Investigation of Oxygen Evolution Reaction at LaRuO_3 , $\text{La}_{3.5}\text{Ru}_4\text{O}_{13}$, and La_2RuO_5

Maria Abreu-Sepulveda¹, Phong Trinh², S. Malkhandi², S. R. Narayanan², Jacob Jorné¹, David J. Quesnel¹, James A. Poston Jr.³, A. Manivannan^{3*} manivana@netl.doe.gov

¹University of Rochester, Rochester, NY 14627

²University of Southern California, Los Angeles, CA

³US-Department of Energy / NETL, Morgantown, WV 26507

*Corresponding author.

Abstract

Development of electrocatalysts is important for reducing the voltage loss due to the oxygen evolution reaction (OER) in metal-air batteries and water electrolyzers. In the present work, the electrocatalytic activity towards oxygen evolution for a series of lanthanum-ruthenium compounds has been investigated by steady-state current-potential measurements in alkaline media to understand the effect of structure, valence state of the transition metal ion, and the role of surface adsorbed hydroxyl species. Compounds of the perovskite family, LaRuO_3 , $\text{La}_{3.5}\text{Ru}_4\text{O}_{13}$, and La_2RuO_5 , were prepared by the Pechini process and calcined at different temperatures to obtain the desired phases. X-ray photoelectron spectroscopy of LaRuO_3 and La_2RuO_5 showed shifts of the Ru-3d peaks towards higher binding energies indicative of a highly oxidized surface with possibly high surface hydroxylation. The electrochemical activity of the compounds at 0.8 V vs. NHE was in the order of 10^{-6} A/cm^2 and the mass specific activity was about 80 mA/g. Tafel slopes were in the vicinity of 60 mV/decade for LaRuO_3 (orthorhombic) and $\text{La}_{3.5}\text{Ru}_4\text{O}_{13}$ (orthorhombic), and about 80 mV/decade for La_2RuO_5 (monoclinic). In addition FT-IR results indicate high surface coverage by hydroxide species. The reaction order with respect to OH^- ions was found to be lower than unity. It is possible that strong interaction of hydroxide groups with ruthenium at the surface of the electrode makes it difficult to dissociate the Ru-OH bond and prevent further interaction with dissolved OH^- even at high overpotentials.

Keywords: water electrolyzer; oxygen evolution; noble transition metal perovskites

1. Introduction

The rate of electrochemical transformations involving oxygen in aqueous media is strongly dependent on the type of catalyst surface, and therefore considerable research has focused on the synthesis of novel electrode materials to increase the rate of these reactions and reduce the voltage losses [1-7]. In this context, transition metal oxides and noble transition metal oxides with the pyrochlore and perovskite structures have been considered as electrocatalysts. Pyrochlore and perovskite structures are of interest because of their high chemical and structural stability, and the possibility of substituting relatively wide range of elements to tune their catalytic properties [8].

Moreover, finding a correlation between the oxygen evolution performance and the electrocatalytic activity of perovskite materials have been the topic of research for decades. Recently, Suntivich et al [9], proposed a design principle based on the e_g filling of the surface transition metal ions due to OH^- adsorption and the covalent bonding of oxygen as a descriptor for the low overpotential associated with OER in perovskite compounds. Lanthanum cobalt oxide and lanthanum nickel oxide perovskites studied in alkaline media showed promising catalytic activities toward OER with good electrochemical stability in full cell configurations [10-13]. Ruthenium metal has also shown encouraging performance supporting OER in comparison to platinum and other noble metals in acid media [14]. Typically, Ru metal is oxidized to RuO_4 that dissolves readily in acid media [15] and in order to avoid further formation of unstable ruthenium oxides, some researchers have proposed its incorporation with other oxides to form ternary systems [16]. Mamaca et al [17], showed the efficacy of $\text{Ru}_{1-x}\text{Ir}_x\text{O}_2$ systems for water splitting for PEM fuel cell applications in acidic environments. The presence of iridium assisted in avoiding catalyst dissolution while keeping favorable electrochemical activities [18]. Other studies have focused on the performance of ruthenium based structures in alkaline media. In particular, Eun-Ok Chi et al. [19], demonstrated a decrease of the Tafel slope value during OER with increase of ruthenium content in the structure for a group of perovskites (Sr or Ca in the A site) and pyrochlores (Bi or Pb in the A site). Although the performance of Ru-Ir oxide materials is superior to that of the lanthanum-based perovskites, the latter showed

increased stability in a variety of operating environments making such compounds more attractive for cost-sensitive applications.

The aim of the present work is to investigate the electrochemical activity of various lanthanum ruthenates (LaRuO_3 , $\text{La}_{3.5}\text{Ru}_4\text{O}_{13}$, and La_2RuO_5) towards OER in alkaline media, since Ru-based compounds are highly active in promoting the OER. Although LaRuO_3 has been previously studied as catalytic material for direct alcohol fuel cells [20], to our understanding, this is the first report of oxygen evolution for such compounds. These compounds were synthesized by the Pechini process and characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge structure (XANES), and Brunauer–Emmett–Teller (BET). The electrochemical properties were tested by quasi steady-state current-potential measurements and by cyclic voltammetry (CV) in alkaline media to determine the Tafel slope and the electrochemical reaction order towards OH^- .

2. Experimental

All lanthanum ruthenates studied in this work were prepared by the Pechini process. The metal precursors used were $\text{LaNO}_3 \cdot 6\text{H}_2\text{O}$ (99.999%, Alfa Aesar) and RuCl_3 (99.9%, Alfa Aesar). Citric acid (anhydrous, 99.5+ %) and ethylene glycol (99.0%) were also purchased from Alfa Aesar. The ratio of these chelating agents and the metal precursors was 1.2:1.2:1.0. Stoichiometric amounts of the metal precursors were dissolved in DI water at room temperature, along with citric acid. The solution was vigorously stirred while the temperature was increased to 65 °C to proceed with the addition of ethylene glycol and kept at this temperature until it became a viscous gel-like substance due to the slow evaporation of water. Then the beaker was transferred into a heating mantle to provide uniform heating. The temperature of the heating mantle was increased to 120 °C which results in the formation of the 3D polymeric structure by the reaction of citric acid with ethylene glycol. Finally the beaker containing the remaining product was placed in an oven at 120 °C overnight to ensure the resulting compound was thoroughly dried. Later, the polymeric structure was crushed with an agate mortar and typically small quantities of the material were calcined at various temperatures such as 800 °C, 1000 °C and 1200 °C for 8 hours to decompose the polymeric compound and obtain the desired oxide phases.

2.1. Structural Characterization

Orthorhombic and monoclinic phases of the lanthanum ruthenates (LaRuO_3 , $\text{La}_{3.5}\text{Ru}_4\text{O}_{13}$, and La_2RuO_5) were confirmed by XRD using a PANalytical X'Pert Powder diffractometer using $\text{Cu K}\alpha$ radiation with a wavelength of 1.54056 Å. FT-IR spectroscopy was performed using a Thermo Scientific Nicolet FT-IR Spectrometer, between 4000-400 cm^{-1} under N_2 atmosphere. Micrographs of the surface morphology were obtained using a JEOL 7600 FE-SEM interfaced to a Thermo-Electron S7 X-ray Microanalysis system. The specific surface area was measured by the surface adsorption of nitrogen (Brunauer-Emmett-Teller, BET) using ASAP 2020 model from Micromeritics. A Physical Electronics (PE) SAM-590 UHV system equipped with a PE spherical capacitor type analyzer with an Omni Focus III Lens and a PE 04-303 Argon (Ar) ion Gun was employed for the X-ray Photoelectron spectroscopy (XPS). System calibrations were in accordance with PE procedures utilizing the photoemission lines EB ($\text{Cu } 2p_{3/2}$) = 932.7 eV, EB ($\text{Au } 4f_{7/2}$) = 84 eV and EB ($\text{Ag } 3d_{5/2}$) = 368.3 eV. The system was operated within a pressure range of 1.3×10^{-7} Pa to 1.3×10^{-6} Pa. Binding energies were referenced to adventitious carbon located at 284.8 eV.

2.2. Electrochemical studies

A typical three-electrode system was employed for all the electrochemical experiments using an Epsilon electrochemical test system. A Pt-wire, saturated calomel, and glassy carbon disk immersed in 1.0 M potassium hydroxide solution were used as counter, reference and working electrodes, respectively. In the case of reaction order determination, pH dependence studies were carried out using 1.0 M, 0.1 M and 0.01 M potassium hydroxide solutions. Electrochemical measurements were performed on the polished surface of the glassy carbon disk electrode (5 mm diameter) modified using the catalyst ink. The catalyst ink was prepared following a procedure used by Malkhandi, et al. [11], in which 4 mg of catalyst powder was dispersed in 1000 μL of a solution containing 10 μL of 5 wt% Nafion, 250 μL of isopropanol and 1.34 mL of DI water and sonicated for at least 30 minutes to form a suspension. A thin film of the catalyst ink was formed on the surface of the GC electrode by depositing 20 μL of the suspension and allowing it to dry for approximately 10 minutes at 120 °C. The loading was estimated to be 80 μg .

The electrolyte was purged continuously with ultra-high purity nitrogen for 15 minutes before and during the experiments. For the steady-state current-potential measurements, the working electrode was cycled between 250 to 700 *mV* vs. 20% potassium hydroxide mercury/mercury oxide reference electrode (MMO, 0.098 *V* vs. NHE at 25 °C) and recording the anodic current after 300 *s* every 25 *mV*. All electrochemical potentials are reported against the Normal Hydrogen Electrode (NHE).

2.3. Area calculation measurements

Electrochemical active surface area (ECSA) of the compounds was calculated using an in situ method based on the double layer capacitance [21]. In the absence of oxygen and in between narrow potential regions, the current response of the electrode is of capacitive nature with negligible Faradaic processes, resulting in a rectangular voltammogram. The value of the current is plotted against scan rate that results in a straight line with a slope equal to the double layer capacitance at constant potential, equation 1. A reference value of 60 $\mu F/cm^2$, typically applied for oxide surfaces [12, 21], has been used to calculate the ECSA of the material by the use of equation 2. All the results are expressed and plotted in terms of the ECSA determined by this method.

$$C_{dl} = \frac{dQ}{dE} = \frac{Idt}{dE} = \frac{I}{\left(\frac{dE}{dt}\right)} \quad (1)$$

$$A_{eff}(cm^2) = \frac{C_{dl}}{C_*} \quad (2)$$

3. Results and Discussion

3.1. Structural characterization

Crystal structures and XRD patterns of the compounds are presented in Figs. 1 and 2, respectively. The lanthanum ruthenate perovskite, LaRuO₃, structure consists of a framework of RuO₆ octahedra sharing corners in all three dimensions linked in zig-zag chains. A lanthanum cation is placed in a cage-like space formed by eight RuO₆ as shown in Fig. 1a. The lattice

parameters were $a = 5.73 \text{ \AA}$, $b = 7.75 \text{ \AA}$, and $c = 5.61 \text{ \AA}$, that are in agreement with previously reported lattice parameters, $a = 5.68 \text{ \AA}$, $b = 7.88 \text{ \AA}$, and $c = 5.54 \text{ \AA}$ [22]. XRD pattern showed the presence of extra peaks that partially matched with other lanthanum oxides, such as La_2O_3 and $\text{La}_3\text{Ru}_3\text{O}_{11}$ that were below 6% as impurity phases (Fig. 2a). The amount of impurity fraction has been calculated based on the comparison ratio of the highest intensity peak of the impurity with the highest intensity peak of the main compound. The structure of La_2RuO_5 can be formally described as layered perovskite in which additional LaO_2 units are placed between every perovskite slab forming a monoclinic crystal phase (Fig. 1b). The lattice parameters are similar to the values reported previously [23], and are $a = 9.17 \text{ \AA}$, $b = 5.81 \text{ \AA}$, and $c = 7.96 \text{ \AA}$. $\text{La}_{3.5}\text{Ru}_4\text{O}_{13}$ having a triple-layered perovskite structure in coexistence with rutile slabs, Fig. 1c, was obtained after calcining stoichiometric amounts of the precursors at 1000°C for 8 hours. The lattice parameters were calculated to be $a = 12.01 \text{ \AA}$, $b = 5.61 \text{ \AA}$, $c = 3.85 \text{ \AA}$, that are comparable to the values reported by Abraham et al. [24], in which $a = 11.94 \text{ \AA}$, $b = 5.60 \text{ \AA}$, and $c = 3.86 \text{ \AA}$. XRD pattern along with impurity peaks and the corresponding Rietveld refinement are presented in Figures 2a and 2b, respectively. For the crystallite size calculation, we used the Scherrer's formula ($\tau = K\lambda / \beta \cos \theta$) applied to the main diffraction peaks. Several scans were analyzed and the average crystallite size value is reported in Table 1. In our current Pechini (sol-gel) synthesis the crystallite sizes were found to be in the range of 100-300 nm after heat treated at high temperatures.

SEM of the three compounds showed a high degree of agglomeration and coarse particles and their surface morphology were similar. Figure 3 represents the SEM morphology for La_2RuO_5 right after calcination at 1200°C for 8 hours. In agreement with crystallite growth due to heat-treatment, the crystallite size of the high temperature compound La_2RuO_5 is large compared to the other compounds. Though, LaRuO_3 and $\text{La}_{3.5}\text{Ru}_4\text{O}_{13}$ were calcined at the same temperature and time (1000°C for 8 hrs), the crystallite size of $\text{La}_{3.5}\text{Ru}_4\text{O}_{13}$ seems to be larger than LaRuO_3 and with less surface area. The preparation conditions, structural characterization, the crystallite size and the surface area of these compounds are summarized in Table 1.

Ex-situ X-ray photoelectron spectroscopy was used to investigate the oxidation states of ruthenium in LaRuO_3 and La_2RuO_5 . The charge correction was made using C1s as the reference peak. It is important to mention that Ru-3d peaks overlap with C1s peaks making the

deconvolution process difficult. XPS was also performed by mixing gold nanoparticles; however it included some error since the charge correction for gold will be different than that of the compound. In this case, the Au-4f peaks were in the expected position but, the C1s peaks were significantly shifted. Therefore, deconvolution was carried out following adventitious carbon peak located at 284.8 eV. After de-convolution, several peaks belonging to C1s, C-O-C, O-C=O and multiple oxidation states of ruthenium were distributed in the range of 280 eV to 290 eV (Figs. 4a and 4b). The peaks for ruthenium were assigned following the energy difference between Ru-3d_{3/2} and Ru-3d_{5/2} doublets to be $\Delta E = 4.2$ eV which is caused by strong spin-spin interaction. The first set of Ru-3d peaks appears at 282.5 eV for the 3d_{5/2} with the 3d_{3/2} positioned 4.19 eV at higher binding energy. The second set of Ru-3d peaks is located at 283.8 eV and the separation between the states 3d_{5/2} and 3d_{3/2} is found to be 4.16 eV [25]. These multiple valence states of ruthenium indicate the possibility of several ruthenium oxidation states at the surface of both compounds and the shift towards higher binding energy could be indicative of a high coverage of electronegative hydroxyl ion species on the surface [25]. The presence of multiple valence states for Ru is also confirmed by two sets of secondary peaks in the Ru-3p region that are also shifted towards higher binding energy values of about 2 eV. The expected binding energies for the valence states of ruthenium in LaRuO₃ is 3+ and for La₂RuO₅ is 4+ located at 280.9 eV and 281.9 eV, respectively. It is important to emphasize that our observed values of 282.5 eV and 283.8 eV for LaRuO₃ and La₂RuO₅ are higher than expected due to strong adsorption of electronegative ions at the surface such as OH⁻.

Oxygen XPS peaks were also investigated to obtain information about these oxides (Fig. 4c). An oxygen peak was present at values higher than 530 eV and this peak is associated to oxygen anions due to the metal oxides [26, 27]. The O1s peak located at 529.0 eV was attributed to adsorbed oxygen or hydroxides at the surface of the material. The high intensity of the 529 eV peak confirms the strong presence of OH⁻ and is consistent with the shift in Ru 3d peaks due to the electronegativity of OH⁻. The characteristic peaks of lanthanum 3d orbital showed no difference among the survey scans of the compounds, consistent with the literature as shown in Fig. 4d [28]. It is relevant to mention that X-ray Absorption Near Edge Structure (XANES) studies performed on the phases showed Ru valence states between 3.5 and 4+. The results have not been included because of the negligible contribution of the bulk material to the surface electrochemistry. XANES studies were performed in the APS facility in Argonne National

Laboratory. To further confirm the presence of OH⁻ on the surface of the compound, FTIR spectra were obtained in the range of 4000- 400 cm⁻¹ under N₂ atmosphere using the reflectance mode to investigate the catalyst surface. The results for the three compounds are presented in Fig. 5, in which a strong and broad band near 3500 cm⁻¹ belonging to OH⁻ is observed. FTIR measurements confirmed the presence of OH⁻ groups on the surface of these compounds, which is consistent with XPS results.

3.2. Electrochemical studies

Electrochemical OER measurements were performed on all the three oxides. All the current density data was calculated by dividing the current by the electrochemical surface area (ECSA). The value for ECSA was obtained by employing the double layer capacitance ratio using 60 $\mu\text{F}/\text{cm}^2$ as the specific reference capacitance for surface oxides, as described section 2.3 and illustrated in Fig. 6. Figure 7 shows the steady-state current measurements in the anodic direction. The curves plotted in Fig. 7 were obtained under UHP N₂ atmosphere. The onset potential of the compounds investigated was in the vicinity of 600 mV vs. NHE.

Fig. 8 shows the specific activity of the compounds with respect to the ECSA at 0.75 and 0.80 V vs. NHE. At 0.75 V, the area specific activity seems to be higher for the La₂RuO₅; however it is surpassed by La_{3.5}Ru₄O₁₃ at 0.80V. The mass specific activity of the compounds, using a calculated catalyst loading of $\sim 0.4 \text{ mg}/\text{cm}^2$, was found to be approximately 80 mA/g; which might indicate that not all the catalytic material is exposed to electrolyte due to two reasons: i) bulk material is not taken into account ii) materials with higher crystallite size having lower surface area. A semi-log plot of current vs. potential, also known as the Tafel plot is shown in Fig. 9. The Tafel slope values were 56, 65 and 83 mV/decade for LaRuO₃, La_{3.5}Ru₄O₁₃ and La₂RuO₅, respectively (Fig. 10). The Tafel slope increases in the order of LaRuO₃<La_{3.5}Ru₄O₁₃<La₂RuO₅ and the Ru-3d peak shift observed from XPS suggests that the hydroxyl species binding strength increases in the same order. Given the significant shift towards higher binding energies in the Ru-3d region, it is possible to have a surface with a strong hydroxylation character and low activity towards OER ($10^{-6} \text{ A}/\text{cm}^2$), therefore it can be assumed that the hydroxide ions are strongly attached to the surface of the perovskites, preventing further interaction of the active sites with ions in solution due to Coulombic repulsion.

Bockris and Otagawa [21] have measured the reactions orders for various perovskite compounds in alkaline media and proposed several mechanisms based on Tafel slopes and reaction order values. We realized that measuring more than one kinetic parameter (Tafel slope) is important for the discrimination between existing OER mechanisms. Therefore, to understand the actual mechanism for OER for our compounds, the reaction order with respect to OH⁻ adsorption on the electrode surface was also investigated at constant overpotential. The reaction order value was obtained from the slope of the log plot of current density versus OH concentration in the bulk solution under constant overpotential [$reaction\ order = \log i / \log(OH)_{\eta}$] with i in A/cm^2 . Figure 11 shows the semi log plot of area specific current density vs. pH at $\eta = 350\ mV$ and $\eta = 400\ mV$ for LaRuO₃, La_{3.5}Ru₄O₁₃ and La₂RuO₅. The reaction order at $\eta = 350\ mV$ has been found to be 0.38, 0.60 and 0.10 for LaRuO₃, La_{3.5}Ru₄O₁₃ and La₂RuO₅, respectively. At overpotential near $\eta = 400\ mV$, the values of the reaction order with respect to OH⁻ decreased. An almost independent behavior towards OH⁻ concentration was observed in the case of La₂RuO₅ at $\eta = 400\ mV$. The fractional values obtained are far from unity and indicate a strong interaction of the surface with the hydroxide ions at all pH values. The value of the Tafel slopes (RT/F) and the reaction order for La_{3.5}Ru₄O₁₃ and LaRuO₃ suggest similar OER mechanism on both surfaces, contrary to La₂RuO₅ which has Tafel slope around $80\ mV/decade$ and reaction order values close to 0. However, extensive coverage by OH⁻ ions might be the predominant surface conditions for all the compounds under the potential window studied. Several reaction mechanisms with reaction order of zero with respect to hydroxide concentration have been postulated by Bockris and Otagawa [21]. We find that the Bockris oxide pathway or the O'Grady pathway are reasonable with the following rate determining steps for the OER mechanism compared to the Tafel slopes and reaction orders observed under Temkin adsorption conditions:

However, we were unable to assign the measured kinetic parameters to a unique OER mechanism. Therefore, we intend to investigate the rate determining step further. The electrochemical and kinetic parameters have been summarized in Table 2.

Despite the similarities in the structure of the compounds, it seems that they possess different electrochemical behavior for oxygen evolution. These differences may be explained in terms of the crystal structure differences, specifically on the local environment of the transition metal ion. In the case of LaRuO_3 , the RuO_6 octahedra shares corner in all three dimensions while forming a zigzag chain in all directions, c.a. 3.97 Å (see Fig. 1). On the other hand, in La_2RuO_5 , the RuO_6 chain is interrupted by additional lanthanum oxide units. In the case of $\text{La}_{3.5}\text{Ru}_4\text{O}_{13}$, ruthenium ions are found in three positions, Ru(1) and Ru(2) in corner-shared octahedral environment, forming a triple layered perovskite along the (100) direction, and the Ru(3) positioned also in a octahedral environment but edge-sharing. The later forms a 1D rutile slab along the (010) direction. The distance between Ru(3)-Ru(3) atoms is about 1 Å less than that of Ru(1) found in LaRuO_3 and La_2RuO_5 , although alternating distance values were found for the semi-rutile slab along the (010) direction [28].

In all three structures, the electro-active ion ruthenium is in a distorted octahedral configuration surrounded by six oxygen anions with the O-Ru distances being very similar among the compounds studied. However, a portion of the RuO_6 octahedra in the $\text{La}_{3.5}\text{Ru}_4\text{O}_{13}$ is edge-sharing in 1D and attached by corners to the second portion of RuO_6 that forms the triple-layered perovskite slabs. Coaquira *et al.* suggested that the edge sharing configuration of RuO_6 is believed to cause the overlap between d bands of adjacent Ru cations to be stronger than in corner-shared configuration [28]. Therefore, the high mass specific activity and higher reaction order obtained from $\text{La}_{3.5}\text{Ru}_4\text{O}_{13}$ could be ascribed to the presence of edge-sharing ruthenium octahedra that increases the filling of electrons in the d bands.

In the perovskite configuration, the transition metal ion is the active cation with respect to the oxygen evolution reaction. It has been shown that the degree of oxidation of the transition metal cation affects significantly the interaction with the hydroxide species due to the electron density in the sigma antibonding (σ^*) states at the surface. The electron density near unity in the e_g - σ^* states results in good electrocatalytic activity due to antibonding interaction of the transition metal cation and the hydroxide ions [9]. In this study, Ru is found to be in higher oxidation states $>4+$, which indicates σ^* are not filled, resulting in a relatively strong bonding interaction of the transition metal ion with hydroxyl ions compared to LaNiO_3 or LaCoO_3 . These results indicate Ru as the transition metal in the B site with La in the A site of the perovskite

configuration is likely to possess low electrocatalytic activity towards the evolution of oxygen [29].

4. Conclusion

A family of lanthanum ruthenates, LaRuO_3 , $\text{La}_{3.5}\text{Ru}_4\text{O}_{13}$, and La_2RuO_5 were synthesized by the Pechini polymerization process. The compounds were characterized using XRD and XPS for phase purity identification and valence state determination, respectively. Lattice parameters obtained from the XRD are consistent with previous studies and XPS data indicates the presence of more than one Ru valence state ($>4+$) and the possibility of a highly hydroxylated surface, which was confirmed by FTIR measurements. The interaction of electronegative species (OH^-) with ruthenium causes high oxidation states for charge neutrality, leading to strong interaction between Ru-OH. The highest specific surface activity ($6.2 \text{ mA/cm}_{\text{ECSA}}^2$) and mass specific activity (80 mA/g) towards OER was obtained for $\text{La}_{3.5}\text{Ru}_4\text{O}_{13}$ in which the ruthenium octahedra were found in both corner-shared and edge-shared configurations. Moreover, a Tafel slope value (RT/F) close to 60 mV/decade and high reaction order (0.62) compared to its analogous phases LaRuO_3 and La_2RuO_5 . The edge-shared character of this compound may enhance the overlapping of the d bands of adjacent ruthenium ions resulting in a higher specific activity toward oxygen evolution. Based on the high hydroxylation observed from FT-IR, higher Ru oxidation states at the surface, reaction orders lower than unity, and the Tafel slopes near RT/F, it can be concluded that the surface is covered with a strongly bound layer of OH^- ions.

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References

- [1] F. Cheng and J. Chen, *Metal-air batteries: from oxygen reduction electrochemistry to cathode catalysis*, Chem. Soc. Rev., 2012, 41, 2172-2192.
- [2] Y-C. Lu, Z. Xu, H.A. Gasteiger, S. Chen, K. Hamad-Schifferli, and Y. Shao-Horn, *Platinum-Gold Nanoparticles: A highly active Bifunctional Electrocatalyst for Rechargeable Lithium-Air Batteries*, J. Am. Chem. Soc., 2012, 132, 12170-12171.
- [3] X. Han, F. Cheng, T. Zhang, J. Yang, Y. Hu, and J. Chen, *Hydrogenated Uniform Pt clusters Supported on Porous CaMnO_3 as Bifunctional Electrocatalyst for Enhanced Oxygen Reduction and Evolution*, Adv. Mater., 2014, 26, 2047-2051.
- [4] W.S. Li, H.Y. Chen, X.M. Long, F.H. Wu, Y.M. Wu, J.H. Yan, and C.R. Zhang, *Oxygen Evolution Reaction on Lead-Bismuth Alloys in Sulfuric Acid Solution*, J. Power Sources, 2006, 158, 902-907.
- [5] Y. Zhang, J. Rosen, G.S. Hutchings, and F. Jiao, *Enhancing photocatalytic oxygen evolution activity of cobalt-based spinel nanoparticles*, Catalysis Today, 2014, 225, 171-176.
- [6] R.R. Mitchell, B.M. Gallant, C.V. Thompson and Y. Shao-Horn, *All-carbon-nanofiber electrodes for high-energy rechargeable Li-O_2 batteries*, Energy Environ. Sci., 2011, 4, 2952.
- [7] C.A.C. Sequeira, D.M.F. Santos, and P.S.D. Brito, *Electrocatalysis of oxygen reduction by lanthanum-strontium manganate*, Russ. J. Electrochem., 2008, 44, 852-856.
- [8] R.A. Rincón, E. Ventosa, F. Tietz, J. Masa, S. Seisel, V. Kuznetsov, and W. Schuhmann, *Evaluation of perovskites as electrocatalysts for the oxygen evolution reaction*, Chem. Phys. Chem., 2014, 15, 2810-2816.
- [9] J. Suntivich, K.J. May, H.A. Gasteiger, J.B. Goodenough, and Y. Shao-Horn, *A perovskite oxide optimized for oxygen evolution catalysis from molecular orbital principles*, Science, 2011, 334, 1383-1385.

- [10] Y. Shimizu, H. Matsuda, N. Miura, N. Yamazoe, *Bifunctional oxygen electrode using large surface area perovskite type oxide catalyst for rechargeable metal-air batteries*, Chem. Lett., 1992, 21, 1033-1036.
- [11] S. Malkhandi, B. Yang, A. Manohar, A. Manivannan, S. Prakash, S.R. Narayan, *Electrocatalytic Properties of nanocrystalline calcium-doped lanthanum cobalt oxide for bifunctional oxygen electrodes*, J. Phys. Chem. Lett., 2012, 3, 967-972.
- [12] R.N. Singh, S.K. Tiwari, S.P. Singh, A.N. Jain, and N.K. Singh, *Electrocatalytic activity of high specific surface area perovskite type LaNiO_3 via sol gel route for electrolytic oxygen evolution in alkaline solution*, Int. J. Hydrogen Energy, 1997, 22, 557-562.
- [13] K.P.C. Yao, Yi-Chun Lu, Chibueze V. Amanchukwu, David G. Kwabi, Marcel Risch, Jigang Zhou, Alexis Grimaud, Paula T Hammond, Fanny Bardé, and Yang Shao-Horn, *The influence of transition metal oxides on the kinetics of Li_2O_2 oxidation in Li- O_2 batteries: high activity of chromium oxides*, Phys. Chem. Chem. Phys., 2014, 16, 2297-2304.
- [14] T. Reier, M. Oezaslan, and P. Strasser, *Electrocatalytic oxygen evolution reaction (OER) on Ru, Ir, and Pt Catalysts: A comparative Study of Nanoparticles and Bulk Materials*, ACS Catalysis, 2012, 2, 1765-1772.
- [15] C. Iwakura, K. Hirao, and H. Tamura, *Anodic evolution of oxygen on ruthenium, in acidic solutions*, Electrochim. Acta, 1977, 22, 329-334.
- [16] R. S. Yeo, J. Orehotsky, W. Visscher, and S. Srinivasan, *Ruthenium-Based Mixed Oxides as Electrocatalysts for Oxygen Evolution in Acid Electrolytes*, J. Electrochem. Soc., 1981, 128, 1900-1904.
- [17] N. Mamaca, E. Mayousse, S. Arrii-Clacens, T.W. Napporn, K. Servat, N. Guillet, K.B. Kokoh, *Electrochemical activity of ruthenium and iridium based catalysts for oxygen evolution reaction*, App Catalysis B: Environmental, 2012, 111-112, 376-380.

- [18] T.I. Valdez, S. Firdosy, B.E. Koel, S.R. Narayanan, *Investigation of ruthenium dissolution in advanced membrane electrode assemblies for direct methanol based fuel cell stacks*, ECS Transactions, 1, Proton Exchange Membrane Fuel Cells V, 2005, 293-303.
- [19] E.Chi, Y. Kwon, and S. Mho, *Oxygen evolution reaction at electrodes of single phase ruthenium oxides with perovskite and pyrochlore structures*, Bull. Korean Chem. Soc., 1997, 18, 972-976.
- [20] A. Lan and A.S. Mukasyan, *Complex $\text{SrRuO}_3\text{-Pt}$ and $\text{LaRuO}_3\text{-Pt}$ catalysis for direct alcohol fuel cells*, Ind. Eng. Chem. Res., 2008, 47, 8989-8994.
- [21] J.O'M. Bockris and T. Otawaga, *Mechanism of oxygen evolution on perovskite*, J. Phys. Chem., 1983, 87, 2960-2971.
- [22] H. Kobayashi, M. Nagata, R. Kano, and Y. Kawamoto, *Structural characterization of the orthorhombic perovskites: $[\text{ARuO}_3 \text{ (A = Ca, Sr, La, Pr)}]$* , Mater. Res. Bull., 1994, 1271-1280.
- [23] S. Ebbinghaus, *High- and Low-temperature La_2RuO_5 by Powder Neutron Diffraction*, Acta Crystallographica C61, 2005, i96-i98.
- [24] F. Abraham, J. Trehoux, and D. Thomas, *$\text{La}_{3.5}\text{Ru}_4\text{O}_{13}$: Un nouveau compose a feuillets de type pérovskite*, J. Solid State Chem., 1980, 32, 151-160.
- [25] C.L Bianchi, V. Ragaini, and M.G. Cattania, *An XPS study on ruthenium compounds and catalysis*, Mat. Chem. and Phys., 1991, 29, 297-306.
- [26] K.Jung, J.Lee, W. Bin Im, S. Yoon, K. Shin, and J.Lee, *Promoting Li_2O_2 oxidation by a $\text{La}_{1.7}\text{Ca}_{0.1}\text{Ni}_{0.75}\text{Cu}_{0.25}\text{O}_4$ layered perovskite in lithium-oxygen batteries*, Chem. Commun., 2012, 48, 9406-9408.
- [27] L. Qiao and X. Bi, *Direct observation of Ni^{3+} and Ni^{2+} in correlated $\text{LaNiO}_{3-\delta}$ films*, Europhys. Lett., 2011, 93, 57002.

- [28] J.A.H. Coaquira, R.L. de Almeida, L.B. Carvalho, S. Quezado, and S.K. Malik, *Physical properties of the novel ruthenate $La_{3.5}Ru_4O_{13}$: Possible mixed valence of Ru ions*, J. Appl. Phys. 2009, 106, 013909.
- [29] I.C. Man, H-Y. Su, F. Calle-Vallejo, H.A. Hansen, J.I. Martínez, N.G. Inoglu, J. Kitchin, T.F. Jaramillo, J.K. Nørskov, and J. Rosmeisi, *Universality in oxygen evolution electrocatalysis on oxide surfaces*, Chem. Cat. Chem., 2011, 3, 1159-1165.

Figure Captions

Fig. 1. Atomic distribution of the studied lanthanum ruthenates: LaRuO_3 (a), La_2RuO_5 (b), and $\text{La}_{3.5}\text{Ru}_4\text{O}_{13}$ (c) (crystal structures generated using the data from references 22-24).

Fig. 2. (a) XRD pattern for LaRuO_3 , La_2RuO_5 , and $\text{La}_{3.5}\text{Ru}_4\text{O}_{13}$. Impurities are denoted by + and * signs, (b) Rietveld refinement of $\text{La}_{3.5}\text{Ru}_4\text{O}_{13}$.

Fig. 3. SEM micrograph of La_2RuO_5 showing coarse particles and high agglomeration.

Fig. 4. XPS peaks of C1s (red) and Ru3d (black) orbitals for LaRuO_3 (a) and La_2RuO_5 (b), and O1s (c) and La3d (d).

Fig. 5. FTIR spectra for the compounds show a prominent OH band near 3500 cm^{-1} .

Fig. 6. (a) CV for area calculation for LaRuO_3 in the region of 0 to 50mV vs. MMO, (b) shows the linear dependence of current and scan rate.

Fig. 7. Current density as function of voltage for the studied compounds in 1M KOH under continuous nitrogen purging.

Fig. 8. Area specific activity based on the electrochemical surface area obtained from double layer measurements 0.75 V and 0.80 V vs. NHE.

Fig. 9. (a) Semi log plots of the compounds; dashed line represents the reversible potential, (b) Enlarged portion of the linear region for the three compounds.

Fig. 10. Tafel values of the compounds.

Fig. 11. Semi log plot of area specific current density vs. pH at $\eta = 350\text{ mV}$ (black) and $\eta = 400\text{ mV}$ (red) of LaRuO_3 , $\text{La}_{3.5}\text{Ru}_4\text{O}_{13}$ and La_2RuO_5 .

Fig. 1.

Fig. 2

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.

Fig. 10.

Fig. 11.

Tables

Table 1. Synthesis conditions and structural parameters for the lanthanum ruthenates.

Compound	Calcination °C/time (hr)	Lattice parameters (Å)			Average Crystallite size (nm)	BET area (m ² /g)
		a	b	c		
LaRuO₃	1000/8	5.7993	7.8224	5.0849	50-100	2.03
La_{3.5}Ru₄O₁₃	1000/8	10.3324	6.6755	6.1439	100-200	1.49
La₂RuO₅	1200/8	9.1972	5.8013	7.9372	150-300	0.98

Table 2. Electrochemical parameters and kinetic data obtained for the compounds.

Compound	ECSA (cm ²)	Tafel (mV/dec)	mA/cm ² 0.8V vs NHE	mA/g 0.8V vs NHE	Reaction order*	
					350mV	400mV
LaRuO₃	1.91	56	5	63	0.28	0.23
La_{3.5}Ru₄O₁₃	0.95	65	6.2	80	0.62	0.41
La₂RuO₅	0.79	83	5.9	57	0.10	0.02

*Reaction order was measured at constant overpotential, i.e. 350 and 400 mV.