Platinum substituted Cobalt(II, III) Oxide: Interplay of tetrahedral Co(II) sites towards electrochemical oxygen evolution activity

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Abstract

Substitution of ionic platinum is carried out in Co$_3$O$_4$ host synthesized by solution combustion strategy. These Pt substituted Co$_3$O$_4$ spinels characterized by XRD show pure crystalline phase of Co$_3$O$_4$ without any separated peaks related to Pt/PtO$_x$. Electrochemical OER activities of these spinels are investigated by cyclic voltammetry, linear sweep voltammetry and chronoamperometry in neutral, alkaline and neutral buffer electrolytes. LSV studies on 1% Pt substituted Co$_3$O$_4$ exhibit a low overpotential ($\eta$) of 455 mV at 20 mA cm$^{-2}$ in KOH, as compared to PBS medium. Tafel slope value of 117 mV dec$^{-1}$ in KOH represents one electron EC mechanism. The detailed XPS studies indicate that Pt doping increases the tetrahedral Co$^{2+}$ sites of Co$_3$O$_4$. XPS studies before and after the OER also infer that the mixed valence of Co in the host (Co$_3$O$_4$) undergoes redox (Co$^{2+}$/Co$^{3+}$) changes with simultaneous reduction in Pt dopant from Pt$^{4+}$ to Pt$^{2+}$ influencing the OER activity.
1. Introduction

Spinels give potential applications in broad technical fields such as in semiconductor [1], magnetism [2-5], oxidation [6-10] and catalysis [6, 11-14]. Large class of spinels exist and researchers have worked on Magnesium spinels [2], Zinc Ferrite spinel [4], Nickel based spinels [15], Cuprospinels [16], Iron-Manganese spinels [17] and so on. Particularly, Co$_3$O$_4$ and its substituted form has been found as an effective electroactive material due to its excellent catalytic activity and corrosion reliability for electrochemical oxygen evolution reaction (OER) in alkaline media [11, 13, 18-22]. Cobalt oxide exists in two distinct forms, Co$_3$O$_4$ and CoO. Co$_3$O$_4$ spinel material exists in cubic close packing array of oxide ions that contains Co(II) ions holding the tetrahedral 8a sites and Co(III) ions in octahedral 16d sites [10, 23]. Both of these oxides show p-type semiconducting behavior but Co$_3$O$_4$ gives greater conductivity than CoO [24].

Atomic substitution is referred as one of the significant techniques to gain the desired physicochemical properties [8]. Through the defect for bearance of the spinel structure, it is feasible to substitute a notable fragment of cobalt cations by other metal ion such as d-and f-block metals [25]. It is found that iron doping improves the activity as catalyst for selective oxidation reactions [8]. Doping of zinc improves the thermal stability of spinel’s core structure [26]. Platinum doping has showed positive results for oxidation and electrode modification for efficiency [9, 27]. In a latest research, computational modeling study of water splitting [6] has revealed the role of morphology based activity of cobalt oxide [28] for OER and ORR (oxygen reduction reaction) under varying pH conditions. However, controversial results still exist regarding its OER performance on size-controllable Co$_3$O$_4$ hexagonal platelets for determining active sites from two different tetrahedral and octahedral sites using density functional theory (DFT) studies and other characteristic techniques [29].
Different synthesis methods have been reported for synthesizing substituted cobalt oxides. He et al. has used the typical oriented aggregation method with binder as water for synthesizing Co₃O₄ nanocrystals [30]. Thermal decomposition method has also been adopted for copper substitution in CoOₓ [31]. A facile and surfactant-free synthesis of 3.5 – 70 nm size controlled Co₃O₄ nanoparticles has been synthesized by altering the ratio of ethanol to water and utilized for the degradation of phenol [12]. Ding et al. followed a two-step procedure for the preparation of Co₃O₄ nanofibers by employing electro-spinning on aluminum foil which is followed by calcination (500°C for 3 h) and employed as an enzyme-free sensor for glucose detection [32]. Beside these, usual methods of synthesis of spinel oxides are sol-gel [33], homogeneous precipitation [34], solvothermal synthesis [35, 36] and hydrothermal method [3, 37, 38]. Among all, solution-combustion method is used because of its unique reliability and easiness for synthesis of transition metals over spinel oxides [39].

In this paper, different percentages of platinum doping in cobalt oxide PtₓCo₃₋ₓO₄ (x = 0.0075 – 0.03) spinel is achieved using solution-combustion method [40, 41]. The aim of this article is (a) how this substitution affects the electrocatalytic OER activity (b) how the OER activity is correlated with the surface chemistry of Co and Pt and (c) plausible mechanism based upon the XPS investigations.

2. Materials and methods

2.1. Materials

Cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O), 98.05 % pure, from Merck Sp. Pvt. Ltd, Mumbai, India. Hexachloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O), 99.00 % pure, Pt content 38-40 % from Sisco Res. Lab, Mumbai, India. Urea (CO(NH₂)₂) 99 % pure Merck Life Sci. Pvt. Ltd. Mumbai, India. All chemicals used for this study were of analytical grade and used without
further purification. All the solutions and electrolytes were prepared using double distilled Millipore water.

2.2. Synthesis

Solution combustion method is one of the efficient and reliable methods for synthesizing the doped metal oxides and pure metal oxides [40, 42, 43]. In this work, Pt-substituted (0.25%, 0.5% and 1%) Co₃O₄ spinels were prepared. Co₃₋ₓPtₓO₄ (x = 0.0075 – 0.03) by dissolving 5.0 g of cobalt nitrate mixed with varying amounts of hexachloroplatinic acid (8.918, 17.9, 35.8 mg) and varied amounts of urea (0.680 – 0.687 g) in a minimal amount of distilled water in a borosilicate glass dish. For Co₃O₄ preparation, 2.0 g of cobalt nitrate is mixed with 0.688 g of urea. The clear solution containing dish is kept in a muffle furnace at 450°C. After 30 minutes, the obtained powder is collected in a silica crucible and kept for calcination at 600°C overnight (approximately 10 h). After calcination a black color powder is obtained and is used for various analyses. Scheme 1 represents the synthesis procedure for the Pt-substituted-Co₃O₄ and undoped pure Co₃O₄ catalysts. The synthesized materials were characterized by using the powder X-ray diffraction (XRD, BRUKER D8 DISCOVER diffractometer in the range of 20-80°), scanning electron microscopy (FESEM, Jeol, Japan), high-resolution transmission electron microscopy with electron energy disperse spectroscopy (HR-TEM: JSM - 2100, Jeol, Japan) and X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD spectroscope (Kratos) with a monochromatic Al Kα radiation (1486.6 eV, line width 0.8eV)).

2.3. Electrochemical Studies

Electrochemical studies were carried out using conventional three-electrode system using an AUTOLAB PGSTAT204 electrochemical workstation at room temperature. The electrolyte solutions were prepared by using double-distilled water. The working electrode was made using
catalyst ink which is a mixture of 100 mg of the catalyst with 100 mg of 5% Nafion solution which acts as a binder for ink. Then 650μL of isopropanol was added to make a thin ink, which was then sonicated for 20 min and then deposited on the glassy carbon (GC) electrode. The geometric area of the working electrode was 0.071cm². Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were carried out using catalyst coated GCE as working electrode, Ag/AgCl (sat. KCl) as reference electrode and platinum wire as counter electrode. Over potentials (η) were calculated by using the equation: \( \eta = E (\text{RHE}) - 1.23 \text{ V} \) where \( E (\text{RHE}) = E (\text{Ag/AgCl}) + (0.196 + 0.059 \times \text{pH}) \).

The electrolytes used in the experiment were, 0.5 M potassium hydroxide solution (KOH; pH=13.6), 0.5 M phosphate buffer (PBS; pH=7) and 0.5 M potassium sulphate solution (K₂SO₄; pH=7). Chronoamperometry study was carried out for 1000 seconds at 1.4 V in K₂SO₄ and PBS medium and at 0.7V in KOH medium. CV (25 scans) and LSV measurements were carried out at fixed scan rates of 40 mV s⁻¹ and 20 mV s⁻¹ under room temperature. The double layer capacitance is of the order of 13 μF cm⁻² for both Co₃O₄ and 1% Pt substituted Co₃O₄ confirming the comparable electroactive surface areas.

3. Results and discussions

The prepared Pt substituted Co₃O₄ (Co₃-xPtₓO₄ (x = 0.0075 – 0.03)) and pure Co₃O₄ catalysts were characterized by XRD (Figure 1a). XRD patterns of Pt-substituted-Co₃O₄ (Co₃-xPtₓO₄ (x = 0.0075 – 0.03)) catalysts showed sharp XRD peaks as seen in the parental Co₃O₄ spinel oxide [40, 41]. No secondary phase or peak related to Pt/PtOₓ is observed however, complete substitution cannot be ascertained if some segregated phase forms on the surface. Materials appeared to be crystalline and depict large crystallite size. The morphological and microscopy analysis of 1% Pt-substituted-Co₃O₄ was characterized by SEM (Figure 1b&c) and HRTEM (Figure 1d-h). As seen in SEM images, 1% doping concentration of Pt showed well-defined
particles with hexagonal geometry with very large agglomerates of 1% Pt-substituted-Co$_3$O$_4$ (Figure 1b&c). Morphology is similar to unsubstituted Co$_3$O$_4$ [40]. Likewise, HRTEM images of 1% Pt-substituted-Co$_3$O$_4$ sample showed hexagonal morphology can be seen (Figure 1d) and the particle shape and boundaries are clearly noticeable with pure Co site and Pt-substituted-Co$_3$O$_4$ (Figure 1e). Size of the particles remain in the range of 60–120 nm and the lattice d-spacing of Pt and Co is ~0.22 and ~0.46 nm, corresponding to Pt(1 1 1) and Co(1 1 1) [44, 45]. Segregation of Pt in Pt substituted Co$_3$O$_4$ explains that complete substitution of Pt in Co$_3$O$_4$ could not be achieved. EDS studies confirms the existence of low concentration of Pt (0.3%) in the 1% Pt-substituted-Co$_3$O$_4$ sample (Figure 1h) which means that either there is heterogeneity or irregular distribution of Pt in the Co$_3$O$_4$ particles.

Similarly, high resolution XPS spectra of the Co 2p and Pt 4f elements of 1% Pt substituted Co$_3$O$_4$ catalyst showed the existence of ionic Pt$^{4+}$ over host Co$_3$O$_4$ with Co$^{2+}$ and Co$^{3+}$ species (Figure 7). The detailed discussion of XPS analysis is available in later section. From the detailed characterizations of the Pt-substituted-Co$_3$O$_4$, as seen in Scheme 1, one can conclude that ionic Pt (i.e., Pt$^{4+}$) is possibly substituted into the Co$^{2+}$ (tetrahedral) and Co$^{3+}$ (octahedral) sites of host Co$_3$O$_4$. This fact can be confirmed as the substitution of Pt$^{4+}$ enhances the Co$^{2+}$ satellite peak at 786.0 eV to maintain the charge balance (Figure 7a, compare lower and middle spectrum).

Cyclic voltammograms (CVs) of Co$_3$O$_4$ and Pt substituted Co$_3$O$_4$ (Co$_{3-x}$Pt$_x$O$_4$) in 0.5M KOH in the potential range of 0.0 to 1.0 V is shown in Figure 2(a-d). Undoped Co$_3$O$_4$ shows OER with a current density of 100 mA cm$^{-2}$ (Figure 2d) at 1.0 volts in the first cycle. Noticeable redox features are seen in the CV at 0.43 and 0.49 volts belonging to Co$^{2+}$/Co$^{3+}$ redox reaction [40, 41]. OER occurs with an onset potential of 0.6 V. CV of 0.25% Pt-substituted Co$_3$O$_4$ also shows cobalt redox peaks at 0.5 V and 0.42 V but the current density is suppressed compared to undoped Co$_3$O$_4$.
(Figure 2a). This justifies that Pt substitution is possibly on the cobalt site. Apart from this, OER starts occurring with an onset potential of 0.6 V and reaches a maximum current density of 52.7 mA cm$^{-2}$ at 1.0 V. This current is almost half of the Co$_3$O$_4$ (Figure 2d) thus Pt substitution decreases the activity in this electrolyte. It is possible that Pt substitution is enhancing the non-reactive tetrahedral sites of Co$^{2+}$ in Co$_3$O$_4$ to maintain the charge neutrality in the substituted compound [29]. In case of 0.5% Pt and 1% Pt substitution, the cobalt redox peaks further suppress and the observed maximum current densities at 1.0 V are 72.3 mA cm$^{-2}$ and 85.3 mA cm$^{-2}$ (Figure 2b,c). Clearly, the current density is lower compared to Co$_3$O$_4$ in spite of increase in the Pt concentration. This confirms that the substituted compound indeed has lesser number of active sites than Co$_3$O$_4$. Increasing trend in the current density among Pt substituted compound is probably due the Pt effect alone.

Likewise, CV of all synthesized catalysts in 0.5M K$_2$SO$_4$ at three different positive potential ranges (from 0 to 1.2 V, 1.4 V, and 1.6 V) was carried out. Since there is no OER activity in the potential range from 0 to 1.2 V, this range was increased up to 1.6 V to accelerate the catalytic responses as shown in Figure 3(a–d). As seen in the CV, peak appearing between 1.2 ~ 1.6 V is belonging to Co$^{2+}$/Co$^{3+}$ redox reaction, as in KOH medium. In case of Co$_3$O$_4$, OER current density is 14.6 mA cm$^{-2}$ at 1.6 V at first cycle. CV appears featureless and no redox features are noticed in this electrolyte medium. Figure 3a shows the CV of 0.25% Pt substituted Co$_3$O$_4$. The current density at 1.6 V is 22.3 mA cm$^{-2}$ at first cycle which is higher than Co$_3$O$_4$ alone. With 0.5% Pt and 1% Pt substituted Co$_3$O$_4$ catalysts, CV appear similar with decrement in current densities. At 1.6 V, the noticed current densities are 20.3 mA cm$^{-2}$ and 17.4 mA cm$^{-2}$ for 0.5 and 1% Pt substituted Co$_3$O$_4$ (Figure 3b,c). Thus, lower doping of Pt in Co$_3$O$_4$ favors OER in 0.5 M K$_2$SO$_4$ neutral
medium and activity decreases with further increases in doping concentration. This again proves that probably ionic Pt is populating the non-reactive tetrahedral site.

Although both basic and neutral electrolyte medium indicates that Pt doping is not significantly increasing the OER activity, one cannot deny the effect of local pH change near the electrode. The justification of catalytic behavior can be verified by using a neutral buffer medium for OER activity as the buffer solution will take care of the local pH effects near the electrode. Thus, the activity will truly reflect the materials property.

CV experiments in 0.5M phosphate buffer (PBS) at three different positive potential ranges (from 0.0 V to 1.2 V, 1.4 V and 1.6 V) are shown in Figure 4(a–d). Undoped Co₃O₄ (Figure 4d) gives 52.6 mA cm⁻² at 1.6 V. For 0.25% Pt-substituted catalyst (Figure 4a) the onset potential for OER is found be around 1.1 V (1.7 V vs. RHE) giving 480 mV of over potential. Beyond this range OER activity starts, the current density at 1.2 V is 6.1 mA cm⁻², at 1.4 V is 28.3 mA cm⁻² and at 1.6 V is 51.8 mA cm⁻². The observed current density in 0.5 M PBS at 1.6 V is similar to undoped Co₃O₄ confirming negligible effect of Pt substituent. Likewise, CV looks similar and OER current densities at 1.6 V on 0.5% Pt, 1% Pt substituted and undoped catalyst Co₃O₄ are 52.9 mA cm⁻², 50.4 mA cm⁻² and 52.6 mA cm⁻² respectively (Figure 4b-d). Clearly, no catalytic effect is noticed after Pt substitution and with increase in the Pt concentration. Thus, the local pH effects probably cause the enhancement in current in the case of KOH and K₂SO₄ and the Pt is mostly inactive.

Usually, steady state responses are more accurate to explain the materials activity compared to potentio-dynamic responses such as CV. Therefore, chronoamperometry studies of OER in 0.5M KOH, 0.5 M K₂SO₄ and 0.5M PBS electrolyte for Pt substituted (0.25%, 0.5% and 1%) and undoped Co₃O₄ catalysts are studies and shown in Figure 5. In order to attain the steady
state current response, the potential is fixed at 0.7 V for KOH (Figure 5a), 1.4 V for K₂SO₄ and PBS medium (Figure 5b, c) for 1000 seconds. Below this potential, the OER activity was insignificant and at higher potentials, noise appears in the measurement. Corresponding steady state current densities (after 1000 s) as a function of Pt doping concentration are shown in Figure 5d. Clearly, Pt doping only marginally change the current density compared to Co₃O₄ alone confirming the inactivity of Pt in Co₃O₄.

In order to further ascertain the true activity trend, LSV experiments and Tafel slope measurements of 1% Pt-substituted-Co₃O₄ have been performed in KOH, PBS and K₂SO₄ mediums (Figure 6). From the comparative LSV, the electrochemical activity of 1% Pt-substituted-Co₃O₄ for OER in KOH medium is highest as compared to K₂SO₄ and PBS medium. The observed overpotential (η) on 1% Pt-substituted-Co₃O₄ in KOH at operationally relevant current density of 20 mA cm⁻² is 455 mV (Figure 6a) which is lower than that in PBS (η=795 mV). The overpotential value is comparable to reported cobalt oxide based materials [46, 47]. The Tafel slope values obtained for 1% Pt-substituted-Co₃O₄ electrode in KOH, PBS and K₂SO₄ are 117 mV dec⁻¹, 153 mV dec⁻¹, 219 mV dec⁻¹, respectively (Figure 6b). Tafel slope value with 120 mV dec⁻¹ is defined for one electron transfer EC mechanism and is probably in the present case. Likewise, the observed overpotential on pure Co₃O₄ at 20 mA cm⁻² is 467 mV in KOH and 804 mV in PBS (Figure 6c). It is undetermined for K₂SO₄. Respective Tafel slopes on Co₃O₄ electrode in KOH, PBS and K₂SO₄ are 141 mV dec⁻¹, 158 mV dec⁻¹, and 295 mV dec⁻¹ (Figure 6d). Both Co₃O₄ and 1% Pt substituted Co₃O₄ show comparable Tafel slope confirming the similarity in the OER mechanism. Further confirmation regarding the rates of OER reaction in 1% Pt substituted Co₃O₄ and Co₃O₄ is evident from the exchange current density (iₒ) calculated from the Tafel plots [48, 49]. Calculated iₒ values on 1% Pt-substituted-Co₃O₄ are 0.63 mA cm⁻², 3.16μA cm⁻², 1.26 μA cm⁻² and on pure Co₃O₄ are
0.39 mA cm\(^{-2}\), 2.51 μA cm\(^{-2}\), 7.9 μA cm\(^{-2}\) for KOH, PBS and K\(_2\)SO\(_4\) electrolytes, respectively. No specific trend is observed in the exchange current density. In KOH Pt substitution is enhancing the activity while in other solvent is decreases. If we consider PBS free from any pH change effects, Co\(_3\)O\(_4\) is more active than 1% Pt-substituted-Co\(_3\)O\(_4\). This verifies the fact that Pt substitution is increasing the non-reactive tetrahedral Co\(^{2+}\) sites.

4. Evolution of Pt substituted Co\(_3\)O\(_4\) surface chemistry

In order to understand the evolution of surface chemistry of Pt substituted Co\(_3\)O\(_4\) catalyst under OER in 0.5 M KOH condition, pre- and post-OER XPS analysis is analyzed for this study. Our aim is to study the doping effect and mechanism by XPS. XPS is done after chronoamperometry study where scan rate is not relevant. High resolution XPS spectra of the Co 2p and Pt 4f elements of 1% Pt substituted Co\(_3\)O\(_4\), before and after the electrochemical measurements and Co 2p of pure Co\(_3\)O\(_4\) catalysts are shown in Figure 7. Co 2p doublets (Co 2p\(^{3/2}\) and Co2p\(^{1/2}\)) along with two shakeup satellites are depicted for Co\(_3\)O\(_4\), pre and post OER analysis of Pt substituted Co\(_3\)O\(_4\) (Figure 7a). Satellite peak at around 786.0 eV belongs to the presence of Co\(^{2+}\) in the sample [41, 50]. After Pt doping, Co 2p\(^{3/2}\), shows two prominent peaks at 779.1 eV and 780.6 eV with enhanced shakeup satellite around 786.1 eV. This indicates the mixed oxidation states of cobalt and change in the composition of both the states after doping or substitution [41, 50]. Noticeably, the satellite peak at about 786.1 eV become intense after Pt substitution confirming the enhancement of Co\(^{2+}\) in the system. This happens to maintain the charge balance after Pt\(^{4+}\) insertion in the lattice. Tetrahedral Co\(^{2+}\) is known to be inactive for catalytic reaction, therefore, Pt substitution did not show significant enhancement in the OER activity. XPS spectrum post-OER of Pt-substituted Co\(_3\)O\(_4\) looks similar to Co\(_3\)O\(_4\) with suppressed satellite at 786.0 eV.
This may indicate that Pt is possibly coming out of the Co$_3$O$_4$ matrix. Thus, Pt substituted Co$_3$O$_4$ is unstable under positive applied potential.

In case of Pt (dopant) before OER, the Pt 4f core level XPS spectra showed two doublets of Pt 4f$_{7/2}$ and Pt 4f$_{5/2}$ peaks at 74.4 and 77.8 eV (Figure 7b). The deconvolution of Pt 4f$_{7/2}$ suggests that the dopant Pt majorly exist in +4 oxidation state [51, 52]. Evidently, the formation of more Co$^{2+}$ after Pt$^{4+}$ substitution is to maintain the charge neutrality because higher valent Pt is replacing lower valent Co. XPS of Pt 4f post-OER is quite noisy and fitting is a challenge. With the best of our ability we tried to deconvoluted and the deconvoluted Pt4f$_{7/2}$ spectrum shows the formation of more Pt$^{2+}$ at 72.4 eV and 75.7 eV [51]. This appears strange as Pt is expected to remain oxidized under positive applied potential [53]. The fact that Co$^{2+}$ in the Pt substituted sample, again converts to Co$^{3+}$ after OER (Figure 7a) probably causing the Pt$^{4+}$ to get reduced and hence it comes out to the surface of Co$_3$O$_4$. During OER activity, the formation of +2 oxidation state of Pt infers the adsorption of hydroxyl group (Pt$^{2+}$(OH)$_{ads}$) over Pt surface [51]. Considering mixed valence states of Co and Pt ions of spinel Pt substituted Co$_3$O$_4$ oxide, OER mechanism can be explained as follows:

$$\text{Co}_{2-2y}^{3+}\text{Co}_{1+y}^{2+}\text{Pt}_y^{4+}O_4^- + 2(OH)^- \rightarrow \text{Co}_{2-2y+6}^{3+}\text{Co}_{1-y-6}^{2+}\text{Pt}_{y'}^{4+}\text{Pt}_{y''}^{2+}O_4^- + O_2 \uparrow + 2H^+ + 2\bar{e} \quad \ldots \quad (1)$$

The overall electrochemical activity of spinel Pt-substituted Co$_3$O$_4$ oxide can be explained by considering that mixed valence Co undergoes redox changes between Co$^{2+}$ and Co$^{3+}$ in agreement with the XPS spectra of Co 2p$_{3/2}$. Formation of Pt$^{2+}$ from Pt$^{4+}$ oxidation state (Figure 7b) is due to the formation of Co$^{3+}$ from Co$^{2+}$ causing some Pt$^{4+}$ to get reduced. At this stage Pt$^{2+}$ comes out of the Co$_3$O$_4$. From this, we can conclude that the interplay of octahedral sites (Co$^{3+}$) and tetrahedral (Co$^{2+}$) along with ionic Pt affects the OER activity. Schematic representation for the surface evolution of the Pt-substituted Co$_3$O$_4$ before and after electrochemical treatment.
(Scheme 1) and the substitution of ionic Pt (i.e., Pt$^{4+}$) into the tetrahedral (Co$^{2+}$) and octahedral (Co$^{3+}$) sites of host Co$_3$O$_4$ which assured the formation of more tetrahedral Co$^{2+}$ sites, Pt substituted Co$_3$O$_4$ is only marginally superior to unsubstituted Co$_3$O$_4$.

5. Conclusion

Highly crystalline, platinum substituted cobalt oxide (Co$_{3-x}$Pt$_x$O$_4$ ($x = 0.0075 – 0.03$)) spinel oxides has been synthesized by solution combustion method. Electrochemical OER is performed using these spinel oxides in KOH, K$_2$SO$_4$, and phosphate buffer medium. CV and chronoamperometric studies have indicated that only marginal or no improvement is noticed in the Pt substituted compound compared to Co$_3$O$_4$. This is attributed to the formation of more tetrahedral Co$^{2+}$ after Pt$^{4+}$ substitution. XPS studies confirmed this phenomenon. LSV experiments infer that the OER overpotential of 1% Pt-substituted-Co$_3$O$_4$ and pure Co$_3$O$_4$ at the current density of 20 mA cm$^{-2}$ in KOH medium are 455 mV and 467 mV as compared to PBS ($\eta=795$ mV for 1% Pt-substituted Co$_3$O$_4$ and $\eta=804$ mV pure Co$_3$O$_4$). Tafel slope indicates one electron transfer EC mechanism in KOH and PBS. Exchange current density ($i_0$) values on 1% Pt-substituted Co$_3$O$_4$ are 0.63 mA cm$^{-2}$ (KOH), 3.16 $\mu$A cm$^{-2}$ (PBS) and 1.26 $\mu$A cm$^{-2}$ (K$_2$SO$_4$). No set trend in the activity is observed in the Pt substituted Co$_3$O$_4$ in comparison to Co$_3$O$_4$. Activity after Pt substitution decreases in regards to the exchange current density. This demonstrates that Pt substitution increases the tetrahedral Co$^{2+}$ sites which do not impart any activity to the substituted compound. Detailed XPS studies indicate that during OER, mixed valence of Co in the host (Co$_3$O$_4$) undergoes redox changes involving Co$^{2+}$ and Co$^{3+}$ influencing the Pt$^{4+}$reduction to Pt$^{2+}$ species. If one can find a suitable dopant which populates the active octahedral sites of Co$_3$O$_4$, activity improvement is expected. For example, Ni substituted Co$_3$O$_4$ has been shown to improve the OER activity of parent Co$_3$O$_4$. 
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Author contributions

A.S. envisaged the idea and S.N. executed the experiments and wrote the manuscript. N.J. synthesized and characterized the materials. S.I. carried out XPS measurements. All the authors contributed to the data analysis and writing and gave approval for the final submission.

Notes

The authors declare no competing financial interest.

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Scheme 1: Schematic representation of combustion synthesized Pt substituted Co₃O₄ and possible mechanism for the evolution of surface chemistry towards OER activity.
Figure 1

Figure 1: XRD patterns of combustion synthesized Pt substituted Co$_3$O$_4$ and pure Co$_3$O$_4$ catalysts (a). Microscope observation of the 1% Pt substituted Co$_3$O$_4$ catalyst: Low and high magnification SEM images of 1% Pt substituted Co$_3$O$_4$ (b & c), HRTEM images of 1% Pt substituted Co$_3$O$_4$ and EDS spectrum with an inset of weight percentage of Co, O, Pt atoms (d-h).
Figure 2: CV of Pt substituted Co$_3$O$_4$ catalyst for different doping percentage of Pt (a) 0.25%, (b) 0.5%, (c) 1%, and undoped Co$_3$O$_4$ (d) and at 40 mV s$^{-1}$ of scan rate in 0.5M KOH electrolyte.
Figure 3: CV of Pt substituted Co₃O₄ catalyst for different doping percentage of Pt (a) 0.25%, (b) 0.5%, (c) 1%, and undoped Co₃O₄ (d) and at 40 mV s⁻¹ of scan rate in 0.5 M K₂SO₄ neutral electrolyte.
Figure 4: CV of Pt substituted Co$_3$O$_4$ catalyst for different doping percentage of Pt (a) 0.25%, (b) 0.5%, (c) 1%, and undoped Co$_3$O$_4$ (d) and at 40 mV s$^{-1}$ of scan rate in 0.5 M PBS neutral electrolyte.
Figure 5: Chronoamperometric responses of Co$_3$O$_4$ and Pt substituted Co$_3$O$_4$ catalysts (a) at 0.7 V in 0.5M KOH and at 1.4 V in 0.5 M K$_2$SO$_4$ (b) and at 1.4 V in 0.5M PBS (c) electrolytes along with their corresponding current density after 1000 seconds with respect to Pt doping concentration (d).
Figure 6: LSV responses of 1%Pt-substituted-Co$_3$O$_4$ (a) and undoped pure Co$_3$O$_4$ (c) at 20 mV s$^{-1}$ of scan rate in 0.5M KOH, 0.5 M K$_2$SO$_4$ and 0.5M PBS electrolyte along with their respective Tafel plot (b and d).
Figure 7: High resolution XPS spectra of Co 2p (a) of pure Co₃O₄ catalyst (before OER) and Pt 4f (b) region of on Pt-substituted-Co₃O₄ catalyst (before and after OER).
Oxygen evolution activity on Pt substituted Co$_3$O$_4$ spinel

Co$_3$O$_4$ spinel:
- Co$^{2+}$
  - Tetrahedral sites ($I_r \sim 0.58$ nm)
- Co$^{3+}$
  - Octahedral sites ($0.61$ nm)

Interplay of Pt$^{2+}$ with Co$^{2+}$ sites:
- Pt$^{4+}$
- Pt$^{2+}$

Pt substitution & reduction:
- $Co^{3+}_{2-2y}Co^{2+}_{3+y}Pt^{4+/2+}_yO_4$

Electrolytes (0.5 M):
- KOH
- K$_2$SO$_4$
- PBS

OER activity:
- Catalytically active
- Catalytically inactive