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Influence of Ruthenium Substitution in LaCoO₃ towards Bifunctional Electrocatalytic activity for Rechargeable Zn-Air Battery

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The rechargeable Zinc-air battery is a clean technology for energy storage applications but is impeded by the slow kinetics of the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) during its cycling. Herein, a series of lanthanum cobaltate based perovskites are synthesised with the B-site cation deficiencies in the structure occupied by Ru substitution: $LaCo_{1-x}Ru_xO_{3-6}$ (x = 0, 0.1, 0.2, 0.3 and 0.5). These compositions were designed to enhance the OER/ORR activities, which are two vital reactions for the rechargeable Zn-air batteries. The powder x-ray diffraction analysis revealed that increasing the Ru substitution >20 % (x > 0.2) alters the LaCoO₃ crystal structure from rhombohedral to orthorhombic. The photoelectron spectroscopy studies reveals that the surface oxygen vacancies increased in the Ru substituted catalyst, a property important for enhancing the OER/ORR efficiency. The LaCo_{0.8}Ru_{0.2}O₃₋₆ (LCRO82) catalyst exhibits a promising electrocatalytic activities in both OER and ORR reactions in 0.1 M KOH solution. Further, the LCRO82 catalyst was evaluated as a cathode for rechargeable Zn-air battery application displaying high power density of 136 mW cm⁻² at a current density of 175 mA cm⁻² and a stable charge-discharge voltage gap of 0.78 V after 1440 cycles, with excellent cycling stability over 240 h.

Introduction

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With the ever-increasing energy demand and depletion of fossil fuels on the earth, the development of clean and sustainable electrochemical energy systems that can store renewable energy through efficient, environmental-friendly and cost-effective ways is paramount.^{1–3} Rechargeable metal-air (M = Li, Al and Zn, etc.) batteries are deemed to be the most propitious candidates for sustainable storage devices because of their higher specific energy densities than present lithium-ion batteries.^{4,5} Among the various metal-air batteries, the rechargeable Zn-air system has attracted intensive attention concerning electrochemical energy storage owing to its reasonably high theoretical specific energy density (1086 Wh kg⁻¹), volumetric energy density (6136 Wh L⁻¹), the high abundance of zinc resources and relatively low cost.^{6,7} Yet, rechargeable Zn-air batteries are still suffering from low energy efficiency, charge-discharge polarization and cycling instability on account of the slow kinetics of the oxygen evolution reaction and oxygen reduction reaction (ORR/OER) on the air electrode side.^{8–10} Thus, a wide range of active and stable non-precious metal, bifunctional electrocatalysts including transition-metal oxides,^{11–15} metal alloys,^{16,17} and metal-free materials^{18,19} have been studied for application in rechargeable Zn-air batteries.

Perovskites have been widely explored owing to their remarkable electrocatalytic activities, Zn-air battery performances and stability in the aqueous electrolytes.^{13,20,21}Perovskite oxides have the chemical formula of ABO₃, where A is a rare earth metal or alkaline earth element and B is a transition element (TM = Co, Ni, Mn, Fe). In particular, LaCoO₃ has been widely employed for electrocatalytic applications. ^{22–24} Unfortunately, single electrocatalytic activity and poor intrinsic property of LaCoO₃ limit its application as an aircathode in rechargeable Zn-air battery. Interestingly, the partial A/B-site substitution of perovskite oxides with other transition metal is an effective strategy to tailor the intrinsic properties like oxygen deficiency, a near unity (σ^* -antibonding) eg orbital filling in a transition metal cation, closer Co 3d-O 2p-band center relative to the Fermi level and higher covalency between transition metal and oxygen bond, which are responsible for enhancing the bi-functional (OER/ORR) activity of perovskite.²⁵⁻²⁹ Also, the presence of mixedvalence states of the B-site cation and oxygen vacancies provides sites for migration of the charge carrier, electron or metal ion (Zn²⁺ or Li⁺), during charging and discharging of the metal-air battery.^{12,30-} ³²Based on correlation between transition metal 3*d*-O 2*p* covalency and eg electron filling on electrocatalytic activity of perovskites, several investigations were proposed to enhance the electrocatalytic activity in A/B-site substituted perovskites. For example, Duan et al.³³ reported Fe substituted in the B-site LaCoO₃ for OER application. They found that 10% Fe substituted $LaCoO_3$ (LaCo_{0.9}Fe_{0.1}O₃) owns increased overlap between Co 3d and O 2p

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states, which results in enhancement of covalency and optimal e_g configuration and promoted OER activity. Similarly, Sun et al.³⁴ introduced Mn in the B-site of LaCoO₃ perovskite lattice, which helps to tailoring the Co 3d-O 2p covalency and the e_g electron filling, promoting the OER reaction kinetics and Shen et al.35 reported the partial substitution of La³⁺ for Sr²⁺ in LaFeO₃ increases the OER activity. The authors attributed the enhanced activity to presence of Fe^{4+} -induced hole states in $La_{1-x}Sr_xFeO_3$ and modification in the Fe 3d-O 2p covalency. On the other hand, many studies were focused to tuning the B-site cation valance state and oxygen vacancies in the structure to boost the electrocatalytic activity. For instance, Wang et al.³⁶ studied the redox pairs, Ni³⁺/Ni²⁺ and Mn⁴⁺/Mn³⁺ and the oxygen vacancies in La_{0.8}Sr_{0.2}MnO₃ by substituting the Ni in the Mn site, which helps to modify the B site M-O bond and the surface configuration and therefore promotes the bi-functional activity. Similarly, Vignesh et al.³⁷ investigated the Ni substitution of the Co-site in the $LaCo_{0.97}O_{3-\delta}$ perovskites, which resulted in the oxygen vacancy and redox pair Ni³⁺/Ni²⁺ and Co²⁺/Co³⁺, thereby enhancing OER activity. Abreu-Sepulveda et al.³⁸ and Malkhandi et al.³⁹ introduced the various changes including the electronic structure, oxygen vacancies as well as the oxidation state of Co in the La_{0.6}Ca_{0.4}CoO₃ structure by means of substituting the Fe and Mn respectively in the Co site to achieve higher OER activity. Liu et al.⁴⁰ engineered abundant oxygen vacancies and also mixed valence of Co²⁺/Co³⁺ and Mn³⁺/Mn⁴⁺ in LaMnO₃ perovskite by replacing Mn in part with Co to realize higher bi-functional activity. These results show that the partial substitution of the A or B-site cation in the perovskite with a transition metal atom could favourably alter the electronic structure, bond strength, oxygen vacancies and synergistic redox couple interaction that induce higher bi-functional catalytic activities for rechargeable metal-air battery applications.

Furthermore, The OER activity as a function of oxygen binding energy resulted in Volcano type plot has been reported based on the DFT calculations. These results show, Ru and Ir catalysts are the closet to the top of the volcano. It also predicted that Ru and Ir based catalysts have optimal balance in the surface-oxygen interaction energies as the activity-controlling parameter. Therefore, Ru and Ir based catalysts are currently best OER catalysts to provide enhanced catalytic activity. To balance the cost and the activity, Ru is the least expensive platinum group metal and appears to be an ideal choice ^{41–44} and in the current scenario, the most trend setting state of the art catalysts Pt-Ru/C with 40 wt. % Pt and 20 wt. % Ru on Vulcan XC-72R carbon was used as a bi-functional catalyst owing to their renowned ORR-OER activity; though, the scarcity pricing, derisory reserve and destitute electrochemical stability of the Pt-Ru/C catalyst have considerably limited its substantial applications. Nevertheless, new type of catalyst is essential to improve the catalytic activity along with cost effectiveness and stability issues. One among them is to reduce the Pt, Ru loading and use highly active catalyst support without affecting the performance.

In this context, substitution of Ru into LaCoO₃ (LaCo_{1-x}Ru_xO_{3- δ}, x = 0, 0.1, 0.2, 0.3 and 0.5) perovskite is reported here. Among these, the LaCo_{0.8}Ru_{0.2}O_{3- δ} catalyst shows superior bi-functional activity in an aqueous alkaline electrolyte medium, which can be attributed to the mixed oxidation state of B-site cations (Co²⁺/Co³⁺ and Ru³⁺/Ru⁴⁺) and oxygen vacancies present in the structure. In addition, the LaCo_{0.8}Ru_{0.2}O_{3- δ} catalyst has been demonstrated to function as a

cathode for the rechargeable Zn-air battery, exhibiting a stable charge-voltage gap even after 1440 cycles and discharge covero 2403 to

Experimental Section

Materials

Lanthanum nitrate hexahydrate $(La(NO_3)_3 \cdot GH_2O, 99.9\%$ Alfa Aesar), cobalt nitrate hexahydrate $(Co(NO_3)_2 \cdot GH_2O, 97.7\%$ Alfa Aesar) ruthenium trichloride trihydrate $(RuCl_3.3H_2O, 30-40\%$ Ru, SRL, India), ethylene glycol (AR, 99 %, SRL, India), citric acid anhydrous (AR, 99 %, SRL, India), Nafion ionomer (Sigma Aldrich), ethanol, Milli-Q water, Pt-Ru/C with 40 wt. % Pt and 20 wt. % Ru on Vulcan XC-72R carbon (Quintech, Germany), Zn (99.95 %, Goodfellow GmbH, Germany), gas diffusion layer carbon electrode (SIGRACET GDL 38 BC).

Perovskite preparation

The LaCo_{1-x}Ru_xO₃₋₆ where x = 0, 0.1, 0.2, 0.3 and 0.5 perovskite oxides denoted as LCO, LCRO91, LCRO82, LCRO73 and LCRO55 respectively were synthesized through a modified citrate sol-gel method (Pechini method).⁴⁵ The stoichiometric amounts of La(NO₃)₃·6H₂O (99.9 % Alfa Aesar), Co(NO₃)₂·6H₂O (97.7 % Alfa Aesar) and RuCl₃.3H₂O (30-40 % Ru, SRL), were dissolved in 50 mL of ethylene glycol together with citric acid (citric acid/metal = 1:2.5 ratio). Then, the mixture was heated at 120 °C with continuous stirring for 12 h. The obtained gel was heated in a preheated muffle furnace at 350 °C for 2 h to decompose the nitrates. Finally, the obtained product was ground and calcined at 800 °C for 4 h.

Material characterization

The powder x-ray diffraction (XRD) data of the samples was collected on a Bruker D8 Advance Da Vinci diffractometer using CuK α (λ = 1.5418 Å) radiation. The morphological features were observed on a Carl Zeiss 130 VP Field Emission Scanning Electron Microscope (FESEM) and a Technai-20 G2 transmission electron microscope (TEM). The oxidation state of the samples was determined from X-ray Photoelectron Spectroscopy (XPS) using a Thermo Fischer K-AlphaTM Spectrometer with non-monochromatic Al K α radiation (1486.7 eV). The C 1s peak of the adventitious carbon (284.8 eV) was used as the reference binding energy for calibration. The oxygen non-stoichiometry (δ) values were obtained from iodometric titration.

Electrochemical activity tests

Rotating-disc electrode experiments were carried out in a PINE RDE setup with glassy carbon as the working electrode, a Pt wire as the counter electrode and an Ag/AgCl (sat. with KCl) electrode with a KNO₃ saturated salt bridge as the reference electrode as the working electrode. The catalyst ink was prepared by mixing 5 mg oxide catalyst and 1 mg Valcan-XC72 carbon in a mixture of 100 μ L of Nafion ionomer, 600 μ L of ethanol and 300 μ L mQ water. The 10 μ L dispersed catalyst ink was coated on the glassy carbon (loading = 0.204 mg cm⁻²). The bi-functional activity (ORR-OER) studies of the catalysts were carried out in both N₂ and O₂ saturated aqueous

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Fig. 1 Rietveld refined powder XRD patterns of the a) LCO, b) LCRO82, c) LCRO73 and d) LCRO55 phases. Experimental data points (red), calculated patterns (black), their differences (green) and Bragg diffraction positions (blue ticks for *R/3c* and purple sticks for *Pbnm* space group) are presented. (*The diffraction peaks marked with '*', "" corresponds to RuO*₂ [JCPDS No.: 01-070-2662] and La₂O₃ [JCPDS No.:00-022-0369] respectively).

 $0.1\,$ M KOH solutions. The potentials recorded and referred to Ag/AgCl in each experiment were calculated using the formula

E_{RHE} = E_{Ag/AgCl} + 0.059 pH + 0.198 V

Where, E_{RHE} is the potential vs. reversible hydrogen electrode (RHE), $E_{Ag/AgCl}$ is the potential vs. Ag/AgCl electrode, and pH is the pH value of electrolyte.

Zn-air battery fabrication and testing

The Zn-air battery studies of the prepared lanthanum-based catalysts were carried out in a homemade cell with an electrochemical workstation (Biologic, VSP/VMP 3B-20, France) at room temperature by galvanostatic and galvanodynamic techniques. The polished zinc foil, 6 M KOH solution, Whatman TM glass microfiber separator and the prepared catalyst coated on the gas diffusion layer were used as anode, electrolyte, separator and cathode, respectively. The air-breathing cathode was prepared by coating the slurry mixture of 1 mg of catalyst (LCO or LCRO82) in ethanol, 1 mL of Milli-Q water and 0.11 mg of 5 wt% Nafion ionomer solution on gas diffusion layer (GDL) carbon electrode and then the coated electrode was dried in a vacuum oven overnight at 80 °C.

Results and discussion

The Rietveld refined XRD patterns of the LaCo_{1-x}Ru_xO_{3- δ} (x = 0.0, 0.2, 0.3 and 0.5) powder samples are presented in Fig. 1. The LCO and LCRO82 diffraction patterns were refined using a rhombohedral

phase with an *R*/3*c* space group. The progressive substitution of Co by Ru results in a broadening of the Bragg peaks, which indicates a decrease in crystal size and substitution is inferred by a shift to lower angles in the peaks. The LCRO73 diffraction pattern has been refined with two phases having a rhombohedral structure (space group: *R*/3*c*) and orthorhombic structure (space group: *Pbnm*) with the ratio between the phases being 55:45. The LCRO55 diffraction pattern could be refined using an orthorhombic structure with *Pbnm* space group. Thus, with increasing Ru substitution, the crystal structure alters from rhombohedral to orthorhombic. These results are consistent with other reported B-site substituted perovskite materials.^{33,46} The obtained crystallographic parameters are summarized in Table S1.

FESEM images of the prepared catalysts are displayed in Fig. 2(a-d). It is seen that there is a significant change in the morphology and grain size in the bare and Ru substituted catalyst. The particles are smaller for LCRO82, LCRO73 could be slightly bigger than LCO and LCRO55 are significantly bigger. The elemental mapping of the LCRO82 sample, confirming the uniform distribution of ruthenium on the surface (Fig. 2). The corresponding Energy Dispersive X-ray Analysis (EDAX) profile is also given in Fig. 2(e). The TEM micrographs of LCO and LCRO82 are presented in Fig. S1. Both LCO and LCRO82 samples exhibit an interconnected agglomerated structure. It should be noted that the LCO sample shows larger particle size about (80-100 nm) than the LCRO82 sample (40-60 nm), these observations are consistent with FESEM results. The relatively smaller crystallite size for the 20% Ru substituted LaCoO₃ samples (LCRO82), could be due to the fact that up to 20 % Ru, it retained the rhombohedral phase whereas beyond 20 % it changed to orthorhombic phase. These structural changes are found to be influencing the particle size too. Lower the particle size higher will

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Fig. 2(a) FESEM images of (a) LCO, (b) LCRO82, (c) LCRO73, (d) LCR055 (e) EDAX profile of LCRO82 and elemental mapping of LCR082 for Mix, La, Co and Ru, respectively.

be the activity due to increased surface area and oxygen vacancies. ^{29,47} Further details of oxygen vacancies and oxidation states of the materials were obtained with X-ray photoelectron spectroscopy (XPS) studies. **Fig. 3(a-b)** shows the survey spectra of LCO and LCR082, respectively. Both display the presence of La 3d, Co 2p, O 1s, and C 1s, and LCR082 has additional Ru 3p and Ru 3d peaks. The corresponding binding energy values are listed in **Table S3**, confirming that Ru substitution was successful. **Fig. 3(c-d)** reveals the Co 2p spectra of LCO and LCR082, which split into two spinorbit doublets around 779 eV (2p_{3/2}) and 795 eV (2p_{1/2}), indicating the presence of mixed oxidation states of Co²⁺ and Co³⁺ in both the catalysts. **Table S4** presents the calculated Co²⁺/Co³⁺ ratios obtained from the area of fitted peaks, which shows that the Co²⁺/Co³⁺ ratio The O 1s XPS spectra of the LCO and LCRO82 catalysts are deconvoluted into four components,^{49–51} lattice oxygen species (O^{2-}), highly oxidative oxygen species (O_2^{2-}/O), hydroxyl groups or the surface adsorbed oxygen (OH/O_2) and adsorbed molecular water (H_2O) at 528.8 eV, 530.2 eV, 531.3 eV and 533.3 eV respectively (Fig. 3(e-f)). The relative area values of all deconvoluted peaks are given in Table S5. The oxidative oxygen species (O_2^{2-}/O^{-}) correlate to surface oxygen vacancies, which are favourable for catalysing OER/ORR activity.^{52,53}

The oxygen non-stoichiometry δ values obtained from iodometric titration of LCO and LCRO82 were 0.23 and 0.31 respectively (Table S2), which further confirms more oxygen vacancies in the LCRO82 sample.⁵⁴ The LCRO82 exhibits a higher O₂²⁻/O⁻ species ratio than LCO which implies surface oxygen vacancies.^{30,55,56}



Fig. 3 XPS spectra of LCO and LCRO82. (a) Survey scan of LCO, (b) survey scan of LCRO82, (c-d) Co 2p region, (e-f) O1s region of LCO and LCRO82, respectively and (g) C 1s for LCO, and (h) for Ru 3d and C 1s region of LCRO82 catalyst.

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Current density (mA cm⁻²)

25

20

15

10

5

0

-5

10

0.0 0.3

(d)

LCO

Current density (mA/cm²)

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Fig. 4 Bi-functional ORR/OER activities of LaCo_{1-x}Ru_xO_{3-δ} (x=0, 0.2, 0.3 and 0.5) in O₂-saturated 0.1 M KOH electrolyte (a) CV curves at 50 mV s⁻¹, (b) LSV curves of LCO catalyst at different rotation rpm (400 -2200 rpm), (c) LSV curves of LCRO82 catalyst at different rotation rpm (400-2200 rpm), (d) comparison of bi-functional activities of LaCo_{1-x}Ru_xO_{3-δ} (x=0, 0.1, 0.2, 0.3 and 0.5) and Pt, Ru/C catalysts, (e) OER and ORR overpotential of LaCo_{1-x}Ru_xO₃₋₆ (x=0.1, 0.2, 0.3 and 0.5) and Pt, Ru/C catalysts, and (f)OER Tafel slopes of all the catalysts (IR corrected).

From these results it is concluded that Ru substitution (LCRO82) creates oxygen vacancies in the structure, these observations correlate with the higher Co²⁺/Co³⁺ ratio and smaller particle size for LCRO82, which may have a great impact on the electrocatalytic activity and are consistent with other reported B-site cation substituted perovskites.57,58

The electrocatalytic activities of the prepared $LaCo_{1-x}Ru_xO_{3-\delta}$ (x=0, 0.1. 0.2. 0.3 and 0.5) catalysts towards oxygen redox were assessed by cyclic voltammetry (CV) and rotating disc electrode (RDE) measurements in O₂ and N₂-saturated 0.1 M KOH solution. Fig. 4(a) shows typical cyclic voltammograms of LCO and LCRO82 measured at a scan rate of 50 mV s⁻¹. The LCRO82 catalyst has an ORR onset potential of 0.73 V vs. the reversible hydrogen electrode (RHE), which is more positive than that of LCO, 0.63 V. Fig. 4(b-c) illustrate the linear sweep voltammograms (LSV) of LCO and LCRO82 in O_2 saturated 0.1 M KOH solution at different rotation speeds. With the increasing rotation speed, the current densities of both the catalysts gradually increase, due to the faster oxygen flux and shorter diffusion length on the electrode surface.⁵⁹ Fig. S2(a) shows the Koutecky-Levich (K-L) plot of LCRO82 at a potential range of 0.3 to 0.4 V. The plot has characteristic linearity and parallelism, suggesting first-order kinetics with respect to dissolved oxygen.47 From the slope obtained from the K-L plot, the number of electrons transferred for overall ORR reaction is found to be ~ 4, indicating reduction to water.

The oxygen evolution reaction (OER) activities (Fig. S2(b)) of $LaCo_{1-x}Ru_xO_{3-\delta}$ (x=0, 0.1, 0.2, 0.3 and 0.5) and commercial Pt, Ru/C catalysts were further examined by LSV experiments in 0.1 M KOH solution at 1600 rpm. The LCRO82 catalyst exhibits superior OER activity (1.69 V vs RHE at a current density of 10 mA cm⁻²) than that of LCO, LCRO73, LCRO55 and commercial Pt, Ru/C catalysts. Fig. 4(d) shows the bi-functional activity of $LaCo_{1-x}Ru_xO_{3-\delta}$ (x= 0, 0.1, 0.2, 0.3 and 0.5) and commercial Pt,Ru/C catalysts.

Table. 1. Summary of the half-cell testing results for the $LaCo_{x}Ru_{1-x}O_{3-\delta}$ (x =0, 0.1, 0.2, 0.3 and 0.5) and Pt, Ru/C.

Catalyst	OER performance		ORR performance	
	E (V) @ i = 10 mA cm ⁻²	i _{max} (mA cm ⁻²) @ E = 1.9 V <i>vs.</i> RHE	E (V) @ i = -3 mAcm ⁻²	i _{max} (mA cm ⁻²) @ E = 0.3 V <i>vs.</i> RHE
X=0	-	3.0	0.16	-2.32
X=0.1	1.80	16.8	0.53	-3.8
X=0.2	1.69	24.0	0.63	-4.75
X=0.3	1.81	15.2	0.41	-4.32
X=0.5	1.83	13.7	0.32	-3.11
Pt, Ru/C	1.75	-	0.72	-3.7

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Fig. 5 Zn-air battery performance of LCO, LCRO82 and Pt, Ru/C catalysts. (a), (b) The deep discharge curve and specific capacity of the primary Zn-air battery studies at current density of 5 mA/cm², (c) discharge polarization and power density curves, (d) rate capability test, (e) rechargeable Zn-air battery cycling data at a current density 5 mA/cm² in short interval (10 min per cycle), (f) Nyquist plots (inset show EIS fitted equivalent circuit) and (g) galvanostatic charge-discharge cyclic stability test .

The bi-functional activities are calculated by taking the potential difference between OER/ORR activity at benchmark current density values (ORR= -3 mA cm⁻² and OER = 10 mA cm⁻²).⁶⁰ The calculated bi-functional activities of Ru substituted catalysts are in the following order LCRO82 (1.06 V) >LCRO91 (1.27 V) > LCRO73 (1.4 V) > LCRO55 (1.51 V) as shown in Fig 4(e). The summary of bifunctional half-cell data of these samples is shown in Table 1. The LCRO82 catalyst also shows a substantial oxygen electrode activity and is compared to other reported perovskites in Table S7. Furthermore, to understand the reaction kinetics of $LaCo_{1-x}Ru_xO_{3-\delta}$

(x=0, 0.1, 0.2, 0.3 and 0.5) and commercial Pt, Ru/C electrocatalysts during OER activity, the Tafel slopes of these samples were compared (Fig 4f). The LCRO82 catalyst displays the Tafel slope of about 43 mV dec⁻¹, which is lower than that of LCRO91 (61 mV dec⁻¹) LCRO73 (66 mV dec⁻¹) LCRO55 (68 mV dec⁻¹) Pt,Ru/C (128 mV dec⁻¹) and LCO (167 mV dec⁻¹). These results reveal that the faster OER reaction kinetics as well as the enhanced OER behavior of LCRO82 catalyst.

Based on the electrocatalytic studies of the $LaCo_{1-x}Ru_xO_{3-\delta}$ compositions, LCRO82 has shown superior bi-functional activity

Journal Name

compared to the other Ru substituted catalysts. Thus, LCO and LCRO82 have been chosen as cathode candidates for Zn-air battery application and compared with the state-of-the-art Pt, Ru/C catalyst. Fig. 5(a-b) presents primary Zn-air battery studies for LCO, LCRO82 and Pt, Ru/C. The open-circuit voltage of LCO and LCRO82 (1.28 V) are lower than that of Pt, Ru/C (1.38 V). LCRO82 exhibited a higher specific capacity and stability (433 mAh g⁻¹ discharged over 33 h) than LCO (304 mAh g⁻¹ discharged over 23 h), whereas commercial Pt, Ru/C discharged over 43 h and delivered the highest discharge capacity of 551 mAh g⁻¹. Fig. 5(c) displays the discharge polarization and power density curves of Zn-air battery using LCO, LCRO82 and Pt, Ru/C cathode catalyst. The LCRO82 catalyst delivers a peak power density of 136 mW cm⁻² at the current density of 175 mA cm⁻², which is much better than that of the LCO catalyst (20 mW cm⁻² at a current density of 105 mA cm⁻²) and is closer to the Pt, Ru/C catalyst (178 mW cm⁻² at current density of 200 mA cm⁻²) respectively. Fig. 5(d) shows current step down and step up discharge rate capability test for the LCO, LCRO82 and Pt, Ru/C catalysts with different current densities (1-30 mA cm⁻²) at 5 min discharge, Fig. 5(e) presents typical galvanostatic charge-discharge cyclic stability tests for the secondary Zn-air battery at a current density of 5 mA cm⁻². The charge and discharge cycling stability of the LCO and LCRO82 shows a comparable voltage gap, higher than that of Pt, Ru/C for the initial few cycles. After 180 cycles, LCRO82 shows a lower charge-discharge gap of 0.78 V with a higher roundtrip efficiency of 60 %, which is a lower than that of LCO (0.82 V, round-trip efficiency 59 %) and comparable to Pt, Ru/C (0.78 V, round-trip efficiency 60 %). Thus, Ru substituted perovskite is a highly promising catalyst for rechargeable Zn-air battery applications, showing higher cycling stability with prominent roundtrip efficiency. To further understand the internal resistance of the constructed Zn-air battery containing LCO, LCRO82 and Pt, Ru/C, electrochemical impedance spectroscopy (EIS) studies were conducted (Fig. 5(f)). The impedance data are fitted using an equivalent circuit and details are given in supporting information (Fig S3 and table S6). The R(QR)(QR)W equivalent circuit is used for fitting of impedance data, where R implies the resistance contributions of different components of cell: solution resistance (Rs), solid-electrolyte interface resistance (R₁), charge transfer resistance (R_2) and Q is the constant phase elements (CPE). Warburg diffusion models cannot be related to M-air batteries as O_2 concentrations tend to vary point to point within cell environments. Thus, W is attributed to the mass transfer of oxygen at the cathode.^{61,62} The simulated resistance values of LCO, LCRO82 and Pt, Ru/C are presented in (Table. S6.). The smaller R₁ of LCRO82 (0.40Ω) than Pt, Ru/C and LCO suggests lower solid electrolyte interface (SEI) resistance.⁶³ The charge transfer resistance value (R_{ct}) of LCRO82 (0.54 Ω) is negligible and lower than that of Pt, Ru/C and LCO. The lower $R_{\rm ct}$ value is a strong indication of improvement in the catalytic kinetics.⁶⁴ Long charge-discharge cycling (10 min per cycle) of the LCRO82 catalyst was performed by mechanically replacing the zinc plate and electrolyte at a current density of 5 mA cm⁻² (Fig. 5(g)). The charge-discharge voltage gap of the constructed Zn-air battery shows a stable charge-voltage gap even after 1440 cycles and discharged over 240 h. This is a clear indication of the stability and efficiency of LCRO82 cathode in Zn-air environment under prolonged operation. Moreover, the rechargeable Zn-air performance of LCRO82 cathode outperforms several reported perovskite catalysts (Table S8.) With facile bi-functional electrocatalytic activity inherited by oxygen vacancies, single phase with superior structural benefits and cobalt redox features

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 $\label{eq:label} LaCo_{0.8}Ru_{0.2}O_{3-\delta} \mbox{ demonstrates itself as a promising candidate for the rechargeable Zn-air batteries.} DOI: 10.1039/D0TA06673G$

Conclusions

The B-site substitution of $LaCoO_3$ with Ru ($LaCo_{1-x}Ru_xO_{3-\delta}x = 0, 0.1,$ 0.2, 0.3 and 0.5) provides a highly efficient non-precious metal bifunctional catalyst for rechargeable Zn-air battery application in alkaline media. The $LaCo_{0.8}Ru_{0.2}O_{3-\delta}$ (LCRO82) catalyst exhibits promising electrocatalytic activities in both OER and ORR reactions in 0.1 M KOH solution with smaller OER Tafel slope of 43 mV/dec and 4 electron transfer of reduction to water. The rechargeable Znair battery studies using the LCRO82 catalyst reveal superior charge and discharge potential and improved round trip efficiency than the LCO catalyst and comparable to state-of-art Pt,Ru/C catalyst. Moreover, the mechanically rechargeable Zn-air battery containing the LCRO82 catalyst shows a stable charge-discharge voltage gap even after 1400 cycles with excellent cycling stability for 240 h. These results strongly suggest that $LaCo_{0.8}Ru_{0.2}O_{3-\delta}$ (LCRO82) can be used as an alternative efficient non-precious metal bi-functional catalyst for Zn-air battery applications.

Conflicts of interest

There are no conflicts to declare

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