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Development of high-temperature electrolyzers: -Search for new efficient electrodes and design of advanced microtubular electrolyzers-

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DEVELOPMENT OF HIGH-TEMPERATURE
ELECTROLYZERS: -SEARCH FOR NEW
EFFICIENT ELECTRODES AND DESIGN OF
ADVANCED MICROTUBULAR ELECTROLYZERS-

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Development of high-temperature electrolyzers:

-Search for new efficient electrodes and design of advanced microtubular electrolyzers-

**Ph.D. Thesis elaborated by:
Miguel Ángel Morales-Zapata**

Development of high-temperature electrolyzers:

-Search for new efficient electrodes and design of advanced microtubular electrolyzers-

by

Miguel Ángel Morales-Zapata

A dissertation submitted in partial fulfillment of the requirements for the degree
of Doctor of Philosophy in Physics

Institute of Nanoscience and Materials of Aragon,
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CERTIFICAN

Que la presente memoria de tesis doctoral elaborada por el Ldo. Miguel A. Morales Zapata titulada “Development of high-temperature electrolyzers: Search for new efficient electrodes and design of advanced microtubular electrolyzers” contiene un trabajo original de investigación y que ha sido realizada bajo nuestra dirección.

Para ello, en cumplimiento con la legislación vigente, autorizamos su tramitación ante la Universidad de Zaragoza para proceder, en su caso, a su posterior defensa.

Zaragoza, 21 de Diciembre de 2022

Fdo. Miguel A. Laguna Bercero

Fdo. Ángel Larrea Arbáizar

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Table of Contents

Abstract	i
Resumen	ii
Chapter 1. Introduction and Fundamentals	1-1
1.1. Motivation	1-2
1.2. Solid Oxide Cells	1-4
1.2.1. Historical Introduction	1-4
1.2.2. Fuel Cells operating principle and main characteristics	1-5
1.2.3. SOC operating principle	1-6
1.2.4. Efficiency, range of power, and fuel versatility	1-8
1.2.5. SOC designs	1-10
1.3. Thermodynamics of SOEC	1-11
1.4. Advantages of High-Temperature Steam Electrolysis	1-12
1.5. Types of resistances affecting the SOC performance	1-14
1.6. SOC Materials	1-16
1.6.1. Electrolyte	1-16
1.6.2. Fuel electrode	1-17
1.6.3. Oxygen electrode	1-18
1.7. Objective and thesis layout	1-20
Chapter 2. Experimental Techniques	2-1
2.1. Introduction	2-2
2.2. Fabrication techniques	2-2
2.2.1. Slip casting	2-2
2.2.2. Powder extrusion molding (PEM)	2-3
2.2.3. Dip coating	2-4
2.2.4. Vacuum infiltration	2-6
2.3. Structural, thermal, and chemical characterizations	2-7
2.3.1. X-ray powder diffraction	2-7
2.3.2. Dilatometry	2-9
2.3.3. Atomic emission spectrometry	2-10
2.4. Microstructural characterization	2-10
2.4.1. Scanning electron microscopy	2-10
2.4.2. Transmission electron microscopy	2-12

2.4.3. Scanning transmission electron microscopy	2-13
2.4.4. EDS-STEM	2-14
2.4.5. Electron energy-loss spectroscopy	2-15
2.5. Electrical characterization techniques	2-17
2.5.1. DC conductivity	2-17
2.5.2. Electrical conductivity relaxation	2-18
2.5.3. Electrochemical impedance spectroscopy	2-20
2.5.4. Distribution of relaxation times	2-24
2.5.5. I-V and I-V-P characteristics	2-26
2.5.6. Chronoamperometric/chronopotentiometry characterization	2-27
Chapter 3. Phase analysis in nickelates and doped ceria composites	3-1
3.1. Introduction.....	3-2
3.2. Preparation of ceramic precursors	3-3
3.3. Structural analysis	3-4
3.4. Compositional analysis	3-7
3.5. Ce and Pr oxidation states	3-10
3.6. Dilatometry measurements.....	3-15
3.7. Electrical conductivity.....	3-18
3.8. Reduction and oxidation kinetics	3-19
3.9. EIS measurements on symmetrical cells	3-26
3.10. Conclusions	3-31
Chapter 4. Production and Characterization of Microtubular Solid Oxide Cells using Extruded Supports	4-1
4.1. Introduction.....	4-2
4.2. Materials employed for cell fabrication	4-2
4.3. Fabrication of single cells	4-5
4.3.1. NiO-YSZ fuel electrode supports	4-5
4.3.2. Electrolyte	4-6
4.3.3. PNO and Ce-based composite air electrodes.....	4-7
4.4. Electrochemical Characterizations	4-10
4.4.1. PNO air electrodes performance.....	4-13
4.4.2. SOC operation.....	4-16
4.4.3. rSOC durability	4-20
4.5. Postmortem microstructural analysis.....	4-26
4.6. Conclusions	4-30

Chapter 5. Production and Characterization of Tubular Solid Oxide Cells with infiltrated nanocatalyst precursors	5-1
5.1. Introduction.....	5-2
5.2. Fabrication of half cells using slip-casting supports	5-3
5.3. Fabrication of air electrodes by infiltration in porous substrates.....	5-6
5.3.1. Fabrication of the scaffolds.....	5-6
5.3.2. Preparation of infiltration solution	5-7
5.3.3. Phase formation analysis.....	5-8
5.3.4. Single-cell description	5-15
5.4. Characterization of SOC with infiltrated air electrode composites.....	5-16
5.4.1. Cell measurement setup.....	5-16
5.4.2. Effect of scaffold type on SOC performance	5-17
5.4.3. Influence of the Ni-YSZ support on SOC performance	5-20
5.4.4. Stability performance	5-24
5.4.5. Influence of infiltrate composition on SOC performance.....	5-28
5.4.6. Influence of gas composition on SOC performance.....	5-31
5.5. Electrolysis and reversible cell performance	5-35
5.6. Conclusions	5-41
Conclusions	iii
Conclusiones	v
References	vii
Nomenclature.....	xxix
Symbols (units).....	xxxi
Published and Submitted Content.....	xxxii

Index of Figures

Figure 1.1. Diagram of SOEC technology integration in energy systems coupled with intermittent electricity from renewable sources.....	1-4
Figure 1.2. Operating principle of the Solid Oxide cell in SOFC (a) and SOEC (b).....	1-7
Figure 1.3. A) TPB fuel electrode composite [23]. B) TPB formation during oxygen reduction for an MIEC electrode over the bulk and surface using an oxide ion conductor as electrolyte.	1-8
Figure 1.4. SOFC geometries.....	1-11
Figure 1.5. Relationships between enthalpy change (ΔH), Gibbs free energy change (ΔG), and entropy change (ΔS) of the electrolysis reaction for H_2O at 1 atm.....	1-12
Figure 1.6. Ideal and actual current density vs. voltage (I-V) characteristics.	1-15
Figure 2.1. Schematic diagram of the slip casting route	2-3
Figure 2.2. Schematic diagram describing a twin-screw extruder under preset temperature zones along the extruder axis.....	2-4
Figure 2.3. The dip coating setup.	2-5
Figure 2.4. Prepared symmetrical SOC components and dimensions.	2-6
Figure 2.5. Schematic of the infiltration process..	2-7
Figure 2.6. Schematic of the Bragg-Brentano diffractometer.	2-8
Figure 2.7. Diagram of operation of a dilatometer.....	2-9
Figure 2.8. a) SEM sample chamber. b) Positions of the Inlens detector, lateral (Everhart-Thornley) detector in the sample chamber, and the BSE detector.....	2-11
Figure 2.9. Schematic of sample preparation for SEM experiments.....	2-12
Figure 2.10. STEM main detectors and standard positions of the spectrometers with contrast mode configurations to obtain DF images.....	2-14
Figure 2.11. a) STEM-EELS instrumentation. b) Useful signals generated by electron-matter interactions in a thin sample. c) Interpretation of EELS main peaks and their relationship with the conduction and valence band structure.....	2-16
Figure 2.12. Four-point probe configuration for DC conductivity tests in a cylindrical sample.....	2-18
Figure 2.13. Nyquist plot (left) and Bode plots (right) <i>as represented in the ZView software</i>	2-21
Figure 2.14. Nyquist plot depicting the high- and low-frequency features of the real axis impedance.	2-22
Figure 2.15. (a) one RCPE element DRT and (b) a DRT of two RCPE elements (with $\tau_2 = 2 \tau_1$ and $R_2 = R_1$), calculated by the Tikhonov regularization using different λ values.....	2-24
Figure 2.16. Equivalent circuit diagram of Voigt elements analyzing the distribution of relaxation times for EIS measurement simulations.....	2-25

Figure 2.17. Typical representation of I-V and I-V-P curves.....	2-26
Figure 3.1. XRD patterns of PNO and PNO-GDC powders collected after annealing for 2 hours at 1450 °C.	3-4
Figure 3.2. Experimental and calculated lattice parameters vs. Pr atomic content in CPGO samples using Kim's empirical method.....	3-6
Figure 3.3. Experimental patterns (black) and fitted spectra (red) in the 3.7-7.3 keV range for PNO (a), GDC (b), and PDC (c).	3-8
Figure 3.4. Set of simultaneously taken STEM-HAADF and EELS Spectrum-Images recorded for: a) C20, b) C80, c) as received PNO, and d) sintered PNO.	3-11
Figure 3.5. Diagram of the conversion of STEM-HAADF image using the 3D data cube for calculating EELS main peaks.....	3-12
Figure 3.6. Thickness mapping of PNO-P and PNO-S.	3-13
Figure 3.7. Background-subtracted EELS of M_4 and M_5 peaks for CPGO particles in C20 and C80, compared with PNO (PNO-S) and GDC references.....	3-14
Figure 3.8. Dilatometry measurements of PNO and PNO-GDC samples (C20 and C80) from RT to 1450 °C. The red circles indicate changes in the slopes.	3-16
Figure 3.9. Temperature dependences of the differential TEC for the PNO-GDC and PNO samples compared with GDC, YSZ, and PNO from 350 to 800 °C.....	3-17
Figure 3.10. Contraction velocity of PNO-GDC and PNO samples obtained from dilatometry tests performed at 1450 °C with a rate of 2 °C·min ⁻¹ for 2 h.	3-17
Figure 3.11. Temperature dependencies of electrical conductivity of PNO-GDC and PNO under air.....	3-18
Figure 3.12. ECR experiments under different ΔpO_2 and temperatures on a) PNO, b) C20, and c) C80.....	3-20
Figure 3.13. Normalized conductivity fittings of ECR data under different ΔpO_2 : a) 0.21→0.10 atm, b) 0.10→0.02 atm, c) 0.02→1.00 atm, and d) 1.00→0.21 atm.	3-21
Figure 3.14. Arrhenius plots of k_{ex} of the samples studied in this work compared with nickelate literature data.	3-22
Figure 3.15. Arrhenius plots of D_{chem} of the samples studied in this work compared with nickelate literature data.	3-22
Figure 3.16. Oxygen partial pressure dependencies of k_{ex} and D_{chem} coefficients at temperature variations for the samples: A) C80; B) C20; C) PNO.	3-25
Figure 3.17. A) R_{pol} temperature variations of PNO and PNO-GDC compounds. B) EIS of PNO-GDC compared to PNO at 850 °C.....	3-26
Figure 3.18. Deconvoluted symmetrical cell DRT data of C20 and C80 at 701 °C (A and B), 751 °C (C and D), 800 °C (E and F), 850 °C (G and H), and PNO at 850 °C (I). The inset indicates the area percent of each peak.	3-29
Figure 3.19. Temperature dependences of R_{pol} and individual DRT fittings in the temperature range of 700-850 °C of C20 (A) and C80 (B).	3-30
Figure 4.1. (a) SEM image of PNO bulk sample: Grey-PNO (matrix); Bright-NiO; Dark-praseodymium silicate; (b) Greyscale histogram showing the counts of the different phases associated with the image; (c) particle size distribution of praseodymium silicate	

(0-40 pixels); (d) particle size distribution of NiO (160-255 pixels); (e) EDS-SEM quantification of the PNO phase.	4-4
Figure 4.2. Twin-screw extruder scheme with the different temperature zones and the microtubular profile at the nozzle exit.....	4-6
Figure 4.3. Optical microscope images of the NiO-YSZ microtubular support co-sintered with the YSZ electrolyte layer.	4-7
Figure 4.4. SEM micrographs of the PNO air electrode and YSZ layers.....	4-9
Figure 4.5. Workflow for rSOC characterizations and analysis.....	4-10
Figure 4.6. Experimental setup for the microtubular SOC electrochemical tests.....	4-11
Figure 4.7. Detail of the tubular cell inside the furnace showing the thermocouple positions and the electrical contacts for fuel and air electrodes.....	4-12
Figure 4.8. I-V-P characteristics of the PNO microtubular cells a) and Nyquist plot b) in SOFC mode at 800 °C.	4-13
Figure 4.9. Postmortem micrograph of PNO01 at 3.0 kV.	4-14
Figure 4.10. Deconvoluted DRT peaks at 800 °C of a) PNO01, and b) PNO02. The inset indicates the DRT peak area percentages.	4-14
Figure 4.11. Nyquist plot b) and DRT peaks b) of PNO02 in SOFC mode under air and oxygen at 800 °C.	4-15
Figure 4.12. I-V characteristics of PNO02 in rSOC mode between 600-800 °C using a fuel electrode gas of 50 vol.% H ₂ and 50 vol.% H ₂ O.	4-17
Figure 4.13. rSOC operation of PNO02 using a fuel electrode gas of 50 vol.% H ₂ and 50 vol.% H ₂ O (a) Nyquist plot under OCV and polarization between 600-800 °C. Deconvoluted DRT peaks under OCV and polarization at 600 °C (b), 700 °C (c), and 800 °C (d).	4-18
Figure 4.14. R _{pol} temperature dependences of PNO02 at OCV between 600 and 800 °C.	4-20
Figure 4.15. Durability tests in SOEC (1.2 V) and SOFC (0.7 V) modes at 800 °C. The different time intervals are shown in the graph (t ₀ -t ₈).	4-21
Figure 4.16. (a) I-V curves of the microtubular cell in SOFC/SOEC modes at 800 °C, collected at different time intervals during the durability test; (b) I-P curves in SOFC mode at the initial state (t ₀), after stabilization (t ₁), and after the durability test completion (t ₈).	4-22
Figure 4.17. Nyquist plots at 800 °C (OCV conditions) were collected at different time intervals during the durability test.	4-23
Figure 4.18. Distribution of relaxation times for durability experiments performed in PNO02 at 800 °C (OCV conditions), collected at different time intervals.	4-24
Figure 4.19. EDS-layered image of the PNO02 cell. The background layer is secondary electron image. The different colors assigned to each phase, using the Ni-K, Zr-L, Pr-L, and Ce-L peaks are indicated in the inset.	4-26
Figure 4.20. SEM images of PNO02 before and after durability studies: a) Detail of the PNO electrode of an identical cell before operation; b) detail of the PNO electrode after operation; c) microstructure of a similar cell before operation showing a homogeneous distribution of porosity in the Ni-YSZ support; d) microstructure of the PNO cell after	

operation showing the evolution of the porosity in the Ni-YSZ support. Letters e-h indicate the approximate region where the subsequent images (magnified) were taken.	4-28
Figure 4.21. SEM images using a BSE detector showing the porosity of PNO02 at different distances from the Ni-YSZ/YSZ interface: before rSOC operation, taken at 0.5 kV (a, c, and e), and after 150 of rSOC operation, taken at 1.5 kV (b, d, and f).	4-29
Figure 5.1. Schematic of the slip casting process for the fabrication of NiO-YSZ supports.	5-4
Figure 5.2. Pre-sintered NiO-YSZ supports. The supports were heat-treated at 850 °C for three hours.	5-5
Figure 5.3. XRD (20 to 90 degrees) of PNO-YSZ and GDC scaffolds in samples annealed between 700 and 1000 °C for 5 hours using one infiltration.	5-9
Figure 5.4. XRD diffractograms (32 to 34 degrees) of PNO-infiltrated GDC scaffolds for samples annealed between 700 and 900 °C.	5-10
Figure 5.5. XRD patterns (26 to 45 degrees) of PrO _x -infiltrated scaffolds from 600 to 800 °C: YSZ (a); GDC (b).	5-11
Figure 5.6. SEM images of SOC before testing: a) PNO/GDC interface; b) PrO _x /GDC interface.	5-12
Figure 5.7. SEM micrograph of a fractured section of a PrO _x -GDC sample sintered at 1000 °C before testing. Yellow marks indicate PrO _x agglomerates and red marks show GDC particles of the scaffold.	5-13
Figure 5.8. XRD patterns (26 to 45 degrees) of NNO-infiltrated YSZ from 600 to 1100 °C.	5-14
Figure 5.9. Comparison of the dimensions of A- and B-series cells (a), dimensions of the SOC configuration for A-series (b), and B-series (c).	5-15
Figure 5.10. SOC electrical test setup	5-16
Figure 5.11. I-V-P curves of A-PNG and A-PNY a), A-NNG and A-NNY cells b).	5-18
Figure 5.12. Comparison of the electrochemical performance of A-series nickelate air electrode composites with YSZ and GDC scaffolds: a) EIS measurements between 650 and 750 °C; b) DRT at 750 °C showing the peak area percentages in the inset.	5-19
Figure 5.13. I-V-P characteristics of A-PNG and A-PG6 (a), and B-PNG and B-PNG (b) between 650 and 750 °C using 50 SCCM of H ₂ (3 vol% humidified) on the fuel electrode side and 100 SCCM air on the air electrode side.	5-21
Figure 5.14. Nyquist plot comparison of A-PNG and B-PNG at 750 °C (a), 700 °C (b), and 650 °C (c). Blue circles and green squares show the fittings on experimental EIS data using the DRT method. Corresponding DRT data for each temperature are plotted in d, e, and f.	5-22
Figure 5.15. (a) Values of polarization resistance and (b) capacitance of individual peaks corresponding to DRT data at different temperatures for A-PNG and B-PNG.	5-24
Figure 5.16. I-V-P, Nyquist plots, and DRT graphs for A-PNG (a, b, and c) and B-PNG (d, e, and f) at 650 °C. Solid lines in (b) and (e) represent EIS experimental data, while the points on the curve show the accuracy of the DRT fitting. Inset in (e) shows the zoomed Nyquist data.	5-26

Figure 5.17. Comparison of the stability between A- and B-cells at 650 °C and 0.7 V. As the water inside the container at the outlet gradually evaporates, refilling the container is needed after a few hundred hours.....	5-27
Figure 5.18. A-PNG and A-PG6 Nyquist plot at different temperatures (a), DRT peaks of A-PNG and A-PG6 (b), B-PNG and B-PG6 Nyquist plot at different temperatures (c), DRT peaks of B-series B-PNG and B-PG6 (d).....	5-29
Figure 5.19. SEM micrographs using a BSE detector of air electrode thickness after tests: A-PNG taken at 15 kV a) and B-PNG taken at 20 kV b).....	5-31
Figure 5.20. B-PNG and B-PG6 DRT peak variations between 650 and 700 °C under different air and oxygen atmospheres.....	5-32
Figure 5.21. DRT graphs of B-PG6 at 650 °C with different air and fuel electrode gas compositions and varying flow rates.	5-34
Figure 5.22. Post-mortem XRD patterns of a) A-PNG and b) B-PNG before and after the potentiostatic test at 650 °C, 0.7 V.	5-35
Figure 5.23. rSOC potentiostatic tests at 700 °C using a fuel composition of 50 vol.% H ₂ O/ 50 vol. % H ₂ , with 0.765 V in SOFC and 1.165 V in SOEC.	5-37
Figure 5.24. rSOC I-V curves using a fuel composition of 50 vol.% H ₂ O/ 50 vol. % H ₂ of A-PG6 and B-PG6 at 700 and 750 °C and A-PNG at 750 °C..	5-38
Figure 5.25. Nyquist plots in rSOC mode of A-PG6 and B-PG6 at 700 °C (a); Nyquist plots of B-PG6 and A-PNG at 750 °C (b); DRT peaks of A-PG6 at 700 °C using 45 vol % of H ₂ O (c); DRT peaks of B-PG6 at 700 °C using 50 vol % of H ₂ O (d).....	5-38
Figure 5.26. DRT peaks of A-PNG evolution on time under continuous SOEC operation at 750 °C.....	5-39
Figure 5.27. Post-mortem SEM micrographs of B-PG6 after rSOC operation at 750 °C: SOC layer distribution taken at 10 kV (a); Fractured sample of the fuel electrode/electrolyte interface taken at 1.0 kV (b).....	5-40

Index of Tables

Table 1.1.: Actual efficiency of hybrid fuel cell systems compared to various electricity generation systems as a function of power.	1-9
Table 2.1. Circuit elements used in modeling with the impedance formulation and associated processes.	2-23
Table 3.1. ICP-OES analysis of the powder samples used in this study.	3-3
Table 3.2. Precursors used in this study.	3-3
Table 3.3. Phase composition and lattice parameters of the samples studied, as calculated from refined XRD.	3-5
Table 3.4. Concentration ratios from ICP-OES and Cliff-Lorimer parameters (k_{AB}) of the standards (in atomic fraction) used for EDS quantification.	3-9
Table 3.5. EDS-STEM Quantifications of CPGO in C80 and C20.	3-9
Table 3.6. EDS-STEM Quantification of PNO in PNO-GDC mixtures compared to PNO sintered at 1450 °C and PNO in as-received powder.	3-10
Table 3.7. Reported Ce and Pr M_5/M_4 ratios for 3+/4+ oxidation states and reference samples used in different EELS studies.	3-15
Table 3.8. Activation energies for D_{chem} and k_{ex} in $Ln_2NiO_{4\pm\delta}$ ($Ln = La, Pr, Nd$) and GDC mixed oxides at selected temperature ranges and $pO_2 = 0.21$ atm.	3-24
Table 3.9. Symmetrical SOC R_{pol} between 700-850 °C, acquired by DRT fittings.	3-27
Table 4.1. Preparation of extruded NiO-YSZ supports for 65 vol. % of solid charge. ..	4-5
Table 4.2. Dimensions and weights of the single cells and its after sintering.	4-8
Table 4.3. DRT fittings for the R_{pol} values of PNO cells at different frequency intervals (in Hz).	4-15
Table 4.4. DRT fittings for R_{pol} values of PNO02 at different frequency intervals (in Hz) under polarization and OCV. The R values are in $\Omega \cdot cm^2$	4-19
Table 4.5. R_{pol} fitting values of the Nyquist plots of PNO02, at 800 °C and OCV.	4-25
Table 4.6. Pore distribution of the Ni-YSZ electrode of PNO02 after operation.	4-30
Table 5.1. Composition and thickness of different supports and layers.	5-5
Table 5.2. Fabricated SOC using catalysts infiltrated in different scaffolds.	5-15
Table 5.3. R_{pol} calculated by DRT area fittings of A-cells using nickelate electrodes.	5-20
Table 5.4. Polarization resistance and capacitance values of different peaks associated with DRT plots for cells A-PNG and B-PNG at different temperatures.	5-24
Table 5.5. Polarization resistances and capacitances calculated from DRT fittings at 650 °C for A-PNG, A-PG6, B-PNG, and B-PG6, before and after stability tests.	5-31
Table 5.6. R_{pol} values of DRT area fittings from EIS data of A-PG6 and B-PG6 operated in rSOC mode at 700 °C.	5-39

Abstract

This work presents nickelate and ceria-based materials as air electrodes for solid oxide electrolyzer cells. These materials, characterized by X-ray diffraction, showed a doped ceria phase product of the interdiffusion of one of the praseodymium nickelate (PNO) decomposition products (Pr_6O_{11}) into the gadolinium-doped ceria (GDC) lattice. The materials also exhibited fast oxygen kinetics, evidenced by their high surface exchange (k_{ex}) and chemical diffusion (D_{chem}) coefficients. The k_{ex} obtained were 7.4×10^{-7} and $2.2 \times 10^{-6} \text{ cm} \cdot \text{s}^{-1}$ at 800 °C and synthetic air for PNO- and GDC-rich composites, respectively. Similarly, the calculated D_{chem} were 5.5×10^{-8} and $7.6 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$ at 800 °C and synthetic air for PNO- and GDC-rich composites, respectively.

The PNO-GDC composite air electrodes' reaction zones were enhanced via nanoengineering of the air electrode microstructure using the infiltration of nanosized electrocatalysts. The resulting cells showed good stability for 260 hours at 650 °C, with a continuous increase in performance for the first 90 hours. A higher porosity in extruded microtubular supports enhanced the performance, especially in electrolyzer mode, using a fuel composition of 50 vol% H_2O . A reduction of 0.13 to 0.02 $\Omega \cdot \text{cm}^2$ in charge transfer resistance and 0.68 to 0.02 $\Omega \cdot \text{cm}^2$ in electrode transport resistance contributions to total polarization resistance was observed. The reversible solid oxide cell performance of microtubular cells using a nickel and yttria-stabilized zirconia (Ni-YSZ) fuel electrode support, a YSZ electrolyte, and a double air electrode layer of PNO-GDC/PNO was measured for over 150 hours, where scanning electron microscopy observations showed no structural degradation of the air electrode layers after the tests. Ni agglomeration and redistribution of porosity away from the fuel electrode/electrolyte were determined as the cause of the degradation.

Resumen

El presente trabajo describe el funcionamiento de electrodos de aire a base de niquelato y ceria para electrolizadores de óxido sólido. Estos materiales, caracterizados por difracción de rayos X, mostraron una fase de ceria dopada producto de la interdifusión de uno de los productos de descomposición del niquelato de praseodimio (PNO) en la estructura de ceria dopada con gadolinio (GDC). Los materiales también exhibieron una rápida cinética de oxígeno, evidenciada por sus altos coeficientes de intercambio superficial (k_{ex}) y difusión química (D_{chem}). Los k_{ex} obtenidos fueron 7.4×10^{-7} y 2.2×10^{-6} $\text{cm} \cdot \text{s}^{-1}$ a 800 °C en aire sintético para composites ricos en PNO y GDC, respectivamente. De forma similar, los D_{chem} calculados fueron 5.5×10^{-8} y 7.6×10^{-8} $\text{cm}^2 \cdot \text{s}^{-1}$ a 800 °C y aire sintético para compuestos ricos en PNO y GDC, respectivamente.

Las zonas de reacción de los electrodos de aire compuestos PNO-GDC se mejoraron empleando técnicas de nanoingeniería de la microestructura del electrodo de aire mediante la infiltración de electrocatalizadores de tamaño nanométrico. Las celdas resultantes mostraron una buena estabilidad durante 260 horas a 650 °C, con un aumento continuo del rendimiento durante las primeras 90 horas. Una mayor porosidad en los soportes microtubulares extruidos demostró mejoras en el rendimiento, especialmente en modo electrolizador, utilizando una composición de combustible de 50% vol H_2O . Adicionalmente, se observó una reducción en la resistencia de transferencia de carga de 0.13 a 0.02 $\Omega \text{ cm}^2$ y en las contribuciones de la resistencia de transporte del electrodo a la resistencia de polarización total de 0.68 a 0.02 $\Omega \text{ cm}^2$. Finalmente, se midió el rendimiento de la celda microtubular de óxido sólido en la configuración de soporte de electrodo de combustible de níquel y circonia estabilizada con itria (Ni-YSZ), electrolito YSZ y doble capa de electrodo de aire de PNO-GDC/PNO durante más de 150 horas. Las observaciones por medio de microscopía electrónica de barrido no mostraron degradación estructural de las capas de electrodos de aire después de las pruebas. La aglomeración de Ni y la redistribución de la porosidad lejos del electrodo de combustible/electrolito se determinaron como la causa de la degradación.

Chapter 1. Introduction and Fundamentals

From the days of William Grove to recent times, fuel cell technology has been a matter of constant research and discussion in the electrochemistry scientific scene. As emerging renewable energy systems have increased worldwide, highly efficient energy conversion mechanisms have become more necessary. In recent years, high-temperature devices like solid oxide electrolyzers have gained the attention of industries and scientific research institutions as a solution for power-to-gas conversion. This process opens multiple strategies for renewable energy excess storage in the form of chemical compounds while producing no contamination. This chapter presents solid oxide electrolyzer technology's state-of-the-art configurations and materials. The included literature covers the status of hydrogen production technologies, a description of the solid oxide cell devices and operating principle, polarization resistances and their respective processes, thermodynamics, materials for cell components, and, to sum up, the prospect of advanced oxygen electrodes for the development of high-temperature electrolyzers, as this is the main topic of the current research work.



1.1. Motivation

Hydrogen is the most abundant element in the universe and the basis of many physical, chemical, and biological processes on Earth. It is also a great energy carrier with a very high energy per unit of mass. H_2 contains a compelling higher calorific value of combustion ($\sim 142 \text{ MJ}\cdot\text{kg}^{-1}$) than natural gas or oil (~ 55 and $42 \text{ MJ}\cdot\text{kg}^{-1}$, respectively) and a high energy per unit mass ($120 \text{ MJ}\cdot\text{kg}^{-1}$) [1]. That is why scientists and industries have been greatly interested in hydrogen production technologies in recent years.

In nature, H_2 is bonded with other elements, such as water and hydrocarbons. To free H_2 from those compounds, a significant amount of energy is needed to break the bonds and force it away from the other elements it has reacted with. Most H_2 is produced by steam methane reforming (grey and blue H_2), bombarding methane or natural gas with steam at high temperatures and pressure to force the carbon and H_2 atoms apart. Still, methane's long-term global warming potential is a concern as mass for mass is a hundred times more potent greenhouse gas than CO_2 [2]. Attention is shifted toward green H_2 as it does not produce greenhouse gas emissions. Here, H_2 is separated from oxygen atoms in water via electrolysis using renewable-only energy sources. This process is much less efficient at low temperatures and about six times more expensive than producing hydrogen from steam-reforming methane [3]. Even so, at high temperatures, steam electrolysis offers several advantages in terms of thermodynamics and kinetics that enhance the efficiency of H_2 production and could result in a cheaper technology over other means of H_2 production by the economy of scale [4].

A key factor in the development of a green H_2 -based economy is the use of Solid Oxide Cells (SOC) not only in fuel cell mode (SOFC) but also as solid oxide electrolysis cells (SOEC) for hydrogen production. When operated reversibly (alternating SOFC and SOEC modes as reversible Solid Oxide Cells or rSOC), a wide range of functionalities is exhibited in combination with renewable energy sources like solar energy, wind turbines, geothermal, etc. (*fig. 1.1*). The most evident is the release of energy in the form of electricity. Still, they also generate valuable energy storage in chemical compounds, providing green hydrogen production with high fuel conversion and efficiency [5,6]. The SOC technology is the basis for the electrochemical conversion of power to gas. Here, the term 'gas' includes steam (H_2O), carbon dioxide (CO_2), H_2 , carbon monoxide (CO), or syngas (H_2 combined with CO).

The concept of power-to-gas presents several advantages over batteries. To begin with, batteries are best suited for being discharged in relatively short hours to a few days,

while H_2 can be stored for weeks or months. These features are needed as renewable technologies are projected to have the most energy grids over the next few decades, also requiring ample seasonal energy storage. H_2 is the perfect candidate to solve this problem as excess energy can be stored when far more electricity than needed is produced from solar and wind. Then, this energy can also be converted back to electricity when the production of renewables is slower.

The cost of producing hydrogen by SOEC is lower than in alkaline and protonic exchange membrane electrolysis (PEMEC), as SOEC is about 20% more efficient without heat integration. With heat integration, SOEC is about 30% more efficient than alkaline electrolysis and PEMEC [7]. All energy required can be produced with renewable energy technologies and scaled up to get a potentially transformational solution for several applications in the industry. Power-to-gas technologies seem to be one of the most plausible radical solutions to reaching zero CO_2 emissions, an extremely challenging goal considering that current annual emissions are set at 33 Gt [8]. The 2020s are a historical time to make the energy transition from the fossil fuel era to a hydrogen economy, mainly due to hydrocarbon deposit shortages and political conflicts over natural gas. The route to take off towards an emission-free hydrogen economy to achieve climate neutrality in 2050 has converged in initiatives such as European Union's Green Deal [9] or similar hydrogen roadmaps in Japan, the USA, and many other countries.

This thesis addresses the electrochemical performance of oxide ion-conducting cells operating as rSOC for hydrogen production and its posterior use as an energy vector, focusing on air electrode materials and nanosized electrocatalysts that stimulate fast oxygen diffusion and studying their degradation phenomena under SOFC/SOEC operating modes. SOC requires materials that simultaneously promote these devices' oxygen reduction and hydrogen oxidation reactions. For this reason, advanced air electrodes that provide versatility under diverse oxygen partial pressure conditions are particularly interesting. In addition, long-term stability in SOC performance is the final goal for these devices' commercial viability, where compatibility between components becomes essential. This introductory section includes a brief description of the operation principle of the SOFCs and SOECs, including performance and polarization losses, a short review of the current materials development, and some aspects of the advantages of SOECs and the perspectives for rSOC in energy systems.

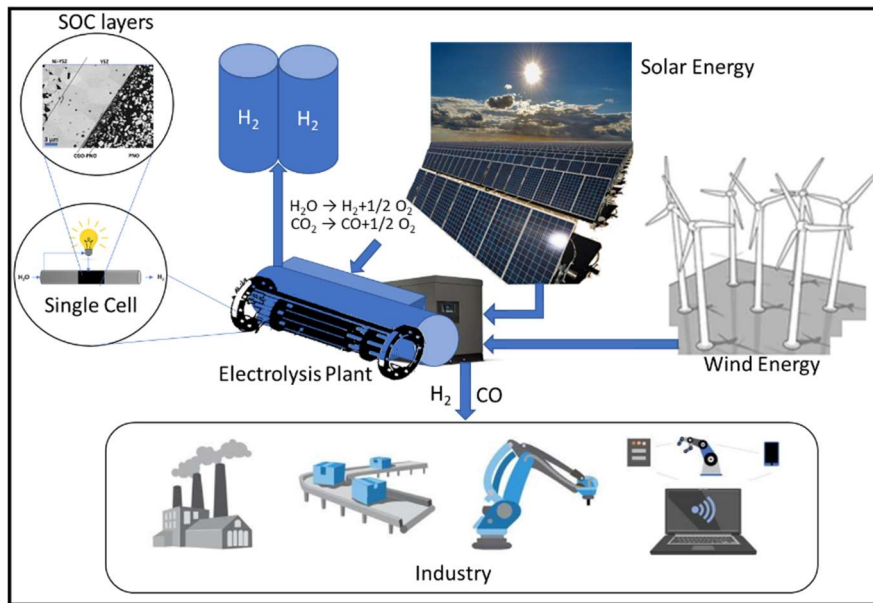


Figure 1.1. Diagram of SOEC technology integration in energy systems coupled with intermittent electricity from renewable sources. Adapted from [10].

1.2. Solid Oxide Cells

1.2.1. Historical Introduction

For almost 200 years, electrolytic cell technology has been studied, starting with Faraday, who observed that aqueous solutions were excellent conductors [11]. He introduced the classification of materials into first and second types of conductors, metallic and electrolytic [12]; the former is nowadays identified as electronic and the latter as ionic. By this time, the chemistry of water was better understood. In 1837, Schönbein and Grove showed that water electrolysis in an acidic medium is a reversible process that generates electricity from hydrogen and oxygen. This was the first comprehensive study about the electrochemical process of electrolytic cells, giving place to Grove's invention of fuel cells, which developed a cell in a series configuration in 1939 [13]. Since the late 19th century, the term "solid electrolyte" has been used to describe dense ceramic ionic conductors as electrolytes [14]. Still, this term was formally introduced in Nernst's investigation of electric incandescent lamps [12,14]. Nernst found that mixtures of insulating oxides, such as zirconia and calcium or yttria, could also exhibit strong ion conduction. Many mixed oxides with high conductivities at elevated temperatures were recognized, including the composition of 85 wt% of zirconia and 15 wt% of yttria, the so-called Nernst mass. Reynolds's thesis of 1902 [12] extended this field by measuring the conductivity of numerous binary and ternary systems in the range of 800-1400 °C, among others, formed by ZrO_2 . After many years, in the early 1960s, Westinghouse Electric

Corporation developed series-connected SOCs of planar and tubular geometry with platinum electrodes [14]. During the same decade, John Bockris [15] coined the term "hydrogen economy" to describe a future where hydrogen fuel cells power everything, which helped promote the fuel cell concept over the following decades. However, one of the main reasons this idea did not gain sufficient impulse was because the anode materials required platinum which made the fuel cell fabrication costly. By 1985, Dönitz and Erdle [16] were the first to report results from a SOEC using a supported tubular electrolyte for the HotElly project at Dornier System GmbH. SOFC design consisted of long tubular cells, electrically interconnected by oxide materials and ductile nickel mesh conductors combined into tube bundles. This design led to the first 5 kW SOFC generators in 1986 and 100 kW SOFC systems in 1998 [17,18]. During the 2000s, new materials were developed, lowering the price of production, and several types of fuel cell configurations have been studied with a better understanding of electrochemical properties and applications.

1.2.2. Fuel Cells operating principle and main characteristics

Fuel cells present several advantages over conventional electricity generation systems. Like any traditional combustion process, they constitute exothermic oxidation reactions in which the fuel acts as an electron donor and the oxidant (generally air) as an electron acceptor. However, they differ considerably in the route to conversion from chemical energy to electrical energy. In the combustion process, many transformation stages are necessary, which involve converting the energy obtained from combustion into mechanical and electrical energy. In an electrochemical cell, the current generated by the flow of electrons during the reaction acts as an electromotive force (EMF), channeling it through an external circuit. In this sense, a fuel cell is a device capable of directly converting chemical energy via oxidation and reduction reactions into electricity, similar to a battery. The downside: continuous fuel must be supplied in fuel cells for the same purposes.

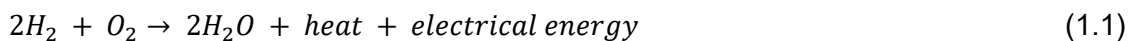
The electrochemical conversion efficiency of fuel cells does not abide by the thermal and mechanical processes restricted by the Carnot cycle, giving place to high fuel-to-electricity conversion efficiencies. The path during energy conversion in a fuel cell is much simpler as it is not necessary to convert the chemical energy of the fuel into mechanical energy and then drive an electric generator. Furthermore, fuel cells also yield negligible pollutant emissions of gases such as SO_2 , NO_x , and CO_2 or other dangerous particles, contrary to power generation from burning coal and oil [19]. Also, their

operation is relatively quiet because of the lack of moving parts and can be located anywhere, including within residential areas.

Fuel cells consist of an anode, an electrolyte, and a cathode. The anode is the fuel cell component where the oxidation reaction happens, while the cathode is where the reduction reaction occurs. There are several different types of fuel cells operating at different temperature ranges. In general, they are named after the type of material and the conductive nature of the electrolyte, which also determine the operating temperature. The most common types [20] are Alkaline fuel cells (AFC), Proton Exchange Membrane fuel cells (PEMFC), Direct methanol fuel cells (DMFC), Phosphoric acid fuel cells (PAFC), and Microbial fuel cells (MFC), which are used in relatively low temperatures (<200 °C). Intermediate-to-high temperature cells include the Molten Carbonate fuel cell (MCFC), operating at ~500 °C, and finally, the Solid Oxide fuel cell (SOFC) [18], which is used at intermediate-to-high temperatures (typically 500-1000 °C). All the cells are, in principle, reversible. Still, in practice, some cells experience a degradation of materials or incapability to handle the required long-term operation to perform the reversible modes.

1.2.3. SOC operating principle

A Solid Oxide Cell (SOC) is built up of two porous, gas, ion, and electron-conducting electrodes separated by a ceramic oxygen ion-conducting electrolyte. Alternatively, proton-conducting electrolytes can also be used for SOC. Still, as this work is focused on oxide ion-conducting electrolytes, only the reactions for the latter will be described in this section. The electrodes are subjected to different types of gases, depending on the operating mode of the SOC. When the cell is operated in SOFC mode, gases such as H₂, CH₄, syngas (H₂ combined with CO), and NH₃ can be used as fuels. In H₂-fueled SOFC, hydrogen is oxidized into H₂O in the fuel electrode, producing a hydrogen oxidation reaction (HOR). The other electrode is fed with O₂ or air and works as an air/oxygen electrode, where the oxygen reduction reaction (ORR) occurs. At the air electrode/electrolyte interface, oxygen molecules are reduced to oxide ions. These oxide ions are conducted through the electrolyte, and the total reaction in the cell (*fig. 1.2a*) is:



Each fuel/oxidant interaction in the electrodes presents a reaction where the Gibbs free energy (ΔG) is related to the theoretical cell voltage [18,20] according to:

$$E_T = -\frac{\Delta G}{nF} \quad (1.2)$$

In eq. 1.2, n is the number of electrons exchanged in the reaction, and F is Faraday's constant. At open circuit voltage (OCV), the reversible cell potential of eq. 1.2 is given by the Nernst equation (eq. 1.3) at the given operating conditions. For the reaction in eq. 1.1, the OCV of the cell can be obtained by:

$$OCV = -\frac{\Delta G}{2F} + \frac{RT}{4F} \ln \left(\frac{(p_{H_2})^2 \cdot (p_{O_2})}{(p_{H_2O})^2} \right), \quad (1.3)$$

The terms inside the logarithm of eq. 1.3 are the partial pressure ratios of the species acting on the components of the cell (H_2 and H_2O in the fuel electrode and O_2 in the air electrode).

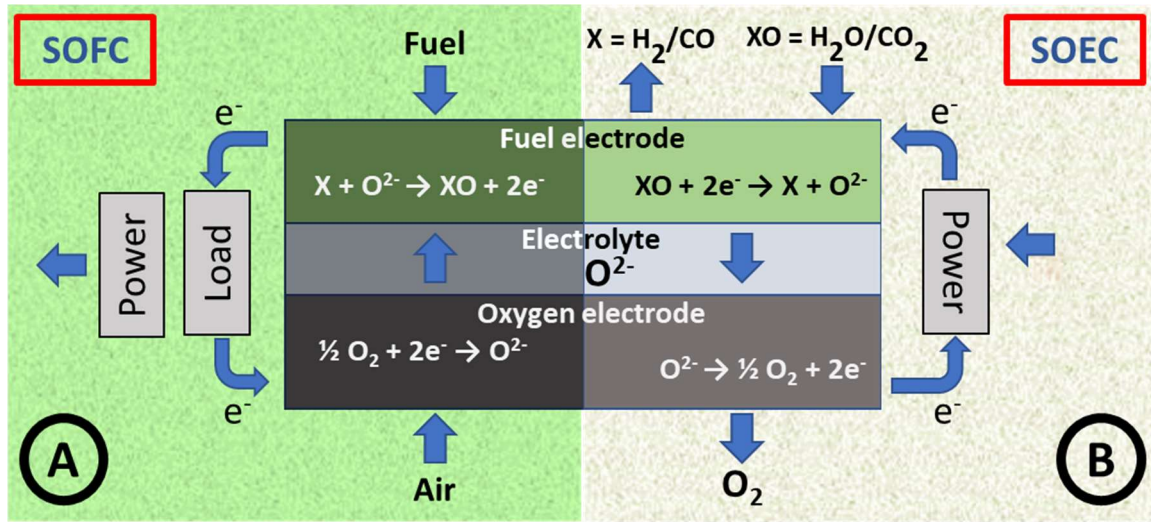


Figure 1.2. The operating principle of the Solid Oxide cell in SOFC (a) and SOEC (b) shows the deactivation and recovery processes involved during rSOC operation.

Adapted from [21].

The inverse reaction of eq. 1.1. constitutes the SOEC mode (fig. 1.2b), where an external power supply between the electrodes of a fuel cell separates steam molecules and induces the reversal of the flow direction of both electrons and ions in the cell [22]. The result is the water electrolysis producing an enrichment of hydrogen and oxygen in the fuel and oxygen electrodes, respectively. As SOEC requires heat, the usual operating range is between 650 - 1000 °C.

In the electrodes, the HOR and ORR processes occur in the triple phase boundary (TPB): the zone where the electronic phase, ionic phase, and gas phase (hydrogen, air) are in contact. Generally, the TPB is seen as a small finite volume that extends inside the electrodes. Their typology depends on if the electrodes are composite or mixed ionic and electronic conductor (MIEC) materials, as their conduction paths differ due to the

different atmospheres and reactions produced (*fig. 1.3*). In both cases, the electrodes catalyze the reactions and provide conductive paths for the electrons. For example, in a typical nickel/yttria-stabilized zirconia (Ni-YSZ) fuel electrode, the TPB is the zone where Ni metallic particles (electronic phase), the YSZ skeleton (ionic phase), and pores (gas phase) are in interaction (*fig. 1.3a*). In MIEC electrodes, the ORR pathway involves the formation of TPBs between MIEC, electrolyte, and pore during the oxide ion transfer (*fig. 1.3b*).

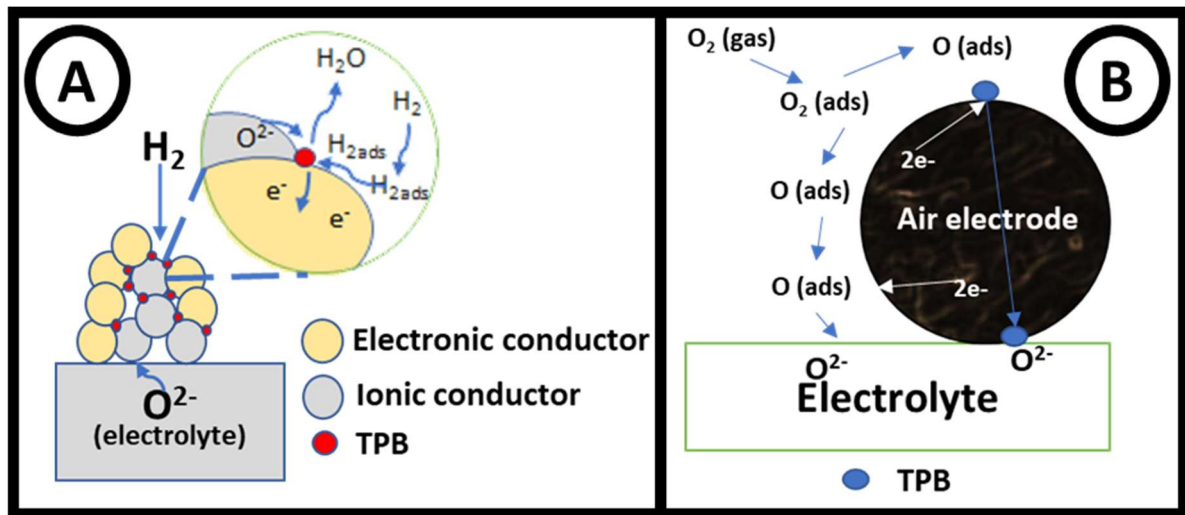


Figure 1.3. A) TPB fuel electrode composite [23]. B) TPB formation during oxygen reduction for an MIEC electrode over the bulk and surface using an oxide ion conductor as electrolyte [24].

The processes present within the TPB zone include gas phase transport (convection and diffusion) from the gas flow in the channels to the porous electrodes, diffusion of molecular porous media (Fick, Dusty, and Knudsen), adsorption of species, desorption, dissociation, grain and surface diffusion, surface reaction, bulk exchange, and charge transfer steps [25]. Often multiple pathways are possible; one is generally preferred depending on the prevailing conditions and the properties of the internal components.

1.2.4. Efficiency, range of power, and fuel versatility

SOFCS have been identified as one of the most likely fuel cell technologies poised to capture a significant market share in future hybrid systems [19,20], where very high efficiencies can be achieved at high temperatures in combination with power systems, theoretically of at least 75%, as shown in *Table 1.1*. A unit consisting of a cell stack, heat exchangers, combustion chamber (or afterburner), and a gas turbine subsystem can provide a technical solution for the use of fuel cells in power generation. In practice,

simple cycles with an efficiency of 65% and a combined cycle with electrical efficiency greater than 75% have been developed in commercial units [22,23]. In addition, emissions of nitrous oxides (NO)_x in waste products have been measured in the order of 0.5 ppm, which is a magnitude lower than in similar technologies [24].

Table 1.1.: Actual efficiency of hybrid fuel cell systems compared to various electricity generation systems as a function of power [26].

System	Power range (MW)	Efficiency range (%)
Fuel cell/gas turbine hybrid	4 – 750	57 – 75
Fuel cells	0.1 – 100	50 – 60
H ₂ -fueled steam turbines	500 – 900	55 – 60
Combined cycles in gas turbine	40 – 600	45 – 50
Heat-recovering gas turbines	0.1 - 6	30 – 42
Internal combustion engines	0.2 - 50	25 – 40
Microturbines	0.4 - 1	25 – 30
Gas turbines	0.8 - 100	12 – 35

Regarding the efficiency of the SOC, as part of the fuel will not react when passing through the cell, to calculate the efficiency, it is necessary to consider the use of fuel:

$$\eta = U_F \frac{E}{E_T} \quad (1.4)$$

U_F is the fuel utilization, E is the operating voltage, and E_T is the theoretical voltage.

The fuel utilization, assuming no electronic conduction in the electrolyte or any gas exchange between the electrodes, can be calculated by:

$$U_F = \frac{I}{2F\dot{m}_{H_2}} \quad (1.5)$$

where $\dot{m}_{H_2}$ is the molar H₂ flow in the fuel electrode inlet.

Typically, single SOFCs have a power density between 0.2 and 2.0 W·cm⁻², and fuel flexibility, because of the possibility of operating in internal reforming, external reforming, partial oxidation, and direct oxidation [27]. In internal reforming, the steam reforming reaction and the exothermic reaction from the oxidation reaction are operated in a single unit, where methane, methanol, CO₂, and other hydrocarbons are converted into H₂ within the fuel electrode volume in both single cells and stacks [28]. The elevated temperature of operation has an additional advantage as highly expensive Pt is not needed to catalyze the reactions and eliminates the need for an external reformer system for fuel processing. Another alternative is indirect internal reforming, where the reform

system recovers heat from the SOC stack. In external reforming, the endothermic steam reforming reaction and the fuel cell reaction occur independently with no direct heat transfer. In hybrid SOFC/gas turbine systems external reforming, the heat required by the endothermic reforming reactions is supplied directly by the fuel cell stack at about 800–900 °C. At last, partial oxidation is applied when hydrocarbon fuels are converted into syngas through steam reforming, dry/CO₂ reforming, partial catalytic oxidation, and oxidative steam reforming. Direct oxidation corresponds to electrochemically oxidation processes on the fuel electrode that complement other reforming operating modes [27].

1.2.5. SOC designs

SOFC designs are varied and usually classified into planar and tubular geometry. In planar geometry, the variants are categorized by the material of support they use (*fig. 1.4*). To reduce the operating temperature, fuel or air/oxygen electrode supports are employed when using a thin electrolyte, however in the former, there are problems with the reoxidation of metallic components and limited mass transport, while in the latter power densities are usually lower. Electrolyte-supported cells tend to have better structural support due to the dense electrolyte. However, characteristic operating temperatures are higher to minimize ohmic losses. Other possibilities are interconnector-supported cells and porous metal substrates (generally stainless steel). The interconnector-supported cells, although having more robust structures, are susceptible to oxidation. In contrast, metal-supported cells usually have a more complex design due to the addition of a new material, which could cause compatibility issues.

The other type of configuration is tubular geometry [29,30]. In this design, the various components of the cell are coated to form layers on a ceramic tube. This configuration allows simpler designs for the collection and distribution of fuel and air and a better ability to withstand higher thermal stresses. This, in turn, provides a high tolerance to diverse fuel supplies and fast response to load changes and interruptions [31,32]. Within the tubular designs are the conventional ones, which use tubes with diameters > 15 mm, and the microtubular cells, which have diameters < 5 mm. The power density per area and volume units can be increased by decreasing the tube diameter [29]. This design favors the sealing area between the different atmospheric conditions of the electrodes, as sealing can be done at the ends of the tubes. However, it presents difficulties in the current collection of electrodes.

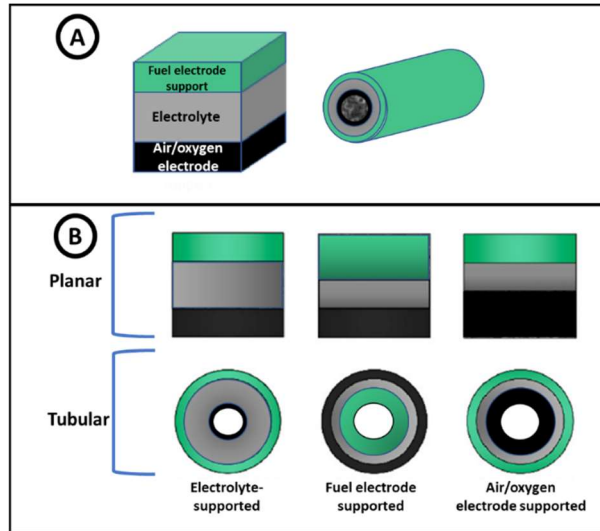


Figure 1.4. SOFC geometries: (a) 3D model of the planar and tubular cell, (b) cross-sections of electrolyte-, fuel electrode-, and air/oxygen electrode-supported cells for both planar and tubular geometry. Compiled from [33].

In summary, SOFC design technology is still under development since higher power densities, reliability, and durability are required while reducing fabrication costs. The microtubular design will be covered in chapters 4 and 5 to identify performance degradation sources and stability in SOFC/SOEC operation.

1.3. Thermodynamics of SOEC

Even though the SOEC is still in the demonstration stage of technology, its attractiveness lies in its unrivaled conversion efficiencies resulting from beneficial thermodynamics at high temperatures. The thermodynamics of steam electrolysis is described by the relationships of enthalpy (ΔH), Gibbs free energy change (ΔG), and entropy (ΔS) variations at 1 atm represented in *fig. 1.5*. Their relationship is expressed by:

$$\Delta G = \Delta H - T\Delta S \quad (1.6)$$

A significant amount of steam electrolysis energy demand can be obtained from the Joule heat produced within the SOC. This heat decreases the electrical energy demand required for H_2 production, increasing efficiency and reducing costs if the price of heat is lower than for electricity or if waste heat sources can be exploited. Otherwise, it is convenient to operate the SOEC at thermoneutral potential (E_{tn}), where the heat generated in the SOC equals the heat consumption for the endothermic electrolysis reaction. For steam electrolysis at 800 °C and 1 atm, using $\Delta H_{H_2O} = 249 \text{ kJ}\cdot\text{mol}^{-1}$ as indicated in *fig. 1.5*, the thermoneutral potential is:

$$E_{tn,SOEC} = \frac{\Delta H_{H_2O}}{nF} = 1.29 \text{ V} \quad (1.7)$$

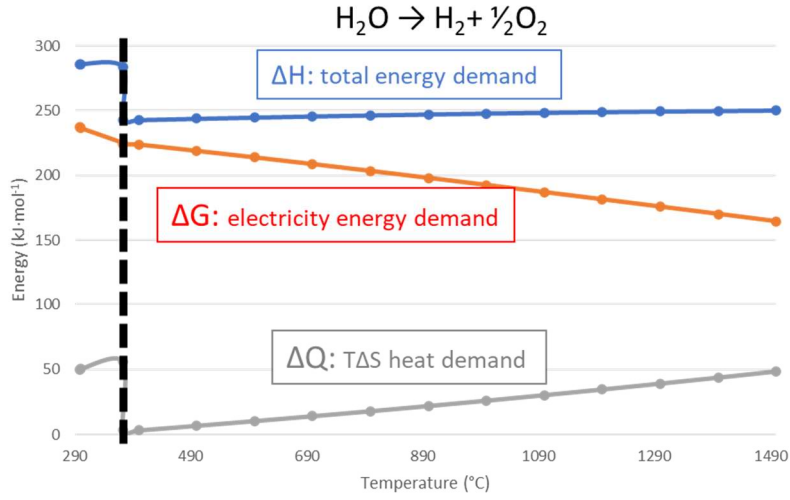


Figure 1.5. Relationships between enthalpy change (ΔH), Gibbs free energy change (ΔG), and entropy change (ΔS) of the electrolysis reaction for H_2O at 1 atm. Data were obtained from [34].

Finally, the kinetics of the reactions involved in high-temperature SOEC and its overall conductivity increase with the temperature [16,35]. This is commonly observed in SOEC electrochemical characterizations, where the internal polarization resistance (R_{pol}) and the area-specific resistance of the cell (ASR) show a decrease with increased temperatures. Consequently, increasing the temperature at a given constant SOEC voltage and fuel electrode composition will increase the current density response and the H_2 production rate.

1.4. Advantages of High-Temperature Steam Electrolysis

High-temperature electrolysis presents many advantages over low-temperature electrolysis technologies. The most relevant are:

- The H_2 rate of production: A SOEC operated at the thermoneutral potential for the splitting of steam (1.29 V) will attain an electrolysis current density of $\sim 1.5 \text{ A}\cdot\text{cm}^{-2}$, whereas a PEMEC operated at the thermoneutral potential for the splitting of liquid water (1.47 V) attains a current density of $\sim 0.5 \text{ A}\cdot\text{cm}^{-2}$ at similar fuel compositions [10]. SOEC H_2 generation systems have achieved a better conversion performance than commercial PEMEC in terms of production rate at

18.3 g·h⁻¹ (corresponding to -0.25 A·cm⁻²) and showing a conversion up to 14% higher than the PEMEC system at -1 A·cm⁻² [36].

- Higher electrolysis efficiencies: The steam electrolysis reaction becomes increasingly endothermic as temperature increases. In these conditions, the total energy demand involves increasing heat and decreasing electrical energy demand [37]. Therefore, when electrolysis is performed at elevated temperatures, it is possible to obtain higher electrolysis efficiencies than any other fuel cell-based electrolysis technology (<110 % [38]), such as alkaline (62-82 % [38]) or polymeric electrolyzers (67-82 % [38]) and other electrolysis routes [10,39]. Combined SOEC/renewable energy systems can potentially improve power plants' efficiency, which is operated most efficiently at constant power output.

In conclusion, efficient steam electrolysis with the lowest possible investment implies a system capable of storing energy in chemical compounds, and the conversion of H₂ back into electricity and H₂O provides a viable solution for power-to-gas technologies. For this reason, cells that can work as rSOC are preferred cost-wise [5]. Under this perspective, SOEC fits more into a solution for surplus energy storage problems in renewable energy systems [40]. Stable performances of long rSOC tests for 4,000 hours are reported for single cells [41] (at 800 °C for 80 cycles of one hour in SOEC and five hours in SOFC) and 9,200 hours for stacks (at 750 °C in SOFC and 820 °C in SOEC) [42]. Also, the economic analysis indicates that the expected cost of SOEC distributed H₂ production (4.4 USD·kg⁻¹) is on par with other H₂ production technologies like natural gas reforming, low-temperature electrolysis, and MCFC/combined heat and power (CHP) systems [43]. Combined with low electricity cost projections (20 USD·MW⁻¹·h⁻¹), an aggressive electrolyzer deployment can make green hydrogen cheaper than any low-carbon alternative (i.e., < USD 1·kg⁻¹) before 2040 [44].

Supposing a rapid scale-up in the following decades, green hydrogen is expected to start becoming competitive with blue hydrogen by 2030 in a wide range of countries (those with electricity prices of 30 USD·MW⁻¹·h⁻¹). At the stack level, the lower cell voltage of SOEC results in three to four times more H₂ production than similar technologies, reportedly within the 45-50 Wh·g⁻¹ range [7]. According to estimates given in the literature, a 5 MW SOEC stack system is currently available at the cost of <2500 EUR·kW⁻¹, and this value is projected to decrease to 1090 EUR·kW⁻¹ by 2030 and 610 EUR·kW⁻¹ by 2050, due to economies of scale [4].

1.5. Types of resistances affecting the SOC performance

The analysis of electrochemical losses allows us to identify which processes are influencing the performance of the SOC, and each type of loss is relevant depending on the operating conditions of the cell. In ideal rSOC conditions, the value of $\frac{\Delta G}{nF}$ would equal the attainable EMF, as represented in the current density vs. voltage plot (I-V) of *fig. 1.6*. However, the cell voltage (E) is typically lower than the EMF due to the existence of irreversibilities when current is drawn from the SOC. This voltage drop is often referred to as cell polarization. One part of the polarization is influenced by the electrode reactions (activation overpotential), and the other occurs due to changes in the reactant concentrations (concentration overpotential). The irreversibilities can also be represented by resistive losses that are functions of the current density (I) due to operation in SOFC (E < OCV) and SOEC (E > OCV). The resistance of the cell is often measured as ASR ($\Omega \cdot \text{cm}^2$) and can be expressed as:

$$ASR = R_{ohm} + R_{pol} \quad (1.8)$$

The SOC internal resistance is generally identified via I-V curves and electrochemical impedance spectroscopy (EIS). In the I-V method, the slope of the curve is associated with the ASR. In the EIS technique, the different contributions to R_{pol} can be disclosed at their respective frequency range.

The ohmic resistance, R_{ohm} , is caused by the resistance to the conduction of ions in the electrolyte, the conduction of electrons in the electrode, and contact resistances. The contact resistances involve processes related to constriction resistances, as current collectors are contacting at different points [45].

R_{pol} is constituted by specific processes [46,47] and expressed as:

$$R_{pol} = R_{elect} + R_{dif} + R_{conv} \quad (1.9)$$

The charge transfer resistance, R_{elect} , appears because of the activation polarization. This polarization is necessary to surpass the limiting energy barrier that slows the electrochemical reaction. Finer electrode microstructures present fewer rate-limiting energy barriers that lower the R_{elect} value. This value describes the kinetics of the electron transfer reaction at the electrode/electrolyte interface. In electrochemistry, the term activation is a generalization for electrode reaction rate limitations like adsorption of

reactant molecules at the electrode, bond breaking in the reactant molecule, surface diffusion of reactant intermediates from the catalytic sites to the TPB limit, diffusion of ions through the bulk of electrode particles with mixed conduction, conduction through/around segregated phases at the surface or TPB, desorption of reaction products, transfer of ions across the electrode/electrolyte interface or transfer of electrons from electrode to a molecule [48–50]. The activation processes are generally identified at higher frequencies than other R_{pol} contributions.

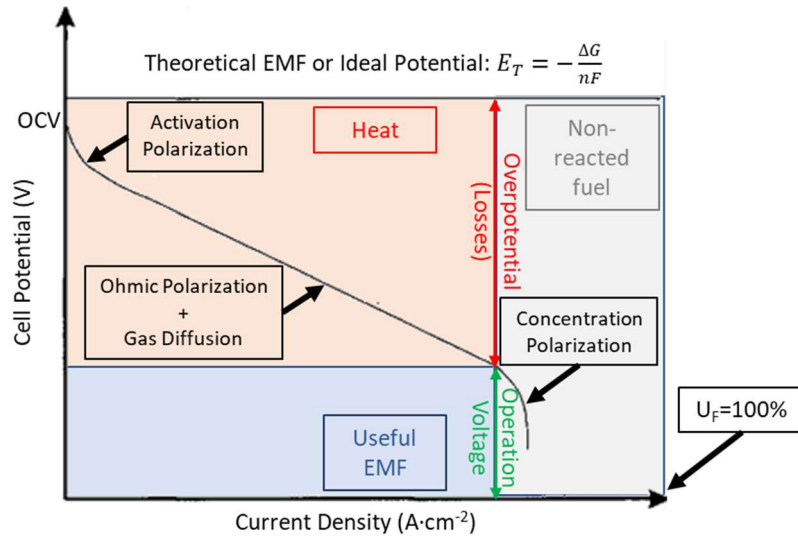


Figure 1.6. Ideal and actual current density vs. voltage (I-V) characteristics showing the types of polarizations affecting the cell. Adapted from [51].

The resistance product of the gas diffusion/concentration polarization is R_{dif} . It describes how sluggish can the electrode reactions be because of mass transport effects due to the transfer of reactants or products either outside an electrode or inside a thick, porous electrode. The R_{dif} value increases proportionally with the current density and decreases using coarser electrode microstructures that facilitate gas transport.

In SOC literature, a gas conversion process seldom appears when there is an insufficient gas concentration (or partial pressure) within fuel and oxygen electrodes' active sites [52,53]. This process produces a gas conversion impedance, R_{conv} , in EIS measurements (at a frequency < 100 Hz).

From the descriptions in this section, it is evident that the cell's internal resistance and polarization losses between the electrodes must be minimized to achieve optimal performance at a given temperature, fuel type, and oxidant composition. However,

obtaining stability over time becomes more important for practical applications in SOC systems. This is subjected to material selection and its specific properties under operating conditions.

1.6. SOC Materials

1.6.1. Electrolyte

The state-of-the-art electrolyte is the cubic stabilized zirconia (mainly 8 mol % of Y_2O_3 , 8YSZ), possessing relatively high ionic conductivity (σ_{ion}) at the traditional high-temperature ranges ($>700\text{ }^\circ\text{C}$) [54] and good electronic insulation. At further reducing potentials, electroreduction is a problem for SOC performance [55] due to electronic leaking through the YSZ. Even so, it is not entirely stable during extended operations because it tends to evolve into tetragonal zirconia and has a significantly lower σ_{ion} than cubic zirconia [56]. However, it is possible to mitigate this effect by doping with additional yttria content. Another alternative is using 10Sc1CeSZ (SSZ), a material with a higher σ_{ion} than 8YSZ [57]. At intermediate-to-low temperatures, ceria-based electrolytes are also good alternatives. However, they are not as suitable for rSOC as YSZ because the electronic conductivity (σ_{el}) is high for the fuel electrode atmospheres due to reduction into Ce^{3+} [58] producing an internal short-circuiting of the cell [59]. Some authors have proposed using a multilayer electrolyte of gadolinium-doped ceria (GDC) separated by an electronic insulator of doped zirconia [60]. Although GDC's ionic conductivity is higher than in YSZ at $<700\text{ }^\circ\text{C}$, the lower densification of these materials constitutes a problem. On the dimensionality of the electrolytes, the advantages and disadvantages of having a thin layer have been studied recently [61]. A thickness between 5 and 15 microns is more appropriate for fuel electrode-supported cells to mitigate the temperature-dependent ohmic resistance of the SOC. For mechanical stability, a thickness between 65 and 200 μm is desirable for electrolyte-supported SOC.

A collection of other electrolyte materials such as scandia-doped ceria (SDC) [62], scandia and alumina stabilized zirconia [63], YSZ/SDC [64], and lanthanum-strontium-gallium manganite (LSGM) [65] have also been tested in various SOC configurations. High ionic-conductive materials like apatites ($\text{La}_{10-x}\text{Ge}_6\text{O}_{26+\delta}$ and $\text{La}_{10-x}\text{Si}_6\text{O}_{26+\delta}$ [66]), $\text{La}_2\text{Mo}_2\text{O}_9$ (LAMOX), $\text{Bi}_2\text{V}_{1.9}\text{Cu}_{0.1}\text{O}_{5.35}$ (BICUVOX.10), and $\text{Bi}_2\text{Mg}_x\text{V}_{1-x}\text{O}_{5.5-3x/2-\delta}$ (BIMEVOX) have also been proposed as electrolytes [67], but not enough has been reported in terms of SOEC or rSOC operation.

On the other hand, proton-conducting electrolytes have proven to be successful in maintaining good electrochemical performance at lower than 650 °C. The most remarkable examples include BCY [68], $\text{La}_6\text{WO}_{12}$ [69], $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_3$ [70], and $\text{Ba}_{0.3}\text{Ti}_{0.7}\text{O}_{2.65}$ [71].

1.6.2. Fuel electrode

The use of noble metals as electrode material, although resulting in better SOFC performances for platinum-based electrodes, is considered too expensive for commercial SOC operation [72]. In consequence, researchers have taken advantage of the high activity of Ni, mainly conducting electrons, where widespread use of Ni-based fuel electrodes has been reported over the years [72]. To increase the reaction area in the fuel electrode, Ni particles are typically mixed with ionic conducting particles of the same material as the electrolyte. The most used layout is a combination of NiO-8YSZ, having a solid charge of about 60 vol. % and between 40 and 50 vol. % pore-fraction after in-situ reduction of NiO into metallic Ni [73]. The latter parameter is configured depending on if the objective is exclusively SOFC operation (35 vol. % is adequate), which would need, in general, less porosity than SOEC fuel electrodes (45 vol. %) [74,75]. The principle of this configuration is to increase the reaction area when Ni particles mix with ionic-conducting particles when charge-transfer reactions occur in the surroundings of the active TPB. H_2 /protons have low solubility and high mobility in Ni, making transport of H_2 species in the bulk of Ni-YSZ possible over short distances (0.1 μm), extending the reaction site up to 100 nm to the physical TPB [76].

The pore-former has an essential influence on the microstructure determined by the chosen additive. This allows enhanced gas diffusion after the reduction of NiO [77,78]. The most frequently reported pore formers are flour, rice, corn starch, wheat, graphite, and organic microspheres [79]. Nevertheless, carbon black and polymethyl methacrylate (PMMA) pore formers stand out. An enhanced open porosity was obtained with activated carbon particle size optimization [80]. On the other hand, PMMA has brought better results over several pore-formers, evidenced by the increasing rate of electrochemical reactions in Ni-YSZ electrodes [75,79].

In an rSOC, handling H_2O and CO_2 is pivotal because, at typical operation temperatures, Ni oxidizes rapidly when exposed to O_2 traces. A notable edge of using platinum electrodes for electrolysis is that the electrode can be operated at conditions where nickel-based electrodes would undergo oxidation, thereby avoiding recycling of H_2 or CO ; however, 99% steam can be applied to the Ni-YSZ electrode at 850 °C without

oxidation of the electrode [35]. Another topic under discussion is the Ni migration away from the vicinity of the electrolyte under SOEC operation [81]. To encapsulate this, at 800 °C is very common to find degradation over 1 A·cm⁻² in any SOC operation mode [82]. When increasing the temperature, Ni migrates from the vicinity of the electrolyte because of the loss of contact between particles [83].

1.6.3. Oxygen electrode

One of this thesis's main objectives is to study oxygen electrodes for advanced SOEC. As prerequisites, air electrode materials must have high electronic and ionic conductivity, similar thermal expansion coefficients (TEC), thermal and chemical compatibility with other SOC components, and thermal stability under oxidizing and reducing atmospheres. Also, their microstructure must be porous to promote gas transport and high catalytic activity for the ORR, and their processing must be reproducible and cost reliable. A critical factor in SOC oxygen electrodes is to introduce MIEC properties at intermediate temperature ranges (500-700 °C) to reduce the chances of degradation in performance due to grain enlargement during operation.

Commonly used oxygen electrodes are based on perovskites (ABO₃ structure, with A = lanthanide, B= transition metal) like the lanthanum-strontium manganite or La_{1-x}Sr_xMnO₃ (LSM, where x is the dopant content on the A-site cation). Additionally, perovskites possessing MIEC properties are also used, such as the double-doped lanthanum-strontium ferrite cobaltite (La_{1-x}Sr_xFe_{1-y}Co_yO₃ or LSFC, where y is the dopant content on the B-site cation) or lanthanum-strontium cobaltite (La_{1-x}Sr_xCoO₃ or LSC) [84]. LSM has been preferred over the years because of its high σ_{el} and thermal stability at usual SOC temperatures; however, at the intermediate temperature range, its σ_{el} decreases significantly [67].

With the increased interest in electrolysis, co-electrolysis, and rSOC, the interest has shifted towards lanthanide nickelates of Ruddlesden-Popper (RP) structure [85] as air electrodes due to several advantages over perovskite and double perovskite materials. For lanthanide nickelate-based electrodes, the oxygen exchange is driven by a cooperative mechanism from both the interstitial oxygen from the rock-salt layers and regular oxygen from the perovskite layers [86]. The rock-salt layers can accumulate large amounts of highly mobile interstitial oxygen, while the perovskite layers, depending on their composition, can contain oxygen vacancies [87]. Although most RP nickelates do not present a high σ_{el} like several perovskite materials, their σ_{ion} is higher at intermediate-to-low temperatures [88]. To demonstrate the viability of these materials as oxygen

electrodes, Bassat *et al.* [89] calculated their σ_{ion} values, finding that $\text{La}_2\text{NiO}_{4+\delta}$ (LNO) presented a higher value than that of $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$ (LSFN) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ (LSFC). The performance of these materials is comparable to LSM electrodes, particularly for LNO and $\text{Nd}_2\text{NiO}_{4+\delta}$ (NNO) [90], with $\text{Pr}_2\text{NiO}_{4+\delta}$ (PNO) exhibiting the lowest cathodic R_{pol} in SOFC mode and highest oxygen permeation rate [66,91,92]. The most recent reviews of lanthanide nickelate materials include studies of air electrodes in combination with proton-conducting SOC [93,94], with highly successful SOEC performances [95–97]. Yet, obtaining stability in these cells can be challenging.

The most prominent issue with nickelate-based electrodes is the reactivity of the nickelate phase with standard electrolyte materials inducing the formation of insulating phases that increase R_{pol} [98]. The phase compatibility of nickelates with electrolytes has been studied for GDC and YSZ [99] and LSGM [100], revealing that YSZ and GDC are highly reactive with PNO and LNO at 900 °C for over 24 hours, while reactivity is not as evident in LSGM for up to 72 h at 1000 °C. An interlayer (or diffusion layer) can prevent reactivity with YSZ and GDC and is also expected to facilitate the transfer of O_2 ions and avoid delamination of the electrode during aging. Doped-ceria interacts with nickelates, decomposing them and producing a Pr-doped ceria phase at 1100 °C [101]. Even with interdiffusion, the degradation rate of the electrodes is expected to be low in the long term [102]. GDC seems more suitable than YSZ and SSZ at intermediate temperatures [54] due to lower densification that can prevent the agglomeration of particles. It was also demonstrated that the Ce-Pr-Gd oxide (CPGO) interlayer diminished nickelate decomposition, finding an increase of 48% in power density [103].

Another aspect that can influence the resulting microstructure and performance of these electrodes is the type of synthesis. This is evidenced in experiments performed by Montenegro-Hernández *et al.* [104], where a series of NNO powders prepared by the solid-state reaction, hexamethylenetetramine, and citrates methods, were used and compared in terms of microstructural features. A low porosity was present for the NNO starting material prepared by solid-state reaction. This influenced the oxygen kinetic and EIS performances, as the bulk diffusion and the combination of adsorption and gas diffusion processes were identified as the rate-determining steps. On the other hand, in the electrodes with the starting powders prepared from the other two methods, the surface oxygen exchange and dissociative adsorption processes were critical for the ORR. The electrocatalysis properties are often improved via infiltration techniques [105] and composite electrodes [82]. For this reason, the use of $\text{Ln}_{n+1}\text{Ni}_n\text{O}_{3n\pm 1}$ ($\text{Ln} = \text{La}, \text{Pr}$ or Nd) infiltrated air electrodes [89,106] has been evaluated for LNO [88,107,108], NNO

[109–112] and PNO [101]. High-ordered ($2 < n < 3$) RP phases $\text{Ln}_3\text{Ni}_2\text{O}_7$ and $\text{Ln}_4\text{Ni}_3\text{O}_{10}$, which usually appear as the high-temperature decomposition of the $\text{Ln}_2\text{NiO}_{4+\delta}$ parent phase, have also been studied for the same purpose [65, 113–117]. These phases exhibit better structural stability at high temperatures, low thermal expansion coefficients (TEC), and better σ_{el} than the parent phases [114]. These materials also have chemical reactivity advantages due to the prevention of SrO surface segregation with Cr vapor from the interconnector, a common cause of degradation in SOC [88].

1.7. Objective and thesis layout

Although rSOC studies have been developed in recent years as the interest in high-temperature electrolysis has increased, suitable air electrode materials for stable long-term operation have included only a few works. Based on previous SOC's fabricated in the Institute of Nanoscience and Materials of Aragón, which have been successfully operated in SOEC, this Ph.D. thesis is dedicated to the research of PNO and doped ceria mixtures for air electrodes and the understanding of the mechanisms that affect their performance and degradation scenarios in rSOC operation.

Chapter 2 describes the experimental techniques and equipment used for the different studies performed in this work.

In *chapter 3*, the PNO and PNO-GDC mixtures are studied to evaluate the main phases' structure and composition and determine if there are detrimental products in the reactivity between the oxides at high temperatures. The formation of the CPGO phase is also studied in terms of microstructural and energy dispersive spectroscopy in scanning transmission electron microscopy (EDS-STEM) analysis of the composition. Also, to determine possible changes in the oxidation state of Ce and Pr in the samples, Electron Energy Loss Spectroscopy (EELS) for the core-loss energy range was carried out. Electrochemical studies are carried out using the electrical conductivity relaxation method (ECR) at different ranges of oxygen partial pressures at high temperatures. Symmetrical cells of the analyzed air electrode composites are prepared to be evaluated in EIS studies and distribution of relaxation times (DRT) analyses.

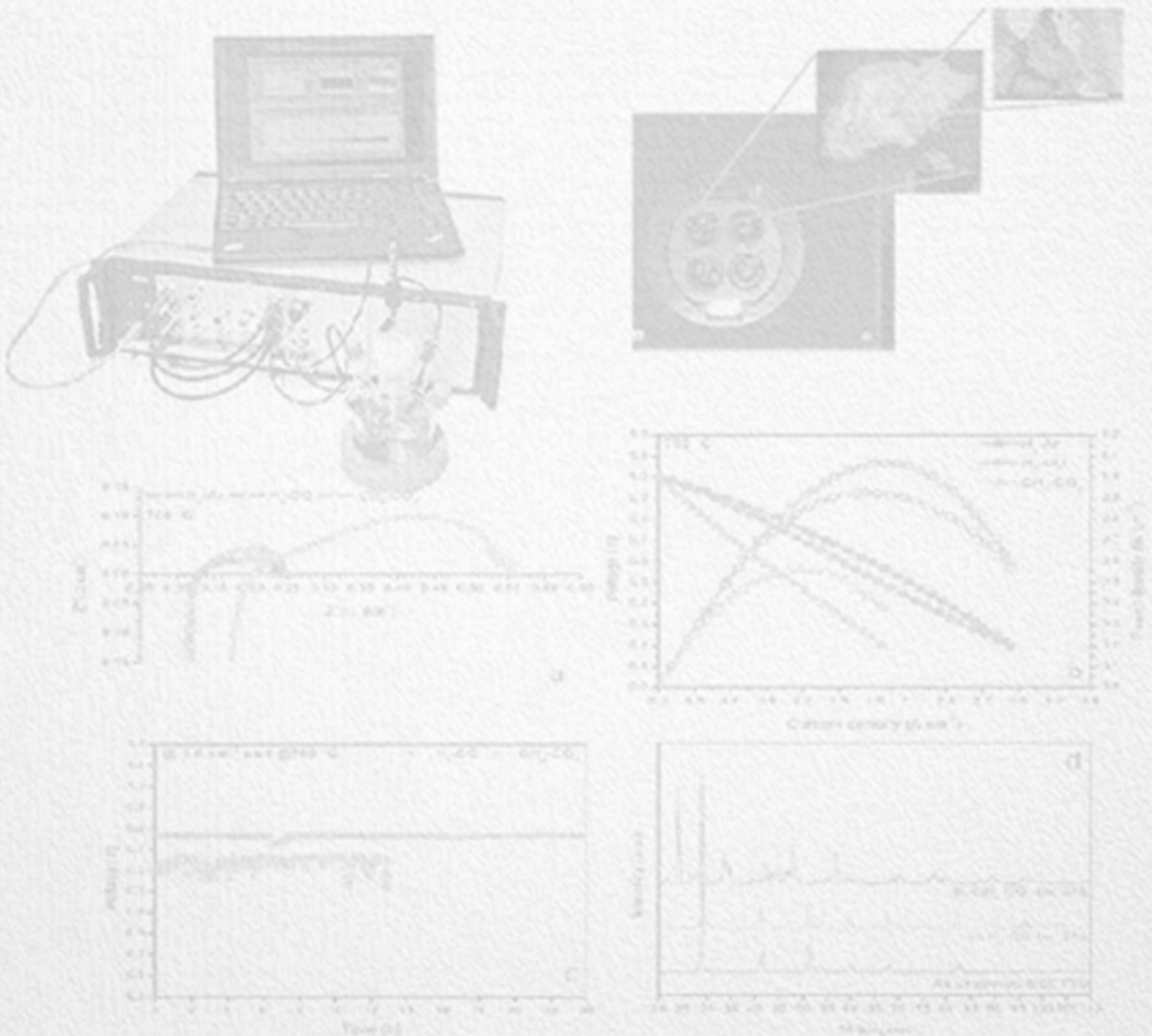
Chapters 4 and 5 employed PNO-GDC mixtures to prepare composite air electrodes in complete tubular SOC's. *Chapter 4* also describes the performance and durability of rSOC's at different operation conditions using conventional solid-state reaction synthesis. The cells are characterized through I-V-P curves, EIS, DRT, and postmortem scanning electron microscopy (SEM). Similar to *chapter 4*, in *chapter 5*, I-V-P curves, EIS, DRT,

and microstructural SEM techniques are employed to characterize polarization losses in single tubular cells with composite air electrodes composed of nickelate and PrO_x infiltrated nanocatalysts. These studies aim to verify the rate-determining processes in the R_{pol} and the stability of rSOC using the selected air electrodes.

Chapter 2. Experimental Techniques

SOC electroceramic components are advanced materials whose physicochemical properties and applications depend on a close control of their structure, composition, surface, and distribution of dopants. For this reason, diverse methods and techniques must be selected accordingly to characterize the materials appropriately.

This chapter intends to give a brief, yet insightful, description of the contextual framework in which the experimental work has been developed for SOC fabrication and their respective structural, microstructural, and electrical characterizations. A more detailed representation of the controls, mechanisms, tests, and media in the manufacturing and characterization processes is presented in *chapters 3 to 5*.



2.1. Introduction

This section includes the selected methodology from the synthesis of ceramic powders, the SOC assembly of components resulting from layer deposition, the subsequent thermal treatment, and the prototypes' structural/microstructural and electrochemical characterization.

2.2. Fabrication techniques

The primary purpose of high-performance SOC component fabrication involves obtaining non-agglomerated powders with uniform size distribution and sintering to near theoretical density without grain growth. In this work, the slurry technique is employed for SOC component fabrication, where efforts were made to ensure appropriate control of the particle size of the starting powders and the stability/homogeneity of the suspension, avoiding the presence of agglomerates and surface contamination [118].

The techniques selected for the SOC support fabrication require producing compositions at a low cost while maintaining control of the green piece shapes. Powder extrusion molding (PEM) and slip casting were the methods that fit these requirements for fuel electrode support fabrication. The dip coating method is employed to fabricate electrolyte, scaffold, and air electrode layers as it is a suitable technique that complements the ones used for the support fabrication. A vacuum is implemented for nanocatalyst infiltration in porous scaffolds to help promote the catalytic activity in air electrode microstructures. These methods were already developed in our group (PEM) and the group of Prof. Thomas Etsell of University of Alberta (slip casting) for the fabrication of tubular cells.

2.2.1. Slip casting

The slip-casting method entails filtration and fluid removal to shape green pieces by pouring a stable suspension (or slurry) into a porous mold [119]. These molds are customarily made of plaster shaped in the form of the desired piece, i.e., with a metallic element (*fig. 2.1a*), and then dried for 48 hours before the casting (*fig. 2.1b*). The cast slurry is poured into the molds after this stage (*fig. 2.1c*), and the excess liquid is removed at the end of the casting process. The piece is dried in two stages: a partial step after depositing the slip and another before sintering. With this process, complex components are adjusted to the design of the mold with high homogeneity of the shaped material while maintaining reasonable control of the thickness of the green parts (*fig. 2.1d*).

The ceramic suspension of the slip must meet specific requirements for a successful cast. To begin with, the particle size of the material in suspension must be small enough ($< 1\ \mu\text{m}$) to prevent sedimentation. In addition, the suspensions must have good stability to avoid agglomerates.

Also, properties like low volatility, no reactivity with dust and additives, and the possibility of dissolving these additives are sought during the optimization of the slurries. A polar liquid such as water is preferably used as a solvent in the suspensions to obtain these characteristics. Typically, homogeneous ceramic suspensions are obtained using dispersing and agglomerating agents and continuous magnetic stirring [119].

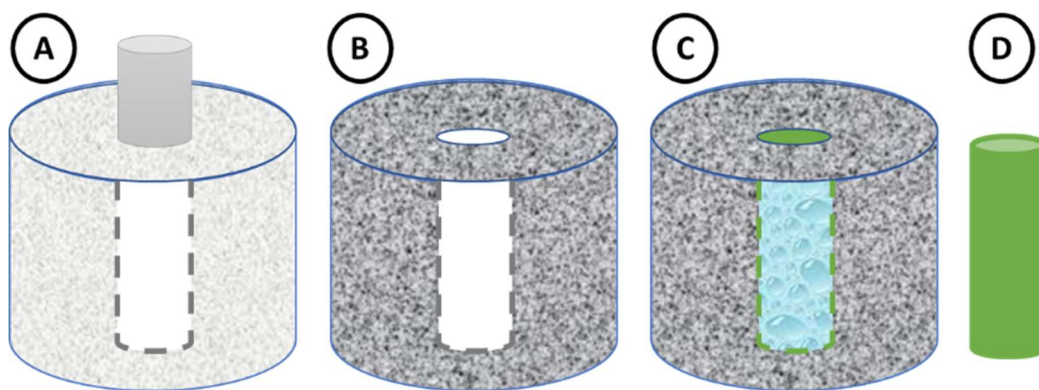


Figure 2.1. Schematic diagram of the slip casting route. a) plaster solution with a metallic test tube to shape the mold. b) dry tubular plaster mold. c) mold filled with the slurry. d) final green piece.

This method was used to fabricate tubular supports at the University of Alberta, and additional details will be given in section 5.2.

2.2.2. Powder extrusion molding (PEM)

The PEM technique, widely used in the industry to form plastic pieces with a constant tubular section, can also produce ceramic pieces [78]. This method embodies passing a material with certain plasticity through a nozzle at high pressures.

The equipment used for the microtubular support fabrication is a twin screw extruder (Haake Rheomex OS). In this type of equipment, the pressure necessary for the process is obtained from the torque to the spindles that rotate in a cylindrical chamber (*fig 2.2*). The temperature in the different zones is controlled independently as it passes from the reactor zone to the compression zone.

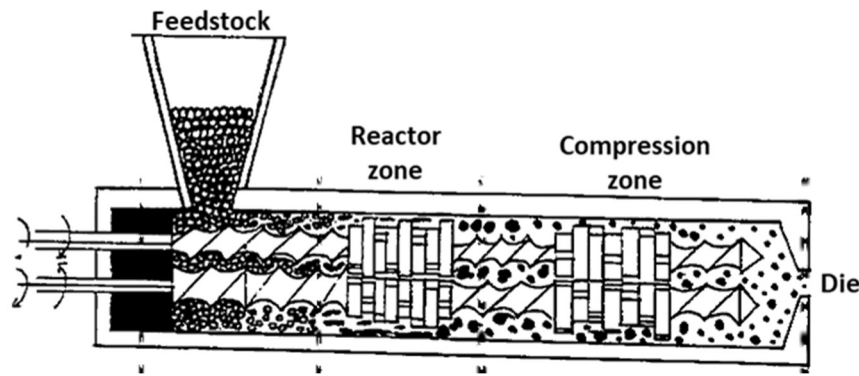


Figure 2.2. Schematic diagram describing a twin-screw extruder under preset temperature zones along the extruder axis [120].

The material must obtain plasticity and creep properties, for which it requires using a binder system composed mainly of extrudable plastics and a certain amount of ceramic powder. The binder system selected for this work was thermoplastic since it presents substantial advantages for the conformation of green parts compared to other binder systems, such as soluble or thermostable ones. Among these advantages are the excellent resistance of the green parts after forming, better contour quality, recyclability of the feedstock, and low abrasion of the machinery. The disadvantage is that the elimination of the thermoplastic system takes longer than the other binder system types. Once the part has been shaped, the binder system can be eliminated using heat and non-polar solvents like heptane.

Section 4.3.1 offers the details for the elaboration of microtubular supports, proportions of the binder system and solids load, thermal profiles of the extruder, and extrusion speed, among others, which have been previously optimized in collaboration with Dr. Alejandro Várez's group at the University Carlos III of Madrid (UC3M) [78,81,121–123].

2.2.3. Dip coating

The dip coating method involves immersing a substrate in a precursor ceramic solution and lifting it vertically with a controlled velocity [119]. Despite its simple appearance, the dip-coating process involves a complex interplay between many counteracting factors: viscous drag upward on the liquid by the moving substrate, the force of gravity on the wet film, surface tension in the concavely shaped meniscus, surface tension gradient along the height of the film due to drying effects, among others [124,125]. Critical parameters like suspension viscosity, extraction speed, the number of immersions, and immersion time must be monitored to control these processes and regulate the thickness of the deposited layers.

This technique was used to fabricate different SOC component layers, including electrolyte, barrier layer, and oxygen electrode layer. For all the layers coated in this work, the zone intended for the coating is left exposed, and the rest is covered by polytetrafluoroethylene (PTFE). A homemade apparatus is adapted with an electric motor to carry out the dip coating procedure. A schematic of the dip coating process used for layer deposition is shown in *fig. 2.3*.

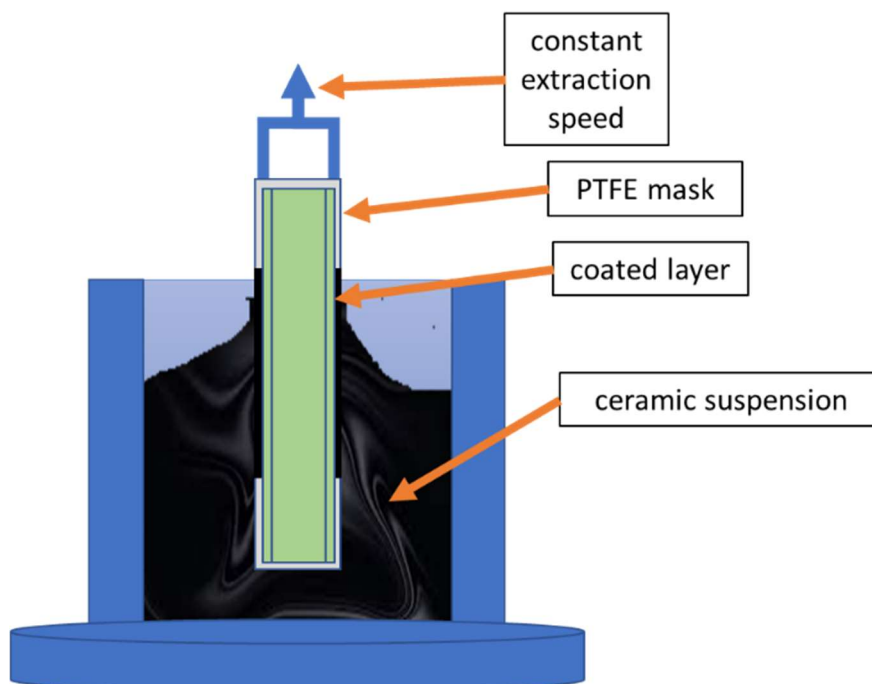


Figure 2.3. The dip coating setup.

Initially, the air electrode ceramic solutions (*fig. 2.4*) are made from 15 ml of ceramic solution, typically ~15 vol. % of solids in an ethanol solution, 2 vol. % α -terpineol, and Polyvinyl Butyral – PVB (2.5 vol. % for Ce-based interlayers and 5 vol.% for nickelate-based electrodes). Magnetic stirring in each solution was carried out by placing a magnetic rod inside a chemical vessel with ethanol for 25 minutes. Then, ultrasound treatment is used to homogenize the ceramic solution with one minute per test and intervals of 15 seconds per cycle. An ice bath is applied to avoid changes in the solution composition due to the temperature effect.

Finally, for the air electrode solutions, two dip coatings were made at $4.5 \text{ mm} \cdot \text{s}^{-1}$, while for electrolyte and interlayers, three immersions at $3.0 \text{ mm} \cdot \text{s}^{-1}$ were performed. For the symmetrical cell fabrication, the nickelate-based electrode layers were coated on

uniaxially-pressed pellets fabricated from a GDC powder (FuelCell Materials) sintered at 1400 °C for 2 h with up/down ramps of 2 °C·min⁻¹. The GDC electrolyte obtained had a diameter of $\approx$ 18 mm and a thickness of $\approx$ 1.2 mm. On single cells, the dip coating process is performed on top of the fuel electrode support for the electrolyte and air electrode layers (in that order), as described in *chapters 4 and 5*.

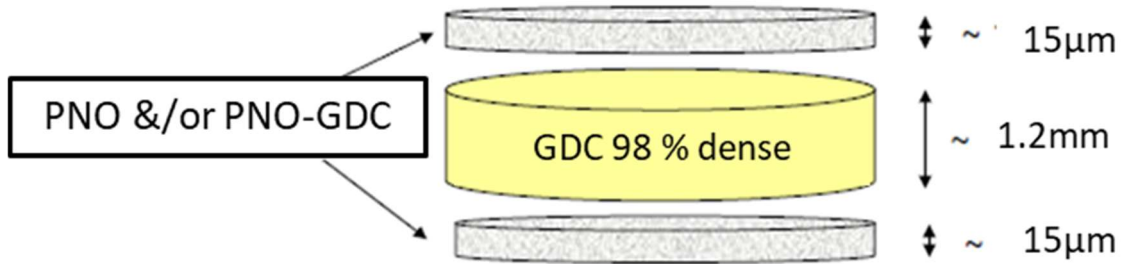


Figure 2.4. Prepared symmetrical SOC components and dimensions.

2.2.4. Vacuum infiltration

Vacuum infiltration is a deposition technique on porous substrates that allows the filling of these substrates with a suspension or solution [126]. This technique has been used for the deposition of nanoparticles in porous scaffolds by infiltration of salts followed by a calcination stage.

The catalyst infiltration in thin and porous scaffolds [126] (*fig. 2.5a*) employs nanosized ceramic powders synthesized by chemical precipitation and reaction routes. The scaffold is first deposited on top of a dense electrolyte and is composed of a high ionic conductor like GDC or YSZ and the addition of pore former to the ceramic suspension. Using this process, a nitrate solution containing a precipitating agent is added to the solution containing the cation of the desired oxide. By applying vacuum infiltration, more particles can penetrate the scaffold surface. In this route, vacuum pressure levels below the liquid boiling point are used to maintain the composition of the liquid before infiltration. When the desired vacuum has been reached, the vacuum line is closed, and the air is slowly allowed to enter through the vacuum intake so that the pressure of this air causes the liquid to flow through the conduit to the empty sample chamber. Once the sample is entirely covered by the infiltrated liquid (*fig. 2.5b*), the vacuum of the entire system can be eliminated.

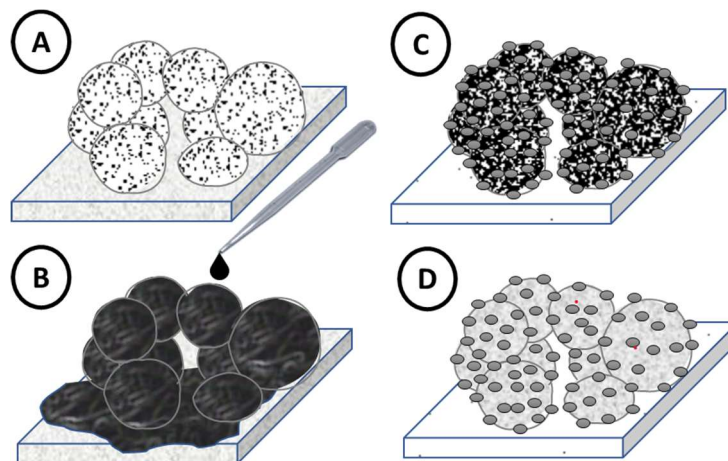


Figure 2.5. Schematic of the infiltration process: a) thin, porous scaffold layer; b) substrate after the vacuum infiltration process; c) after firing, the calcination residual excess surges on the top of the scaffold surface; d) composite appearance after cleaning of residual excess. Based on [126].

The firing of the precipitates follows this step to decompose the nitrates. The calcination process promotes the redox reaction between the organic component and metal nitrates. Eventually, it releases the residual carbonate and the decomposition of metal nitrates, resulting in a composite nanopowder with small grain size and homogeneous microstructure. The residual carbonate excess surge to the scaffold surface must be cleaned as it does not contribute to the catalysis (*fig. 2.5c-d*). This process is repeated until the solid loading of the nitrates inside the scaffold reaches the desired weight gain of the infiltrates. For composite nanopowder fabrication, this method is superior to other techniques for its low processing temperature, low cost, precise control of cationic composition, and homogeneous phase distribution [127].

2.3. Structural, thermal, and chemical characterizations

2.3.1. X-ray powder diffraction

The X-ray powder diffraction (XRD) approach involves several interferences that produce X-ray waves at specific directions in space after being diffracted by ordered electric charge distributions [128]. This way, it is possible to determine the crystallographic structure of a compound, quantify the phases present in a mixture, identify the size of the crystal grains, preferential orientations, and study crystallographic transitions as a function of temperature.

The employed powder diffractometer has a Bragg-Brentano type geometry (*fig. 2.6*) in which the electronic counter can form a variable angle (typically $2\theta = 3^\circ\text{--}110^\circ$) with the incident X-ray beam. The sample is in the center of the axis of a precision goniometer, whose angular velocity is in a 2:1 ratio to the detector.

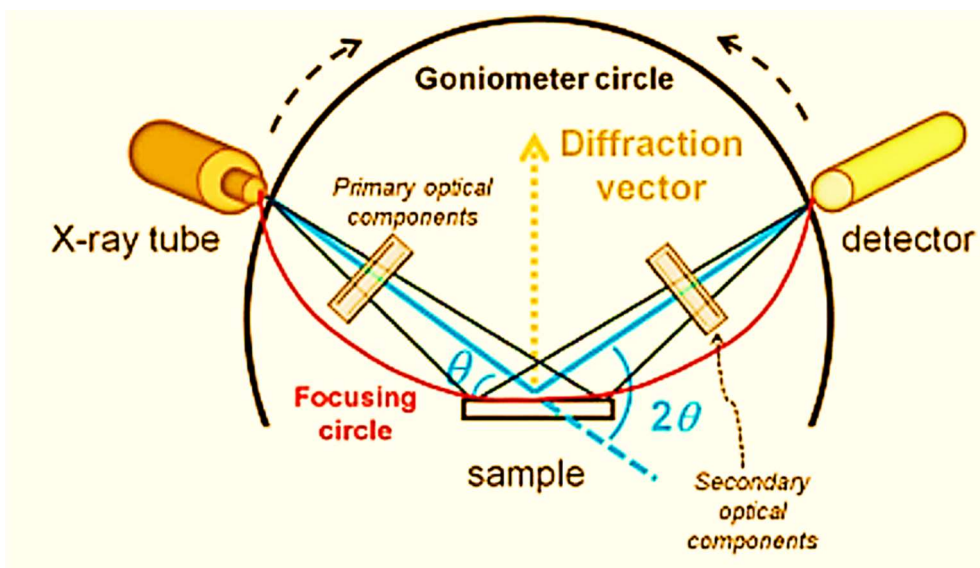


Figure 2.6. Schematic of the Bragg-Brentano diffractometer [129].

The graphic record or diffractogram is formed by a series of peaks distributed according to the angular value 2θ and corresponds to characteristic reflections of a compound. The height and width of these peaks will indicate the intensity of each reflection. Most of the XRD analyses of this work use a D-Max Rigaku detector with a low-voltage rotating copper anode, except for the results in chapter 5, where a cobalt anode was used instead.

The lattice parameters and phase quantification information can be extracted from XRD data by comparing the theoretical and the experimental diffraction patterns and minimizing (refining) the differences between the data sets by the least square method. Common differences between data sets include peak width, intensity, and shifts. The refinement method often employs a peak shape function fitting (Pseudo Voigt, Lorentzian, or Gaussian) of a reference XRD pattern to minimize discrepancies. A Lorentzian function is applied to the XRD data refinements in our fittings using the Fullprof [130] and Profex [131] software.

2.3.2. Dilatometry

Dilatometry is a technique that measures the variation in a sample size subjected to a thermal process [132]. During the sintering of solid parts, a volume contraction is induced on the material because of the filling of the empty spaces between particles. The use of dilatometry allows real-time monitoring of length variations during heat treatment. The length variation of the sample is described by:

$$\Delta L = \frac{L - L_0}{L_0} \quad (2.1)$$

where L is the length after the dilatometry test and L_0 , is its reference length.

This technique is essential to adjust the sintering treatments of materials with different properties and evaluate their thermal compatibility. It is critical to know the thermal compatibility of materials since their contraction at different rates produces delamination of the components. The thermal expansion coefficient (TEC) is obtained from the contraction data generated in eq. 2.1, through its heating or cooling ramp. With this method, it is possible to identify different layer configurations that suit the thermal compatibility between the cell components, such as modifying the materials' granulometry and using functional layers and additives.

The dilatometer consists of a furnace in which the sample is placed in contact with an alumina pushrod directed at a position sensor, as shown in *fig. 2.7*. The equipment used is a thermomechanical dilatometer SETSYS 200 from Setaram.

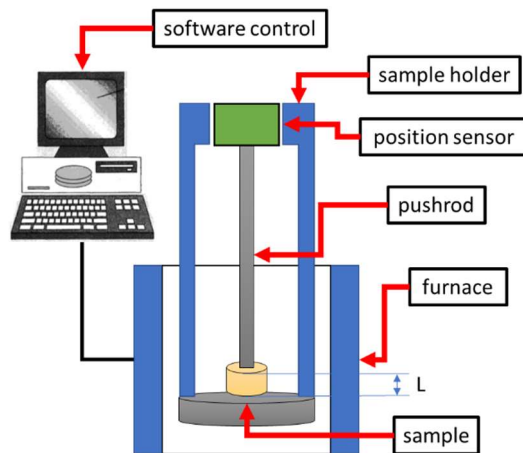


Figure 2.7. Diagram of operation of a dilatometer.

2.3.3. Atomic emission spectrometry

The atomic emission spectrometry technique was employed to accurately determine the composition of the starting oxides [133]. The optical emission spectrometer with an inductively-coupled plasma excitation source (ICP-OES) SPECTRO Arcos was employed for the chemical characterization of the samples. The measurements were performed at the Geological Techniques Unit of the Complutense University of Madrid.

The sample powders are digested and projected into a nebulization chamber using a peristaltic pump. The digestion methods involved using HNO₃, HF, and HCl for the rare earth materials studied in this work. The powders are then vaporized and excited, resulting in the emission of optical radiation. In detail, this method uses an ICP, an ionized gas formed by the working gas (Ar) in a high-frequency electromagnetic field when high-frequency current flows through an induction coil. At temperatures of around 9700 °C, the generated plasma torch emits electromagnetic radiation in the optical range, which is dispersed by a monochromator, forming a spectrum. The element quantification depends on the relation between the signal intensity and analytes concentration. This study's typical wavelength values for rare earth materials are 393-446, 390-423, and 303-377 nm for Ce, Pr, and Gd, respectively.

This method presents low detection limits (in ng/mL) mainly determined by the standard deviation of background signal and equivalent background concentration, about 1–2 magnitudes lower than that obtained by techniques like graphite furnace atomic absorption spectrometry (GFAAS) for all but a few elements. Even for these elements, the simplicity with which the ICP-OES instrument is operated often outweighs the loss in sensitivity [134].

2.4. Microstructural characterization

2.4.1. Scanning electron microscopy

Scanning electron microscopy (SEM) entails the incidence of a focused electron beam (generally between 0.2 and 40 kV) scanning a region of the sample placed in a vacuum chamber (*fig. 2.8a*). The SEM explores the surface of the image point by point, unlike the TEM and the Optical Microscope, which simultaneously illuminate the entire area of the sample [135].

Upon striking the sample, the electrons scatter through the surface, emit a signal picked up by the detector specified by the user, and generate an image. The most common particles emitted by the sample to produce the image are secondary electrons (SE), back-scattered electrons (BSE), and characteristic X-rays.

The SE are those low-energy electrons produced in the collision between electrons. Therefore, those electrons that penetrate deep into the sample are absorbed, and only SE close to the surface can escape from the specimen. The emission is higher on surfaces not perpendicular to the beam, resulting in images with high morphological contrast. SE signals collected by Everhart-Thornley detectors integrate an electron collector formed by a positively biased grid to attract them toward a scintillator.

On the contrary, BSE electrons are detected by a semiconductor device usually placed surrounding the electron beam exit piece. They are commonly used to get compositional contrast between the different phases.

Fig. 2.8b shows the positions of the main detectors used in SEM: Everhart-Thornley in the sample chamber, Inlens, and BSE.

In this work, we have used a Merlin Field Emission SEM (Carl Zeiss) capable of operating at electron acceleration voltages up to 30 kV. This instrumentation is equipped with an INCA 450 EDS detector (Oxford Instruments).

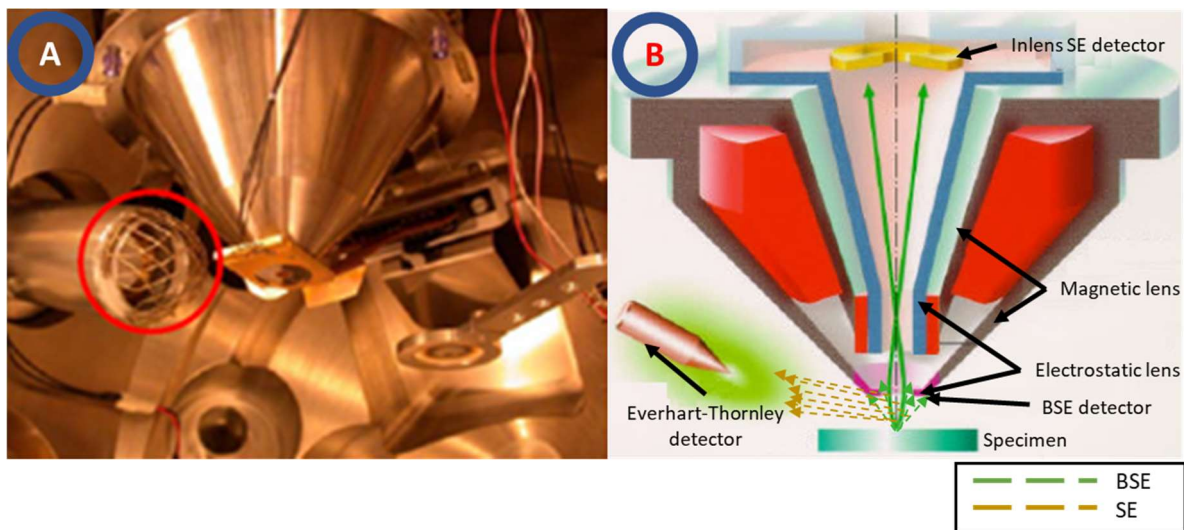


Figure 2.8. a) SEM sample chamber [136]. b) Positions of the Inlens detector, lateral (Everhart-Thornley) detector in the sample chamber, and the BSE detector [137].

The steps for SEM sample preparation are shown in *fig. 2.9*. Initially, the samples are cut using a STRUERS Secotom-10 cutter with a BUEHLER diamond blade in transverse or longitudinal sections to obtain manageable dimensions for the experimental image. Next, the samples are embedded in an EPOFIX epoxy resin (STRUERS) inside a vacuum chamber. Afterward, the SEM sample is polished (STRUERS Laboforce-1) with SiC papers of decreasing grain size. Subsequently, diamond paste of 3 and 1 μm is applied, followed by a colloidal silica solution. During polishing, optical microscopy is used to observe if any defects or lines are present in the polished sample.

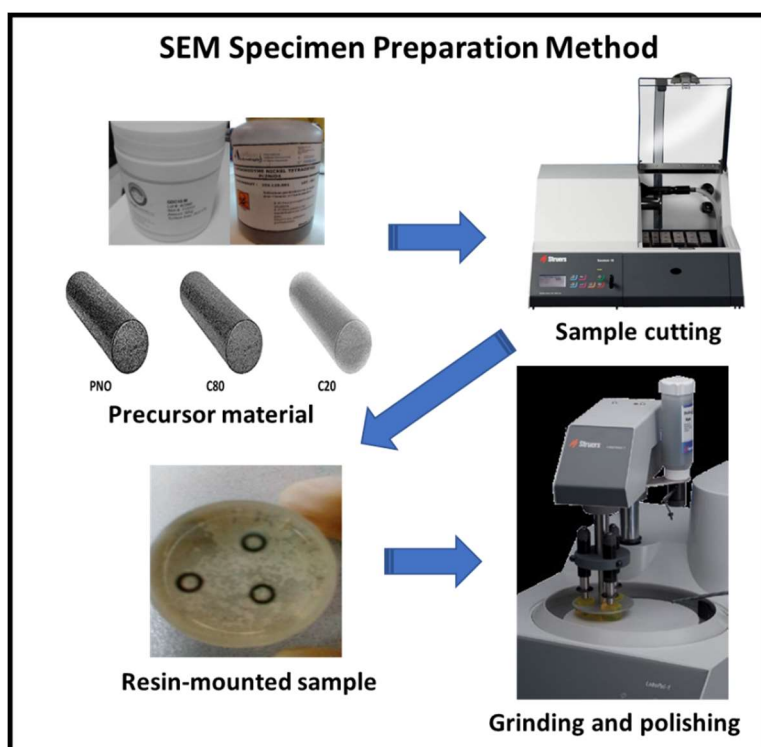


Figure 2.9. Schematic of sample preparation for SEM experiments.

Occasionally, fractured samples have also been observed. In this case, a section of interest in the sample is broken into pieces and added to the sample holder using carbon tape.

The samples observed with high-energy electrons (>3 kV) have been coated by evaporating a carbon filament in a vacuum chamber to prevent them from charging during observation.

2.4.2. Transmission electron microscopy

The transmission electron microscopy (TEM) operating principle is based on irradiating a thin sample with an electron beam of energy typically between 80 and 300 kV [138].

Using this technique is possible to achieve atomic resolution and use the transmission of electrons to form images, electron diffraction to obtain information about the crystalline structure, and characteristic X-ray emission to determine the chemical composition of the sample through EDS.

For the analysis of our samples, we used the imaging mode, where electrons are emitted by an electron filament and focused by condenser lenses on the thin sample. Electrons passing through the sample are collected and focused by the objective lens into an enlarged intermediate image. This image is magnified by projection lenses, controlling the magnification of the image on the projection screen. The observation screen is covered with a phosphorescent material that, when exposed to the electron beam, emits a green light proportional to the beam's intensity, allowing the final image to be viewed. A charge-coupled device (CCD) type sensor digitally records the image.

2.4.3. Scanning transmission electron microscopy

Scanning transmission electron microscopy (STEM) is an extension of the TEM technique. The electron beam is portrayed in a fine spot (0.05 – 0.2 nm range) scanned over the specimen using a raster illumination system parallel to the optical axis. This feature makes STEM suitable for several imaging techniques, such as bright field (STEM-BF), annular dark field (STEM-ADF), and high-angle ADF (STEM-HAADF) imaging, as shown in *fig. 2.10*. Also, spectroscopic mapping by EDS or electron energy loss spectroscopy (EELS) can be obtained simultaneously, allowing a direct correlation of images and spectroscopic data.

The STEM-BF collects the electron beam directly in STEM through a circular detector. STEM-ADF uses an annular detector slightly larger than the direct beam in STEM-BF. STEM-HAADF, on the other hand, uses an annular detector with a larger hole to collect the scattering produced at a high angle. In this technique, diffraction contrast disappears using a Z-contrast image ($\text{intensity} \propto Z^{1.7}$) instead.

For our specimens, STEM-HAADF images were acquired using a Titan 80–300 (Thermo Fisher Scientific) STEM equipped with a Fischione detector and a CEOS DCOR probe spherical aberration corrector (CEOS GmbH) operated at 300 kV.

STEM samples were prepared using a suspension of the powder sample in acetone. This suspension was poured onto holey carbon Cu grids and Au grids and then carbon-coated to avoid charging.

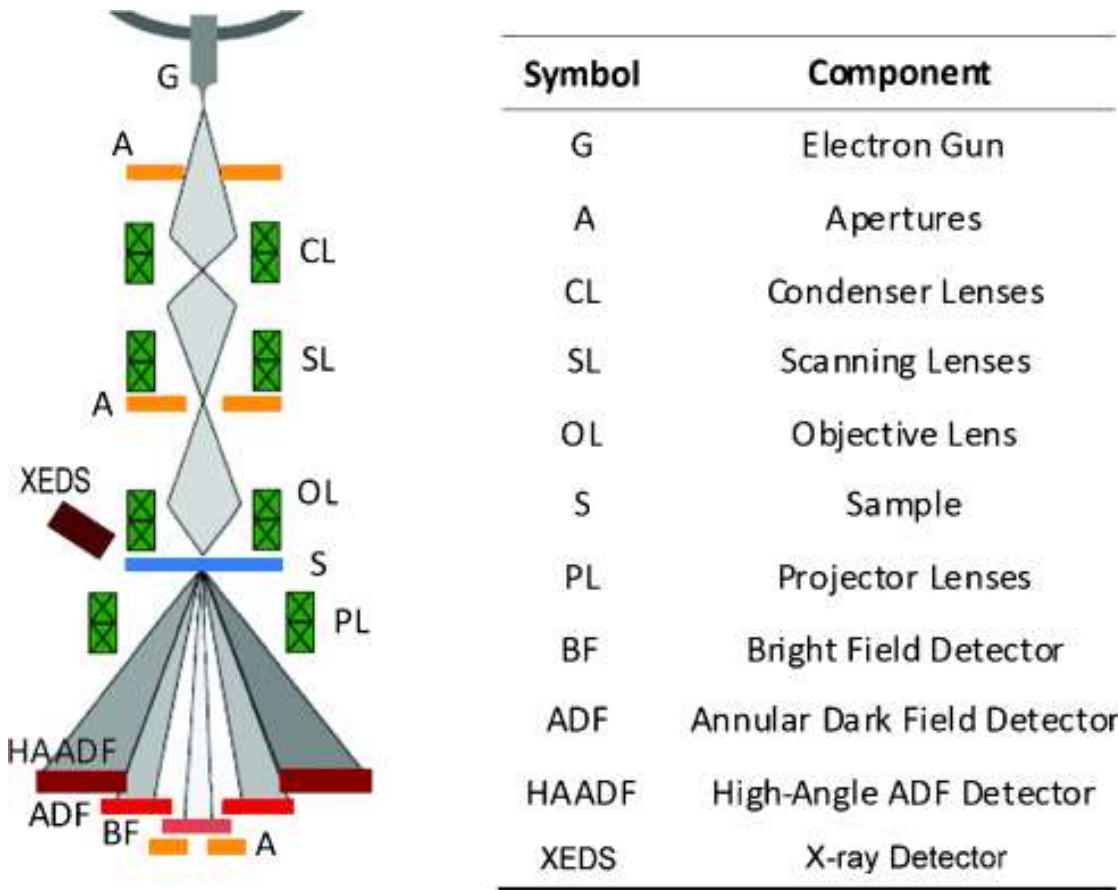


Figure 2.10. STEM main detectors and standard positions of the spectrometers with contrast mode configurations to obtain DF images [139].

2.4.4. EDS-STEM

The energy-dispersive X-ray spectroscopy (EDS) technique is based on the X-rays generated as a product of the electron beam interaction with the sample, allowing the elements present to be identified and their concentration to be established. When a sufficiently accelerated electron beam strikes the surface of a solid, the ionization of the atoms present occurs, that is, the loss of internal electrons. In this state, an electron from an outermost shell immediately jumps to the deficient inner shell filling the gap produced. This jump implies a release of energy whose value equals each electron’s energy difference in its corresponding orbital. This energy is manifested in Auger electrons or X-rays and is unique to each element. When the intensity of this electromagnetic radiation is plotted against its energy, an X-ray spectrum is obtained. This spectrum comprises a

series of peaks, designated as lines of variable intensity, which we call characteristic X-rays, superimposed on a continuous background of lower intensity (continuous X-rays).

The main difference between EDS microanalysis in SEM and STEM is spatial resolution. Since the samples in STEM are extremely thin, fluorescence-driven X-ray emission and electron scattering processes in the sample itself are highly unlikely. This implies that, while the spatial resolution of the microanalysis in the SEM is of the order of a few microns, in the STEM, this resolution improves to even atomic resolution. For this reason, we performed most of the quantitative microanalyses in STEM.

For the compound quantification in EDS-STEM, the thin foil criterion was applied. This criterion states that the TEM sample is thin enough, so X-ray absorption and fluorescence within the specimen are negligible [138,140]. The Cliff-Lorimer technique [140] is a qualitative measurement method that uses sensitivity parameters k_{AB} related to the atomic number correction factor under the thin foil criterion. In binary systems, the concentration of element A concerning element B is related to their respective X-ray energy intensities by a sensitivity parameter:

$$\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B} \quad (2.2)$$

where C and I denote the elements' concentrations and X-ray intensities, respectively. k_{AB} is not considered a constant because their value can change between EDS-TEM detector configurations.

In this work, we have used the Cliff-Lorimer sensitivity parameter method with both experimental profiles and standard compounds to improve our EDS-STEM quantification accuracy. The INCA software was employed for the fitting of the experimental profiles.

2.4.5. Electron energy-loss spectroscopy

Electron energy loss spectroscopy (EELS) uses the energy-loss distribution of electrons that pass through a thin sample to analyze their content (*fig. 2.11a*). This feature is a powerful technique that provides compositional and chemical information from the sample's sub-nanometer areas [141].

EELS instrumentation is usually incorporated into STEM. In this equipment, high-energy electrons interacting with the sample produce myriad signals (*fig. 2.11b*) due to elastic (no energy exchange) and inelastic processes where some incident beam electrons lose energy. The inelastic scattering interactions generate X-rays and other secondary

electrons (caused by the sample relaxation after the inelastic event) and processes that result from collective interactions with many atoms or electrons. The EELS were acquired using a Tridiem spectrometer (Gatan) in this work.

EELS data typically consists of either detailed, energy-loss spectral information from the sample (spectroscopy) or images that have contrast created by the energy-loss properties of the distribution of the material in the sample (energy-filtered TEM). These methods can be combined in a technique called spectrum imaging, where spectral information is collected in a spatially resolved manner. This data from EELS signals can extract specimen information using the 3D data cube method (*fig. 2.11a and 2.11c*) that analyzes the 2D image and creates a third dimension of energy loss along the plane. A more detailed explanation of how this method works is presented in chapter 3.

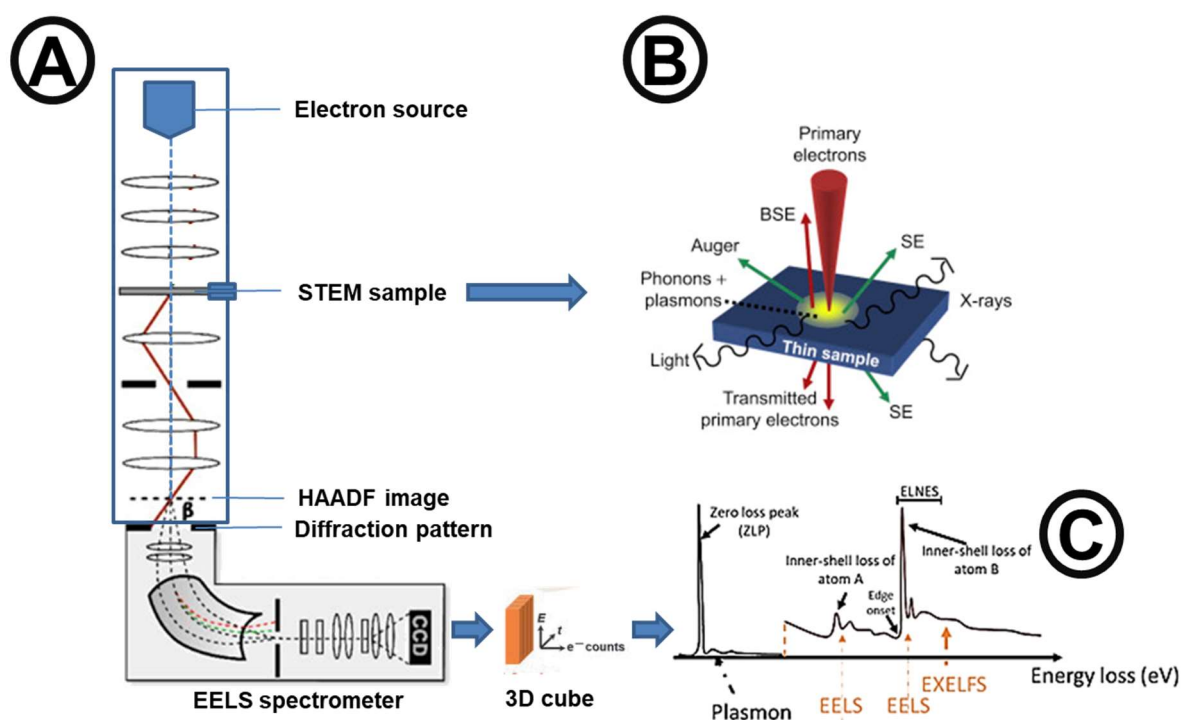


Figure 2.11. a) STEM-EELS instrumentation [142]. b) Useful signals generated by electron-matter interactions in a thin sample [143]. c) Interpretation of EELS main peaks and their relationship with the conduction and valence band structure.

The energy loss spectrum (*fig. 2.11c*) is typically separated into three regions: electrons that have not lost energy (zero-loss peak or ZLP), electrons that have interacted with the weakly bound electrons in the sample (low-loss distribution), and the electrons that have interacted with the tightly bound core electrons of the atoms (the ionization edges or

core-loss region). From the ZLP and low-loss zones, the specimen thickness can be calculated using different methods like the Kramers-König sum rule [141] or the Log-ratio method [144]. The low-loss distribution includes valence/conduction electron density as plasmon peaks (collective free-electron oscillations) produced due to beam electron interactions with the specimen.

The elemental information of the specimen is given in the core loss region (> 50 eV), where the energy-loss edges increase with increasing atomic number, and we can quickly find out what elements constitute the part of the specimen interacting with the electron beam and calculate the amount of each element in quite a straightforward manner. When a high-energy electron encounters an atom, it first penetrates the outer, loosely bound electron cloud, passes the more tightly bound inner (or core) shell electrons, and finally, may encounter the nucleus. The deeper the electron interaction, the greater the energy that may be lost. Bonding and oxidation state information (density of unoccupied states) can be found in the near-edge fine structure (ELNES). This is done, for instance, by analyzing the peak intensity M_5/M_4 ratios in the core-loss spectrum range, which determines the oxidation states of the cations in the specimen. The extended energy loss fine structure (EXELFS) is where small intensity oscillations may be detectable due to diffraction effects from the atoms. In addition to these spectrally related signals, contrast and resolution enhancements of the images can be created by filtering in energy space (e.g., allowing only the zero-loss electrons to form the image) [141].

The main limitation of the EELS technique is the effect of sample thickness. As the sample thickness increases, the strong interaction of primary electrons within the sample results in the electrons undergoing multiple energy loss events. This tends to reduce the signal-to-background ratio of the EELS edges and the visibility of the edges.

2.5. Electrical characterization techniques

2.5.1. DC conductivity

The DC conductivity measurements of this work were performed using the four-point technique to account for the contact resistance contribution (*fig. 2.12*), as many of the materials studied are good electronic conductors. This technique involves applying a potential difference and measuring the current through separate contacts. Usually, platinum wires are connected at the edges of the samples (current terminals) and in the

center (voltage sensing) with equidistant separation. The resistivity R_0 of the sample is calculated as follows:

$$R_0 = \frac{\rho L}{S} \quad (2.3)$$

where ρ is the resistivity of the material, L is the length between the contacts and S is the cross section where the electrical current is passing.

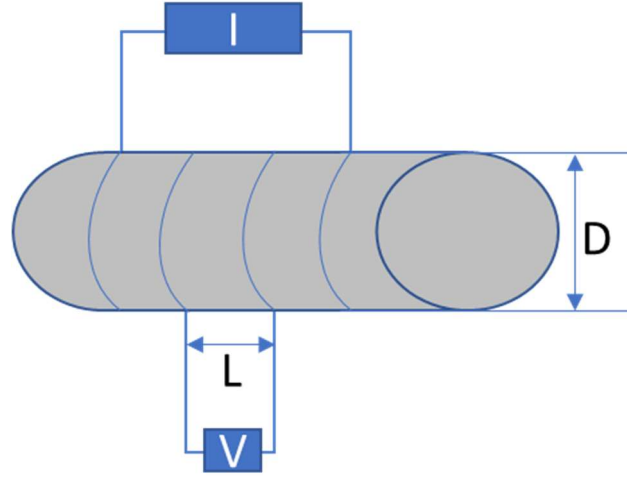


Figure 2.12. Four-point probe configuration for DC conductivity tests in a cylindrical sample.

2.5.2. Electrical conductivity relaxation

Electrical conductivity relaxation (ECR) is the measurement of electronic conductivity under a fixed voltage and different oxygen partial pressure changes (ΔpO_2) until a relaxation time is achieved. ECR is one of the experimental procedures in solid-state electrochemistry for estimating ceramic materials' oxygen chemical diffusion (D_{chem}) and surface reaction exchange (k_{ex}) coefficients of materials. Its principle derives from the solution of Fick's 2nd law of diffusion describing the rate of accumulation (or depletion, $\frac{\partial c}{\partial t}$) of concentration (c) within a volume as proportional to the local curvature of the concentration gradient (eq. 2.4) [145]. This accumulation is proportional to the diffusivity (D):

$$\frac{\partial c}{\partial t} = D \nabla^2 c \quad (2.4)$$

The relaxation process is determined by the rate of the oxygen exchange reaction at the surfaces and the degree to which the materials adapt their oxygen stoichiometry to attain

equilibrium under ΔpO_2 . This process is modeled by the expression of eq. 2.4 using linear absorption boundary conditions:

$$\begin{aligned}
-D_{chem} \frac{\partial c}{\partial x} \Big|_{x=\pm l_x} &= k_{ex} (c_\infty - c(t, x = \pm l_x, y, z)) \\
-D_{chem} \frac{\partial c}{\partial y} \Big|_{y=\pm l_y} &= k_{ex} (c_\infty - c(t, x, y = \pm l_y, z)) \\
-D_{che} \frac{\partial c}{\partial z} \Big|_{z=\pm l_z} &= k_{ex} (c_\infty - c(t, x, y, z = \pm l_z))
\end{aligned} \tag{2.5}$$

where, c_∞ is the oxygen concentration at $t \rightarrow \infty$ corresponding to the equilibrium concentration after ΔpO_2 . $c(t, x, y, z)$ is the oxygen concentration at time ' t ' and position (x, y, z) . l_x , l_y , and l_z are the dimensions in x, y and z directions, respectively.

This process involves the incorporation of oxygen and migration inside the MIEC material that induces simultaneous changes observed in the conductivity measurements. In this manner, the O_2 concentration field can be related to the electronic conductivity $\sigma_t(t)$ and the normalized electronic conductivity $\sigma_n(t)$:

$$\sigma_n(t) = \frac{\sigma(t) - \sigma_0}{\sigma_\infty - \sigma_0} \tag{2.6}$$

which is a function of the conductivity at the time ' t ', the start of experiments σ_0 ($t = 0$), and the end σ_∞ ($t \rightarrow \infty$) [146].

The eq. 2.7 is fitted to the theoretical expression outlined by Yasuda *et al.* [147]:

$$\begin{aligned}
\sigma_n &= 1 - \sum_{p=1}^{\infty} \frac{2L_x^2}{\beta_{p,x}^2 (\beta_{p,x}^2 + L_x^2 + L_x)} \exp \left[-\frac{\beta_{p,x}^2}{l_x^2} dt \right] \\
&\times \sum_{q=1}^{\infty} \frac{2L_y^2}{\beta_{q,y}^2 (\beta_{q,y}^2 + L_y^2 + L_y)} \exp \left[-\frac{\beta_{q,y}^2}{l_y^2} dt \right] \\
&\times \sum_{r=1}^{\infty} \frac{2L_z^2}{\beta_{r,z}^2 (\beta_{r,z}^2 + L_z^2 + L_z)} \exp \left[-\frac{\beta_{r,z}^2}{l_z^2} dt \right]
\end{aligned} \tag{2.7}$$

where $L_x = l_x \frac{k_{ex}}{D_{Chem}}$; $L_y = l_y \frac{k_{ex}}{D_{Chem}}$; $L_z = l_z \frac{k_{ex}}{D_{Chem}}$, and β are the positive roots of $\beta_i \tan \beta_i = L_i$. D_{chem} and k_{ex} are the variable fitting parameters.

The model has one fundamental limitation, as it only applies to small ΔpO_2 that simulate the linearity of the kinetic exchange. Conversely, the experiment can be adjusted to identify the time until conductivity relaxation is reached.

The electrical conductivity measurements were performed using the four-point technique as in DC conductivity experiments. Further details of the setup are given in chapter 3.

2.5.3. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a technique that allows monitoring of the impedances that result from electrochemical reactions produced by Faradaic (largely charge transfer processes) and non-Faradaic processes (mainly mass transport) over a range of frequency (usually between 10^{-2} to 10^7 Hz). The electrical properties observed in each system are generally the consequence of many fundamental microscopic processes related to the movement of charged species and the transfer of these charges to other species. These processes occur at different frequency intervals, and it is possible to discriminate the contribution of each of them to the total impedance by observing the response times to a disturbance introduced into the system. For a system to be characterizable in terms of impedance, it must meet three conditions: linear, causal, and time-invariant.

EIS can be determined through many routes, but the conventional one is applying an AC voltage across a sample and a standard resistor in series. Thus, the in- and out-of-phase voltage components across the sample are measured. Dividing these components by the magnitude of the current gives the resistive and reactive components of the impedance. The measurements are repeated as a stepwise function of frequency [148].

EIS is often represented in Nyquist plots depicting real vs. imaginary parts of the impedances in rectangular coordinates and Bode plots that show the module and phase shift in polar coordinates vs. frequency on a logarithmic scale. The software used for the EIS analysis is ZView (*fig. 2.13*).

In the Nyquist plot (*fig. 2.14*), the first noticeable features are the real axis impedance at high frequencies ($\omega=\infty$) and low frequencies ($\omega=0$). The former corresponds to the ohmic resistance, and the difference between the values at these two frequencies is the polarization resistance (R_{pol}) value.

One strategy to analyze impedance diagrams is using equivalent circuits to extract the R_{pol} values. *Table 2.1* lists the most employed equivalent circuit elements in the literature to represent a particular microscopic process at different frequency intervals. The equivalent circuit model uses components like ohmic resistors (R), capacitors (C), inductors (L), Warburg and Gerischer components, and constant phase elements (CPE) that describe non-uniform properties in real electrochemical systems.

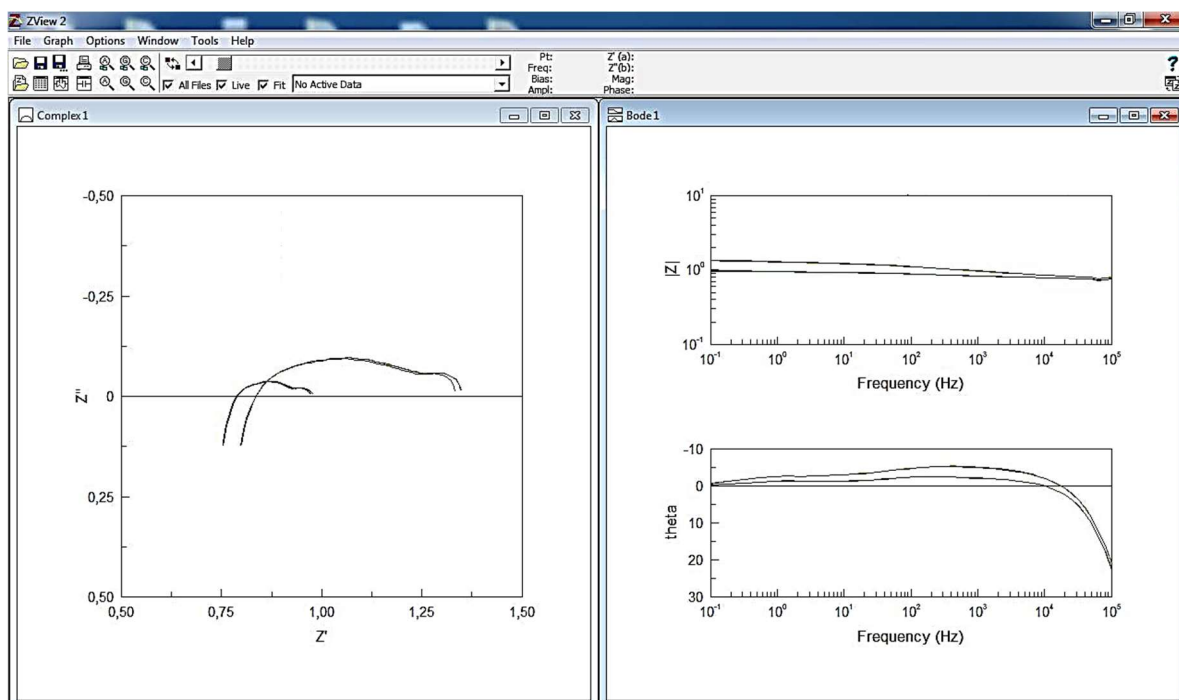


Figure 2.13. Nyquist plot (left) and Bode plots (right) as represented in the ZView software.

It is usual to obtain inductive parameters at the high-frequency end of the spectrum. The typical range of values in fitting inductances is 10^{-7} to 10^{-20} H·cm². It may also happen that low-frequency inductive loops appear due to the electrocatalytic activity of the electrodes. These low-frequency inductive loops usually disappear after cathodic polarization [149].

A capacitive element C simulates the dielectric nature of conductive materials separated by an insulator. However, in SOC electrodes, surface behavior is explained by the double-layer capacitance effect and must be simulated by a CPE. The parallel combination of a resistor with a CPE produces the impedance in an R_{CPE} element, given by:

$$Z_{CPE} = \frac{R_{CPE}}{1 + R_{CPE}(Q\omega j)^\rho} \quad (2.8)$$

Q as a value equivalent to the capacitance in a capacitor

ρ an ideal capacitor exponent with value 0 and 1, being 1 for the ideal case

ω is the frequency in Hz.

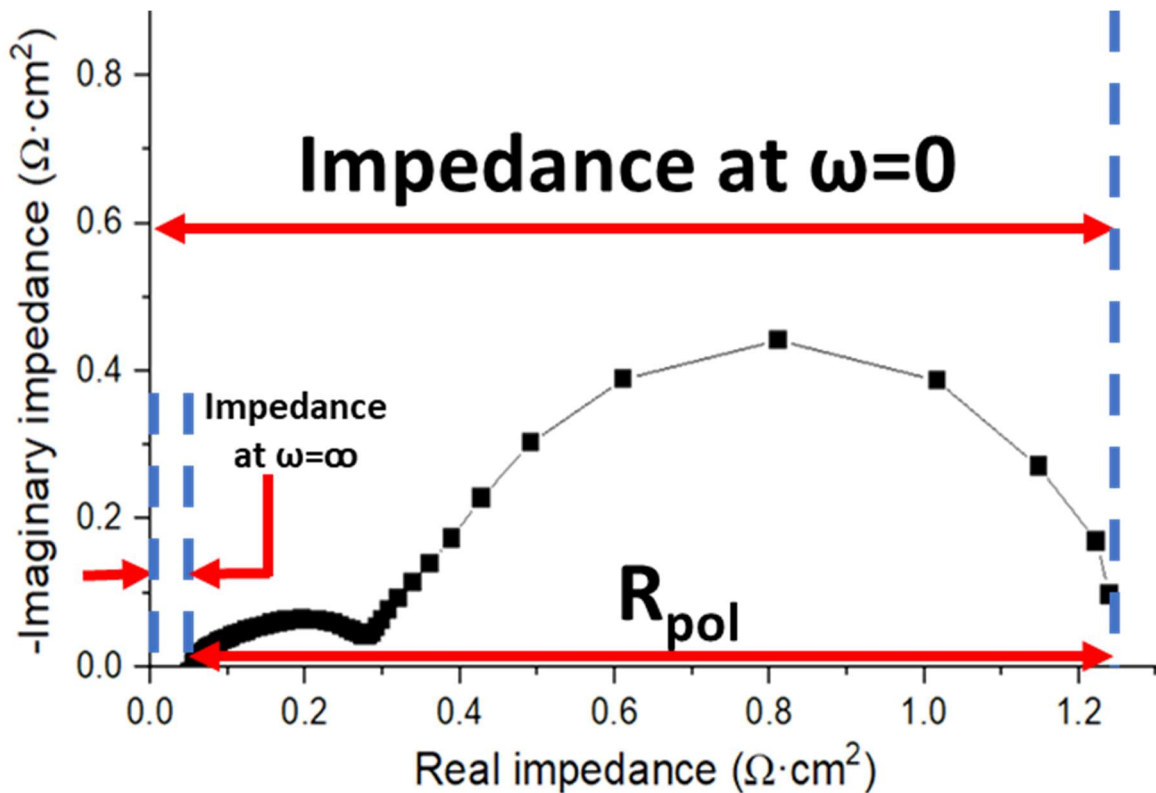


Figure 2.14. Nyquist plot depicting the high- and low-frequency features of the real axis impedance.

Faradaic processes represent resistance elements driven by electrolyte thickness and electrical contacts simulated by only a resistor R (such as R_{ohm}). R_{CPE} elements simulated the potential drop, modeling the response of an RC element through the distribution of values, in contrast to RC, which uses a single value. The R_{CPE} model can simulate H_2 electro-oxidation, ionic transport, and air electrode gas diffusion. In this characterization, elements in parallel occur in the same spatial location, while elements in series are interpreted as a physical sequence. On the other hand, Gerischer and Warburg's elements enable a physical representation of transport and reaction processes in multiple-phase gas diffusion electrode processes at low frequencies. This work did not cover these elements, as the low-frequency fittings were made with R_{CPE} representations with similar accuracy and more direct interpretation.

Table 2.1. Circuit elements used in modeling with the impedance formulation and associated processes [150].

Elements	Symbol	Impedance	Associated process
R		R	Ohmic resistance of the electrolyte, electrical contacts, and real impedances
L		$L\omega j$	Appear due to contributions from measurement probes. Impedance increases as the frequency raise
C		$\frac{1}{C\omega j}$	Charges separated by an insulator form a capacitor. Impedance decreases as the frequency rises. Have only an imaginary impedance component
CPE		$\frac{1}{Y_{CPE}(\omega j)^\rho}$	Simulates the electrochemical double-layer effect
Warburg		$\frac{1}{Y_W\sqrt{\omega j}}$	H ₂ /H ₂ O gas diffusion
Gerischer		$Y_G\sqrt{k + \omega j}$	Oxygen reduction in air electrode
C is the capacitance in F·cm⁻² ω is the frequency in Hz L is the inductance in H·cm² R is the resistance in Ω·cm² k is the Gerischer rate constant parameter in s⁻¹ Y_i is the admittance parameter in S·s^{1/2}			

The disadvantage of the EIS method is that the locally linear assumption of the model assumes average bulk system properties to simplify the approximations, and it does not always apply the actual electrochemical phenomena. EIS requires more information about the system and measures under different conditions to make correct interpretations. The literature sometimes found that the adjustments generate elements without physical meaning. To avoid these inconveniences, parameters are adjusted in an empirical approach. However, it is known that in many cases, the adjustments do not guarantee that the mechanism obtained is the one occurring during the process.

DC electrical tests in dense precursors and symmetrical cell characterizations were performed in a Probostat (NORECS) electrochemical station. DC and AC responses

were recorded using a Zahner Zennium potentiostat in symmetrical cell and single-cell electrical characterizations.

2.5.4. Distribution of relaxation times

Another strategy for interpreting the EIS data is the distribution of relaxation times (DRT) [151] peak analysis. The polarization resistance values of individual DRT peaks are measured by multiplying the surface area fraction of each peak times the total polarization resistance. This method helps to identify the rate-determining processes that could undermine the total resistance of the cell and supports the identification of the equivalent circuit models.

The calculation of the DRT consists of an ill-posed problem that can obtain many possible solutions; for this reason, the function based on the Tikhonov regularization is employed in the model. This function is regulated by the parameter λ , which weights the function and determines the smoothness of the DRT while avoiding artificial peaks. The model requires identifying the λ value for each set of impedance data. Decreasing this parameter changes the DRT peak in width and height and increases the DRT peak resolution (*fig. 2.15*). Also, the same value of λ should be used for all impedance curves within the DRT analysis to maintain a basis for comparison.

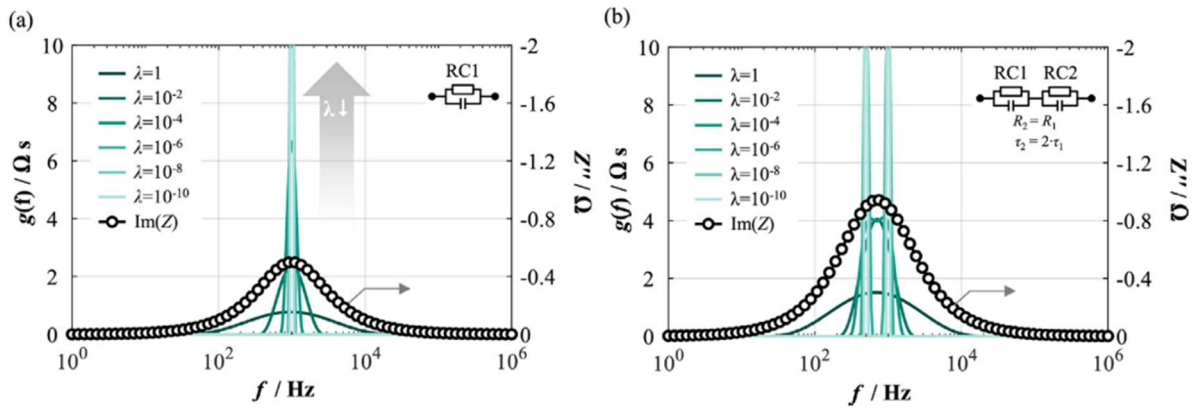


Figure 2.15. (a) one RCPE element DRT and (b) a DRT of two RCPE elements (with $\tau_2 = 2 \tau_1$ and $R_2 = R_1$), calculated by the Tikhonov regularization using different λ values. Reproduced from [150].

The DRT model [152–154] is composed of a series of Voigt elements (*fig. 2.16*) simulating a sum of a finite number of R_{CPE} elements per decade through the equation:

$$Z_{\text{model}}(x, f) = R_{\text{ohm}} + \sum_{n=1}^N \left[x_n \int_{-\infty}^{+\infty} \frac{1}{1+(2\pi f\tau)^2} \phi_n(\ln\tau) d\ln\tau \right] - i \sum_{n=1}^N \left[x_n \int_{-\infty}^{+\infty} \frac{2\pi f\tau}{1+(2\pi f\tau)^2} \phi_n(\ln\tau) d\ln\tau \right] + e_z(f) \quad (2.9)$$

where R_{ohm} is the ohmic resistance in $\Omega \cdot \text{cm}^2$, $\phi_n = 1$ is the phase angle in the ideal model, f is the frequency, $e_z(f)$ is the error and τ is the relaxation time.

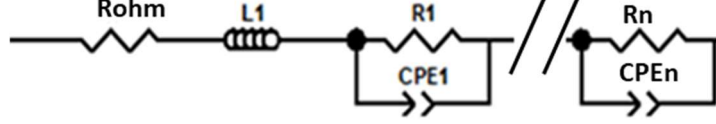


Figure 2.16. Equivalent circuit diagram of Voigt elements analyzing the distribution of relaxation times for EIS measurement simulations.

The estimates of the variable x_n are conducted by adjusting the model with the impedance data using the expression:

$$S(x) = \sum_{n=1}^N \left[\frac{1}{w'_n} (Z'_{\text{exp}}(f_n) - Z'_{\text{model}}(x, f_n))^2 + \frac{1}{w''_n} (Z''_{\text{exp}}(f_n) - Z''_{\text{model}}(x, f_n))^2 \right] \quad (2.10)$$

where w'_n and w''_n are weighted identity matrices to simplify calculations. The super indexes ' and ' ' indicate real and imaginary impedance data, respectively. The function requires a minimization of the equation with the general form:

$$\sum_{n=1}^N [x_n - h(x_1, x_2, \dots, x_N, f_n)]^2 + \lambda P(x_1, x_2, \dots, x_N, f_n) \geq 0 \quad (2.11)$$

for N data points in f_n frequencies and a regularization function $h(x_1, x_2, \dots, x_N, f_n)$. The penalization parameter $P(x_1, x_2, \dots, x_N)$ employs the regularization parameter $\lambda \geq 0$.

As in equivalent circuit modeling, the DRT interpretation is challenging because high-performance electrodes have low impedances (10–100 m Ω), and the concept of a unique rate-limiting step is usually not applicable. This is because the fuel and air electrodes' charge transfer and transport processes often overlap in the 10^2 - 10^4 frequency domain.

Furthermore, another reason for focusing on R_{CPE} elements instead of Warburg and Gerischer elements is that by applying them to calculate the DRT, the side peaks are less regularized and can be better resolved. Dierickx *et al.* [150] also reported asymmetric equivalent circuit elements in Warburg and Gerischer elements that broaden the DRT curves over several frequency decades, complicating individual minor processes' identification.

Chapters 4 and 5 present the analytical DRTs of the characterized impedance spectra for the determination of rate-determining processes.

2.5.5. I-V and I-V-P characteristics

In fuel cells, several irreversibilities occur that limit the amount of useful energy extracted from the system. Some of these limitations depend on the current drawn from the cell (higher losses at higher currents), so it is common to characterize cells based on their current density-voltage (I-V) and power density-voltage (I-V-P) curves, as shown in *fig. 2.17*. It is usual to present the electrical power on the secondary vertical axis of the same graph. Current and power density are represented in surface units as $\text{A}\cdot\text{cm}^{-2}$ and $\text{W}\cdot\text{cm}^{-2}$, respectively.

Before I-V characterizations, the OCV of the cell is measured under the operating condition in SOFC and SOEC modes, which depend on fuel composition. The approximation of the experimental OCV value to the theoretical value predicted by the Nernst equation (*eq. 1.3*) gives an idea of the sealing quality since the difference in values usually originates from leaks between the electrodes that modify the partial pressures in the components.

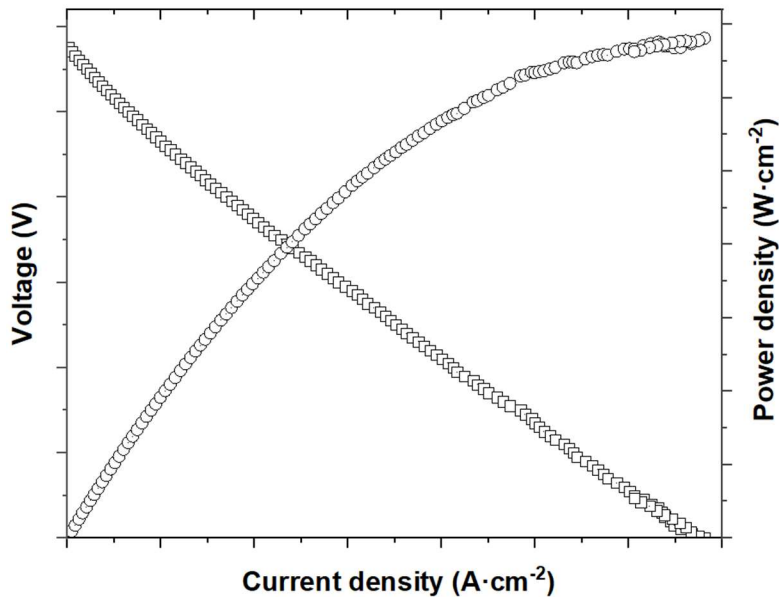


Figure 2.17. Typical representation of I-V and I-V-P curves.

In SOFC and SOEC modes, to perform I-V measurements of single cells, the cell is heated in a tubular furnace and connected to the potentiostat that acts as an electronic load. The DC and AC responses were recorded at different temperatures using a Zahner

Zennium potentiostat in single-cell electrical characterizations. In SOFC mode, the electrical power generated by the cell is represented by the I-V-P curve, which can be calculated by multiplying the voltage by the current at the selected operating point, this power being equal to the area of the rectangle defined by this point.

2.5.6. Chronoamperometric/chronopotentiometry characterization

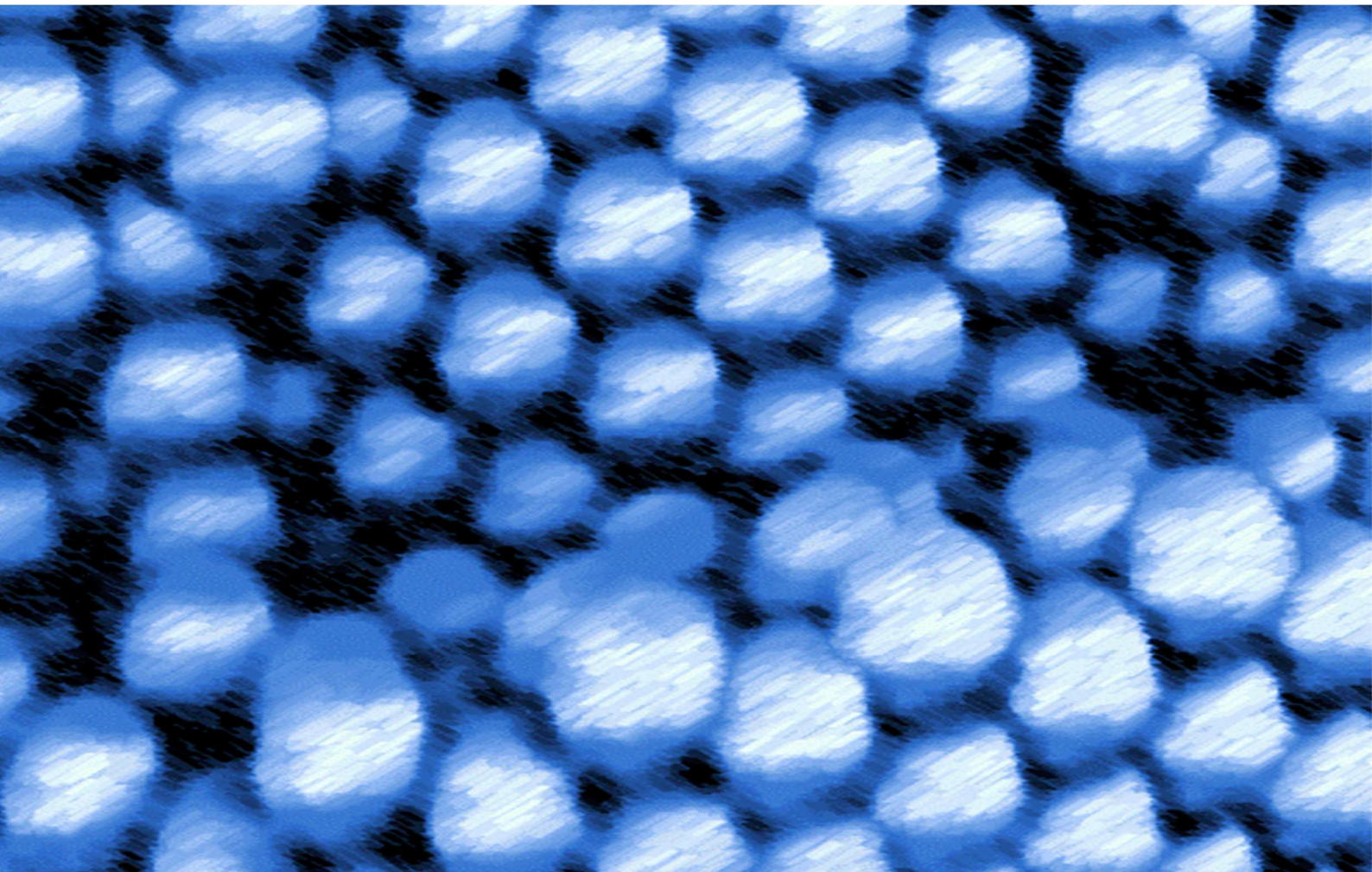
The same experimental setup as in the I-V-P characterizations described in the previous section is used for this type of measurement. The difference in the technique is that a constant potential is applied, or a certain amount of current is forced between the electrodes, and the system's response is characterized over time. This technique is a good indicator of the cell's electrochemical performance over a given period and the stability of the electrodes under given operating conditions. Possible evolutions in cell performance are recorded as increases or decreases in current at a constant voltage or vice versa. At the same time, complementary EIS analysis can help with the identification of rate-determining processes in case of degradation events.

The chronoamperometric electrochemical tests of microtubular single cells were performed in a tubular furnace, and the setup descriptions are detailed in *section 4.4*. DC responses were recorded using a Zahner Zennium potentiostat in single-cell electrical characterizations.

Chapter 3. Phase analysis in nickelates and doped ceria composites

Lanthanide nickelate oxygen electrodes are currently of interest as Solid Oxide Electrolysis Cells materials for their capacity to accumulate interstitial oxygen under high oxygen partial pressures, sustain oxygen losses, and their fast oxygen chemical diffusion. However, they present reactivity problems with commonly used stabilized zirconia electrolytes, forming insulating phases. Including an alternative ionic conductor as a diffusion barrier in the interface between the oxygen electrode and the electrolyte prevents the formation of electrochemically detrimental phases. Praseodymium nickelate and gadolinium-doped ceria mixtures, which react at typical sintering temperatures to form praseodymium- and gadolinium-doped ceria, present kinetic and electrochemical properties that could improve the SOC performance over lanthanide nickelates. These newly-formed oxide mixtures have no detrimental reactivity between the formed phases, which could improve long-term air electrode stability.

In this chapter, a phase study of the electrochemical properties of different compositions of Pr and Gd-doped cerium oxides is conducted and compared with the nickelates to determine their compatibility as SOC air electrode materials.



3.1. Introduction

Several strategies have been developed to improve the stability of lanthanide nickelate electrodes [101]. This work reported that one possible strategy was to apply a mixture of doped ceria and PNO as a diffusive layer to repel the formation of insulating phases. In the presence of GDC, decomposition into PrO_x and $\text{Pr}_4\text{Ni}_3\text{O}_{10-\delta}$ without further formation of NiO at 800 °C, as well as the formation of cubic fluorite Pr- and Gd-doped ceria phases (CPGO) [101], provides good electrochemical performance [155]. The Pr-Ce system is known for its high oxygen availability [156,157], possessing a higher electrical conductivity than undoped ceria [158,159]. Pr content increase in $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ (PDC) enhances the oxygen vacancy concentration and the total conductivity of the material [160]. For example, the Department of Energy of the United States of America (DOE) has discussed the implementation of a nanoscale Pr-Ce barrier layer between the air electrode and electrolyte in SOFC stack systems, where an important cost reduction trade-off using praseodymium oxide (PrO_x)-based electrodes has been identified [161]. Given this enticing background, we further evaluated the prospect of using nickelate and ceria-based precursors as air electrode materials for SOC studies.

To compare the unique electrochemical features of Ce-rich (an ionic conductor) and Pr-rich (an electronic conductor), we studied two PNO-GDC samples with different compositions: a PNO-rich with 20 wt% GDC + 80 wt% PNO (named C20), and a GDC-rich containing 80 wt% GDC + 20 wt% PNO (from now on called C80). Using different methodologies and analytical techniques, these samples are compared with a PNO precursor in comprehensive structural, microstructural, and electrochemical characterizations. The structural features were analyzed by the X-ray diffraction (XRD) technique, a quantitative analysis of the cation interdiffusion of Pr into the ceria lattice via Energy Dispersive Spectroscopy in a Scanning Transmission Electron Microscopy (EDS-STEM), and the determination of the oxidation states of Ce and Pr in the samples through Electron Energy Loss Spectroscopy (EELS). Also, electrochemical studies have been carried out using the electrical conductivity relaxation method (ECR) at different ranges of oxygen partial pressures at high temperatures. Changes in oxygen ion transfer performance are observed through variations in the oxygen kinetic coefficients and their respective activation energies. Finally, to validate their electrochemical performance, symmetrical cells have been manufactured with each of the compositions studied and characterized by electrochemical impedance spectroscopy (EIS) measurements.

3.2. Preparation of ceramic precursors

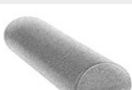
Before preparing the precursors, we verified the composition of the as-received commercial powders: $\text{Pr}_2\text{NiO}_{4+\delta}$ (PNO, Marion Technologies), $\text{Ce}_{0.90}\text{Gd}_{0.10}\text{O}_{1.95}$ (GDC10-M, Fuelcell Materials), and $\text{Ce}_{0.8}\text{Pr}_{0.2}\text{O}_{2-\delta}$ (PDC, Sigma Aldrich) by the ICP-OES technique as shown in *Table 3.1*. These constituents also served as standards for calculating the Cliff-Lorimer sensibility parameters.

Table 3.1. ICP-OES analysis of the powder samples used in this study.

Powder Sample	Ce (at.%)	Pr (at.%)	Gd (at.%)	Ni (at.%)
GDC	88.80±0.12		11.20±0.12	
PDC	79.00±0.08	21.00±0.08		
PNO		67.00±0.10		33.00±0.10

To form the PNO-GDC ceramic precursors, the powders were initially mixed with polyvinyl alcohol (PVA) in an agate mortar at a ratio of 0.15 ml per gram of the powder mixture until a uniform compound was visible and then inserted into a latex sheath to form cylindric-like precursors. The prepared precursors were uniaxially pressed into cylindrical bars at 2000 bar and then sintered in air at 1450 °C for 2 h at a rate of 5 °C·min⁻¹ to ensure the densification of the ceria. After sintering, the studied samples with different PNO and GDC content are detailed in *Table 3.2*.

Table 3.2. Precursors used in this study.

Sample	Precursor Composition	Length (mm)	Diameter (mm)	Density after sintering
PNO 	Pr_2NiO_4	7.0	2.5	>99%
C20 	20 wt% $\text{Ce}_{0.90}\text{Gd}_{0.10}\text{O}_{1.95}$ 80 wt% Pr_2NiO_4	7.0	3.0	>98%
C80 	80 wt% $\text{Ce}_{0.90}\text{Gd}_{0.10}\text{O}_{1.95}$ 20 wt% Pr_2NiO_4	6.0	2.5	>95%

All the samples had a density of over 95%, making them adequate for structural and electrochemical studies. The cylindrical precursors were cut at the dimensions indicated in *Table 3.2* and selected for electrochemical tests, while the rest was pulverized in an agate mortar for structural and microstructural characterizations.

3.3. Structural analysis

Refined XRD patterns (*fig. 3.1*) were deployed for calculations of lattice parameters and the phase quantification of the samples. The XRD analyses of the milled powders were performed with a low-voltage rotating copper anode in the XRD detector. XRD powder refinements resulting values are shown in *Table 3.3*.

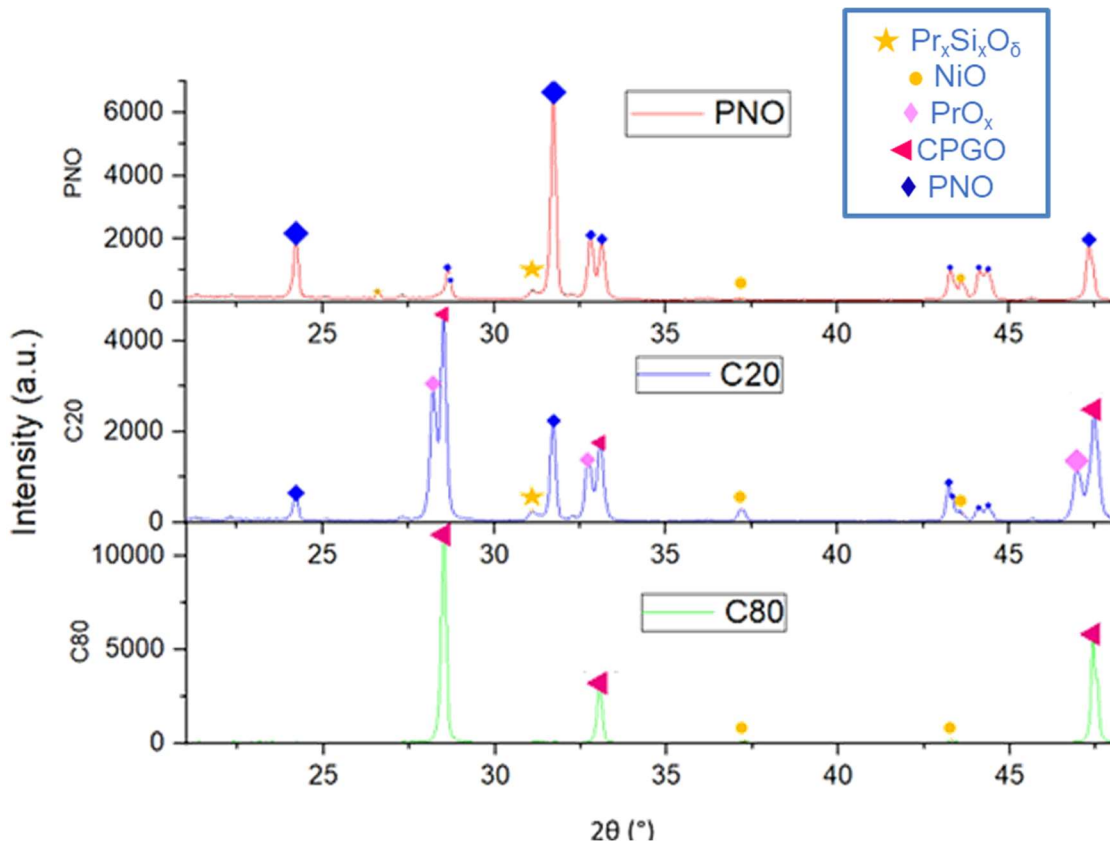


Figure 3.1. XRD patterns of PNO and PNO-GDC powders collected after annealing for 2 hours at 1450 °C.

After sintering, the PNO sample contained two minor secondary phases (NiO and $\text{Pr}_2\text{Si}_2\text{O}_7$). The silicate phase was most likely formed during the processing of the raw powder and has also been observed in the analog NNO [162].

The C20 sample presented several secondary phases, with two fluorite-type phases corresponding to CPGO and PrO_x representing the majority. This is consistent with the studies of Ce-Pr mixed oxides, where coexistence is expected even as the Pr content in the ceria is higher [158,163]. Non-reacted NiO and non-decomposed PNO are also present.

The C80 sample is formed mainly by CPGO, also presenting PrO_x and NiO as minor secondary phases. Comparing the PNO decomposition between both PNO-GDC samples shows that decomposition is influenced by the temperature and increasing GDC content in the mixture [101,156,157]. In C80, the PNO phase is no longer present. Previous studies [163] mentioned that in Pr-doped ceria, the secondary phases disappear as the Pr content diminishes under 65 at.%. Tsai *et al.* [155] confirmed this behavior in CPGO under operating conditions (800 °C), concluding that this phase degrades away from the PNO/GDC interface. At the same time, they described partial time-dependent Pr diffusion occurring in GDC.

Table 3.3. Phase composition and lattice parameters of the samples studied, as calculated from refined XRD.

Sample	Phase Composition	Spatial Group	Lattice Parameters (Å)
PNO	94 wt% PNO (primary phase)	$Fmmm$	5.3966(6); 5.4474(8); 12.4332(12)
	NiO		-
	$\text{Pr}_4\text{Si}_3\text{O}_{12\pm\delta}$		-
C20	38 wt% CPGO	$Fm\bar{3}m$	5.4013(5)
	27 wt% PrO_x ($\text{Pr}_6\text{O}_{11-\delta}$)	$Fm\bar{3}m$	5.4577(7)
	9 wt% PNO	$Fmmm$	5.3913(9); 5.4439(5); 12.4395(7)
	25 wt% NiO		-
C80	96 wt% CPGO (primary phase)	$Fm\bar{3}m$	5.4146(5)
	PrO_x ($\text{Pr}_6\text{O}_{11-\delta}$)		-
	NiO		-

As we want to study the effect of the cation constituents on the structural properties of CPGO, a relationship between the lattice parameter and the Pr content was established using Kim's empirical method (eq. 3.1) based on Vegard's rule [164]. This states that two phases must have a fluorite-type cubic crystal structure and similar ionic radii.

$$d_{Ce} = 0.5413 + \sum_k (0.0220\Delta r_k + 0.00015\Delta z_k) \cdot m_k \quad (3.1)$$

In eq. 3.1, d_{Ce} (in nm) is the lattice constant of the ceria solution at RT, Δr_k (nm) is the difference in ionic radius ($r_k - r_h$) of the k^{th} dopant (r_k) and the host cation (r_h) in eightfold coordination from Shannon's compilation [165], Δz_k is the oxidation state difference ($z_k - z_h$), and m_k is the mol % of the k^{th} dopant represented by:

$$m_k = \frac{n_k \cdot M_k}{100 + \sum_k (n_k - 1) \cdot M_k} \times 100 \quad (3.2)$$

where n_k is the number of cations in the k^{th} solute oxide and M_k is the mol % of the k^{th} dopant oxide.

Assuming the incorporation of PrO_x into the ceria lattice, as the lattice parameters of CPGO and PrO_x have similarities in their crystal structure and ionic radii (Pr^{4+} and Ce^{4+}), the two phases follow Vegard's rule. The results are compared with previous CPGO [166] experiments (*fig. 3.2*). As there is no literature data for CPGO with a high Pr content, PDC data [160] was used to compare with the doped ceria lattice parameters.

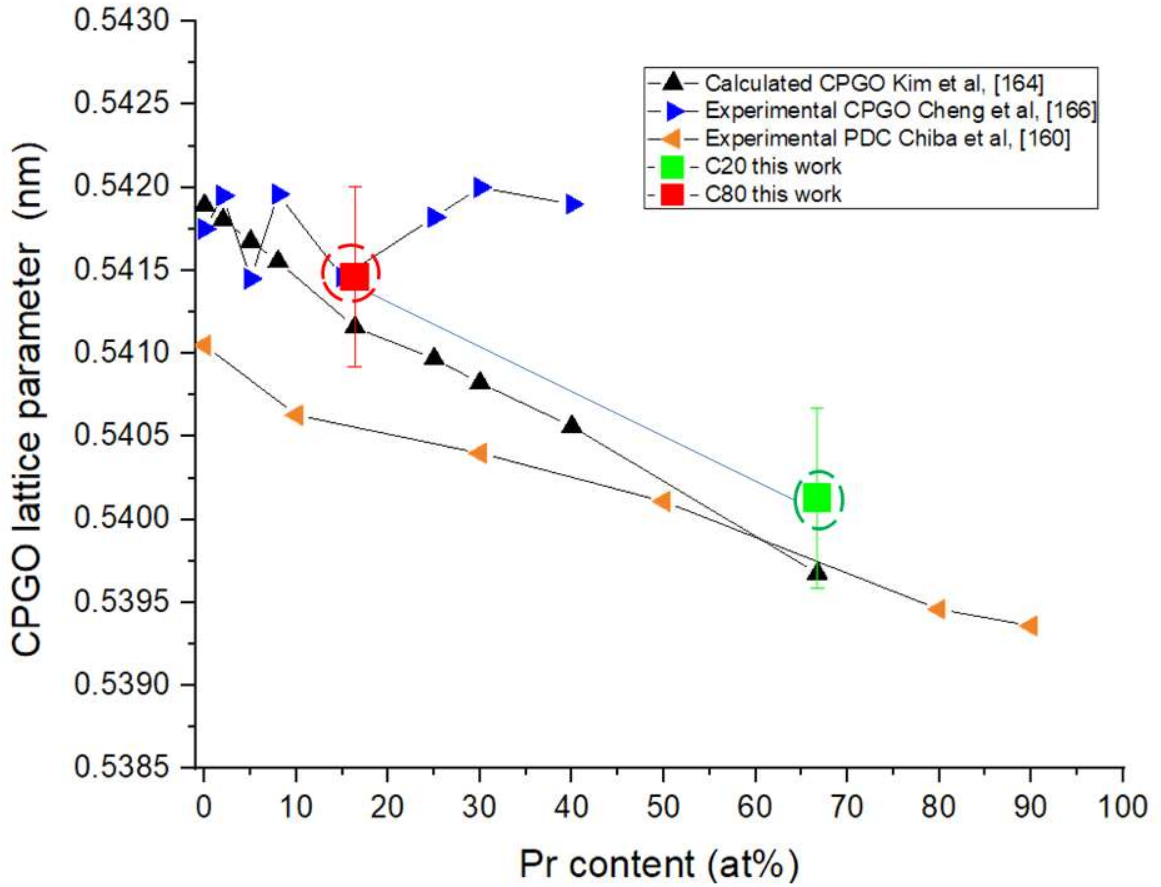


Figure 3.2. Experimental and calculated lattice parameters vs. Pr atomic content in CPGO samples using Kim's empirical method for Pr^{4+} . Data reproduced from [160,166].

The obtained experimental value in C80 ($a=5.4146 \text{ \AA}$) is also compatible with the one reported by Cheng *et al.* [166] ($a=5.4146 \text{ \AA}$ for 15 at. % Pr). While Kim's method (black triangles) adjusts well with our experimental data for both C20 and C80, the data from Cheng *et al.* (blue triangles) does not follow this kind of linearity because the Gd content is constant (10 at. %). In this study, the Gd content decreases as the Pr content

increases. On the other hand, our C20 data adjust better to the high Pr content range in PDC. This suggests that the main difference between the lattice parameter data in this work and PDC data is induced by the Gd content in the dopants. For the lattice parameters obtained experimentally, the average Pr oxidation state is 3.94 in C80 and 3.97 in C20 following *eq. 3.1*.

3.4. Compositional analysis

To determine the cation interdiffusion in the ceria lattice of the C80 and C20 samples, we performed an EDS-STEM quantitative analysis. Experimental profiles and Cliff-Lorimer sensitive factors (k_{AB}) were employed from standards of known stoichiometry for maximum accuracy.

For thin samples in TEM, the required standards must be stable under the electron beam and high vacuum conditions, and the exact stoichiometry must be known before the experiments. The cation ratios of these powders were previously determined by the ICP-OES method and are shown in *Table 3.1*.

For CPGO particles, the selected peaks for fitting were Ce-L, Pr-L, Gd-L, and Cu-K (to account for the Cu grid contribution). In PNO, the peaks of interest were Pr-L, Ni-K, and Cu-K. Experimental profiles were used for maximum accuracy because of overlapping peaks of Gd-L α^1 (6.058 keV) and Ce-L γ^1 (6.052 keV). The experimental profiles used for the fittings were obtained from CeO₂, Pr₂O₃, Gd₂O₃, NiO, and CuO compounds. Spectra with more than 400,000 counts in the selected peaks were used. The Cliff-Lorimer sensitivity factors were determined according to the *eq. 2.4*, using PNO, GDC, and PDC powders (*fig. 3.3*).

The spectra for k_{AB} determination contained more than 500,000 counts in the selected peaks to get a signal-to-noise ratio of $\sim 1 \times 10^{-3}$. The results are compiled in *Table 3.4*, where the experimental errors were estimated using the two-sigma criterion (95% confidence level).

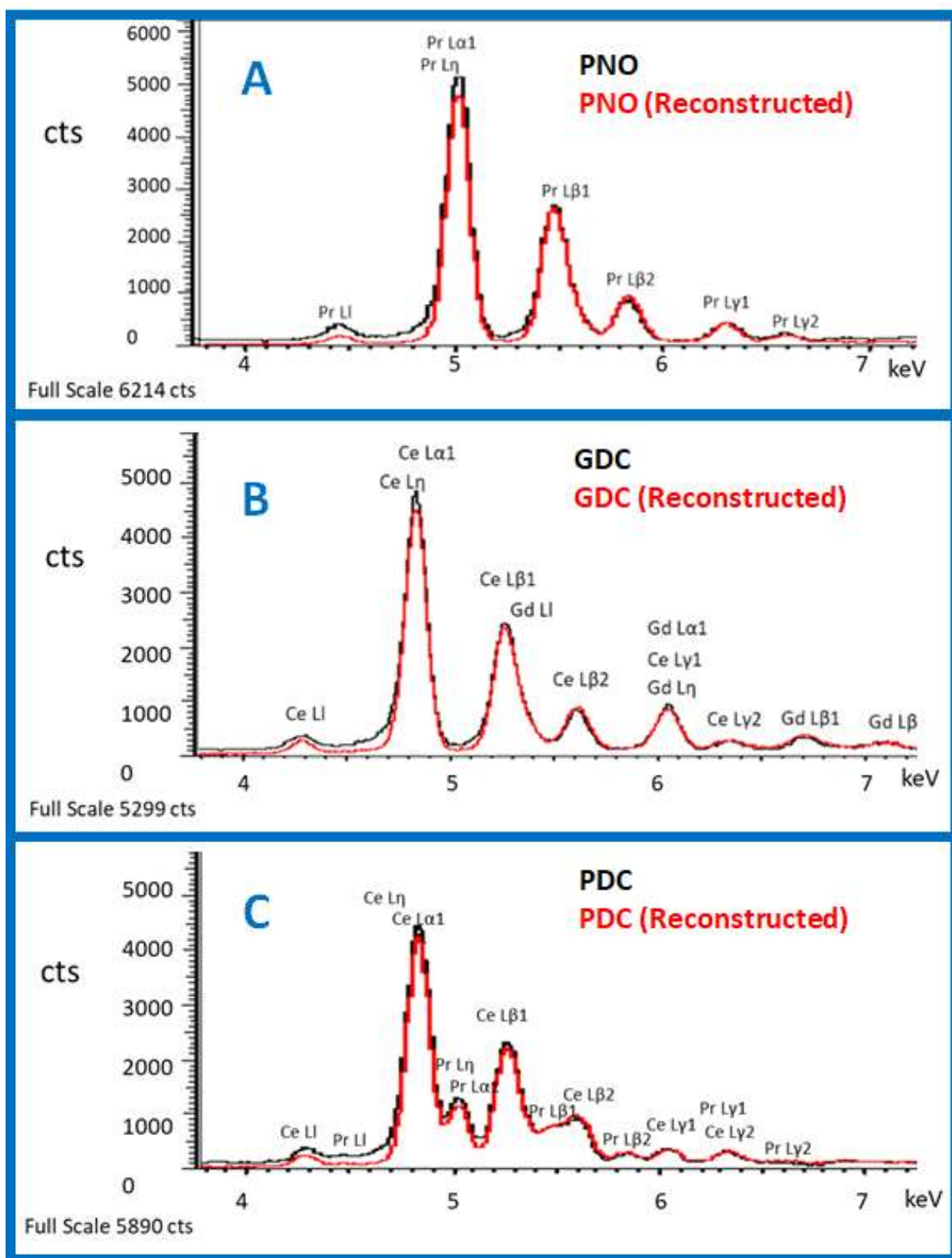


Figure 3.3. Experimental patterns (black) and fitted spectra (red) in the 3.7-7.3 keV range for PNO (a), GDC (b), and PDC (c).

Table 3.4. Concentration ratios from ICP-OES and Cliff-Lorimer parameters (k_{AB}) of the standards (in atomic fraction) used for EDS quantification.

Standard	Concentration ratio	Cliff-Lorimer ratio
GDC	$\frac{Ce}{Gd} = 7.93 \pm 0.09$	$k_{Gd-Ce} = 1.007 \pm 0.010$
PDC	$\frac{Ce}{Pr} = 3.76 \pm 0.02$	$k_{Pr-Ce} = 0.971 \pm 0.010$
PNO	$\frac{Pr}{Ni} = 2.03 \pm 0.01$	$k_{Pr-Ni} = 0.509 \pm 0.003$

The sensitivity factors of *Table 3.4* were used to quantify the CPGO phases of C20 and C80 accumulating counts in 15 and 18 spectra, respectively, to gain statistical significance. The resulting compositions are displayed in *Table 3.5*. Comparing these results with the ones in *section 3.3*, the Ce content in the CPGO phase of C20 (30.1 at. % or 24.3 wt%) is slightly higher than the calculated for the GDC precursor in the previous section (20 wt% of Ce), indicating possible underestimations of the amount of CPGO in C20 calculated by XRD refinements. The Ce content of the CPGO phase in C80 (74.7 at. % or 60.1 wt%) is compatible with the GDC precursor content (80 wt%, roughly 58 wt% of Ce in the mixture) as C80 is mostly CPGO. Additionally, the calculated Pr content in the CPGO phase of C20 (67.2 at. % or 54.7 wt%) confirms the reported limits of solubility of Pr into ceria at around 70 at. % under ambient conditions [158].

Table 3.5. EDS-STEM Quantifications of CPGO in C80 and C20 with 95% confidence level.

Sample	Case 1 Composition
C80	$Ce_{0.747 \pm 0.004} Pr_{0.162 \pm 0.004} Gd_{0.092 \pm 0.004} O_{2-5}$
C20	$Ce_{0.301 \pm 0.006} Pr_{0.672 \pm 0.006} Gd_{0.028 \pm 0.006} O_{2-5}$

The same analysis was performed for PNO, in as-received powder (PNO-P) and after sintering at 1450 °C (PNO-S) to compare with the unreacted PNO particles in C20. Similar PNO compositions (*Table 3.6*) were obtained for each case, and the values coincide with the composition calculated by ICP-OES.

Table 3.6. EDS-STEM Quantification of PNO in PNO-GDC mixtures compared to PNO sintered at 1450 °C and PNO in as-received powder.

Sample	Case 1 Composition
C20 (PNO phase)	$\text{Pr}_{0.669 \pm 0.002} \text{Ni}_{0.331 \pm 0.002} \text{O}_{4+\delta}$
PNO-S	$\text{Pr}_{0.671 \pm 0.001} \text{Ni}_{0.328 \pm 0.001} \text{O}_{4+\delta}$
PNO-P	$\text{Pr}_{0.670 \pm 0.001} \text{Ni}_{0.330 \pm 0.001} \text{O}_{4+\delta}$

Considering all the facts, the two different composition quantification methods of sections 3.3 and 3.4 showed compatibility in the results, particularly for C80. Even so, the EDS-STEM proved to be a more accurate assessment for quantifying CPGO compositions.

3.5. Ce and Pr oxidation states

Electron Energy-Loss spectra (EELS) were acquired to determine the influence of composition changes on the variations of the oxidation state of Ce and Pr in the CPGO particles present in C20 and C80. The oxidation state of Pr was also evaluated in PNO, as no similar studies determined by EELS are available in the literature for this compound. For this purpose, we estimated the intensity ratios of the characteristic M_4 and M_5 EELS edges of Ce and Pr. These lines represent the $3d_{3/2} \rightarrow 4f_{5/2}$ (M_4) and $3d_{5/2} \rightarrow 4f_{7/2}$ (M_5) electronic transitions [167] and their respective spin-orbit splitting. The edge ratio points out the oxidation state [168] so that a tall M_4 edge is due to a 4+ oxidation state. In contrast, a taller M_5 edge signals a significant presence of a 3+ oxidation state. This analysis is not focused on gadolinium or nickel as its oxidation state is not expected to change because of its stability in dry air. Simultaneous STEM-HAADF images were taken to ensure that the EELS analysis was performed in the same CPGO and PNO particles quantified by EDS-STEM (*fig. 3.4*).

STEM-EELS spectrum images are compiled point-by-point using the 3D data cube method shown in *fig. 3.5*. In this figure, x and y are the plane dimensions of the image, and ΔE represents the energy loss projected in the z-direction. The collection semi-angle employed was $\Theta_3 = 51.3$ mrad with a convergence semi-angle of $\Theta_1 = 24.8$ mrad and an aperture of 70 μm . The data were acquired with an energy dispersion of 0.20 eV per channel.

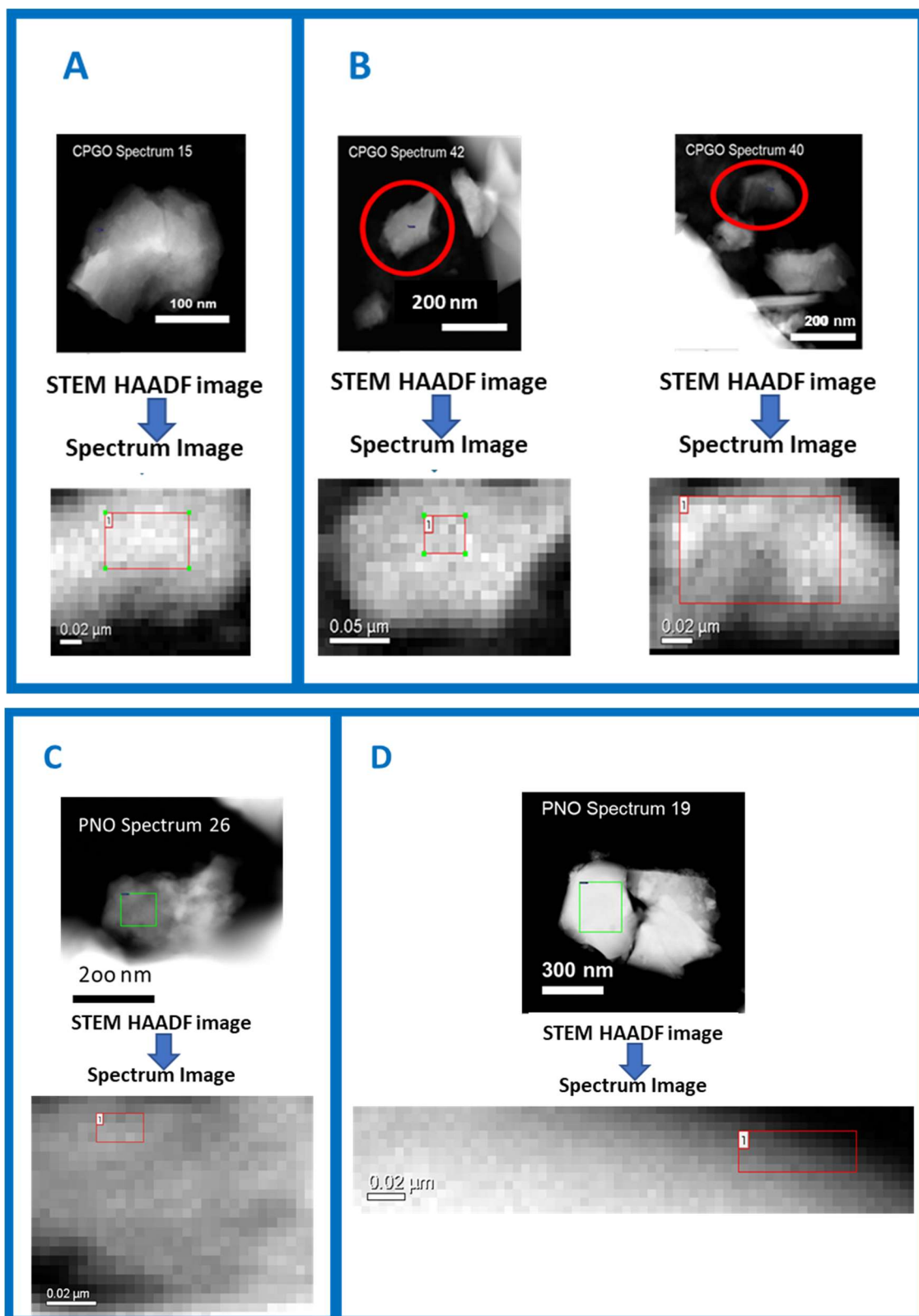


Figure 3.4. Set of simultaneously taken STEM-HAADF and EELS Spectrum-Images recorded for: a) C20, b) C80, c) as received PNO, and d) sintered PNO.

The obtained spectrum images were analyzed using the Gatan® Digital Micrograph (DM) software. Thickness estimations were performed using the log-ratio method [144], where the mean free paths were estimated using the tools provided by Mitchell and Schaffer [169]. The core-loss peak intensity error is calculated according to Egerton [141]. The background is sampled using the power law method on the low-energy side of the ionization edge, extrapolated to higher energies. As the edge over the background ratio decreases dramatically with the increase of the sample thickness, the particle size selected for this study was procured to be below 300 nm. This way, the measured thickness in the zones where the information was obtained from the EELS was generally under 100 nm (*fig. 3.6*).

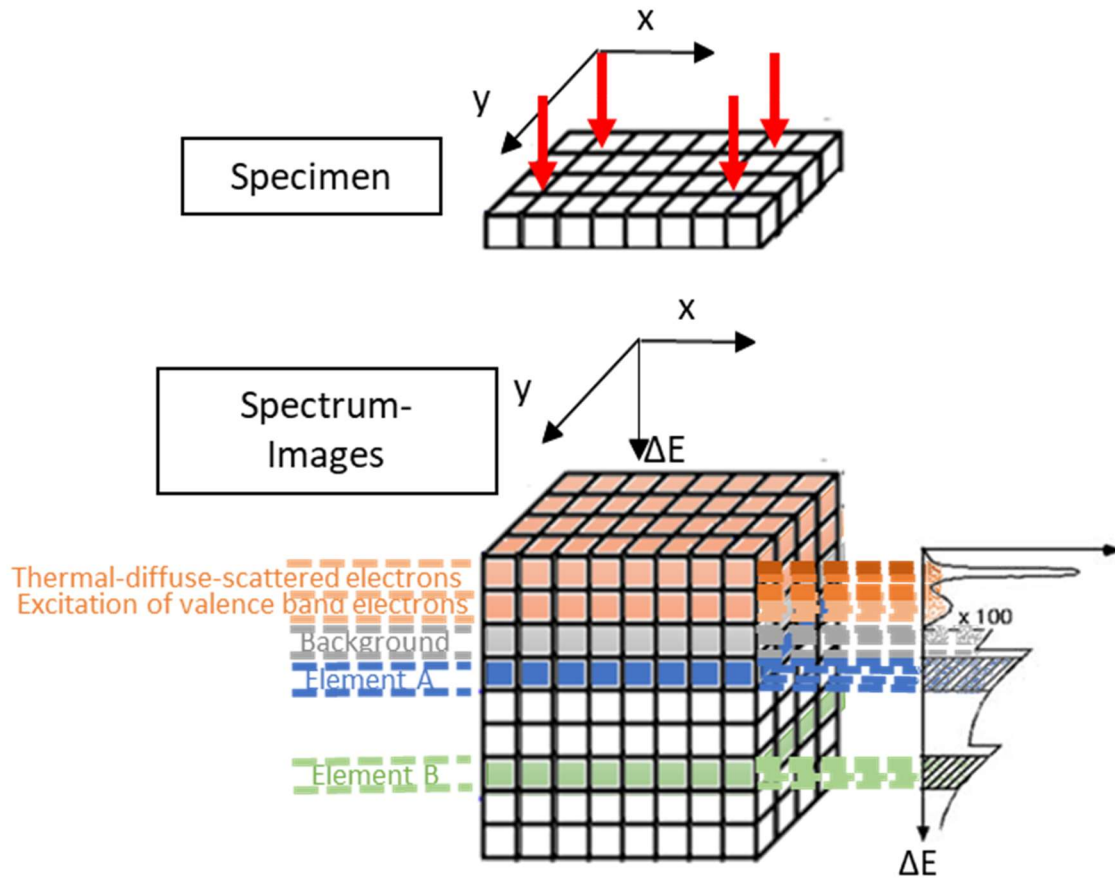


Figure 3.5. Diagram of the conversion of STEM-HAADF image using the 3D data cube for calculating EELS main peaks. Based on [19].

On the other hand, in the PNO reference samples of *fig. 3.6*, the Pr M_5/M_4 peak intensity values obtained for as received powder (PNO-P) and sintered at 1450 °C (PNO-S) were 1.55 ± 0.10 and 1.52 ± 0.07 , respectively. These values indicate a mixed 3+/4+ oxidation

state for Pr according to the expected values in the literature for the Pr M_5/M_4 ratio [167,170,171].

Regarding the Ce oxidation state, we compared the Ce M_5/M_4 peak intensity ratios obtained with GDC (Ce^{4+}) and PNO-S reference samples with the values obtained for CPGO in C20 and C80 (*fig. 3.7*). The net Ce M_5/M_4 ratio in GDC was calculated as 0.88 ± 0.06 , in good agreement with previous experiments [172], while for CPGO was 0.79 ± 0.03 in both samples. In *fig. 3.7*, the Ce $M_{4,5}$ peaks in C20, C80, and GDC have virtually the same area relationship, showing a tendency in the Ce^{4+} state. Other authors also found Ce^{4+} in PDC solid solutions under oxidation conditions using EELS [173] and X-ray absorption near-edge spectra (XANES) [174] experiments.

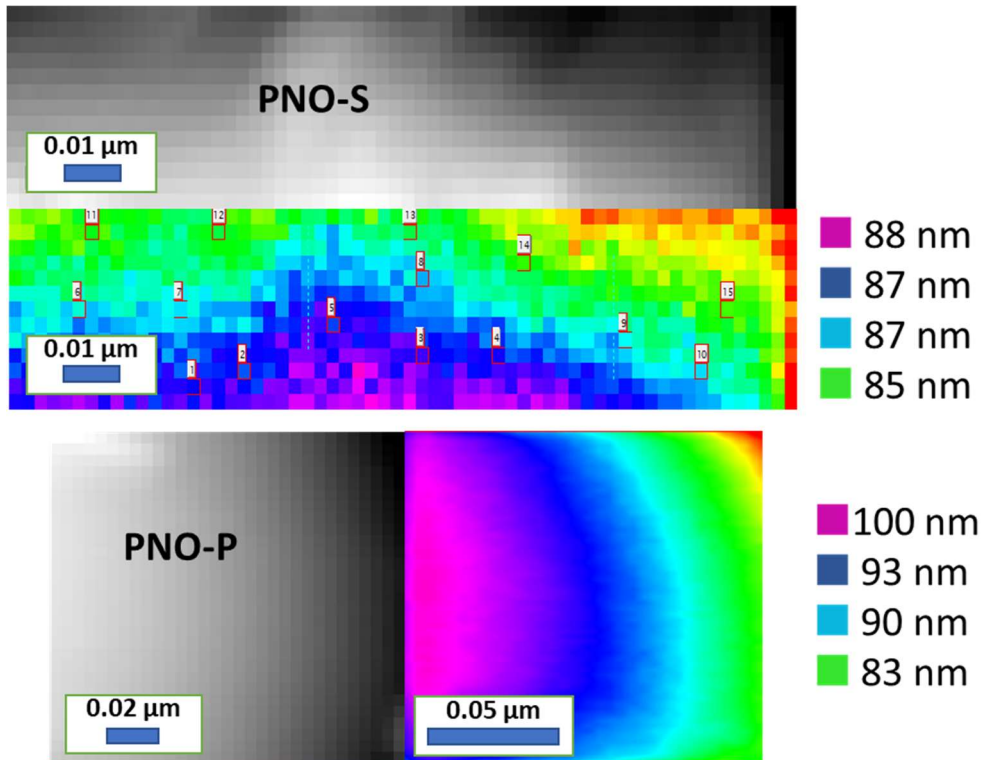


Figure 3.6. Thickness mapping of PNO-P and PNO-S.

For their part, the Pr M_5/M_4 ratio is 1.25 ± 0.07 for C20 and 1.25 ± 0.20 for C80. Although the relative error in C80 is high due to the low Pr M_4 and Pr M_5 peak height, both values are compatible with the one obtained by Fortner *et al.* for Pr^{4+} ($M_5/M_4 \sim 1.28$) [167]. As reported in other works, these results confirm the expected Pr oxidation state ($4+$) for Pr-doped ceria [158,163,166]. A recollection of the EELS M_5/M_4 ratios in literature is presented in *Table 3.7*, and most values are compatible with the results obtained in this

analysis. On the other hand, EELS M_5/M_4 ratio analyses consistently match the results obtained for Pr^{4+} in CPGO according to Vegard's rule prediction from eq. 3.1.

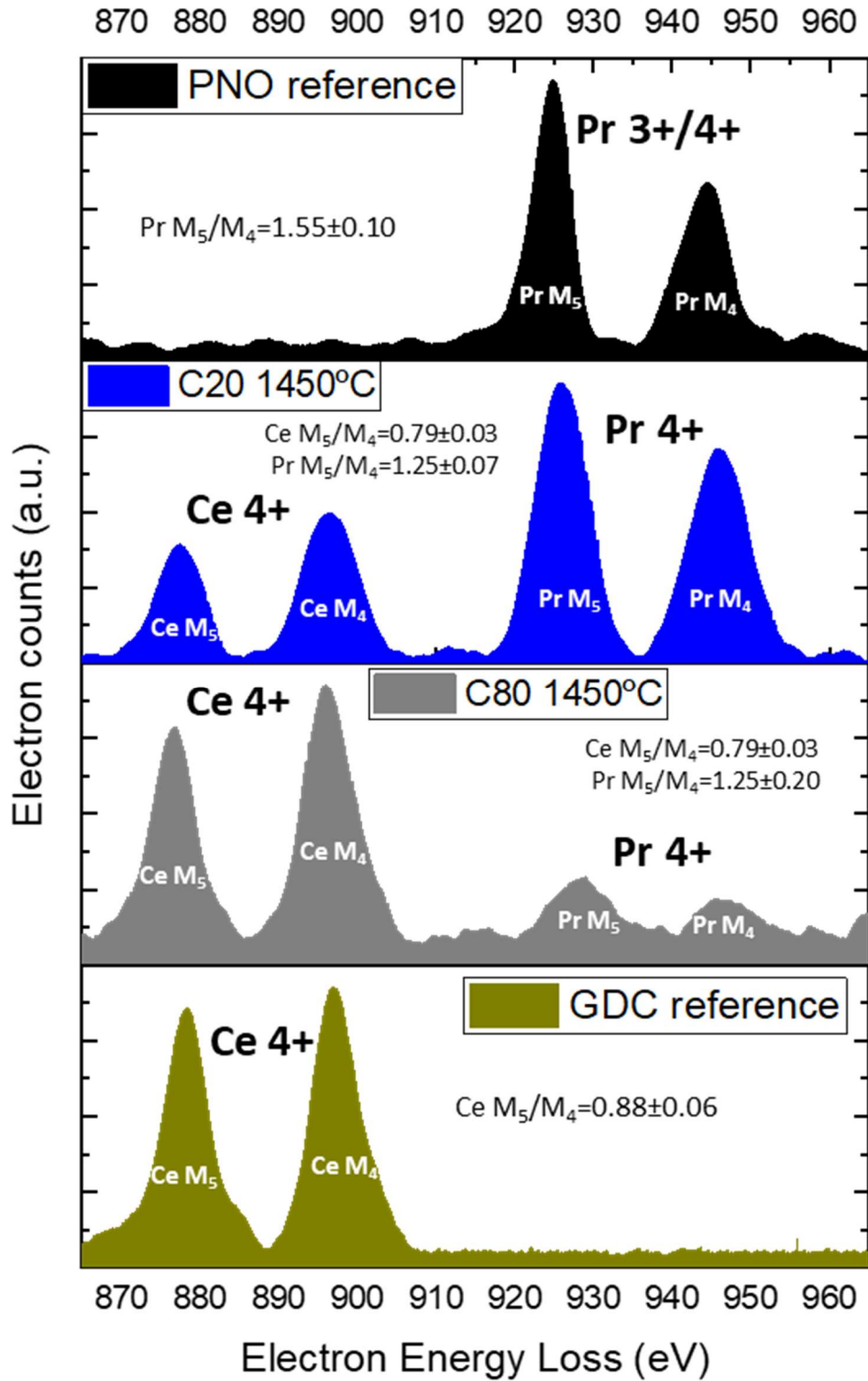


Figure 3.7. Background-subtracted EELS of M_4 and M_5 peaks for CPGO particles in C20 and C80, compared with PNO (PNO-S) and GDC references.

Schaube *et al.* [175] elaborated on the Pr oxidation state in PDC (20 at. % Pr), mentioning that as temperature increases, the Pr³⁺ incorporated into the ceria tends to approximate the total Pr content, while at increasing pO₂ (10⁻⁴ → 1 atm) the Pr⁴⁺ content increases as an effect of point defects for oxygen surface reaction kinetics on doped ceria. At pO₂ = 0.21 atm, the Pr⁴⁺ content was >90%, which is compatible with our results for C80. Other authors imply that the Pr oxidation state at the surface of PDC deviates greatly from that of the bulk [176,177]. We did not observe this effect during our experiments.

Table 3.7. Reported Ce and Pr M₅/M₄ ratios for 3+/4+ oxidation states and reference samples used in different EELS studies.

Reference	Ce ⁴⁺ M ₅ /M ₄	Ce ³⁺ M ₅ /M ₄	Pr ⁴⁺ M ₅ /M ₄	Pr ³⁺ M ₅ /M ₄	Sample
Merrifield <i>et al.</i> 2013 [178]	0.82±0.03	1.23±0.05			CeO ₂ (IV), Ce (III) NO ₃
Collins <i>et al.</i> 2017 [179]	0.89	1.14			CeO ₂ (IV), CeF ₃ (III)
Feng <i>et al.</i> 2015 [173]	0.90	1.25			CeO ₂ (IV), CeF ₃ (III)
Wu <i>et al.</i> 2004 [168]	0.91	1.33			CeO ₂ (IV), Ce (III) PO ₄
Yang <i>et al.</i> 2015 [180]			1.30	1.90	PrO ₂ (IV), Pr ₂ O ₃ (III)
Fortner <i>et al.</i> 1996 [167,170]	0.89	1.14	1.28	1.82	CeO ₂ (IV), Ce (III) PO ₄ , PrO ₂ (IV), Pr ₂ O ₃ (III)
This work	0.79±0.03		1.25±0.20		Ce _{0.75} (IV) Pr _{0.16} (IV) Gd _{0.09} (III) O ₂
This work	0.79±0.03		1.25±0.07		Ce _{0.30} (IV) Pr _{0.67} (IV) Gd _{0.03} (III) O ₂

3.6. Dilatometry measurements

Dilatometry tests under air were performed on the prepared precursors at a rate of 2 °C·min⁻¹ from RT to 1450 °C to calculate the thermal expansion of PNO-GDC samples (*fig.* 3.8) with the differential method [181]. In the chosen temperature threshold, the average TEC was estimated at 14.16×10⁻⁶ K⁻¹ for C80 and 14.78×10⁻⁶ K⁻¹ for C20, slightly higher than for YSZ and GDC electrolytes ~ 12×10⁻⁶ K⁻¹ [182], but suitable for SOC operation conditions. Identical values were obtained in the 500-700 °C range (14.1×10⁻⁶ K⁻¹ for C80 and 14.8×10⁻⁶ K⁻¹ for C20), as seen in *fig.* 3.9. Nevertheless, the value of these coefficients rises to 18.1×10⁻⁶ K⁻¹ and 19.1×10⁻⁶ K⁻¹ for C80 (at 700 °C) and C20 (at 800 °C), respectively. This increase indicates that the intermediate temperature range

is more suitable for the SOC operation of these materials. Several authors noticed similar changes [157,160,183–185], suggesting a phase transition and could explain the differences identified in *fig. 3.8* at 450 °C and 650 °C for C20 and C80, respectively.

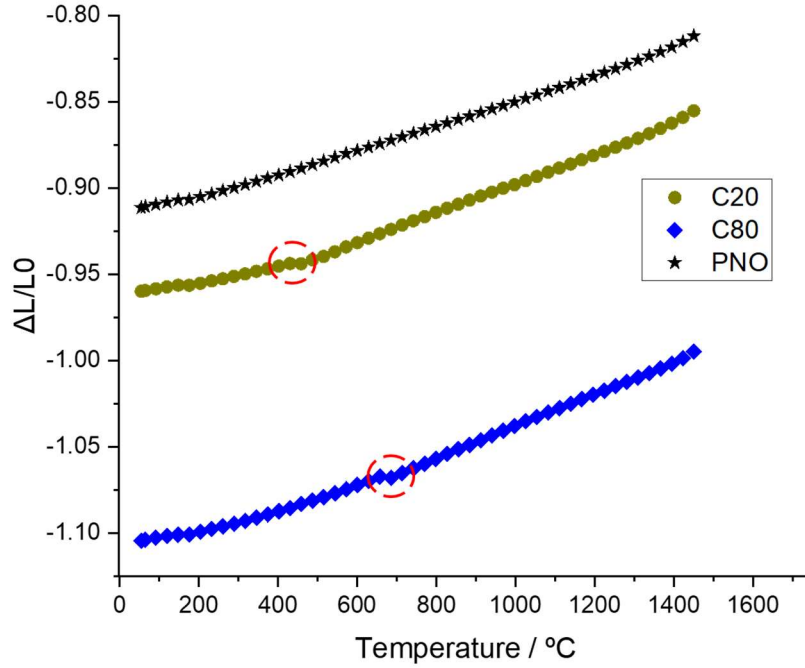


Figure 3.8. Dilatometry measurements of PNO and PNO-GDC samples (C20 and C80) from RT to 1450 °C. The red circles indicate changes in the slopes.

In a previous CPGO study, Chockalingam *et al.* [185] noted the same transition at 650 °C in the composition $\text{Ce}_{0.75}\text{Pr}_{0.20}\text{Gd}_{0.05}\text{O}_{2-\delta}$, a similar composition to C80. Also, Chiba *et al.* [160] observed similar transitions at 450 °C for the Pr-rich ceria composition $\text{Ce}_{0.3}\text{Pr}_{0.7}\text{O}_{2-\delta}$ and ~550 °C for $\text{Ce}_{0.8}\text{Pr}_{0.2}\text{O}_{2-\delta}$. These transition temperatures are within the range of the ceria reduction temperatures at the surface (around 420 °C) and in the bulk (about 720 °C) [186].

The increase in the slope of the curves over 700 °C may have been caused by the loss of lattice oxygen [185], while Pr doping in the ceria induces a significant chemical expansion [185,187,188] that affects the thermomechanical stability of the material. This change of slope on TEC for PNO-GDC samples in *fig. 3.9* indicates that Pr is introduced into the cubic ceria fluorite structure. The PNO decomposition into Pr and Ni oxides initiates this process that starts at 700 °C [189], expelling PrO_x at 800 °C [190], which is incorporated into the ceria lattice, producing a lattice expansion and forming the CPGO phase. *Figure 3.10* shows a peak in the contraction velocity calculations from dilatometry tests due to the CPGO formation at around 1100 °C. Other authors have reported a high

thermal and chemical expansion for these oxides [166,185]. For $x < 0.2$, the thermal and chemical expansions seem more suitable for SOC operation [191].

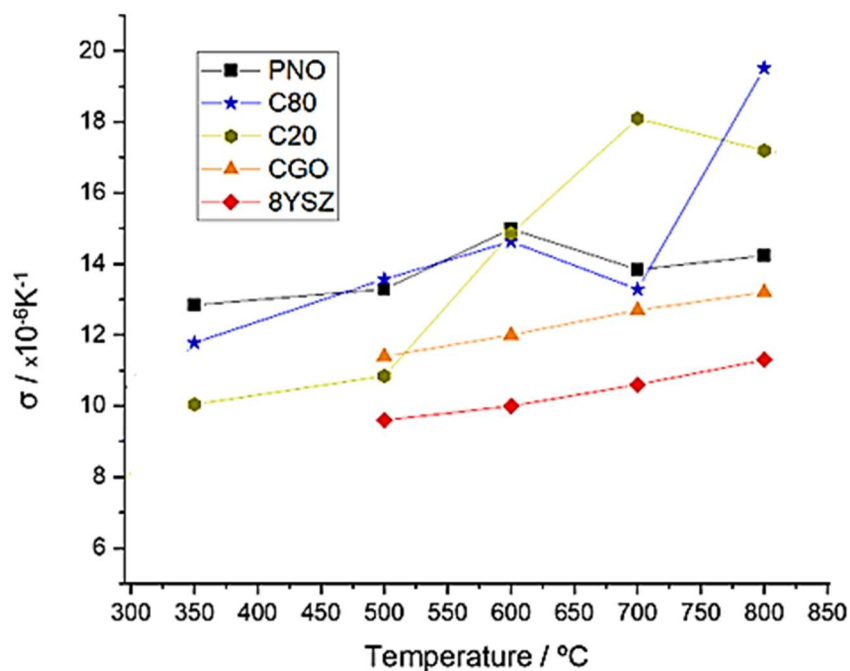


Figure 3.9. Temperature dependences of the differential TEC for the PNO-GDC and PNO samples compared with GDC [192], YSZ [182], and PNO from 350 to 800 °C.

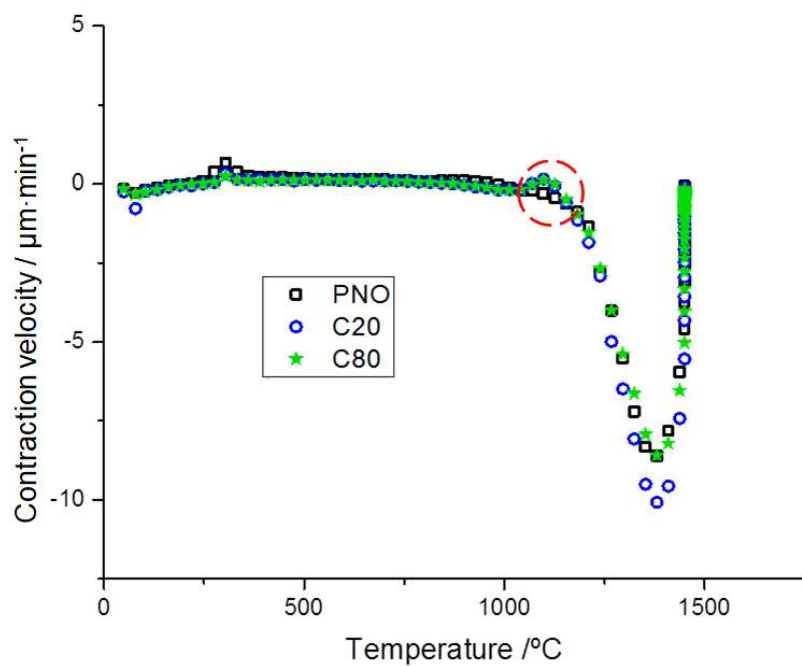


Figure 3.10. Contraction velocity calculations on PNO-GDC and PNO samples obtained from dilatometry tests performed at 1450 °C with a rate of 2 °C·min⁻¹ for 2 h.

3.7. Electrical conductivity

The electrical conductivity (σ_{el}) was characterized by the four-point probe method in the cylindrical PNO, C20, and C80 precursors. The temperature was measured with a thermocouple positioned in the vicinity of the sample (within 2 mm). The cylindrical samples were placed into a Probostat test cell inserted vertically into a tubular furnace. The dimensions of the samples are described in *Table 3.2*. The electrical current of the potentiostat was fixed at 100 mA for PNO and C20 and 10 mA for C80, and the voltage was recorded to calculate σ_{el} in air. PNO showed the highest electrical conductivity with a $\sigma_{el} = 93.19 \text{ S}\cdot\text{cm}^{-1}$ at 800 °C. C20 showed a maximum value of $\sigma_{el} = 0.81 \text{ S}\cdot\text{cm}^{-1}$ at 800 °C under air, while C80 registered a $\sigma_{el} = 0.13 \text{ S}\cdot\text{cm}^{-1}$ at 800 °C as shown in *fig. 3.11*. Those values agree with the literature values for PNO [193], PDC [160,194], and CPGO [160,185]. GDC's electrical conductivity may vary at 800 °C under air (5×10^{-4} to $2 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$) [195–197], while PDC σ_{el} seems to increase proportionally to the Pr content [198]. This makes sense in the fact that the contribution of the electron/hole conductivity to the total conductivity increases with temperature, being the activation energy for ionic conduction (0.7–0.8 eV) significantly lower than the p-type electronic transport (1.1–1.7 eV) [199]. The activation energies for σ_{el} in C80 and C20 were 1.40 eV and 0.56 eV, respectively. The C80 activation energy for σ_{el} is within the value for low Pr content in CPGO (1.10 eV [196]).

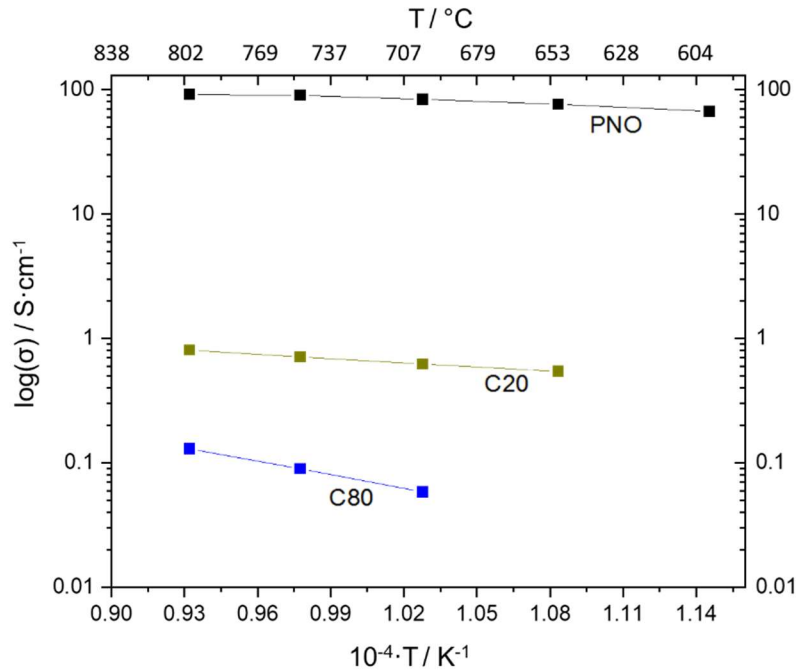


Figure 3.11. Temperature dependencies of electrical conductivity of PNO-GDC and PNO under air.

The temperature dependence of conductivity seems to be controlled by the mobility of the electrons, even at temperatures lower than 800 °C. In doped ceria, the Pr-ion electron hopping between Pr^{3+} and Pr^{4+} cations in the lattice helps to increase oxygen vacancy concentrations at high temperatures [187]. It is important to consider that in doped ceria [199,200], Pr doping facilitates electronic transitions by the formation of an impurity band in between the O-2p valence band and the Ce-4f conduction band, which explains the higher σ_{el} than GDC.

3.8. Reduction and oxidation kinetics

The ECR technique was selected to calculate oxygen chemical diffusion (D_{chem}) and surface exchange (k_{ex}) coefficients. The fittings were made by employing Ciucci's ECRTTOOLS MATLAB script [152–154], which uses a regression model to validate the simultaneous calculations of D_{chem} and k_{ex} coefficients from ECR data. Although non-linear ECR modeling [201] can solve some of the linear ECR deficiencies like the non-linearity of the transport of charged species and surface reaction rates [146], we chose the more straightforward Ciucci's model as an approach for the identification of patterns in the oxygen kinetic parameters of PNO and PNO-GDC specimens. The oxygen transport properties were measured via the conductivity by changing the temperature stepwise from 800 to 600 °C in PNO, from 800 to 650 °C in C20, and from 800 to 700 °C in C80.

Using the four-probe technique, electrical contacts were made by high-purity (99.99%) platinum wires connected at the edges of the samples (current terminals) and in the center (voltage sensing) with equidistant separation. The testing atmosphere was a dry N_2/O_2 mixture. All the experiments were done by changing the oxygen partial pressure ranges ($\Delta p\text{O}_2$) from 0.21 (synthetic air) to 0.10 atm, 0.10 to 0.02 atm, 0.02 to 1.00 atm, and 1.00 to 0.21 atm as shown in *fig. 3.12*. The total flux stream was fixed at $83.5 \text{ ml} \cdot \text{min}^{-1}$. The experimental values were monitored automatically and logged with a sampling rate of two seconds per measure point.

During the experiments, we ensured a controlled response time for oxygen reduction/flush time of fewer than 20 seconds. This correction in flushing time must be applied to maintain similar time constraints associated between oxygen transport and atmosphere re-equilibration [202].

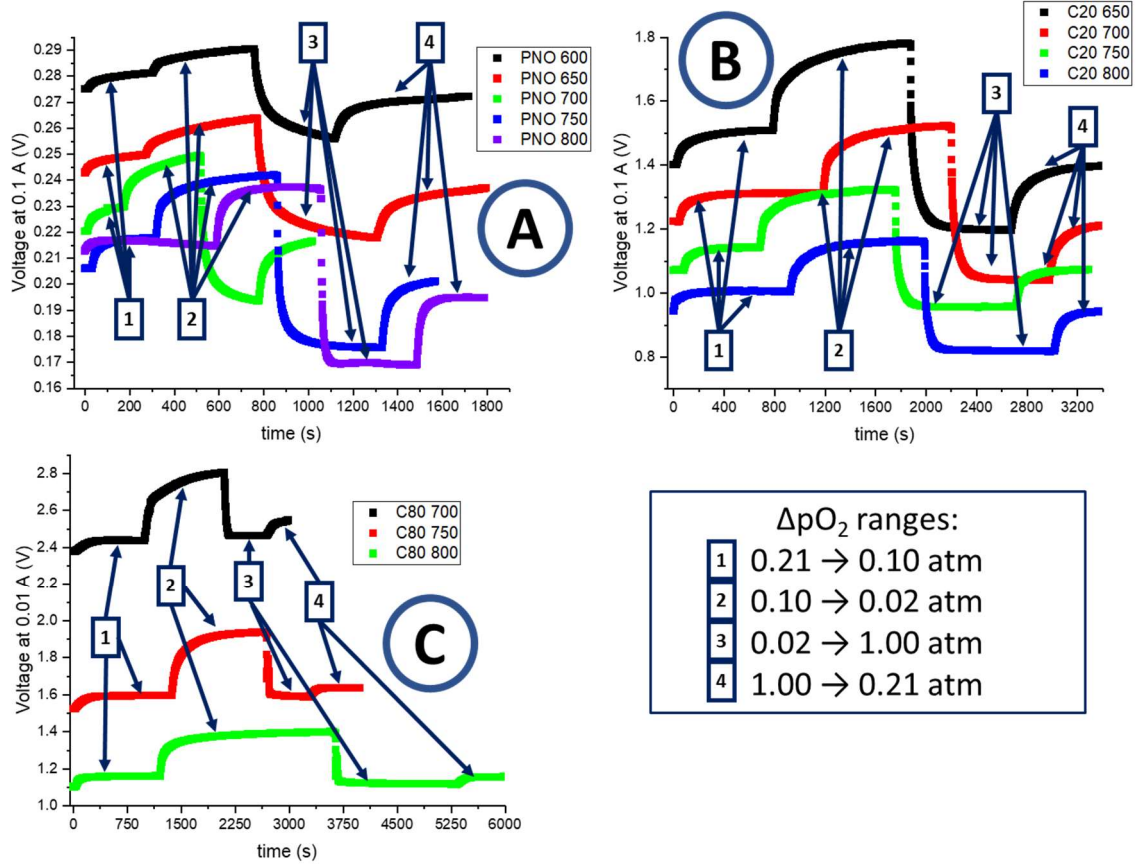


Figure 3.12. ECR experiments under different ΔpO_2 and temperatures on a) PNO, b) C20, and c) C80. The numbers indicate the pO_2 range in which the measurement was taken.

In *fig. 3.13a* results, the electronic conductivity relaxation time was in the order of $PNO < C20 < C80$ from $\Delta pO_2 = 0.21 \rightarrow 0.10$ atm (usual pO_2 under SOC operation). In PNO, the faster relaxation time is owed to higher electronic conductivity under these conditions. Similar results were obtained in the electronic relaxation under ΔpO_2 from 0.10 to 0.02 atm (*fig. 3.13b*). However, different behavior in the normalized conductivity is observed as further ΔpO_2 is induced. For example, as pO_2 increases from 0.02 to 1 atm (*fig. 3.13c*), the C20 sample presents the slowest normalized electronic conductivity relaxation, especially at 700 °C. It also seems that the PNO phase in the C20 sample contributes to the fast electronic relaxation at 800 °C and under reducing conditions (as seen in *figs. 3.13a* and *3.13b*).

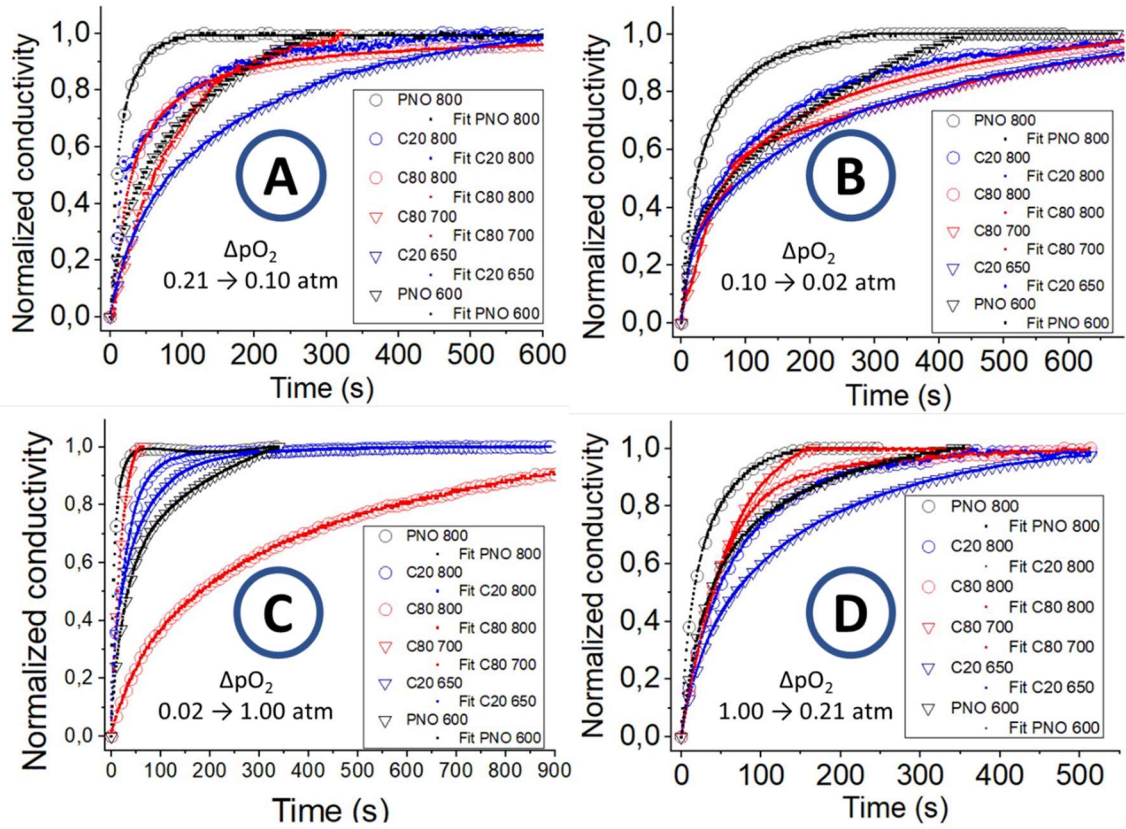


Figure 3.13. Normalized conductivity fittings of ECR data under different ΔpO_2 : a) 0.21→0.10 atm, b) 0.10→0.02 atm, c) 0.02→1.00 atm, and d) 1.00→0.21 atm.

At low temperatures and oxidation conditions ($\Delta pO_2 = 0.02$ to 1.00 atm), the behavior of the C20 sample is worse than in C80 (mainly CPGO). In C80, we observed a generally faster electronic relaxation at lower temperatures and increasing ΔpO_2 (700 °C and $\Delta pO_2 = 0.02 \rightarrow 1.00$ atm).

The k_{ex} , obtained were 3.15×10^{-6} , 7.42×10^{-7} , and $2.20 \times 10^{-6} \text{ cm} \cdot \text{s}^{-1}$ at 800 °C for PNO, C20 and C80, respectively. The D_{chem} were 1.40×10^{-7} , 5.54×10^{-8} , and $7.60 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$ at 800 °C for PNO, C20 and C80, respectively. The temperature dependences of these coefficients are compared with similar works reported in the literature for lanthanide nickelates [89,106,193,203–209] in *fig. 3.14* and *3.15*. *Table 3.8* summarizes the activation energies for k_{ex} and D_{chem} . The D_{chem} activation energies of PNO are lower than the reported for secondary ion mass spectroscopy (SIMS) [193] and pulsed isotope exchange (PIE) [209] methods. Still, the activation energies were in good agreement with other lanthanide nickelates [89,193,204] and doped ceria [175,208,210–216]. The activation energies of k_{ex} and oxygen kinetic coefficients obtained in PNO do not differ significantly from Boehm *et al.* [193]. In addition, the activation energies in D_{chem} and k_{ex} are similar to the published values for LNO.

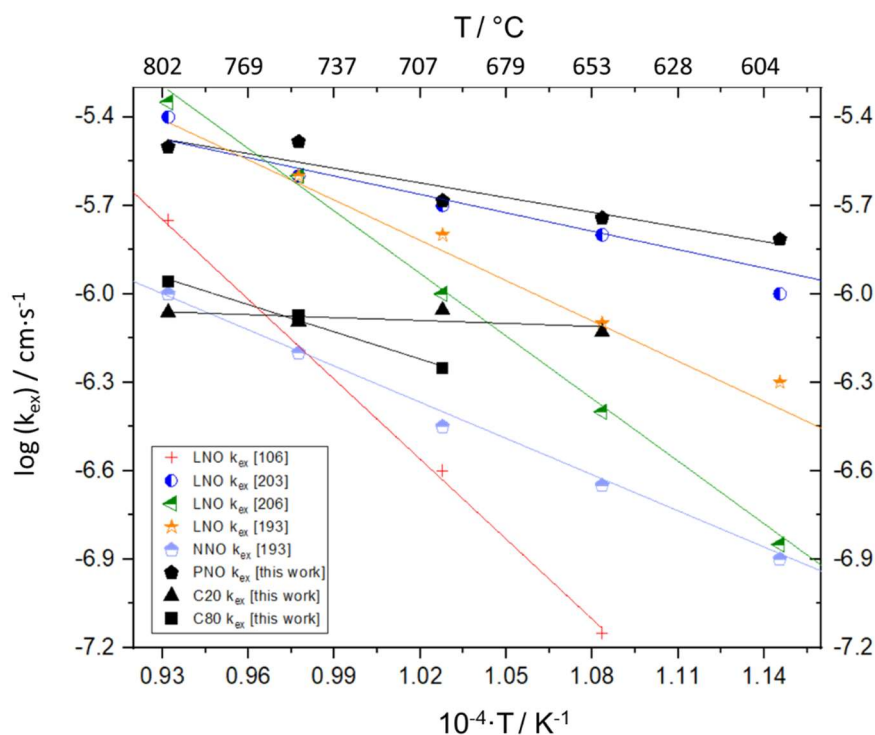


Figure 3.14. Arrhenius plots of k_{ex} of the samples studied in this work compared with nickelate literature data.

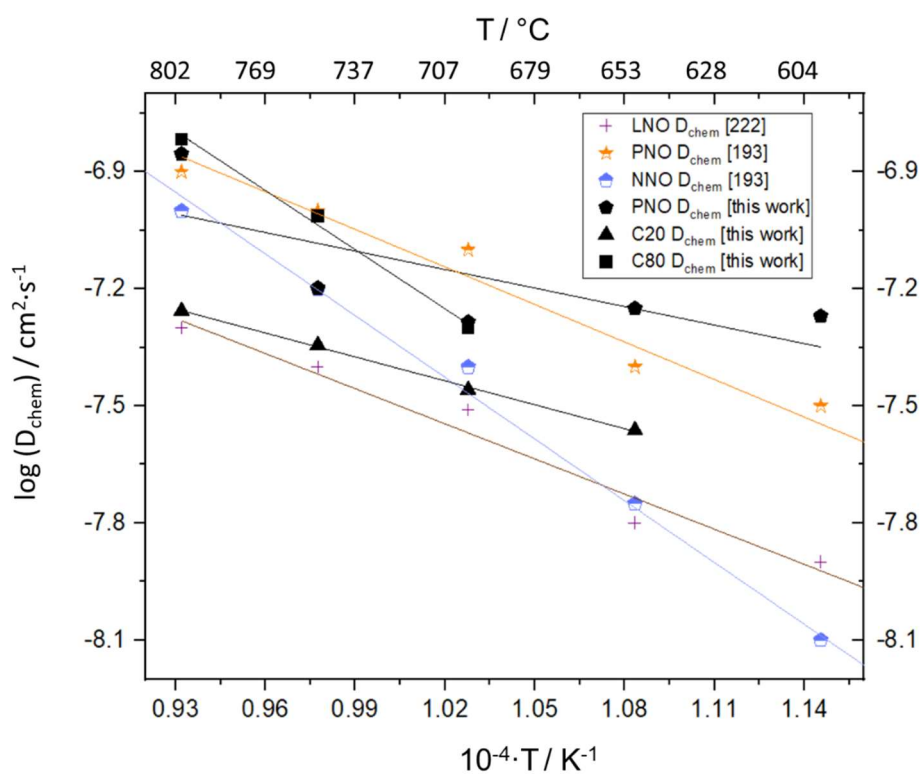


Figure 3.15. Arrhenius plots of D_{chem} of the samples studied in this work compared with nickelate literature data.

Regarding the low activation energies for k_{ex} in C20 (0.10 eV), one hypothesis is that it occurs due to several secondary phases interacting between 650 and 800 °C, which modifies the diffusion processes in the sample at this temperature range. This kind of result is unusual and has been explained before by Adler *et al.* [217], as absorbed $^{18}\text{O}_2$ could swap one labeled O_2 atom for an unlabeled atom to form $^{18}\text{O}^{16}\text{O}$ without crossing the dissociation barrier. Maier *et al.* [218] implied that if the process has low activation energy, it will occur at a faster rate (effective rate constants), and the source of the mechanism turns out to involve an energetic barrier to O_2 dissociation. This mechanism would occur at the same time as bulk incorporation. This would also entail a high availability of free electrons to transfer charge for O_2 incorporation into the bulk. Adler *et al.* [217] also mentioned that this is not usually a possibility and is more likely a source of uncertainty. It is essential to point out that in ECR, the measurements can be in surface, diffusion, or mixed control regime. Fittings to relaxation data with a lower than 3 % standard error mean a re-equilibration in a hybrid regime in oxygen kinetic coefficients [219]. The surface-controlled regime, where the estimation of D_{chem} has higher uncertainty, is usually found at low temperatures, while diffusion control can be seen at higher temperatures. This means that k_{ex} values have a more considerable uncertainty at temperatures higher than 650 °C as it enters the diffusion regime.

In C80, under similar conditions, the reported value of GDC activation energy in D_{chem} is 1.1 eV, while for k_{ex} is 1.0 eV [220,221] below 650°C. The same authors suggested a change in activation energies over 650°C at 2.4 eV. This activation energy change was not evident in our calculations for these temperatures. In voltage relaxation experiments at very low Pr contents, where the D_{chem} for n- and p-type conductivities were modeled, Lubke and Wiemhofer [196] calculated values of $D_{chem(n)} < 2 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ and $D_{chem(p)} < 8 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ at 600 °C. These values were in good agreement with ours and, to our knowledge, are the only values reported for the CPGO phases. Nonetheless, it is sufficient to say that C20 and C80 have a higher concentration of electrons than GDC, evidenced by higher k_{ex} and D_{chem} values. Under SOC operating conditions, this could be beneficial for their use as an air electrode [101].

Table 3.8. Activation energies for D_{chem} and k_{ex} in $\text{Ln}_2\text{NiO}_{4\pm\delta}$ (Ln = La, Pr, Nd) and GDC mixed oxides at selected temperature ranges and $p\text{O}_2 = 0.21$ atm.

Oxide	$\Delta T, ^\circ\text{C}$	Activation energy (eV)		Method	Reference
		Diffusion (D_{chem})	Exchange (k_{ex})		
LNO	450-800	0.62	1.29	SIMS	Kilner <i>et al.</i> [222] Bouwmeester <i>et al.</i> [206]
	600-800	n/a	1.35	PIE	
	520-800	0.71	0.41	SIMS	Boehm <i>et al.</i> [193]
	550-700	1.05	1.46	PIE, ECR	Saher <i>et al.</i> [209]
PNO	550-750	0.91	1.44	PIE, ECR	Sadykov <i>et al.</i> [208]
	600-800	0.40	0.29	ECR	this work
C20	650-800	0.41	0.10	ECR	this work
C80	700-800	1.00	0.61	ECR	this work
NNO	520-800	1.07	0.78	SIMS	Boehm <i>et al.</i> [193]

To better understand the influence of oxygen activity on the oxygen kinetic coefficients, we analyzed its dependence on $p\text{O}_2$ at the different temperatures studied (*fig. 3.16*). The diffusivity seems stable in C80 at $p\text{O}_2 > 0.21$ atm, while higher D_{chem} values are calculated under a lower oxygen evolution (*fig. 3.16a*), where oxygen uptake takes place primarily due to the reduction of Pr, in contrast to the reduction of Ce [223]. This occurs because low $p\text{O}_2$ ($<10^{-30}$ atm at RT) and higher temperatures (>1700 °C at ambient pressure) are required to remove oxygen from CeO_2 [224]. The increase in D_{chem} at low $p\text{O}_2$ is consistent with the experiments of D'Angelo *et al.* [223], who found that oxygen vacancy concentration increased when Pr was added to CeO_2 , further increasing with Pr content. According to their conclusions, at low $p\text{O}_2$, the C80 reduction enhances oxygen uptake due to the presence of oxygen vacancies from the addition of Pr to the ceria. On the other hand, the D_{chem} values in C20 and PNO increase with the temperature and $p\text{O}_2$, obtaining maximum values at 800 °C. At low $p\text{O}_2$, the D_{chem} is lower for C20 and PNO as the defect formation differs from the vacancy-driven C80 due to the presence of the PNO phase in both samples. The effect of the interstitial oxygen in this phase contributes to a higher D_{chem} and k_{ex} at higher $p\text{O}_2$.

In the k_{ex} calculations for each sample, a thermally driven pattern is observed as $p\text{O}_2$ increases. In C20, the k_{ex} decreases by 1.5 orders of magnitude as the temperature and $p\text{O}_2$ increase to 800 °C and 1 atm, respectively (*fig. 3.16b*). In PNO, the opposite effect is observed (*fig. 3.16c*), although a slightly lower k_{ex} is calculated at 800 °C. According to these results, a $p\text{O}_2 > 0.21$ atm during SOC operation could improve the oxygen kinetic

processes in PNO-based electrodes at the 600-800 °C temperature range. In contrast, C20 and C80 oxygen kinetics are generally more suitable for <800 °C.

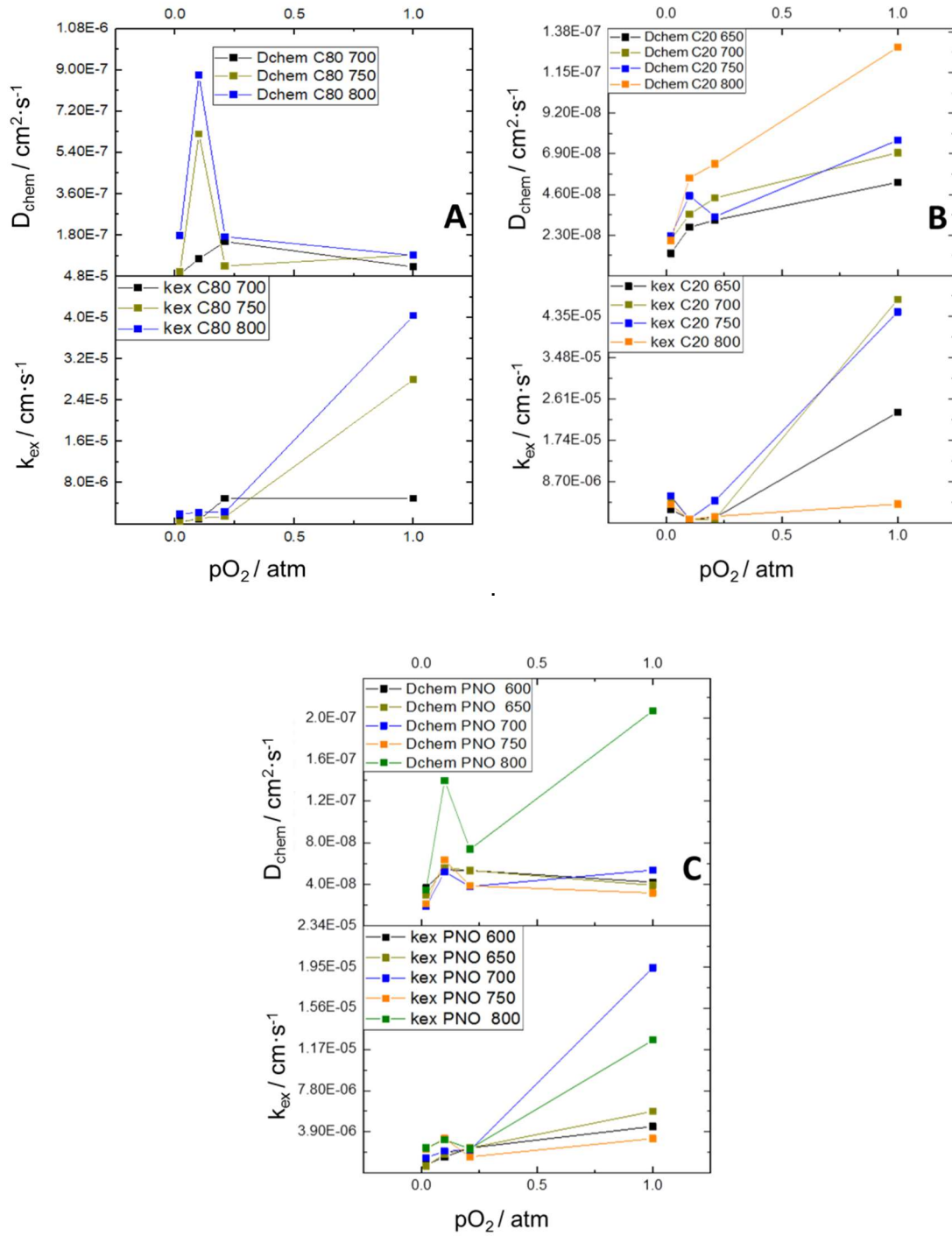


Figure 3.16. Oxygen partial pressure dependencies of k_{ex} and D_{chem} coefficients at temperature variations for the samples: A) C80; B) C20; C) PNO.

3.9. EIS measurements on symmetrical cells

To verify the electrochemical performance of the materials as air electrodes, symmetrical cells were characterized by EIS to determine the R_{pol} under typical operating conditions in high-temperature SOC (700-850 °C at 1 atm). In this study, the electrochemical performance of C20 and C80 electrodes is compared with PNO symmetrical cells as a fingerprint, where five types of cells were manufactured: 3 single-layer (PNO, C20, and C80) and two double-layer (C20/PNO and C80/PNO) air electrode prospects. The air electrode layers were sintered (at 1100 °C for 2.0 h) on GDC pellets with up/down ramps of 2 °C·min⁻¹.

The measurements were performed under OCV conditions with a 20 mV of AC sinusoidal amplitude and a frequency range from 100 kHz to 100 mHz. The calculated R_{pol} values and EIS measurements are shown in *fig. 3.17a* and *b*.

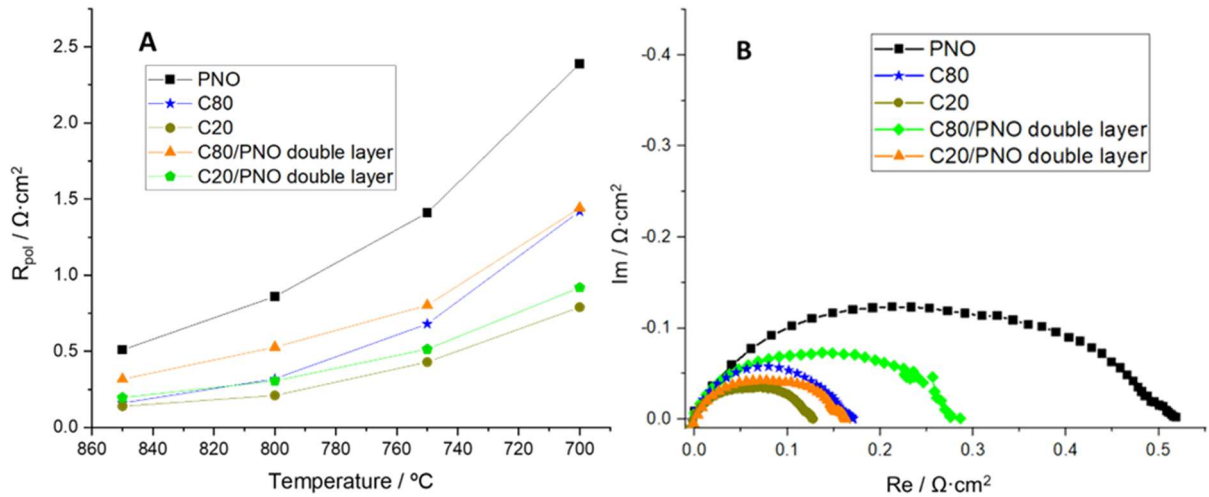


Figure 3.17. A) R_{pol} temperature variations of PNO and PNO-GDC compounds. B) EIS of PNO-GDC compared to PNO at 850 °C.

Resistance-constant phase elements (R_{CPE}) are employed to account for the entire frequency range of processes. The cells were fitted using the distribution of relaxation times (DRT) fitting method, and the R_{pol} values are presented in *Table 3.9*. The DRT parameters of full width half maximum (FWHM = 0.5) and regularization parameter ($\lambda = 0.001$) were constant for each cell. Capacitance and frequencies for each contribution were calculated according to the equations listed in reference [107]:

$$C = (R_{pol}^{1-n} Q)^{\frac{1}{n}} \quad (3.3)$$

$$f_0 = \frac{(R_{pol} Q)^{-\frac{1}{n}}}{2\pi} \quad (3.4)$$

where C is the capacitance, n is an exponent with a value between 0 and 1 that considers the deviation from the ideal capacitor behavior, Q is the fit parameter of the constant phase element, and f_0 is the relaxation frequency.

The resistance values of individual (*i*) peaks (R_i , with typically five identified peaks or $i = 1, \dots, 5$) are calculated by multiplying the surface area fraction of each peak times the R_{pol} of the cell. Using this method, in most cases, four R_{CPE} elements were needed for the fittings.

Table 3.9. Symmetrical SOC R_{pol} values between 700-850 °C, acquired by DRT fittings of EIS data.

850 °C									
Cell	R1	C1	R2	C2	R3	C3	R4	C4	R_{pol}
	($\Omega \cdot \text{cm}^2$)	($\text{F} \cdot \text{cm}^2$)	($\Omega \cdot \text{cm}^2$)	($\text{F} \cdot \text{cm}^2$)	($\Omega \cdot \text{cm}^2$)	($\text{F} \cdot \text{cm}^2$)	($\Omega \cdot \text{cm}^2$)	($\text{F} \cdot \text{cm}^2$)	($\Omega \cdot \text{cm}^2$)
	(3x10 ⁴ -5x10 ⁴ Hz)		(1000-8000 Hz)		(100-1000 Hz)		(10-100 Hz)		
PNO	0.23	2x10 ⁻⁵	0.15	2x10 ⁻⁴	0.11	2x10 ⁻³	0.03	0.08	0.53
C20	0.06	9x10 ⁻⁵	0.04	1x10 ⁻³	0.03	0.01	0.01	0.20	0.13
C80	0.11	3x10 ⁻⁵	0.05	4x10 ⁻⁴	0.00	0.08	0.01	0.17	0.17
800 °C									
Cell	R1	C1	R2	C2	R3	C3	R4	C4	R_{pol}
	($\Omega \cdot \text{cm}^2$)	($\text{F} \cdot \text{cm}^2$)	($\Omega \cdot \text{cm}^2$)	($\text{F} \cdot \text{cm}^2$)	($\Omega \cdot \text{cm}^2$)	($\text{F} \cdot \text{cm}^2$)	($\Omega \cdot \text{cm}^2$)	($\text{F} \cdot \text{cm}^2$)	($\Omega \cdot \text{cm}^2$)
	(1x10 ⁴ -5x10 ⁴ Hz)		(1000-9000 Hz)		(100-1000 Hz)		(10-100 Hz)		
C20	0.07	7x10 ⁻⁵	0.06	7x10 ⁻⁴	0.09	2x10 ⁻³	0.01	0.04	0.23
C80	0.07	5x10 ⁻⁵	0.21	8x10 ⁻⁵	0.05	3x10 ⁻³	0.01	0.18	0.34
751 °C									
Cell	R1	C1	R2	C2	R3	C3	R4	C4	R_{pol}
	($\Omega \cdot \text{cm}^2$)	($\text{F} \cdot \text{cm}^2$)	($\Omega \cdot \text{cm}^2$)	($\text{F} \cdot \text{cm}^2$)	($\Omega \cdot \text{cm}^2$)	($\text{F} \cdot \text{cm}^2$)	($\Omega \cdot \text{cm}^2$)	($\text{F} \cdot \text{cm}^2$)	($\Omega \cdot \text{cm}^2$)
	(3x10 ⁴ -9x10 ⁴ Hz)		(1000-7000 Hz)		(100-1000 Hz)		(10-100 Hz)		
C20	0.05	1x10 ⁻⁵	0.11	2x10 ⁻⁴	0.11	1x10 ⁻³	0.16	5x10 ⁻³	0.42
C80	0.08	4x10 ⁻⁵	0.27	8x10 ⁻⁵	0.22	4x10 ⁻⁴	0.08	4x10 ⁻³	0.65
701 °C									
Cell	R1	C1	R2	C2	R3	C3	R4	C4	R_{pol}
	($\Omega \cdot \text{cm}^2$)	($\text{F} \cdot \text{cm}^2$)	($\Omega \cdot \text{cm}^2$)	($\text{F} \cdot \text{cm}^2$)	($\Omega \cdot \text{cm}^2$)	($\text{F} \cdot \text{cm}^2$)	($\Omega \cdot \text{cm}^2$)	($\text{F} \cdot \text{cm}^2$)	($\Omega \cdot \text{cm}^2$)
	(3x10 ⁴ -9x10 ⁴ Hz)		(1000-9000 Hz)		(100-1000 Hz)		(10-100 Hz)		
C20	0.04	1x10 ⁻⁵	0.18	1x10 ⁻⁴	0.17	9x10 ⁻⁴	0.39	2x10 ⁻³	0.79
C80	0.08	4x10 ⁻⁵	0.07	2x10 ⁻⁴	0.84	9x10 ⁻⁵	0.40	1x10 ⁻³	1.40

The resulting impedance values for PNO, C20, and C80 cells are evaluated by the DRT technique to assess the changes of either PNO or the doped ceria composition on the electrode microstructure and the contribution of the deconvoluted peaks to R_{pol} (*fig. 3.18*). The deconvolution was performed using the multiple peaks fit Gaussian function of Origin [225].

At 850 °C, the R_{pol} value of PNO ($0.51 \Omega \cdot \text{cm}^2$) is almost four times higher than in C20 ($0.13 \Omega \cdot \text{cm}^2$) and three times higher than in C80 ($0.17 \Omega \cdot \text{cm}^2$). Similar results are obtained at lower temperatures for the C20 and C80. Also, the double-layered symmetrical cells (C20/PNO and C80/PNO) presented a similar behavior with a slight R_{pol} increase over single-layer cells (*fig. 3.17b*), indicating that the outmost current collector PNO layer does not affect the performance significantly. The PNO secondary phase in C20 could be beneficial for electrode activation, enhancing its electrical conductivity and accounting for the low R_{pol} values compared to PNO [101].

DRT adjustments were attempted at less than 850 °C in the PNO cells; however, due to the anomaly produced by the instability effect due to nickelate decomposition, the processes overlapped at low frequencies without giving a definitive result, which is why no comparison with C20 and C80 at lower temperatures was performed

The fitting peak designations of the polarization resistances in the correspondent frequency ranges are generally in concordance with the results found in the literature for SOC's [101,111,226,227].

In *fig. 3.18*, The R1 peak in the frequency range of 10^4 and 10^5 Hz is affected by the composition or temperature. Such a high-frequency mechanism is typically associated with interfacial effects in the electrode [228]. In the PNO cell at 850 °C, the R1 peak is higher, and this process is thermally driven in the order of PNO>C20>C80, possibly influenced by the nickelate decomposition.

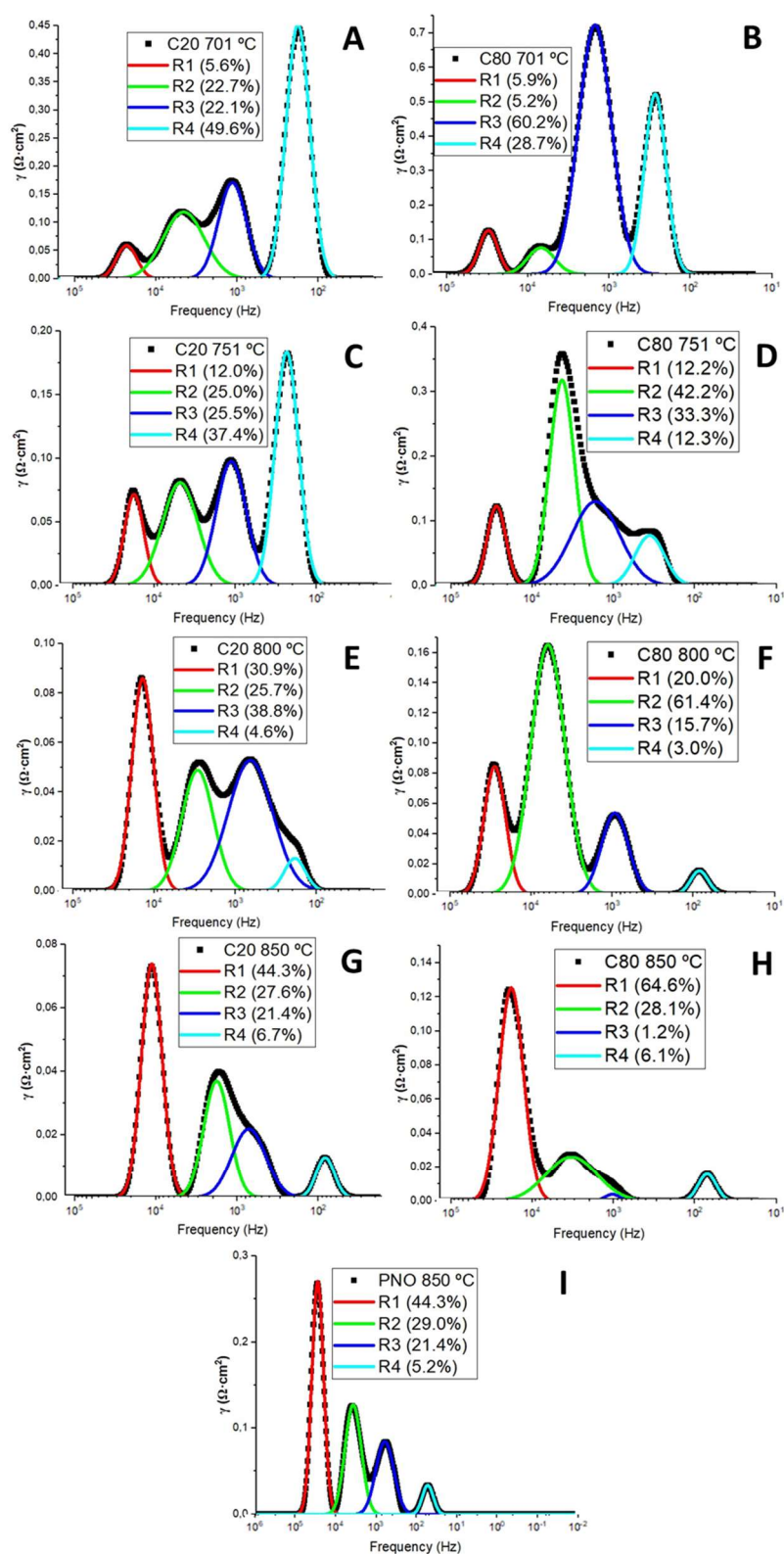


Figure 3.18. Deconvoluted symmetrical cell DRT data of C20 and C80 at 701 °C (A and B), 751 °C (C and D), 800 °C (E and F), 850 °C (G and H), and PNO at 850 °C (I). The inset indicates the area percent of each peak.

Temperature dependences of each R_{pol} contribution are shown in *fig. 3.19*. In C20's R2 peak, a temperature increase reduces the value, while in C80, this effect is not observed. These peaks overlap with R3 regardless of the sample and can be associated with charge transfer polarization in the electrode/electrolyte interface at this frequency threshold. The R3 peak between 100-1000 Hz is usually associated with the transport of gases in fuel and oxygen electrodes. This peak decreases with a higher Ce content and over 800 °C, where the R_{pol} reduces in the following compositional order: C80<C20. In C80, this process is heavily influenced by temperature (activation energy, $E_a = 349 \text{ kJ}\cdot\text{mol}^{-1}$, *fig. 3.19b*), likely due to more oxygen vacancy formation. The R4 peak usually pertains to a mix of O^{2-} surface exchange and charge transfer processes inside the oxygen electrode. This peak diminishes at low temperatures in the order of C80<C20 with similar E_a (240 vs. 257 $\text{kJ}\cdot\text{mol}^{-1}$, respectively, *fig. 3.19a and b*).

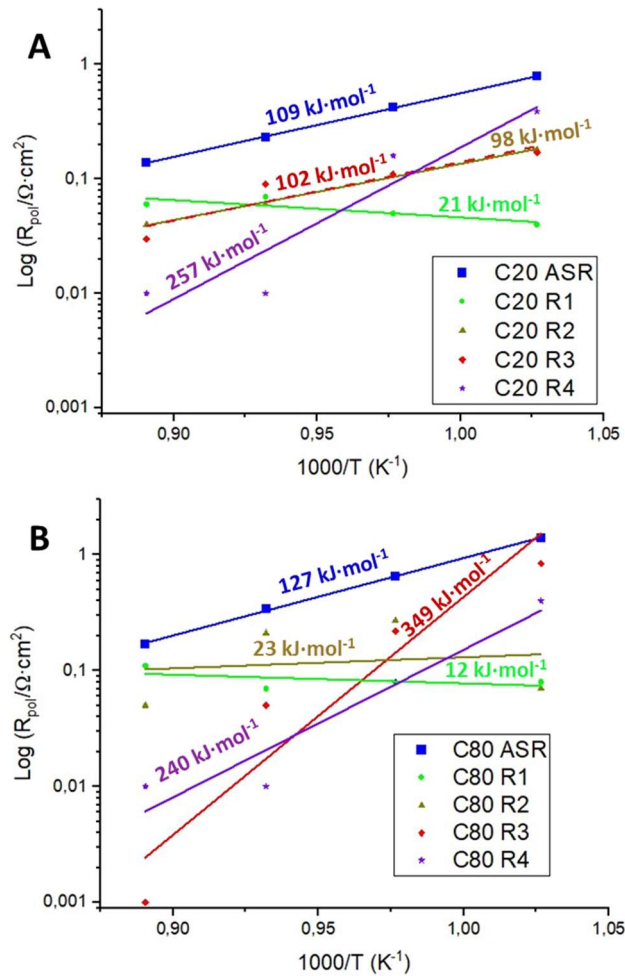


Figure 3.19. Temperature dependences of R_{pol} and individual DRT fittings in the temperature range of 700-850 °C of C20 (A) and C80 (B).

In PNO-GDC electrodes, lower than 1 Hz peaks did not appear, likely due to the extension of the TPB area for electrochemical oxygen reduction reaction [229], which reduces the gas diffusion polarization resistance.

In general, even though a significant reduction of the PNO R_{pol} is obtained with the use of PNO-GDC electrodes, further analyses in single SOCs need to be performed before designating a definitive mechanism for all R_{pol} contributions under standard SOFC/SOEC operation.

3.10. Conclusions

This chapter has focused on the prospect of PNO and PNO-GDC oxide precursors as SOC air electrodes. Ceramic precursors from these materials were fabricated by isostatic pressing. PNO-GDC mixtures were structurally characterized using XRD, where cubic lattice structure compatibility of CPGO and PrO_x phases with Vegard's rule allowed predicting the Ce and Pr oxidation states based on experimental results. We have also evaluated the compromise between oxygen exchange kinetics and the thermal expansion of PNO-GDC. The results indicate that PNO-GDC TEC values of $14 \times 10^{-6} \text{ K}^{-1}$ for C80 and $15 \times 10^{-6} \text{ K}^{-1}$ for C20 are more suitable in the operation range of 500 to 700 °C with standard electrolyte materials, as well as PNO oxygen electrodes.

EDS-STEM experiments were performed to quantify the ensuing cation CPGO composition at $Ce_{0.75}Pr_{0.16}Gd_{0.095}O_{2.5}$ for C80 and $Ce_{0.30}Pr_{0.67}Gd_{0.03}O_{2.5}$ for C20. The structural findings agreed with EELS' Ce and Pr oxidation states, where tetravalence is present in both Ce and Pr cations in the PNO-GDC samples.

The oxygen exchange kinetics of PNO-GDC was also evaluated using ECR to understand better the oxygen surface exchange and diffusion in these materials for SOC applications. The surface exchange value, k_{ex} , obtained were 7.4×10^{-7} and $2.2 \times 10^{-6} \text{ cm} \cdot \text{s}^{-1}$ at 800 °C for C20 and C80, respectively. Moreover, the D_{chem} in PNO-GDC showed some of the highest values in literature amongst doped ceria at 5.5×10^{-8} and $7.6 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$ at 800 °C for C20 and C80, respectively. These results highlight the influence of Gd in the oxygen transport of CPGO, as C80 has higher Gd content. The C20 sample showed a generally faster oxygen exchange in the 650 to 800 °C threshold, especially under decreasing pO_2 , whereas C80 samples showed better performance under increasing pO_2 and a temperature < 800 °C. In addition, PNO-GDC composites show enhanced electrochemical performance, where we found R_{pol} values of $0.13 \Omega \cdot \text{cm}^2$ in

the C20 oxygen electrode and $0.17 \Omega \cdot \text{cm}^2$ in C80, both about 3 to 4 times less than PNO. These studies remain to be determined in the following chapters of this work. Given this context, PNO-GDC mixtures are confirmed as excellent candidates as oxygen electrodes for SOFC/SOEC applications.

Chapter 4. Production and Characterization of Microtubular Solid Oxide Cells using Extruded Supports

SOC's most enticing application is on devices capable of operating reversibly. The biggest challenge in rSOC operating mode is that optimal oxygen kinetics and mixed ionic and electronic conductivity properties in electrodes are often achieved at high temperatures, where the materials' integrity could be compromised in the long term. With so many parameters to control, a fair approach would be to focus on one of the components. Considering this, our implementations focus on SOC air electrodes and their medium-to-long-term stability.

Based on the results detailed in the preceding chapter, a combination of nickelate- and ceria-based materials is proposed to endure the electrochemical processes inherent in the reversible cell operating mode. In this chapter, these air electrode compositions are studied on extruded Ni-yttria-stabilized zirconia fuel electrode supports, which are further covered in chapter 5 using a different fuel electrode fabrication.

4.1. Introduction

The current research in advanced electrodes for intermediate-to-low temperature SOC (between 600 and 800 °C) operation is centered around lowering long-term degradation for its implementation on a vast industrial scale. Single cells employing a thin YSZ electrolyte and Ni-YSZ support often present a performance limitation at lower operating temperatures, evidenced by the air electrode's high polarization resistance [230,231].

Lanthanide nickelate materials have been proposed as oxygen electrodes for electrolysis applications in standard planar cells for LNO [232], NNO [233], and PNO [99]; nevertheless, reversible cycling studies have yet to be demonstrated in detail. We have demonstrated in chapter 3 that these materials are suitable for SOC operation. When using PNO-GDC mixtures as oxygen electrodes, it was determined that a reaction between PNO and GDC occurs during sintering, forming a mixed oxide of cerium doped with Gd and Pr, which presents good electrochemical and oxygen kinetic properties. Thus, implementing this mixed oxide in SOC configurations as an interlayer helps prevent electrode degradation, as the interaction of lanthanide nickelates with YSZ and GDC [98,234] results in insulating secondary phases at the interface (grain boundaries), which decrease the conductivity of the electrolytes.

This chapter will focus on developing PNO-based air electrodes in microtubular single-cell configuration and their electrochemical performance in rSOC mode. The extruded support fabrication method is featured as they have proven to be suitable in terms of cost, manufacturing time, and production efficiency of Ni-YSZ cermets. Also, as already covered in chapter 1, this configuration presents significant advantages over the conventional planar configuration. Several studies can be found in the literature regarding microtubular SOECs [101,235,236]; however, only a few involve long-term reversibility studies, and none use this type of oxygen electrode. The fabrication of the extruded NiO-YSZ supports was part of a research collaboration with Dr. Alejandro Vázquez's group at the University Carlos III of Madrid (UC3M), Spain.

4.2. Materials employed for cell fabrication

Nickel oxide was used as a precursor to metallic Ni to make the cermet that constitutes the fuel electrode support of the cells. The starting material had a $dp_{50} = 0.65 \mu\text{m}$, supplied by Hart Materials.

YSZ was present in the fuel electrode and the electrolyte and is made up of zirconia with 8 mol% Y_2O_3 (distributed by Tosoh and under the trade name TZ-8YS). The supplier indicates that the specific area of the ceramic powders is $7 \pm 2 \text{ m}^2 \cdot \text{g}^{-1}$. The particle size distribution is $\text{dp}_{50} = 0.96 \text{ }\mu\text{m}$. As previously studied by Monzón [121], the Ni-YSZ cermets present a conductivity of $\sigma_{\text{Ni-YSZ}} = 9,300 \text{ S} \cdot \text{cm}^{-1}$ due to considerably high particle connectivity with NiO of $\text{dp}_{50} \leq 1 \text{ }\mu\text{m}$ and open porosity of $\sim 34 \text{ vol. } \%$. As their properties are favorable for SOC operation, these materials were selected for fuel electrode fabrication.

The selected oxygen electrode material is based on the studies of the structural and kinetic properties of PNO-based materials, determining them as a viable prospect for SOC air electrodes. The PNO powder (Marion Technologies, $\text{dp}_{50} \sim 0.1\text{-}0.5 \text{ }\mu\text{m}$) maintained a stoichiometry of Pr to Ni of 2:1 atomic ratio. Their measured electric conductivity was $93 \text{ S} \cdot \text{cm}^{-1}$ at $800 \text{ }^\circ\text{C}$. In addition, PNO presents high oxygen surface exchange ($3.1 \times 10^{-6} \text{ cm} \cdot \text{s}^{-1}$) and oxygen chemical diffusion ($1.4 \times 10^{-7} \text{ cm} \cdot \text{s}^{-2}$) coefficients at $800 \text{ }^\circ\text{C}$ and atmospheric air, as described in *section 3.8*.

As previously reported, sintered PNO shows the presence of small amounts of NiO and $\text{Pr}_4\text{Si}_3\text{O}_{12}$. The materialographic SEM analysis of *figures 4.1a* and *b* displays an after-sintering bulk PNO with particles of these secondary phases. These phases correspond to $\sim 3 \text{ vol. } \%$ of the total content in bulk (*fig. 4.1b*), and the calculated dp_{50} of these particles was below the $1 \text{ }\mu\text{m}$ range (*figs. 4.1c* and *d*).

Finally, we have selected praseodymium nickelate and Gadolinium-doped Ceria mixtures based on the studied reactivity of PNO and GDC and their chemical compatibility, as described in chapter 3. GDC ceramic powders were supplied by FuelCell Materials. The nominal particle size of the supplied powder has a dp_{50} between 0.1 and $0.4 \text{ }\mu\text{m}$, with a surface area of $35.6 \text{ m}^2 \cdot \text{g}^{-1}$. As ceria is highly refractory, GDC presents sinterability problems. Its melting point is $2300 \text{ }^\circ\text{C}$, which reduces densification kinetics even at temperatures as high as $1600 \text{ }^\circ\text{C}$. As a result, many of the GDC-based layers presented in the literature are relatively porous compared to YSZ.

In this study, the PNO: GDC weight ratio is 4: 1, as increasing the Pr content enhances the vacant oxygen concentration and overall conductivity of the material. The calculated density of the mixed oxide is $7.06 \text{ g} \cdot \text{cm}^{-3}$. The PNO-GDC mixture used in the single SOC fabrication contains the CPGO composition of $\text{Ce}_{0.30}\text{Pr}_{0.67}\text{Gd}_{0.03}\text{O}_{2-\delta}$ formed by the interaction of the powders at $1100 \text{ }^\circ\text{C}$ in air. This composition is preferred since it

presents an excellent correlation between conductivity and catalytic activity. This composition also prevents the formation of praseodymium zirconate on contact in the YSZ electrolyte while showing high O_2 surface exchange and diffusion coefficients of $7.42 \times 10^{-7} \text{ cm} \cdot \text{s}^{-1}$ and $5.54 \times 10^{-8} \text{ cm} \cdot \text{s}^{-2}$, respectively. Not all the Pr-oxide diffuses into the ceria lattice; nevertheless, the unreacted phases (PNO and Pr_6O_{11}) are beneficial in the overall conductivity of the mixed oxide.

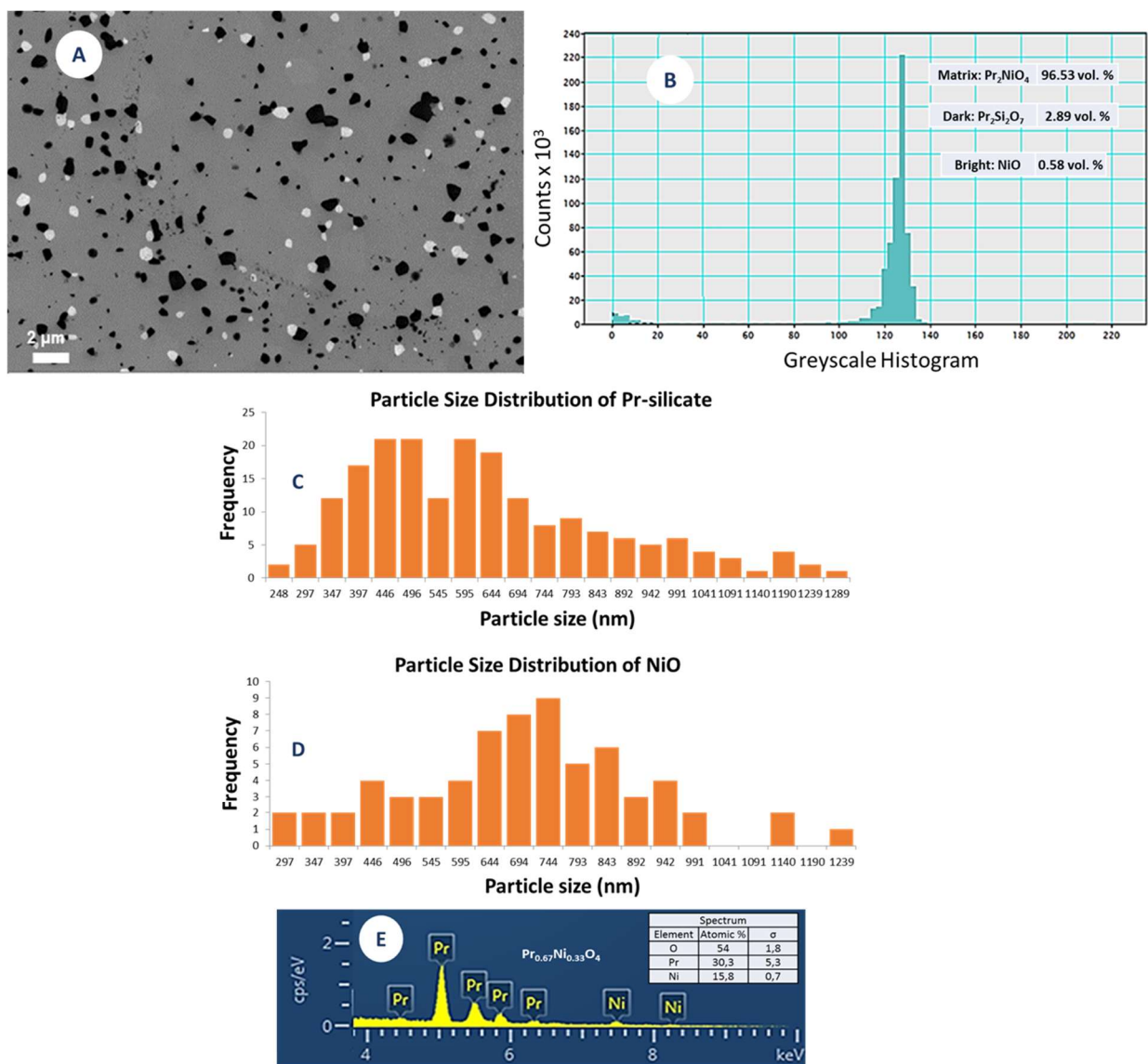


Figure 4.1. (a) SEM image of PNO bulk sample: Grey-PNO (matrix); Bright-NiO; Dark-praseodymium silicate; (b) Greyscale histogram showing the counts of the different phases associated with the image; (c) particle size distribution of praseodymium silicate (0-40 pixels); (d) particle size distribution of NiO (160-255 pixels); (e) EDS-SEM quantification of the PNO phase.

4.3. Fabrication of single cells

4.3.1. NiO-YSZ fuel electrode supports

NiO-YSZ supports were fabricated by the powder extrusion molding (PEM) method, whose optimization parameters were based on the developments of Jardiel *et al.* [237], Arias-Serrano *et al.* [78], and Monzón [121]. In the PEM process, a twin-screw extruder was employed for the extrusion molding, using four heating areas along the barrel from the feeder to the nozzle in which the temperature can be programmed individually. The most important aspect of this process is the acquisition of suspension stability with a solid charge as high as possible to induce a large density of the green tube. For this to happen, the screw speed and the temperature profile to obtain a self-sustaining plastic rod must be carefully controlled.

Initially, the feedstocks were mixed and fed gradually into the extruder feeder. The exact proportion is detailed in *Table 4.1*. The solid charge (65 vol. %) constituted YSZ added to NiO and corn starch (particle sizes between 4-10 μm) and is first shaken for 10 minutes using a turbula mixer. This feedstock is mixed with a binding system consisting of a thermoplastic multicomponent mixture of a polymer (polypropylene, Repsol), wax (paraffin wax, Panreac), and surfactant (stearic acid, Panreac).

Table 4.1. Preparation of extruded NiO-YSZ supports for 65 vol. % of solid charge.

Component	Polypropylene	Stearic Acid	Paraffin Wax	NiO	YSZ	Corn Starch
ρ ($\text{g}\cdot\text{cm}^{-3}$)	0.89	1.01	0.91	6.96	5.90	1.50
vol. % binder	50.00	4.00	46.00	-	-	-
vol. % mixture	17.50	1.40	16.10	26.98	15.92	22.10
wt% mixture	4.58	0.42	4.33	53.15	27.74	9.79

The mixture was then passed three times through the twin-screw extruder to ensure a good blend between the components, as it was observed that there were some non-molten polymers at a faster velocity. The temperature was programmed from feeder to nozzle from 185, 180, 180, and 164 $^{\circ}\text{C}$ in four different zones, as shown in *fig. 4.2*. The slurry was cooled with water at the exit from the nozzle (6 mm width and 0.5 thickness die) in a vertical position with a plane profile at the end of the tube.

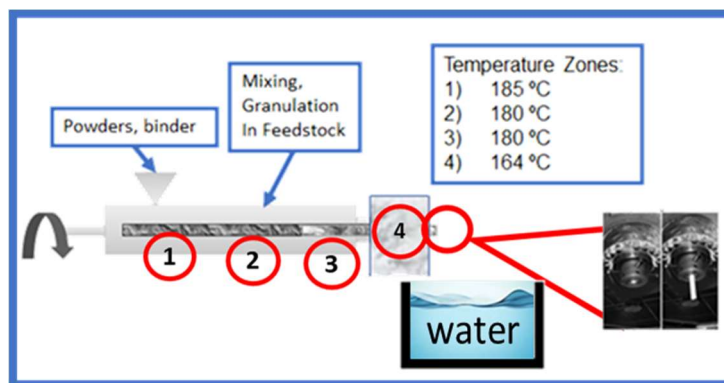


Figure 4.2. Twin-screw extruder scheme with the different temperature zones and the microtubular profile at the nozzle exit.

After extrusion and cooling, the microtubes were dried with compressed air. The final length was cut to 6 cm leaving sufficient length (5mm) to place the electrical contacts and the sealing at the ends of the microtube. This is convenient for preventing fuel depletion, a common problem with larger tubes.

The binding material was removed by submerging the supports in an n-heptane solution and leaving them in an oven at 80 °C overnight to turn the green piece into a brown piece. The supports presented an average outer diameter of 3.2 mm with a wall thickness of 640 μm . Afterward, holes with bits between 1.0-2.0 mm were made with diamond drill bits to facilitate electric contacts.

Afterward, the microtubular support was prepared for the placement of the YSZ ceramic electrolyte solution by dip coating. The ends of the microtubes were covered with PTFE (Teflon) so that the YSZ layer did not adhere inside the holes that would be used for the electrical contacts during the electrical characterization.

In the configuration used in the cell studied in this chapter, no functional layer was employed. The reasoning behind this is that in previous studies using PEM Ni-YSZ supports, no improvements in gas diffusion were identified within the fuel electrode [238].

4.3.2. Electrolyte

The electrolyte was coated on top of the NiO-YSZ support using the dip coating process, using a similar fabrication method as Monzón et al. [123]. The prepared ceramic suspensions consisted of YSZ and propanol (1.25:1 weight ratio), 1 wt% Beycostat, and binder (5 wt% polyvinyl butyral -PVB- in propanol). The suspension was mixed using a

magnetic stirrer at 300 rpm for 15 minutes. The suspension was sonicated for 1.25 minutes using an ultrasound probe on point (Sonics VibraCell).

The viscosity values were compared to previous suspension recipes stored in our database by rheology studies. This served to verify the reproducibility of the thickness in the electrolytic medium. YSZ ceramic suspensions within 0.026 and 0.038 Pa.s were selected for dip coating in the NiO-YSZ supports.

Afterward, the fuel electrode support was dipped three times into the electrolyte suspension for about 3 seconds. The extraction speed was set to $3 \text{ mm}\cdot\text{s}^{-1}$, subjecting the prototype to drying between each immersion. This process yielded an electrolyte thickness of about $20 \text{ }\mu\text{m}$ measured by observation in an SEM. The fuel electrode supports were co-sintered (in a Hobersal S.L. furnace) with the YSZ coating at $1500 \text{ }^{\circ}\text{C}$ for 2h ($4 \text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$). The co-sintering was done vertically using an alumina rod of 0.1 mm diameter inside the contact hole at the tube's end. If sintered horizontally, the weight of the material causes deformation on the tubular support. The sintering program included a $600 \text{ }^{\circ}\text{C}$ (0.5 h) ramp with a rate of $1 \text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ to ensure the complete removal of organic components. The appearance of the co-sintered sample is shown in *fig. 4.3*. The holes at the end of the tube are to coil the electrical contacts made with gold or silver wires.

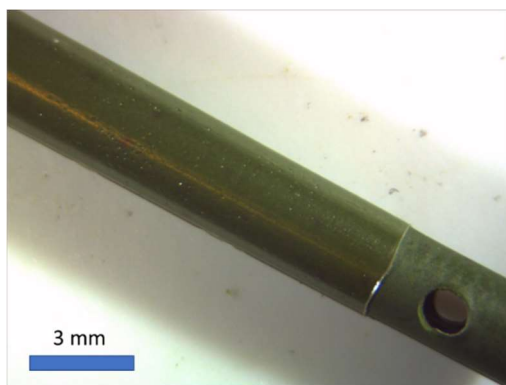


Figure 4.3. Optical microscope images of the NiO-YSZ microtubular support co-sintered with the YSZ electrolyte layer.

4.3.3. PNO and Ce-based composite air electrodes

Single microtubular SOC with two types of air electrode materials previously compared in *section 3.9* (PNO-GDC and PNO) were prepared in NiO-YSZ support configurations with a YSZ electrolyte. The selected SOC design featured a PNO-GDC/PNO (double cathode layer) employed for a two-fold purpose. The PNO-GDC layer has the functionality of an interlayer that prevents reactivity between PNO and YSZ. It also

stabilizes the reactions of these compounds with the medium while contributing to the oxygen electrode's electrochemical activity. The PNO layer was the outmost layer, and its function was primarily as a current collector and the major contributor to the air electrode oxygen evolution.

After the support and electrolyte co-sintering, the PNO-GDC and PNO slurries were deposited to fabricate the air electrode component. The air electrode was composed of an external layer of PNO and a thin PNO-GDC layer with a 4:1 wt% composition. The powders were mixed with ethanol at a 1.45:1 weight ratio for PNO, and a 1.18:1 weight ratio for PNO-GDC. 2 wt% of Beycostat was added to the mixture. After 1 minute in the ultrasound bath, 2.5 wt% of a solution containing PVB dissolved in ethanol (16 wt% PVB) is included. An ultrasonic probe was used to reduce the size of the agglomerates. To ensure reproducibility, the ceramic solutions are kept within an average viscosity of 0.048 Pa·s and 0.056 Pa·s for PNO-GDC and PNO, respectively. The dip coating speed rate is settled at $3.0 \text{ mm}\cdot\text{s}^{-1}$ (1 dip) and $4.5 \text{ mm}\cdot\text{s}^{-1}$ (2 dips) for PNO-GDC (getting a thickness of $\sim 3 \text{ }\mu\text{m}$ after sintering) and PNO ($\sim 30 \text{ }\mu\text{m}$), respectively.

Due to the dimensions of the single cell used in the prototypes, there is an area capacity for the layer deposition of 3 cm^2 . Larger areas can lead to fuel depletion at the end of the microtube. To simplify the characterizations, an air electrode of an active area of 1 cm^2 is used to ease measurement and calculate current and power densities.

The air electrode layers must be sintered at lower temperatures than the fuel electrode and the electrolyte to avoid the decomposition of the electronic conductive material and the formation of insulating phases at the interfaces between the air electrode and electrolyte. Both layers were sintered in two steps at $1100 \text{ }^\circ\text{C}$ ($2 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$) for 2 hours. *Table 4.2* presents the dimensions of single cells prepared with the configuration Ni-YSZ/YSZ/PNO-GDC/PNO.

Table 4.2. Dimensions and weights of the single cells and their layers after air electrode coatings and sintering.

Prototype	Interlayer	diameter (mm)	Active length (mm)	Fuel electrode thickness (μm)	Air electrode thickness (μm)	Electrolyte thickness (μm)
PNO01	PrO _x -GDC	3.215	9.91	640	30	25
PNO02	PNO-GDC	3.215	9.92	650	30	25

The PNO01 cell included a PrO_x -GDC layer fabricated using the same methodology described in this section with a PrO_x : GDC weight ratio of 4:1 (NiO-YSZ/YSZ/ PrO_x -GDC/PNO). This cell was prepared to compare the effect of the nickel phase on the performance of PNO02, which is the main configuration studied in this work (NiO-YSZ/YSZ/PNO-GDC/PNO). The results of the fabrication process are shown in *fig. 4.4*, illustrating the dimensions of the different layers for the Ni-YSZ support, the YSZ electrolyte, the PNO-GDC interlayer, and the PNO electrode, respectively.

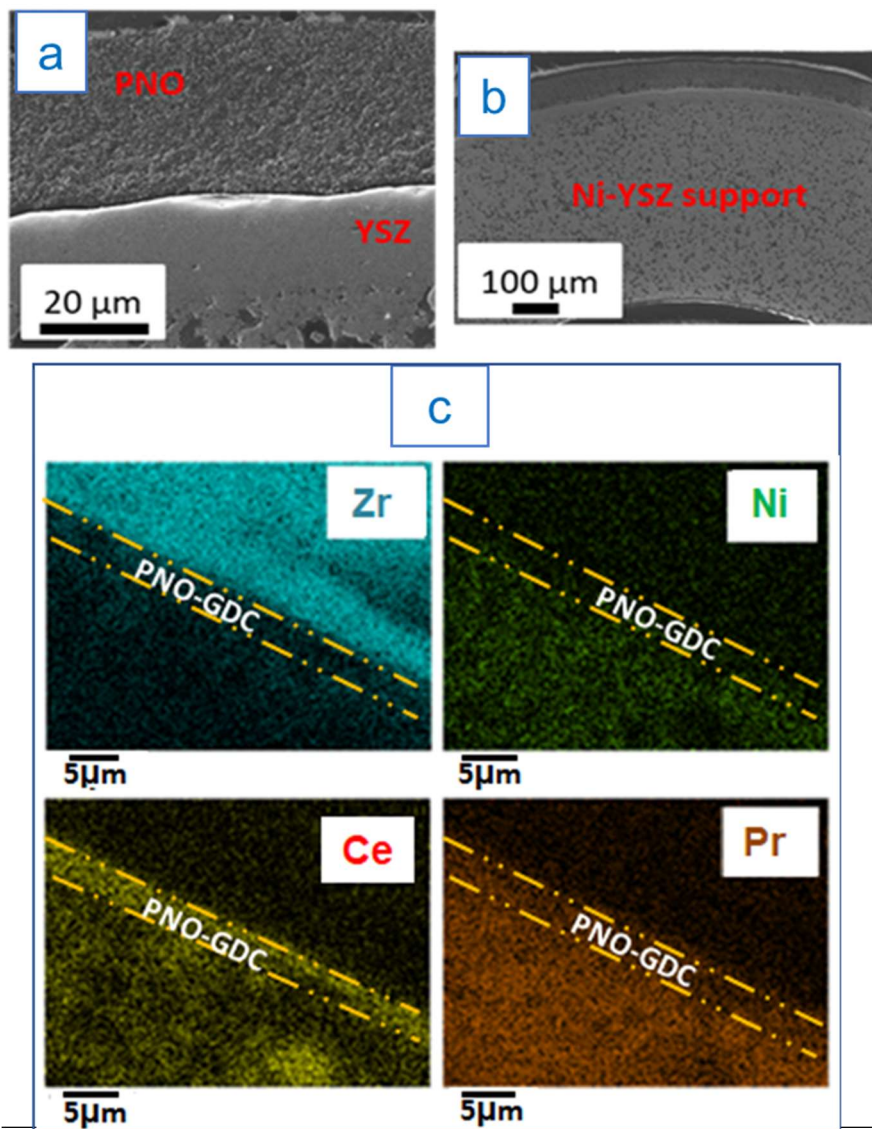


Figure 4.4. SEM micrographs of the PNO air electrode and YSZ layers a), Ni-YSZ support [81] b), and elemental map of the SOC layers showing the PNO-GDC interlayer c).

4.4. Electrochemical Characterizations

The electrochemical characterizations were performed in a four-probe setup with a potentiostat at temperatures between 600 and 800 °C, and the test conditions, parameters, methods, and results obtained, are summarized in *fig. 4.5*. The experimental setup can be seen in *fig. 4.6*. The system had connectors to place the voltage and current outlets and the possibility of placing thermocouples in areas close to the sample to know its temperature accurately. Additionally, there were gas inlets and outlets with mass flow controllers to regulate the atmosphere where the measurement was to be carried out.

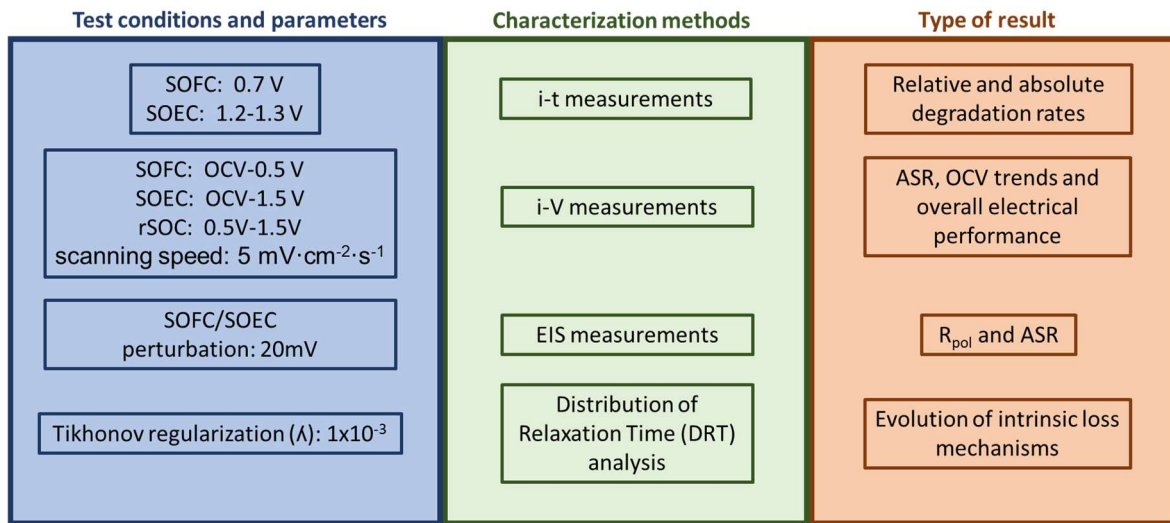


Figure 4.5. Workflow for rSOC characterizations and analysis.

To make good electrical contact with each electrode, the ~5 mm uncoated section at the end of the microtubular support was coiled with gold wires using the featured holes on both ends. The air electrode active area (1 cm²) was coiled with Au wire, and Au paste was added to improve the electrical contact and current collection.

After the contacts were installed, alumina tubes of 5 mm diameter were connected to the microtube on each end (covering the electrical contacts) and sealed with a ceramic sealant (Aremco, Ceramabond 503) to provide separation between the atmospheres of both electrodes. After 1 hour of drying the sealant at RT, the cell was inserted in a furnace at 260 °C for 2 hours each to ensure good sealing. *Fig. 4.7* shows the detail of the inner electrode contact after sealing.

The inlet of feed gases was connected to one end of the cell through the alumina tube and placed inside a small tubular furnace. Since a homogeneous temperature must be

maintained in the cell region covered by the oxygen electrode, the tubular furnace featured three temperature-controlled zones [121]. Due to the small dimensions of the furnace, the convection cooling, and the cooling effect of the gas flow, the temperature in the cell's active area differed from that of the furnace reference. Therefore, a thermocouple (Pt-10% Rh) was placed next to the oxygen electrode (*fig. 4.7*) to display the actual cell temperature in the active zone. In this arrangement, the sealing was placed 3 cm away from the oven to keep the temperature below 200 °C. The oxygen electrode was left exposed to static air.

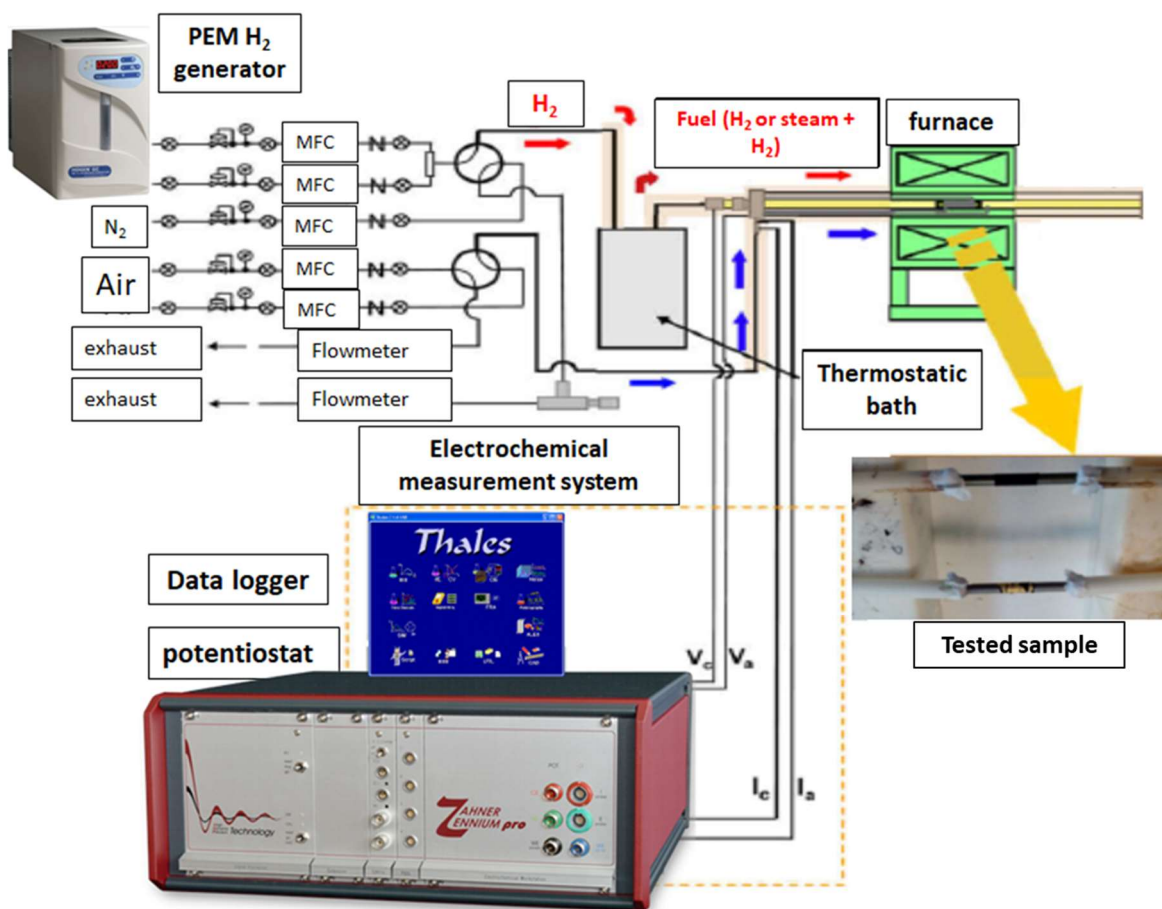


Figure 4.6. Experimental setup for the microtubular SOC electrochemical tests.

Before introducing H₂ to the system, a supply of N₂ (66.0 ml·min⁻¹) was fed to provide a neutral atmosphere and clear the ducts from oxygen to prevent combustion at high temperatures. As the temperature in the furnace regions stabilizes, nitrogen gas is exchanged for humidified hydrogen to reduce NiO to metallic Ni at the fuel electrode. The H₂ gas flow of 88 ml·min⁻¹ was supplied by a PEMFC electrolyzer (Heliocentris PGH2 250). The addition of water to the reaction was carried out by passing the gas stream

through a bubbler at RT. This step contributes an amount of water vapor in the gas stream of ~3 vol.% H₂O.

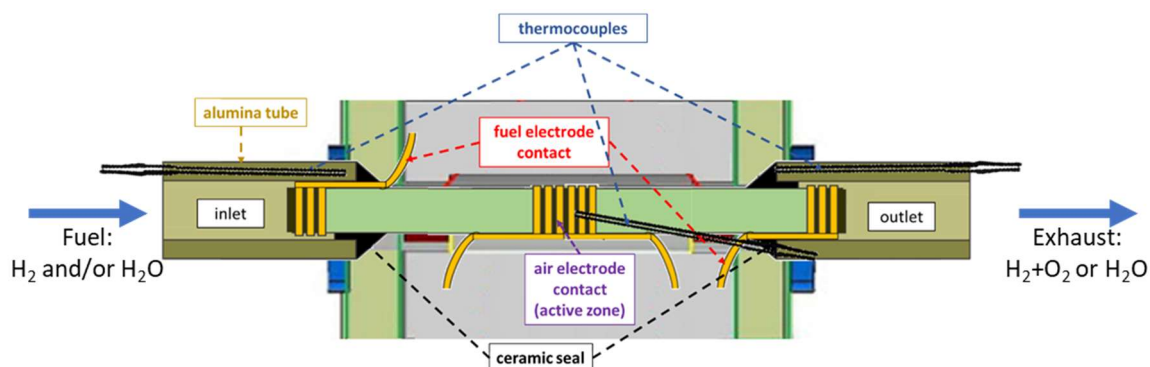


Figure 4.7. Detail of the tubular cell inside the furnace showing the thermocouple positions and the electrical contacts for fuel and air electrodes.

In SOFC operating mode, the cell microstructure was allowed to stabilize after NiO reduction for 20 hours [121]. Afterward, the cell's OCV (1.10 V at 800 °C) was measured to verify the sealing with the alumina tubes and insulation in the feed gas entering the fuel electrode, ensuring an efficient reduction of the NiO. The reduction of NiO to Ni produces a volume shrinkage of ~41 vol.%. Here a metallic nickel phase and a pore phase occur in the region previously occupied by the NiO phase. Finally, the fuel electrode theoretical composition is 25 vol.% Ni, 25 vol.% YSZ, and 50 vol.% porosity. The connectivity of these phases is influenced by the conditions under which the reduction occurs [239].

To measure the I-V and I-V-P characteristics, a voltage was applied to the SOC through the potentiostat, measuring the current density in the active area. The range of I-V-P measurements was between OCV to 0.5 V in SOFC, with scanning speeds of 5 mV·cm⁻²·s⁻¹ to keep the system in a steady state. The slope of the I-V curve has units of specific resistance, ASR, in Ω·cm², and the total contributions to the R_{pol} of single cells were characterized by EIS. The measurements were performed without current load using 20 mV of AC sinusoidal amplitude and a frequency range from 100 kHz to 100 mHz in the electrochemical station. The EIS measurements were characterized by DRT using a Tikhonov regularization parameter of λ = 0.001 to compare with the results obtained for symmetrical cells in *section 3.9*. Finally, chronoamperometry experiments were conducted, fixing the voltage at 0.7 V to test the stability of the cells over time.

4.4.1. PNO air electrodes performance

The PNO cells were initially characterized in SOFC mode with a fuel composition of 97 vol.% H₂ and 3 vol.% H₂O. The I-V-P curves were measured at 800 °C (*fig. 4.8a*), where the PNO02 cell showed a performance improvement of more than double the result of PNO01. The maximum power density (MPD) generated in these cells at 0.5 V were 0.27 W·cm⁻² and 0.56 W·cm⁻² for PNO01 and PNO02, respectively. Similarly, *fig. 4.8b* depicts the Nyquist plot of the PNO cells, where a R_{pol} of 1.4 Ω·cm² and 1.0 Ω·cm² was recorded for PNO01 and PNO02, respectively. There was also an increase in the ohmic resistance of PNO01 produced by issues with the electric contacts (gold wires).

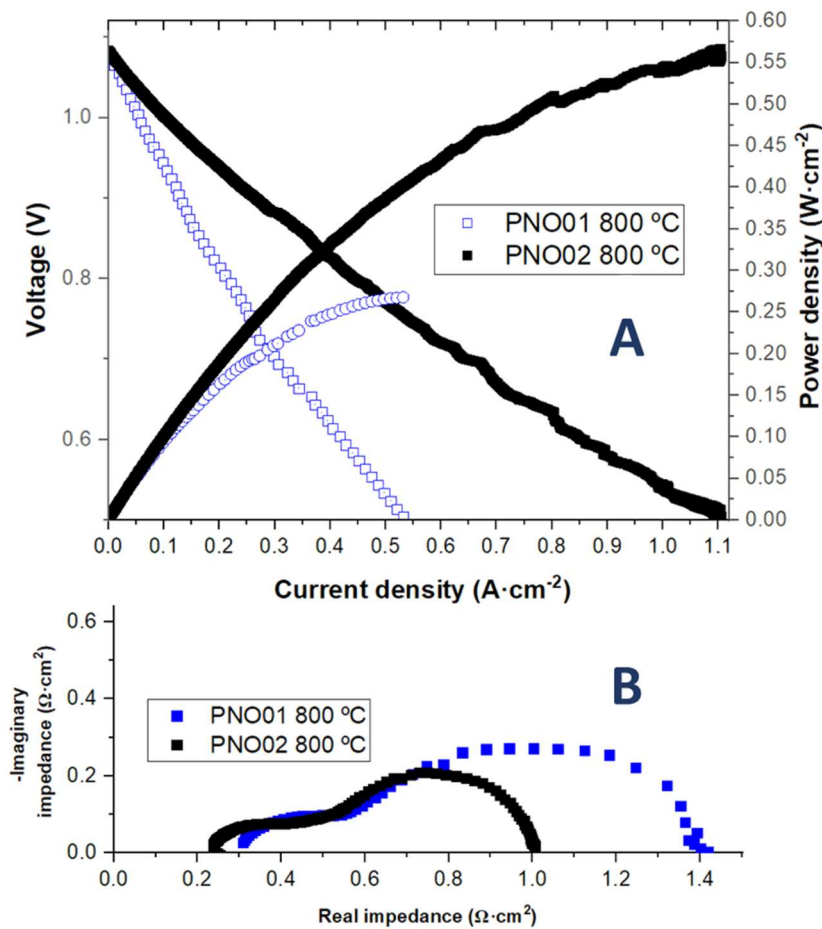


Figure 4.8. I-V-P characteristics of the PNO microtubular cells a) and Nyquist plot b) in SOFC mode at 800 °C.

The degradation of the PNO01 was evidenced in SEM analysis, where in *fig. 4.9*, the postmortem microstructure of the cell showed delamination of the PNO electrode. For this reason, further experiments focused on the configuration employed for PNO02.

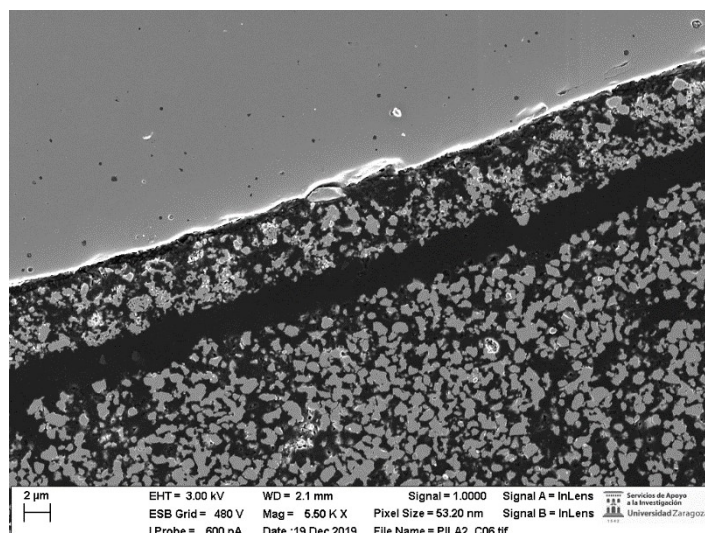


Figure 4.9. Postmortem micrograph of PNO01 using an InLens detector at 3.0 kV.

Fig. 4.10 breaks down the deconvoluted DRT peaks at their respective frequency ranges, and the DRT peak area calculations for the R_{pol} of each cell are presented in Table 4.3. In PNO01 (fig. 4.10a), a lower R1 peak implies a lower interfacial reactivity contribution to R_{pol} than in PNO02 (fig. 4.10b). Similar behavior was observed in the comparison of symmetrical PNO-GDC and PNO cells at 850 °C (in section 3.9). The differences were attributed to the influence of the nickelate decomposition at high temperatures. However, the PNO02 impedance values were lowered in the other three peaks. The R2 peak area was diminished by two times, by about a quarter in R3, and R4 completely disappeared when using the PNO-GDC/PNO double-layered air electrode configuration of PNO02 instead of the PrO_x -GDC interlayer of PNO01.

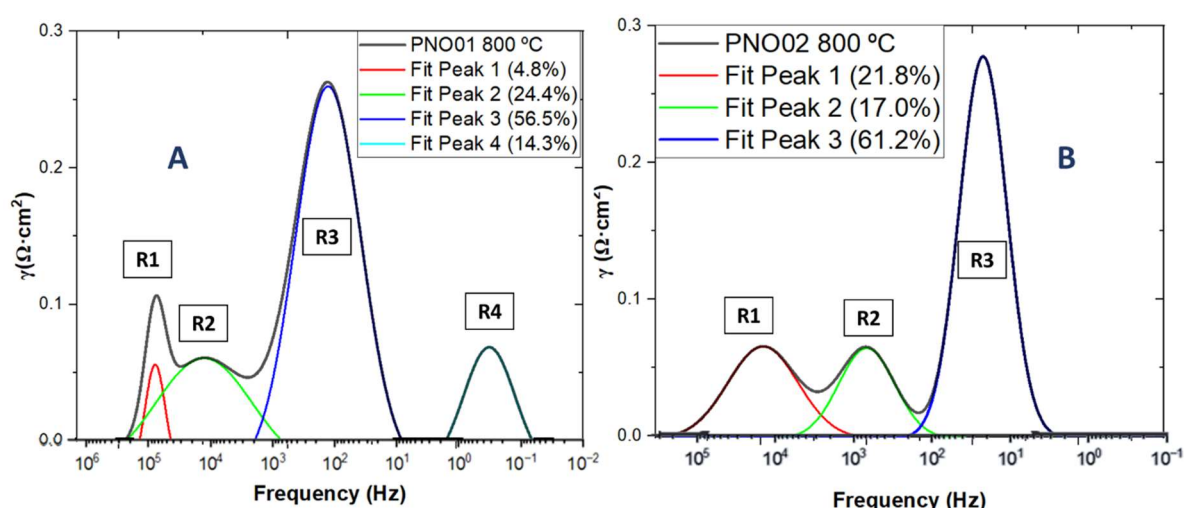


Figure 4.10. Deconvoluted DRT peaks at 800 °C of a) PNO01 and b) PNO02. The inset indicates the DRT peak area percentages.

Table 4.3. DRT fittings for the R_{pol} values of PNO cells at different frequency intervals (in Hz). The R values are in $\Omega \cdot \text{cm}^2$, and the C values are in $\text{F} \cdot \text{cm}^{-2}$.

Cell	R _{ohm}	R1	C1	R2	C2	R3	C3	R4	C4	R _{pol}	ASR
		3x10 ⁴ -9x10 ⁴ Hz		1x10 ³ -1x10 ⁴ Hz		30-100 Hz		<1 Hz			
PNO01	0.31	0.05	3x10 ⁻⁵	0.27	6x10 ⁻⁴	0.61	3x10 ⁻³	0.16	5.00	1.09	1.40
PNO02	0.24	0.17	3x10 ⁻⁵	0.13	1x10 ⁻³	0.46	1x10 ⁻²	0.00	0.00	0.76	1.00

Another trend observed during the impedance characterizations of PNO02 is that the highest contribution to R_{pol} is identified in the R3 peak (61%). Delving further into this result, a pure oxygen flow of $83 \text{ ml} \cdot \text{min}^{-1}$ was applied to the air electrode of a slightly degraded PNO02 cell configuration to see the variations of the DRT peaks. *Fig. 4.11a* shows that the low-frequency arc is reduced under O_2 flow in the air electrode. This is also evident in *fig. 4.11b*, where a major reduction is visible in peaks R2 and R4, whereas peak R3 is almost merged with R4 and is also significantly diminished. The lower frequency peak R5 also decreased when using O_2 flow in the air electrode. These results confirmed that gas diffusion at low $p\text{O}_2$ transport in reforming mixtures influences the behavior of low-frequency peaks, increasing the impedance [47,53].

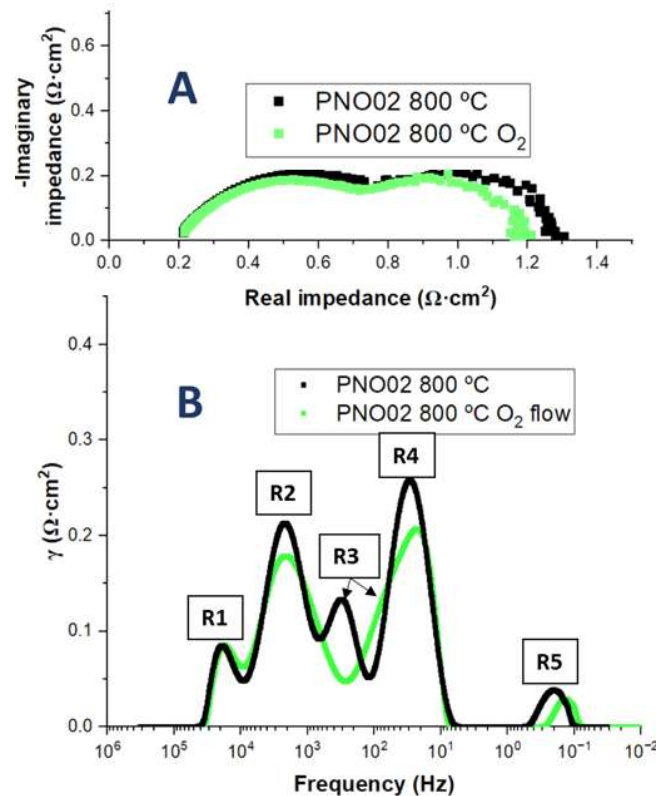


Figure 4.11. Nyquist plot b) and DRT peaks b) of PNO02 in SOFC mode under air and oxygen at 800 °C.

4.4.2. SOC operation

In our experiments, a 50 vol.% H₂ and 50 vol.% H₂O fuel composition was applied. The steam bath temperature was stabilized at 83 °C to obtain the desired H₂O volume ratio, using a typical H₂ gas flow of 88 ml·min⁻¹. In this manner, steam is supplied by a thermostatic bath controlling the temperature. The amount of water fed is relative to the pressure of H₂O in the bath (0.5 atm = 380 mmHg) as a function of temperature, according to:

$$T_b = \frac{1730.63}{8.07131 - \log p_{H_2O}} - 233.426 \quad (4.1)$$

where T_b is the bubbler temperature in °C and p_{H_2O} is the steam pressure in mmHg. All gas lines downstream of the humidifier were externally heated (at temperatures greater than 100 °C) to prevent vapor condensation.

I-V measurements ranged between OCV to 1.5 V for SOEC and 0.5-1.5 V for rSOC. The measured OCV of PNO02 (employing the double PNO-GDC/PNO air electrode layer) under the applied fuel composition was about 0.90 V at 800 °C. Initial I-V characteristics in rSOC mode (*fig. 4.12*) showed an electrolysis current density of 0.94 A·cm⁻² at 800 °C at an operation voltage of 1.3 V, an increase of over 990% (0.09 A·cm⁻²) and 140% (0.38 A·cm⁻²) at operating temperatures of 600 °C and 700 °C, respectively. The Nyquist plot of *fig. 4.13a* was compatible with the I-V slope as R_{pol} values of 2.7, 0.6, and 0.2 Ω·cm² were obtained at 600, 700, and 800 °C, respectively.

To study the passivation (a R_{pol} increase) and activation (a beneficial decrease in R_{pol}) effects of the electrodes under the 50 vol.% H₂ and 50 vol.% H₂O fuel composition, a current density of ±0.20 A·cm⁻² between 700 and 800 °C, and ±0.10 A·cm⁻² at 600 °C were applied. Under polarization at -0.20 A·cm⁻² (SOEC), a reduction of 16% in the low-frequency arc obtained in OCV was observed (*fig. 4.13a*). A slight decrease in the high-frequency range is seen when measuring the impedance spectrum at a current density of 0.20 A·cm⁻² (SOFC). This effect was even more visible as the temperature decreased from 800 to 600 °C.

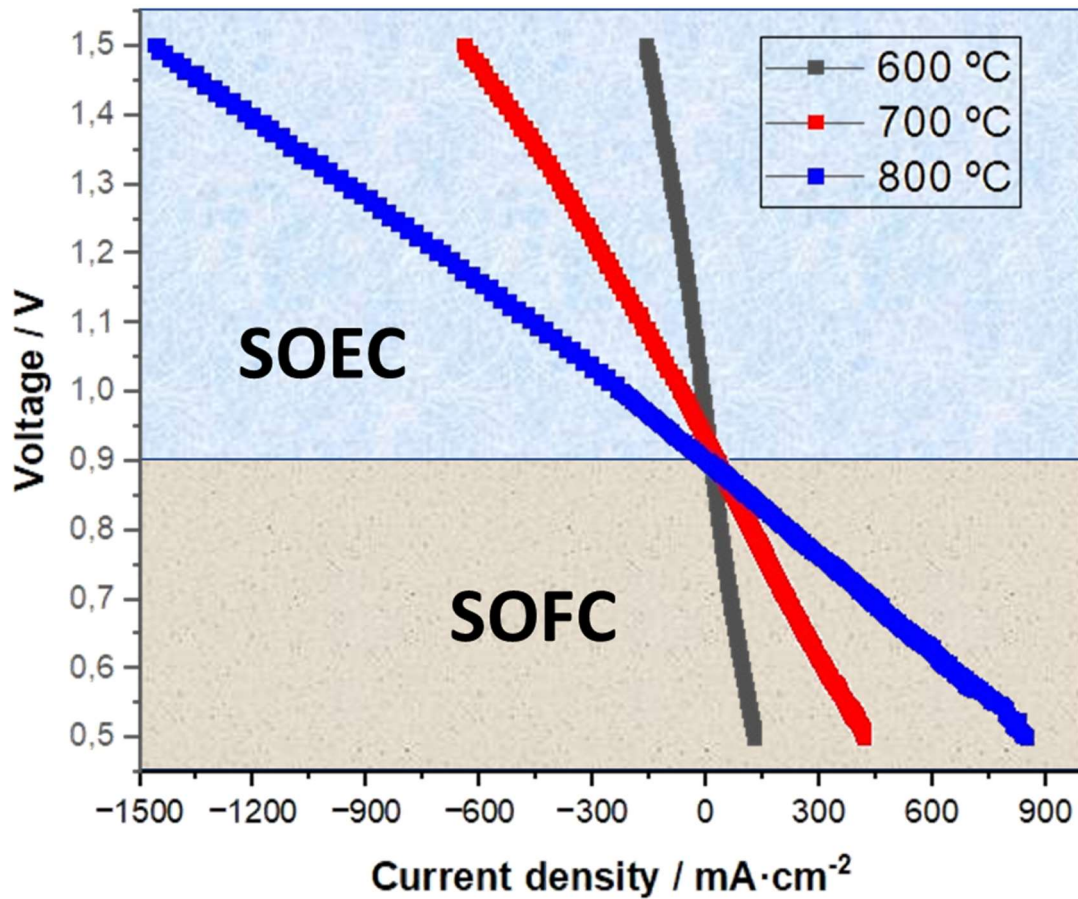


Figure 4.12. I-V characteristics of PNO02 in rSOC mode between 600-800 °C using a fuel electrode gas of 50 vol.% H₂ and 50 vol.% H₂O.

Air electrode activation commonly affects processes between 1 and 100 Hz [240]. Usually, processes at higher than 100 Hz are not affected by the activation/passivation effect during cell polarization. In this analysis, R_{pol} decreases slightly in peaks R1 and R2 under SOFC mode. When analyzing *figs. 4.13b to c*, it is evident that operating in SOEC mode barely shows changes in the high-frequency peaks.

Table 4.4 shows the R_{pol} results of the DRT area calculations in *fig. 4.13b to d* for each peak. The R1 and R2 values were activated in SOFC mode at 600 °C. Nevertheless, passivation was found in R4 and R5, where the latter appears as a gas conversion process. This process also appeared at 700 °C, although the values are low and could have been caused by an artifact due to the error of the DRT technique.

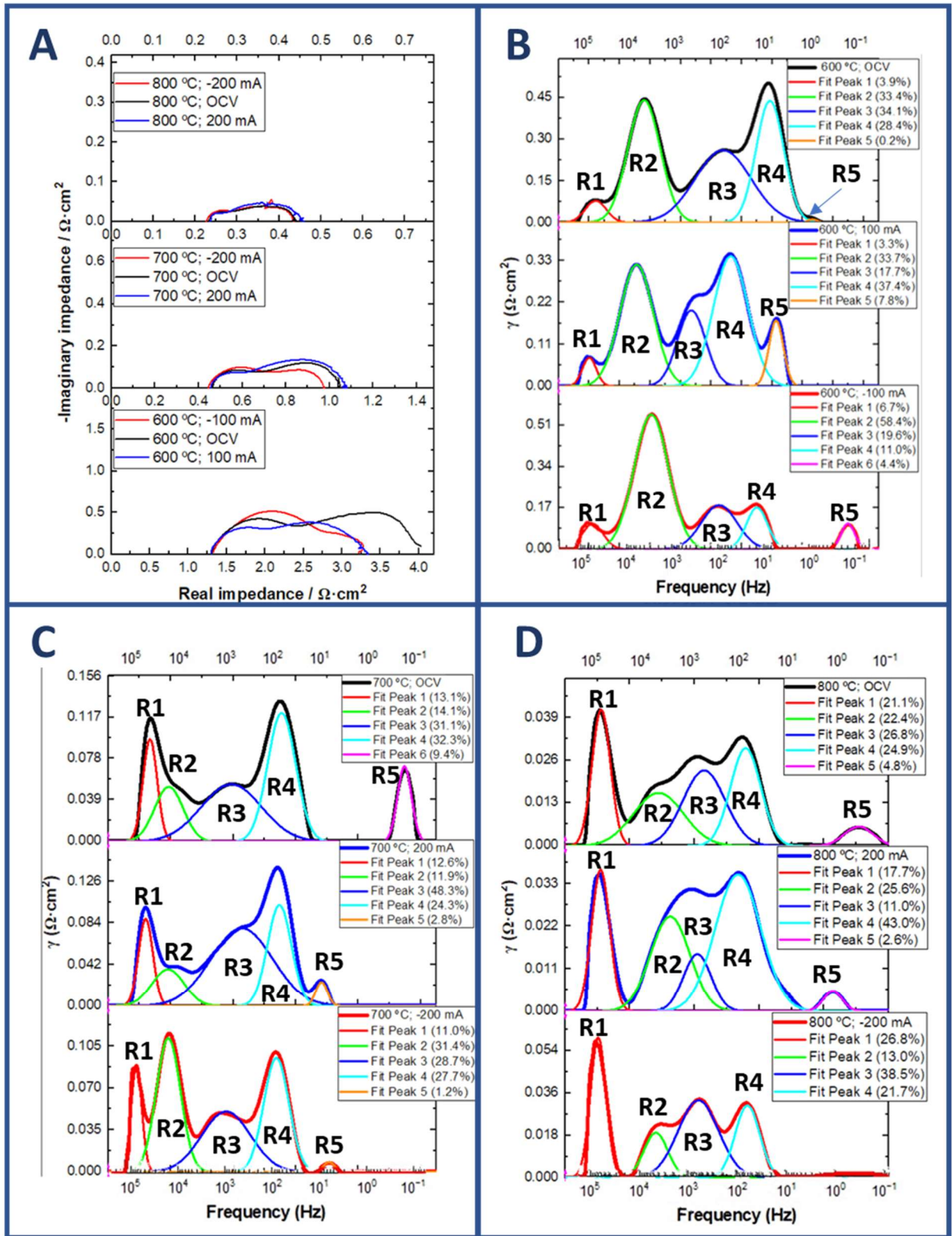


Figure 4.13. rSOC operation of PNO02 using a fuel electrode gas of 50 vol.% H_2 and 50 vol.% H_2O (a) Nyquist plot under OCV and polarization between 600-800 °C. Deconvoluted DRT peaks under OCV and polarization at 600 °C (b), 700 °C (c), and 800 °C (d). The inset indicates the DRT fitting peak area percent.

Under SOEC polarization, the PNO02 cell was generally activated, as shown by a decrease in R3, R4, and R5. R3 and R4 diminished about 2.5 and 3.5 times, respectively, at 600 °C. Also, R5 was eliminated at 800 °C. This confirms that SOEC polarization mainly influences the low-frequency processes in the cell's R_{pol} .

Table 4.4. DRT fittings for R_{pol} values of PNO02 at different frequency intervals (in Hz) under polarization and OCV. The R values are in $\Omega \cdot cm^2$.

Condition	R1	R2	R3	R4	R5	R_{pol}
	10^4 - 10^5 Hz $10^{-5} F \cdot cm^{-2}$	10^3 - 10^4 Hz $10^{-4} F \cdot cm^{-2}$	100-600 Hz $10^{-3} F \cdot cm^{-2}$	20-100 Hz $10^{-2} F \cdot cm^{-2}$	<10 Hz $10^{-1} F \cdot cm^{-2}$	
OCV, 600 °C	0.11	0.90	0.92	0.77	0.01	2.70
100 mA	0.07	0.67	0.35	0.75	0.16	2.00
-100 mA	0.13	1.14	0.38	0.21	0.09	1.95
OCV, 700 °C	0.08	0.08	0.19	0.19	0.06	0.60
200 mA	0.08	0.08	0.31	0.16	0.02	0.64
-200 mA	0.06	0.17	0.15	0.15	0.01	0.54
OCV, 800 °C	0.04	0.05	0.05	0.05	0.01	0.20
200 mA	0.04	0.06	0.02	0.09	0.01	0.22
-200 mA	0.05	0.02	0.07	0.04		0.19

The temperature dependences of PNO02 polarization resistances are summarized in *fig. 4.14*. At OCV, R2, R3, and R4 have the highest activation energies, while low energies are calculated in R1. At 600 °C, a high R4 value is observed in both OCV and under SOFC conditions; nevertheless, these values are diminished over four times when applying SOEC polarization. At 600 °C, a high R2 value indicates possible fuel electrode charge transfer issues and partially contributes to the species transport in both electrodes. These results imply that temperature changes influence the charge transfer and transport in the electrodes, contributing to cell passivation under OCV and SOFC conditions, mainly in processes between 20 and 10^4 Hz.

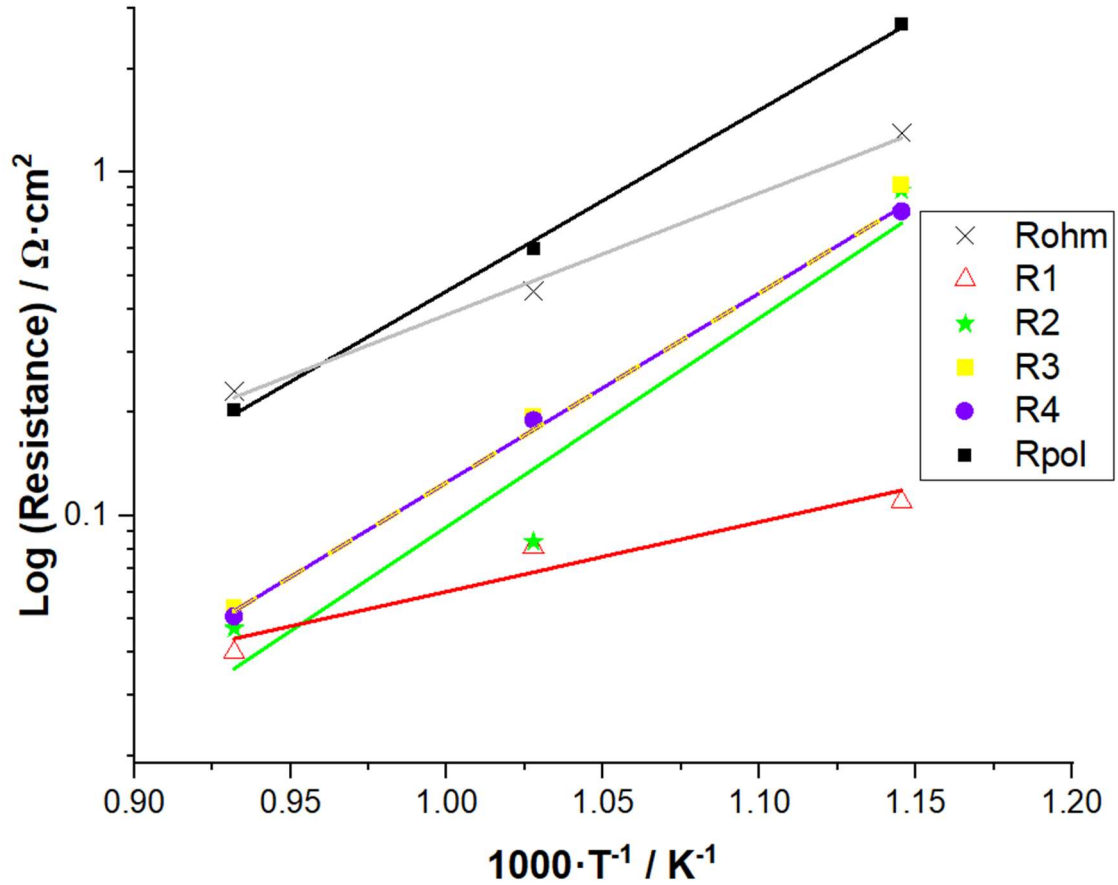


Figure 4.14. R_{pol} temperature dependences of PNO02 at OCV between 600 and 800 °C.

4.4.3. rSOC durability

Further tests involved the cycling between SOFC/SOEC modes to study the degree of recovery of the double air electrode layered PNO02 cell. As seen in the I-V curves at 800 °C in *fig. 4.15*, fuel concentrations modify OCV behavior. Initially, the obtained current densities were about $0.50 \text{ A} \cdot \text{cm}^{-2}$ at 0.7 V in SOFC mode and about $-0.80 \text{ A} \cdot \text{cm}^{-2}$ at 1.2 V in SOEC mode ($ASR_{SOFC} = 0.40 \text{ } \Omega \cdot \text{cm}^2$ and $ASR_{SOEC} = 0.32 \text{ } \Omega \cdot \text{cm}^2$). This performance was enhanced after 20 hours under SOEC operation: $0.58 \text{ A} \cdot \text{cm}^{-2}$ at 0.7 V in SOFC mode, and about $-0.98 \text{ A} \cdot \text{cm}^{-2}$ at 1.2 V in SOEC mode. The SOEC results outperform previous reversible microtubular cells using either LSM-YSZ ($-0.48 \text{ A} \cdot \text{cm}^{-2}$ at 1.2 V and 820 °C) or LSFC ($-0.67 \text{ A} \cdot \text{cm}^{-2}$ at 1.2 V and 800 °C) as oxygen electrodes [123,235,236,241]. This partially validates the previous reports implying that lanthanide nickelate electrodes are believed to be suitable for effective oxygen evolution in the SOEC mode [242] due to their flexible oxygen hyperstoichiometry product of the Ruddlesden–Popper crystal structure. After the 20-hour initial characterization, durability experiments were carried out in rSOC mode: alternating SOFC and SOEC cycles by

fixing their voltage at 0.7 and 1.2 V, respectively. The total duration of the test was about 150 hours under the current load.

After the first 20 hours, no degradation was observed in SOEC mode, but in the second cycle (from t_2 to t_3), an apparent decrease in performance was perceived. Despite this degradation, the ensuing SOFC cycle (2nd cycle from t_3 to t_4) seems beneficial, as the current density increases with time until reaching a quasi-stationary state. As shown in *fig. 4.16*, the degradation observed in SOEC mode is then recovered after the second SOFC cycle, and no apparent degradation was observed up to about 100 hours. This behavior also occurs in both the third and fourth cycles. It is then clear that the system recovers its performance to a large extent by reversing between SOEC/SOFC modes.

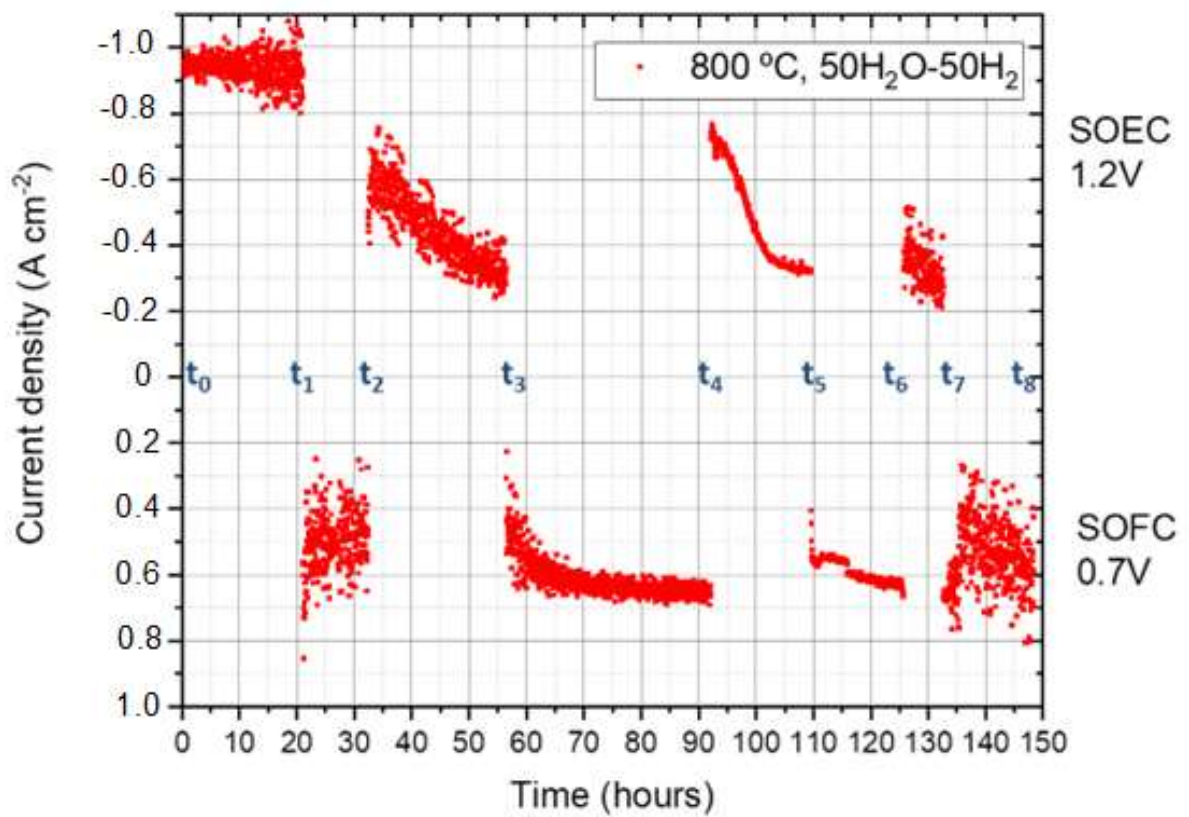


Figure 4.15. Durability tests in SOEC (1.2 V) and SOFC (0.7 V) modes at 800 °C. The different time intervals are shown in the graph (t_0 - t_8) [81].

The most plausible explanation found in the literature for cell recovery is offered by Graves *et al.* [41]. They imply that the formation of O_2 bubbles is being produced during extended SOEC operation by high internal pressures at the oxygen electrode/electrolyte interface, generating pore formation. Therefore, continuous operation under electrolysis mode can carry out the complete separation of the YSZ particles at this interface. The

reversible operation either mitigates this mechanism or reverses its formation. Nevertheless, in our experiments, not all the degradation is fully recovered, and some decay is irreversible.

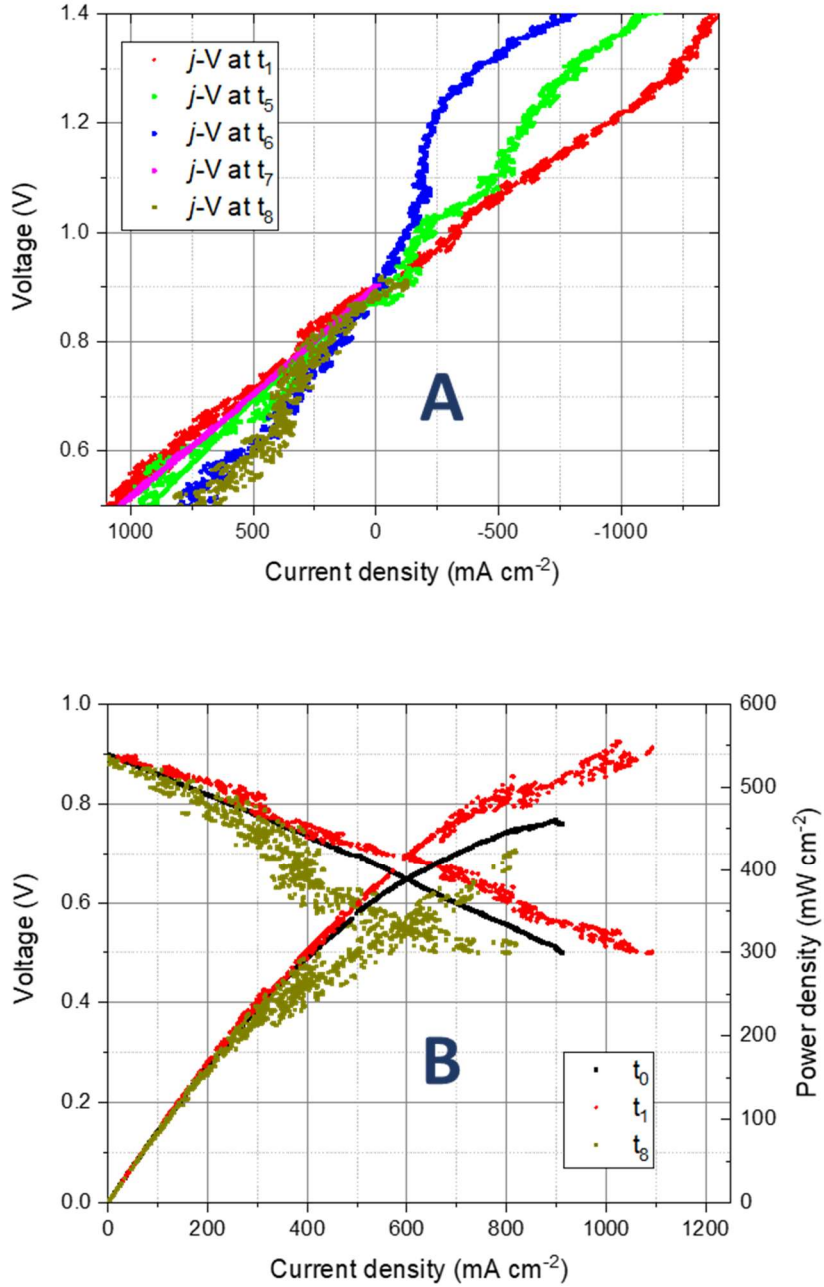


Figure 4.16. (a) I-V curves of the microtubular cell in SOFC/SOEC modes at 800 °C, collected at different time intervals during the durability test; (b) I-P curves in SOFC mode at the initial state (t_0), after stabilization (t_1), and after the durability test completion (t_8) [81].

Two aspects of the I-V curve in *fig. 4.16* should be discussed at this point. To begin with, current fluctuations are observed as an outcome of partial contact losses in the inner current collector (within the seal). The fuel electrode contact was rebuilt after 60 hours (t_3), and then the fluctuations disappeared, only to reappear after 125 hours (t_6). In addition, at t_6 , a concave shape emerges in SOEC mode. This resulted from SOC operation under low current densities, where concentration polarization tends to appear because of the deterioration of the Ni-YSZ-pore microstructure. Hence, the I-V slope decreases at high current densities caused by the electroreduction of the YSZ in the presence of the low pO_2 at the fuel electrode chamber [55,243].

EIS measurements (*fig. 4.17*) were also recorded at the end of each cycle to study the evolution of the cell. The Nyquist plots were fitted using the following equivalent circuit:

$$L - R_{ohm} - (R_1 CPE_1) - (R_2 CPE_2) - (R_3 CPE_3) - (R_4 CPE_4) \quad (4.2)$$

where L is inductance, R_{ohm} is the ohmic resistance, and R_{1-4} , CPE_{1-4} are resistances (R_i) in parallel with constant phase elements (CPE_i).

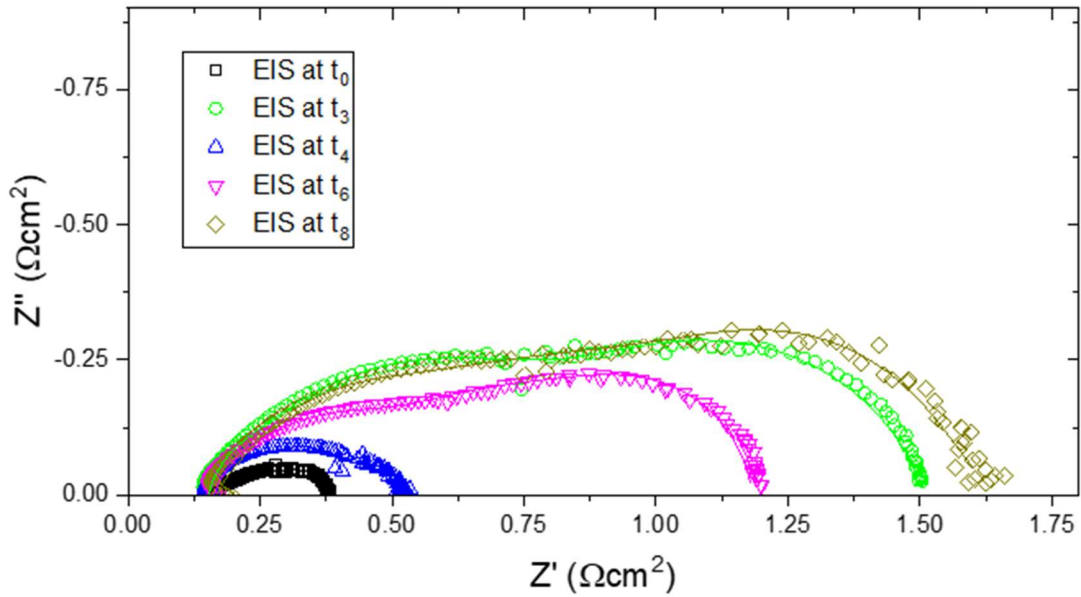


Figure 4.17. Nyquist plots at 800 °C (OCV conditions) were collected at different time intervals during the durability test [81].

The DRT peaks of *fig. 4.18* illustrate the frequencies at which each process contributes to R_{pol} . The calculated values are compiled in *Table 4.5* and compared with R_{pol} values obtained in the equivalent circuit method. It is observed that, although there is a similar pattern in the data, the intermediate values of R_2 , R_3 and R_4 are distributed differently in the DRT method. For these cells, EIS fittings are represented using four arcs for the

MIEC behavior of the oxygen electrode composite. The DRT analysis also validates the presence of the four components in most calculations. The latter method seems more reliable; thus, the selected approach is represented in the results.

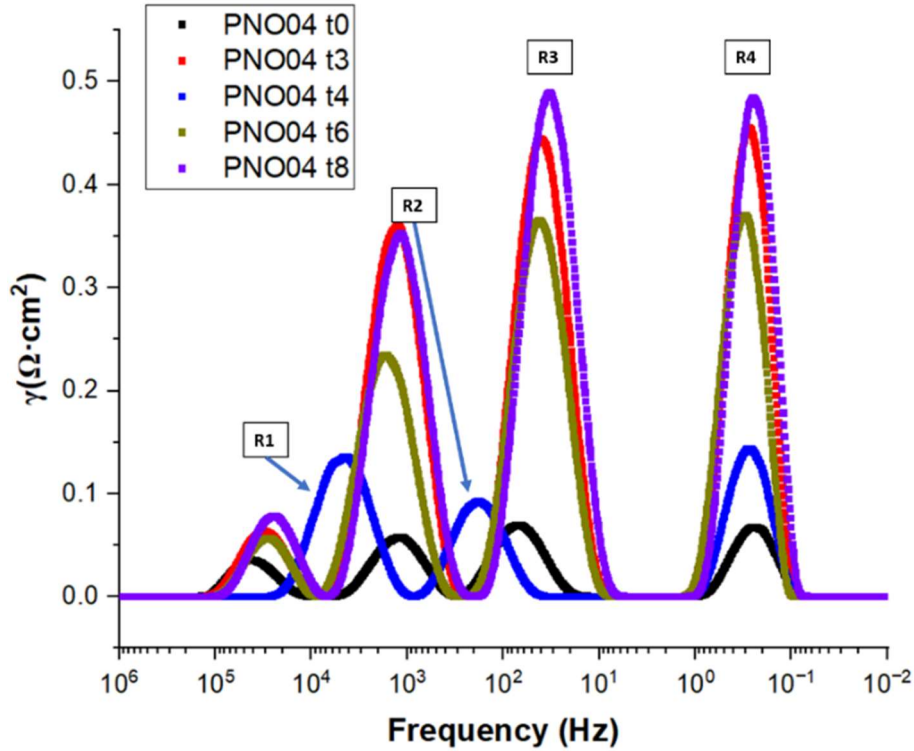
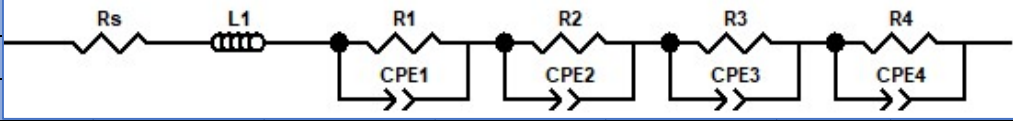


Figure 4.18. Distribution of relaxation times for durability experiments performed in PNO02 at 800 °C (OCV conditions), collected at different time intervals [81].

The R_{ohm} value increased slightly during the degradation test. It is believed that this could be related to coarsening of the Au paste of the oxygen electrode current collector during characterization since no porosity was detected inside the YSZ electrolyte, a common source found by other authors [244]. The R1 parameter is about constant with time after the first cycle, as depicted in *Table 4.5*. This component is heavily influenced by interface impurities such as $Pr_2Zr_2O_7$. This is probably evolving at grain boundaries during sintering or even throughout SOFC operation under the current load. The R2 and R3 parameters were designated to charge transfer processes at the fuel and oxygen electrodes, respectively. In R2, the variation of this component is more likely related to Ni growth and the formation of hydroxides [245], influenced by the agglomeration/expansion of Ni particles in the fuel electrode caused by pH_2O variations. In this experiment, R2 values decreased after the SOFC cycles, while in SOEC conditions, the opposite occurred, indicating a direct relationship with the increase of steam. As a general norm in SOEC mode, the R_{pol} is lower due to higher H_2O content.

Charge transfer drawbacks explain this during increasing "H₂ spill" on an OH⁻ group in YSZ on SOEC operation. At this stage, increased exchange current in higher concentrations of H₂O occurs as an effect of the increase in the number of H₂ sites susceptible to proton acceptance.

Table 4.5. Fitting values of the Nyquist plots of PNO02, collected at 800 °C and OCV using equivalent circuits. The values in parenthesis are the calculated DRT peak area fittings [81]. Typical frequency ranges and capacity values for each contribution are also indicated.

Circuit							
Time collected	R _{ohm}	R1 (7-10x10 ⁴ Hz) (10 ⁻⁴ F cm ⁻²)	R2 (300-7000 Hz) (~10 ⁻³ F.cm ⁻²)	R3 (10-100 Hz) (~10 ⁻² F.cm ⁻²)	R4 (<1 Hz) (~10 ⁻¹ F.cm ⁻²)	R _{pol}	ASR _{cell}
t ₀ initial state	0.15 (0.15)	0.03 (0.04)	0.01 (0.06)	0.14 (0.07)	0.05 (0.07)	0.23 (0.23)	0.38 (0.38)
t ₃ (56 h). after SOEC	0.16 (0.15)	0.09 (0.07)	0.24 (0.37)	0.29 (0.45)	0.73 (0.46)	1.35 (1.34)	1.51 (1.49)
t ₄ (90 h). after SOFC	0.17 (0.16)	0.09 (0.12)	0.10 (0.09)	0.09 (0.00)	0.07 (0.14)	0.35 (0.35)	0.51 (0.51)
t ₆ (125 h). after SOFC	0.18 (0.16)	0.11 (0.06)	0.19 (0.24)	0.17 (0.37)	0.56 (0.37)	1.02 (1.03)	1.20 (1.19)
t ₈ (150 h). after SOFC	0.18 (0.17)	0.12 (0.09)	0.25 (0.36)	0.26 (0.49)	0.81 (0.48)	1.43 (1.43)	1.61 (1.60)

The evolution of the R3 parameter is interesting, particularly at t₄. By the calculations of this parameter in *Table 4.5*, the R3 value either disappeared or was greatly diminished at t₄. In the DRT peaks, this R3 parameter absence is accompanied by partial displacements of the high-frequency peaks to the right. According to the rSOC test results in *fig. 4.15*, the cell improved and stabilized from t₃ to t₄ (34 hours), which signifies the most stable stage during the experiments. A possible combination of fuel electrode diffusion/oxygen electrode reactions is evolving during this stage.

The R4 parameter remained in the same low-frequency range (0.1 to 1 Hz) throughout the experiments. At such low frequencies, the only possible explanation for this process is the conversion diffusion at low pO_2 transport in the reforming gas mixture. R4 increased over time, with partial improvements under switching SOC operating modes, as seen in t_4 (*Table 4.5*). It is also worth noticing that no gas conversion resistance (in the 1 to 10 Hz frequency range) was observed. This effect was successfully eliminated under the operation conditions selected for these experiments, as with flows greater than $40 \text{ ml} \cdot \text{min}^{-1}$, there is no variation in the internal resistance in EIS measurements [121], signaling no fuel depletion at high current intensities. Due to the nature of the experiments, it is concluded that the internal resistances related to the feeding flow are diffusive limitations. The impedance increase at low frequencies could be mitigated by increasing fuel and air electrode gas flow and pressure.

4.5. Postmortem microstructural analysis

The PNO02 cell showed no microstructural degradation between the layers after SOC operation, as observed in *fig. 4.19*. In the EDS elemental map, no interdiffusion is observed in the YSZ/PNO-GDC interface.

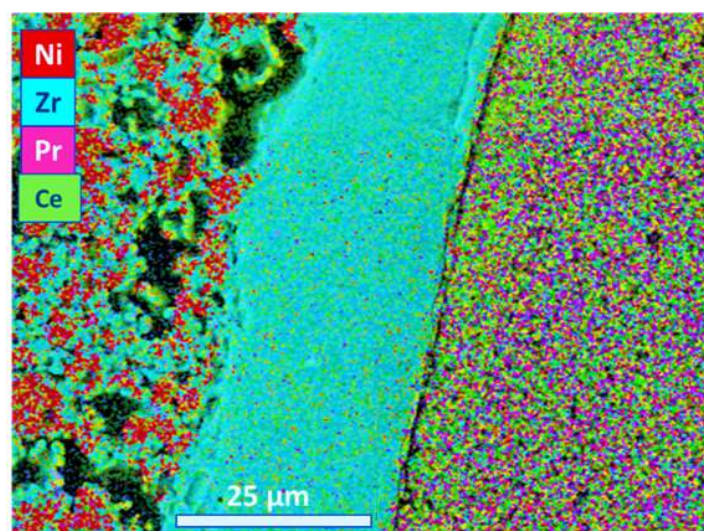


Figure 4.19. EDS-layered image of the PNO02 cell. The background layer is a secondary electron image. The different colors assigned to each phase, using the Ni-K, Zr-L, Pr-L, and Ce-L peaks, are indicated in the inset. The energy of the incident electron beam was 15 kV.

Even so, visible degradation occurs mainly in the Ni-YSZ fuel electrode, as evidenced in *fig. 4.20c* and *d*, where SEM images of the cells are shown (samples were polished after

epoxy infiltration, and the images were taken using a BSE in-lens detector using a 1.5 kV electron beam). The agglomeration of nickel particles results in a gradient distribution of porosity and accumulation of pores observed in the inner part of the tube (*figs. 4.20d* and *h*). This demonstrates that the degradation could be partially removed by reversible cycling between the electrolysis and fuel cell modes, in agreement with previous results [55,246,247].

In addition, the double-layer oxygen electrode (PNO-GDC/PNO) shows no apparent microstructural evolution after the reversible durability test (*fig. 4.20b*). Continuous electrolysis operation results in an accumulated degradation associated with Ni coarsening, and the SEM observations confirm the source of this degradation.

Of important notice is the effect induced by large pores product of the pore former, as observed in *fig. 4.20d* and in the magnified images (*figs. 4.20e-h*), that is probably causing the current density decrease, which is also consistent with the EIS results. Additional experiments will be needed to find the limits under continuous SOEC operation to avoid this irreversible damage.

Ultimately, the pore distribution of the reduced Ni-YSZ electrode was analyzed in an identical cell as PNO02. The pore distribution analysis was made using Gatan DigitalMicrograph to identify the pore variation as a function of electrode distance to the electrolyte interface. Previously, the porosity of the samples had been calculated by Hg porosimetry experiments, obtaining values between 38 and 44 vol. % of pores before reduction and 50 vol % after NiO reduction in the extruded support.

The image analysis was performed in SEM micrographs of the fuel electrode in a cell with a similar fabrication to PNO02 (*fig. 4.21a, c, and e*). The analysis was made as a qualitative approximation of the pore distribution since it was performed on a single image. Specimen preparation observation conditions were the same used for the images in *fig. 4.20*. The resulting pores can be seen as holes (dark particles). In each case, the pores are formed by spherical particles, deformed during the sintering process, leaving sizes of $\sim 5 \mu\text{m}$ in diameter. During reduction, pores with a size of $<1\mu\text{m}$ are created between the phases (*fig. 4.21a*). The YSZ phase has a dark gray appearance, and the nickel phase is light gray. The resulting pore fractions in the Ni-YSZ electrode before operation (*Table 4.6*) are compatible with the ones generated in the Hg porosimetry analysis.

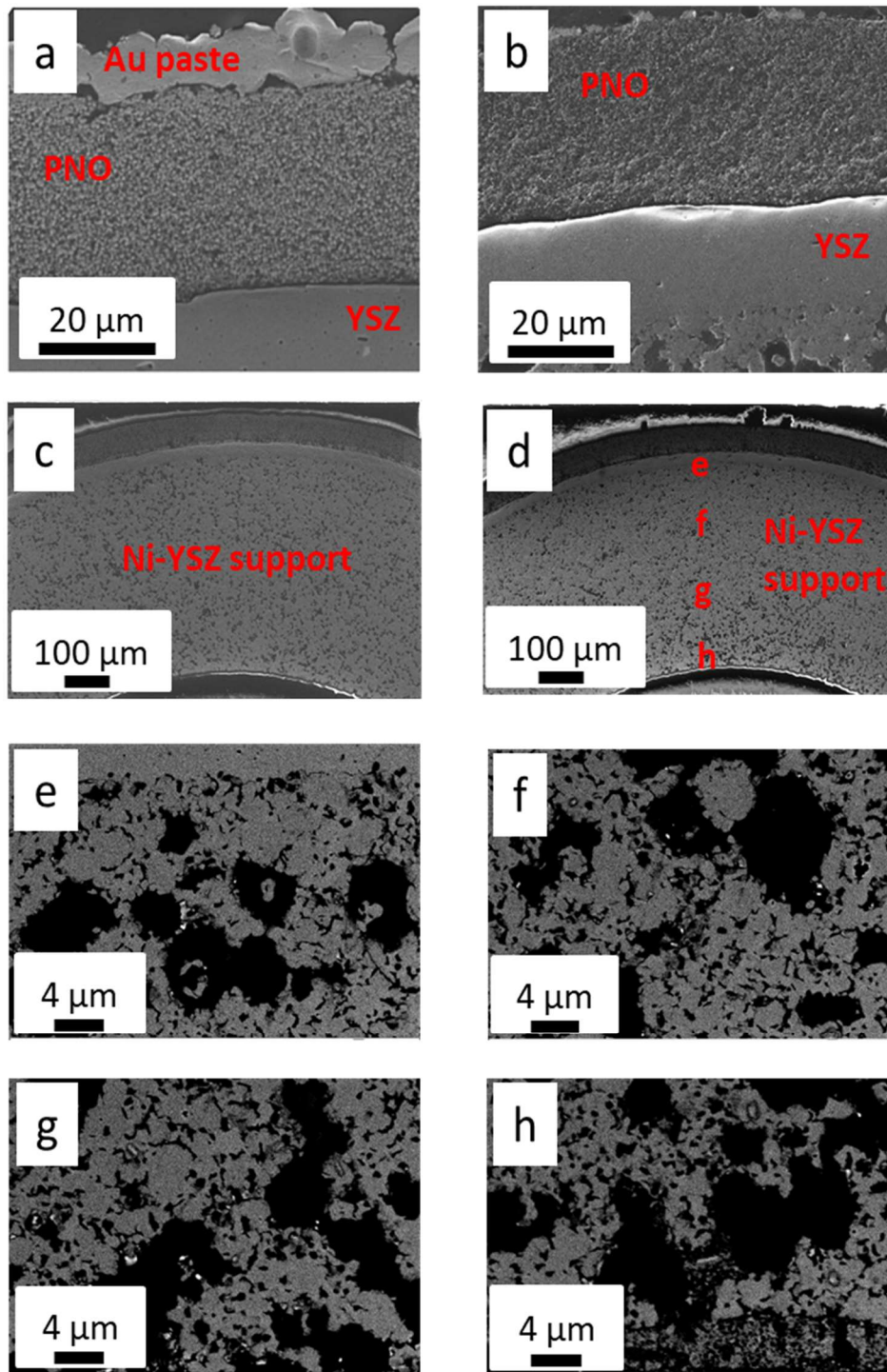


Figure 4.20. SEM images of PNO02 before and after durability studies: a) Detail of the PNO electrode of an identical cell before operation; b) detail of the PNO electrode after operation; c) microstructure of a similar cell before operation showing a homogeneous distribution of porosity in the Ni-YSZ support; d) microstructure of the PNO cell after operation showing the evolution of the porosity in the Ni-YSZ support. Letters e-h indicate the approximate region where the subsequent images (magnified) were taken [81].

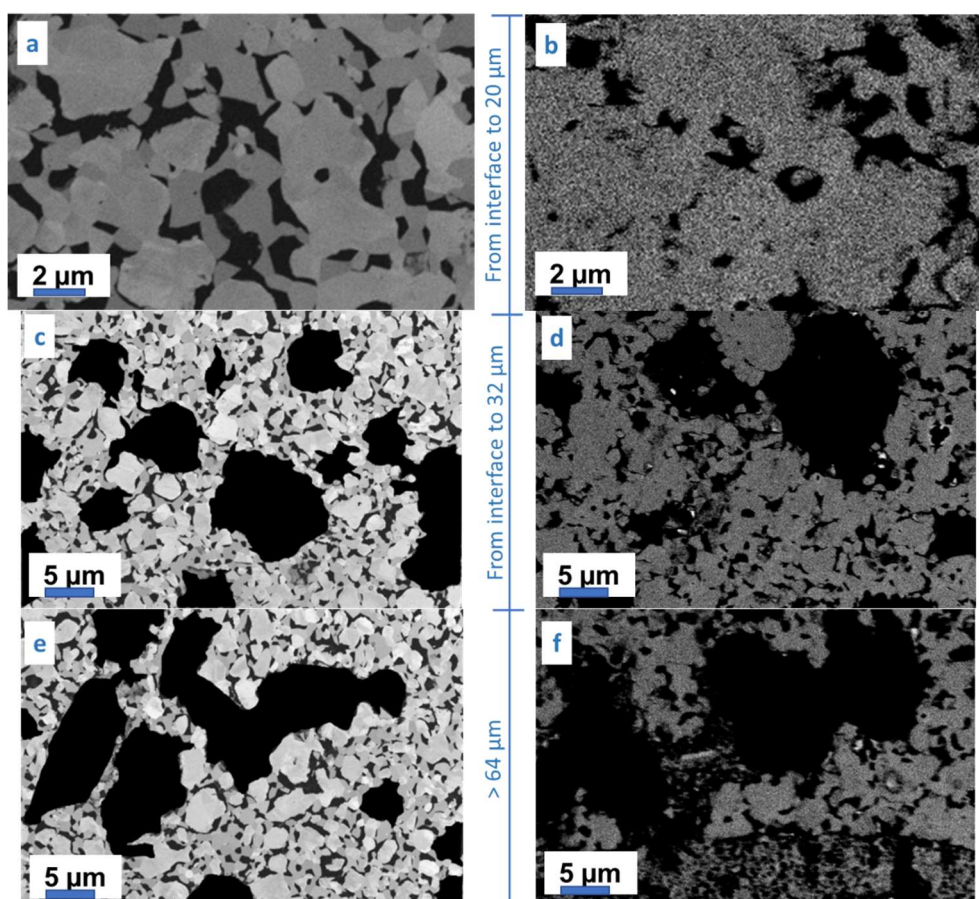


Figure 4.21. SEM images using a BSE detector showing the porosity of PNO02 at different distances from the Ni-YSZ/YSZ interface: before rSOC operation, taken at 0.5 kV (a, c, and e), and after 150 of rSOC operation, taken at 1.5 kV (b, d, and f).

Figures 4.21 a and b illustrate the Ni-YSZ/YSZ interface where only pores produced in the NiO reduction are visible. The fuel electrode nickel coarsening after 150 of rSOC operation (fig. 4.21b) is mainly located at the 20-micron range from the Ni-YSZ/YSZ interface and is the primary source of degradation in the cell in rSOC mode. Although the results in Table 4.6 show little difference in the porosity (considering the error), important variations in pore distribution are identified away from the interface after 150 hours of rSOC operation. Comparing the total porosity results at 0 h and after 150 h, the pore-former-induced pores seem to decrease their distribution closer to the Ni-YSZ/YSZ interface. The pore distribution in Table 4.6 and figures 4.21c to f show the Ni-YSZ electrode distance to the electrolyte from 0 to 64 μm . The most noticeable change in pore distribution after rSOC operation is the progressive increment in the pore volume fraction as the distance from the electrolyte increases (from ~ 37 to ~ 54 vol. %). This result suggests that Ni mobility affects pore distribution in prolonged rSOC operation.

This could also be related to the loss of TPB contact at the electrolyte interface due to the degradation of the fuel electrode.

Table 4.6. Pore distribution of the Ni-YSZ electrode of PNO02 after rSOC operation.

NiO reduction pores at Ni-YSZ/YSZ interface		
Distance to Electrolyte, μm	Reduction pores vol. % (0 h)	Reduction pores vol. % (150 h)
0-20	~19	~14
Total porosity in the Ni-YSZ		
Distance to Electrolyte, μm	Pore vol. % (0 h)	Pore vol. % (150 h)
32 to 64	~48	~37
>64	~42	~54

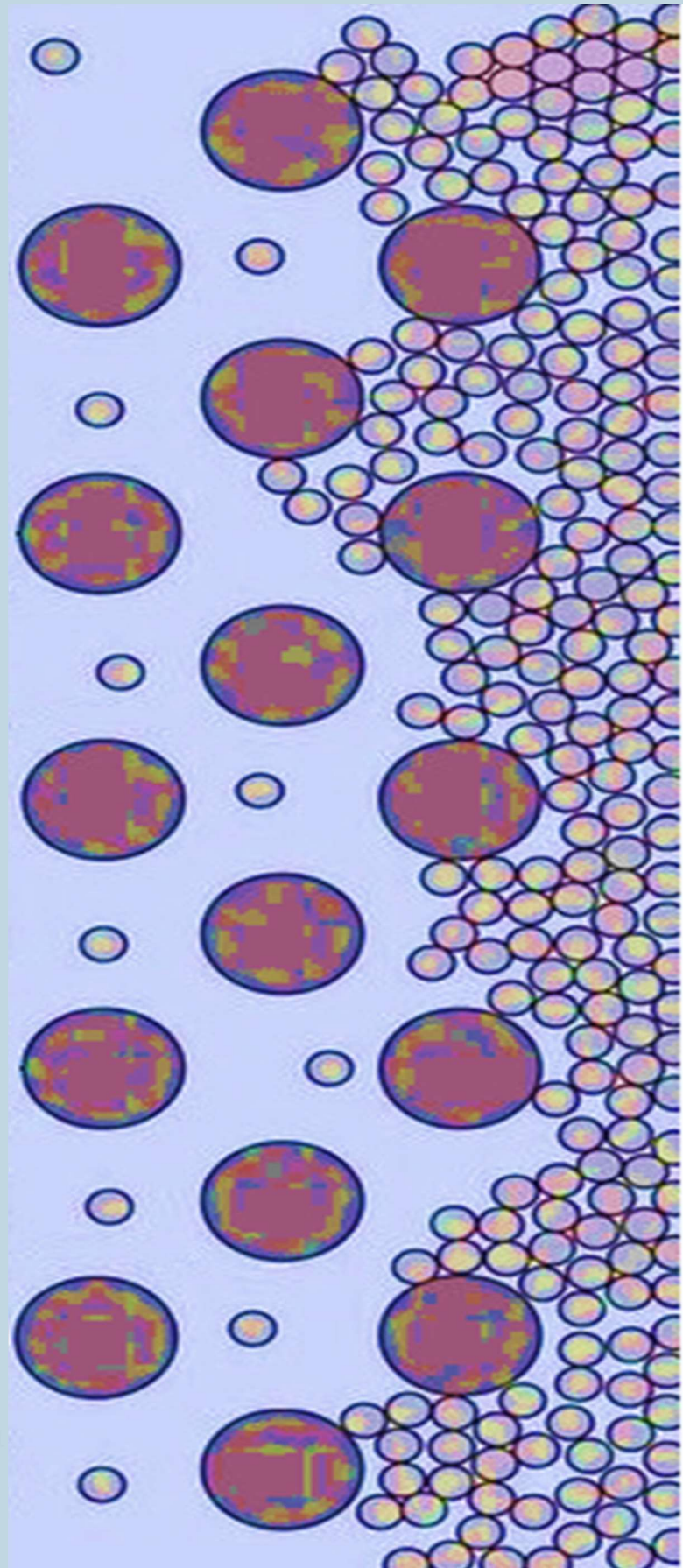
4.6. Conclusions

This chapter described the fabrication processes and SOC configuration strategies to tally the reversible operation of a microtubular SOC with a nickelate-based oxygen electrode. The cell was composed of Ni-YSZ microtubular support, a YSZ dense electrolyte, and a double oxygen electrode formed by a first composite layer of PNO-GDC and the second one of PNO. Good cell performance was obtained at 800 °C for both SOFC and SOEC operation modes and was especially promising for electrolysis. The current density in SOEC mode at 800°C was measured at $-0.98 \text{ A}\cdot\text{cm}^{-2}$ at 1.2 V with 50 vol. % steam, being one of the highest reported values for a microtubular electrolyzer [248].

Current density versus voltage curves (I-V) in electrolysis mode showed an ASR of $0.32 \text{ }\Omega\cdot\text{cm}^2$. The stability of PNO as an oxygen electrode has been confirmed by switching the voltage from 0.7 V to 1.2 V, where no apparent degradation was observed in fuel cell mode and SOEC mode for up to 100 hours. Although some degradation was observed during SOEC operation, part of this degradation was recovered when cycling to SOFC mode. However, after this period, especially in the electrolysis mode, there is an accumulated degradation probably associated with Ni coarsening, as confirmed by additional SEM and EIS experiments. SEM micrograph analysis identified nickel mobility as the cause of the degradation at the fuel electrode under high steam partial pressures. Overall, the electrochemical characterization results confirm that PNO-GDC mixtures are excellent candidates as oxygen electrodes for SOFC/SOEC applications.

Chapter 5. Production and Characterization of Tubular Solid Oxide Cells with infiltrated nanocatalyst precursors

Air electrodes developed through nanoparticle infiltration could provide significant advantages over conventional fabrication methods; among them are mechanical stability and the ability to control the phase formation within the microstructure of a porous substrate, which has become of great importance in SOC studies. In this chapter, the lookout of air electrode enhancement through the infiltration method is evaluated from the fabrication of the cells to an electrochemical performance standpoint.



5.1. Introduction

Taking advantage of the nickelate and doped ceria kinetic and electrochemical properties, we implement the method of tailoring the air electrode microstructure and electrochemical properties via the infiltration of nanoparticles for performance enhancement. This method has been successfully applied over the last decade by several research groups [110,249,250]. In this process, a thin, porous scaffold layer (TPL) is first deposited on top of a dense electrolyte, and another solid phase is introduced in the form of nanoparticles. An infiltration solution of active components usually results in a significant increase in the air electrode TPB density. Most of the electrochemical reaction occurs in that part of the air electrode.

The cells presented in this chapter are of two types of support fabrication: extruded microtubular supports (with openings on both ends), already explained in chapter 4, and tubular supports fabricated by slip casting (enclosed on one end) at the University of Alberta. However, the main goal of the study is not to compare two different cells with different fabrication methods, as the Ni-YSZ in the support and the thicknesses of the electrolyte and air electrodes are different. The purpose of the study is to focus on the viability of using PNO-infiltrated air electrodes for stable Ni-YSZ-based SOFCs, using the two aforementioned supports as a benchmark, as their single-cell stability is a topic that has yet to be studied. A consensus among SOC researchers is that the main drawback of their development and commercialization is the lack of experimental data on long-term stability [161]. In addition, it is interesting to study how different tubular geometries and microstructural parameters, such as changing the thickness of the air electrode or the addition of a functional layer in the Ni-YSZ support (AFL), affects the internal resistance.

The first approach of this study involves the fabrication of SOC components (fuel electrode supports, electrolytes, functional layers). Phase analysis of the infiltrated scaffolds via XRD in composites is performed before electrochemical tests. Afterward, electrochemical characterizations are conducted in SOFC, SOEC, and rSOC operating modes. The fabrication of several cells and all the characterizations presented in this chapter were performed in a research collaboration with Dr. Thomas Etsell's group at the Department of Chemical and Materials Engineering of the University of Alberta, Canada.

5.2. Fabrication of half cells using slip-casting supports

In this study, we incorporated SOC's using NiO-YSZ tubular supports fabricated by the slip-casting technique. The tubular NiO-YSZ supports were prepared using milled NiO mixed with YSZ (Tosoh TZ8Y, 8 mol% Y_2O_3) with a 1.86:1 weight ratio of NiO: YSZ. The cells using this support constituted the A series of samples of this chapter's study.

With the help of plaster slip-cast molds, the NiO-YSZ solution was turned into a solid support. These molds had a gypsum/deionized (DI) water weight ratio of 3:2. An open polyethylene (PE) tube was first cleaned and taped. The gypsum/water mixture was soaked for 2 minutes and shaken in a Retsch MM200 stirrer. The mixture was then cast into the PE tube, pushing a fixed mandrel inside the cast. After about 20 minutes, the molds were dried to a point where the mandrels could be retired. The molds dried entirely for three days in a humidity-controlled room and were inspected for impurities and defects before being used for slip casting. The details of tubular NiO-YSZ support preparation via slip casting are depicted in fig. 5.1 following the details of reference [75].

The NiO powder used (from Fuel Cell Materials) had an average particle size of 1 μm . The NiO was milled for 24 h. The powders were added to DI water (1:1 weight ratio), and zirconia balls were included in the mixture to ensure good mixing (1.5 times the weight of the suspension). The suspension is stirred for 2 hours using a ball mill at 70 rpm. After this, the rest of the DI water is included in the suspension. Following this step, the pH is measured using a pHmeter (Mettler Toledo FiveGo) and settled at 4 with hydrochloric acid to gain a stable slip.

Graphite (Graphit Kropfmühl AG, 4.5 μm particle size) was added with a weight proportion of 6.5 wt. % to act as pore-former. The resulting suspension was mixed for 15 minutes in the stirrer with an ensuing sonication for 3 minutes. As a result, a stable NiO-YSZ ceramic was obtained. This suspension was slip-casted in the plaster molds using a dwell time of 40 seconds (constantly filling the mold with suspension without saturating its capacity). The cast was formed, and almost immediately, the mold was drained of the suspension excess, as shown in *fig. 5.1*.

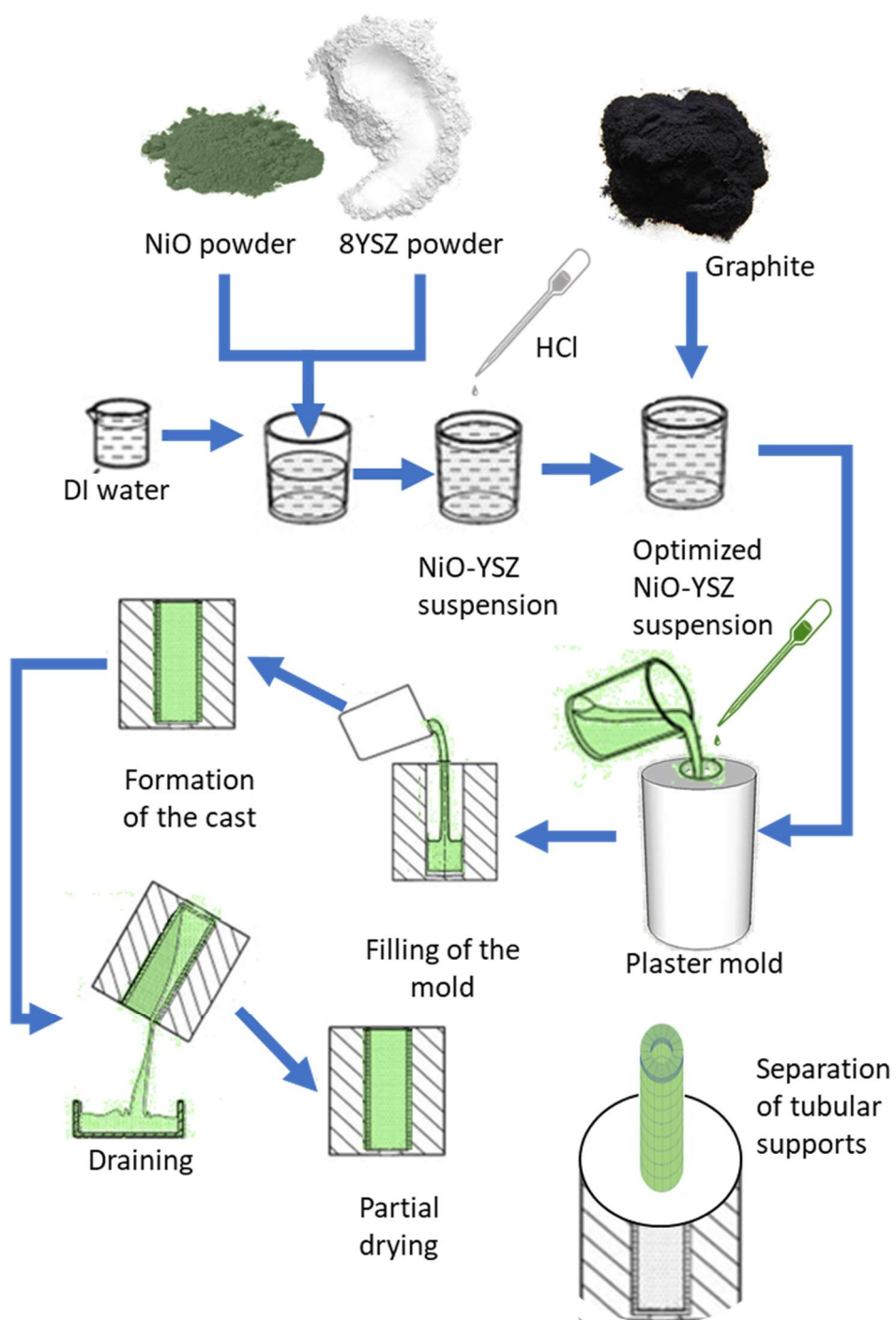


Figure 5.1. Schematic of the slip casting process for the fabrication of NiO-YSZ supports [75].

The slip casts were partially dried for three hours and carefully retired from the molds. Supports were dried at RT and pre-sintered at 850 °C ($5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$) for 3h. The resulting NiO-YSZ tubular supports are shown in *fig. 5.2*.

Microtubular extruded NiO-YSZ supports described in *section 4.3.1* were used for comparison purposes (B series). They differed in tube diameter as the A series cells had a diameter of 5.3 mm, while the B series cells had a diameter of 3.1 mm on average. The two types of supports, their composition, volume ratios, and thicknesses are described in *Table 5.1*.

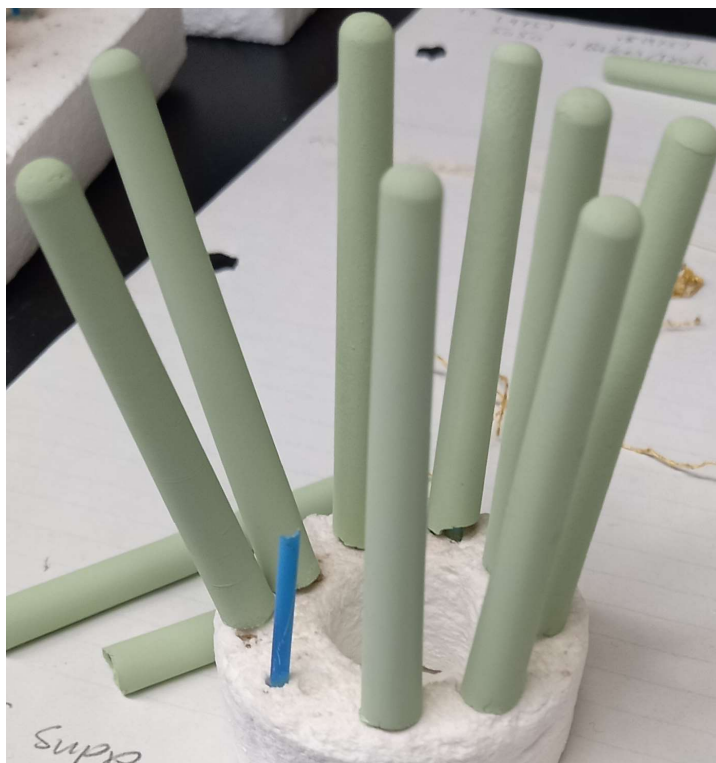


Figure 5.2. Pre-sintered NiO-YSZ supports. The supports were heat-treated at 850 °C for three hours.

Table 5.1. Composition and thickness of different supports and layers.

Sample series	Fuel electrode Support			
	Method	Composition	volume ratio	Thickness
A	Slip-cast	Ni:YSZ: Graphite	30:30:40	390 μm
B	Extrusion	Ni:YSZ: Starch	25:25:50	640 μm

In the NiO-YSZ support fabricated by slip casting, a functional layer (AFL) was coated onto the support of the cell by the dip coating method. As mentioned in chapter 4, the cells with extruded supports do not show noticeable performance improvements, so there is no need to add an AFL in these types of cells.

The AFL slurry was prepared by mixing NiO (J. T. Baker, average particle size of 250 nm): YSZ powders (65:35 weight ratio), ethanol (1:4 powder: ethanol weight ratio), binder (6 wt% ethyl cellulose in terpineol) using zirconia balls in a planetary mill for 2h. The slurry was homogenized in an ultrasound bath for one minute before the coatings.

A dip coat for about 10 seconds equaled 6-7 μm . Three dip coats were needed to obtain a thickness of $\sim 20 \mu\text{m}$. After drying at RT, the layers were pre-sintered at 850 $^{\circ}\text{C}$ (5 $^{\circ}\text{C}\cdot\text{min}^{-1}$) for 3h.

The thin YSZ electrolyte layer was coated into the NiO-YSZ slip using the dip coating method in two steps, consisting of YSZ-to-ethanol weight ratios of 1:7 and 1:10 for the first and second steps, respectively. The suspension for the first set of coatings was made of YSZ with ethanol (1:7 weight ratio) and binder (6 wt% ethyl cellulose in terpineol), milled using zirconia balls in a planetary mill at 300 rpm for 1 hour. The suspensions were sonicated for 3 minutes using an ultrasound bath. The tubular supports were dipped once into the electrolyte suspension for about 10 seconds. The YSZ-coated supports were dried at RT and then co-sintered at 1400 $^{\circ}\text{C}$ (3 $^{\circ}\text{C}\cdot\text{min}^{-1}$) for 3 h. Afterward, another set of coatings was applied using the same methodology as before, with a YSZ: solvent suspension of a 1:10 weight ratio. The sintering program remains the same as in the first set, and by applying this layer, a gas-tight YSZ electrolyte was ensured. The approximate electrolyte thickness of the A series cells is $\sim 7 \mu\text{m}$. The details of the electrolyte coating applied in the extruded supports are already described in section 4.3.2. The electrolyte thickness for the B series cells was between 30-35 μm .

5.3. Fabrication of air electrodes by infiltration in porous substrates

We prepared SOC air electrodes on each cell using infiltration solutions in porous scaffolds to form nickelate-based composites. Different composites were chosen during the initial approach, and their sintering temperatures at which the single phases form in the scaffold were identified by XRD analysis.

5.3.1. Fabrication of the scaffolds

Based on the previous experience on YSZ scaffolds [75,79], the first approach was to characterize and compare two similar cells varying the scaffold material. The porous, thin scaffolds were made of GDC and YSZ and coated onto the cell's electrolyte using dip coating. The suspensions were prepared by milling powders of different scaffold types: calcined-milled YSZ (CMYSZ) and GDC with added pore-former. In each case,

the dispersant used was Menhaden fish oil in an azeotropic solution of 60 wt. % ethanol with 40 wt. % toluene, and the binder was 6 wt. % ethyl cellulose in terpineol.

The CMYSZ powder was calcined at 1500 °C for 3 hours and milled for 48 hours. Afterward, the powder (37 wt% of solid loading) is combined with 14.8 wt% of dispersant, 21 wt% of ethanol, and 27.2 wt% of binder, respectively. We used three dips of the CMYSZ solution for about 10 seconds to obtain 10 µm of thickness. The scaffold was dried at RT and sintered at 1300 °C for 3 hours.

The GDC scaffold was fabricated using 2.5 wt. % pore-former (PMMA of $d_{50} = 1.5 \mu\text{m}$) to enhance pore distribution, keeping the same powder, ethanol, dispersant, and binder weight proportions as the previous scaffold. For the B cells (extruded supports), we used two dips ($\sim 20 \mu\text{m}$), and for the A series, we used only one dip ($\sim 10 \mu\text{m}$). After each dip, a heat gun is used to maintain a homogeneous temperature distribution along the coating. At last, the scaffold was dried at RT and sintered at 1300 °C for 3 hours.

5.3.2. Preparation of infiltration solution

The infiltration solution is composed of stoichiometric ratios of the nickelates (PNO and NNO) and the Pr-based oxides. Initially, a magnetic stirrer mixed the infiltrates with DI water and surfactant. For example, PNO infiltrates, Pr, and Ni nitrates with stoichiometric ratios were mixed in a magnetic stirrer with water (7 M), and the surfactant used was Triton-X. This improved the surface tension in the highly polar solution. The molar concentration of the infiltrate concentration ensured a more homogenous solution than using a different concentration. The same procedure was followed when using NNO and PrO_x infiltrates.

The cells were dipped into the infiltrate suspension and enclosed inside a vacuum chamber (until 1.5 atm) for 2 minutes. The excess of the infiltrate (on the surface) was removed using damp tissue. The heat treatment procedure is performed in two stages: first, the calcination, where the organic is eliminated and the solid infiltrates are deposited in the TPL, and second, sintering at the temperature where the infiltrates form the single-phase in the TPL. The calcination is performed in a furnace for 15 minutes to allow the decomposition of the nitrates, and this was achieved at 350 °C for PNO and 450 °C for PrO_x . The infiltration procedure was repeated until the solid loading reached 30 wt. % [251].

5.3.3. Phase formation analysis

Surface modifications via the infiltration of nanocatalysts can generate a formation of phases at lower temperatures than conventional fabrication routes like solid-state reactions. The PNO, NNO, and PrO_x infiltrates were prepared in scaffolds to identify at which temperature the single phase is formed. For this purpose, dense YSZ and GDC scaffolds are prepared using the slip-casting technique only for the XRD analysis. The fabrication and heat treatment of the TPLs is similar to the one described in *section 5.3.1*.

In the YSZ scaffolds, the PNO infiltration solution formed the PNO-YSZ composite (*fig. 5.3a*). Below 1000 °C, increasing X-ray energy counts of a PrO_x -related phase (specifically Pr_6O_{11}) are formed along the main peaks of the YSZ scaffold.

The PNO phase is identified at 1000 °C, with a Pr-zirconate peak appearing at 33.2°, as previously reported by other researchers [98]. The extent of the reaction is weak, yet the non-conducting phase can be detrimental to an infiltrated electrode. The composite air electrode reactivity is highly dependent on the surface area of the catalyst particles, and most of the bulk is made of pores/scaffolds. For this reason, we decided to move forward with the GDC scaffold.

Unlike the PNO-YSZ composite, PNO-GDC (*fig. 5.3b*) has more secondary phases at 1000 °C. Nevertheless, Pr_6O_{11} and NiO are expected, as we identified them in *chapter 3* as co-existing un-reacted secondary phases. The advantage of using the GDC scaffold with the PNO catalyst is that the insulating zirconate phase is avoided. The disadvantage is that to obtain a higher PNO content after sintering, it is necessary to increase the temperature to over 1000 °C. This route is opposed to the purpose of the infiltration technique, which is used to reduce the heat treatment temperature of the conventional fabrication methods. Hence, the most reasonable sintering temperature of PNO-GDC infiltrated composites is kept at 1000 °C. Although we previously observed the formation of this phase in PNO and GDC mixtures at 1100 °C with the non-infiltrated air electrode [101], using infiltration, the particles are smaller than in the solid-state fabrication process, and reactivity can occur at lower temperatures. In addition to these phases, a Ce-Pr-Gd (CPGO) phase is also present, being more noticeable when increasing the calcination temperature, as illustrated in *fig. 5.4* (between 32-34 degrees).

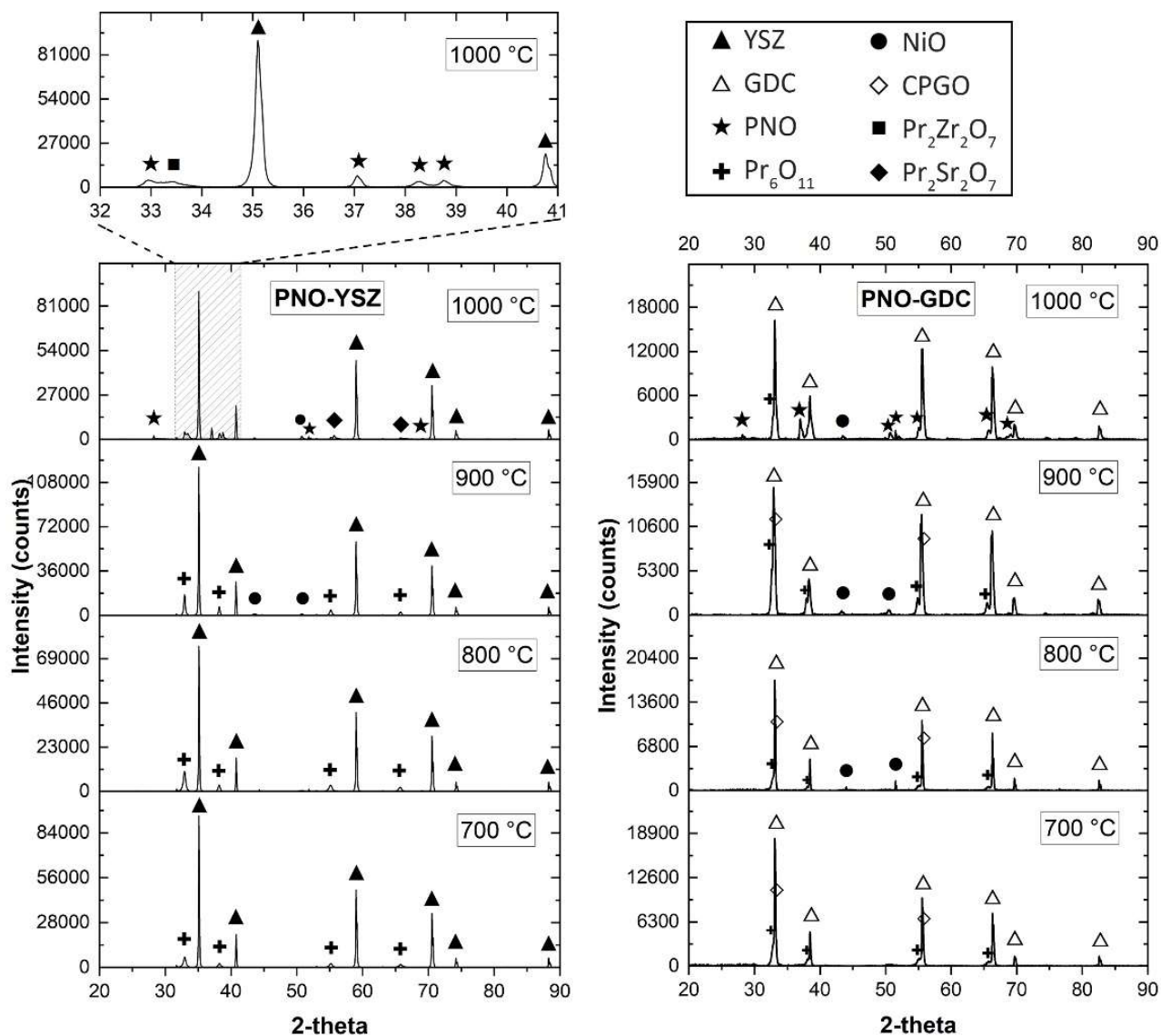


Figure 5.3. XRD (20 to 90 degrees) of PNO-YSZ and GDC scaffolds in samples annealed between 700 and 1000 °C for 5 hours using one infiltration [252].

At 900 °C, the GDC peak is broadening, and a secondary ceria peak is taking shape. At lower temperatures, this effect is not as evident. The lattice parameter of the ceria phase changes from 5.412 to 5.402 Å when reaching 900 °C, similar to the lattice parameter of CPGO in the C20 sample (5.4013 Å, *Table 3.3 in chapter 3*). This serves as evidence of the presence of a coexisting secondary ceria phase.

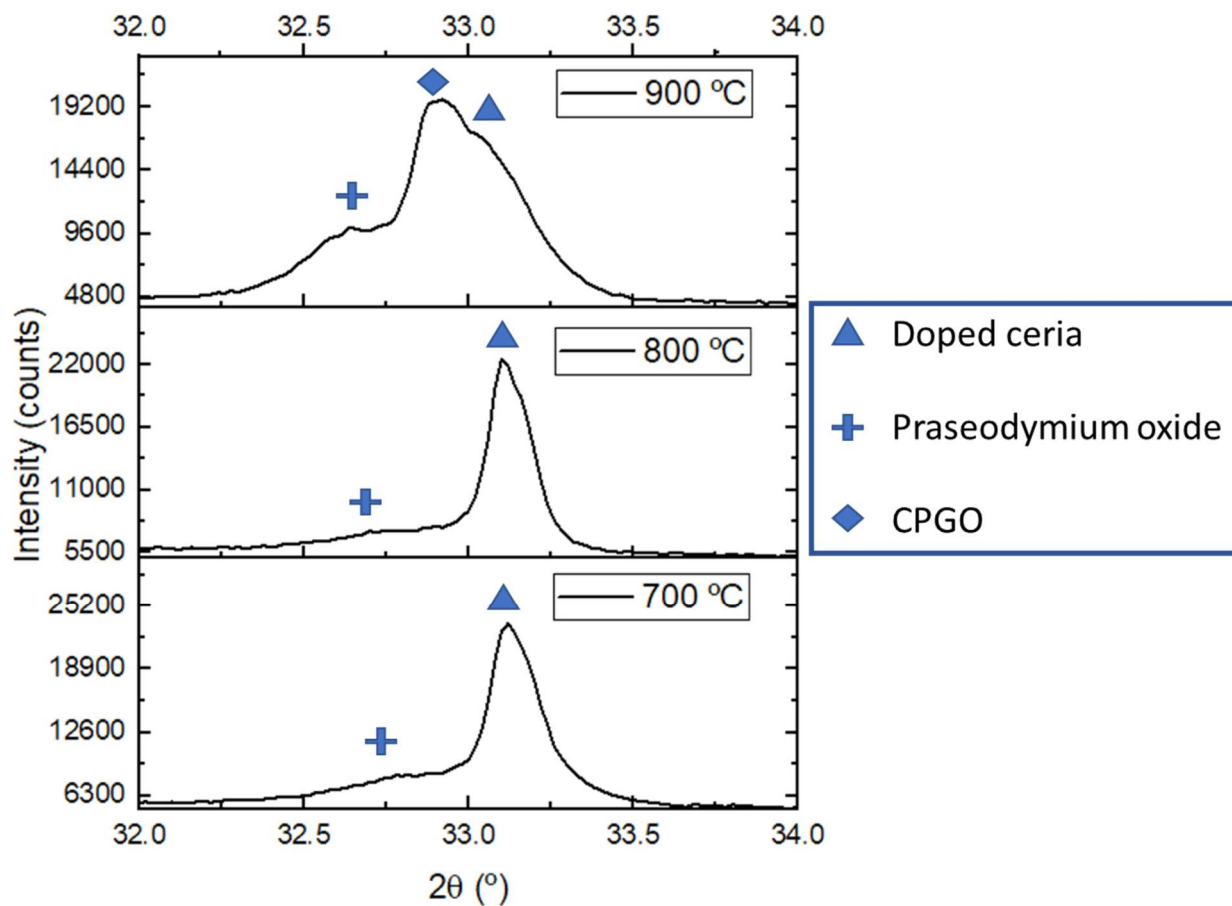


Figure 5.4. XRD diffractograms (32 to 34 degrees) of PNO-infiltrated GDC scaffolds for samples annealed between 700 and 900 °C.

The XRD analysis of the composites formed by the infiltration of PrO_x nanoparticles into CMYSZ and GDC scaffolds was performed in the temperature range of 600 to 800 °C. PrO_x -YSZ (fig. 5.5a) and PrO_x -GDC (fig. 5.5b) composites showed a single Pr_6O_{11} phase regardless of temperature.

The lower temperature end could avoid increasing the catalyst particle size. In this case, the sintering of PrO_x -based composites prepared by infiltration is performed at 600 °C, where the PrO_x single phase is already formed.

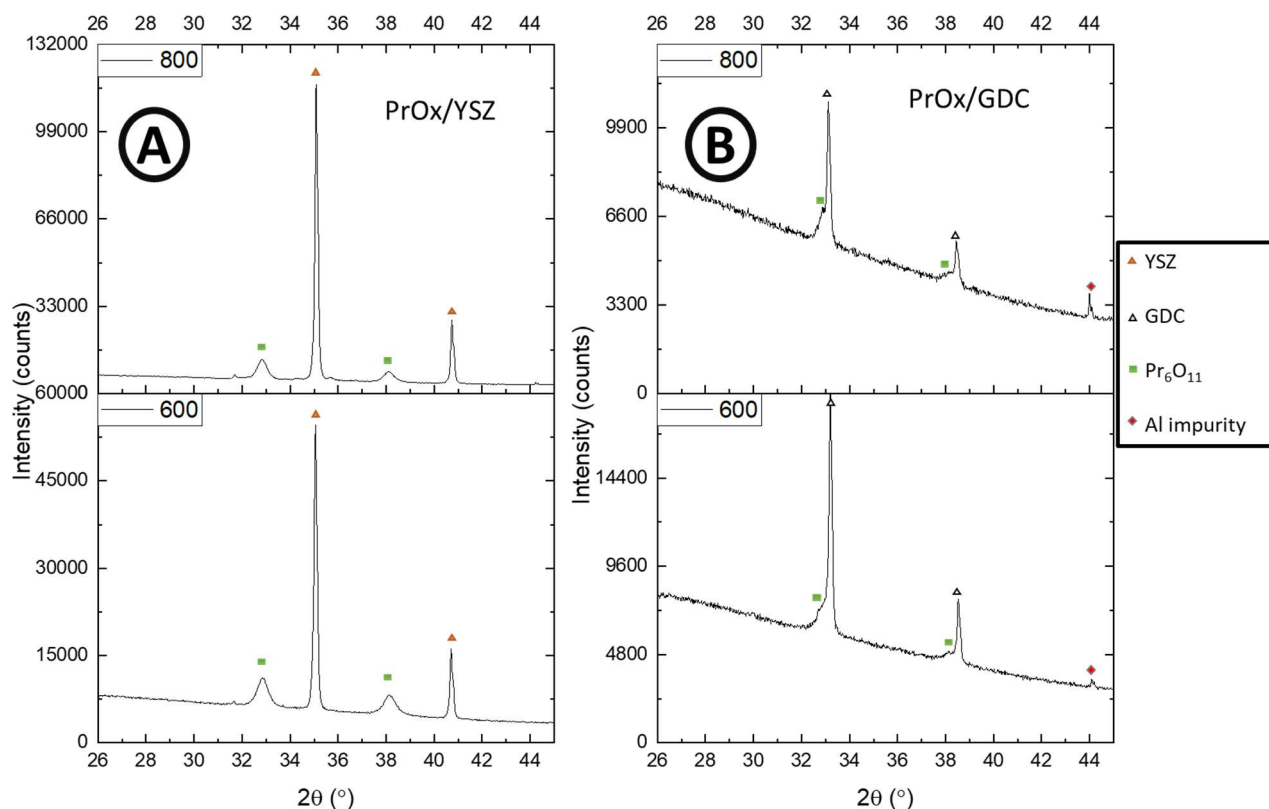


Figure 5.5. XRD patterns (26 to 45 degrees) of PrO_x-infiltrated scaffolds from 600 to 800 °C: YSZ (a); GDC (b).

The particle size of the PNO and PrO_x infiltrates in the GDC scaffold was observed in SEM micrographs. Before testing, the infiltrate particle size is similar for PNO (*fig. 5.6a*) and PrO_x-GDC (*fig. 5.6b*) composites, at around 60 nm. The particle size was taken on a PNO sample sintered at 1000 °C and a PrO_x sample sintered at 600 °C. These temperatures are ideal for the heat treatment of the material selected as infiltrated composites for SOC air electrodes in our study.

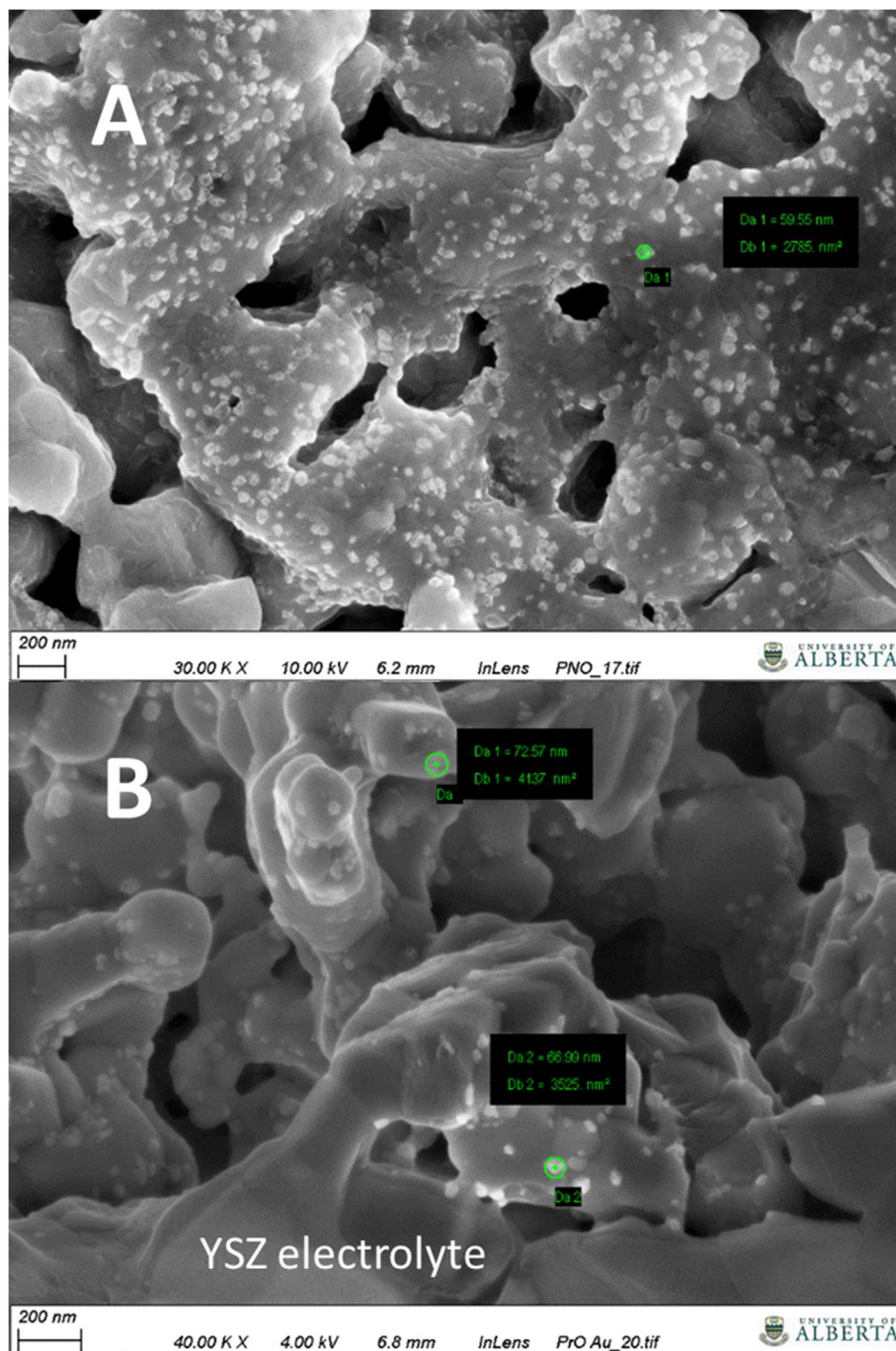


Figure 5.6. SEM images of SOCs before testing: a) PNO/GDC interface; b) PrO_x/GDC interface.

Also, as illustrated in *fig. 5.7*, PrO_x agglomerates are formed with particle sizes between 1-4 μm in the PrO_x-GDC sample sintered at 1000 $^{\circ}\text{C}$. In practice, a particle size under 100 nm would be more desirable to mitigate the increase in the infiltrates' particle size. Thus the sintering temperature of the PrO_x-Gd composite was selected at 600 $^{\circ}\text{C}$.

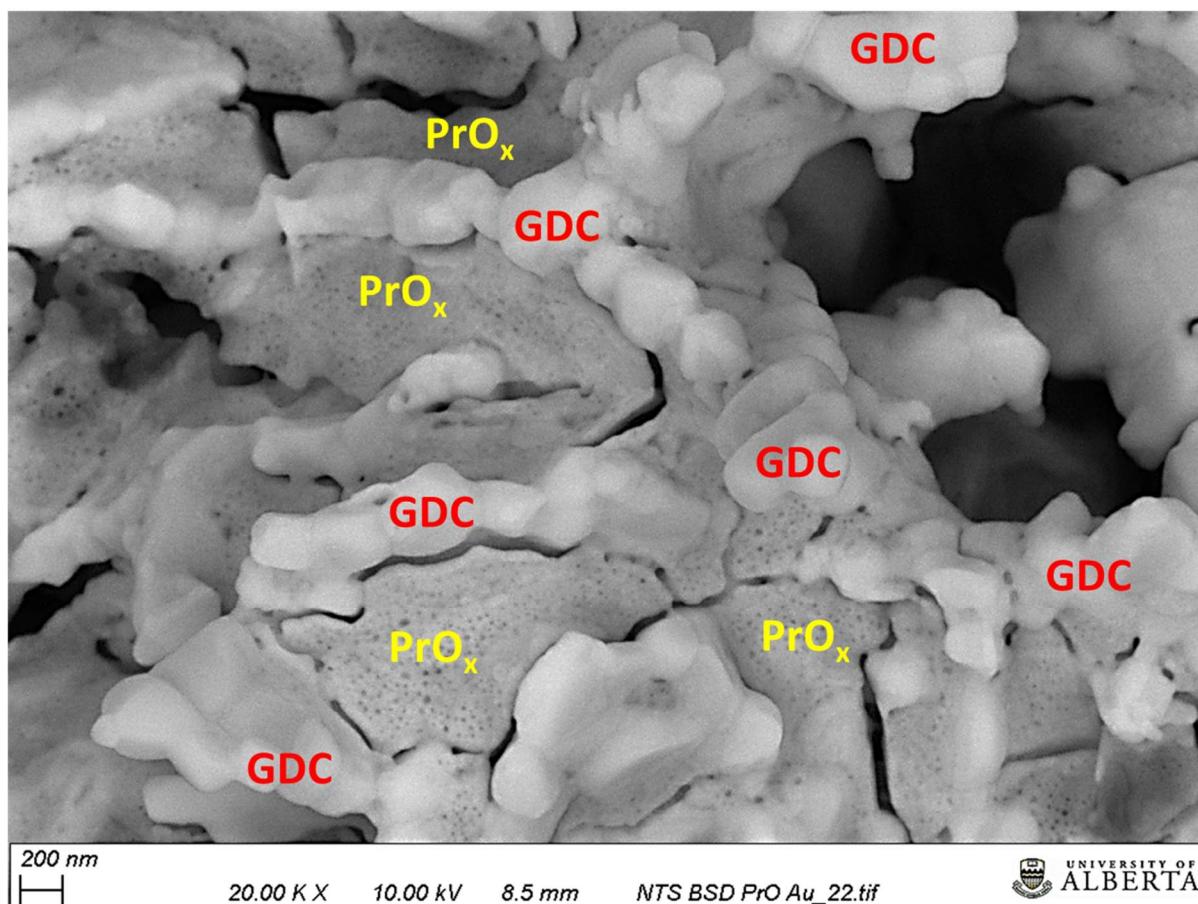


Figure 5.7. SEM micrograph of a fractured section of a PrO_x -GDC sample sintered at 1000 °C before testing. Yellow marks indicate PrO_x agglomerates, and red marks show GDC particles of the scaffold.

The NNO single phase is formed in the YSZ scaffold at 1000 °C, as seen in *fig. 5.8*, with no secondary phases detected. However, at 1100 °C, there is a small contribution of $\text{Nd}_2\text{Zr}_2\text{O}_7$, which could derail the electronic conductivity of the formed composite. As a consequence, 1000 °C was selected as the maximum calcination temperature.

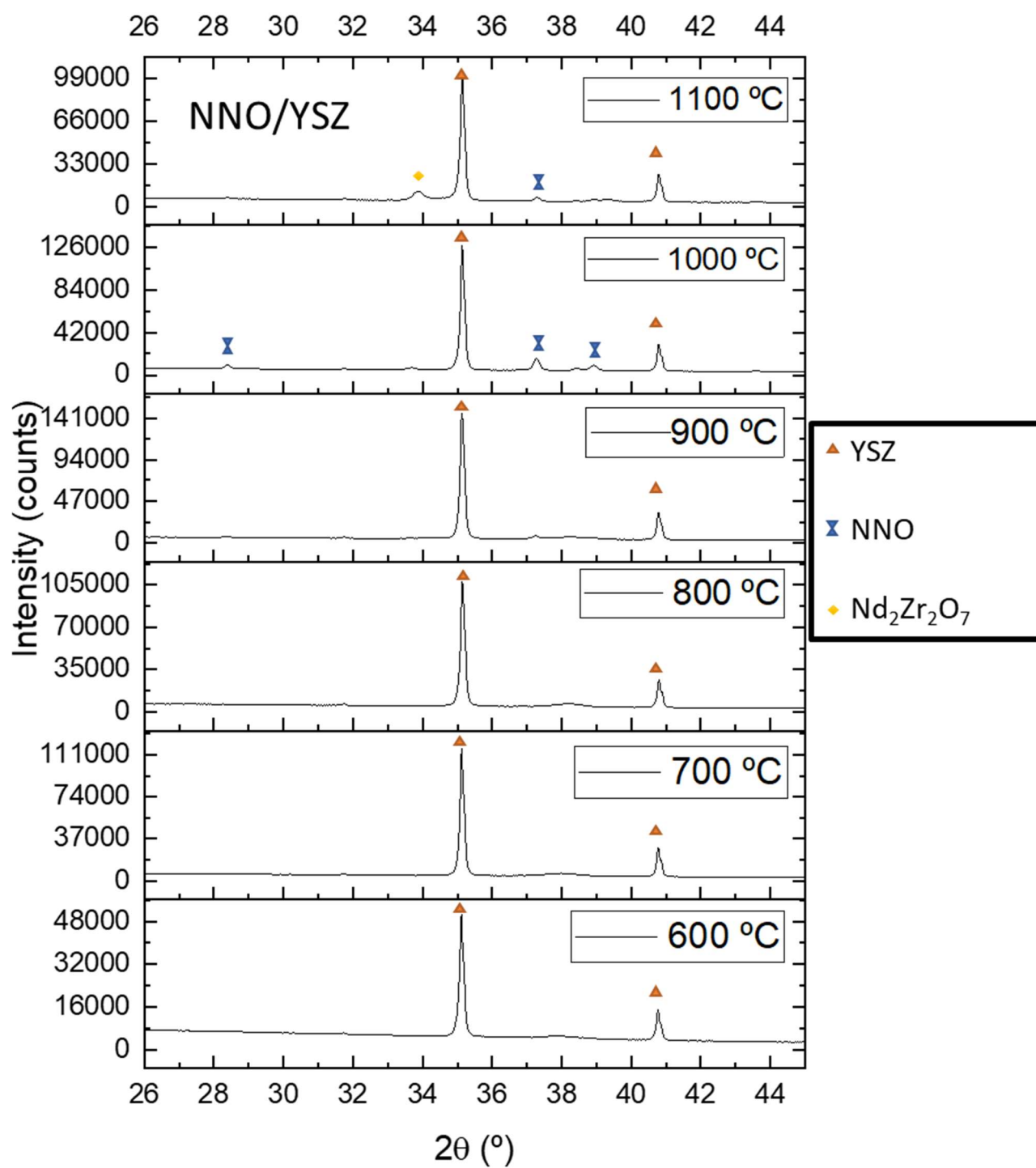


Figure 5.8. XRD patterns (26 to 45 degrees) of NNO-infiltrated YSZ from 600 to 1100 °C.

5.3.4. Single-cell description

A summary of the samples and relevant infiltration parameters is presented in *Table 5.2*. *Fig. 5.9* shows the actual dimensions of the prepared cells after the heat treatments. As seen in *fig. 5.9a*, the A-series cell is closed on one end due to the shape of the plaster mold, while the B-series cell is open on both ends. The dimensions of both cell types are illustrated by the SEM micrographs in *fig. 5.9b* (A-series), and *fig. 5.9c* (B-series).

Table 5.2. Fabricated SOC using catalysts infiltrated in different scaffolds.

Series	Nomenclature	Scaffold	Infiltrate	N° of infiltrations	Solid loading (wt%)	Sintering temperature (°C)
A	A-PNY	CMYSZ	PNO	3	36	1000
	A-NNY	CMYSZ	NNO	3	35	1000
	A-PNG	GDC	PNO	2	32	1000
	A-NGG	GDC	NNO	2	30	1000
	A-PG6	GDC	PrO _x	2	32	600
B	B-PNG	GDC	PNO	4	33	1000
	B-PG6	GDC	PrO _x	4	33	600

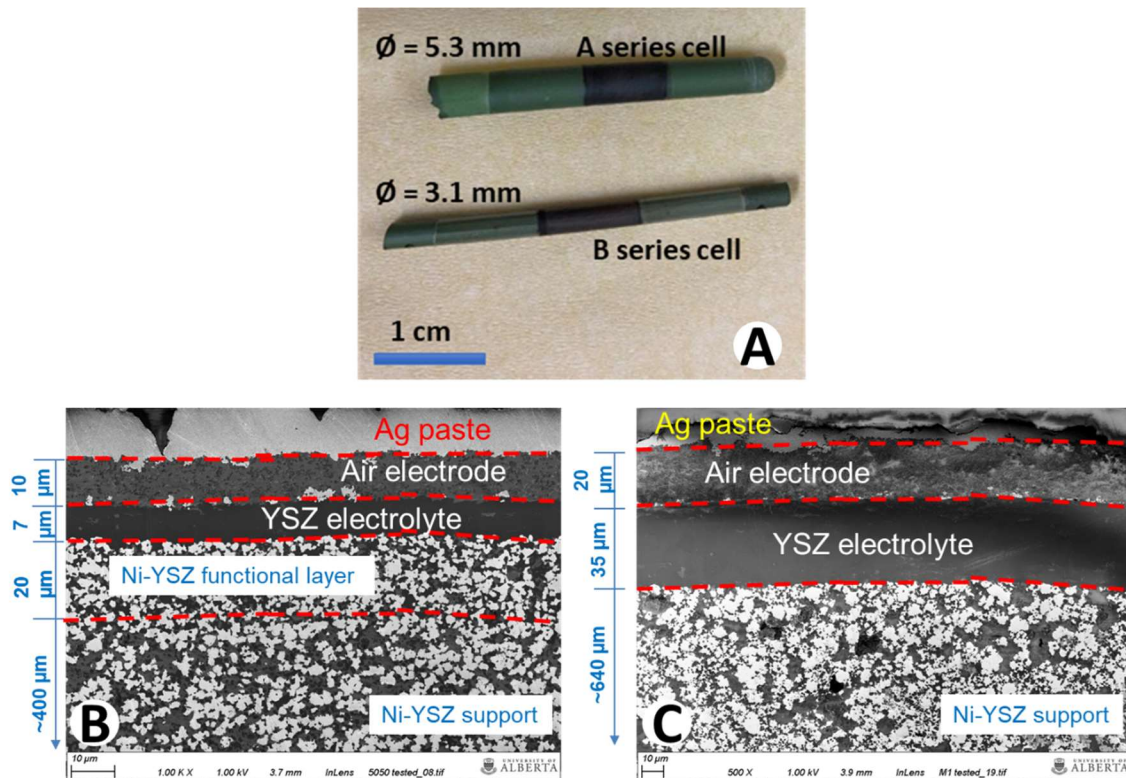


Figure 5.9. Comparison of the dimensions of A- and B-series cells (a), dimensions of the SOC configuration for A-series (b), and B-series (c).

5.4. Characterization of SOC with infiltrated air electrode composites

5.4.1. Cell measurement setup

In the cells of the A series, Cu mesh (Alfa Aesar) was inserted as the inner fuel electrode support current collector. Silver wire and paste (Fuel Cell Materials) were also coated onto the fuel electrode support, and an Ag wire (Alfa Aesar) was wrapped around the open end of the support. This way, the fuel electrode current collector has contact on two sites of the support in order to ensure good electrical contact with the external circuit. Both tubular cell types were coupled to mullite tubes using Ceramabond 552 (Aremco) cement, and hot glue was used to seal the outlet of the mullite tube (*fig. 5.10a*). Then, the Ag paste was coated onto the air electrode with a paintbrush and dried at 200 °C. A silver mesh was tightly wrapped around the active zone using Ag wires (*fig. 5.10b* and *c*). The active area is 1.5 cm² for the A cells and 1 cm² for the B cells.

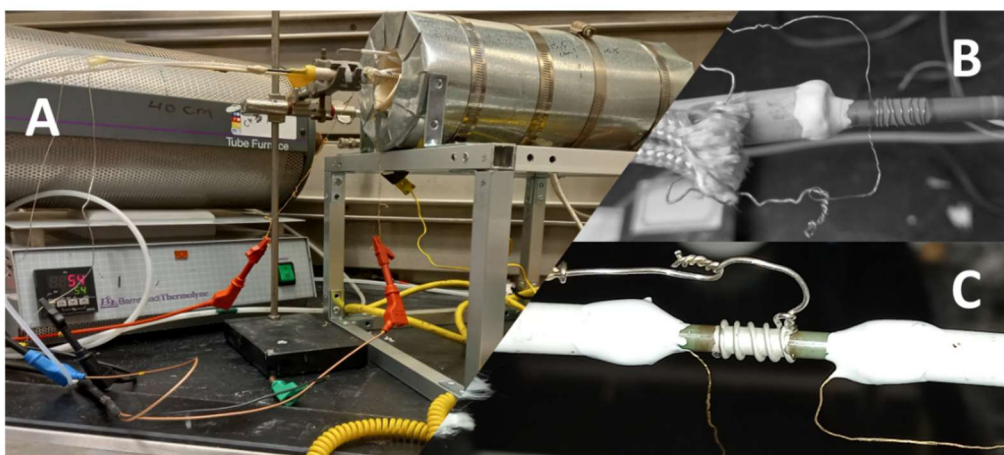


Figure 5.10. SOC electrical test setup: a) Installed cell within the tubular furnace, temperature controllers, and electrical connections used in the experiments; b) Setup of the A cells showing the electrical connections in the air electrode; c) Setup of the B cells with the corresponding Ag electrical contacts.

The cells were placed in the hot zone of a tubular furnace, and a thermocouple was placed close to the air electrode to monitor the temperature. The inlet was connected to the H₂ gas using a bubbler to provide humidified hydrogen to the fuel electrode side of the cell, while the air electrode side was exposed to airflow. The NiO phase in the fuel electrode was reduced at 750 °C for 20 h using a mixture of nitrogen and humidified hydrogen (3 vol% H₂O) with flow rates of 43 and 7 standard cubic centimeters per minute (SCCM), respectively. At standard 1 atm and RT conditions, this flow is equivalent to ~7 ml·min⁻¹. Then the gas mixture was gradually switched to 0 SCCM of nitrogen and 50

SCCM of hydrogen in 1 hr. Synthetic air with 100 SCCM was used on the air electrode side.

The electrochemical measurements were performed in a potentiostat with a 10A booster and frequency response analysis (FRA32M). The temperature range of the test was made in runs from 750 °C to 650 °C, where stability tests were performed. In EIS, a 20 mV of AC sinusoidal amplitude and a frequency range from 100 kHz to 100 mHz were used. The EIS data were analyzed by the DRT method (with a fixed regularization parameter $\lambda=1 \times 10^{-3}$), typically representing four processes. Surface area fractions underneath individual DRT peaks are calculated using peak analysis in Origin software. Similar to chapters 3 and 4, the polarization resistance values of individual peaks (R_i , with $i = 1, \dots, 4$) are calculated by multiplying the surface area fraction of each peak times the total polarization resistance (R_{pol}). Capacitance values for each peak are measured using the characteristic frequencies and R_i values in eqn. 3.3 and 3.4. Based on chapter 4 results, this method has proven more accurate and straightforward than equivalent circuit modeling [152].

The first series of tests were performed in A-cells, where we intended to measure the performance of the different scaffolds fabricated with two infiltrated nickelates, PNO and NNO. These infiltrations formed the PNO-GDC (A-PNG), PNO-YSZ (A-PNY), NNO-GDC (A-NNG), and NNO-YSZ (A-NNY) composites.

Once the OCV is reached (~1.10 V at 750 °C and 1.14 V at 650 °C), the initial characterizations in SOFC mode are conducted.

5.4.2. Effect of scaffold type on SOC performance

As the objective of this study is to determine the cell's performance and the stability of the air electrode, we decided to focus the subsequent study on single cells rather than on symmetrical cells. It is worth noting that in a symmetrical cell configuration, it is impossible to make conclusions about the stability of air electrodes as more factors affect cell performance. The polarization resistances, oxygen reduction and oxidation states of the air electrode catalysts, and heat generated during the potentiostatic test are all different in a symmetrical cell compared to a single cell test. Any conclusions with a symmetrical cell won't guarantee a successful stability test in a single SOC configuration. For instance, Brus *et al.* [253] reported on the microstructure and performance of a Ni-YSZ/YSZ/LSFC-GDC cell configuration and noticed a stable performance regardless of the apparent degradation in the fuel electrode: *"Even though a decrease in the TPB*

length was observed, the performance of the cell does not change significantly. Moreover, the measured power density increases slightly during the operation". The plausible explanation of this effect was "the compensation by overlapping strong improvement of the air electrode and decay mechanism of the fuel electrode." This fact shows that a definite conclusion should be restrained when proposing a unique solution for SOFC electrochemical performance.

In fig. 5.11a and b, the I-V characteristics show the initial performance of A-PNG, A-PNY, A-NNY, and A-NNG. At 750 °C and 0.5 V (fig. 5.11a), the maximum power density (MPD) registered values of 0.70, and 0.55 W·cm⁻² for A-PNOG and A-PNY, respectively. At lower temperatures, the MPD is almost identical in both cells at 0.27 and 0.43-0.45 W·cm⁻² at 650 and 700 °C, respectively.

In the A-NNY and A-NNG cells, the performance was measured at 750 °C for both cells, but at lower temperatures, only results for A-NNY were measured. The MPD performance of both cells was similar at 750 °C at 0.35 and 0.32 W·cm⁻² for A-NNY and A-NNG, respectively. At this temperature, however, the results are lower than those obtained for the PNO-infiltrated cells.

In the A-PNY cell, at all the temperatures measured, the shape of the I-V curve at higher than 0.90 A·cm⁻² showed mass transfer limitations that were not visible in the A-PNG cell.

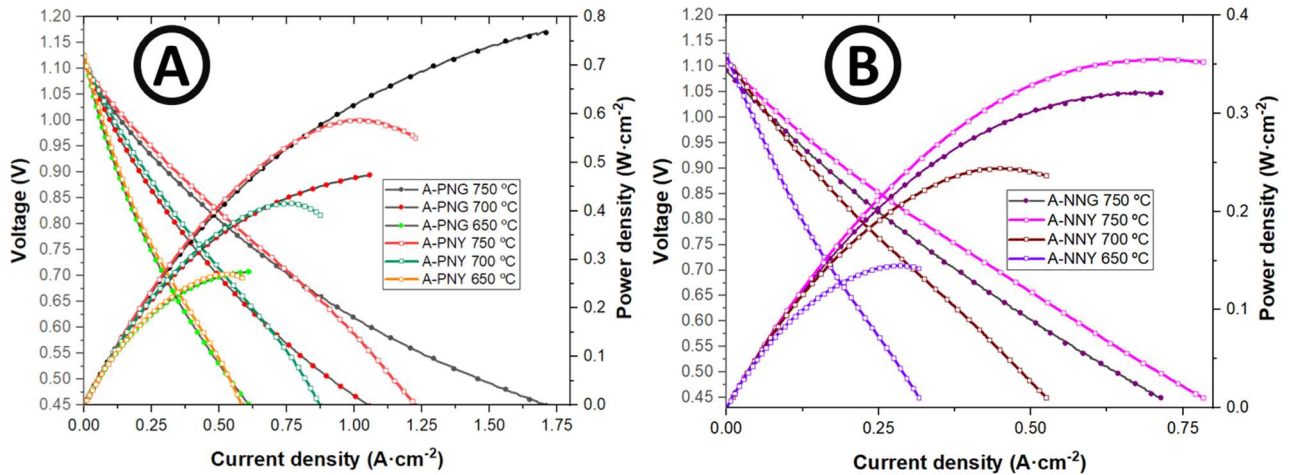


Figure 5.11. I-V-P curves of A-PNG and A-PNY cells a), A-NNG and A-NNY cells b).

The OCV remained within the same value at their respective temperature in each cell, indicating no sealing problems. At 650 °C, the slope indicates a high ASR value

compared to temperatures over 700 °C. *Fig. 5.12a* shows that the R_{pol} generally follows the order A-PNY < A-PNG < A-NNY in all the temperatures tested. At 750 °C, A-NNG had the lowest R_{pol} , but a high ohmic resistance was observed ($0.43 \Omega \cdot \text{cm}^2$ compared to $0.15\text{-}0.20 \Omega \cdot \text{cm}^2$ of the other cells), probably due to poor inner contact of the fuel electrode with the Cu mesh.

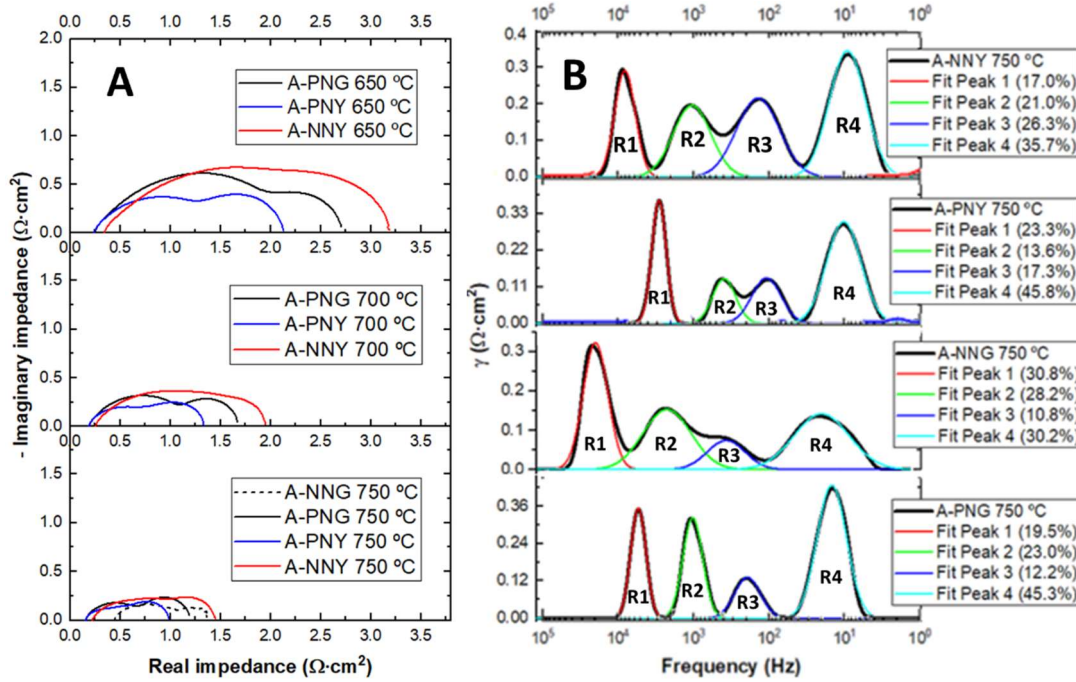


Figure 5.12. Comparison of the electrochemical performance of A-series nickelate air electrode composites with YSZ and GDC scaffolds: a) EIS measurements between 650 and 750 °C; b) DRT at 750 °C showing the peak area percentages in the inset.

The DRT peak analysis of the EIS data is shown in *fig. 5.12b*. Peak R1 (> 1000 Hz) is not generally different between the cells, except for A-NNG, which is at least 10% higher than the other cells. The A-PNY cell showed the lowest areas in peaks R2 (between 300-3000 Hz) and #3 (between 30-300 Hz). This result suggested a better O^{2-} transfer resistance product of airflow (in the air electrode) and fuel flow (in the fuel electrode) [47,254]. Meanwhile, peak R3 contribution is owed to the combination of mechanisms of oxygen-surface exchange and O^{2-} transport resistance in the air electrode. A similar peak R3 area was obtained in the A-PNG cell.

Peak R4 is also similar in peak area in the four cells studied. The A-NNG cell had the lowest value among the studied cells. This cell showed peak shifts, consistent with the high ohmic resistance obtained. The A-NNY cell had the highest R_{pol} in every temperature and the highest DRT peak area in this analysis.

The corresponding R_{pol} values of the mechanisms are detailed in *Table 5.3*. The A-PNY cell had the lowest R_{pol} values among the studied cells. Notably, the R2 value was more than half of the value obtained in A-PNG and A-NNY. Both A-PNG and A-NNY showed similar tendencies in R2 and R3 as temperature decreased, while A-PNY experienced an increase of the R2 value from $0.11 \Omega \cdot \text{cm}^2$ at 750°C to $0.64 \Omega \cdot \text{cm}^2$ at 650°C .

Table 5.3. R_{pol} calculated by DRT area fittings of A-series cells using nickelate composite air electrodes.

650 °C					
Sample	R1 ($\Omega \cdot \text{cm}^2$)	R2 ($\Omega \cdot \text{cm}^2$)	R3 ($\Omega \cdot \text{cm}^2$)	R4 ($\Omega \cdot \text{cm}^2$)	R_{pol} ($\Omega \cdot \text{cm}^2$)
A-PNG	0.26	0.45	1.01	0.73	2.45
A-PNY	0.30	0.64	0.13	0.82	1.89
A-NNY	0.28	0.41	1.03	1.11	2.83
700 °C					
Sample	R1 ($\Omega \cdot \text{cm}^2$)	R2 ($\Omega \cdot \text{cm}^2$)	R3 ($\Omega \cdot \text{cm}^2$)	R4 ($\Omega \cdot \text{cm}^2$)	R_{pol} ($\Omega \cdot \text{cm}^2$)
A-PNG	0.23	0.56	0.12	0.57	1.47
A-PNY	0.26	0.24	0.15	0.48	1.13
A-NNY	0.24	0.56	0.47	0.42	1.69
750 °C					
Sample	R1 ($\Omega \cdot \text{cm}^2$)	R2 ($\Omega \cdot \text{cm}^2$)	R3 ($\Omega \cdot \text{cm}^2$)	R4 ($\Omega \cdot \text{cm}^2$)	R_{pol} ($\Omega \cdot \text{cm}^2$)
A-PNG	0.20	0.24	0.12	0.46	1.03
A-PNY	0.19	0.11	0.14	0.37	0.82
A-NNY	0.21	0.25	0.32	0.43	1.21
A-NNG	0.29	0.30	0.05	0.27	0.90

In general, Although the A-PNY cell performed better than A-PNG, we further focused this study on the latter composite due to mass transfer issues in the former, which were evident at high current densities, as shown in the I-V characterization. Also, as identified in *section 5.3.3*, the Pr-Zr reactivity remains a concern in mid-to-long-term SOC operations.

5.4.3. Influence of the Ni-YSZ support on SOC performance

In this section, the slip casting and extruded Ni-YSZ supports used in the tubular SOC are evaluated regarding the cell's electrochemical performance, R_{pol} , and stability. In this approach, we compared the A-PNG cell with B-PNG [252].

Figures 5.13a and b show the initial performances of A-PNG and B-PNG cells recorded in I-V-P curves between 650 and 750°C . Cell A's MPD was measured at 0.77 , 0.47 , and $0.27 \text{ W} \cdot \text{cm}^{-2}$ at 750 , 700 , and 650°C , respectively.

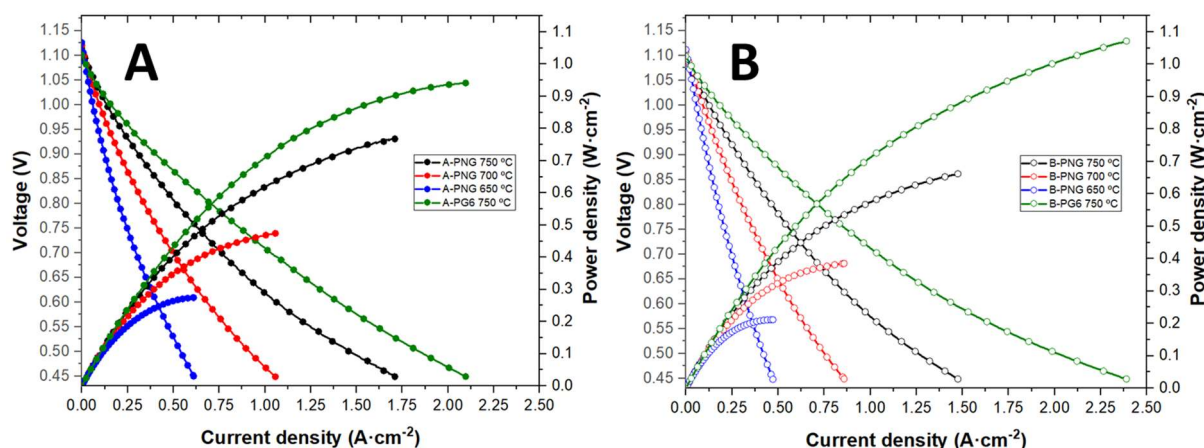


Figure 5.13. I-V-P characteristics of A-PNG and A-PG6 (a), and B-PNG and B-PNG (b) between 650 and 750 °C using 50 SCCM of H₂ (3 vol% humidified) on the fuel electrode side and 100 SCCM air on the air electrode side [252].

The performance of B-PNG was slightly lower than A-PNG, as shown in *fig. 5.13b* with MPDs of 0.66, 0.38, and 0.21 at 750, 700, and 650 °C, respectively. These values resulted in an MPD increase of cell A-PNG of 17, 23, and 30 % more than B-PNG at 750, 700, and 650 °C, respectively. The OCV remained constant at each temperature during all the characterizations, showing no signs of leakage in the ceramic seal. The initial electrochemical characterizations of the PrO_x-GDC composite air electrodes show higher performance than PNO-GDC air electrodes. *Figure 5.13* shows an MPD at 750 °C of 0.81 and 1.13 W·cm⁻² for A-PG6 (*fig. 5.13a*) and B-PG6 (*fig. 5.13b*), respectively. This represents an increase over A-PNG and B-PNG cells (0.77 and 0.66 W·cm⁻², respectively).

Nyquist plots of the two cells were studied between 650 and 750 °C and compared in *fig. 5.14a* to *5.14c*. As illustrated in these figures, the lowest ohmic resistance values were obtained in A-PNG at each temperature studied. The B-PNG cell showed lower R_{pol} values, especially in the high-frequency component. The difference in ohmic resistance is related to the thinner electrolyte of A-PNG (7 microns) compared to B-PNG (30-35 microns). Even so, the maximum difference is 50% at 650 °C. Due to geometrical differences, the Ni-YSZ support silver current collector was attached to one end of the tube for the A-PNG cell. In contrast, for the B-PNG cell, the support silver current collector was attached to both ends of the tube, which could have helped to improve the electrical contact. As these cells are diverse in the fabrication method of the supports (extrusion vs. slip cast), pore former thickness and the use of different NiO powders could have also affected the ohmic contact resistance.

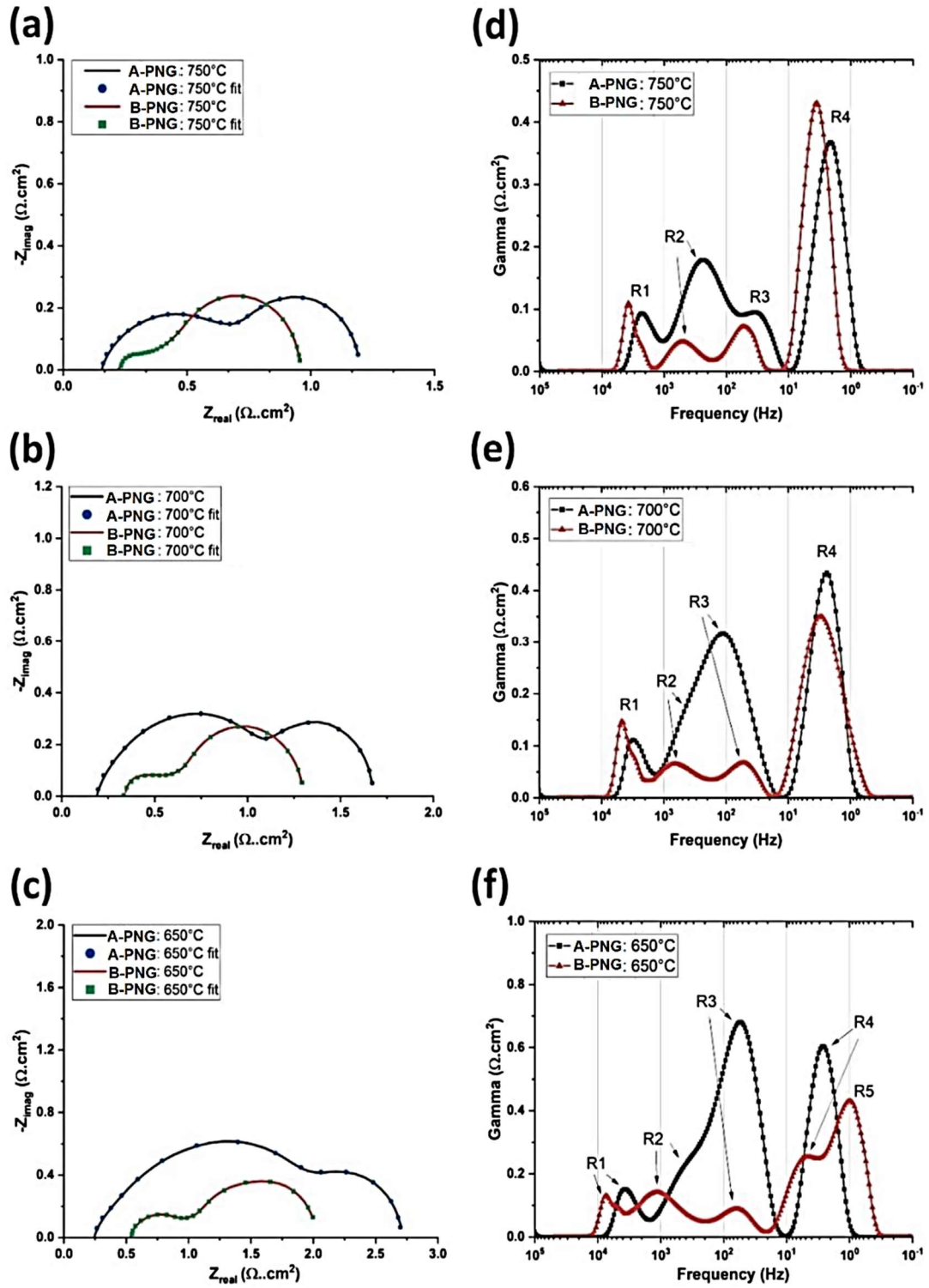


Figure 5.14. Nyquist plot comparison of A-PNG and B-PNG at 750 °C (a), 700 °C (b), and 650 °C (c). Blue circles and green squares show the fittings on experimental EIS data using the DRT method. Corresponding DRT data for each temperature are plotted in d, e, and f [252].

Consistent with the EIS data, the DRT of *fig. 5.14d* to *f* generally shows a reduction of peaks R2 and R3, particularly at 650 °C. Additional features are worth mentioning from the DRT analysis: first, the high-frequency peak (R1) in B-PNG is shifted to the left, which is due to a higher ohmic resistance than A-PNG as indicated in the Nyquist plots of *fig. 5.14a* to *c*; second, at 650 °C, a fifth peak appeared at <1 Hz. This peak also surged in the symmetrical PNO cells tested in *section 3.9* and the single cells characterized in *section 4.4.1* as a product of a gas diffusion resistance and disappeared as temperature increased. As mentioned in *section 4.4.2*, SOFC operation does not significantly influence this effect as SOEC does.

The DRT peak area contributions to total R_{pol} have been discussed extensively in previous chapters, and some similarities have been identified. Generally, four peaks are detectable in the DRT data. The resistances (R values) with their respective activation energies (*fig 5.15a*) and capacitances (C values in *fig. 5.15b*) are calculated by the DRT peak area and are summarized in *Table 5.4*. These results are discussed in the following lines:

- The R1 value, almost unaltered with temperature, especially in B-PNG (low activation energy of 0.7 and 38 kJ·mol⁻¹ for B-PNG and A-PNG, respectively), is assigned to oxygen ion transfer in air and fuel electrodes.
- The R2 resistance presented higher activation energies in A-PNG (54 kJ·mol⁻¹) and B-PNG (121 kJ·mol⁻¹). The latter energy indicates a fuel electrode charge transfer process heavily dependent on temperature.
- The R3 value in A-PNG, which uses a relatively thinner air electrode (~10 microns), is more affected by temperature variations than in B-PNG. *Fig. 5.15a* shows that the activation energy is much higher than in B-PNG (168 vs. just 23 kJ·mol⁻¹). Reduction in the air electrode thickness of A-PNG negatively affected the performance at lower temperatures. The same pattern was observed in symmetrical cells in *fig. 3.18* and *fig. 3.19*, with high activation energy. In those cells, the thicknesses were ~15 microns. The R3 value is associated with O²⁻ surface exchange [254] and charge transfer inside the air electrode, implying that this process is not occurring as seamlessly in A-PNG as in B-PNG. According to *Table 5.4*, the values of R3 for A-PNG and B-PNG at 650 °C are 0.85 and 0.12 Ω·cm², respectively. Increasing the temperature to 750 °C, the corresponding resistance values get closer (0.10 and 0.09 Ω·cm², respectively).
- R4 has the largest characteristic DRT peak area at 750 °C in both cells. As R5 calculated from peak R5 is only present at a very low-frequency range (< 1 Hz),

these results suggest that R5 (capacitance of $0.2 \text{ F}\cdot\text{cm}^{-2}$) can be related to concentration polarization.

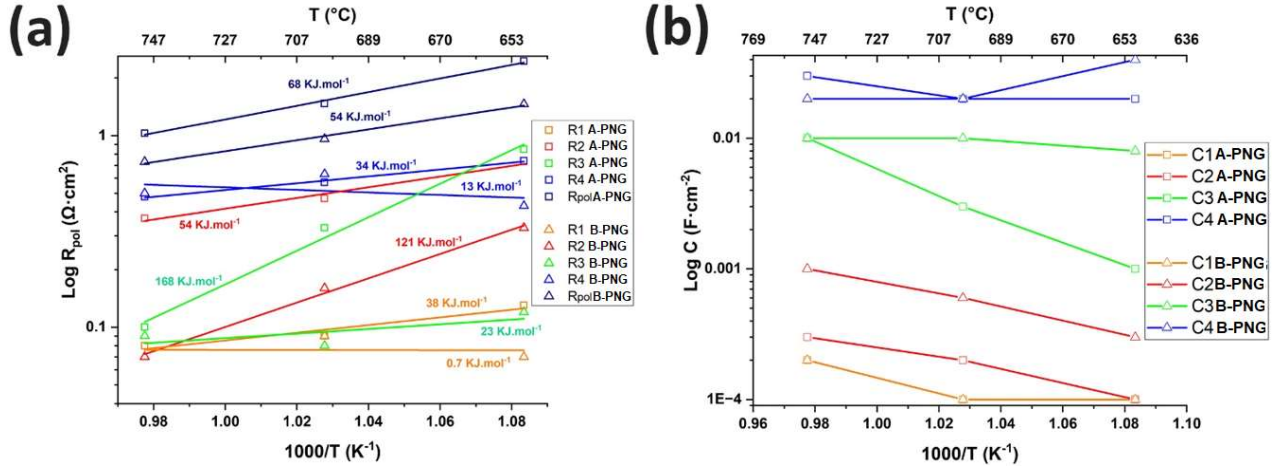


Figure 5.15. (a) Values of polarization resistance and (b) capacitance of individual peaks corresponding to DRT data at different temperatures for A-PNG and B-PNG [252].

Table 5.4. Polarization resistance and capacitance values of different peaks associated with DRT plots for cells A-PNG and B-PNG at different temperatures.

Sample	R1 ($\Omega\cdot\text{cm}^2$)	C1 ($\text{F}\cdot\text{cm}^2$)	R2 ($\Omega\cdot\text{cm}^2$)	C2 ($\text{F}\cdot\text{cm}^2$)	R3 ($\Omega\cdot\text{cm}^2$)	C3 ($\text{F}\cdot\text{cm}^2$)	R4 ($\Omega\cdot\text{cm}^2$)	C4 ($\text{F}\cdot\text{cm}^2$)	R5 ($\Omega\cdot\text{cm}^2$)	C5 ($\text{F}\cdot\text{cm}^2$)	R _{pol} (total)
	(3x10 ³ -2x10 ⁴ Hz)		(300-3000 Hz)		(25-300 Hz)		(1-25 Hz)		(<1 Hz)		
A-PNG: 750 °C	0.08	2E-04	0.37	3E-04	0.10	1E-02	0.48	3E-02	-	-	1.03
B-PNG: 750 °C	0.07	2E-04	0.07	1E-03	0.09	1E-02	0.50	2E-02	-	-	0.73
A-PNG: 700 °C	0.09	1E-04	0.47	2E-04	0.33	3E-03	0.57	2E-02	-	-	1.47
B-PNG: 700 °C	0.09	1E-04	0.16	6E-04	0.08	1E-02	0.63	2E-02	-	-	0.96
A-PNG: 650 °C	0.13	5E-05	0.73	2E-04	0.85	1E-03	0.74	2E-02	-	-	2.45
B-PNG: 650 °C	0.07	1E-04	0.33	3E-04	0.12	8E-03	0.43	4E-02	0.51	0.2	1.46

5.4.4. Stability performance

In SOC literature, there is little reported about PNO-infiltrated air electrode stability. Some experiments have been performed with PNO air electrodes [255–260]; however, their stability with composites fabricated by infiltration in single-cell operation had not yet been thoroughly tested over a medium-to-long-term operation; only a 168-hour test at 750 °C has been reported in symmetrical cells using SDC-infiltrated PNO scaffolds [260].

Figures 5.16a and d show the I-V-P performance of A-PNG and B-PNG, respectively, before and after the potentiostatic tests at 650 °C. In *fig. 5.16a*, the A-PNG performance increased from 0.27 to 0.36 W·cm⁻², equaling a 31% improvement during the test. On the other hand, *fig. 5.16d* shows how the performance of cell B-PNG improves during the first 161 hours of the test from 0.21 to 0.28 W·cm⁻², an identical 31% improvement to A-PNG. After 161 hours, the performance slightly decreases from 0.28 to 0.27 W·cm⁻².

Fig. 5.16e shows the Nyquist plot at different stability test time intervals for B-PNG. The R_{pol} decreases from the initial value of 1.46 Ω·cm² to 0.95 Ω·cm² after 260 hours. However, ohmic resistance increases from 0.50 to 0.60 Ω·cm² for the final 100 hours of the test. A plausible reason is the deterioration of the internal silver contact in the fuel electrode at prolonged operation at high temperatures, as no evidence of a loosened electrical contact was observed. Contrary to this, the Nyquist plots in *fig. 5.16b* and *c* reveal a reduction of the A-PNG R_{pol} after 91 h of the stability test without changes in the ohmic resistance. *Fig. 5.16c* shows the corresponding DRT in *fig. 5.16b*, where the cause of R_{pol} reduction is the decrease of peaks R3 and R4. This demonstrates that oxygen evolution within the air electrode over the duration of the experiment is helping in the performance increase of A-PNG.

In the case of B-PNG, the DRT data in *fig. 5.16f* shows a continuous reduction in peak R4, while peak R5 is eliminated after 60 h into the test. The most interesting feature in this figure is that peak R2 slightly increases from the start of the test to 160 h, returning to the initial value at 260 h. This behavior has already been discussed in *chapters 3 and 4*, as the process that drives the charge transfer resistance in the fuel electrode. It is inferred that this process is accelerated by operating at high temperatures and steam content. The increasing values of peaks R1 and R2 at 60 and 160 hours can be attributed to the microstructure evolution (TPBs) of the Ni-YSZ electrode [254].

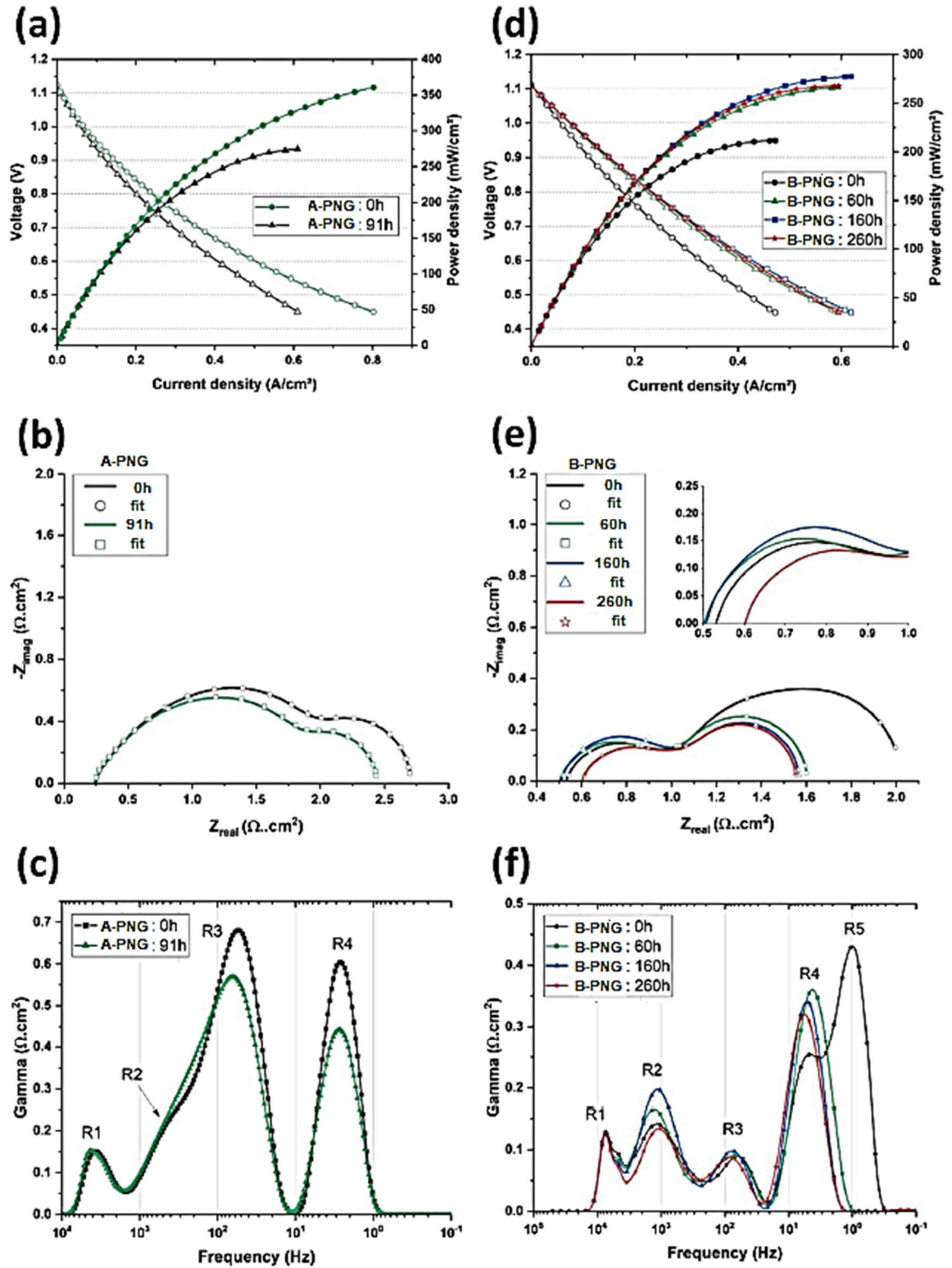


Figure 5.16. I-V-P, Nyquist plots, and DRT graphs for A-PNG (a, b, and c) and B-PNG (d, e, and f) at 650 °C. Solid lines in (b) and (e) represent EIS experimental data, while the points on the curve show the accuracy of the DRT fitting. Inset in (e) shows the zoomed Nyquist data [252].

Stability tests on SOC using PNO-infiltrated GDC air electrodes were compared over 90 and 260 hours for A-PNG and B-PNG, respectively (*fig. 5.17*). The tests were performed at 0.7 V and 650 °C, with fuel and air flows of 50 and 100 SCCM, respectively. An increase in the current density is noticeable for all cells at the beginning of the stability test, with similar behavior in both cells for the initial 90 h, demonstrating the repeatability of the test. According to *fig. 5.17*, the B-PNG current density was continuously improving for about 186 hours. After this, a sudden jump in the current density of B-PNG is observed due to a slight increase in the fuel pressure (p_{H_2}) inside the fuel chamber. The fuel outlet gas (composed of unreacted H_2 and produced H_2O) was placed inside a water container. As reported by Vafaeenezhad *et al.* [252], the proper bubbling of the fuel outlet during the stability test ensures gas-tight sealings. The A-PNG cell did not degrade over the duration of the 90 hours test. The degradation rate of the A-PG6 was $32.1 \text{ mA} \cdot \text{kh}^{-1}$ ($78\% \cdot \text{kh}^{-1}$). The B-PG6 cell, similarly to B-PNG, showed jumps in the current density at 100 hours as a product of a slight increase in p_{H_2} inside the fuel chamber. After 100 hours, the cell presented a degradation rate of $3.5 \text{ mA} \cdot \text{kh}^{-1}$ ($10\% \cdot \text{kh}^{-1}$) for the duration of the test. As a reference, Khoshkalam *et al.* [261] reported a degradation rate of $29\% \cdot \text{kh}^{-1}$ for 200 h at 650 °C in a cell using a Pr_6O_{11} -infiltrated LNF/CGO air electrode. Stability implies degradation rates well below $1\% \cdot \text{kh}^{-1}$, as in air electrodes like LSFC, where a $0.4\% \cdot \text{kh}^{-1}$ was obtained in a cell configuration using a Ni-GDC fuel electrode [262]. For this reason, full stability has not been achieved yet in PrO_x -GDC electrodes using our cell configurations, while, for the most part, PNO-GDC electrodes did not show degradation.

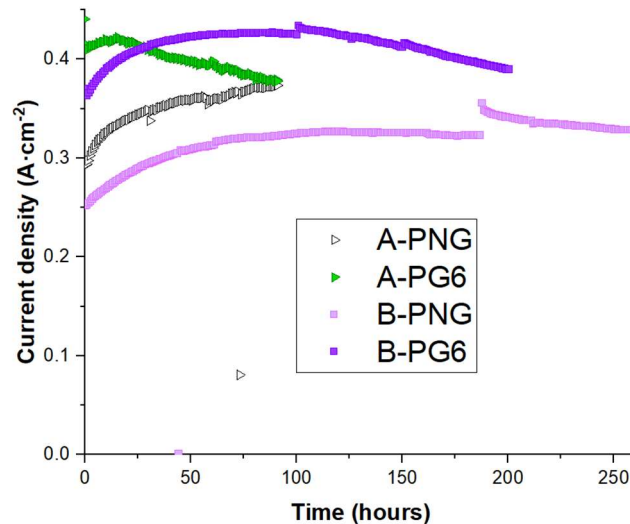


Figure 5.17. Comparison of the stability between A- and B-cells at 650 °C and 0.7 V.

As the water inside the container at the outlet gradually evaporates, refilling the container is needed after a few hundred hours.

5.4.5. Influence of infiltrate composition on SOC performance

In this section, the PrO_x -GDC composite is compared with PNO-GDC to evaluate the behavior of both electrodes. The changing of the air electrode infiltrate in the composite is employed to isolate the DRT peaks related to the processes that affect its internal resistances. Due to the novelty of the PNO-infiltrated air electrode, limited data is available in the literature; however, changing any of the SOC component microstructures can help to understand the contribution of each DRT peak, as suggested by other authors [263]. Cells A-PG6 (slip cast supports) and B-PG6 (extrusion molding supports), both with PrO_x -GDC air electrodes sintered at 600 °C, were selected for comparison with cells A-PNG and B-PNG (both with PNO-GDC air electrodes), as a similar GDC scaffold is used on each of them, so only the infiltrate composition can be contrasted between these cells. The rest of the variables (porosity, thickness, etc.) were kept similar in each cell. These variations are detected in the DRT peaks R3 and R4, as just these two peaks generally respond to changing the air electrode catalyst and gas composition [263].

The EIS result of *fig. 5.18a* shows a similar ohmic resistance in cells A-PNG and A-PG6 ($0.18 \Omega \cdot \text{cm}^2$). *Table 5.5* shows the DRT peak area fitting results for individual R_{pol} (R values) and capacitance (C values) calculations. The fittings are consistent with the EIS data, where a major increase in the low-frequency arc was observed at each temperature. A-PG6 R_{pol} values were 0.83, 1.15, and $1.79 \Omega \cdot \text{cm}^2$ at 750, 700, and 650 °C, respectively. These values are significantly lower than in A-PNG (*Table 5.5*). A prevalent trend in the EIS data is that the nickelate influence on cell performance increases the R_{pol} and is especially notable at 650 °C. *Fig. 5.18c* displays the EIS results of the B-series cell comparison. Between B-PNG and B-PG6, there is a difference in the value of the ohmic resistance of more than 20%. Contrary to the A-cells, the thicker electrolyte in these cells is also affected by temperature variations as their value increases by almost 100%.

The increase of ohmic resistance (*fig. 5.18a*) could have been due to silver paste (current collector) sintering or slight detachment of silver mesh, as well as detaching the contact between silver and potentiostat device wires. The R_{pol} values of B-PG6 are twice as low as in B-PNG (*Table 5.5*) at 0.52, 0.65, and $0.86 \Omega \cdot \text{cm}^2$ at 750, 700, and 650 °C, respectively. To round out this summary of EIS results, the cell A-PNG R_{pol} decreased from 2.45 to $2.20 \Omega \cdot \text{cm}^2$, and cell A-PG6 R_{pol} presented an increase from 1.79 to $2.24 \Omega \cdot \text{cm}^2$. The B-PNG R_{pol} decreased from 1.46 to $0.95 \Omega \cdot \text{cm}^2$, while in B-PG6, the R_{pol} slightly diminished from 0.92 to $0.86 \Omega \cdot \text{cm}^2$ after the stability test.

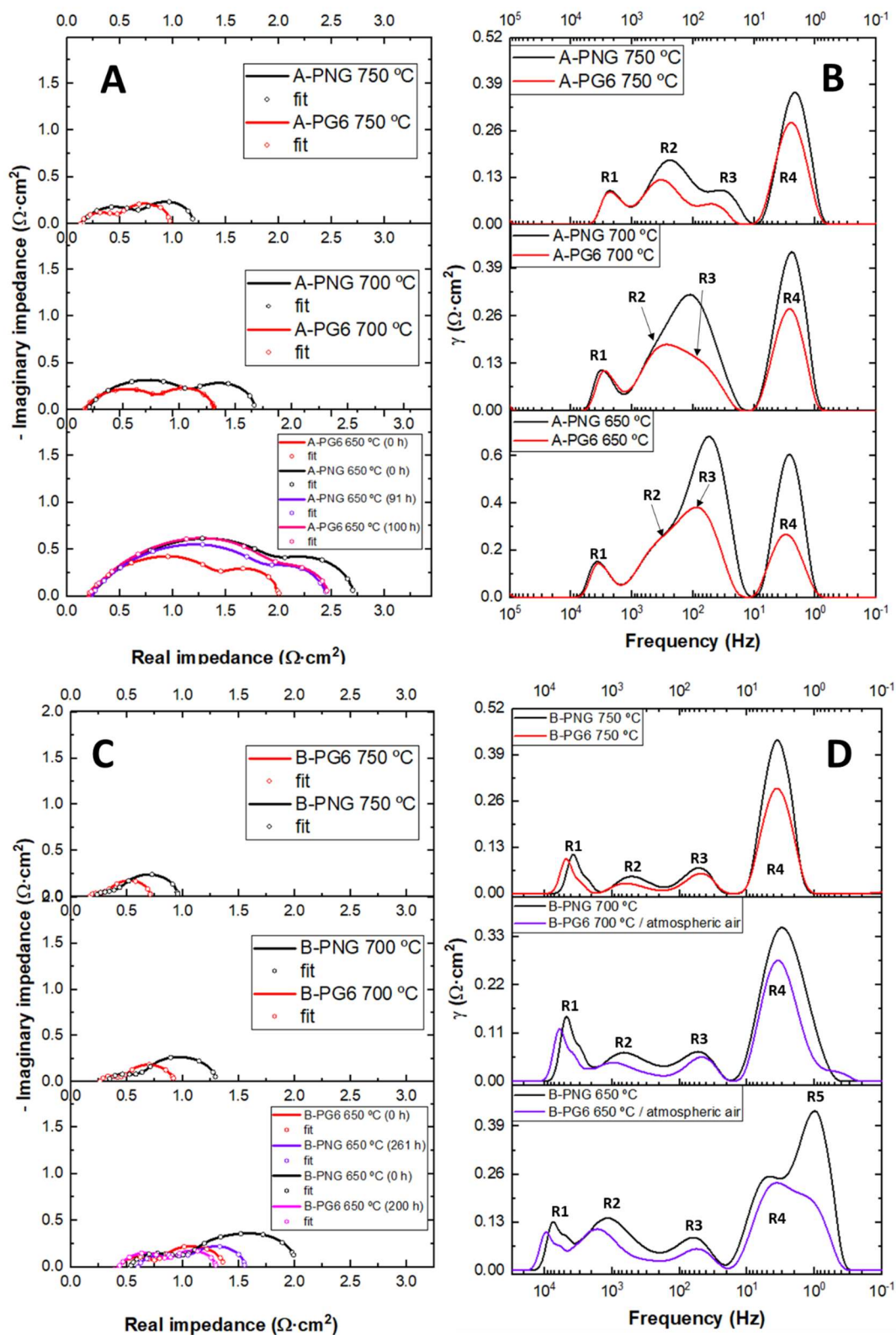


Figure 5.18. A-PNG and A-PG6 Nyquist plot at different temperatures (a), DRT peaks of A-PNG and A-PG6 (b), B-PNG and B-PG6 Nyquist plot at different temperatures (c), DRT peaks of B-series B-PNG and B-PG6 (d).

DRT data comparison of A-PNG and A-PG6 is shown in *fig. 5.18b*. On A-PG6, lower peaks R1 and R2 are observed, suggesting better charge transfer and electrode transport. The high-frequency peak R1 is barely affected by changing the infiltrate as A-PNG and A-PG6 peak area values are similar.

Peak R2 is also unaffected by changing the air electrode composition, especially at 650 and 700 °C. Increasing the temperature to 750 °C, R2 is slightly reduced. This result confirms the hypothesis that peak R2 is associated with charge transfer resistance at the fuel electrode/electrolyte interface, as referenced several times in the previous chapters [254].

In both A-cells, peaks R2 and R3 overlapped between 650-700 °C. Peaks R3 and R4 of A-PNG showed the most notable variations. Upon lowering the temperature, a sharp increase of the peak is visible in these peaks at 650 °C. This implies that the rate-determining process is compromised by fuel and oxygen electrode transport, as suggested by some authors [47,254].

During the DRT peak analysis, A-series DRT peaks R3 and R4 were reduced using PrO_x as an infiltrate. Peak R3 is associated with O^{2-} surface exchange [254] and charge transfer inside the air electrode.

Contrary to A-PNG, peak R3 for B-PNG was not much affected by changing the infiltrated nanocatalyst. At 750 °C, the main difference between the DRT peaks B-PNG and B-PG6 is in the low-frequency peak R4. Also, a slight shift to the right in peak R1 of B-PNG is caused by the increase in ohmic resistance shown in the Nyquist plots *fig. 5.18c* (probably due to loss of contact in the fuel electrode current collector).

Peak R5 contribution was non-existent in A-PNG and A-PG6 cells, where the SEM micrographs of *fig. 5.19* show a more homogeneous pore distribution (in a 10-micron electrode) than in B-series cells (using a 20-micron electron). A thinner air electrode thickness provides a better O_2 distribution in the composite. Also, from the post-mortem SEM microstructural images of *fig. 5.19a* (A-PNG) and *fig. 5.19b* (B-PNG), no delamination or cracks are observed between the air electrode and the electrolyte after the stability test.

Table 5.5. Polarization resistances and capacitances calculated from DRT fittings at 650 °C for A-PNG, A-PG6, B-PNG, and B-PG6, before and after stability tests.

Sample	R1 ($\Omega\cdot\text{cm}^2$)	C1 ($\text{F}\cdot\text{cm}^2$)	R2 ($\Omega\cdot\text{cm}^2$)	C2 ($\text{F}\cdot\text{cm}^2$)	R3 ($\Omega\cdot\text{cm}^2$)	C3 ($\text{F}\cdot\text{cm}^2$)	R4 ($\Omega\cdot\text{cm}^2$)	C4 ($\text{F}\cdot\text{cm}^2$)	R5 ($\Omega\cdot\text{cm}^2$)	C5 ($\text{F}\cdot\text{cm}^2$)	R _{pol} (total)
	(3x10 ³ -2x10 ⁴ Hz)		(300-3000 Hz)		(25-300 Hz)		(1-25 Hz)		(<1 Hz)		
A-PNG	0.13	5E-05	0.73	2E-04	0.85	1E-03	0.74	2E-02	-	-	2.45
*A-PNG (91 h)	0.28	5E-05	0.47	2E-04	0.86	1E-03	0.59	2E-02	-	-	2.20
A-PG6	0.22	1E-04	0.32	1E-03	0.69	1E-02	0.56	2E-02			1.79
*A-PG6 (91 h)	0.22	1E-04	0.39	1E-03	1.10	1E-02	0.53	2E-02			2.24
B-PNG	0.07	1E-04	0.33	3E-04	0.12	8E-03	0.43	4E-02	0.51	0.2	1.46
*B-PNG (260 h)	0.16	8E-04	0.20	5E-04	0.10	1E-02	0.49	2E-02	-	-	0.95
B-PG6	0.12	1E-04	0.26	1E-03	0.08	1E-02	0.45	2E-02			0.92
*B-PG6 (200 h)	0.12	1E-04	0.28	1E-03	0.09	1E-02	0.38	2E-02			0.86

* Following the stability test

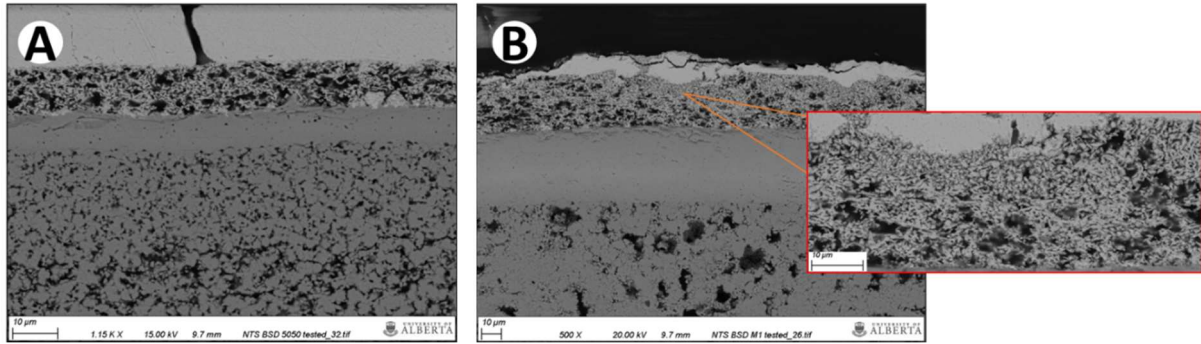


Figure 5.19. SEM micrographs using a BSE detector of air electrode thickness after tests: A-PNG taken at 15 kV a) and B-PNG taken at 20 kV b).

5.4.6. Influence of gas composition on SOC performance

For a better understanding of peaks R3 and R4, the air electrode gas atmosphere is changed for B-PG6. This experiment used three different air electrode atmospheres at 650 °C and 700 °C: atmospheric air, air at 100 ml·min⁻¹, and oxygen at the same flow rate as the latter. The DRT data for B-PNG and B-PG6 cells is shown in *fig. 5.20*. Generally, the DRT peaks of B-PG6 are lower than B-PNG. More characteristically, the low-frequency peak R5 is reduced in B-PG6 at 650 °C (black vs. red graphs in *fig. 5.20*). This peak was effectively eliminated during the stability test (*fig. 5.16f*), and together with this result, suggests that oxygen concentration positively affects the PNO-based air electrodes over time. By using a pure O₂ flow (green color in *fig. 5.20*), peak R5 disappears. Conversely, when atmospheric air (purple line) is used in B-PG6 instead of

air at 100 SCCM air (red line), R5 increases. Although R5 also appears in B-PG6 at lower frequencies (0.7 Hz) at 700 °C when atmospheric air is used (purple line), under the predetermined conditions of this experiment, this peak barely appeared. The effect could also be associated with an artifact due to the experimental DRT technique.

Regarding the DRT peak fitting, the R1 value after the stability test increased more than twice its original value in the cells using PNO-infiltrated GDC composites (0.13 to 0.28 $\Omega \cdot \text{cm}^2$ in A-PNG and 0.07 to 0.16 $\Omega \cdot \text{cm}^2$ in B-PNG). This resistance remained the same after the tests for both, A-PG6 and B-PG6. The difference between the two types of air electrodes is likely because no detrimental reactivity is expected between PrO_x and GDC. At the same time, PNO decomposition probably expels the NiO phase that is non-conductive.

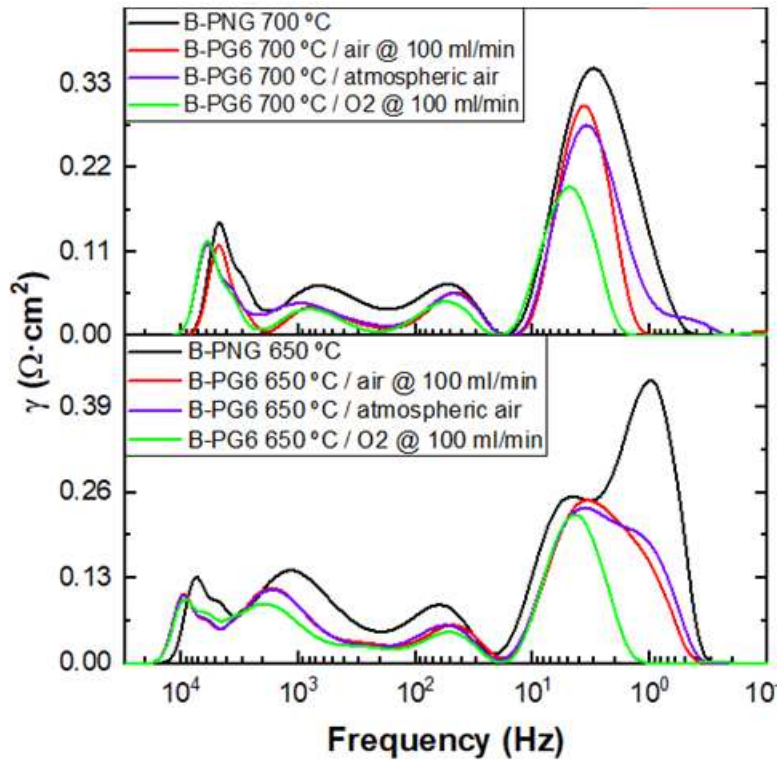


Figure 5.20. B-PNG and B-PG6 DRT peak variations between 650 and 700 °C under different air and oxygen atmospheres.

The R2 value of cell B-PNG is less than half the R2 in A-PNG, while B-PG6 is also lower than A-PG6. The analysis of the R2 value illustrates the importance of pore content on the performance of SOFC, which has already been discussed by other researchers [264], as the B-series support contains a higher pore volume than the A-series (50 vs. 40 vol. %). This might compensate for the lack of AFL in B-series cells by providing fuel channels

with faster flow rates inside the fuel electrode up to the contact with the electrolyte interface.

The R3 value of B-PNG is considerably lower than A-PNG, and both barely changed after the stability test. R3 presented variations in B-PG6 (from 0.08 to 0.09 $\Omega \cdot \text{cm}^2$) and in A-PG6, where an increase from 0.69 to 1.10 $\Omega \cdot \text{cm}^2$ was observed after the test. The R4 value is generally reduced after the stability experiments, where the elimination of the R5 value compensates for the apparent higher R4 value of B-PNG after 260 h. Some possible reasons for this positive change are the PNO phase oxygen stoichiometry, phase evolution, and the formation of defects that enhance oxygen exchange kinetics.

The variation of the DRT graph for B-PG6 upon changing the H₂ flow rate is shown in *fig. 5.21*. Here, peak R4 is affected by changing the H₂ flow rate on the fuel electrode side and the O₂ flow rate on the air electrode side. Additionally, increasing the total flow rates increases the characteristic frequency of peak R5 from 2 to 10 Hz. This behavior at low frequencies is attributed to gas conversion impedance, which according to several sources, gas conversion impedance and flow rates have an inverse relation [47,265,266]. As the operation in SOFC mode involves low p_{H₂O} (3 vol%), gas conversion can be the highest contributor to R_{pol} in most cases [47,266]. The experimental setup becomes an even more pivotal aspect, as, in an EIS setup with an unsuitable gas diffusion network, the gas conversion contribution (1-10 Hz) will dominate, especially at low pO₂. This makes sense in most tubular cell test setups because the air at the air electrode side is not pressurized compared to planar configurations [53].

When atmospheric air is changed to pure oxygen (using an H₂ flow of 50 SCCM as fuel), the low-frequency peak R5 reappears in *fig. 5.21* as a gas diffusion contribution in the air electrode. This result backs up the hypothesis that conversion and diffusion mechanisms in SOFC operation are coupled [47,266]. Also, judging by this result, the R4 peak is more affected by the gas conversion at the fuel electrode.

Some similarities in our studies with single cells were found with symmetrical cell studies in *chapter 3*. The most noticeable was that in thinner air electrodes, the thermal activation energy was generally high in R3 and R4. The initial performance of SOCs with more PNO content in the composites presented a higher DRT peak area than in PrO_x-GDC and PNO-GDC composites.

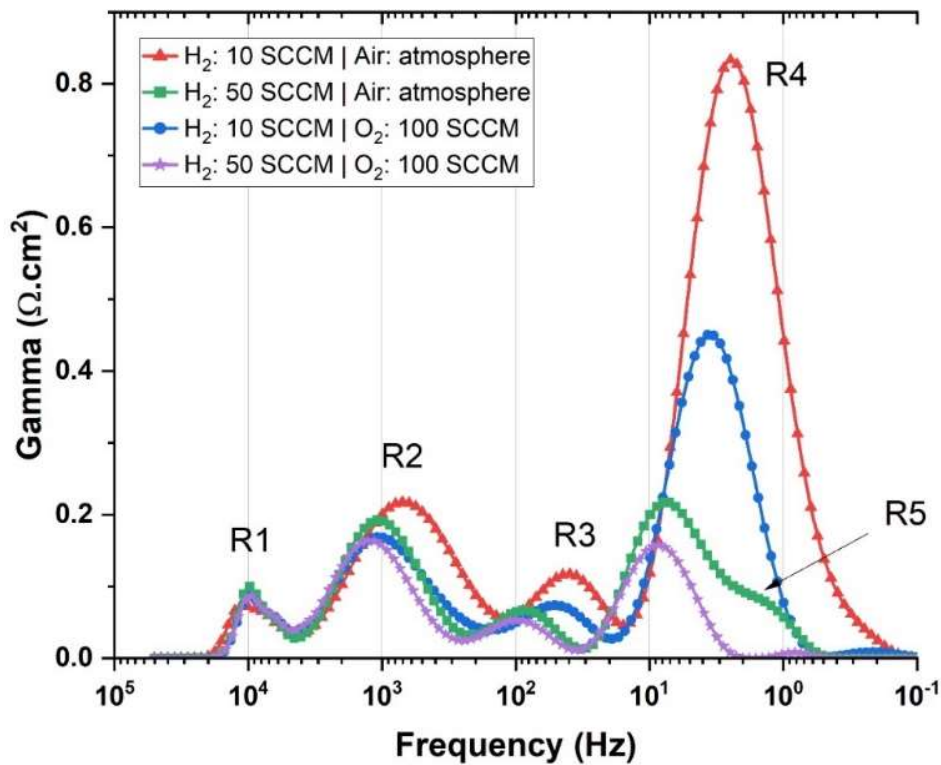


Figure 5.21. DRT graphs of B-PG6 at 650 °C with different air and fuel electrode gas compositions and varying flow rates [252].

Finally, the post-mortem XRD analysis (*fig. 5.22*) of both samples showed little evolution of the PNO phase, with the possible formation of a higher-order nickelate ($\text{Pr}_4\text{Ni}_3\text{O}_{10.5}$) due to a prolonged operation under air at high temperatures. This phase has one of the highest electronic conductivities among RP nickelates [267,268] and could be the reason for the increased initial performance of A-PNG and B-PNG. Even so, the intensity of $\text{Pr}_4\text{Ni}_3\text{O}_{10.5}$ is low and interferes with the base PNO peaks, so a definitive conclusion should be reached with caution. As referenced in our previous work [252], the same phase was detected by other researchers. In any case, these points must be considered:

- The rate of reaction for the $\text{Pr}_4\text{Ni}_3\text{O}_{10.5}$ phase is not expected to be high. However, the appearance of this phase could be attributed to the initial improvement of the air electrode, which for A and B cells took place during the initial period of the test (90 h). Further phase transformation might have been stopped.
- Cell B-PNG had microtubular geometry with an outer diameter of 3.1 mm. This can increase the background counts and, consequently, increase the noise in the XRD data of this sample. For this reason, a tentative peak designation is made in post-mortem XRD. In any case, we observed in cell A-PNG an increase in the PrO_x phase after the 90-hour test (*fig. 5.22a*), and according to Montenegro-

Hernández et al. [98], that could be a good indicator of the formation of a high-order nickelate as the former is a secondary product of the decomposition of PNO.

Most of the secondary phases formed from the composite precursor are good MIEC. This is a good underlying reason for the general low-frequency DRT peak decrease, particularly in peak R4. Nevertheless, no conclusive determinations can be made besides the increase in the intensity of the Pr_6O_{11} peak product of the partial PNO decomposition. It is also possible that part of this decomposition reacts with the ceria to form a mixed ceria oxide, but this hypothesis could not be demonstrated during this XRD analysis.

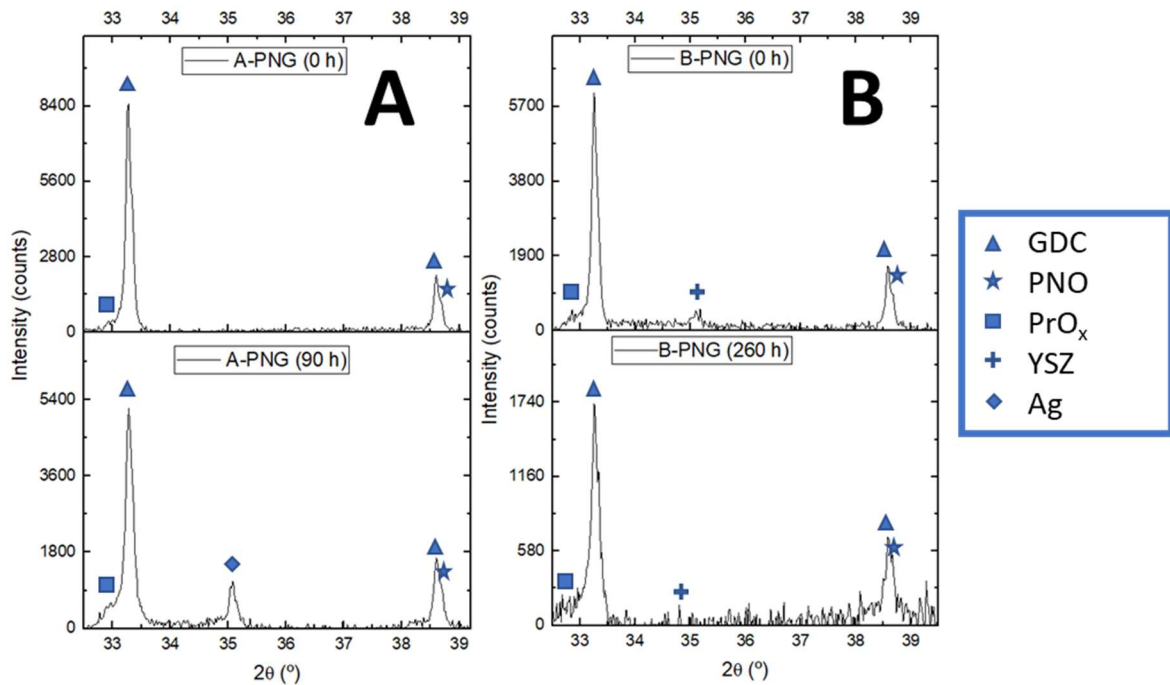


Figure 5.22. Post-mortem XRD patterns of a) A-PNG and b) B-PNG before and after the potentiostatic test at 650 °C, 0.7 V [252].

5.5. Electrolysis and reversible cell performance

Given the promising stability results in SOFC mode, the next step is to switch reactions and test the cells in SOEC mode. For this purpose, the electrochemical setup is changed so that sufficient steam is fed to the fuel electrode side. In the new setup, the difference is the inclusion of a thermostatic bath, and heating tape covers the inlet duct from the bath to avoid steam condensation.

For the SOEC and rSOC characterizations, A-PNG, A-PG6, and B-PG6 were selected. Both the fuel and the outlet pressure rate are 1.1 atm. The cells were reduced at 750 °C under a fuel composition of 97 vol% H₂ and 3 vol% H₂O for SOFC tests. The thermostatic bath is set at 79 and 83 °C to produce 45 and 50 vol% of steam, respectively. After switching compositions to operate in SOEC mode (1:1 volume ratio of H₂O: H₂) in B-PG6, the OCV registered was 0.96 and 0.94 V for 700 and 750 °C, respectively. Finally, rSOC tests alternating SOFC (0.765 V) and SOEC (1.165 V) modes are performed periodically to identify the cell's recovery capacity upon degradation.

The potentiostatic rSOC test result of B-PG6 is shown in *fig. 5.23a*. The switch between SOFC and SOEC was done every 10 h. After 100 hours of testing in rSOC, B-PG6 displayed an OCV = 0.83 V, owing to a much higher steam content at the end of the experiment. In A-PG6 (*fig. 5.23b*), the tubular slip-casted cells endure changes in steam composition equivalent to 45 vol.% of steam. The test was done by switching operating modes from SOFC to SOEC after 20 hours. Subsequently, in SOEC mode, the current density remained relatively stable for about 48 hours.

The degradation rate in SOEC for A-PG6 was 104 mA·kh⁻¹, lower than in B-PG6 (179 mA·kh⁻¹). The decrease in performance in rSOC is due to condensation produced at the inlet, as insufficient heating was initially provided in the experimental setup. Also, Ni migration could be an issue, as demonstrated in our previous rSOC tests (*section 4.4.3*). This behavior was more evident in the A-PNG cell, which was tested in rSOC for 52 hours using a fuel composition of 1:1 in H₂:H₂O. An OCV of 0.94 V at 750 °C was recorded. The performance of this cell showed constant degradation for 52 hours. A comparison of the rSOC performance is depicted in the I-V graph of *fig. 5.24*. The SOEC current density performance of A-PNG at 750 °C (at 1.3 V) is comparable to a cell using PNO/PNO-GDC composite, as reported by Laguna-Bercero *et al.* [101].

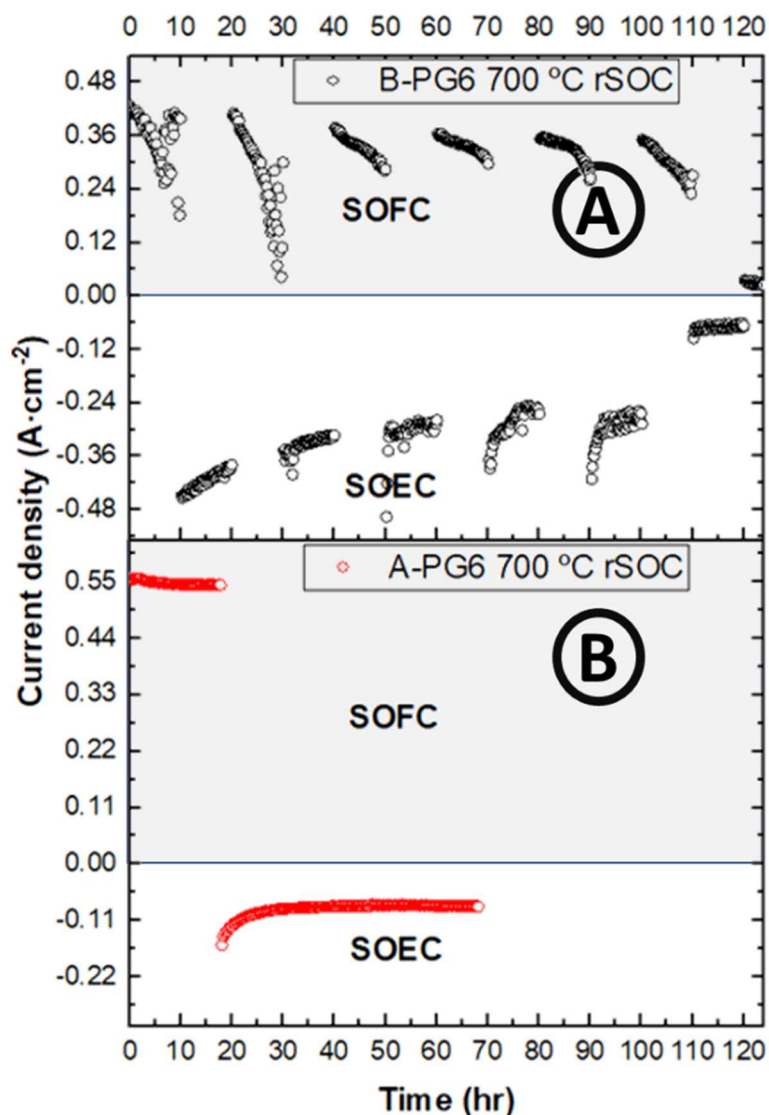


Figure 5.23. rSOC potentiostatic tests at 700 °C using a fuel composition of 50 vol.% H₂O/ 50 vol. % H₂, with 0.765 V in SOFC and 1.165 V in SOEC: a) B-PG6; b) A-PG6.

The best SOEC performance in this study was obtained for B-PG6 at 750 °C and 1.3 V, obtaining a current density of -0.86 A·cm⁻². Fig. 5.25c and d compare the DRT of the two cells with PrO_x-infiltrated GDC air electrodes at different steam content in fuel composition at the inlet. The R_{pol} of A-PG6 and B-PG6 were 1.10 and 0.17 $\Omega\cdot\text{cm}^2$, respectively. After 100 hours, B-PG6 R_{pol} increases to 0.70 $\Omega\cdot\text{cm}^2$, and the R_{pol} of processes associated with fuel and air electrodes and R3 are significantly decreased in B-PG6 (as displayed in the R_{pol} values of Table 5.6), especially in R3, where the value dropped from 0.68 $\Omega\cdot\text{cm}^2$ in A-PG6 to just 0.02 $\Omega\cdot\text{cm}^2$ in B-PG6. This difference explains the different rSOC performance between these two cells. Also, the appearance of an R5 peak is present at a different frequency range, suggesting gas conversion mechanisms. In B-PG6, this peak is barely noticeable.

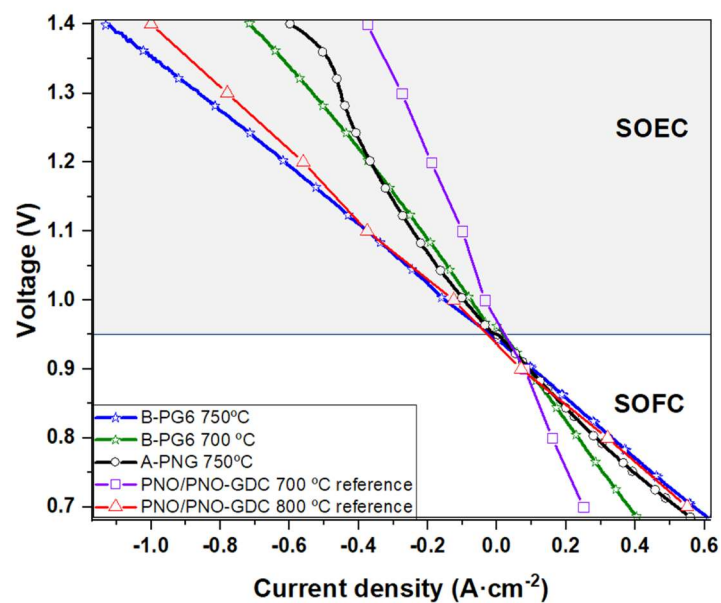


Figure 5.24. rSOC I-V curves using a fuel composition of 50 vol.% H₂O/ 50 vol. % H₂ of A-PG6 and B-PG6 at 700 and 750 °C and A-PNG at 750 °C. The PNO/PNO-GDC reference between 700 and 800 °C is obtained from [101].

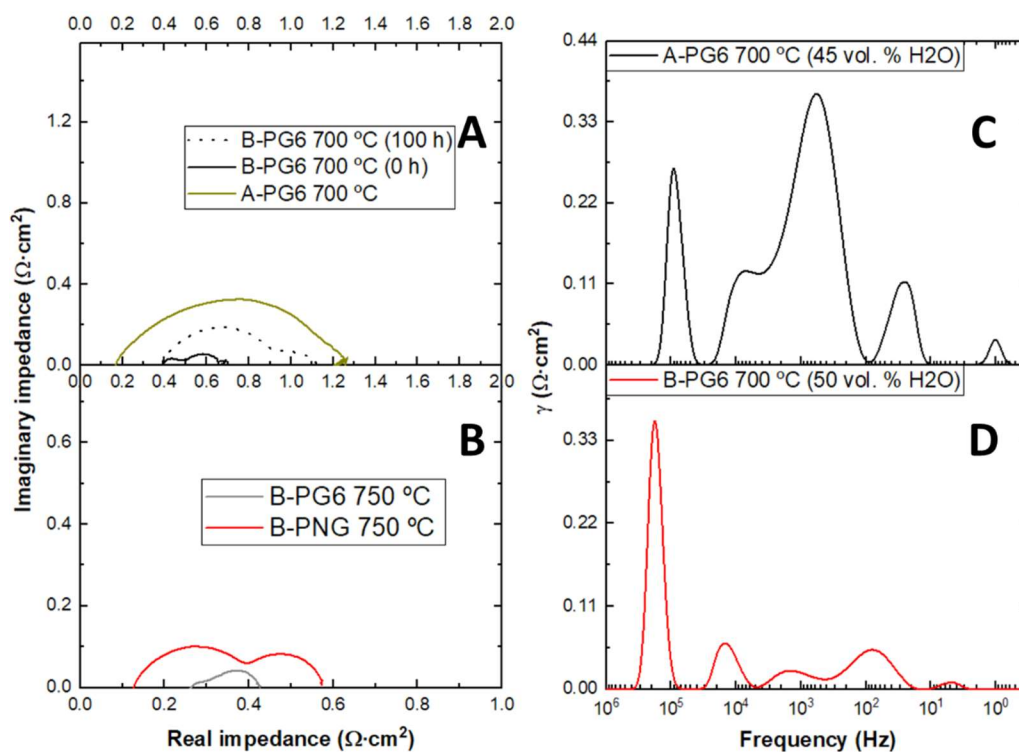


Figure 5.25. Nyquist plots in rSOC mode of A-PG6 and B-PG6 at 700 °C (a); Nyquist plots of B-PG6 and A-PNG at 750 °C (b); DRT peaks of A-PG6 at 700 °C using 45 vol % of H₂O (c); DRT peaks of B-PG6 at 700 °C using 50 vol % of H₂O (d).

Table 5.6. R_{pol} values of DRT area fittings from EIS data of A-PG6 and B-PG6 operated in rSOC mode at 700 °C.

Sample	R1 ($\Omega \cdot \text{cm}^2$)	R2 ($\Omega \cdot \text{cm}^2$)	R3 ($\Omega \cdot \text{cm}^2$)	R4 ($\Omega \cdot \text{cm}^2$)	R5 ($\Omega \cdot \text{cm}^2$)	R_{pol} ($\Omega \cdot \text{cm}^2$)
A-PG6	0.16	0.13	0.68	0.11	0.02	1.10
B-PG6	0.08	0.02	0.02	0.04	0.01	0.17

Finally, a DRT analysis from the EIS data of A-PNG is conducted to determine the cell mechanisms or components that most impact the degradation of the cell under SOEC mode. *Fig. 5.26* represents the DRT peaks of A-PNG at the start and after 28 and 52 hours of SOEC testing. After 28 hours, peaks R2 and R3 increase drastically, while at 52 hours of operation, R3 has the highest increase and R4 decreases. This effect is consistent with reports explaining that at high steam content, the gas conversion peak tends to disappear [47,266]. These results imply that at 28 hours, a degradation corresponds to both fuel and air electrodes, which is more evident at 52 hours, where peak R3 shifts and increases even more. Contrary to *section 4.4.3* results, no peak R5 evolution (< 1 Hz) was present during this experiment (using the PNO-infiltrated composite as air electrode), suggesting an improved gas diffusion over the chapter 4 cells (which used PNO-GDC/PNO layers) in SOEC mode. The air electrode microstructure has been improved, and the gas diffusion effect has also been minimized.

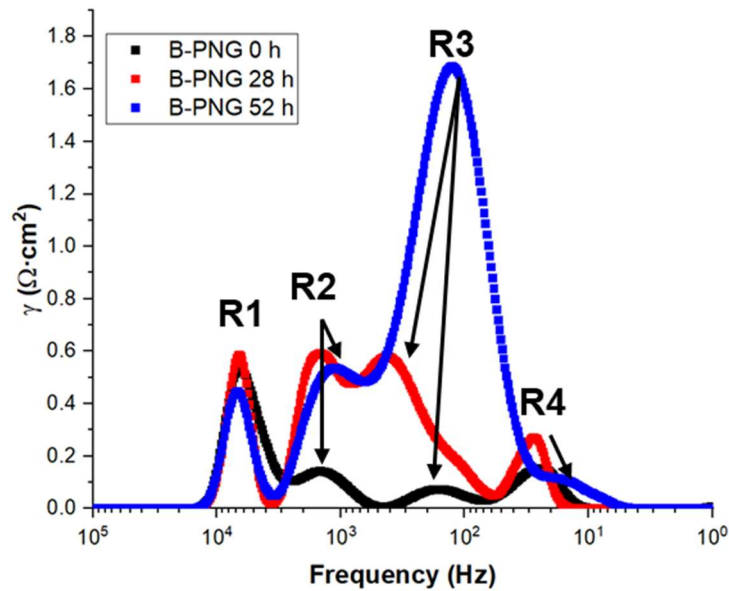


Figure 5.26. DRT peaks of A-PNG evolution on time under continuous SOEC operation at 750 °C.

SEM studies were performed in all the studied cells after SOC operation. In *fig. 5.27a*, the SEM micrograph shows the effect of the pore-former-induced pores in the microstructure, and also, in the fuel electrode/electrolyte interface, the Ni particles have agglomerated significantly. Consequently, most of the pores have been allocated to the inner part of the support (a $\sim 120\ \mu\text{m}$ zone), backing up some of these asseverations in the discussion of the electrochemical test. This is consistent with the results obtained for the SOEC characterizations in chapter 4 (*section 4.4.3*), where Ni mobility was an issue in the long term. As explained in that chapter, a possible mechanism occurring during operation is that NiOH^+ species, a product of the exposure to steam at the fuel electrode, move to high pH_2 zones and reduce forming Ni agglomeration in those zones.

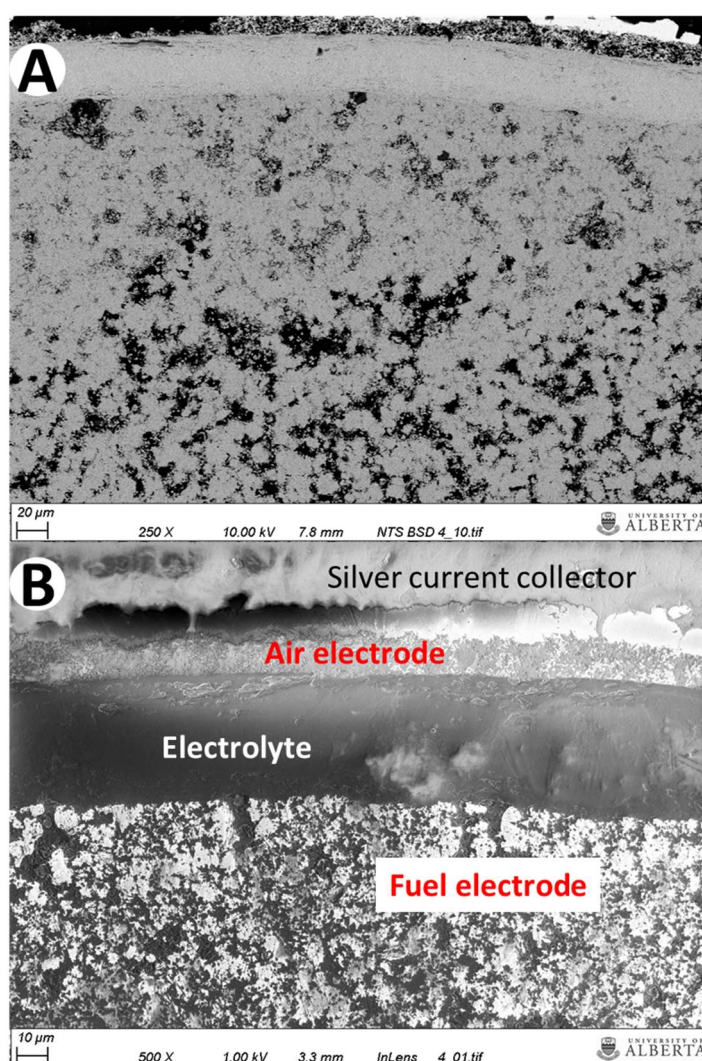


Figure 5.27. Post-mortem SEM micrographs of B-PG6 after rSOC operation at 750 °C: SOC layer distribution taken at 10 kV (a); Fractured sample of the fuel electrode/electrolyte interface taken at 1.0 kV (b).

Fig. 5.27b reveals no microstructural degradation/delamination of the air electrode with the YSZ electrolyte, which is also a result we observed in SOFC tests. In this regard, the reproducibility of the air electrodes fabricated during this chapter and microstructural stability was achieved.

5.6. Conclusions

During this chapter, technical aspects of SOC component fabrication mainly focused on the SOC performance of single cells using infiltrated nickelates, and praseodymium oxide nanoparticle-infiltrated air electrodes were satisfactorily identified and evaluated. Its application in the different SOC operating modes was also successfully demonstrated, where mid-term air electrode stability was achieved on GDC porous substrates.

The influence of fabrication parameters like scaffold thickness and infiltrate concentration was successfully characterized via electrochemical tests. A 7 M infiltrate concentration of PNO and PrO_x provided good SOC stability in a 30 wt. % solid loading cell with a 10-20 μm thickness of GDC porous substrate. This scaffold was selected because of its lower reactivity than YSZ scaffolds. The optimal temperature of phase formation of infiltrated catalysts in the scaffolds was determined before the electrochemical characterizations. The XRD analysis allowed us to identify a suitable sintering temperature for the air electrodes. For PNO infiltrates, the phase formation was optimized at 1000 $^{\circ}\text{C}$, while for PrO_x , the minimum sintering temperature is 600 $^{\circ}\text{C}$.

The performance of the air electrode composites was compared on two tubular SOFCs with different fuel electrodes and electrolyte microstructures, showing promising results between 650-750 $^{\circ}\text{C}$. The stability of PNO-infiltrated cells has been demonstrated during 90 h and 260 h of potentiostatic tests at 650 $^{\circ}\text{C}$ and 0.7 V in different fuel electrode supports of tubular geometry. The low-frequency gas diffusion polarization resistance (< 1Hz) was eliminated as time elapsed due to the optimized microstructure. The polarization resistance of the cells decreased during the first 90 hours of tests product of the improved oxygen reduction reaction and gas conversion rate according to DRT results and EIS fittings. Also, PrO_x nanoparticles infiltrated in GDC proved beneficial for medium-to-term stability. No apparent microstructural degradation was shown in post-mortem SEM micrographs, and no delamination occurred in the air electrode/electrolyte interface. Post-mortem XRD analysis of the air electrodes showed partial PNO phase evolution into a higher-order nickelate phase, $\text{Pr}_4\text{Ni}_3\text{O}_{10}$, which has a higher conductivity and thermal stability than PNO.

Reversible SOC operation was also demonstrated in the prepared cells. A SOEC current density of $-0.86 \text{ A}\cdot\text{cm}^{-2}$ was obtained for single cells using PrO_x/GDC air electrodes at 750°C and 1.3 V , with a polarization resistance as low as $0.17 \Omega\cdot\text{cm}^2$ in a microtubular extruded support. Test conditions proved crucial for controlling steam condensation to prevent the degradation of the cells during testing. Also, the performance of cells using PNO-GDC air electrodes under SOEC operation at 750 and 1.3 V is comparable with the one obtained for PNO/PNO-GDC configurations between 700 and 800°C . Like previous SOEC results, Ni agglomeration in the fuel electrode/electrolyte interface was observed as the product of the Ni mobility under a high steam content.

No significant discrepancy in the low-frequency impedances was observed in the behavior of different DRT peaks in two different tubular cells when parameters were changed (changing fuel or air composition, changing the air electrode thickness, or adding AFL). This result is uniquely interesting as it provides new insights for infiltrated air electrodes with Ni-YSZ fuel electrode supports and YSZ electrolytes.

Based on the results of this study, air electrodes fabricated by the infiltration of nanocatalysts of high Pr content (in either nickelate or PrO_x form) on GDC scaffolds are promising air electrodes for low-to-medium temperature SOC operation due to their high performance and stability. In any case, more extended tests in the cell configuration studied and improved SOEC setups remain to be performed to exceed the obtained results. In this regard, efforts for improved stability and steam conversion under SOEC are part of future work on this topic.

Conclusions

From the results presented in the previous chapters, the following main conclusions can be drawn:

- PNO-GDC composite materials were successfully characterized by XRD structural and STEM microstructural analysis, where the formation of a Pr- and Gd-doped ceria or CPGO was identified. Through EDS-STEM quantifications, the obtained compositions were $\text{Ce}_{0.30}\text{Pr}_{0.67}\text{Gd}_{0.03}\text{O}_{2.5}$, and $\text{Ce}_{0.75}\text{Pr}_{0.16}\text{Gd}_{0.09}\text{O}_{2.5}$ for PNO- and GDC-rich composites, respectively. These phases are the product of the interdiffusion of cations of the PNO decomposition products, Pr_6O_{11} , into the GDC lattice. These phases coexist in PNO-rich composites, while GDC-rich composites are almost entirely composed of CPGO. PNO-rich composites showed several secondary phases, of which PNO and a praseodymium oxide phase contributed to a higher electrical conductivity than GDC-rich composites. PNO and CPGO phases were characterized by STEM-EELS techniques where the particles presented oxidation states of mixed $\text{Pr}^{3+}/\text{Pr}^{4+}$ in PNO and Pr^{4+} and Ce^{4+} in CPGO.
- Compared to the literature, the air electrode materials exhibited fast oxygen kinetics, evidenced by their relatively high diffusion and surface exchange coefficients. The oxygen surface exchange coefficients, k_{ex} , obtained were 7.4×10^{-7} and $2.2 \times 10^{-6} \text{ cm} \cdot \text{s}^{-1}$ at 800°C and $p\text{O}_2=0.21 \text{ atm}$ for PNO- and GDC-rich composites, respectively. Similarly, the calculated oxygen diffusion coefficients, D_{chem} , were 5.5×10^{-8} and $7.6 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$ at 800°C $p\text{O}_2=0.21 \text{ atm}$ for PNO- and GDC-rich composites, respectively.
- The degradation of cell components was analyzed using EIS characterizations in symmetrical cells using PNO-GDC composites. The cells demonstrated low R_{pol} values in the temperature range of $700\text{--}850^\circ\text{C}$. The measured impedances were $0.13 \Omega \cdot \text{cm}^2$ in the PNO-rich electrode and $0.17 \Omega \cdot \text{cm}^2$ in the GDC-rich electrode, about 4 and 3 times less than the PNO electrode, respectively.
- The rSOC performance of cells using a Ni-YSZ fuel electrode support, a YSZ electrolyte, and a double air electrode layer of PNO-GDC/PNO was measured for over 150 hours, with no structural degradation of the dual air electrode layer after the tests. Ni agglomeration and redistribution of porosity away from the fuel electrode/electrolyte was the cause of the degradation.
- The thermal expansion coefficient of the PNO-GDC layer was calculated at $19.1 \times 10^{-6} \text{ K}^{-1}$, which is a higher value than. for both YSZ and GDC ($13 \times 10^{-6} \text{ K}^{-1}$)

between 700 and 800 °C. This value was reduced to $14.8 \times 10^{-6} \text{ K}^{-1}$ when operating between 500-700 °C. Maintaining this temperature range can help with long-term stability during operation.

- The PNO-GDC composite air electrodes' reaction zones were enhanced via nanoengineering of the air electrode microstructure using the infiltration of nanosized electrocatalysts, where stable MIEC air electrodes were fabricated and implemented in single cells.
- Phase analyses of the infiltrated composite electrodes were characterized by XRD, where the PrO_x and PNO nanocatalysts single-phase formation was identified at 600 and 1000 °C, respectively.
- PrO_x -GDC composite air electrodes performed favorably to PNO-GDC composites (R_{pol} of 1.79 vs. 2.45 $\Omega \cdot \text{cm}^2$ for A cells and 0.92 vs. 1.46 $\Omega \cdot \text{cm}^2$ for B cells using a fuel composition of 97 vol% H_2 / 3 vol% H_2O). Still, the latter cells showed better stability for 260 hours at 650 °C. This was attributed to the possible formation of a non-reversible high-order nickelate phase ($\text{Pr}_4\text{Ni}_3\text{O}_{10 \pm 6}$) product of the decomposition of the PNO phase. This phase influenced the performance and stability of the single cell over time, with an improvement of 31% for 90 h in two different cell designs at 650 °C.
- A higher Ni-YSZ fuel electrode porosity in Ni-YSZ extruded supports enhanced the rSOC performance, especially in SOEC using a fuel composition of 50 vol% H_2O , where a reduction of 0.13 to 0.02 $\Omega \cdot \text{cm}^2$ in charge transfer and 0.68 to 0.02 $\Omega \cdot \text{cm}^2$ in electrode transport contributions to total R_{pol} was observed. Low-frequency mechanisms affecting R_{pol} were heavily influenced by fuel and air electrode gas flow and pressure. The difference in performance between A- and B-cells in SOFC mode was mainly attributed to the air electrode difference in thickness, and in SOEC to a higher porosity in the fuel electrode and its compactness product of the extrusion process.

Conclusiones

De los resultados presentados en los capítulos anteriores, se pueden extraer las siguientes conclusiones principales:

- Los materiales compuestos PNO-GDC se caracterizaron con éxito mediante análisis estructural XRD y microestructural STEM, donde se identificó la formación de una ceria o CPGO dopada con Pr y Gd. A través de cuantificaciones de EDS-STEM, las composiciones obtenidas fueron $\text{Ce}_{0.30}\text{Pr}_{0.67}\text{Gd}_{0.03}\text{O}_{2-\delta}$, y $\text{Ce}_{0.75}\text{Pr}_{0.16}\text{Gd}_{0.09}\text{O}_{2-\delta}$ para compuestos ricos en PNO y GDC, respectivamente. Estas fases son el producto de la interdifusión de cationes de los productos de descomposición de PNO, Pr_6O_{11} , en la estructura GDC. Estas fases coexisten en compuestos ricos en PNO, mientras que los compuestos ricos en GDC están formados casi en su totalidad por CPGO. Los compuestos ricos en PNO mostraron varias fases secundarias, de las cuales el PNO y una fase de óxido de praseodimio contribuyeron a una conductividad eléctrica más alta que los compuestos ricos en GDC. Las fases de PNO y CPGO se caracterizaron mediante STEM-EELS, en donde las partículas presentaron estados de oxidación de $\text{Pr}^{3+}/\text{Pr}^{4+}$ en PNO y Pr^{4+} y Ce^{4+} en CPGO.
- En comparación con la literatura, los materiales de los electrodos de aire exhibieron una cinética de oxígeno rápida, evidenciada por sus coeficientes de intercambio de superficie y difusión relativamente altos. Los coeficientes de intercambio superficial de oxígeno, k_{ex} , obtenidos 7.4×10^{-7} y $2.2 \times 10^{-6} \text{ cm} \cdot \text{s}^{-1}$ a 800°C y $p\text{O}_2=0.21 \text{ atm}$ para compuestos ricos en PNO y GDC, respectivamente. De manera similar, los coeficientes de difusión de oxígeno calculados, D_{chem} , fueron 5.5×10^{-8} y $7.6 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$ a 800°C $p\text{O}_2=0.21 \text{ atm}$ para compuestos ricos en PNO y GDC, respectivamente.
- La degradación de los componentes de la celda se analizó mediante caracterizaciones EIS en celdas simétricas utilizando compuestos PNO-GDC. Las celdas demostraron valores bajos de R_{pol} en el rango de temperatura de $700\text{--}850^\circ\text{C}$. Las impedancias medidas fueron $0.13 \Omega \cdot \text{cm}^2$ en el electrodo rico en PNO y $0.17 \Omega \cdot \text{cm}^2$ en el electrodo rico en GDC, aproximadamente 4 y 3 veces menos que el electrodo PNO, respectivamente.
- El rendimiento de rSOC de las celdas que utilizan un soporte de electrodo de combustible Ni-YSZ, un electrolito YSZ y una capa de electrodo de aire doble de PNO-GDC/PNO se midió durante más de 150 horas, sin degradación estructural de la capa de electrodo de aire doble después de las pruebas. La causa de la

degradación fue la aglomeración de Ni y la redistribución de la porosidad lejos del electrodo de combustible/electrolito.

- El coeficiente de expansión térmica de la capa de PNO-GDC se calculó en $19.1 \times 10^{-6} \text{ K}^{-1}$, el cual es mayor al valor para YSZ y GDC entre 700 y 800 °C ($13.0 \times 10^{-6} \text{ K}^{-1}$). Este valor fue disminuido a $14.8 \times 10^{-6} \text{ K}^{-1}$ al operar entre 500-700 °C. Mantener este rango de temperatura puede ayudar con la estabilidad a largo plazo durante la operación.
- Las zonas de reacción de los electrodos de aire compuestos PNO-GDC se mejoraron mediante la nanoingeniería de la microestructura del electrodo de aire utilizando la infiltración de electrocatalizadores de tamaño nanométrico, donde se fabricaron e implementaron electrodos de aire MIEC estables en celdas individuales.
- Los análisis de fase de los electrodos compuestos infiltrados se caracterizaron por DRX, donde se identificó la formación monofásica de los nanocatalizadores PrO_x y PNO a 600 y 1000 °C, respectivamente.
- Los electrodos de aire compuestos PrO_x -GDC se desempeñaron favorablemente frente a PNO-GDC (R_{pol} de 1.79 frente a $2.45 \Omega \cdot \text{cm}^2$ para celdas tipo A y 0.92 frente a $1.46 \Omega \cdot \text{cm}^2$ para celdas tipo B usando una composición de combustible de 97 % vol H_2 / 3 vol % H_2O). Aun así, estas últimas celdas mostraron una mejor estabilidad durante 260 horas a 650 °C. Esto se atribuyó a la posible formación de una fase de niquelato de no reversible ($\text{Pr}_4\text{Ni}_3\text{O}_{10 \pm \delta}$) producto de la descomposición del PNO. Esta fase influyó en el rendimiento y la estabilidad de la celda individual a lo largo del tiempo, con una mejora del 31 % durante 90 h en dos diseños de celda diferentes a 650 °C.
- Una mayor porosidad del electrodo de combustible de Ni-YSZ en los soportes extruidos de Ni-YSZ mejoró el desempeño de rSOC, especialmente en SOEC que usa una composición de combustible de 50 % en volumen de H_2O , donde se produjo una reducción de 0.13 a $0.02 \Omega \cdot \text{cm}^2$ en la resistencia por transferencia de carga y de 0.68 a $0.02 \Omega \cdot \text{cm}^2$ en la resistencia asociada a fenómenos de transporte en los electrodos. Los mecanismos de baja frecuencia que afectan a R_{pol} estuvieron fuertemente influenciados por el flujo y la presión del gas del electrodo de aire y combustible. La diferencia de rendimiento entre las celdas A y B en modo SOFC se atribuyó principalmente a la diferencia de espesor del electrodo de aire, y en SOEC a una mayor porosidad en el electrodo de combustible y su compacidad obtenida en proceso de extrusión.

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Nomenclature

8YSZ 8 mol% Yttria-stabilized Zirconia	LSFC Lanthanum-Strontium Ferrite Cobaltite
ADF Annular Dark Field detector	LSFN Lanthanum-Strontium-Ferrium Nickelate
AFC Alkaline Fuel Cell	LSGM Lanthanum-Strontium-Gallium Manganite
ASR Area-specific Resistance	MCFC Molten Carbonate Fuel Cell
BF Bright Field detector	MFC Microbial Fuel Cell
BSE Back-scattered Electron	MIEC Mixed Ionic and Electronic Conductor
CCD Charge-coupled Device	NNO Neodymium Nickelate
CHP Combined Heat and Power	OCV Open Circuit Voltage
CPE Constant Phase Element	ORR Oxygen Reduction Reaction
CPGO Praseodymium- and Gadolinium-doped Ceria	PAFC Phosphoric Acid Fuel Cell
DMFC Direct Methanol Fuel Cell	PDC Praseodymium-doped Ceria
DRT Distribution of Relaxation Times	PEM Powder Extrusion Molding
ECR Electrical Conductivity Relaxation	PEMEC Protonic Exchange Membrane Electrolysis Cell
EDS Energy Dispersive Spectroscopy	PEMFC Proton Exchange Membrane Fuel Cell
EELS Electron Energy Loss Spectroscopy	PIE Pulsed Isotope Exchange
EIS Electrochemical Impedance Spectroscopy	PMMA Polymethyl Methacrylate
ELNES Energy Loss Near-edge Structure	PNO-P as-received Praseodymium Nickelate Powder
EMF Electromotive Force	PNO-S sintered Praseodymium Nickelate Powder
EXELFS Extended Energy Loss Fine Structure	PTFE Polytetrafluoroethylene
FWHM Full Width at Half Maximum	PVA Polyvinyl Alcohol
GDC Gadolinium-doped Ceria	PVB Polyvinyl Butyral
GFAAS Graphite Furnace Atomic Absorption Spectrometry	RP Ruddlesden-Popper structure
HAADF High-angle Annular Dark Field detector	rSOC Reversible Solid Oxide Cell
HOR Hydrogen Oxidation Reaction	SE Secondary Electrons
ICP-OES Inductively-coupled Plasma Optical Emission Spectroscopy	SEM Scanning Electron Microscopy
LNO Lanthanum Nickelate	SDC Scandia-doped Ceria
LSC Lanthanum-Strontium Cobaltite	

SIMS Secondary Ion Mass Spectroscopy
SOC Solid Oxide Cell
SOEC Solid Oxide Electrolysis Cell
SOFC Solid Oxide Fuel Cell
SSZ Scandia-stabilized Zirconia
STEM Scanning Transmission Electron
Microscopy (STEM)
TEC Thermal Expansion Coefficients
TPB Triple Phase Boundary
XANES X-ray Absorption Near-edge
Spectroscopy
XRD X-ray Powder Diffraction
YSZ Yttria-stabilized Zirconia
ZLP Zero-loss Peak

Symbols (units)

ΔG Gibbs free energy ($\text{kJ}\cdot\text{mol}^{-1}$)

ΔH enthalpy change ($\text{kJ}\cdot\text{mol}^{-1}$)

ΔpO_2 oxygen partial pressure changes (atm)

ΔS entropy change ($\text{kJ}\cdot\text{mol}^{-1}$)

σ_{el} electronic conductivity ($\text{S}\cdot\text{cm}^{-1}$)

σ_{ion} ionic conductivity ($\text{S}\cdot\text{cm}^{-1}$)

σ_n normalized electronic conductivity ($\text{S}\cdot\text{cm}^{-1}$)

σ_t time-dependent electronic conductivity ($\text{S}\cdot\text{cm}^{-1}$)

ω frequency (Hz)

C capacitance per unit area ($\text{F}\cdot\text{cm}^{-2}$)

D_{chem} oxygen chemical diffusion ($\text{cm}^2\cdot\text{s}^{-1}$)

E_a - activation energy ($\text{kJ}\cdot\text{mol}^{-1}$ or eV)

E_T - theoretical cell voltage (V)

E_{tn} thermoneutral potential (V)

F - Faraday's constant

k Gerischer rate constant parameter (s^{-1})

k_{AB} - Cliff-Lorimer sensibility parameters

k_{ex} oxygen surface reaction exchange ($\text{cm}\cdot\text{s}^{-1}$)

L inductance ($\text{H}\cdot\text{cm}^2$)

$\dot{m}_{H_2}$ - molar H₂ flow at fuel electrode inlet ($\text{mol}\cdot\text{s}^{-1}$)

p_{H_2} - hydrogen partial pressure (atm)

p_{O_2} - oxygen partial pressure (atm)

p_{H_2O} - steam partial pressure (atm)

n number of electrons exchanged in the reaction

R - ideal gas constant

R_{ohm} - ohmic resistance ($\Omega\cdot\text{cm}^2$)

R_{pol} internal polarization resistance ($\Omega\cdot\text{cm}^2$)

U_F - fuel utilization (vol.%)

Y_i admittance parameter ($\text{S}\cdot\text{s}^{1/2}$)

Published and Submitted Content

Published work:

M.A. Morales-Zapata, A. Larrea, M.A. Laguna-Bercero, Reversible operation performance of microtubular solid oxide cells with a nickelate-based oxygen electrode, *Int. J. Hydrogen Energy*. 45 (2020) 5535–5542. <https://doi.org/10.1016/j.ijhydene.2019.05.122>

M.A. Laguna-Bercero, A. Orera, M. Morales-Zapata, A. Larrea, Development of Advanced Nickelate-Based Oxygen Electrodes for Solid Oxide Cells, *ECS Trans.* 91 (2019) 2409–2416. <https://doi.org/10.1149/09101.2409ecst>

S. Vafaeenezhad, M.A. Morales-Zapata, A.R. Hanifi, M.A. Laguna-Bercero, Á. Larrea, P. Sarkar, T.H. Etsell. Stability of infiltrated cathodes using $\text{Pr}_2\text{NiO}_{4+\delta}$ precursor for low-temperature fuel cell applications, *Int. J. Hydrogen Energy*. 47 (82) (2022), 35081–35095. <https://doi.org/10.1016/j.ijhydene.2022.08.108>

Submitted work:

M.A. Morales-Zapata, A. Larrea, M.A. Laguna-Bercero, Review: Lanthanide nickelates for their application on Solid Oxide Cells, *Electrochim. Acta* (2023).

M.A. Morales-Zapata, A. Larrea, M.A. Laguna-Bercero, Structural and Electrochemical Studies of Praseodymium Nickelate and Doped Ceria Composites for Solid Oxide Cell Oxygen Electrodes, *J. Phys. Energy* (2023), Manuscript Number JPENERGY-100598

Conferences:

Oral presentation. 1st Physics Doctoral Conference, Faculty of Sciences, University of Zaragoza, Zaragoza, Spain, June 20th, 2019. Optimization of performance in microtubular solid oxide cells: developing air electrodes based on nickelates.

Oral presentation. 2nd HiTesea Meeting, University of Zaragoza, Zaragoza, Spain, June 25th, 2019. High-temperature microtubular electrolyzers with a nickelate-based oxygen electrode.

Oral presentation. 7th Symposium on Hydrogen Technologies and Fuel Cells, HYCELTEC, at the Faculty of Chemistry of the University of Barcelona, Barcelona, Spain, from July 1st to 3rd, 2019. Optimization of microtubular solid oxide cells by the development of nickelate air electrodes.

Poster presentation. 3rd HiTESEA Meeting, Campoblanco, Madrid, January 29th, 2020. Determination of Oxygen Chemical Diffusion and Surface Exchange Coefficients in mixed Cerium and Praseodymium oxides for SOC applications.

Oral presentation. LVII congress of the Spanish Society of Ceramics and Glass, Castellón, Spain, October 26th to 29th, 2020. Study of cerium oxide doped with praseodymium and gadolinium (CPGO) as an Oxygen Electrode in Solid Oxide Cells (SOC).

Oral presentation. XV Spanish National Meeting on Electroceramics, Vitoria-Gasteiz, Álava, Spain, July 7th to 9th, 2021. Pr and Gd-doped Ceria as Oxygen Electrode in Solid Oxide Cells (SOC).

Oral presentation. XVI Spanish National Congress of Materials, Ciudad Real, Spain, June 28th to July 1st, 2022. Study of the infiltration of nickelates and praseodymium oxide in porous substrates as oxygen electrodes in solid oxide cells (SOC).