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Short Communication

Electrocatalytic Activity of Nanoporous Perovskite $La_{1-x}Ca_xCoO_3$ Towards Hydrogen Peroxide Reduction in Alkaline Medium

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Perovskite-type series of $La_{1-x}Ca_xCoO_3$ compounds were synthesized by a modified amorphous citrate precursor method. Their catalytic activities for hydrogen peroxide electroreduction in 3.0 mol dm^{-3} KOH at 25 °C were evaluated by cyclic voltammetry and galvanostatic measurement. The influence of x in $La_{1-x}Ca_xCoO_3$ on their catalytic performance was investigated. Among these compounds, $La_{0.6}Ca_{0.4}CoO_3$ calcined at 650 °C exhibited the highest catalytic activity. An aluminum-hydrogen peroxide cell containing 0.4 mol dm^{-3} H_2O_2 as oxidant and using $La_{0.6}Ca_{0.4}CoO_3$ as cathode catalyst achieved a peak power density of 201 mW cm^{-2} at 150 mA cm^{-2}.

Keywords: Perovskite; Hydrogen peroxide electroreduction; Aluminium-hydrogen peroxide cell

1. INTRODUCTION

Oxygen reduction reaction (ORR) in alkaline medium is a critical electrochemical process in fuel cells. Generally, pure oxygen is used as oxidant in fuel cells. However, due to the inconvenient use of compressed oxygen and the higher activation energy for ORR causing lower oxygen electro-reduction rates, the application of oxygen is to some extent limited. Hydrogen peroxide (H_2O_2) is a relatively easy handing liquid and its reduction is a faster kinetic process involved in a two-electron transfer. And the mechanism of the H_2O_2 reduction at perovskite electrodes can be described as the following equations [1,2]

$$HO_2^- + H_2O + 2e^- = 3OH^- \qquad (1)$$

or

$$HO_2^- = 2\ OH^- + O_2 \qquad (2).$$

As a potential alternative to the cathodic reaction in direct liquid fuel cell, electrochemical reduction of hydrogen peroxide has been paid much attention. [3,4]

Usually, noble metals are known to be fairly active for H_2O_2 electroreduction.[5] Noble metals catalysts, however, have some serious problems to be overcome before worldwide spread of fuel cells, such as expensive cost and limited resources. Perovskite-type (ABO_3) oxides, especially $La_{1-x}Ca_xCoO_3$, have captured considerable attention due to their low cost, wide availability and stability in alkaline solution.[6,7] Their catalytic activity, ionic and electronic conductivity can be tuned by partially replacing the elements in either A-site (such as La and Ca) or B-site (such as Co, Mn and Ni). Recently, Wang *et* al.[8] reported the electrocatalytic activity of $La_{1-x}Sr_xMnO_3$ towards hydrogen peroxide reduction in alkaline electrolyte, and found that the $La_{0.4}Sr_{0.6}MnO_3$ exhibited the best catalytic activity for hydrogen peroxide reduction. To date, the electrocatalytic behavior of $La_{0.6}Ca_{0.4}CoO_3$ towards oxygen reduction in alkaline electrolyte has been reported by our group and the results showed that the homogeneous nanoporous $La_{0.6}Ca_{0.4}CoO_3$ exhibited good catalytic activity for oxygen reduction.[9] Hence, it would be significant to study the catalytic behavior of perovskite-type $La_{1-x}Ca_xCoO_3$ for H_2O_2 reduction.

The aim of this work is to explore the possibility for the application of perovskite-type compounds as H_2O_2 cathode. Nanoporous perovskite $La_{1-x}Ca_xCoO_3$ were synthesized by a modified amorphous citrate precursor (ACP) method. The electrocatalytic activity and stability of $La_{1-x}Ca_xCoO_3$ for H_2O_2 reduction in alkaline medium were investigated by cyclic voltammetry and chronoamperometry. The performances of $La_{1-x}Ca_xCoO_3$ as the cathode catalysts in alkaline aluminun-H_2O_2 cells were evaluated.

2. EXPERIMENTAL

The catalyst $La_{1-x}Ca_xCoO_3$ powders were synthesized by a modified-ACP method according to the similar procedure described in our previous report.[9] Phase identifications of the synthesized powders were conducted by a MXPAHF X-ray diffractometer from 20 º to 80 º with a Cu *Kα* of 1.54056 Å. Both the morphologies and energy dispersive X-ray spectroscopy (EDS) of the as-prepared $La_{1-x}Ca_xCoO_3$ particles were observed by a Hitachi S-4800 scanning electron microscope equipment. Specific surface area was measured by nitrogen adsorption-desorption with the Brunauer-Emmett-Teller (BET) method.

To prepare $La_{1-x}Ca_xCoO_3$ electrodes, $La_{1-x}Ca_xCoO_3$ powder and carbon black (Vulcan XC-72) were dispersed in anhydrous ethanol by sonication for 10 min to obtain a suspension, to which a polytetrafluorethylene (PTFE, 10 wt.% in H_2O) emulsion was added. This mixture was blended for another 30 min with ultrasonic agitation and then dried at 80 °C to obtain a dough–like paste, which was finally rolled into a thin layer of about 200 μm in thickness. These thin layers had the same geometrical area of 1.0 cm^2 (10 mm × 10 mm) and the catalyst loading was about 0.2 mg cm^{-2}. Two pieces of the identical thin layers were finally pressed together with a nickel foam current collector under 10 MPa pressure for 30 s and then sintered for 30 min at 340 °C. The obtained electrodes consisted of 75 wt.% $La_{1-x}Ca_xCoO_3$, 15 wt.% carbon black and 10 wt.% PTFE.

Electrochemical measurements were performed in a standard three-electrode electrochemical cell with a saturated Ag/AgCl reference electrode and a bright platinum (2 cm^2) foil as the counter electrode. The electrolyte was 3.0 mol dm^{-3} KOH containing 0.4 mol H_2O_2. Cyclic voltammetry and galvanostatic profiles were conducted by Parstat 2273. The $La_{1-x}Ca_xCoO_3$ electrodes had been rested in the electrolyte for 24 h to assure that the electrolyte had sufficient time to penetrate into the structure of the electrodes. And then all cyclic voltammetry curves were obtained until they were repeatable. The reported current densities were calculated using the geometrical area of the electrode.

The performances of $La_{1-x}Ca_xCoO_3$ as cathode catalysts of the Al-H_2O_2 cells were examined by using a home-made flow through test cell as shown in Fig. 1.

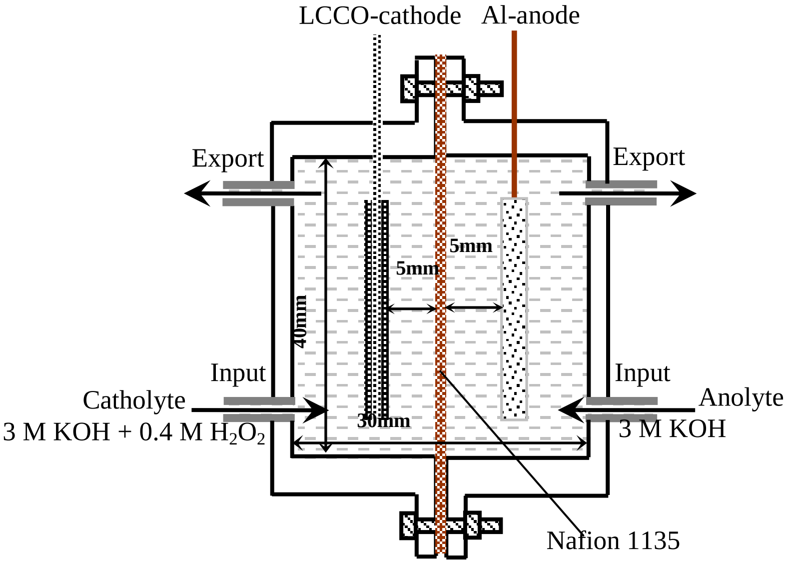

Figure 1. Schematic diagram of the plexiglass cell used for electrochemical measurements. The dimensions of the cell are 30 mm ×40 mm ×40mm (L×W×H), the distances from the electrodes to the membrane are both 5mm.

The aluminum alloy LF6 (91.9%Al, 6.5%Mg, 0.6%Mn, 0.3%Fe, 0.3%Si, 0.2%Zn, 0.1%Ti) served as anode. Both the aluminum alloy anode and the $La_{1-x}Ca_xCoO_3$ cathode had the same geometrical area of 4.0 cm^2 (20 mm × 20 mm). Nafion-1135 (DuPont) membrane was used as the separator. The anolyte (3.0 mol dm^{-3} KOH) and the catholyte (3.0 mol dm^{-3} KOH + 0.4 mol dm^{-3} H_2O_2) were pumped into the bottom of the anode and the cathode compartment, respectively, using an individual peristaltic pump, at a flow rate of 80 cm^3 min^{-1}, and exited at the top of the compartments. The electrochemical performance of the Al-H_2O_2 was recorded at 25 °C on a battery test instrument (Wuhan Land Electronic Co. Ltd., China).

3. RESULTS AND DISCUSSION

XRD analysis was performed to obtain information about the formation of crystallographic phase and about the influence of the ratio of La to Ca on the structure of $La_{1-x}Ca_xCoO_3$ compounds.

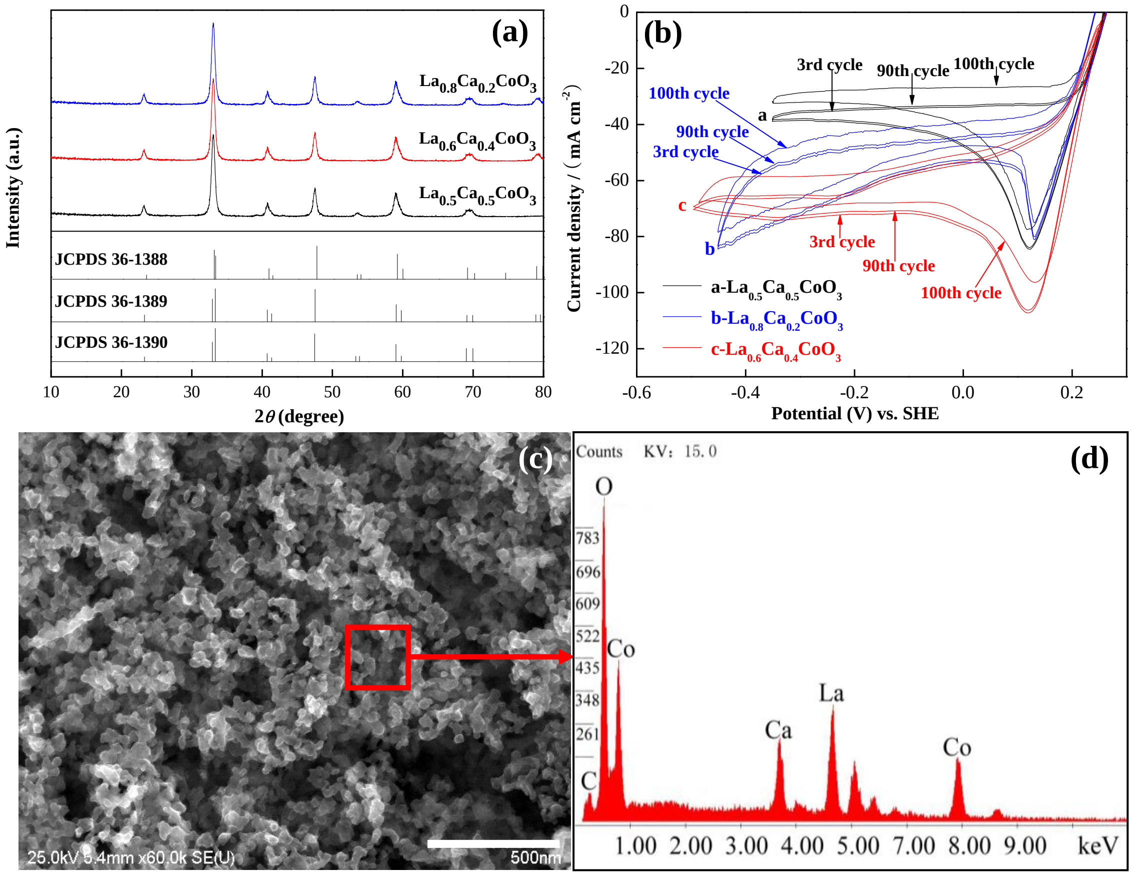

Figure 2. XRD patterns of $La_{1-x}Ca_xCoO_3$ with x equal to 0.2, 0.4 and 0.5 calcined at 650 °C (a), SEM image of $La_{0.6}Ca_{0.4}CoO_3$ calcined at 650 °C (c), the EDS spectrum collected onto the square zone of image (d) and cyclic voltammograms of $La_{1-x}Ca_xCoO_3$ recorded in 3.0 mol dm^{-3} KOH containing 0.4 mol dm^{-3} H_2O_2 with the scan rate of 5 mV s^{-1} (b).

Fig. 2a presents the XRD patterns of a series of $La_{1-x}Ca_xCoO_3$ compounds calcined at 650 °C (x = 0.2, 0.4 and 0.5) along with their standard patterns (JCPDS 36-1388, 36-1389, 36-1390). As shown in Fig. 2a, the XRD patterns were all in good agreement with their corresponding JCPDS standard patterns respectively, without any impurity, indicating that these three samples presented pure perovskite phases and were all well crystallized at 650 °C. The average crystalline size of the calcined samples at 650 °C, calculated based on the Scherrer equation, was between 34 and 40 nm. In addition, the specific surface areas of $La_{1-x}Ca_xCoO_3$ determined by the BET technique were about 205, 210 and 212 m^2/g for x = 0.2, 0.4 and 0.5, respectively. Such a high specific surface area supplied a number of surface active sites, which could facilitate material's electrocatalytic properties.

Fig. 2c and 2d shows the morphology of $La_{0.6}Ca_{0.4}CoO_3$ sample calcined at 650 °C, together with the EDS spectrum of the particles in the selected regions. EDS only detected trace amount of the carbon element (Fig. 2d), which might come from the carbon tap during the EDS test. As shown in Fig. 2c, most of the particles were in irregular shape, but presented novel nanoporous structure with the particle size of about 40 nm. In the modified-ACP preparation process, the carbon can not only hinder the growth of solid particles during heating but also act as the pore-forming material which caused pore structure forming after burning out when the calcination temperature reached above 600 °C. Because the interconnected pore could form channels, it would be convenient for the electrolyte and H_2O_2 to move onto the internal surfaces of the nanoporous catalysts.[10]

Fig. 2b shows the effect of the ratio of La to Ca on the electrocatalytic activities of $La_{1-x}Ca_xCoO_3$. The three different compositions were tested by cyclic voltammetry for 100 cycles. The cyclic voltammograms were recorded at a scan rate of 5 mV s-1 in 3.0 mol dm-3 KOH containing 0.4 mol dm-3 H_2O_2. As shown in Fig. 2b, H_2O_2 electroreduction started at around +0.23 V vs. SHE, being independent of the composition of $La_{1-x}Ca_xCoO_3$. For these three samples, the cyclic voltammograms were very stable from the 2nd cycle to the 90th cycle. After the 90th cycle, the cathodic peak current density gradually declined, which is due to the exfoliation of the active materials from the surface of the electrodes.

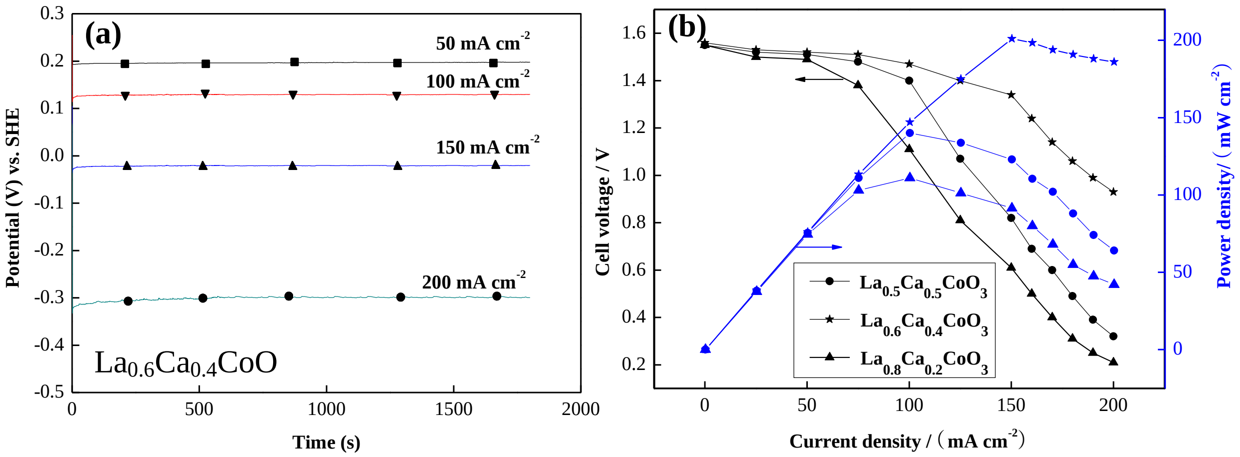

Figure 3. Galvanostatic curves for H_2O_2 electroreduction on $La_{0.6}Ca_{0.4}CaO_3$ electrode at different current densities in 3.0 mol dm^{-3} KOH + 0.4 mol dm^{-3} H_2O_2 (a), performance of Al-H_2O_2 single semi-fuel cell with $La_{1-x}Ca_xCaO_3$ electrodes (b). Anolyte: 3.0 mol dm^{-3} KOH at a flow rate of 80 cm^3 min^{-1}. Catholyte: 3.0 mol dm^{-3} KOH + 0.4 mol dm^{-3} H_2O_2. Operation temperature: 25 °C.

It is well known that the electroreduction of H_2O_2 can proceed through direct and indirect pathways. The direct reduction occurs via a two-electron process ($H_2O_2 + 2e^- \rightarrow 2OH^-$). The indirect reduction consists of the decomposition of H_2O_2 to O_2 followed by electroreduction of the latter. As shown in Fig. 2b, the current densities varied with the mole ration of La to Ca, for example, the current densities at 0.1 V vs. SHE was -56, -99 and -76 mA cm^{-2} with x = 0.2, 0.4 and 0.5 which were all higher than those reported by Cao *et al.*[11]. Among these three samples, the $La_{0.6}Ca_{0.4}CoO_3$ sample presented the highest cathodic peak current density, indicating that the sample $La_{0.6}Ca_{0.4}CoO_3$ sample exhibited the best catalytic activity for H_2O_2 electroreduction. This might be related to more oxygen vacancy on the surface structure of $La_{0.6}Ca_{0.4}CoO_3$.[12]

The stability of $La_{0.6}Ca_{0.4}CoO_3$ electrode for H_2O_2 electroreduction was also investigated by galvanostatic measurements. Fig. 3a shows galvanostatic curves of H_2O_2 electroreduction on $La_{0.6}Ca_{0.4}CoO_3$ calcined at 650 °C with various current densities. At these four current densities, the voltage readings agreed well with the results of cyclic voltammograms. As shown in Fig. 3a, the voltage reached to steady state after a few seconds and did not decrease within 30 min test period, indicating that the catalytic performance of $La_{0.6}Ca_{0.4}CoO_3$ was stable and sustainable for hydrogen peroxide electroreduction. These galvanostatic results demonstrated that perovskite $La_{1-x}Ca_xCoO_3$ possesses considerable catalytic activity and stability towards electroreduction of H_2O_2 in alkaline medium at 25 °C.

The electrochemical performances of $La_{1-x}Ca_xCaO_3$ as the cathode catalyst in Al-H_2O_2 cells were investigated. Fig. 3b presents plots of cell voltage and power density against current density. The cells were operated at 25 °C with 0.4 mol dm^{-3} H_2O_2 feeding to the cathode compartment. All the cells exhibited an open circuit voltage of around 1.55 V. In alkaline media, the cell reaction of an Al-H_2O_2 battery is

$$2Al + 3H_2O_2 + 2OH^- \rightarrow 2Al(OH)_4^- \qquad (3)$$

The theoretical voltage of the reaction is 2.3 V. However, the actual voltage that can be achieved typically falls in the range of 1.0-2.0 V.[13] It was observed that with the increase of current density, the voltages of the cells decayed almost linearly until reaching to the mass transport control region and then dropped drastically. It was indicated that the cell performances were limited by both the poor mass transport within the cathode and the large ohmic resistance.[8] Among these three electrodes, the $La_{0.6}Ca_{0.4}CaO_3$ as the cathode catalyst of Al-H_2O_2 cell presented the best electrochemical performance, delivering a peak power density of 201 mW cm^{-2} at 150 mA cm^{-2} and 1.34 V, which was comparable with that of Al-H_2O_2 cell using nanoparticle Co_3O_4 cathode catalyst.[10] It is worth to mention that $La_{1-x}Ca_xCoO_3$ can also be used as cathode catalysts for other types of fuel cells using H_2O_2 as oxidant such as direct methanol-H_2O_2 fuel cell[14] and borohydride-H_2O_2 fuel cell[15].

4. CONCLUSIONS

Nanoporous perovskite $La_{1-x}Ca_xCoO_3$ compounds were prepared by a modified-ACP method. Their catalytic activities for H_2O_2 electroreduction in alkaline medium were evaluated at 25 °C. The results showed that the sample $La_{0.6}Ca_{0.4}CaO_3$ calcined at 650 °C exhibited the best catalytic activity. The Al-H_2O_2 fuel cell using $La_{0.6}Ca_{0.4}CaO_3$ as cathode catalysts displayed an open circuit voltage of 1.55V and a peak power density of 201 mW cm^{-2}.

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