Short communication

LaNi$_{0.8}$Co$_{0.2}$O$_3$ as a cathode catalyst for a direct borohydride fuel cell

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ABSTRACT

A perovskite-type oxide LaNi$_{0.8}$Co$_{0.2}$O$_3$ is prepared as a direct borohydride fuel cell (DBFC) cathode catalyst. Its electrochemical properties are studied by cyclic voltammetry. The results demonstrate that LaNi$_{0.8}$Co$_{0.2}$O$_3$ exhibits excellent electrochemical activity with respect to the oxygen reduction reaction (ORR) and good tolerance of BH$_4^-$ ions. Maximum power densities of 114.5 mW cm^{-2} at 30 °C and 151.3 mW cm^{-2} at 62 °C are obtained, and good stability (300-h stable performance at 20 mA cm^{-2}) is also exhibited, which shows that such perovskite-type oxides as LaNi$_{0.8}$Co$_{0.2}$O$_3$ can be excellent catalysts for DBFCs.

1. Introduction

Fuel cells have attracted significant attention for their high efficiency in converting chemical energy into electricity compared with the efficiency of hydrogen combustion engines. However, the successful large-scale commercialisation of fuel cells has been hindered by the scarcity of precious metal catalysts [1,2] and the easy degradation of these catalysts by contamination originating in the fuel [3,4]. Therefore, great interest has been focused on the research of non-precious metal catalysts as a substitute in fuel cells. Direct borohydride fuel cells (DBFCs) are fuel cells that can use non-precious metal catalysts for both their cathode and anode. The low-cost catalyst MnO$_2$ has been reported to exhibit sufficient oxygen reduction reaction (ORR) activity and feeble activity with respect to BH$_4^-$ oxidation [5,6]. Moreover, macrocyclic compounds, including Fe/CoTMPP [7,8], Fe/CoPc [9,10] and Fe/Co-PPY-C [11], have been reported to exhibit good electrocatalytic activities toward the ORR. The results revealed by Lefevre et al. show that Fe–N–C catalysts can match the performance of an outstanding Pt/C catalyst system [12,13]. Apart from these metal–support catalysts, non-metal catalysts, such as vertically aligned nitrogen-containing carbon nanotubes, could also be used as efficient ORR electrocatalysts [14].

Perovskite-type oxides were considered as promising catalysts for ORR due to their sufficient electrical conductivity and good electrochemical properties [15]. LaNi$_x$Co$_{(1-x)}$O$_3$ (x = 0.1–0.9) is one of these type oxides. It can serve as an excellent catalyst in some high-temperature reaction such as the reaction of solid oxide fuel cells cathode [16] and the oxidation of light hydrocarbons including CO$_2$ reforming of methane [17], carbon monoxide oxidation [18], propane deep oxidation [19] and so on. However, the data regarding LaNi$_x$Co$_{(1-x)}$O$_3$ (x = 0.1–0.9) applications in the low-temperature ORR are still scarce. This paper reports new progress in the research of the perovskite-type oxide LaNi$_{0.8}$Co$_{0.2}$O$_3$ as a cathode catalyst for DBFCs.

2. Experimental details

2.1. Catalyst preparation

The preparation of the perovskite-type oxide is described in previous works [15,20,21]. LaNi$_{0.8}$Co$_{0.2}$O$_3$ was synthesised by the sol–gel method. LaCoO$_3$ and LaNiO$_3$ were also prepared as references. Lanthanum nitrate (La(NO$_3$)$_3$·6H$_2$O), nickel nitrate (Ni(NO$_3$)$_2$·6H$_2$O) and cobalt nitrate (Co(NO$_3$)$_2$·6H$_2$O) were used as raw materials.

The anode catalyst cobalt (II) oxide [22] was purchased from J&K Chemical Ltd.

2.2. Electrode preparation

The cathode consisted of a gas diffusion layer, a current collector and an active layer. The gas diffusion layer was prepared by mixing 60 wt.% acetylene black and 40 wt.% polytetrafluoroethylene (PTFE) (solid quality), then pressing the slurry into a 0.3-mm membrane and heating at 340 °C for 1 h. The active layer was prepared by mixing 30 wt.% catalyst, 45 wt.% carbon nanotubes and 25 wt.% PTFE (solid quality) into a paste. The pastes was then smeared onto a

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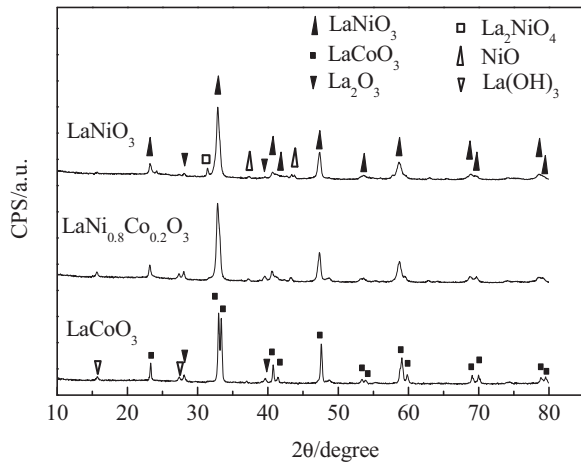
Fig. 1. XRD patterns of the perovskite-type oxides LaCoO$_3$, LaNi$_{0.8}$Co$_{0.2}$O$_3$ and LaNiO$_3$.

nickel foam and dried at 80 °C for 2 h under vacuum. The cathode electrode was finished by rolling the gas diffusion layer and the prepared nickel foam into a 0.6-mm sheet.

The anode was prepared by the following steps: 97 wt.% cobalt (II) oxide and 3 wt.% PTFE were mixed together. The mixture was pasted onto the nickel foam, then dried at 80 °C for 2 h under vacuum. The anode electrode was then pressed under a pressure of 3 MPa for 1 min.

2.3. Characterisation of catalyst

The X-ray diffraction of LaCoO$_3$, LaNi$_{0.8}$Co$_{0.2}$O$_3$ and LaNiO$_3$ were conducted with a diffractometer (D/MAX-2400, Japan) using

a CuKα ($\lambda = 1.5444$ Å) source, and the diffraction signals were recorded in the 2θ ranging 10–80°. The particle size and morphology of the samples were observed by field emission scanning electron microscope (FE-SEM, JSM-6700F).

2.4. Electrochemical measurements

Cyclic voltammetry (CV), which was measured using an electrochemical workstation (CHI650C, ChenHua, Shanghai, China), was employed to characterise the electrochemical properties of LaNi$_{0.8}$Co$_{0.2}$O$_3$. A standard three-electrode system was used in these electrochemical measurements. In the CV tests, a glassy carbon (GC) electrode modified with a cathode catalyst, a graphite electrode or Pt wire and a Hg/HgO electrode were used as the working electrode, counter electrode and reference electrode, respectively. The modified GC electrode was fabricated as following: a catalyst ink was prepared by ultrasonically mixing 3 mg catalyst, 0.5 ml ethanol and 15 μl Nafion (5 wt.%) into a slurry, then spreading 10 μl of the slurry onto the surface of the glass carbon electrode. Before the tests, oxygen was eliminated or enriched by bubbling nitrogen gas or air into the electrolyte solution for 20 min.

To evaluate the performance of the cells that consisted of these perovskite-type oxides as cathodes and cobalt (II) oxide as anodes, polarisation curves were collected by a battery testing system (from Neware Technology Limited, Shenzhen, China). The test was conducted in a container with a 1-cm^2 window, where the cathodes were placed. The gas diffusion layer of the cathode was exposed to air, whereas the active layer was in contact with the electrolyte fuel. The anode was placed inside the container, facing the cathode and 2 cm away from it. The detailed structure of the fuel cell can be verified in [9]. The oxygen and fuel flow rates were 5 sccm and 20 ml min^{-1}, respectively.
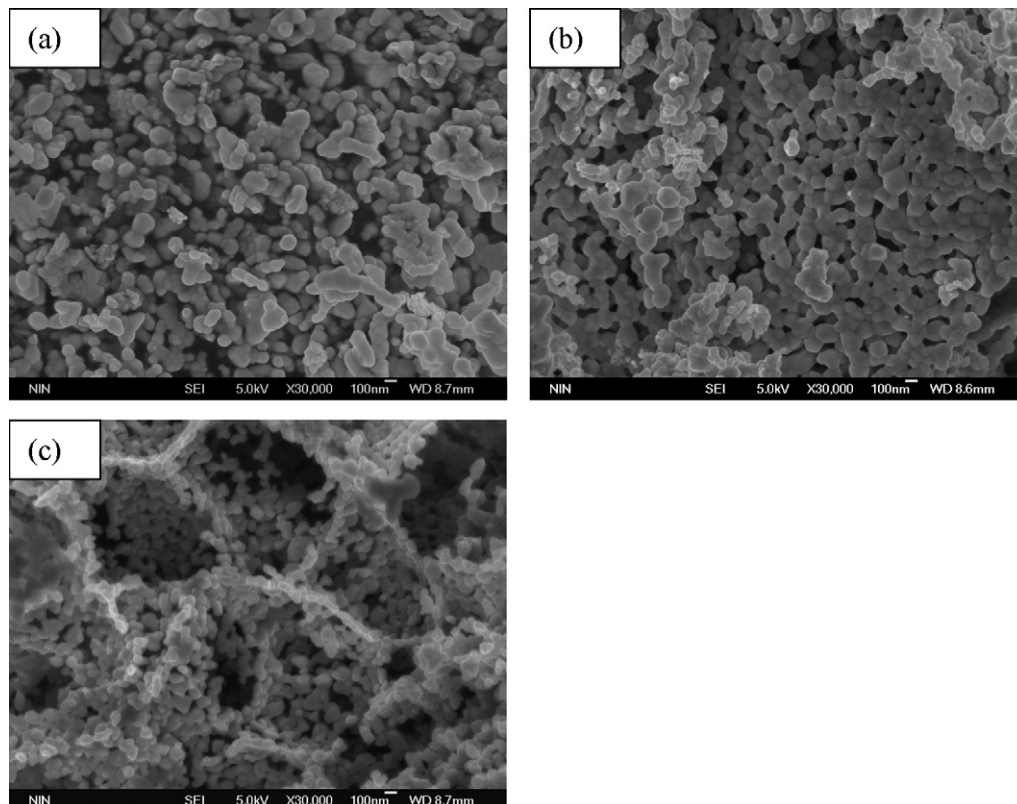
Fig. 2. SEM image of the prepared catalyst (a) LaCoO$_3$; (b) LaNi$_{0.8}$Co$_{0.2}$O$_3$; (c) LaNiO$_3$.
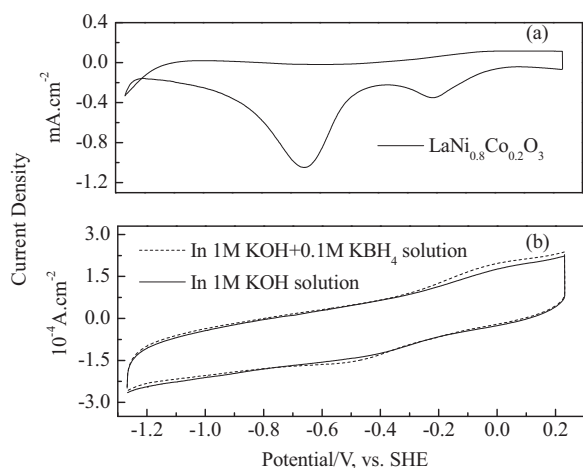
Fig. 3. (a) Cyclic voltammograms of $LaNi_{0.8}Co_{0.2}O_3$-modified glassy carbon in 1 M KOH solution saturated with air at room temperature. Scan rate: $100\,mV\,s^{-1}$. Counter electrode: Pt wire. Reference electrode: Hg/HgO electrode; (b) cyclic voltammograms of $LaNi_{0.8}Co_{0.2}O_3$-modified glassy carbon in 1 M KOH solution and 1 M KOH + 0.1 M KBH_4 solution saturated with N_2 at room temperature. Scan rate: $100\,mV\,s^{-1}$. Counter electrode: graphite electrode. Reference electrode: Hg/HgO electrode.

3. Results and discussion

Fig. 1 shows the XRD patterns of $LaCoO_3$, $LaNi_{0.8}Co_{0.2}O_3$ and $LaNiO_3$. The patterns change from the perovskite-type $LaCoO_3$ phase (JCPDS, PDF code: 048-0123) to the perovskite-type $LaNiO_3$ phase (JCPDS, PDF code: 33-0710) with increasing Ni concentration, which indicates that the synthesis method can be used to obtain perovskite-type oxides. It is also found that minor peaks of La_2O_3 phase (JCPDS, PDF code: 01-089-4016), NiO (JCPDS, PDF code: 00-044-1159), $La(OH)_3$ (JCPDS, PDF code: 00-006-0585) and La_2NiO_4 (JCPDS, PDF code: 01-080-0065) in Fig. 1 which suggests that the samples are not a single phase structure. Fig. 2 shows the morphology of $LaCoO_3$, $LaNi_{0.8}Co_{0.2}O_3$ and $LaNiO_3$ and globular particles is displayed uniformly with average diameter around 80–100 nm.

Fig. 3(a) shows cyclic voltammograms of the glassy carbon (GC) electrode modified with a $LaNi_{0.8}Co_{0.2}O_3$ catalyst in 1 M KOH solution under air saturation. It has deducted the background currents which were obtained with a GC in the nitrogen-saturated electrolyte. The result shows two intense reduction peaks at ca. −0.246 V and ca. −0.688 V (vs. Hg/HgO, 6 M KOH), which represents the reduction of O_2 to $O_2^{\bullet-}$ (reaction (1)) and O_2 to HO_2^- (reaction (2)), respectively [23–26].

$$O_2 + e^- \rightarrow O_2^{\bullet-} \tag{1}$$

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \tag{2}$$

It can be concluded from Fig. 3(a) that $LaNi_{0.8}Co_{0.2}O_3$ has excellent electrochemical activity toward the ORR. Another essential characteristic for the cathode catalyst is tolerance of the fuel solution (KBH_4 + KOH), which makes DBFCs successful membraneless structures that avoid using precious ion exchange membranes [6,9,10]. Fig. 3(b) shows the cyclic voltammograms of the GC electrode modified with $LaNi_{0.8}Co_{0.2}O_3$ in fuel solution (0.1 M KBH_4 + 1 M KOH) and electrolyte solution (1 M KOH), respectively. To eliminate the influence of the oxygen reduction reaction, the solution was saturated with nitrogen gas to exclude oxygen. There is no apparent oxidation peak, which indicates that $LaNi_{0.8}Co_{0.2}O_3$ does not react with BH_4^- and can, therefore, tolerate BH_4^-.

The performances of the cells fabricated with $LaCoO_3$, $LaNi_{0.8}Co_{0.2}O_3$ and $LaNiO_3$ as their cathode and CoO as their anode are illuminated in Fig. 4, and the maximum power densities of 87.7, 114.5 and 106.9 mW cm^{-2} were obtained at room
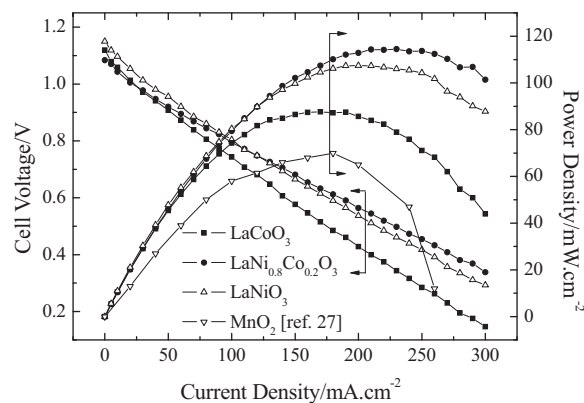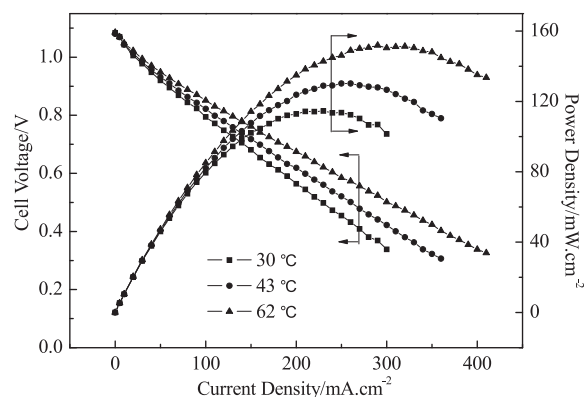

Fig. 4. Performance of DBFCs: using $LaCoO_3$, $LaNi_{0.8}Co_{0.2}O_3$ and $LaNiO_3$ as cathode and CoO as anode materials; MnO_2 as cathode and hydrogen storage alloys as anode materials [27], at room temperature. Fuel solution: 6 M KOH + 0.8 M KBH_4, O_2 flow rate: 5 sccm, fuel flow rate: 20 ml min^{-1}.

temperature for each cell, respectively. For comparison, some published data of DBFC using MnO_2 as cathode and hydrogen storage alloys as anode [27] was also demonstrated in Fig. 4. It is obvious that much higher max power densities were obtained when $LaNi_xCo_{(1-x)}O_3$ ($x = 0, 0.8, 1$) were used as cathode. To the best of our knowledge, the electrochemical activity of perovskite-type oxide is determined by electrical and ionic conductivity [16]. $LaNiO_3$ and $LaNi_{0.8}Co_{0.2}O_3$ have higher maximum power densities than $LaCoO_3$ because $LaNiO_3$ has a low electrical resistance and metallic-like conductivity [16,28]. $LaNi_{0.8}Co_{0.2}O_3$ as a cathode in the membraneless DBFC showed the best performance due to Ni substitutions, which induce lattice defects and consequently increase the concentration of oxygen vacancies. Thus, both ionic conductivity and the presence of main active sites are enhanced by the increased concentration of oxygen vacancies. Therefore, $LaNi_{0.8}Co_{0.2}O_3$ shows the best electrochemical activity among these series catalysts.

Fig. 5 shows the performance of a $LaNi_{0.8}Co_{0.2}O_3$-catalysed cathode at different temperatures. It distinctly shows that the maximum power density increases with increasing temperature due to the enhanced kinetics of the oxidation/reduction reaction and mass transfer of the reactant. The maximum power densities are 114.5, 130.3 and 151.3 mW cm^{-2} at 30, 43 and 62 °C, respectively.

The stability of the $LaNi_{0.8}Co_{0.2}O_3$-catalysed cathode has been studied through life-time experiments. The fuel solution was refreshed every 24 h, and data points were randomly picked. Fig. 6 shows that $LaNi_{0.8}Co_{0.2}O_3$ maintains good stability over a 300-h test, which is ascribed to its outstanding tolerance for BH_4^- and

Fig. 5. Performance of DBFCs using a $LaNi_{0.8}Co_{0.2}O_3$ cathode and CoO anode at different temperatures. Fuel solution: 6 M KOH + 0.8 M KBH_4, O_2 flow rate: 5 sccm, fuel flow rate: 20 ml min^{-1}.
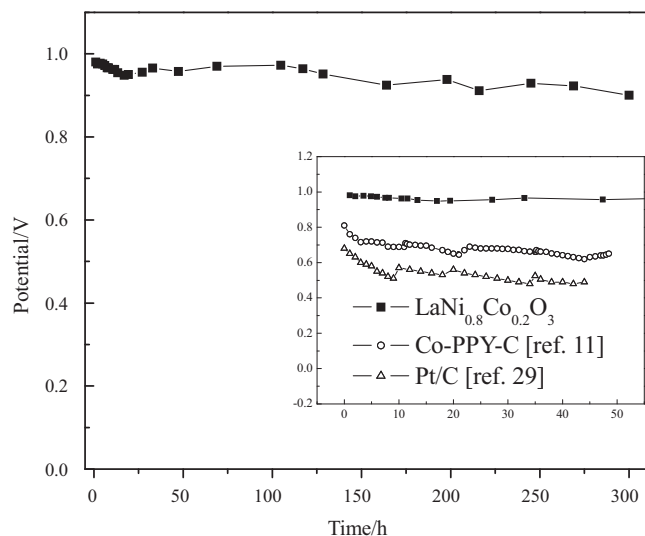
Fig. 6. Life-time test of DBFCs using a $LaNi_{0.8}Co_{0.2}O_3$ cathode and CoO anode under ambient atmosphere. Referenced performance stabilities using $Co(OH)_2$-PPY-C [11] and Pt/C [29] catalyst were measured at a current density of 50 and 20 mA cm^{-2}, respectively. Fuel solution: 6 M KOH + 0.8 M KBH$_4$, current discharge: 20 mA cm^{-2}.

remarkable corrosion-proof ability against OH$^-$. As a comparison, Fig. 6 also shows the DBFC life-time experiments of $Co(OH)_2$-PPY-C [11] and Pt/C [29] as the cathode catalyst. It obviously shows that fuel cell have much better performance stability when $LaNi_{0.8}Co_{0.2}O_3$ was used as cathode.

4. Conclusions

In summary, a perovskite-type oxide $LaNi_{0.8}Co_{0.2}O_3$ was synthesised by the sol–gel method. The electrochemical measurements show that $LaNi_{0.8}Co_{0.2}O_3$ has excellent catalytic activity for the oxygen reduction reaction and good borohydride tolerance. Maximum power densities of 114.5 mW cm^{-2} at 30 °C and 151.3 mW cm^{-2} at 62 °C were obtained. In addition, good stability was shown through galvanostatic discharge testing under ambient conditions.

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