

Electrochemical evaluation of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ cathode material for zinc air batteries application

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Received: 17 May 2007 / Accepted: 18 March 2008 / Published online: 18 April 2008
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Abstract We synthesized nano-sized $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ ($x=0.1-0.4$) cathode catalysts for zinc air secondary batteries by the citrate method, and measured electrochemical characteristics of the cathodes according to the cathode catalyst's calcium content. We heat treated the prepared precursor at a calcination temperature of 700°C , and examined it by XRD analysis and electrochemical evaluation. We examined the prepared $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ catalyst powder's oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and cycle-stability performance. When we consider ORR, OER and cycle-stability performance simultaneously, $\text{La}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$ catalyst showed the best performance because of its lowest voltage deference between charge and discharge, and its lowest degradation according to cycle.

Keywords Zinc air batteries · Oxygen reduction · Oxygen evolution · Cathode

1 Introduction

Bifunctional oxygen electrodes play a key role in the development of electrically rechargeable metal/air batteries. Many kinds of electrocatalysts have been investigated for

oxygen reduction and evolution reactions. Compared to noble metal catalysts, metal oxides in the form of perovskites, pyrochlores and spinels have the advantages of avoiding gassing on the zinc electrode when they act as bifunctional electrodes for the oxygen reduction and evolution reactions [1–3].

Perovskites, having a general formula of ABO_3 , are interesting oxygen electrode catalysts because of their high oxide ion mobility. By partially substituting a cation A' for A, or a cation B' for B, with different valence, ionic defects or changes in the valence states of the catalytically active metal B can be induced in the perovskite to influence its catalytic activity and conductivity [4, 5].

Calcium-doped LaCoO_3 perovskite has been considered for bifunctional cathode applications. Bi-functional cathodes for zinc air secondary batteries should promote oxygen reduction and evolution reactions simultaneously. The Substitution of Ca^{2+} for La^{3+} increases the oxygen vacancy concentration and, thus, supports increased oxygen ion conductivity [6]. To decide the contents of Ca^{2+} which is substituted to La^{3+} , we prepared calcium-doped LaCoO_3 perovskite and investigated its electrochemical performance according to Ca doping level.

2 Experimental

2.1 Preparation of catalyst precursor

Calcium-doped LaCoO_3 perovskite powder was prepared by the citrate method. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and citric acid were used as starting materials. Metal nitrates were mixed in a stoichiometric molar ratio of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ ($x=0.1-0.4$) and dissolved in deionized water. Then citric acid was added as a chelating

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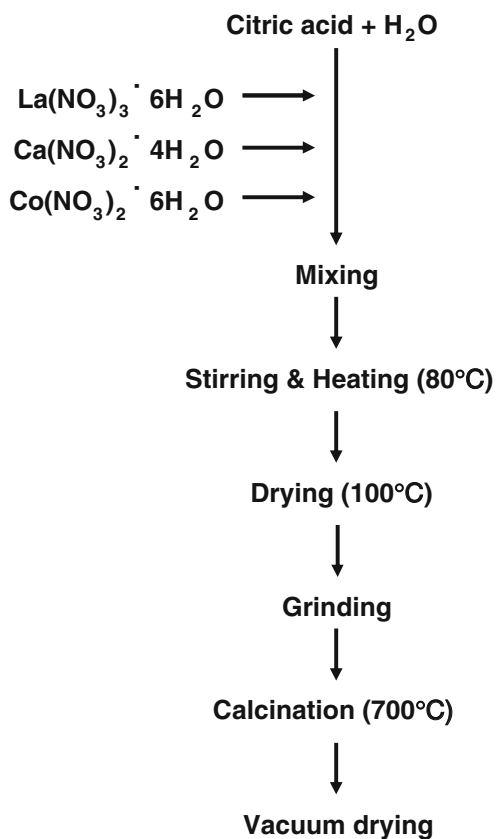


Fig. 1 Process of manufacturing the cathode catalyst

agent while stirring constantly. After mixing the starting materials, the solution containing a mixture of citric acid and constituent metal nitrates, $\text{La}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was heated at 80°C for several hours in order to evaporate the excess solvents, to promote polymerization and to achieve gel precursor, which

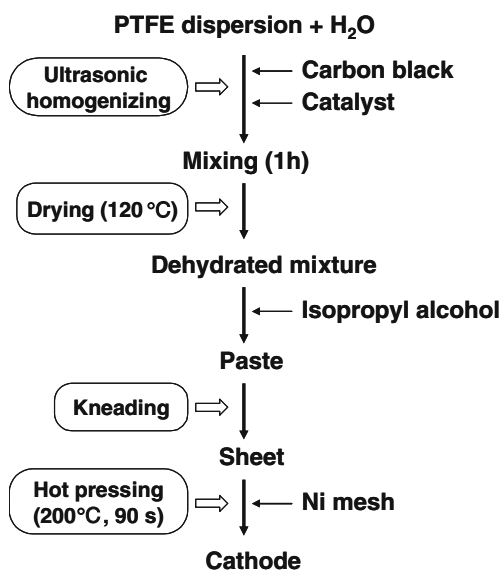


Fig. 2 Process of manufacturing the cathode

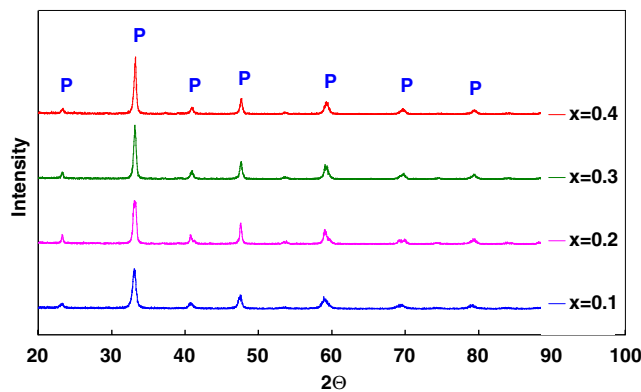


Fig. 3 XRD patterns of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ ($x=0.1-0.4$) catalyst after calcination

was dried at 100°C for 12 h and then calcined for 2 h at 700°C (Fig. 1).

2.2 Preparation of cathode and half cell fabrications

To manufacture the cathode, we first mixed the PTFE dispersion with distilled water, and then added Vulcan XC-72 carbon and the $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ catalyst to that mixture in sequence. The mixed slurry was then dried at 120°C . After dropping 15 cc of isopropyl alcohol into the dehydrated mixture, we pasted and kneaded it with a roll presser, making a layer $300\ \mu\text{m}$ thick. These cathode sheets were attached to both sides of the Ni mesh, and finally were hot pressed at a temperature of 200°C to remove residual moisture. To prevent moisture from penetrating from the outside and flooding out the electrolyte from the inside, we attached a gas-diffusion layer electrode to one side of the cathode. This gas-diffusion layer electrode supplies airflow channels and reaction sites in the cathode of zinc air batteries. Figure 2 shows the process of manufacturing the cathode.

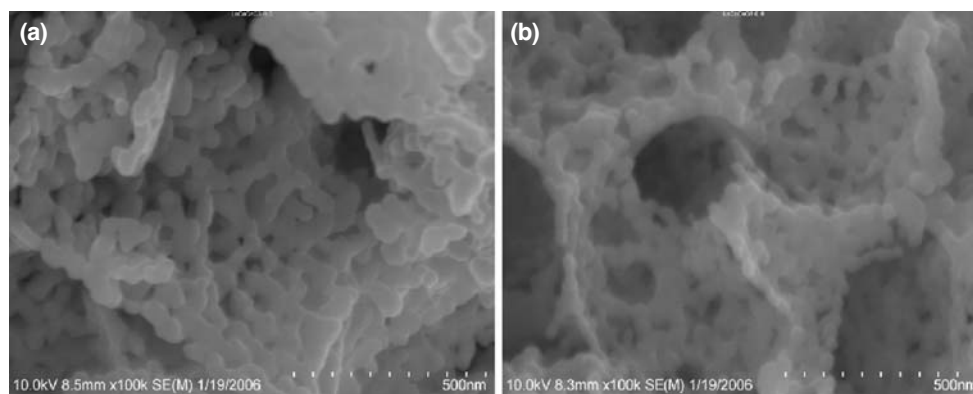
The prepared disk-type cathode as a working electrode was placed into an electrochemical cell. On the opposite side, the platinum mesh as a counter electrode was placed with an Hg/HgO electrode as a reference electrode. The electrolyte was prepared by 8.5 M KOH of potassium hydroxide (KOH) and filled the cell.

2.3 Electrochemical experiments

Electrochemical characterizations were performed in a three-electrode half cell. The scan rate for linear sweep voltammograms (LSV) and cyclic voltammograms (CV) were 2 and 5 mV/s, respectively.

The cathode's surface morphology was examined through a scanning electron microscope (S-2700, Hitachi, Japan). The XRD patterns were determined by an X-ray diffractometer (1830 X-ray diffractometer, Philips) using Ni

Fig. 4 SEM images of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ ($x=0.1-0.2$) catalyst; (a) $x=0.1$, (b) $x=0.2$



filtered Cu $K\alpha$ radiation ($\lambda=1.5406\text{\AA}$) in the 2θ range of $20-90^\circ$ at a scan rate of $0.1^\circ/\text{s}$. A potentiostat (VMP3, Princeton Applied Research) was used for electrochemical measurement of the half cell.

3 Results and discussion

3.1 Physical properties

In a previous study we found that only when we calcined the catalyst at 700°C could we achieve a pure single-phase perovskite structure [7]. Through the XRD analysis shown in Fig. 3, we checked that calcined powder at 700°C had the $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ perovskite structures.

Figure 4 shows the morphology of the $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ ($x=0.1-0.2$) catalyst. The powders calcined at 700°C contained homogeneous and nano-sized particles (average particle size was 50 nm). The citrate method is a useful process for synthesizing fine powder because it can reduce the calcination temperature and increase the surface area, resulting in increasing ORR and OER.

3.2 Cathodic and anodic polarization performance

The activity of ABO_3 perovskite type catalyst material could be modified by doping the A and B positions [8]. Cathodic polarization was carried out for the oxygen reduction reaction. Figure 5 shows the polarization curves for a series of calcium-doped perovskites, $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$, $\text{La}_{0.7}\text{Ca}_{0.3}\text{CoO}_3$, $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$. At a current density of $50\text{ mA}/\text{cm}^2$, 346 mV for $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$, 360 mV for $\text{La}_{0.7}\text{Ca}_{0.3}\text{CoO}_3$, 494 mV for $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and 246 mV for $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$ were achieved as the cathodic overpotentials. These results mean that $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$ has the best activity for the oxygen reduction reaction.

A partial substitution of La^{3+} by Ca^{2+} can improve the catalytic behavior. The lattice parameter decrease, with

increasing Ca content. Because, the ionic radius of Ca^{2+} (0.99 Å) is smaller than that of La^{3+} (1.14 Å). So BET surface area can be increased with increasing Ca content, and it gives rise to improvement of catalytic performance. But, A. Kahoul et al. [9] reported that when they use water as a solvent to synthesize the catalyst precursor, they could not observe the significant variation of surface area in the $0.1 \leq x \leq 0.4$ range. Furthermore, the heterogeneity in the material could be increased for higher Ca concentration.

Therefore, as shown in Fig. 5, the poor electrochemical performance for oxygen reduction reaction was caused from heterogeneity in the range of $0.2 \leq x \leq 0.4$.

Figure 6 shows the anodic polarization curves. According to Ca doping level, the activity for oxygen evolution changed slightly. At a current density of $50\text{ mA}/\text{cm}^2$, 658 mV for $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$, 686 mV for $\text{La}_{0.7}\text{Ca}_{0.3}\text{CoO}_3$, 494 mV for $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and 648 mV for $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$ were achieved as the anodic overpotentials. $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ showed the best activity for the oxygen evolution reaction.

Bi-functional catalysts for cathodes should act to reduce the irreversibility occurring when the battery is charged and

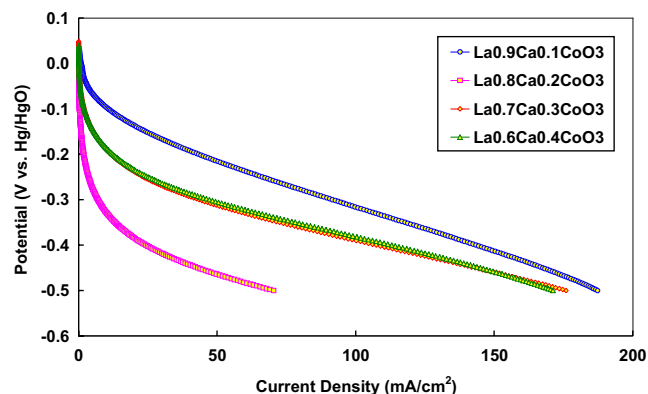


Fig. 5 Cathodic polarization curves of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ ($x=0.1-0.4$) cathode

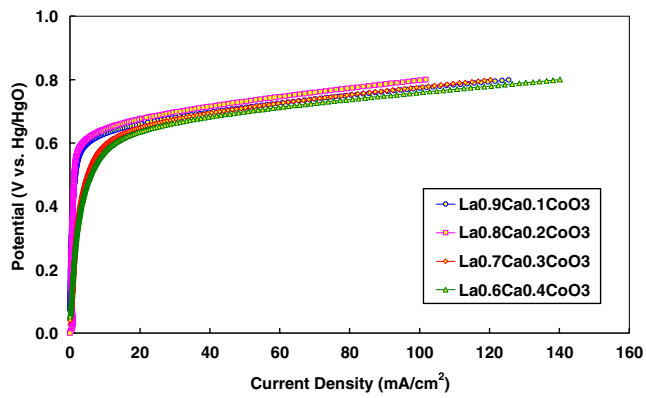


Fig. 6 Anodic polarization curves of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ ($x=0.1-0.4$) cathode

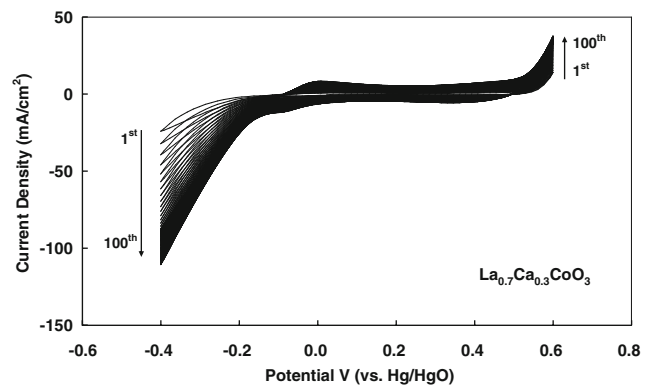


Fig. 9 Cyclic voltammogram of $\text{La}_{0.7}\text{Ca}_{0.3}\text{CoO}_3$ cathode at a sweep rate of 5 mV/s

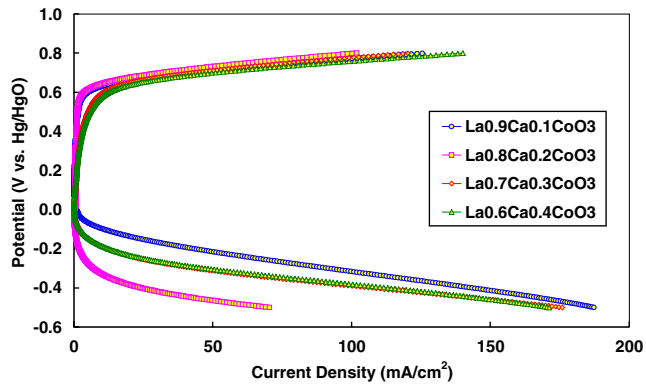


Fig. 7 Anodic and cathodic polarization curves of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ ($x=0.1-0.4$) cathode

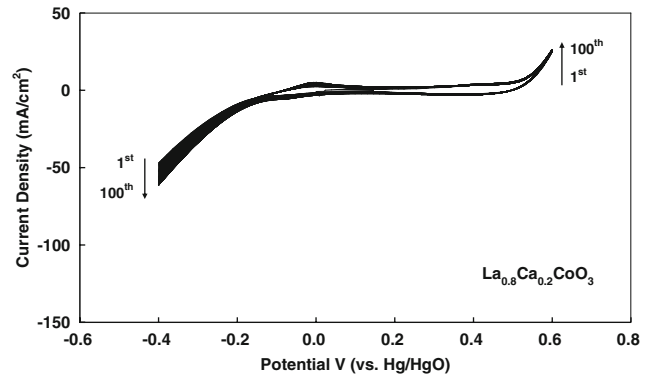


Fig. 10 Cyclic voltammogram of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ cathode at a sweep rate of 5 mV/s

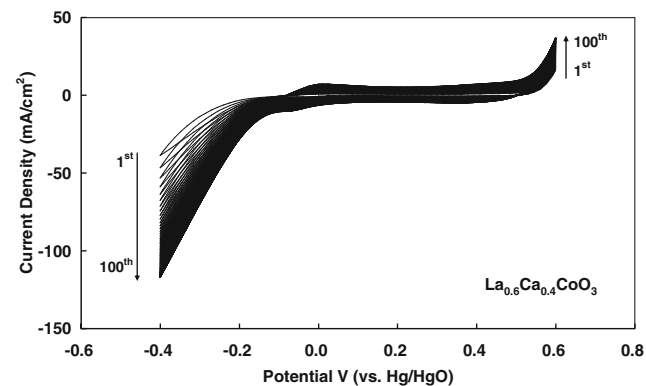


Fig. 8 Cyclic voltammogram of $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ cathode at a sweep rate of 5 mV/s

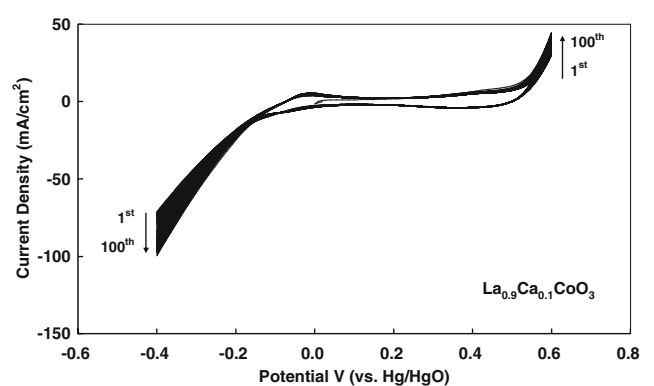


Fig. 11 Cyclic voltammogram of $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$ cathode at a sweep rate of 5 mV/s

discharged. Oxygen evolution and reduction in aqueous solutions occur at a high overpotential [$E(\text{O}_2, \text{gen.}) > E(\text{O}_2, \text{red.})$]. This irreversibility of the reactions is the main problem in the development of cathodes. Development of bi-functional catalysts for cathodes is an important prerequisite for a zinc air secondary battery [10]. Some researchers have studied and reported the irreversibility of the charge and discharge reaction. Kannan et al. reported 0.6 V of potential difference between charge ($i=100 \text{ mA/cm}^2$) and discharge ($i=30 \text{ mA/cm}^2$) for LaNiO_3 ; and Shimizu et al. reported 1V for $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ ($i=100 \text{ mA/cm}^2$) [4].

Figure 7 shows anodic and cathodic polarization curves of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ ($x=0.1-0.4$). In this measurement, the potential differences between charge (oxygen evolution, $i=50 \text{ mA/cm}^2$) and discharge (oxygen reduction, $i=50 \text{ mA/cm}^2$) were 1.00 V for $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$, 1.05 V for $\text{La}_{0.7}\text{Ca}_{0.3}\text{CoO}_3$, 0.99 V for $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and 0.89 V for $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$. The activities of calcium-doped LaCoO_3 perovskite in the oxygen reduction and evolution reactions were found to decrease in order of $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3 > \text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3 > \text{La}_{0.7}\text{Ca}_{0.3}\text{CoO}_3 > \text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$. So considering only initial performance, we chose $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$ as a good candidate for the bifunctional catalyst in a zinc air secondary battery.

3.3 Cycleability

Figure 8, 9, 10, and 11 show the results of 100 cyclic voltammetric curves of both oxygen reduction and evolution reactions on the cathode containing prepared perovskite catalysts. The cyclic voltammetry was conducted in a potential range of -0.4 V to $+0.6 \text{ V}$ with a scan rate of 5 mV/s .

The perovskite $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ and $\text{La}_{0.7}\text{Ca}_{0.3}\text{CoO}_3$ have unstable cyclic voltammetric curves, as shown in Figs. 8 and 9. Repeating the cycle number increased not only anodic current, but also cathodic current. This was probably caused by a degradation in the perovskite's structural properties during cycling. However, $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$ have very stable cycling compared to $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ and $\text{La}_{0.7}\text{Ca}_{0.3}\text{CoO}_3$, as shown in Figs. 10 and 11. But the perovskite $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ has lower cathodic and anodic current than $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$.

4 Conclusions

We prepared nano-sized catalysts for oxygen reduction and evolution by the citrate method.

Considering oxygen reduction and evolution reactions simultaneously, $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$ could be taken as a good bi-functional catalyst for cathodes. The potential difference between charge (oxygen evolution, $i=50 \text{ mA/cm}^2$) and discharge (oxygen reduction, $i=50 \text{ mA/cm}^2$) was 0.89 V.

Because of the heterogeneity in material, in the higher Ca concentration range ($0.2 \leq x \leq 0.4$), it showed reduced catalytic performance compare to $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$.

Considering initial electrochemical performance and cycling simultaneously, $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$ and $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ could be taken as good bi-functional catalysts for cathodes but, because of its low cathodic and anodic current, $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ should be excluded. In conclusion, the optimum calcium-doped LaCoO_3 for a bi-functional catalyst for cathodes was $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$ in our study.

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