



Short communication

The use of polypyrrole modified carbon-supported cobalt hydroxide as cathode and anode catalysts for the direct borohydride fuel cell

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ABSTRACT

A polypyrrole modified carbon-supported cobalt hydroxide (Co(OH)₂-PPY-C) has been prepared by the impregnation-chemical method and used as the electrode catalyst in a direct borohydride fuel cell (DBFC). The microstructure of Co(OH)₂-PPY-C has been characterized by X-ray diffraction and transmission electron microscopy. The cell performance and short-term performance stability of the DBFC using the Co(OH)₂-PPY-C as catalysts have been investigated. A maximum power density of 83 mW cm⁻² has been achieved at 0.6 V under ambient conditions. The Co(OH)₂-PPY-C catalyst demonstrates a smaller value of polarization than the carbon-supported Co(OH)₂ catalyst. Results from electrochemical impedance spectrum analysis confirm that the polypyrrole addition to the cathode effectively decreases its resistance. During operation of the DBFC using Co(OH)₂-PPY-C as catalyst, the Co(OH)₂ tends to be converted into CoHO₂.

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1. Introduction

The development of non-precious catalysts to replace Pt in fuel cells has been carried out over many years for the development of fuel cell technologies. The direct borohydride fuel cell (DBFC) has attracted much interest as a potential power source due to its high electromotive force of 1.64 V, high capacity of 5.67 Ah g⁻¹ [1,2], and the possibility of using non-Pt metals as electro-catalysts [3,4]. Several studies on Ag [5,6] and MnO₂ [7,8] as cathode catalysts have been carried out. Although these inorganic catalysts exhibited good initial performance similar to that of Pt, they were of low stability and not tolerant to borohydride [5,7]. On the other hand, metal complexes with macrocyclic ligands, such as porphyrins and phthalocyanines, are expected to be alternatives to the conventional carbon-supported Pt as cathode catalysts [9–11]. In the study of non-precious metals as anode catalysts, several transition metals (Ni, Cu, Ag) [3,12–14] and hydrogen storage alloys [14–20] have been investigated. Besides the catalyst material itself, some studies have focused on the conductivity of the electrode which significantly influences the cell performance. Cheng and Scott [21] suggested using titanium mesh-supported gold and silver anodes and found that they showed higher current densities and higher cell power densities than carbon-supported anodes in DBFCs.

Polypyrrole (PPY) is a well-known electrically conducting polymer with a conductivity of about 1 S cm⁻¹ [22]. PPY has been successfully applied as a conducting material to support catalysts such as metal oxides [23,24] and complexes [25]. Yuasa et al. [26] has developed a carbon supported Co catalyst with surface modification of PPY. The catalyst demonstrated fairly good electro-catalytic activity for the four-electron reduction of O₂ and demonstrated high stability against degradation.

Co(OH)₂ as a normal cobalt compound has been used as a cathode material in batteries [27] and as an electro-catalyst in electro-synthesis [28–30]. Recently, it was reported that Co(OH)₂ modified glassy carbon electrodes could be used for the electro-catalytic oxidation of methanol in alkaline solutions [28]. It is considered that the PPY modified carbon-supported Co(OH)₂ (Co(OH)₂-PPY-C) can be used as a catalyst in DBFCs.

This work describes the first attempt to use Co(OH)₂ as the electrode catalyst in a DBFC. It was known that the electrical conductivity of Co(OH)₂ was not as good as that of the metallic catalysts so the PPY was applied to improve the electrical conductivity of the electrodes. The PPY modified carbon-supported catalysts were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The polarization behavior of the electrodes and performance stability of the DBFC using the as-prepared Co(OH)₂-PPY-C were investigated.

2. Experiment details

The polypyrrole modified carbon (PPY-C) was synthesized following the method described by Rasika Dias and Mokrane [26,31].

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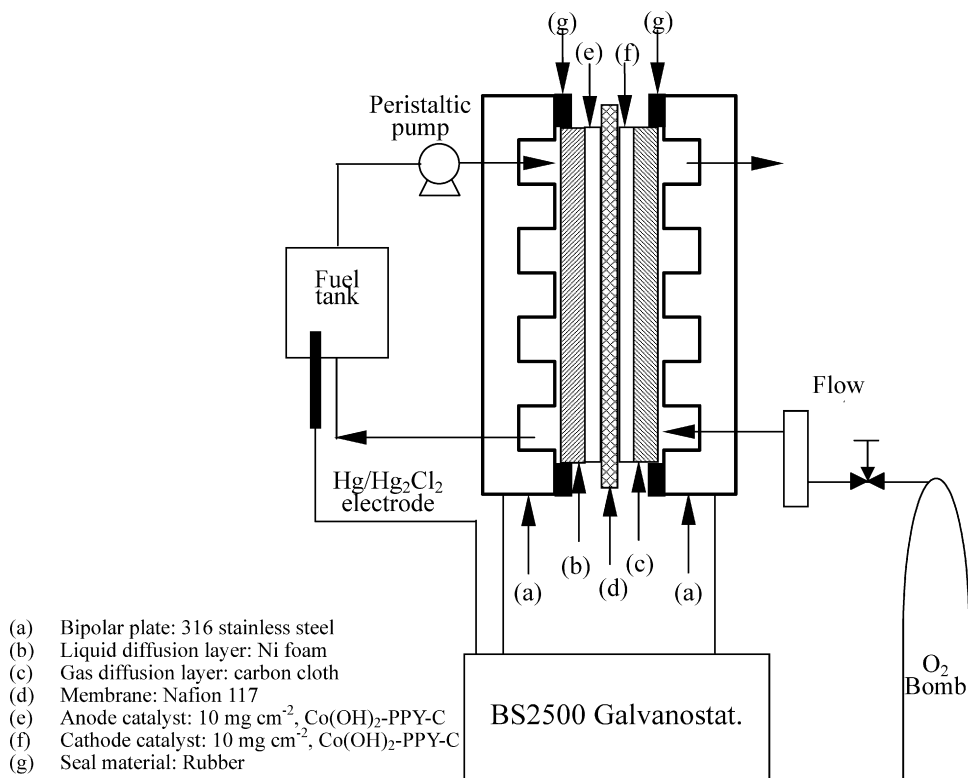


Fig. 1. Schematic image of the test system for the DBFC.

Firstly, a carbon dispersion solution was prepared by adding 10 g of acetylene black and 2.5 mL of glacial acetic acid to 150 mL of de-ionized water and stirring for 20 min at room temperature. Then 2 g of pyrrole and 10 mL of H_2O_2 solution (10 wt.%) were added to the carbon dispersion solution and then stirred at room temperature for 3 h to form polypyrrole on carbon particles. The pH value of the solution was controlled to around 3. The PPY-C powders obtained were then filtered, washed and dried at 90°C under vacuum for 10 h. The loading of polypyrrole on the carbon black was about 17 wt.%. The PPY-C (12 g) was placed in a three-necked round-bottom flask and mixed with 60 mL of $\text{Co(NO}_3)_2$ solution (10 wt.%). The mixture was stirred for 30 min at 80°C . Then 400 mL of NaOH solution (1 wt.%) was added at a rate of 20 mL min^{-1} with a peristaltic pump. The catalyst obtained was filtered and washed several times with warm de-ionized water and finally dried at 90°C under vacuum for 12 h. The loading of Co(OH)_2 was calculated to be about 15 wt.%. Co(OH)_2 -C was prepared by a similar method in order to load Co(OH)_2 on the carbon powders.

The catalyst structures were identified by powder X-ray diffraction with a Rigaku-D/MAX-2550PC diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The catalyst morphology was observed with a JEM-2010 transmission electron microscope operated at 200 kV.

Cathodes were prepared by coating the catalyst slurry on to a piece of hydrophobic carbon cloth with a catalyst loading of 10 mg cm^{-2} . Anodes were prepared by pasting the catalyst slurry on to a piece of Ni foam with a catalyst loading of 10 mg cm^{-2} . The hydrophobic carbon cloth was prepared by immersing it in a polytetrafluoroethylene (PTFE) emulsion (20 wt.%) for 3 min and then sintering at 350°C for 1 h. The catalyst slurry was prepared by mixing the catalyst with de-ionized water, a Nafion suspension (5 wt.%) and anhydrous ethanol with a mass ratio of 1:3:7:3. The Nafion membrane was pretreated by boiling it in H_2O_2 solution (3 wt.%) and then in de-ionized water for 1 h. The scheme of the cell test system is given in Fig. 1.

An alkaline NaBH_4 solution (5 wt.% of NaBH_4 , 10 wt.% of NaOH) was used as the fuel. The cell performance and electrode polarization were measured at a fuel flow rate of 10 mL min^{-1} and a dry O_2 flow rate of 150 mL min^{-1} under ambient conditions. Polarization measurements and electrochemical impedance spectrum (EIS) analyses were carried out on a Zahner IM6 analyzer using a calomel electrode as the reference electrode in a three-electrode system. The AC frequency was varied from 100 kHz to $30 \mu\text{Hz}$ with an amplitude of 5 mV. The calomel electrode was inserted in the fuel tank and separated from the fuel by a Nafion membrane N117. The saturated KCl solution was used as the electrolyte in the reference electrode.

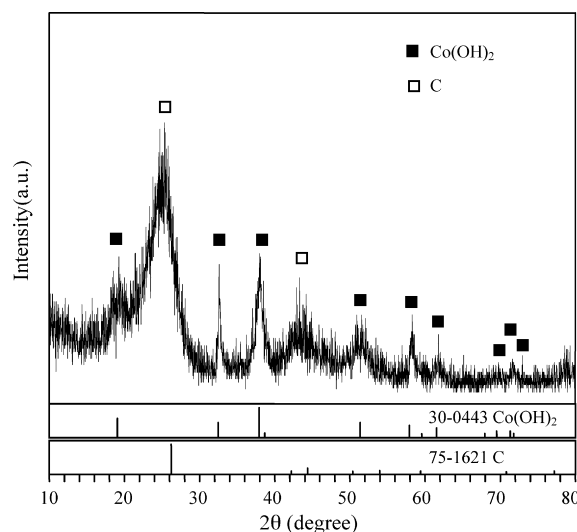


Fig. 2. XRD patterns of the as-prepared Co(OH)_2 -PPY-C.

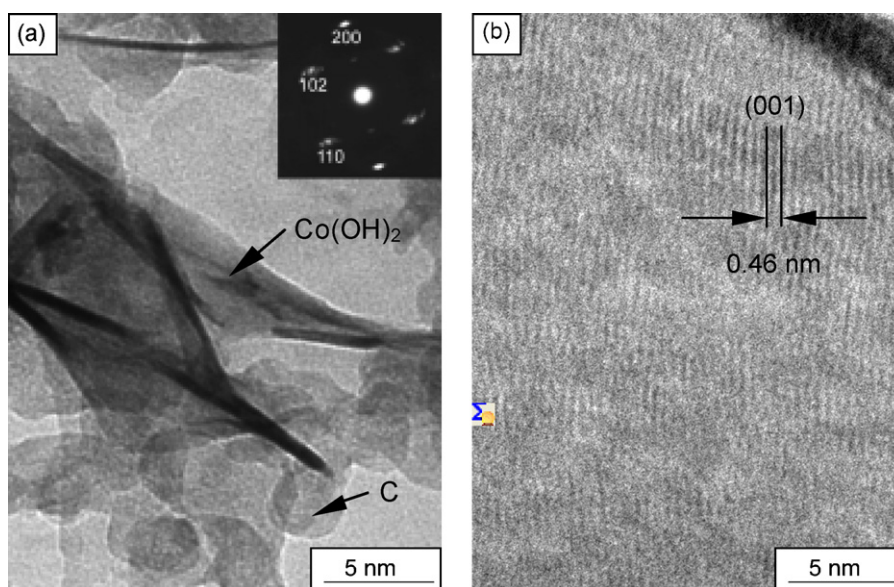


Fig. 3. (a) TEM image of the as-prepared Co(OH)_2 -PPY-C with the SAED patterns of a single platelet and (b) HRTEM image of a single platelet.

3. Results and discussion

3.1. Characterization of Co(OH)_2 -PPY-C

Fig. 2 shows the XRD pattern of the as-prepared catalyst along with standard XRD patterns of β - Co(OH)_2 and carbon. The XRD analysis confirmed the existence of β - Co(OH)_2 . The morphology of the as-prepared catalyst was characterized by TEM as shown in Fig. 3. It was found that there were some platelets dispersed on carbon particles. The inset in Fig. 3(a) gives the selected area electron diffraction (SAED) pattern of a single platelet, showing the hexagonal structure of Co(OH)_2 . The diffractions from the (1 1 0), (1 0 2) and (2 0 0) crystal planes of β - Co(OH)_2 identified by SAED agree well with the X-ray diffraction peaks at 57.9° , 51.4° and 67.9° , respectively. Fig. 3(b) shows the high-resolution transmission electron microscopy (HRTEM) image of a single platelet. The interplanar spacing of about 0.46 nm agrees well with the spacing of the (0 0 1) planes of β - Co(OH)_2 .

3.2. Electrochemical properties of Co(OH)_2 -PPY-C

We constructed test cells using the as-prepared Co(OH)_2 -C and Co(OH)_2 -PPY-C as catalysts for both cathode and anode. The performances of the test cells using Co(OH)_2 -PPY-C and Co(OH)_2 -C are illustrated in Fig. 4. Compared with the cell using the Co(OH)_2 -C as catalysts, the cell using Co(OH)_2 -PPY-C demonstrated a higher performance. A maximum power density of 83 mW cm^{-2} was achieved at 0.6 V. The electrode polarization showed that the slope of the linear voltage–current relationship of the Co(OH)_2 -PPY-C cathode was noticeably lower than that of the Co(OH)_2 -C cathode, as shown in Fig. 5. It was considered that the ohmic resistance of the Co(OH)_2 -PPY-C electrode might have decreased because of the good electrical conductivity of the polymer PPY and so the cell performance was improved when using it as the catalyst.

To understand the effect of the addition of PPY on the cell performance, EIS analyses were performed under open circuit conditions in a three-electrode system. Fig. 6(a) shows the EIS analysis results

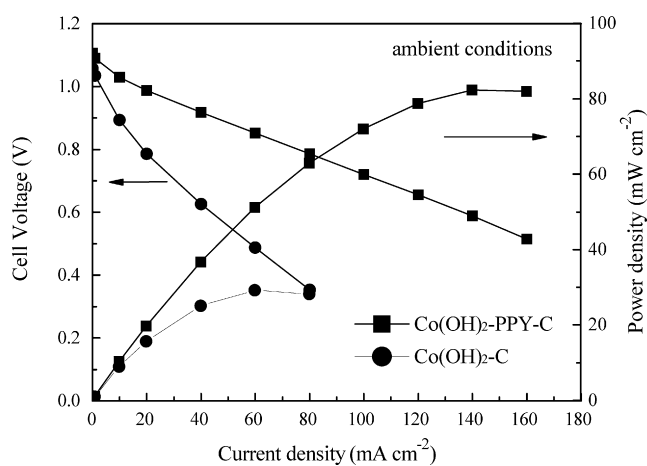


Fig. 4. Cell performance of the DBFC using Co(OH)_2 -PPY-C or Co(OH)_2 -C as the cathode and anode catalyst under ambient conditions. Cathode: catalyst loading is 10 mg cm^{-2} , dry O_2 at a flow rate of 150 mL min^{-1} (1 atm). Anode: catalyst loading is 10 mg cm^{-2} , 5 wt.% of NaBH_4 , 10 wt.% of NaOH at a fuel flow rate of 10 mL min^{-1} . Membrane: N117.

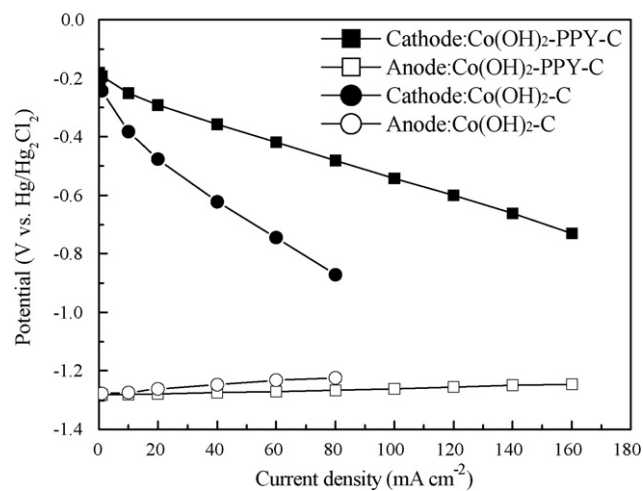


Fig. 5. Cathode and anode polarization curves of the DBFC using Co(OH)_2 -PPY-C and Co(OH)_2 -C as the cathode and anode catalyst under ambient conditions. Cathode: catalyst loading is 10 mg cm^{-2} , dry O_2 at a flow rate of 150 mL min^{-1} (1 atm). Anode: catalyst loading is 10 mg cm^{-2} , 5 wt.% of NaBH_4 , 10 wt.% of NaOH at a fuel flow rate of 10 mL min^{-1} . Membrane: N117.

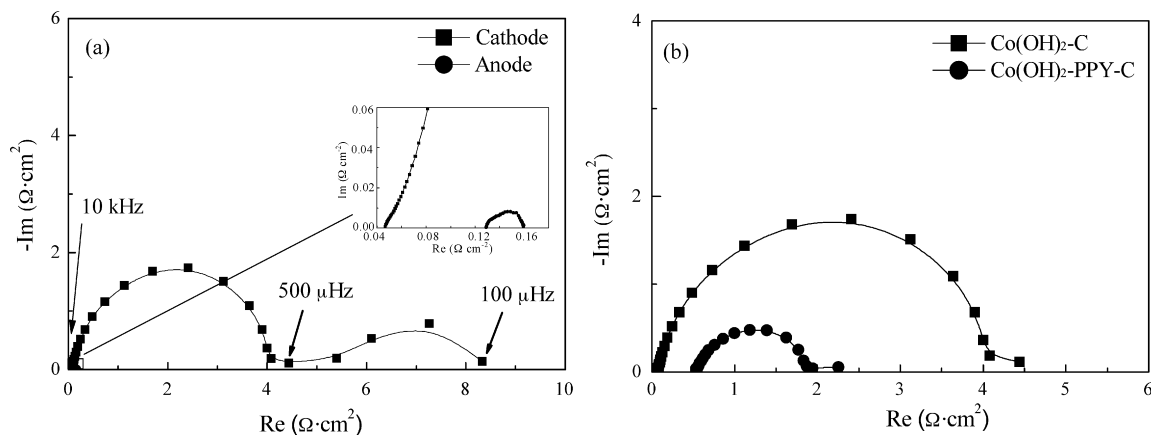


Fig. 6. Electrochemical impedance spectra of the $\text{Co(OH)}_2\text{-C}$ and $\text{Co(OH)}_2\text{-PPY-C}$ electrodes. (a) $\text{Co(OH)}_2\text{-C}$ as the catalyst of cathode and anode; (b) $\text{Co(OH)}_2\text{-C}$ and $\text{Co(OH)}_2\text{-PPY-C}$ as the catalyst of cathode.

using $\text{Co(OH)}_2\text{-C}$ as anode and cathode catalysts in the cells corresponding to Fig. 4. There are two arcs as shown in Fig. 6(a). According to EIS studies of porous electrodes, the semicircle at high frequencies is related to the ohmic resistance of the electrolyte together with all the external resistances; the semicircle at low frequencies is attributed to the electrochemical reaction on the electrodes [32,33]. The anode demonstrated smaller ohmic resistance and reaction resistance than the cathode when $\text{Co(OH)}_2\text{-C}$ was used as the anode and cathode catalyst. Comparing with the electrode polarization behavior shown in Fig. 5, it was reconfirmed that the cell polarization was dominated by the cathode polarization. The ohmic resistance of the cathode would significantly influence the performance of the DBFC. The EIS analysis results shown in Fig. 6(b) reveal that the ohmic resistance of the $\text{Co(OH)}_2\text{-PPY-C}$ cathode was smaller than that of the $\text{Co(OH)}_2\text{-C}$ cathode. It is believed that the addition of PPY decreased the ohmic resistance of the cathode so that its electrical conductivity was improved. As a result, the cell using $\text{Co(OH)}_2\text{-PPY-C}$ as catalyst demonstrated higher performance than the cell using $\text{Co(OH)}_2\text{-C}$ as catalyst.

Fig. 7 gives a comparison of the DBFC performance stability when using $\text{Co(OH)}_2\text{-PPY-C}$, Pt/C and Ag/C [6] as the cathode catalyst. It was found that the cell using $\text{Co(OH)}_2\text{-PPY-C}$ as the cathode cat-

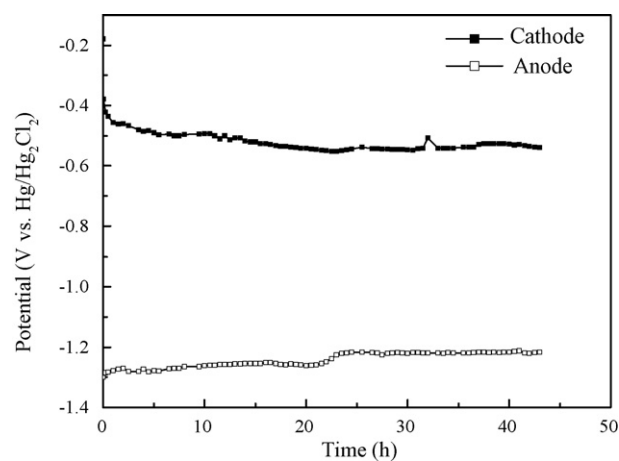


Fig. 8. Polarization stabilities of the anode and cathode of $\text{Co(OH)}_2\text{-PPY-C}$ at a current density of 50 mA cm^{-2} under ambient conditions. Cathode: $\text{Co(OH)}_2\text{-PPY-C}$ loading is 10 mg cm^{-2} , dry O_2 at a flow rate of 150 mL min^{-1} (1 atm). Anode: $\text{Co(OH)}_2\text{-PPY-C}$ loading is 10 mg cm^{-2} , 1 L 5 wt.% of NaBH_4 , 10 wt.% of NaOH solution at a fuel flow rate of 10 mL min^{-1} . Membrane: N117.

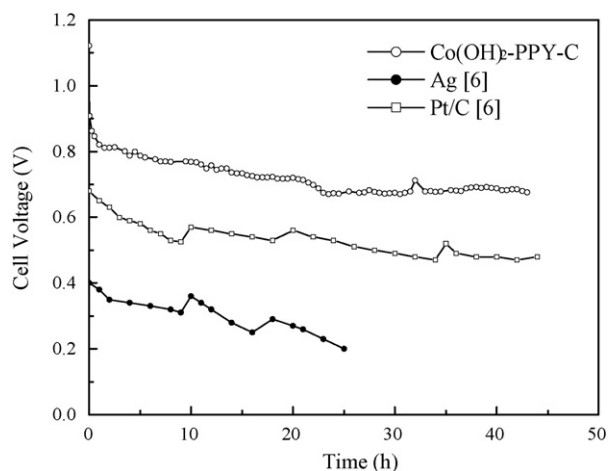


Fig. 7. Performance stability of the DBFC using $\text{Co(OH)}_2\text{-PPY-C}$ as the catalyst at a current density of 50 mA cm^{-2} under ambient conditions. Referenced performance stabilities using Pt/C and Ag/C catalyst were measured at a current density of 20 mA cm^{-2} at 25°C [6]. Cathode: $\text{Co(OH)}_2\text{-PPY-C}$ loading is 10 mg cm^{-2} , dry O_2 at a flow rate of 150 mL min^{-1} (1 atm). Anode: $\text{Co(OH)}_2\text{-PPY-C}$ loading is 10 mg cm^{-2} , 1 L 5 wt.% of NaBH_4 , 10 wt.% of NaOH solution at a fuel flow rate of 10 mL min^{-1} . Membrane: N117.

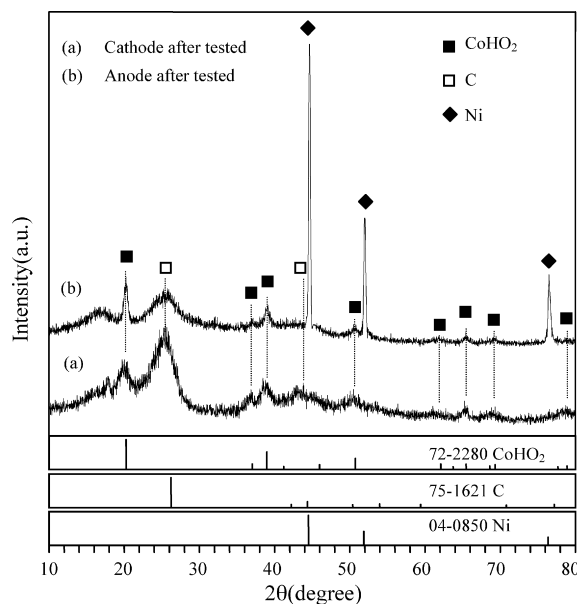


Fig. 9. XRD patterns of (a) cathode after use and (b) anode after use in the DBFC.

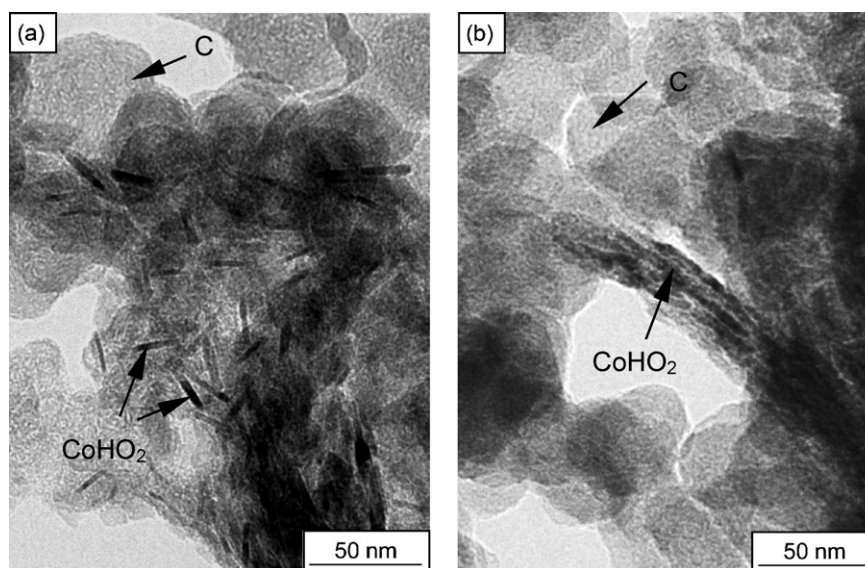


Fig. 10. TEM images of (a) cathode catalyst after use (b) anode catalyst after use in the DBFC.

alyst demonstrated better performance stability than the others. The operating potentials of cathode and anode showed comparable polarization stabilities, as shown in Fig. 8.

3.3. Ex situ characterization of $\text{Co}(\text{OH})_2$ -PPY-C after use

In order to understand the function of $\text{Co}(\text{OH})_2$ -PPY-C as cathode and anode catalysts in the DBFC, the microstructure of the electrodes after operation was examined by XRD and TEM. It was found that the diffraction peaks of $\text{Co}(\text{OH})_2$ had disappeared but diffraction peaks of CoHO_2 had appeared (Fig. 9). The TEM images revealed the formation of needle-like crystals in the cathode and anode, as shown in Fig. 10. Since $\text{Co}(\text{II})$ in $\text{Co}(\text{OH})_2$ could be oxidized to $\text{Co}(\text{III})$ under alkaline conditions [21,34,35], it was supposed that the cathode catalyst of the as-prepared $\text{Co}(\text{OH})_2$ would be oxidized during operation of the DBFC as follows:



It has been reported that the change of cation valences of the cathode catalyst could accelerate the electrochemical oxygen reduction reaction (ORR) [25]. It was considered that the as-prepared $\text{Co}(\text{OH})_2$ catalyst would be converted into CoHO_2 during operation, and then CoHO_2 was presumed to act as the cathode catalyst for ORR.

For the anode catalyst, it was proposed that $\text{Co}(\text{OH})_2$ would be chemically reduced to metallic Co by BH_4^- in the fuel when using it as the anode catalyst. However, it was found that the as-prepared $\text{Co}(\text{OH})_2$ was also converted into CoHO_2 . It is possible that the metallic Co was electro-oxidized to CoHO_2 when the DBFC was operated in alkaline solutions at a lower voltage. Further detailed investigations will be necessary to understand this phenomenon.

4. Conclusions

The catalyst $\text{Co}(\text{OH})_2$ -PPY-C was synthesized by an impregnation-chemical method and used as the cathode and anode catalyst in a DBFC. A maximum power density of 83 mW cm^{-2} was achieved when using $\text{Co}(\text{OH})_2$ -PPY-C as electrode catalyst at 0.6 V and under ambient conditions. The $\text{Co}(\text{OH})_2$ -PPY-C catalyst showed a smaller electrochemical polarization than the $\text{Co}(\text{OH})_2$ -C catalyst because PPY modification improved the electric conductivity of the electrode. It was found that $\text{Co}(\text{OH})_2$ -PPY-C had good short-term

durability as electrode catalyst in the DBFC. $\text{Co}(\text{OH})_2$ is converted into CoHO_2 during operating the DBFC.

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