Characterization and Electrocatalytic Properties of
Titanium-Based Ru$_{0.3}$Co$_{0.7-x}Ce_x$ Mixed Oxide Electrodes for
Oxygen Evolution in Alkaline Solution

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Ti-supported RuO$_2$-Co$_3$O$_4$-CeO$_2$ (Ru$_{0.3}$Co$_{0.7-x}$Ce$_x$ oxide, 0 ≤ x ≤ 0.7) electrodes were prepared by sol-gel process. The phase structure, surface morphology, and microstructure of the oxide layer were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Electrocatalytic activity and oxygen evolution reaction (OER) kinetics on these electrodes in 1.0 mol·dm$^{-3}$ KOH solution were studied by recording open-circuit potential, cyclic voltammetry, and polarisation curves. The results showed that the appropriate content of CeO$_2$ could reduce the grain size and increase active surface area. The electrocatalytic activity shows a strong dependence on the CeO$_2$ content in the film. Catalytic performance of mixed oxide electrodes with 40 mol % CeO$_2$ was the best, with the greatest voltammetric charge, 86.23 mC·cm$^{-2}$, and the smallest apparent activation energy for OER at 0.60 V was 22.76 kJ·mol$^{-1}$.

1. Introduction

The oxygen evolution reaction (OER) is one of the most intensively studied electrochemical reactions due to its importance in practical applications such as water electrolysis, chloralkali cells, fuel cells, and secondary metal air batteries. The OER is a very interesting process because of its high activation overpotentials in aqueous solutions. Ruthenium is well known as one of the most active and promising elements, and RuO$_2$ has been shown to possess interesting electrocatalytic properties for the OER both in acid and alkaline solutions [1–4]. Although RuO$_2$- and IrO$_2$-coated Ti electrodes are known to possess high catalytic activity, they lack the stability required for practical applications [5]. The long-term performance of RuO$_2$ and IrO$_2$ may be improved by the addition of Co$_3$O$_4$ [6, 7]. The interest in these electrode materials is mainly due to low cost, wide disposability, stability in alkaline solution, and good electrocatalytic properties. The performance in alkaline solution of a spinel structure Co$_3$O$_4$ electrode can be optimized introducing a small amount of RuO$_2$, an oxide which itself shows poor stability in alkaline solutions [3, 7]. In many investigations, a third oxide is added to either enhance the selectivity or to optimize the activity, selectivity, and stability. CeO$_2$ is a promising candidate to modulate the electrocatalytic activity of oxide electrodes due to its high redox potential (Ce$^{III}$/Ce$^{IV}$) [4, 8–11]. In this paper, we report the investigation of the influence of nominal cerium dioxide concentration [CeO$_2$]$_x$, respectively, on surface, kinetics, and electrocatalytic properties of Ti supported Ru$_{0.3}$Co$_{0.7-x}$Ce$_x$ oxide electrodes for the OER in alkaline medium.

2. Experimental

2.1. Electrode Preparation. Thin film electrodes of nominal compositions were prepared by the sol-gel process (Calcination: 400°C). The polymeric precursor was prepared by mixing citric acid (CA) (Merck) in ethylene glycol (EG) (Merck) at 60°C. The precursor salt (RuCl$_3$·nH$_2$O (Stream Chemicals), Co(NO$_3$)$_2$·6H$_2$O (≥99.0%), and Ce(NO$_3$)$_3$·4H$_2$O (≥99.0%)) dissolved in ethanol) was then added slowly, at an M/CA/EG molar ratio of 1:3:12, where M refers to...
ruthenium, cobalt, or cerium ions. After total dissolution of the precursor salt, the temperature was raised to 90°C and kept at this level for 2 hours, under vigorous stirring. The solutions were prepared separately and mixed in the proper nominal ratio of ruthenium, cobalt, and cerium ions. Duplicate samples were prepared for each electrode composition. Sandblasted Ti supports were degreased with alkali solution by ultrasonic and etched for 2 h with boiling 10% (w/w) oxalic acid. The precursor mixtures were applied by brushing on one side of a pretreated Ti support. After application of each coating, the electrode was heated in air to 130°C for 10 minutes, for polymerization to occur, and then fired at 400°C for 10 min. This procedure was repeated until the desired nominal oxide loading (1.5–2.0 mg oxide cm⁻²) was achieved. The final structure received 1-hour annealing at 400°C. Duplicate samples were prepared for each electrode composition. Details of the electrode preparation and final mounting are described elsewhere [12–14].

2.2. Cell, Equipment, and Solutions. Electrochemical studies were performed using 1.0 mol·dm⁻³ KOH aqueous solution as the supporting electrolyte and prepared volumetrically using Milli-Q plus quality water. Solutions were deaerated before and during each experiment using ultrapurified nitrogen gas. All of the experiments were carried out at room temperature. An experimental setup consisting of a conventional electrolytic cell with a main body (∼50 mL), one platinum sheet serving as counter electrode (2.5 cm × 2.5 cm size), and an Ag/AgCl electrode (CH, 3 mol·dm⁻³ KCl, 0.207 V versus SHE at 25°C) reference electrode was used throughout the experiments.

2.3. Techniques and Instruments. Ti supported Ru₀ₓCo₃₀₋ₓCeₓ oxide layers were characterized through X-ray analysis using a Rigaku D/MAX-2200 Model instrument using Cu (Kα) radiation (λ = 0.15418 nm) from 10 to 70° at a scanning speed of 10°·min⁻¹. Morphological information was attainted from scanning electron microscopy (SEM, Shimadzu SSX-550). The open-circuit potential (E_oc) of freshly prepared electrodes was measured during 20 min after electrode immersion in the electrolyte. In all cases, a stationary E_oc-value was reached after 15 min. Electrochemical experiments were carried out using a BAS 100 B/W instrumentation. The surface response of the electrodes was examined by cyclic voltammetric curves and potentiodynamic curves. Voltammetric curves were recorded at 50 mV s⁻¹ covering the −0.6 and 0.4 V (versus Ag/AgCl in 1.0 mol·dm⁻³ KOH) range. The voltammetric charge content in this potential range was determined by integration of the i/E profiles by Origin (version 8.0) software. When the potential was swept between 0.3 and 0.8 V (versus Ag/AgCl), potentiodynamic curves were recorded in 1.0 mol·dm⁻³ KOH at 1 mV s⁻¹.

Reaction-order experiments with respect to OH⁻ were carried out while keeping the electrode at 0.45 V and 0.75 V for 15 min. These electrode potentials were selected because they fell in the linear current domain of the tafel curves. Experiments were carried out with solutions at several different pOH values obtained by systematic substitution of KOH by KClO₄, keeping the total ionic concentration constant at 1.0 mol·dm⁻³.

3. Results and Discussions

3.1. Morphological Characterization. SEM photomicrographs presented in Figures 1(a), 1(b), 1(d), 1(e), 1(g), and 1(h) show clearly the difference in microporosity among the three samples. It was found that a deposited Ru₀₄Co₃₀₋₄Ce₄ (x = 0) oxide layer appears to be more or less severely cracked, while Ru₀₃Co₃₋₃Ce₃ (x = 0.4, 0.7) oxide deposits appeared to be more porous.

Figures 1(c), 1(f), and 1(i) show the X-ray diffraction patterns for different compositions of electrodes prepared at 400°C. For all the investigated samples, well-defined Ti peaks can be observed. Because Ti was not previously incorporated into the coating mixture, the presence of these peaks can be attributed to the Ti substrate. As shown in Figure 1(c), the RuO₂ presents a well-defined crystallinity in the rutile form, characterized by the main peaks at the positions 2θ = 28.26° and 35.24°; the Co₃O₄ spinel structures are at 2θ = 18.88°, 30.98°, 36.98°, 54.94°, and 58.94°. On the other hand, the different values of the crystallographic parameters between the RuO₂ rutile and the Co₃O₄ spinel structures lead low probability to forming a solid solution.

Compared with the non-CeO₂ electrodes, diffractograms of mixed oxide films exhibit somewhat broader peaks suggesting a lower crystallinity of active component as shown in Figures 1(f) and 1(i). The results show that CeO₂ does not form solid solutions with the rutile phase (e.g., RuO₂ and TiO₂), acting solely as a dispersant matrix for this phase, which is expected to lead to a strong increase of the electrochemically active surface area [10].

3.2. Open-Circuit Potential. Figure 2 shows the dependence of the open potential, E_oc, on the film composition for freshly prepared electrodes, measured in 1.0 mol·dm⁻³ KOH. RuO₂ and Co₃O₄ are both active materials for oxygen evolution reaction. As shown in Figure 2, introduction of CeO₂ into the binary RuO₂ and Co₃O₄ mixture causes a slight increase in E_oc.

3.3. Voltammetric Curves. Figure 3 shows representative voltammetric curves of the electrodes at different CeO₂ content. A substitute of 40 mol% Co₃O₄ by CeO₂ leads to a significant increase in the voltammetric current density; as the concentration of CeO₂ increases, the symmetry of redox peaks increases. The band located at ∼0.27 V is attributed to the Ru³⁺/Ru⁴⁺ redox couple. As discussed by Fernandes [15], the nonsymmetric profile of the broadbands located in the −0.6 to −0.3 V interval, which are also present in alkaline solution, can be correlated with a slow irreversible Faradaic reduction occurring on the oxide surface. The apparent irreversibility of the surface solid-state redox transitions can be associated with the instability of a small electrode. But it is denoted by the nonsymmetric profile of the broadbands located in the more cathodic region [15, 16].
Figure 1: XRD patterns and SEM images of the surface of \( \text{Ru}_{0.3}\text{Co}_{0.7-x}\text{Ce}_x \) oxide electrodes (a, b, c) \( x = 0.0 \); (d, e, f) \( x = 0.4 \); (g, h, i) \( x = 0.7 \).

Figure 2: Open-circuit potential on the nominal CeO\(_2\) content in 1.0 mol·dm\(^{-3}\) KOH.

When the integration of anodic and cathodic currents of the voltammetric profile is limited to more anodic regions, the ratios of \( q_a/q_c \)-ratios \( \geq 0.956 \), for all the oxide compositions. This high ratio close to unity indicates that the oxide surface is stable under the conditions applied during this work. Therefore, the addition of the CeO\(_2\) could be related to an increase in the surface area possibly by the mechanisms of the inhibition of the grain growth process or a decrease in the sintering process rate.

The voltammetric charge was obtained by integration of voltammetric cures and is plotted as a function of CeO\(_2\) content in Figure 4. The only processes occurring in the
0.6~0.4 V potential range are the surface redox transitions of Ru species and double-layer charging at the oxide-solution interface. Since the latter is as a rule small compared to the former, it measures the number of surface area active sites. This is different from the concept of surface area that also includes Ti-containing sites, but it can be defined as proportional to the electrochemically active surface area [17].

Figure 4 shows that for fresh electrodes $q^*$ goes through a maximum at about 40 mol% CeO$_2$. This can be related with morphological and microstructural changes due to the oxide mixture. As the anodic charge is proportional to the number of electrochemically active sites in the electrode surface, and CeO$_2$ presents no electrochemical activity in this potential range, it is proposed that the voltammetric charge is a function of RuO$_2$ active sites density in the electrode surface, related to an increase in the surface area possibly by the mechanisms of the inhibition of the grain growth process and/or a decrease in the sintering process rate. But the excess content of CeO$_2$ destructs the integrity of the lattice and impacts the surface active areas.

3.4. Oxygen Evolution Reaction
3.4.1. Tafel Lines. The obtained tafel plots showed a deviation from the linearity at high overpotentials. A linear tafel plot should be expected in the studied potential range, in the absence of an ohmic drop expressed as $IR_Ω$. This $IR_Ω$ value was used to fit the corrected ohmic drop polarization curve at high overpotential [18]. The influence of ohmic drop, $IR_Ω$, on the polarization curve can be written as

$$ E - IR_Ω = a + b \log i, $$

where $R_Ω$ is the total ohmic resistance, $E$ is the electrode potential, $a$ is the constant, and $b$ is the tafel slope.

Figure 5(a) shows a typical quasistationary potential sweep curve before and after $IR_Ω$ correction. The optimum $R_Ω$ values randomly distributed in the 0.2~1.8Ω interval were obtained. The $R_Ω$ values found are in excellent agreement with other RuO$_2$-based oxide electrodes submerged in similar supporting electrolyte [15]. As the resistance of the film is negligible due to the metallic conductor nature of RuO$_2$, the $R_Ω$ values can be attributed only to the solution resistance.

After the ohmic drop correction, all curves show two linear regions for all the investigated electrodes. Figure 5(b) gathers tafel slope data, $b$, determined in the low and high overpotential domains as a function of [CeO$_2$]$_x$. Tafel data reveal that the influence of [CeO$_2$]$_x$ on OER kinetics strongly depends on the overpotential domain. This behaviour is in agreement with literature reports [19] on oxide electrodes containing noble metals (e.g., Ru and Ir) as the active component. Figure 6 clearly shows that tafel slopes in the low and high overpotential domains, $b_{low}$ and $b_{high}$, are little affected by the [CeO$_2$]$_x$. At low overpotentials, tafel slopes close to 50 mV were observed. At high overpotentials, after $IR_Ω$ correction, a second tafel slope is observed randomly distributed around 120 mV for all compositions. The change of the tafel slope indicates that deviation of the experimental
3.4.2. Reaction Order with Respect to OH\(^-\), \(\zeta\)\(_{\text{OH}^-}\). Reaction order determination provides useful information to elucidate the electrode mechanism. The reaction order with respect to OH\(^-\), \(\zeta\)\(_{\text{OH}^-}\), was determined in both the low and high overpotential domains as a function of nominal oxide composition. To be significant, reaction orders must be determined at constant ionic strength to avoid diffuse double-layer effects [19]. To accomplish this, KOH concentration was varied between 0.1 and 1.0 mol·dm\(^{-3}\) keeping the ionic strength constant at 1.0 mol·dm\(^{-3}\) by systematic substitution of OH\(^-\) by ClO\(_4^-\) ions.

Keeping constant the electrode potential and considering negligible changes in water activity, the reaction order with respect to OH\(^-\), \(\zeta\)\(_{\text{OH}^-}\), for conditions of the high-field approximation, \(\eta \geq 0.1\) V, was determined using next equation:

\[
\zeta_{\text{OH}^-} = -\left[\frac{\partial \log i}{\partial \text{pOH}}\right]_{E,T},
\]

where \(\text{pOH} = -\log(\text{OH}^-)\).

Representative plots of current density as a function of OH\(^-\) concentration at constant ionic strength are reported in Figure 6 for both low (0.45 V) and high (0.75 V) overpotentials.

Figure 6 clearly shows that the linear segments in the log \(i\) versus \(\text{pOH}\) plots are parallel, revealing that \(\zeta_{\text{OH}^-}\) values are independent of \([\text{CeO}_2]_x\). Figure 7 presents the \(\zeta_{\text{OH}^-}\) data as function of \([\text{CeO}_2]_x\), showing the data are randomly scattered around unity on changing \([\text{CeO}_2]_x\) (\(\zeta_{\text{OH}^-} \approx 1\) in all cases), which show that the reaction order with respect to OH\(^-\) does...
not vary with the concentration of OH\(^-\) and the content of CeO\(_2\).

3.5. Apparent Activation Energy. The effect of temperature on the kinetic parameters of the electrocatalyst is of paramount importance for the oxygen evolution reaction of anode. The influence of temperature on the kinetics of oxygen reduction was examined by linear sweep voltammetry (LSV) measurements at different temperature ranging from 18\(^\circ\)C to 55\(^\circ\)C. The apparent activation energy, \(\Delta E_a\), for the oxygen reduction reaction on Ti/Ru-Co-Ce cluster catalyst was calculated from a linear regression analysis of the slope of the Arrhenius equation represented by the following relationship:

\[
i = k \exp \left( -\frac{(-\Delta E_a)_{\eta}}{RT} \right) \rightarrow (-\Delta E_a)_{\eta} = -2.303R \left( \frac{\partial (\log i)}{\partial (1/T)} \right).
\]

Representative plots of current density as a function of \(T\) at constant overpotential (0.6 V) are reported in Figure 8. Figure 8 clearly shows that the linear correlation coefficient could be very close to one \((r > 0.999)\). Also, for all catalysts, the current densities increase rapidly with the increase of temperature. The enhanced reaction rate is reasonably understood in that elevated temperature. According to slope from Figure 8, we can calculate \(\Delta E_a\) for each electrode (see Table 1). The doping of CeO\(_2\) can decrease the apparent activation energy of OER; the electrode with 40 mol% CeO\(_2\) has the smallest \(\Delta E_a\) which is 22.76 kJ/mol.

4. Conclusions

XRD study shows that CeO\(_2\) does not form solid solutions with the rutile phase (e.g., RuO\(_2\) and TiO\(_2\)), only acts as a dispersant, and causes diffractograms with somewhat broader peaks and a strong increase in the oxide surface roughness, suggesting lower crystallinity and higher surface area of active component.

"In situ" studies of the conductive metallic oxide electrodes reveal that an introduction of CeO\(_2\) into the binary RuO\(_2\) and Co\(_3\)O\(_4\) mixture changes the electrode morphology and surface properties, increasing the electrode surface area and slightly increasing \(E_{oc}\). Electrocatalytic activity of electrodes with 40 mol% CeO\(_2\) nominal composition is the best, with the greatest voltammetric charge, 86.23 mC cm\(^{-2}\), and the smallest apparent activation energy for OER at 0.60 V was 22.76 kJ/mol.

The kinetic study of the OER revealed that while overpotential domain affects the electrode process, it is unrelated to CeO\(_2\). Experimental tafel slope and reaction order data with respect to [OH\(^-\)], combined with the theoretical analysis based on the concept of the apparent electronic transfer coefficient, support the electrode mechanism proposed by Yeager adequately describes the OER in alkaline medium. Experimental tafel slopes at low and high overpotentials were 40 mV and 120 mV, respectively. The reaction orders with respect to [OH\(^-\)] are both 1.0.

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References


