



Surficial reconstruction in bimetallic oxide SrCoO_x through Ce-doping for improved corrosion resistance during electrocatalytic oxygen evolution reaction in simulated alkaline saline water

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ABSTRACT

Transition metal based bimetallic oxides are good candidates for electrocatalytic oxygen evolution owing to their variable oxidation states, synergistic effects, good conductivity, convincing electrochemical stability, and low cost. However, these materials are highly susceptible to corrosion during saline seawater electrolysis. This work, for the first time, highlights the role of cerium (Ce) doping in bimetallic strontium cobalt oxide (SrCoO_x) electrocatalyst for electrochemically stable and corrosion-resistant oxygen evolution reaction (OER) in simulated saline water. The experimental results reveal that 0.5% Ce-doped 5% SrCoO_x has the best corrosion resistant ability with respect to the undoped SrCoO_x and various other Ce-doped samples. The growth of CeO_2 nanoparticles and the generation of CeO_x passivation layer through Ce doping were supposed to block the corrosive ions on the surface, thereby hindering chlorine evolution reaction (CER). The Ce^{3+} ions doped inside the SrCoO_x lattice created multiple defects and vacancies which sacrificially facilitate the OER while mitigating the CER. The suppression of corrosive reactions was indicated through low corrosion current ($-1.10 \mu\text{A}\cdot\text{cm}^{-2}$) and high corrosion potential (0.90 V vs. RHE) values suggesting slowest corrosion rate and least tendency towards CER in 0.5% Ce-doped 5% SrCoO_x . Consequently, it demonstrated the least Tafel slope of $81.7 \text{ mV}\cdot\text{dec}^{-1}$ in saline OER electrolysis with respect to the $121.0 \text{ mV}\cdot\text{dec}^{-1}$ was obtained for undoped 5% SrCoO_x . Moreover, the electrochemical stability demonstrated in chronoamperometric OER for 45 h and the cyclic voltammetry (500 cycles) confirmed that 0.5% Ce-doped SrCoO_x electrocatalyst possesses enhanced anticorrosive properties, which was further supported by post-use linear sweep voltammetry, cyclic voltammetry, and X-ray diffraction analyses. Linear polarization resistance study was also employed on the seawater sample, collected locally, to assess the validity of the present work in real marine systems. In view of the observed results, this work can open an alternate pathway to investigate various transition metal oxide systems as potential corrosion resistant electrocatalysts for seawater.

KEYWORDS

bimetallic oxide, SrCoO_x , cerium doping, oxygen evolution reaction (OER), chlorine evolution reaction, passivation layer

1 Introduction

The unabating depletion of global fossil fuels and subsequent environmental pollution with global warming has prompted the scientific community to shift the focus on using the abundant renewable energy resources such as wind, solar light, and water. In this direction, water splitting into hydrogen and oxygen gases by the aid of light or electrical bias has been the focus of researchers as clean energy source. However, there have been lot of challenges in terms of designing suitable catalysts for water splitting process. The electrocatalytic water splitting involves the application of an

electrical bias across the cathode and anode in an electrochemical cell. At the cathode, reduction of H_2O forms H_2 gas via hydrogen evolution reaction (HER); while the oxidation reaction at the anode produces O_2 gas via oxygen evolution reaction (OER). Since H_2 gas is a green and energy extensive source, it is considered as one of the most promising solution for alternative energy production [1]. However, the rate of electrochemical HER at the cathode relies heavily on the activity of OER occurring at the anodic compartment; due to the kinetic limitations to OER, as being a 4-electron process against the 2-electron process in HER

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[2–4]. Therefore, the design of highly active and stable anodic material for electrochemical water splitting is highly desired. The use of surplus saline/sea-water against the scarce freshwater resources at the industrial-scale water splitting in arid coastal regions can be a game-changing technology for sustainable energy goals [5–8]. Other than fluctuations to the local pH and presence of impurities, the vast presence of chloride ions in sea-water poses the biggest challenge to the anodic OER as it initiates a competing reaction, called the chlorine evolution reaction (CER), that is thermodynamically more favorable than OER and leads to corrosion of electrodes, hindering its large-scale implementation [9–13]. The CER is a two-step and two-electron transfer reaction occurring between pH 3–7.5 while the hypochlorite formation is highly favored over pH of 7.5 [14]. Oxidation of chloride ions in water systems can be suppressed if the overpotential is kept below 480 mV at a specific pH [15]. The drawbacks of CER is that it drastically lowers the activity and efficiency of the overall water-splitting system since it highly corrodes and erodes the anodic material through adsorption followed by dissolution as metal hydroxides in the electrolyte solution [16, 17].

Transition metal oxides are considered attractive anodic materials for OER owing to their variable oxidation states, robustness, high abundance, and corrosion-resistance properties, among which oxides of cobalt is considered one of the highly active materials for OER [18, 19]. Their OER performance depends on the morphology, composition, oxidation state, 3d electronic configuration, surface binding energy to oxygen, and energy required to undergo transition from lower to higher oxidation states [18]. These performance deciding factors can be optimized by synergistic combination of cobalt oxides with a suitable metal to form a bimetallic oxide [20, 21]. The physical and chemical properties of bimetallic oxides can be modulated by altering their cations as well as the synthesis methods [22–25]. However, the bimetallic oxide based anodic materials are highly susceptible to corrosion in saline OER conditions, due to high concentration of chloride and other ions in sea-water, which mainly interfere through pitting and stress corrosion [16]. Furthermore, in bimetallic oxides, there is a risk of the electrocatalytically active layer being peeled off and undergoing metal dissolution, thereby reducing the efficiency of OER [26]. On the other hand, use of layered double hydroxides (LDHs) and two-dimensional (2D) materials as potential seawater electrocatalysts is also not encouraged owing to their inadequate active sites, inferior electrical conductivity (e.g., LDHs) [27], weak adsorption to the reaction intermediates (e.g., graphene) [28] and susceptibility towards degradation due to fast oxidation (e.g., MXenes) [29]. Therefore, development of efficient and corrosion resistant bimetallic oxide based OER anodic electrode material is highly desired which demands sufficient attention from the researchers.

Recently, many strategies have been employed to enhance corrosion resistance in seawater including electronic structural modulation, creation of a passivation layer and oxygen vacancy generation. Rare earth metal ion doping in bimetallic oxides based anodic materials can enhance corrosion resistance in seawater by incorporating these aforementioned strategies by facilitating creation of defect-rich sites, adsorption, and conversion of OER reaction intermediates [30]. Gao et al. [31] doped NiS_2 with Ce ion to introduce higher active sites and better durability which eventually enhanced electrocatalytic OER performance. They obtained 87 mV lower overpotential in Ce-doped NiS_2 with respect to the pure NiS_2 , owing to the probable formation of a corrosion resistant CeO_2 passivation layer [32]. Obata and

Takanabe [33] deposited a perm-selective CeO_x layer on bimetallic NiFeO_x to fend off corrosive chloride ions alleviating OER corrosion in saline electrolyte, by selectively allowing hydroxide and hydrogen peroxide anions to the catalytically active inner layer. Even though these studies suggested the possible advantages of using Ce ion doping, the corrosion suppression mechanism was not discussed in detail through investigating the corrosion rate and tendency of the electrocatalyst. Therefore, development of corrosion resistant electrocatalysts by rare-earth metal doping in bimetallic oxides and understanding the underlying mechanism can realise the direct use of this technology in sea-water which will have dual benefits in terms of abundant energy and fresh water preservation [5].

Herein, this study is aimed to develop efficient anodic OER electrode materials with good corrosion resistance against the unwanted CER. We, for the first time, chose bimetallic SrCoO_x as the primary anode material for saline electrochemical OER, owing to the fact that oxides of cobalt and strontium are highly active towards OER according to the volcano plot [34]. Moreover, cobalt and strontium are predicted to form passivated oxides thereby preventing the dissolution of their ions in the electrolyte through chloride adsorption as per their Pourbaix diagram, which imparts anti-corrosive properties in them. The compositional ratio between strontium and cobalt were varied and the electrochemically best performing composition of SrCoO_x was obtained for OER. The as obtained best OER electrocatalyst, 5% SrCoO_x , was doped with Ce ions to enhance its corrosion resistance towards CER in simulated seawater electrolysis. After optimizing, the 0.5% Ce-doped 5% SrCoO_x electrocatalyst exhibited the best corrosion resistance and OER selectivity with respect to the undoped 5% SrCoO_x .

2 Experimental section

2.1 Chemicals

Strontium nitrate ($\text{Sr}(\text{NO}_3)_2$, 99.0%, Sigma-Aldrich), Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.999%, Sigma-Aldrich), Cerium (III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\geq 99.99\%$, Sigma-Aldrich), Iridium (III) chloride hydrate ($\text{IrCl}_3 \cdot x\text{H}_2\text{O}$, reagent grade), Potassium hydroxide (KOH, Sigma-Aldrich), Oxalic acid dihydrate ($\geq 99.5\%$, Scharlau), Hydrochloric acid (HCl, 37%, Merck) Ethanol (Merck) and Ethylene glycol (Merck) and Nickel metal foam (NF, 2 mm thickness, American Elements). Milli-Q ultrapure water with a resistance of 15 $\text{M}\Omega\cdot\text{cm}$ was used for whole duration of this study.

2.2 Synthesis of SrCoO_x bimetallic oxides

In a typical sol-gel synthetic route (Scheme S1 in the Electronic Supplementary Material (ESM)), $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, oxalic acid dihydrate and ethylene glycol were mixed in calculated stoichiometric amounts. The two nitrate salts were mixed in ethylene glycol thoroughly and a gel was formed after the addition of oxalic acid and stirring at 85 °C. The gel was then dried in an oven at 150 °C and then calcined at 830 °C in a muffle furnace for 4 hours with a ramping rate of 5 °C·min⁻¹. Different compositions of SrCoO_x were obtained by altering the molar ratios of Sr and Co. The undoped SrCoO_x (designated as SCO hereafter) catalysts prepared include 0.5% SCO, 1% SCO, 2.5% SCO, 5% SCO, 10% SCO, and 20% SCO, as per the feed ratio. The same sol-gel protocol was used to prepare pure cobalt oxide (Co_3O_4) and strontium oxide (SrO_x). All the samples were powdered for

thorough characterizations and finally electrocatalytic OER application was employed.

2.3 Synthesis of Ce-doped 5% SrCoO_x

Various dopant concentrations of Ce ions were used for synthesizing different Ce-doped SrCoO_x (Ce-doped SCO) samples by a similar sol-gel method (Scheme S1 in the ESM). Definite dopant concentrations of cerium (III) nitrate hexahydrate were mixed with the nitrate salts in ethylene glycol. The remaining steps were the same as those carried out for the synthesis of SCO samples. The as-synthesized Ce-doped SCO electrocatalysts include 0.5% Ce-SCO, 1% Ce-SCO, and 2% Ce-SCO, as per the feed ratio. The actual doping amount was confirmed using ICP-MS, as presented in Table S5 in the ESM, as the Ce content in the acid-digested samples increases linearly with the feed ratios.

2.4 Synthesis of IrO₂

A similar sol-gel route was used where Iridium (III) chloride hydrate was mixed in ethylene glycol thoroughly, and a gel was formed after the addition of oxalic acid and stirring at 85 °C. The gel was then dried in the oven at 120 °C for 24 hours and then calcined at 600 °C in a muffle furnace for 2 hours with a ramping rate of 2 °C·min⁻¹ [35]. The calcined powder was then ground before being used for electrode preparation.

2.5 Preparation of electrodes for OER

A nickel foam support was cut into rectangular pieces of 0.5 cm × 1.0 cm and sequentially washed by sonication in 3.0 M HCl, deionized (DI) water and then ethanol for 5 minutes each. The electrocatalyst ink was prepared by dispersing 4 mg of the electrocatalyst in ethanol (500 μL) along with the addition of Nafion (10 μL) as the binder. The resulting mixture was ultrasonicated for 30 minutes and finally drop-casted on already cut Ni foam substrates over an active area of 0.5 cm×0.5 cm. Finally, the as fabricated electrodes were air dried before being applied for electrocatalytic OER measurements as working electrodes.

2.6 Physical characterizations

X-ray diffractograms were obtained from a diffractometer (PANalytical Empyrean diffractometer) with a Cu tube ($K\alpha = 1.54059 \text{ \AA}$) radiation as the X-ray source. Data were collected in the range of 2θ values from 5° to 80° at a beam voltage of 30 kV and a beam current of 10 mA. Powder XRD data analyses were done using PANalytical X'Pert High Score Plus software. Field emission scanning electron micrographs were obtained from two different microscopes (JEOL JSM-7610F FEG-SEM and FEI QUANTA 250 FEG SEM) at varying voltages and magnifications. Energy dispersive X-ray spectroscopy (EDS) analyses were performed on the JEOL JSM-7610F FEG-SEM at 30 kV accelerating voltage. High resolution transmission electron microscopy (HR-TEM) and assembled EDS analyses were performed at varying voltages and magnifications on Titan 80-300ST instrument. X-ray photoelectron spectroscopy was employed using XPS instrument (Thermo Scientific–ESCALAB Xi') with monochromatic Al $K\alpha$ as the X-ray source (100 eV pass energy, 0.3 eV step size, Mono 650 μm power). The survey spectrum was carried out over a binding energy range of 0 to 1350 eV. ICP-MS (Perkin Elmer NexION 2000 with Nickel cones and associated with Syngistix software) was employed to confirm the extent of cerium doping. The samples were digested in strong

acidic mixture and diluted before the ICP measurements. Further, the Ce ion leaching of 0.5% Ce-SCO was also studied using the same technique to confirm the stability of Ce- doped SCO.

2.7 Electrochemical measurements

The electrochemical measurements were performed using a 3-electrode setup from Multichannel Autolab PGSTAT204 (AUTM204.S). The setup consisted of a Pyrex single chamber electrochemical cell mounted with Pt foil as a counter electrode, Ag/AgCl as a reference electrode and electrocatalyst deposited Ni foam as a working electrode, which was attached to the tip of an electrode holder. All the potentials were calibrated to the reversible hydrogen electrode (RHE) with the aid of the equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + (0.0591 \times \text{pH})$. All the acquired current (I) data were converted to current density (j) using the formula: $j = 1000I/\text{surface area}$ having the units of mA·cm⁻². Linear sweep voltammetry (LSV) was performed in alkaline electrolyte (1.0 M KOH) and alkaline saline water (1.0 M KOH+ 0.5 M NaCl) at a scan rate of 10 mV·s⁻¹ within potential range of 0.8 to 2.2 V (vs. Ag/AgCl). Cyclic voltammetry (CV) was performed in alkaline and alkaline saline water at scan rates varying from 10 to 100 mV·s⁻¹ at a fixed potential window of 0.2 V (between 0.97 to 1.17 V vs. RHE) involving the non-Faradaic region. Electrochemical impedance spectroscopy (EIS) measurements were carried out from 10⁶ Hz to 1 Hz with 10 frequency points per decade and an amplitude of 0.01 V_{RMS}. Chronoamperometry was performed in alkaline and alkaline saline electrolyte solutions at an applied potential of 1.62 V vs. RHE for 10 hours. Linear polarization resistance (LPR) experiments were performed on the electrochemical workstation with varying potential windows and a scan rate of 10 mV·s⁻¹ for the determination of corrosion current and corrosion voltage.

3 Results and discussion

3.1 Characterizations

The crystalline structure of pristine Co₃O₄, SrO_x, undoped SCO and Ce-SCO, along with other counterparts were investigated using X-ray diffraction (XRD) analysis (Fig. 1 and Fig. S1 in the ESM). The diffractogram of Co₃O₄ revealed the presence of (111), (220), (311), (400), (422), (511) and (440), thereby matching the ICDD reference code 04-003-2613. The cell cubic parameters suggest the formation of Co₃O₄ phase with a cubic crystal system having a $Fd\bar{3}m$ space group and space number of 227.

The a , b and c values are 8.05 Å. When Sr was doped into cobalt oxide, the 2θ values of peaks slightly shifted to a lower angle, indicating expansion of the lattice probably due to the larger size of Sr²⁺ than Co²⁺. The characteristic peaks for SrO_x are not visible in the SCO bimetallic oxides which might be due to the large background obtained for Co₃O₄ containing moieties or absence of a separate SrO_x phase as demonstrated in Fig. S2 in the ESM. It concludes that there is no separate SrO_x phase accumulated on the Co₃O₄ surface, but Sr has been successfully doped into the lattice. Subsequently, when the SCO samples were doped with Ce, the XRD peaks shifted back to higher 2θ values, to the values corresponding to those of pristine cobalt oxide. This indicates successful doping of Ce ions, replacing Sr in the lattice and not Co as highlighted in the upcoming SEM-EDX studies, and subsequent contraction of the lattice due to smaller size of Ce³⁺ than Sr²⁺ [36]. The slight shift of all the characteristic peaks present in Co₃O₄ to lower 2θ values in undoped (5% SCO) and

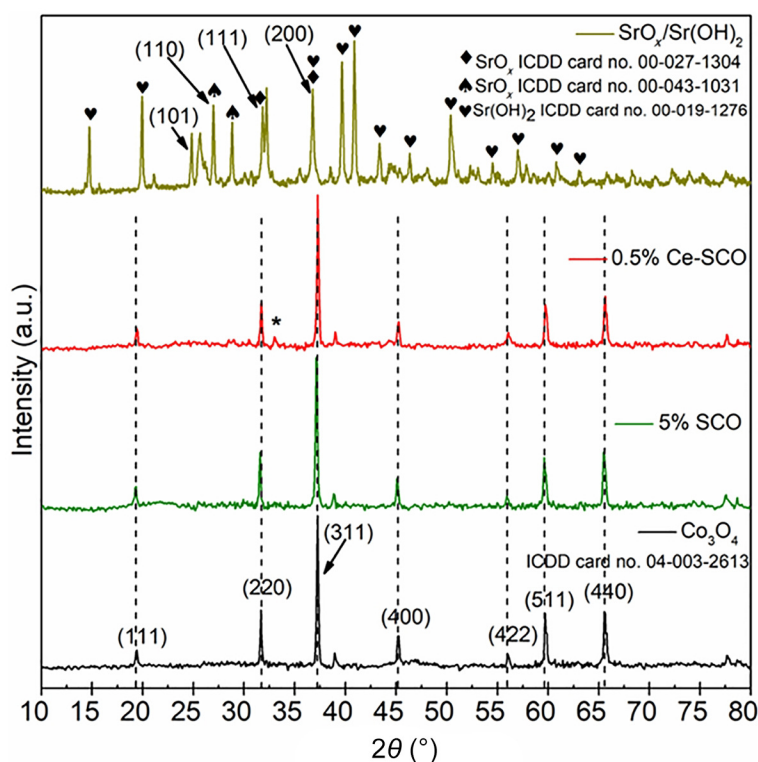


Figure 1 Powdered X-ray diffractograms of pristine Co_3O_4 , SrO_x , 5% SCO ($\text{Sr}_{0.05}\text{Co}_{0.95}\text{O}_x$), and 0.5% Ce-SCO ($\text{Ce}_{0.005}\text{Sr}_{0.05}\text{Co}_{0.945}\text{O}_x$). (200) phase of CeO_2 is denoted as * in 0.5% Ce-SCO XRD pattern.

then to higher 2θ values in doped SCO (0.5% Ce-SCO can suggest the plausible incorporation of SrO_x followed by successful Ce doping (Fig. S3 in the ESM). Along with the shift in 2θ , d -spacing of (220) and (311) phases increase slightly with the incorporation of Sr into Co_3O_4 . However, doping of Ce into the 5% Ce-SCO sample shows the d -spacing, crystallite sizes and FWHM reverting to the values like those of Co_3O_4 . Interestingly, there is appearance of a peak at 2θ value of 33.0° (denoted as * in Fig. 1 and Fig. S3(d) in the ESM) which could correspond to the (200) phase found in CeO_2 (ICDD-04-015-2674) and might indicate the formation of CeO_2 nanoparticles from surplus Ce on doping [37].

The surface morphology of the prepared electrocatalysts was probed using field emission scanning electron microscopy (FESEM). The SEM image of pristine Co_3O_4 (Figs. 2(a) and 2(b)) shows the formation of uniform and finely divided granular flakes. It appears that the SrO_x sample exhibits rod like morphology, apparently developed by fusing of elongated rectangular nanosheets (Figs. 2(c) and 2(d)). The introduction of strontium into cobalt oxide seems to maintain the flake-like morphologies into the bimetallic oxide, as is evident from Figs. 2(e) and 2(f). However, addition of higher Sr content in the SCO indicates dominance of rod shaped SrO_x with the Co_3O_4 flakes distributed over its surface (Figs. S4(a) and S4(b) in the ESM). Therefore, 5% SCO (Figs. 2(e) and 2(f)) might represent the appropriate amount of Sr content in the bimetallic oxide to maintain the appropriate morphology and grain boundaries which could provide higher electrochemical surface area and active sites. The doping of Ce into 5% SCO exhibits reversion of granular morphology with better uniformity and dispersion with respect to the undoped SCO (Figs. 2(g) and 2(h)). This suggests successful doping of Ce into the SCO matrix and its influence on crystallinity and nucleation of SCO nanoparticles [38, 39].

The morphology and crystalline features of the synthesized

bimetallic oxides were further investigated using HRTEM. As can be seen from Fig. 3, pristine Co_3O_4 shows roughly granular flake-like morphology (Fig. 3(a)). Contrarily, SrO_x exhibits elongated thin rectangular nanosheets fused together (Fig. 3(b)). The introduction of SrO_x in Co_3O_4 resulted in the formation of bimetallic SrCoO_x oxide, mostly with square and hexagonal shapes (Fig. 3(c)). Cerium-doping has led to the dominance of hexagonal morphology with sharper edges, with anchored small CeO_x nanoparticles from excessive Ce-doping, along with subsequent CeO_x sheath around the hexagonal flakes (Figs. 3(d)–3(f)).

The HRTEM and selected area electron diffraction (SAED) were further employed to know the d -spacing and were correlated with the XRD cards to elucidate the crystalline phases. The HRTEM with d -spacings was determined for all the samples, including the pristine Co_3O_4 and SrO_x (Fig. S8 in the ESM). As can be seen in Fig. 4(a), 5% SCO exhibits fringes with d -spacings of 0.155 and 0.242 nm corresponding to the (511) and (311) planes of cubic 5% SrCoO_x . The d -spacings obtained from the SAED pattern were also in good agreement with the HRTEM results (Fig. 4(b)). The doping of Ce into 5% SCO showed almost similar arrangement of fringes, with emergence of d -spacings of 0.237 and 0.466 nm corresponding to the (311) and (200) crystalline planes, respectively, which are responsible for the dominated existence of hexagonal morphology. The CeO_2 nanoparticle grown on the 5% SCO exhibits d -spacings of 0.321 and 0.272 nm corresponding to the (111) and (200) crystal planes of CeO_2 (Fig. 4(c)). These results were again in coherence with the SAED data (Fig. 4(d)). The elemental mapping derived from the TEM-HAADF analysis indicates the sparse distribution of constituent elements in the 5% SCO, as shown in Fig. S9 in the ESM. Further, the elemental mapping indicates more of a uniform distribution of Ce in the SCO matrix with surface localized CeO_x nanoparticles, as can be seen as lumps in the mapping

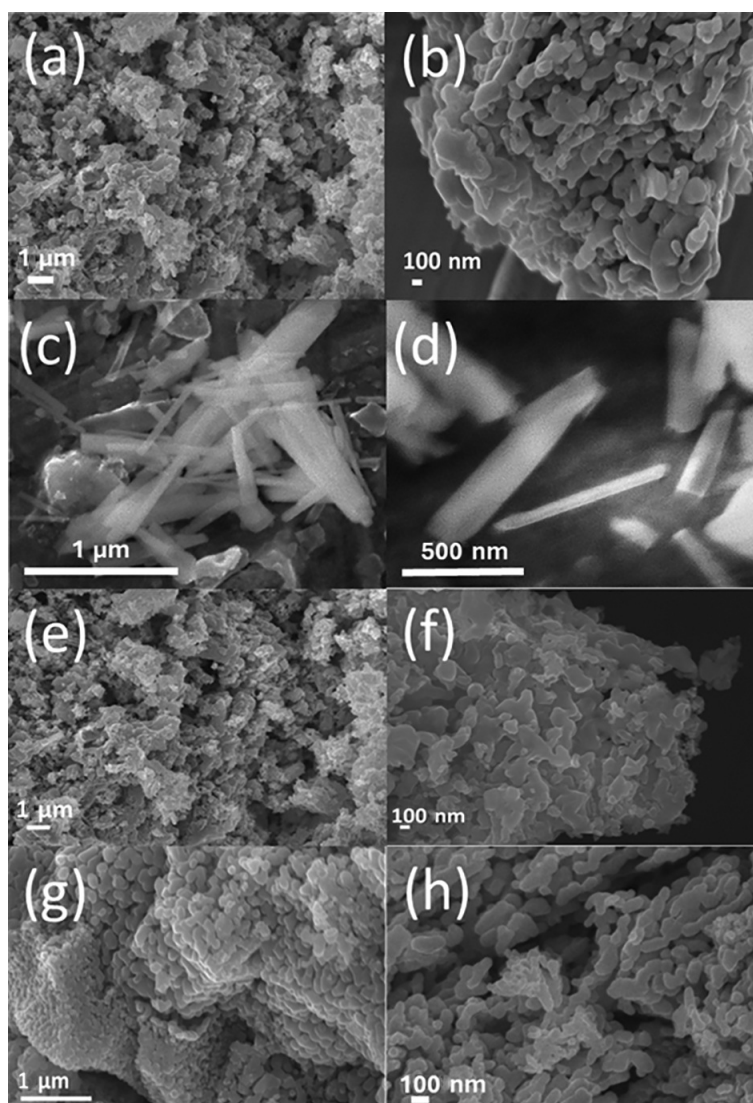


Figure 2 FESEM images at different magnifications. (a) and (b) Co_3O_4 showing granular flake-like morphology; (c) and (d) SrO_x showing elongated rod-like morphology; (e) and (f) 5% SCO showing finer flakes with diffused sheet-like morphology; (g) and (h) 0.5% Ce-doped SCO exhibiting uniform granular like morphology.

micrographs (Fig. 4 (bottom)) and Fig. S10 in the ESM; most likely matching the anchored morphology shown in Figs. 3(d)–3(f).

The EDS analysis obtained from the FESEM machine confirmed the presence of Sr, Co, and O in the as-prepared SCO electrocatalysts, as shown in Fig. S6 in the ESM. It is pertinent to mention that the atomic percentage obtained from the EDS results is in close agreement with the ratios as anticipated during the synthesis process (Tables S6–S9 in the ESM). Further, the EDS for 0.5% Ce-SCO also confirms the presence of all the constituent elements (Fig. S6(d) in the ESM), almost in the same atomic ratios as taken during synthesis (Table S9 in the ESM). The atomic percentages for Co, Sr and Ce were 95.32%, 4.12% and 0.56%, respectively, which are in accordance with the feed ratios. The SEM-EDS mapping results complement the results from TEM-EDS mapping, as shown in Fig. S7 in the ESM, where all the constituent elements are uniformly distributed, while Ce also exists as CeO_x nanoparticles. Interestingly, these results reveal that Ce doping has exclusively replaced the Sr atoms and has kept the Co_3O_4 lattice intact (Tables S8 and S9 in the ESM). This agrees with the results obtained in XRD, HRTEM, and SAED, where the

d-spacings and corresponding phases pertaining to Co_3O_4 or SCO remains intact. The EDS line scan indicates uniform distribution of Co and O atoms while Ce and Sr atoms have a small atomic fraction with some spikes indicating the doping as well as the accumulation of CeO_x and SrO_x as nanoparticles on the surface of 5% SCO (Fig. S11 in the ESM). The atomic ratio for 0.5% Ce-SCO was also determined by ICP-MS to validate the above results. ICP-MS results are presented in Table S5 in the ESM, which reveal that Sr doping in 0.5% Ce-SCO ranges between 6.0% to 7.0% which is almost comparable to the feed ratio, while the proportion of Ce came out to be 1.40% instead of 0.5% feed ratio which may be due to the partial leaching out of Sr and Co during the *in-situ* reaction. It is necessary to mention that the total feed ratio of Ce doesn't dope into the SCO lattice, and the excessive Ce accumulated as $\text{CeO}_2/\text{CeO}_x$ on the SCO surface.

The oxidation state, chemical structure, and elemental composition were investigated using XPS. We performed XPS analyses of pristine Co_3O_4 , SrO_x , 5% SCO and 0.5% Ce-doped 5% SCO samples to elucidate the electronic states of the synthesized samples with their molar atomic ratios. The XPS results for the former three samples are provided in the supplementary

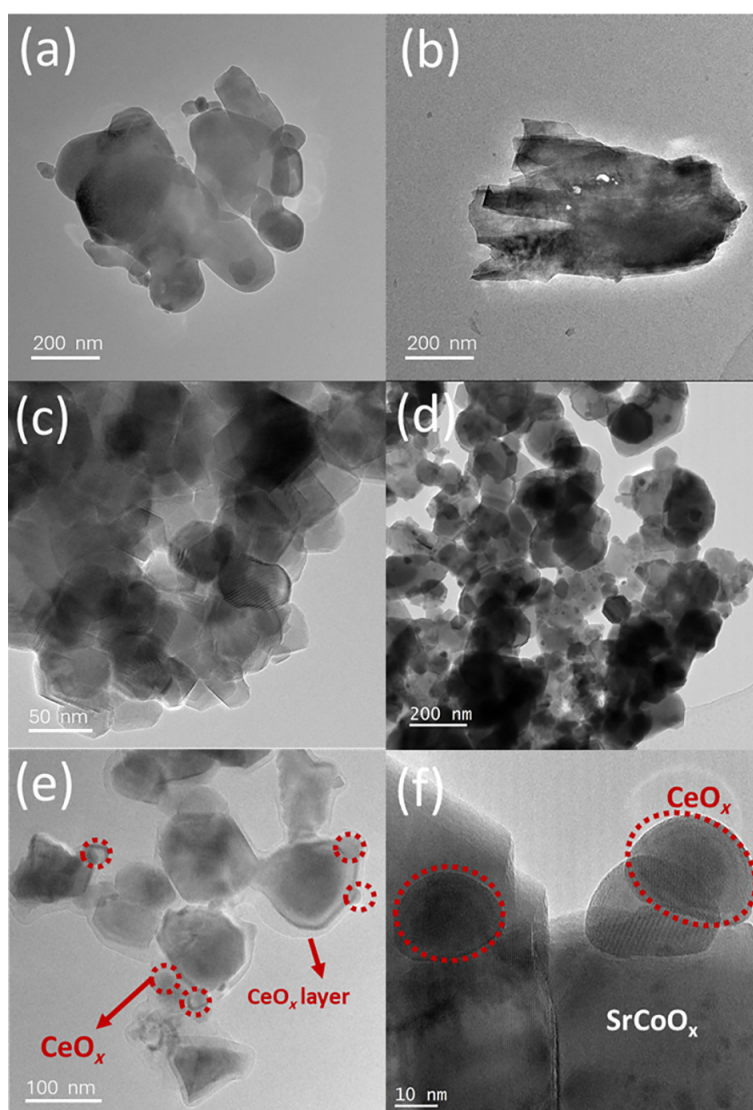


Figure 3 TEM micrographs of (a) Co_3O_4 showing roughly granular flakes; (b) SrO_x showing elongated rod-like morphology; (c) 5% SCO exhibiting hexagonal and square flakes; (d) 0.5% Ce-5% SCO exhibiting growth of small Ce nanoparticles throughout the 5% SCO nanoparticles; (e) and (f) 0.5% Ce-5% SCO sample indicating dominance of hexagonal flakes with anchored CeO_x nanoparticles and a thin sheath of CeO_x covering the flakes.

information (Figs. S12–S14 in the ESM). The survey spectrum for 0.5% Ce-doped 5% SCO sample (Fig. 5) reveals the presence of all the constituent elements i.e., Ce, Sr, Co and O in the synthesized electrocatalyst. In the high resolution XPS of Co 2p, we can see two major peaks at 779.4 and 794.5 eV corresponding to Co $2p_{3/2}$ and Co $2p_{1/2}$, respectively. The deconvolution of the individual core level Co 2p peaks exhibits two strong peaks in each major peak. The pair of peaks from the Co $2p_{3/2}$ located at 778.7 and 779.8 eV can be ascribed to the Co^{3+} and Co^{2+} in Co_3O_4 . Another pair of peaks in Co $2p_{1/2}$ located at 793.6 and 794.6 eV are again assigned to the Co^{3+} and Co^{2+} states in Co_3O_4 . Further, three broad peaks located at 784.3, 788.7, and 803.7 eV are assigned to the shakeup satellite peaks for Co^{2+} and Co^{3+} with a higher predominance for Co^{2+} [40, 41]. A small peak at 775.8 eV can be due to the Co^{2+} of lower oxidation state viz; CoO. For Sr 3d, a broad peak centred at 133.7 eV can be observed. The deconvolution resolved into three prominent peaks centred at 132.0, 133.7, and 135.5 eV which can be ascribed to Sr $3d_{5/2}$, Sr $3d_{3/2}$ and $\text{Sr}(\text{OH})_2$ respectively. The Sr $3d_{5/2}$ corresponds to the Sr–O bond in the lattice while the Sr $3d_{3/2}$ peak corresponds to the Sr–O states on the surface [40, 42, 43]. The Ce 3d XPS spectrum

exhibits characteristic peaks at 881.9 and 926.4 eV corresponding to the $\text{Ce}^{4+} 3d_{5/2}$ and $\text{Ce}^{4+} 3d_{3/2}$, respectively. This indicates that Ce exists as CeO_2 or CeO_x on the catalyst surface [44–47]. The XPS spectrum for O 1s exhibits a prominent peak at 529.1 eV with two shoulder peaks at 530.5 and 532.2 eV. The deconvolution resolved these peaks into three peaks centred at 529.1, 530.4, and 532.3 eV respectively which can be ascribed to the lattice Co–O, defective vacancies and the adsorbed O–H, respectively [41, 48]. It can be seen that there is significant shift of binding energy values in case of undoped and Ce-doped bimetallic SrCoO_x samples due the lattice expansion on introduction of SrO_x into the Co_3O_4 lattice. The major O 1s peaks of the pristine SrO_x and Co_3O_4 have shifted from 537.5 eV (Fig. S14 in the ESM) and 532.7 eV (Fig. S13 in the ESM) to 529.1 eV in the 0.5% Ce-SCO. The major Co 2p peaks of the Co_3O_4 have shifted from 782.3 and 797.5 eV (Fig. S13 in the ESM) to 779.4 and 794.5 eV in 0.5% Ce-SCO samples. The major Sr 3d peak of SrO_x has been shifted from 143.6 eV (Fig. S14 in the ESM) to 134.2 eV in the 0.5% Ce-SCO sample. These results confirm the successful formation of the bimetallic oxide and suggests that the bond lengths have increased on binary oxide formation due to lattice expansion which has resulted in decrease

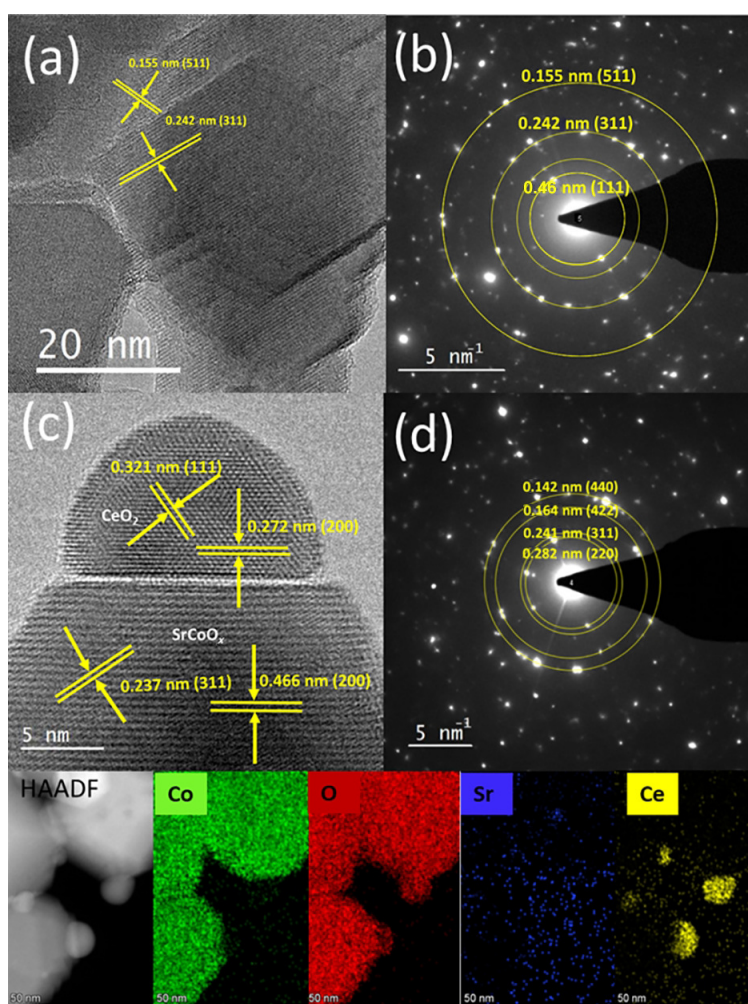


Figure 4 (a) HR-TEM image of 5% SCO exhibiting the dominant d -spacings corresponding to (511) and (311) planes. (b) SAED pattern showing different lattice patterns corresponding to various d -spacings and crystalline planes of 5% SCO. (c) HRTEM of 0.5% Ce-SCO; and (d) corresponding SAED pattern of 0.5% Ce-SCO. EDS elemental mapping at the bottom derived from TEM-HAADF analysis showing successful doping of Sr and Ce in the Co_2O_3 matrix with localized CeO_x nanoparticles distributed on its surface.

of their binding energies, as reflected from the XPS spectra [49]. The percent atomic ratios were also determined using XPS studies (Table S10 in the ESM). The molar ratios obtained were roughly in agreement with the values obtained from EDX studies; as shown in Tables S6–S9 in the ESM.

To confirm the formation of defects in the Ce-doped SCO samples, the photoluminescence (PL) analyses were applied. In the PL analysis, an excitation wavelength of 325 nm was applied, and two prominent emission peaks in the range of 400–410 nm and 650–680 nm were observed for all the samples. The first emission is believed to emerge from the Ce^{4+} (5d to 4f) transition, while the later comes from the lattice defects of the bulk SCO. The results reveal that Ce-doping in the 5% SCO enhances the PL emission which can be indicative of emergence of defects and vacancies in the SCO lattice (Fig. S15 in the ESM).

3.2 Electrocatalytic OER performance

3.2.1 In alkaline water

The OER electrochemical activity of the as-prepared catalysts was investigated using a 3-electrode setup mentioned above, using an alkaline electrolyte (1.0 M KOH). The LSV polarization curves (Fig. 6(a)) demonstrate that 5% SCO requires the lowest overpotential of 350.0 mV at $10 \text{ mA}\cdot\text{cm}^{-2}$ which indicates its

superior electrochemical activity among the undoped SCOs. The satellite peak presented before 1.5 V represents the characteristic oxidation of nickel foam from Ni^0 to Ni^{2+} [50]. The best dopant concentration of Ce into SCO was also determined using polarization curves (Fig. 6(c)) and 0.5% Ce-SCO was found to exhibit the least overpotential among the Ce-doped SCOs. However, its overpotential was slightly higher (410.0 mV vs. RHE) @ $10 \text{ mA}\cdot\text{cm}^{-2}$ current density with respect to 350.0 mV obtained for 5% SCO, indicating a small decrease in current response. Tafel plots are an important parameter to derive the electrochemical OER activity and kinetics. Tafel slope values obtained near the onset potential of the undoped SCOs show that the 5% SCO demonstrates the fastest OER kinetics and activity having the lowest Tafel slope of $121.0 \text{ mV}\cdot\text{dec}^{-1}$; as shown in Fig. 6(b) and Fig. S16(a) in the ESM. Interestingly, Ce-doped SCO increased the OER kinetics further with respect to the undoped SCO. Specifically, 0.5% Ce-SCO showed the lowest Tafel slope value of $81.9 \text{ mV}\cdot\text{dec}^{-1}$ (Fig. 6(d)) with respect to all the undoped and doped counterparts. The electrochemical adsorption of OH^- ions onto the active sites initiates the oxidation of water molecules in alkaline electrolytes. These aforementioned Tafel results reveal that 0.5% Ce-SCO demonstrates the most efficient OER activity as it probably contains the optimal energy and favourable OH^- affinity essential for the formation of OER intermediates and equilibrium

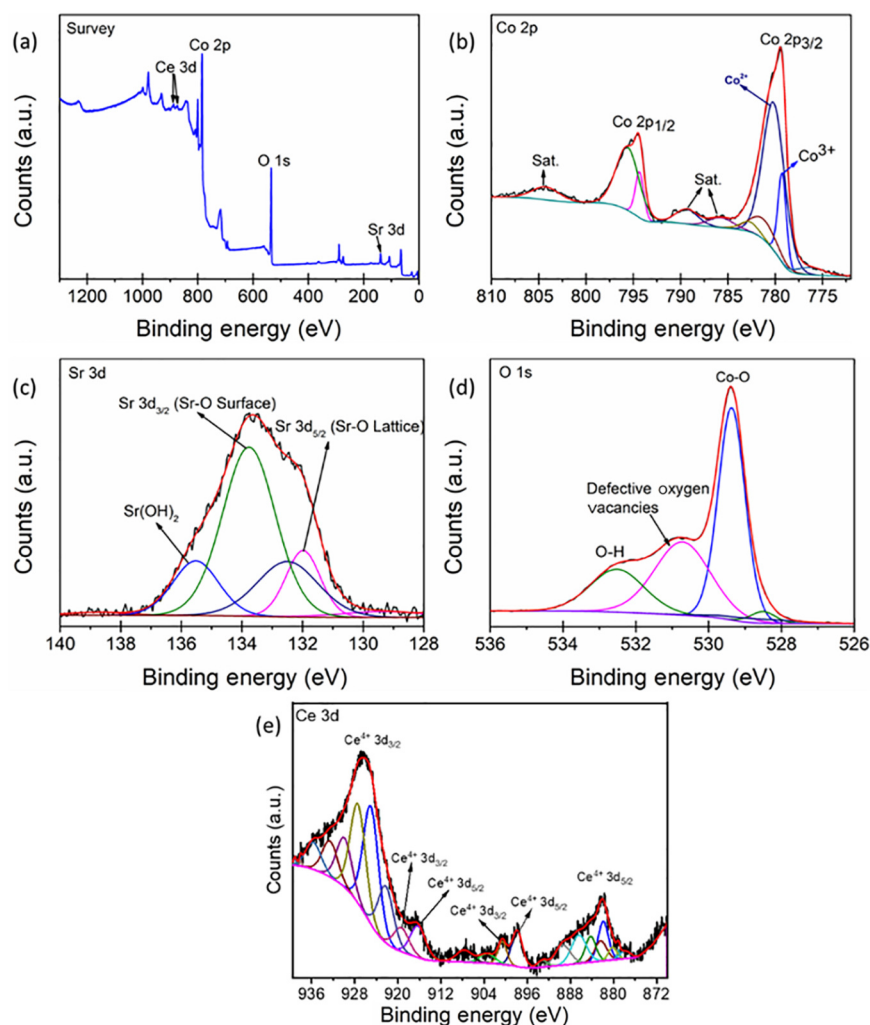


Figure 5 High-resolution XPS spectra of 0.5% Ce-SCO with deconvoluted peaks of (a) survey, (b) Co 2p, (c) Sr 3d, (d) O 1s, and (e) Ce 3d.

coverage of the active sites [51]. We predict that Ce replaces the Sr ions in the lattice leading to the formation of defects, which facilitates OER intermediates leading to better OER kinetics (i.e., lower Tafel slope).

To further assess the electrochemical performance of the Ce-doped and undoped SCO, their electrochemical surface area (ECSA) was determined, which is directly proportional to the capacitance of the double layer (C_{dl}) values, calculated from the CVs taken at different scan rates in the non-Faradaic region (Fig. 6(e) and Fig. S17 in the ESM) [52]. The ECSA is an important parameter in direct electrochemical sea-water splitting, where the aggressive Cl^- ions attack the exposed active sites through adsorption and permanently poisoning the surface of the electrocatalyst [53]. The results exhibit that 0.5% Ce-SCO possesses higher ECSA and C_{dl} than undoped 5% SCO, indicating that Ce-doping into SCO has significantly enhanced the active sites for electrochemical OER in alkaline electrolyte. This higher ECSA could have resulted from the generation of lattice defects responsible for OER.

Transition metals are known to hinder oxygen evolution due to their aerophilic feature. As a result, the detachment of oxygen molecules from the active sites are hampered due to their blockage, inefficient surficial contact between the electrode and electrolyte and leaching out of the metal electrocatalyst from the support at high potential at the anodic double layer due to corrosive metal oxide formation with low conductivity [54].

Therefore, turnover frequency (TOF) is an important parameter in evaluating the oxygen desorption capability of the as-prepared electrocatalyst as it approximates the gas bubbles released per unit time. Both 5% SCO and 0.5% Ce-SCO exhibit a higher TOF in saline electrolyte (15.3 s^{-1}) with respect to that in the non-saline electrolyte (13.3 s^{-1}) (Fig. 6(e)). Therefore, it can be considered that more gas molecules are released in saline electrolytes than in non-saline electrolytes due to the higher concentration of ions in saline water. This superior OER performance of 5% SCO and 0.5% Ce-SCO in saline electrolyte prompted us to investigate them in harsher conditions containing corrosive Cl^- ions [55].

To probe the charge transfer kinetics and conductivity of the as synthesized electrocatalysts, EIS was performed (Fig. S18 in the ESM). The EIS results in alkaline aqueous solution reveal that 5% SCO exhibited the least ohmic/bulk resistance among the as-prepared SCO electrocatalysts. Meanwhile, 0.5% Ce-SCO exhibited the least ohmic resistance among the Ce-doped 5% SCO. Furthermore, both 0.5% Ce-SCO and 5% SCO showed lower ohmic resistance in saline electrolyte than in non-saline electrolyte which could be due to the presence of higher concentration of ions in alkaline saline water than in alkaline water.

3.2.2 Corrosion inhibition in simulated alkaline saline water

To emulate the harsh conditions encountered in seawater, the best electrochemically performing catalysts in alkaline water were again

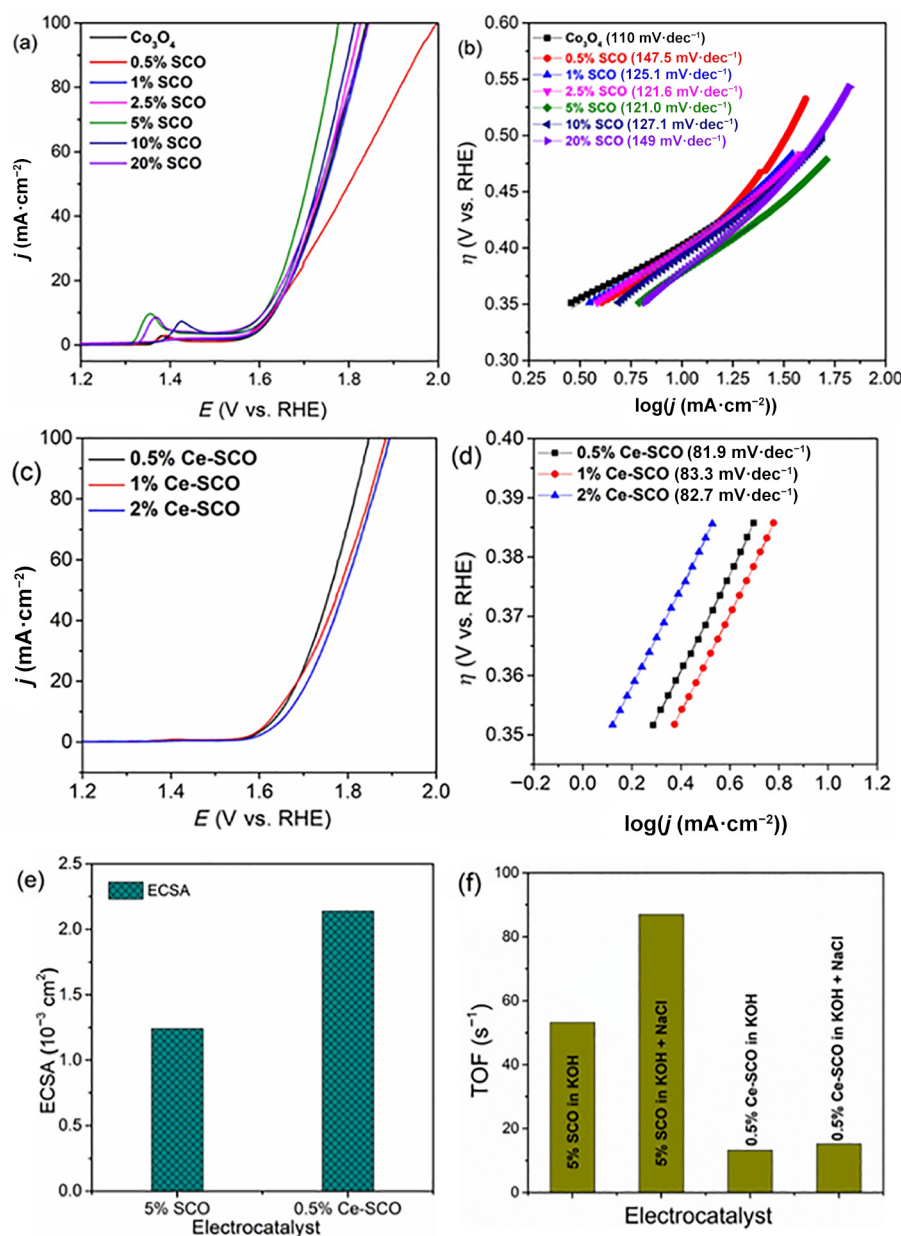


Figure 6 Electrochemical OER analyses: (a) LSV curves for the as-prepared SCO and Co₃O₄ catalysts in 1.0 M KOH. (b) The corresponding Tafel plots and Tafel slopes. (c) LSVs for the as-prepared Ce-doped SCO catalysts in 1.0 M KOH, and (d) their corresponding Tafel plots along with their Tafel slopes. (e) ECSA of best-performing electrocatalysts in 1.0 M KOH electrolyte. (f) TOF at 1.6 V vs. RHE of undoped SCO and 0.5% Ce-SCO in saline and non-saline electrolytes.

investigated in alkaline saline water (1.0 M KOH + 0.5 M NaCl). The polarization curves indicate that the undoped 5% SCO and Ce-doped in 5% SCO exhibit a higher electrochemical activity near the onset potential in saline electrolyte than in the non-saline counterpart, as demonstrated in Fig. 7(a). As can be seen from the results in Figs. 7(a) and 7(b), 0.5% Ce-SCO exhibits significant corrosion resistance by retarding the CER in the saline electrolyte. On the contrary, undoped 5% SCO contributes majorly to CER and is also prone to nickel foam corrosion, as can be seen from Fig. 7(a) and Fig. S19 in the ESM. The LSV of 0.5% Ce-SCO after 1000 CV cycles in saline electrolyte indicate that there is a minimal decrease in OER performance after 1000 CV cycles (Fig. S22 in the ESM).

As mentioned earlier, the LSV results indicate that the onset potential for OER has increased from 350.0 to 410.0 mV for 10 mA·cm⁻² current density for 5% SCO to 0.5% Ce-doped 5%

SCO, respectively. This implies that activity has slightly decreased on introduction of Ce as a protective layer of CeO_x was formed around the active OER electrocatalyst. However, the selective permeation of H₂O and blockade of chloride ions by CeO_x layer has suppressed the competitive CER (Scheme 1). This has selectively enhanced OER kinetics in saline conditions, which also reflects from the decreased Tafel slope. Moreover, from the LSV and CV of 5% SCO and Ce-doped SCO samples in 1.0 M KOH, and 1.0 M KOH + NaCl electrolytes, respectively; it was found that Ce-doped SrCoO_x has remarkably diminished the CER (Fig. 7(a)).

3.2.3 Theoretical mechanism of corrosion inhibition

The results suggest that Ce-doping has a role in corrosion resistance in the saline electrolyte. Ce doping in 5% SCO is expected to introduce structural stability owing to the reduced

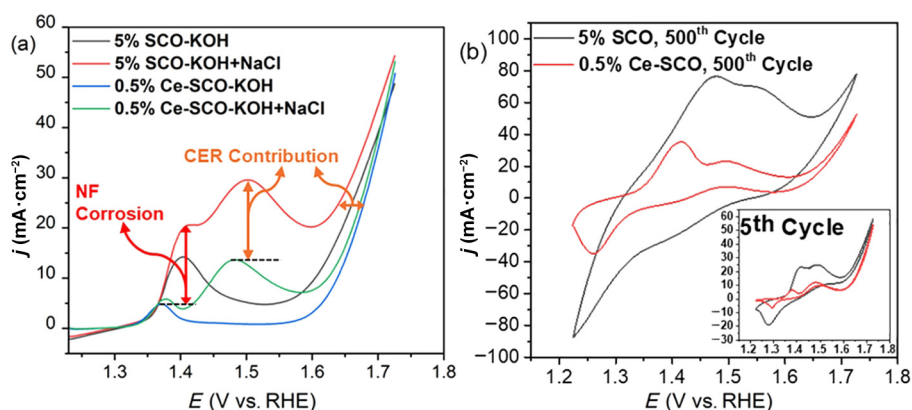
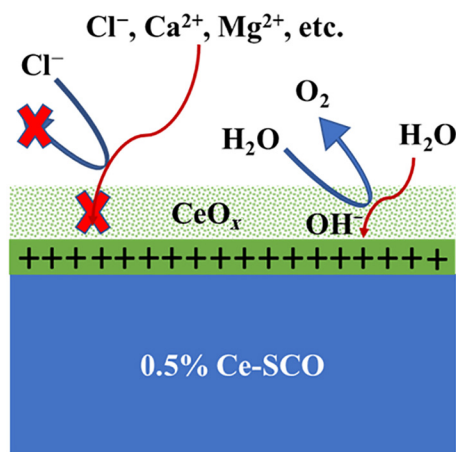


Figure 7 Determination of CER contribution. (a) LSV of 5% SCO and 0.5% Ce-doped SCO in saline and non-saline electrolytes portraying the CER and NF corrosion faced by undoped 5% SCO, and (b) CVs of 5% SCO and 0.5% Ce-SCO in saline electrolyte after 500 cycles (inset: 5 cycles).



Scheme 1 Schematic representation of corrosion mechanism of Ce-SCO as anodic OER material.

lattice strain on exchange of Sr²⁺ and Co²⁺/Co³⁺ with the Ce³⁺/Ce⁴⁺ ions due to the comparable ionic radii. Ce doping was found to reduce the leaching of Sr and Co ions under corrosive conditions by stabilizing their oxidation states, as observed in the ICP-MS results which confirms the occurrence of corrosion resistance.

As the Ce ions contribute electrons via its 4f orbitals, the electronic structure of Ce-doped SrCoO_x modifies due to the migration of the fermi level closer to the conduction band, thereby enhancing the overall electronic conductivity and electrocatalytic activity.

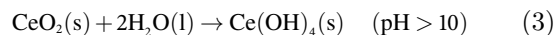
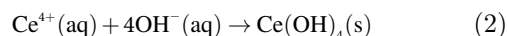
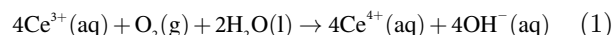
We propose that introduction of Ce in SrCoO_x has led to the generation of defect-rich sites which facilitates the formation of positively charged passivation layer near the surface of the electrocatalyst. This passivation layer sacrificially dissipates the tendency of chloride ions towards CER at the electrocatalyst surface. Further the presence of CeO_x nanoparticles and subsequent formation of CeO_x sheath around the SCO electrocatalyst can hydrolyse in extreme alkaline conditions (as shown in possible Eqs. (1)–(3)) [56–58] at the corrosion potential of 0.90 V vs. RHE according to the Pourbaix diagram of cerium [59]; induces the formation of a semi-permeable layer which allows faster entry of the beneficial OH⁻ ions compared to the corrosive Cl⁻ ions. The formation of wide hydration layer on the SrCoO_x surface may hamper the Cl⁻ ions from adsorption and transport to the bulk lattice. This can be further corroborated by the fact that the ionic radius of Cl⁻ is larger than that of OH⁻ and O²⁻ which could impede the entry of Cl⁻ ions. The CeO_x layer is also self-repairing, as Ce can switch between Ce³⁺ and Ce⁴⁺,

stabilizing the protective CeO_x layer under dynamic corrosive conditions. The Ce³⁺/Ce⁴⁺ redox pair may provide enhanced active sites for OER, to exhibit higher OER activity while maintaining the structural integrity.

From the LSV results, it was confirmed that although Ce-doping slightly increase the onset for OER, but it significantly improves the Tafel slope which can be attributed to the selective permeation of ions to the catalyst surface, avoiding the competitive reactions like CER.

Thus, Ce-doping was found to undergo the surface reconstruction of the SCO electrocatalysts for OER process [60]. Furthermore, cobalt and strontium are predicted to form passivated oxides thereby preventing the dissolution of their ions in the electrolyte through chloride adsorption as per their Pourbaix diagram [61, 62]. This strongly coupled interaction between the OH layer (and/or H₂O molecules) with the bimetallic oxide surface in the alkaline electrolyte can fend off the corrosive ions from interacting with the electrocatalyst's active sites [63, 64].

At 0.90 V vs. RHE:



To further examine its anti-corrosion ability, the undoped 5% SCO and various Ce-doped SCO samples including 0.5% Ce-SCO was subjected to corrosion experiments using linear polarization technique in saline and non-saline electrolytes, as depicted in Fig. 8(a), Figs. S20 and S21 in the ESM. It was found that 0.5% Ce-SCO exhibited a least corrosion current with respect to undoped 5% SCO and its counterparts in saline electrolyte, proving the beneficial anti-corrosive properties of the Ce ions. Also, the j_{corr} was found to decrease with increasing Ce dopant concentration. The 0.5% Ce-doped SCO showed the lowest corrosion current (−1.10 μA·cm⁻²) among the Ce-doped SCO, which indicates an effective suppression of corrosive CER.

3.2.4 Corrosion inhibition in real seawater

We have also carried out electrocatalytic water splitting on real seawater samples collected from a local beach in Abu Dhabi, UAE (Al Hudaibat Island; 24°24'34.2"N, 54°21'13.9"E). The seawater sample collected was centrifuged three times to remove any unwanted particulate matter. After mixing with 1.0 M KOH, OER was performed for up to 45 hours. LSVs were taken before and

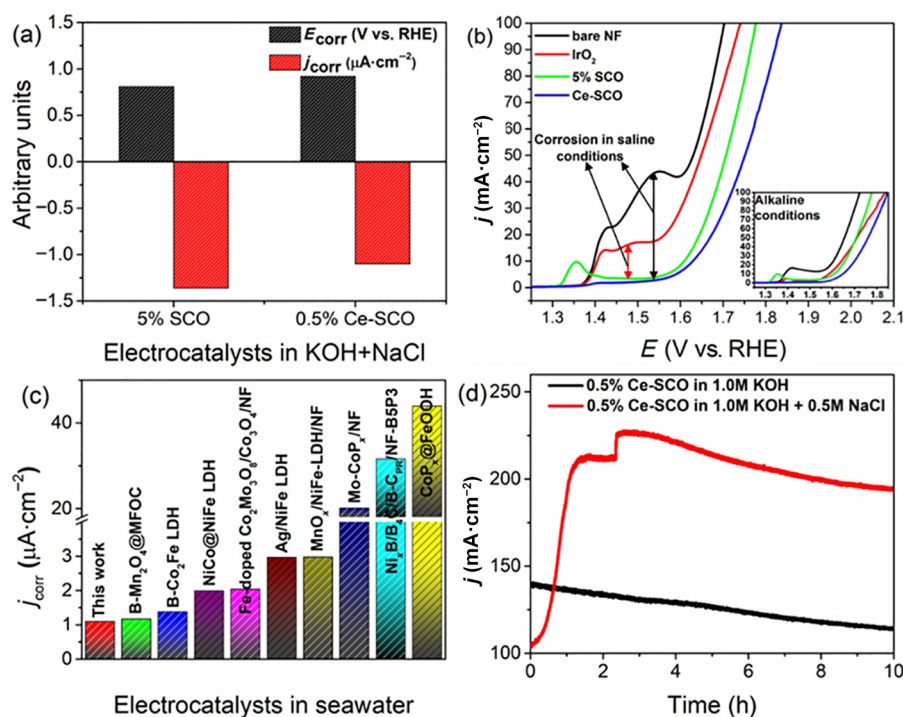


Figure 8 Electrochemical OER corrosion. (a) Corrosion potential (E_{corr} in V vs. RHE) and corrosion current density (j_{corr} in $\mu\text{A}\cdot\text{cm}^{-2}$) for 5% SCO and 0.5% Ce-SCO in alkaline saline water (1.0 M KOH + 0.5 M NaCl). (b) LSV curves under saline conditions indicate the 5% SCO and 0.5% Ce-SCO exhibits better corrosion resistance with respect to the benchmark IrO_2 or nickel foam (inset: corresponding LSV curves under alkaline conditions). (c) Comparative representation of corrosion performance of 0.5% Ce-SCO against other reported electrocatalysts in seawater-based electrolytes (references in Table S11 in the ESM). (d) Chronoamperometric stability curves of 0.5% Ce-SCO in alkaline water (1.0 M KOH) and alkaline saline water (1.0 M KOH + 0.5 M NaCl).

after the 45 hours of OER, as shown in Fig. S22 in the ESM. Linear polarization resistance showed a slight increase in corrosion current in seawater compared to simulated saline water, as expected, due to more corrosive ions in seawater than in saline water. ICP-MS of seawater was also done to ascertain the composition of seawater. Results reveal that Mg and Ca are the major cations available in seawater after Na ions. The results are provided in Table S13 in the ESM.

3.2.5 Stability of the electrocatalysts in simulated saline water/sea water

To further study the effect of saline water corrosion on the durability of electrochemical OER performance, LSV was employed before and after 1000 CV cycles which indicated a minimal shift in the onset of OER, as shown in Fig. S23 in the ESM. To find the structural stability and the probable deterioration of the crystal structure, XRD was employed on the used electrocatalysts after 1000 cycles of CV (in saline electrolyte). It was found that the Ce doping in 0.5% Ce-SCO has maintained the overall crystal structure after saline electrolysis of 1000 CV cycles, whereas the characteristic peaks from SrCoO_x have diminished in the case of the undoped 5% SCO (Fig. S24 in the ESM). While analysing the XRD spectrum, it was found that the peak at $2\theta = 28.5^\circ$ corresponds to SrO_x as per the ICDD 00-043-1031 database. It reveals that the undoped 5% SCO sample has resulted in leaching out of Sr, which has led to the formation of a separate SrO_x phase. However, in Ce-doped 5% SCO, no such peak was observed, which reveals that Ce doping has led to the structural and crystalline stability of the electrocatalyst under harsh saline conditions. This again confirms the role of Ce-doping for not only slowing down the saline water corrosion but also bringing in structural stability to the electrocatalyst.

In addition to PXRD, SEM and TEM analysis was also done after using the electrocatalysts for OER in seawater, to confirm the change in catalyst morphology. It was again observed that the Ce doping and/or CeO_x sheath had maintained the integrity of the 0.5% Ce doped 5% SrCoO_x electrocatalyst. As shown in Fig. S25 in the ESM, the doped electrocatalyst has no significant change in morphology with respect to its unused one; however, the undoped 5% SrCoO_x electrocatalyst has undergone a visible change in surface morphology. Cracks and pits corrosion are evident along with some separate individual phases accumulating on the electrocatalyst surface.

The electrocatalytic OER performance of 0.5% Ce-SCO and 5% SCO samples were compared to the benchmark OER catalyst, IrO_2 . As can be seen from Fig. 8(b), although IrO_2 exhibits a slightly smaller/better onset potential for OER in alkaline electrolytes. However, 5% SCO and 0.5% Ce-SCO show better OER kinetics as reflected from the Tafel slopes (Fig. S21(a) in the ESM), indicating faster proliferation of O_2 molecules. While comparing the corrosion resistance behaviour in saline electrolyte, it was found that 5% SCO and 0.5% Ce-SCO has remarkably diminished the CER/oxidative corrosion with respect to benchmark IrO_2 or nickel foam substrate. It is evident from the prominent oxidation humps obtained from the latter two in the polarization curves (Fig. 8(b)). Further, the linear polarization studies indicate that the synthesized 5% SCO and 0.5% Ce-SCO samples exhibit better corrosion inhibition than IrO_2 based on the calculated E_{corr} values obtained (Fig. S21(c) in the ESM). Again, the Ce-doping, which led to successful generation of a protective sheath in the bimetallic oxide, has significantly contributed to the diminishing the likelihood of CER occurrence unlike in IrO_2 . The chronoamperometry of 0.5% Ce-SCO and IrO_2 was performed in real seawater up to 45 hours of OER. The 0.5% Ce-SCO exhibited

a convincing stability with slight degradation for 45 hours of OER. On the other hand, IrO₂ had a significant dip in current within 5 hours of OER operation, as shown in Fig. S26 in the ESM. Hence, IrO₂ most likely gets corroded more easily in seawater electrolyte than our synthesized 0.5% Ce-SCO electrocatalyst, although it shows better OER activity in the alkaline electrolyte.

The electrochemical stability of an electrocatalyst is a vital factor in determining the scaling and economic feasibility of the process. The 0.5% Ce-SCO demonstrates slightly better durability (Fig. 8(d)) under corrosive saline conditions as the chronoamperometry reveals a more stable current output compared to non-saline conditions over a period of 10 hours. The increase in current density could be attributed to the presence of extra conducting ions in the saline electrolyte. The electrocatalyst showed extensive amounts of gas bubbles released throughout the duration of chronoamperometry experiment. Interestingly, almost similar decrement in current density of 0.5% Ce-SCO was observed in alkaline water and saline-alkaline water after 10 hours of the experiment, demonstrating the role of Ce for corrosion resistance in brine water electrolysis. Furthermore, the stability of Ce in SrCoO_x can be confirmed through the ICP-MS method where a low Ce content was leached out when the Ce-doped SrCoO_x samples were dispersed in the alkaline electrolyte (Table S12 in the ESM).

To further assess the scalability of 0.5% Ce-SCO for seawater electrolysis, it was compared against other electrocatalysts mentioned in the literature as shown below in Fig. 8(c) (and Table S11 in the ESM). The 0.5% Ce-SCO shows the least corrosion current ($j_{\text{corr}} = -1.10 \mu\text{A}\cdot\text{cm}^{-2}$), among the reported ones, which suggests that it might incur the slowest corrosion rate. It also shows a high corrosion potential (0.90 V vs. RHE) which could indicate towards an inferior corrosive tendency [65].

In view of the above results, the strategy of rare earth metal doping in various bimetallic oxide systems can broaden the scope of anticorrosive materials for wider applications in the marine and terrestrial ecosystems.

4 Conclusion

This work highlights the anticorrosive properties of bimetallic SrCoO_x on Ce doping in the simulated alkaline saline and seawater electrocatalyst systems. We found that Ce-doping can generate defects in the SrCoO_x lattice and forms a thin protective layer of CeO_x which acts as a passivation layer for suppression of corrosive CER, while still maintaining a high OER activity. The incorporation of Ce in the 5% SrCoO_x lattice was confirmed from the XRD analysis as revealed from the shift of peaks to higher 2θ values due to lattice expansion. The TEM-EDS further confirmed the doping of cerium in the SrCoO_x lattice while the surplus Ce has deposited on its surface as CeO_x nanoparticles. XRD also revealed reflections for CeO₂ phase, which was also evident from HR-TEM and SEM-EDX results. XPS and EDX data further revealed that the elemental compositions are in close agreement to the feed ratios; and Ce doping selectively replaced Sr in the lattice, and not Co. High resolution XPS analyses suggested formation of Ce⁴⁺, Sr²⁺ and Co²⁺ as preferred oxidation states, confirming the formation of CeO₂ on the electrocatalyst surface; and the generation of defective vacancies when Ce³⁺ replaces Sr²⁺ in the lattice.

The Ce-doped SCO electrocatalysts were found to show enhanced OER activity in alkaline and saline alkaline electrolytes. The 0.5% Ce-SCO exhibited the least Tafel slope (81.9 mV·dec⁻¹)

with respect to its counterparts and the benchmark IrO₂, suggesting its superior OER kinetics. Ce-doping was found to enhance the electrochemically active surface area through successful generation of defects as indicated by its higher ECSA compared to the undoped SCO. The superior TOF values of both 5% SCO and 0.5% Ce-SCO in saline electrolyte than in alkaline electrolyte can be attributed to the faster O₂ release. Doping of 0.5% Ce in 5% SCO led to the least corrosion current ($j_{\text{corr}} = -1.10 \mu\text{A}\cdot\text{cm}^{-2}$) and a high corrosion potential (0.90 V vs. RHE), which indicates its enhanced ability in decelerating the corrosive CER, even better than the benchmark IrO₂ electrocatalyst. The best obtained electrocatalyst, 0.5% Ce-SCO, exhibited convincing stability for at least 45 hours of seawater OER; and showed minimal degradation after 500 CV cycles. The structural stability tests performed through XRD and diminished leaching of the ions in the alkaline electrolytes revealed through ICP-MS analyses also confirm the viability of the current electrocatalyst materials.

In conclusion, we believe using environmentally friendly and low cost SrCoO_x as a superior electrocatalyst for saline water splitting, while exploring the mechanism of CER suppression by Ce-doping through a passivation layer formation may encourage the exploration of rare-earth elements in minute quantities for development of robust and efficient seawater electrodes. These electrodes can use abundant marine water resource for overall water splitting which can conserve freshwater reserves, keeping upscaling of this technology into consideration. The current work can have broader applications in other corrosion-prone systems operated in marine platforms.

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Declaration of conflicting interests

The authors declare no conflicting interests regarding the content of this article.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Supplementary Materials. Additional data related to this paper may be requested from the corresponding author upon request.

Electronic Supplementary Material: Supplementary material (further details of the XRD patterns; SEM and TEM images and elemental analysis; high resolution XPS; Tafel plots, cyclic voltammograms, impedance spectrographs and stability tests) is available in the online version of this article at <https://doi.org/10.26599/NRE.2025.9120162>.

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