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Amorphous cobalt-cerium binary metal oxides as high performance electrocatalyst for oxygen evolution reaction

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Abstract: The amorphous Co-Ce binary metal oxides $\text{Co}_{1-y}\text{Ce}_y\text{O}_x$ prepared by the photochemical metal-organic deposition (PMOD) method is developed as high performance electrocatalysts for oxygen evolution reaction (OER). The influence of Ce content on the OER activity is investigated in terms of geometric and electronic factors. Ce can remarkably enhance the OER activity of CoO_x due to the synergistic effect of surface area, Co^{3+} content, and metal-OH bond strength when the content of Ce is less than 60%. $\text{Co}_{0.9}\text{Ce}_{0.1}\text{O}_x$ supported on fluorine-doped tin oxide (FTO) coated glass substrate shows overpotential of 320 (2) mV at 10 mA cm^{-2} in 1 M KOH solution. The OER mechanism exploration reveals that the rate determining step changes with the Ce content due to the variation of metal-OH bond strength. This work sheds light on the design of high-performance yet cost-effective OER catalysts.

Keywords: Hydrogen production; Oxygen evolution reaction; Cobalt oxide; Cerium

1. Introduction

Electrochemical water splitting has been deemed as a promising technology for H₂ production with electricity generated from intermittent and renewable energy sources such as solar and wind [1]. Two half reactions in terms of hydrogen evolution reaction (HER, $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ in acid; $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ in base) at the cathode and oxygen evolution reaction (OER, $2\text{H}_2\text{O} - 4\text{e}^- \rightarrow 4\text{H}^+ + \text{O}_2$ in acid; $4\text{OH}^- - 4\text{e}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O}$ in base) at the anode are involved in the overall water splitting. Compared to HER, the kinetics of OER is very sluggish due to the transfer of four-proton and four-electron and is always the performance determining factor [2]. Therefore, high overpotential is required to achieve desirable activity for practical application but results in low efficiency. Accordingly, it is of great importance to develop highly active OER catalysts in order to reduce the overpotential and thus improve the efficiency. The recent years have witnessed the rapid development of non-noble metal-based OER catalysts (oxides, oxyhydroxides, etc.) as alternatives to noble-metal oxides (IrO₂ and RuO₂) [3].

The cobalt-based materials are among the most studied OER catalysts due to their excellent electrocatalytic activity. Recent results reveal that compared with NiO_x and FeO_x, CoO_x shows higher intrinsic activity [4]. Its OER activity can be further improved. Generally, the OER activity is determined by both geometric and electronic factors. The geometric factor pertains to the specific surface area and concentration of active sites whilst the electronic factor to the nature of active sites and electronic structure. High surface area Co-based materials generally show higher OER activity

[5]. Since OER happens only after the active species (e.g., Fe^{4+} , Co^{4+} , Ni^{4+}) [6] have been formed, the potential at which O_2 starts to evolve from the catalyst surface is closely associated with the potential of the conversion of metal/metal oxide or lower metal oxide/higher metal oxide couples [7, 8]. The ideal couple has redox potential lower or similar to the theoretical potential of OER. Accordingly, $\text{Co}_2\text{O}_3/\text{CoO}_2$ with low potential is good OER catalyst [7, 8]. The electrocatalytic activity is closely associated with the metal-OH bond strength for oxides and further analysis reveals that it depends on the occupancy of the 3d electron with an e_g symmetry of surface transition metal cations in the oxide [9, 10]. The peak OER activity is at an e_g occupancy close to unity, which has been proved in $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ [11]. Its measured intrinsic OER activity is higher than that of IrO_2 nanoparticles by at least an order of magnitude. Furthermore, the content of M^{3+} in the spinel oxides such as Li-doped Co_3O_4 and NiCo_2O_4 has been suggested to determine the OER activity [12, 13]. Higher content of M^{3+} contributes to the enhanced activity [14]. Such conclusion is also applicable to the amorphous LaCoO_x oxides. The amorphous $\text{La}_{0.7}\text{Ca}_{0.3}\text{CoO}_x$ shows the highest OER activity among the Ca-containing catalysts owing to the higher concentration of Co^{3+} [15]. In addition, increasing the electrical conductivity can also enhance the OER activity by doping and/or employing highly conductive supports [16-19].

CeO_2 is an interesting material with feasible conversion between Ce^{3+} and Ce^{4+} and high oxygen storage capacity (OSC), which has been widely employed in catalysis [20]. Actually, it is found that Ce species can modify the activity of the OER

catalysts through different mechanisms [18, 21-28]. For example, the high performance of the FeOOH/CeO₂ heterolayered nanotubes supported on nickel foam is attributed to the abundant heterostructure interface of FeOOH/CeO₂ and high OSC [22]. CeO_x deposited on the CoO_x film promotes the effective formation of CoOOH by perturbing the electronic structure of surface Co species and optimizing the binding energy of intermediate oxygenated adsorbates [23]. The high throughput screening found that the Ce-rich composition Ni_{0.3}Fe_{0.07}Co_{0.2}Ce_{0.43}O_x demonstrated high OER activity[26]. All those results demonstrate that Ce can be employed to tune the OER catalysts. However, most studies are based on the crystalline materials. For example, the genuine structure of the Ce-modified transition metal oxide catalysts is actually nanocrystalline [26-28]. They are stable two-phase nanostructure composed of 3-5 nm diameter crystalline of fluorite CeO₂ intimately mixed with 3-5 nm crystallites of transition metal oxides alloyed in the rock salt NiO structure [27]. There are very limited studies of the effect of Ce-addition on the amorphous OER catalysts although they generally show higher activity compared with their crystalline counterparts [17, 29]. High-performance amorphous Ni_{0.95}Ce_{0.05}O_x has been prepared by electrodeposition. However, Ce enrichment is found at the surface [18]. In addition, the electrodeposition technique is not necessarily applicable to every metal and is rather sensitive to the voltage protocol, which makes the accurate control of composition difficult.

Herein, the influence of Ce content on the OER performance of amorphous CoO_x, Co_{1-y}Ce_yO_x (y = 0-1), was systematically studied over the whole composition range.

The Co-Ce binary metal oxides were fabricated by the photochemical metal-organic deposition (PMOD) process, which has been used to prepare unitary, binary, ternary, and quaternary amorphous metal oxides with accurate composition and homogeneous elemental distribution [15, 29-34]. The apparent OER activity of CoO_x can be enhanced by < 60% Ce addition, which is superior to or comparable with that reported other ions-modified Co-based catalysts. The activity-composition relationship and the OER mechanism are discussed based on various characterization results.

2. Experimental section

2.1. Catalyst fabrication

The amorphous materials were prepared by the PMOD process on the fluorine-doped tin oxide (FTO) coated glass substrates ($\text{Co}_{1-y}\text{Ce}_y\text{O}_x/\text{FTO}$, $y = 0-1$), which have been cleaned sequentially with detergent, deionized water ($\text{DI-H}_2\text{O}$) and ethanol. The cobalt (II) 2-ethylhexanoate (approx. 65% (w/v) in mineral spirits, Alfa Aesar) and cerium (III) 2-ethylhexanoate (49% in 2-ethylhexanoic acid, Strem) precursors were prepared into 15% w/w solution at different molar ratios with hexane (Alfa Aesar, 98%+) as the solvent. After mixed under ultrasonication, the precursor solutions were spin-coated on the FTO substrates (3000 rpm, 1 min). The samples were then irradiated for 12 h under an ultraviolet (UV) lamp ($\lambda = 185$ and 254 nm) to decompose the organic ligands. This process was monitored by Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer). The samples were calcined at 100 °C for 1 h before use.

The nickel foam (NF, 30 mm × 30 mm × 1 mm, hole: $\Phi 0.2$ mm) was also used as

the support ($\text{Co}_{1-y}\text{Ce}_y\text{O}_x/\text{NF}$, $y = 0-1$), which was treated by 3 M HCl, DI- H_2O and ethanol successively before use. The NF was immersed in the precursor solution (5% w/w) for 5 min, followed by UV irradiation for 24 h. The mass loading of catalysts on NF support is $\sim 1.8 \text{ mg cm}^{-2}$.

2.2. Electrochemical characterization

The electrochemical performance of $\text{Co}_{1-y}\text{Ce}_y\text{O}_x$ ($y = 0-1$) was measured by an electrochemical workstation CHI 760E with a three-electrode system, where the catalyst films on FTO and NF substrates, Pt mesh, and Ag/AgCl (saturated KCl solution) are the working, counter, and reference electrodes, respectively. Unless otherwise specified, the electrolyte is 0.1 M KOH solution. The linear sweep voltammetry (LSV) curves were measured from 1.00 to 1.68 V vs. RHE at the scan rate of 10 mV s^{-1} . The cyclic voltammetry (CV) was tested in the potential range of 0.88-1.65 V vs. RHE at the sweep rate of 10 mV s^{-1} for activity evaluation. To measure the double-layer capacitance (C_{dl}), the CV was scanned in the non-Faradaic potential range (1.16-1.23 V vs. RHE for $\text{Co}_{1-y}\text{Ce}_y\text{O}_x/\text{FTO}$ and 1.09-1.19 V for $\text{Co}_{1-y}\text{Ce}_y\text{O}_x/\text{NF}$) at various sweep rates ($10-70 \text{ mV s}^{-1}$). The reaction order was determined by LSV in KOH of different concentration (0.1, 0.2, 0.3, and 0.35 M) with KNO_3 as the supporting electrolyte to keep the ionic strength constant. The impedance spectra were recorded with an AC amplitude of 10 mV and various DC potentials in the frequency range of 10^6-10^{-2} Hz . The results were fitted with the ZSimpWin software. The durability test was performed with the chronopotentiometric technique at the current density (J) of 1 mA cm^{-2} for $\text{Co}_{1-y}\text{Ce}_y\text{O}_x/\text{FTO}$ and 5 mA cm^{-2}

for $\text{Co}_{1-y}\text{Ce}_y\text{O}_x/\text{NF}$ over 100 h.

All potentials and overpotentials were corrected with 100%- iR_s drop. The potentials are converted to RHE by $E \text{ (vs. RHE)} = E \text{ (vs. Ag/AgCl)} + E_{\text{Ag/AgCl}} \text{ (vs. NHE)} + 0.059 \times \text{pH} - iR_s$. The reference electrode potential ($E_{\text{Ag/AgCl}} \text{ (vs. NHE)}$) was calibrated with the method reported elsewhere [29]. The solution resistance (R_s) was measured by impedance spectroscopy. The current density (J or J_{ge}) was based on the geometric surface area of the films. The specific current density (J_{sp}) was calculated with the relative roughness factor normalized to that of Ce-free samples [15]. When calculating J or J_{ge} for catalysts loaded on NF, the area was multiplied by 2 because both sides of NF can participate in the OER reaction.

2.3. Other characterization

The surface and cross-section microstructures of the catalysts were observed by scanning electron microscopy (SEM, JSM-7800F) equipped with an energy dispersive spectroscopy (EDS) unit. The X-ray photoelectron spectra (XPS) of catalyst films were recorded on a Thermo ESCALAB-250 spectrometer with monochromatic Al K α radiation (1486.6 eV). The binding energy (BE) is calibrated with the adventitious C 1s peak at 284.6 eV. All XPS data were analyzed with the CasaXPS software.

3. Results and discussion

3.1. Microstructure of catalyst films

The amorphous catalyst films were prepared by the facile and scalable PMOD process. The ligands of the precursors absorb UV light and decompose into CO_2 and H_2O . The metal, formed by the electron transfer from ligand to metal center [33], is

oxidized to metal oxide under ambient air atmosphere. The decomposition of ligands can be traced by FTIR and is completed within 12 h (Fig. S1). The thickness of the resultant films is found to be ~200 nm (Fig. S2), which is in agreement with previous report [29]. The surface of $\text{Co}_{1-y}\text{Ce}_y\text{O}_x/\text{FTO}$ ($y = 0-1$) films (Fig. S3) is featureless except cracks ($y = 0-0.2$) and also mesh-grid on the surface of sample with $y = 0.2$. The surface roughness is decreased for samples with $y > 0.2$, which will be discussed below. The elements distribute homogeneously through the films (Fig. S4).

3.2. OER activity of catalyst supported on FTO

The electrocatalytic activity of $\text{Co}_{1-y}\text{Ce}_y\text{O}_x/\text{FTO}$ ($y = 0-1$) towards OER is first evaluated by LSV in 0.1 M KOH and the results are shown in Fig. 1a. The corresponding Tafel plots derived from LSV are given in Fig. 1b. The parameters to evaluate the activity, i.e., Tafel slope, overpotential (η) at 1 and 10 mA cm^{-2} , are illustrated in Fig. 1c and d as a function of Ce content, respectively. The pure CeO_x is almost completely inactive for OER over the potential range studied here (Fig. S5). However, addition of 10% Ce enhances the activity of CoO_x remarkably. The activity decreases with further Ce content but is still higher than that of pure CoO_x when $y \leq 0.5$. Excessive Ce ($y > 0.5$) results in decreased activity. The sample with $y = 0.1$ ($\text{Co}_{0.9}\text{Ce}_{0.1}\text{O}_x$) exhibits the highest activity, $\eta = 213$ (2) and 353 (4) mV at 1 and 10 mA cm^{-2} , respectively. The activity is increased in higher concentration of electrolyte, $\eta = 158$ (1) and 320 (2) mV at 1 and 10 mA cm^{-2} , respectively, in 1 M KOH (Fig. S6). The activity in 0.1 M KOH is higher than that of other elements added amorphous CoO_x -based catalysts prepared with the same PMOD procedure, $\text{Co}_{1-y}\text{Fe}_y\text{O}_x$,

Co_{1-y}Ni_yO_x [29, 30], LaCoO_x [15, 32], La_{0.7}Ca_{0.3}CoO_x [15], Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_x [31], which shows the advantage of the Ce element in promoting the OER activity. Furthermore, the activity of the present amorphous Co_{0.9}Ce_{0.1}O_x in 1 M KOH is superior to or comparable with that reported Co-based OER catalysts at 10 mA cm⁻² [21-25, 35, 36]. For example, η is 313 mV for Ce-deposited CoO_x on Ti substrate [23], 310-410 mV depending on the preparation method for Ni_{0.3}Fe_{0.07}Co_{0.2}Ce_{0.43}O_x supported on GC [26], 340 mV for amorphous Co-MoO_x on GC [23], 360 mV for the ultrafine monolayer Co-containing layered double hydroxide nanosheet [35], 340 mV for the S, N co-doped carbon nanotube-encapsulated core-shelled CoS₂@Co nanoparticles [36]. In addition, Co_{0.9}Ce_{0.1}O_x/FTO ($y = 0.1-0.5$) outperforms the benchmarked water oxidation catalysts reported by the Jaramillo's group [37]. The detailed comparison with the commercial IrO₂ and RuO₂ and some recently reported representative OER catalysts can be found in Table S1. The high OER activity of Co_{1-y}Ce_yO_x here is closely associated with its uniformly amorphous nature, with more coordinately unsaturated cation sites available for reaction and the isotropic and single-phase characteristics [38].

Except the slight increase from 95.6 (1.1) mV dec⁻¹ for $y = 0$ to 104.7 (1.7) mV dec⁻¹ for $y = 0.1$ and 105.9 (2.5) mV dec⁻¹ for $y = 0.2$ samples at low Ce content, the Tafel slope decreases quickly with higher Ce content, from 86.7 (1.8) mV dec⁻¹ for $y = 0.4$ to 73.8 (0.1) mV dec⁻¹ for $y = 0.8$. Such Tafel slope values are common for the Co-based OER catalysts [9, 10, 16, 23, 25, 39, 40]. The variation of the Tafel slope is an indicator of the change of rate determining step (RDS).

3.3. Double layer capacitance

To explore the reasons for the variation of OER activity of $\text{Co}_{1-y}\text{Ce}_y\text{O}_x/\text{FTO}$ ($y = 0-1$) with Ce content, both geometric and electronic factors are taken into account. Considering the differences in the surface roughness (Fig. S3), C_{dl} , which is proportional to the surface area and can be deemed as a geometric factor, is measured by CV in the non-Faradaic potential range with various scan rates (Fig. S7). The variation of C_{dl} with Ce content is presented in Fig. 2a. C_{dl} increases with 10% addition of Ce but then declines dramatically with Ce content. The high activity for sample with $y = 0.1$ (Fig. 1) can be ascribed to the large C_{dl} [17, 18, 25]. However, C_{dl} should not be the sole factor for the activity because the samples with $y = 0.2-0.5$ have lower C_{dl} but show higher OER activity than the sample with $y = 0$. To remove the influence of surface area on the activity, the specific current density (J_{sp}) at η of 0.25 and 0.35 V, calculated with C_{dl} , is provided in Fig. 2b. The corresponding geometric current density J_{ge} is also included for comparison. J_{sp} exhibits distinctively different dependence on Ce content compared with J_{ge} . It increases with Ce slowly when $y \leq 0.2$ and then quickly when $y \geq 0.4$. It suggests that the intrinsic activity of CoO_x can be significantly improved by Ce addition through tailoring the electronic factors. Accordingly, the OER activity of samples with $y = 0.2-0.5$ is mainly dominated by the electronic factors (i.e., intrinsic activity) whereas by geometric factors for samples with $y > 0.5$. Both geometric and electronic factors are important for sample with $y = 0.1$.

3.4. CV results

To further explore the electronic factors, the CV curves of $\text{Co}_{1-y}\text{Ce}_y\text{O}_x/\text{FTO}$ ($y = 0-1$) were recorded (Fig. S8). The CV results in the potential range of 0.9-1.3 V vs. RHE are shown in Fig. 3a. The redox peaks (0.95-1.15 V vs. RHE) correspond to the conversion between Co^{2+} and Co^{3+} [15, 29, 32]. Two obvious oxidation peaks are found for samples with $y = 0-0.2$, which is probably due to the slight differences in the local environment of Co^{2+} . No redox peaks are found for the sample with $y = 0.8$. In addition, no redox peaks related with $\text{Ce}^{4+}/\text{Ce}^{3+}$ are observed because it is beyond the potential scope studied here. The position of redox peaks varies with Ce content, indicating that the electronic structure of cobalt is modulated by Ce adding, which has been widely reported [18, 21-24].

For the samples $\text{Co}_{1-y}\text{Ce}_y\text{O}_x/\text{FTO}$ ($y = 0.4, 0.5$, and 0.6) with only one oxidation peak, the oxidation peak potential increases in the order of $y = 0.4 < y = 0.5 < y = 0.6$. Although Co^{4+} has been suggested to be the OER active species for the Co-based OER catalysts [2, 6], it is difficult to observe from CV because of the overlapping of $\text{Co}^{3+} \rightarrow \text{Co}^{4+}$ with the OER process. Therefore, the potential of $\text{Co}^{2+} \rightarrow \text{Co}^{3+}$ is used to estimate the potential of $\text{Co}^{3+} \rightarrow \text{Co}^{4+}$, i.e., lower potential for $\text{Co}^{2+} \rightarrow \text{Co}^{3+}$ means lower potential for $\text{Co}^{3+} \rightarrow \text{Co}^{4+}$. According to Tseung and coworkers, the lower the redox potential, the higher the activity [7, 8]. The order of the oxidation potential is well agreement with the OER activity (Fig. 1), $y = 0.4 > y = 0.5 > y = 0.6$.

The sample with $y = 0.1$ shows the highest redox current density. The total charge involved in the redox peaks (Q_{ox}) is an estimation of the amount of Co^{2+} in the samples, which is calculated by integration of the oxidation peaks and shown in Fig.

3b. Q_{ox} is maximum for the sample with $y = 0.1$ and then decreases with higher Ce content; it is 0 for sample with $y = 0.8$. It should be noted that the total cobalt content is different for samples $Co_{1-y}Ce_yO_x$ with different Ce level. The obtained Q_{ox} is just a reflection of the absolute content of Co^{2+} in the samples. To explore the relative content of Co^{2+} in the catalyst films, the oxidation charge is calculated considering the difference in Co content and marked as $Q_{ox/Co}$. It is interesting that $Q_{ox/Co}$ shows similar dependence on Ce content with Q_{ox} . The samples with $y = 0.2-0.8$ possess higher concentration of Co^{3+} , which is favorable for the higher intrinsic OER activity [12-15].

3.5. XPS results

XPS is a powerful technique to detect the oxidation state of metal ions at the surface, which is closely associated with the catalysis process. The high resolution XPS spectra of Co 2p and Ce 3d along with the fitting curves are shown in Fig. 4a and b, respectively. The results for O 1s and C 1s are given in Fig. S9 and Table S2. For the Co 2p spectra, the peaks with *BE* at $\sim 780.0/795.1$ eV and $\sim 781.4/796.7$ eV (Table S3) are assigned to Co^{3+} and Co^{2+} , respectively. The satellites at 785.3 and 790.3 eV are attributed to the shake-up peaks of Co^{3+} and Co^{2+} , respectively [41]. No peaks related with Co^{2+} are found for sample with $y = 0.8$. For the Ce 3d spectra, the peaks at 901.0 and 882.5, 907.0 and 888.2, 916.8 and 898.4 eV are assigned to the u and v, u'' and v'', u''' and v''' vibrations of Ce^{4+} , respectively, and those at 904.0 and 885.6 eV to the u' and v' vibrations of Ce^{3+} [42].

The surface concentration ratio of $Co^{3+}:Co^{2+}$ and $Ce^{4+}:Ce^{3+}$ as a function of Ce

content is shown in Fig. 4c. $\text{Co}^{3+}:\text{Co}^{2+}$ and $\text{Ce}^{4+}:\text{Ce}^{3+}$ shows almost complementary dependence on Ce content. $\text{Co}^{3+}:\text{Co}^{2+}$ remains relatively constant when $y \leq 0.4$. However, it increases sharply with Ce content (no Co^{2+} in sample with $y = 0.8$). $\text{Ce}^{4+}:\text{Ce}^{3+}$ shows the reverse trend. It is noted that the atomic ratio of $\text{Ce}^{4+}:\text{Ce}^{3+}$ varies in the range of 2.46-7.70, i.e., the Ce species exists mainly as Ce^{4+} in the as-prepared amorphous materials $\text{Co}_{1-y}\text{Ce}_y\text{O}_x$ ($y = 0-1$). It indicates that the Ce addition perturbs the electronic structure of Co species probably through the charge transfer to the nearest oxygen [18, 21-24], resulting in higher content of Co^{3+} , which is in agreement with the CV results (Fig. 3).

3.6. EIS results

EIS is used to explore the processes during OER. As shown in Fig. 5a, the spectra of all samples at 1.458 V vs. RHE show two semicircles, which can be fitted with the equivalent circuits inset in Fig. 5b. The intercept of the spectra with the real axis at the highest frequencies is the solution resistance (R_s). The semicircles at the high frequency, which maintains constant with potentials applied (Fig. S10), is related with the dielectric property of the film [15] and are fitted with resistance and capacitance of the films (R_{film} , Q_{film}). The OER process results in the semicircles at the medium to low frequencies, which are very sensitive to the potentials applied (Fig. S10) and are fitted with the charge transfer resistance (R_{ct}) and double-layer capacitance (Q_{dl}). Although the change is slight, R_{film} increases with Ce content, similar with that of Ce-doped $\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ [21]. The Ce content has a significant influence on R_{ct} . It decreases dramatically with only 10% Ce addition and remains

almost constant for samples with $y = 0.1-0.5$. It increases quickly for samples with $y > 0.5$. R_{ct} of sample with $y = 0.8$ is even higher than that of CoO_x . The variation of R_{total} with Ce content is consistent with the OER activity (Fig. 1).

3.7. OER mechanism

DFT is a powerful tool to explore the OER mechanism [18]. The difficulty of employing DFT for this work is the amorphous nature of the $Co_{1-y}Ce_yO_x$ catalysts, which makes it extremely hard to construct the actual structure for modeling. The Tafel slope combined with reaction order is an alternative for mechanistic study, for example, in the seminal work of Bockris and Otagama [9, 10]. Such methodology is adopted by many groups, the Tseung's group [12, 13], the Trasatti's group [21], the Chartier and Singh's group [39, 40, 43, 44], and recently by the Shao-Horn's group [45], just to name a few. Accordingly, to get an insight into the OER mechanism, the reaction orders of two materials $Co_{1-y}Ce_yO_x/FTO$ ($y = 0.1$ and 0.4) are measured by LSV in KOH solutions of different OH^- activity (Fig. S11) and the results are shown in Fig. 6. The reaction orders are unity and 1.3 for samples with $y = 0.1$ and 0.4 , respectively, when the potential is vs. NHE. When calculated with potential vs. RHE, it is 0.8-0.9, in consistent with that reported [45].

Based on the Tafel slopes ($70-110 \text{ mV dec}^{-1}$) and reaction orders, a possible OER mechanism is proposed and expressed with Eqs. (1-4) [10].

The theoretical Tafel slope and reaction order are 120 mV dec⁻¹ and unity if step 1 is the RDS. The case of Step 2 is complex depending on the bond strength of metal-OH and coverage. They are 60 mV dec⁻¹ and 1.25 under the Temkin isotherm with intermediate metal-OH bond strength [10], which have been found in LaCoO₃, La_{1-x}Sr_xCoO₃ and Co₃O₄ [9, 10, 39, 40].

The M-OH bond strength for the present amorphous Co_{1-y}Ce_yO_x was calculated based on the eq. (5) proposed by Ruetschi and Delahay [46] with corrections of the electronegativity term suggested by Conway and Bockris [47].

$$D(\text{M-OH}) = 38.96 - \Delta H_{\text{M}_y\text{O}_x}^0 / 2x + 23.06 (X_{\text{M}} - X_{\text{OH}})^2 \quad (5)$$

Where $\Delta H_{\text{M}_y\text{O}_x}^0$ is the negative heat of formation of the oxide M_yO_x at 298 K; X_{M} is the electronegativity of metal element and X_{OH} is 3.3.

The bond strength of Co³⁺-OH (Co²⁺-OH) and Ce⁴⁺-OH (Ce³⁺-OH) is 490.4 (529.1) and 919.5 (946.7) kJ mol⁻¹, respectively [9, 46, 48]. The addition of Ce to CoO_x increases the metal-OH bond strength of this system [21]. Considering the high concentration of coordinately unsaturated cation sites at the surface of amorphous catalysts films, high surface coverage of OH⁻ (0.2 < θ < 0.8) is likely [17, 38]. For the present Co_{1-y}Ce_yO_x system, the Tafel slope decreases from 95.6 (1.1) to 73.8 (0.1) mV dec⁻¹ when the Ce content increases from 0 to 0.8 accompanied with increased metal-OH bond strength. It infers that a combination of step 1 and step 2 is the RDS with the contribution of step 2 increasing especially at high Ce content. Based on the analysis above, it is possible to reduce the Tafel slope and thus increase the OER

activity of the amorphous $\text{Co}_{1-y}\text{Ce}_y\text{O}_x$ catalysts by tailoring the metal-OH bond strength of this system appropriately, which can pave the way to the development of high-performance OER catalysts. Such work is in progress in our group and the results will be reported elsewhere.

3.8. OER activity of catalyst supported on nickel foam

To further improve the OER activity, the amorphous catalysts are loaded onto NF, which has higher surface area and electrical conductivity compared with FTO [2]. Homogeneous catalyst films are loaded on the surface of NF support with whole coverage except cracks (Fig. S12). The LSV curves of $\text{Co}_{1-y}\text{Ce}_y\text{O}_x/\text{NF}$ ($y = 0, 0.1, 0.4$) are shown in Fig. 7a and the corresponding parameters to evaluate the OER activity are listed in Table S1. The Tafel slope remains almost unchanged compared with that on FTO support, suggesting the same OER mechanism. The OER activity is markedly increased. η to achieve 10 mA cm^{-2} decreases by $\sim 80 \text{ mV}$ compared with that on the FTO support. It is only 269 (1) mV at 10 mA cm^{-2} for $\text{Co}_{0.9}\text{Ce}_{0.1}\text{O}_x$ in 0.1 M KOH, which decreases further to 175.2 (0.1) mV in 1 M KOH (Fig. S6). The activity is higher than that reported for $\text{FeOOH}/\text{CeO}_2$ heterolayered nanotubes supported on NF ($\eta = 250$ and 350 mV at 31.3 and 140.2 mA cm^{-2} , respectively) [22], $\text{CoO}_x(\text{Ce})$ electrostatic spray deposited on carbon fiber paper ($\eta = 261$ and 302 mV at 20 and 100 mA cm^{-2} , respectively) [25] in 1 M KOH. It is also comparable with that reported recently (Table S1). EIS analysis (Fig. 7b) reveals that both R_{film} and R_{ct} decreases substantially, which contributes to the high OER activity.

3.9. Stability

The durability of $\text{Co}_{1-y}\text{Ce}_y\text{O}_x$ supported on FTO and NF is examined by the chronopotentiometry technique. As shown in Fig. 8, the samples $\text{Co}_{1-y}\text{Ce}_y\text{O}_x$ /FTO ($y = 0.1$ and 0.4) and $\text{Co}_{0.9}\text{Ce}_{0.1}\text{O}_x$ /NF show stable durability at 1 and 5 mA cm^{-2} over 100 h , respectively. Post-mortem SEM results (Fig. S13) show that cracks form during test, which are probably due to the leaching of the active cations to the solution. It is a common issue for the OER catalysts, especially for the amorphous materials [15, 17, 30, 31], which remains to be addressed.

4. Conclusions

The OER activity of amorphous CoO_x catalyst can be optimized by Ce addition ($\text{Co}_{1-y}\text{Ce}_y\text{O}_x$) through the synergistic effect of geometric and electronic factors. Ce adding enhances the activity when $y \leq 0.5$ through the modification of surface area, Co^{3+} content, and metal-OH bond strength. Excessive Ce addition ($y > 0.5$) results in declined activity due to the seriously smaller surface area although they possess high intrinsic activity. The performance can be further enhanced by loading the amorphous oxides on NF. The OER mechanism study shows that the combination of discharge of OH^- at the oxide forming adsorbed OH radicals and its subsequent electrochemical transform into a physisorbed H_2O_2 are the RDS related to metal-OH bond strength. The Ce-added catalysts exhibit excellent durability. This work shows that by tailoring the geometric and electronic factors through composition, it is probable to develop high-performance yet cost-effective OER catalysts for practical applications.

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Figure captions

Fig. 1. Electrochemical performance of $\text{Co}_{1-y}\text{Ce}_y\text{O}_x/\text{FTO}$ catalysts with different Ce content in 0.1 M KOH. (a) LSV curves at a scan rate of 10 mV s^{-1} . (b) Tafel plots and the corresponding fitted lines. (c) Tafel slopes and (d) overpotential required to attain 1 and 10 mA cm^{-2} as a function of Ce content.

Fig. 2. (a) Double-layer capacitance (C_{dl}) of $\text{Co}_{1-y}\text{Ce}_y\text{O}_x/\text{FTO}$ films with different Ce content. (b) Variation of geometric current density (J_{ge}) and specific current density (J_{sp}) with Ce content for $\text{Co}_{1-y}\text{Ce}_y\text{O}_x/\text{FTO}$ catalysts at the overpotential of 0.25 and 0.35 V in 0.1 M KOH.

Fig. 3. (a) CV curves of $\text{Co}_{1-y}\text{Ce}_y\text{O}_x/\text{FTO}$ films in the potential range of 0.9-1.3 V vs. RHE at a scan rate of 10 mV s^{-1} in 0.1 M KOH. (b) Total charge passed through the oxidation peaks in panel A and that normalized to the Co content.

Fig. 4. (a) XPS spectra of Co 2p. (b) XPS spectra of Ce 3d. (c) Variation of the $\text{Co}^{3+}:\text{Co}^{2+}$ and $\text{Ce}^{4+}:\text{Ce}^{3+}$ ratios with the Ce content.

Fig. 5. (a) Impedance spectra of $\text{Co}_{1-y}\text{Ce}_y\text{O}_x/\text{FTO}$ films at the potential of 1.458 V vs. RHE in 0.1 M KOH. (b) Variation of solution resistance R_s , film resistance R_{film} and charge transfer resistance R_{ct} with Ce content. Equivalent circuit inset in b is used to fit the impedance spectra in a and the fitting lines are also included.

Fig. 6. Reaction order for $\text{Co}_{1-y}\text{Ce}_y\text{O}_x/\text{FTO}$ ($y = 0.1$ and 0.4) films. (a) $\log J$ vs $\log a_{\text{OH}^-}$ at the potential of 0.72 V vs. NHE. (b) $\log J$ vs pH at the potential of 1.50 V vs. RHE.

Fig. 7. The electrocatalytic activity of $\text{Co}_{1-y}\text{Ce}_y\text{O}_x/\text{NF}$ ($y = 0, 0.1, \text{ and } 0.4$) in 0.1 M KOH . (a) LSV curves at a scan rate of 10 mV s^{-1} . (b) Impedance spectra at the potential of 1.459 V vs. RHE .

Fig. 8. Durability test of the $\text{Co}_{0.6}\text{Ce}_{0.4}\text{O}_x/\text{FTO}$, $\text{Co}_{0.9}\text{Ce}_{0.1}\text{O}_x/\text{FTO}$ and $\text{Co}_{0.9}\text{Ce}_{0.1}\text{O}_x/\text{NF}$ samples by the chronopotentiometry technique over 100 h in 0.1 M KOH .

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.