



## Short communication

# A cobalt polypyrrole composite catalyzed cathode for the direct borohydride fuel cell

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## ABSTRACT

A cobalt polypyrrole carbon (Co-PPY-C) composite has been attempted for use as a cathode catalyst in a direct borohydride fuel cell (DBFC). A Co-PPY-C composite has been fabricated in laboratory and characterized by the field emission scanning electron microscopy, transmission electron microscopy, as well as X-ray photoemission spectroscopy. Fabricated Co-PPY-C catalyst demonstrates good short-term durability and activity which are comparable to those obtained from the Pt/C catalyst. A maximum power density of  $65 \text{ mW cm}^{-2}$  has been achieved at ambient conditions. This research concludes that metallo-organic coordination compounds would be potential candidates for use as cathode catalysts in the DBFC.

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## 1. Introduction

Usually fuel cells such as the proton exchange membrane fuel cell (PEMFC) and the direct methanol fuel cell (DMFC) working at ambient conditions, have to use precious metals as electrode catalysts. Recently, the direct borohydride fuel cell (DBFC) has attracted significant attention as a potential power source due to the possibility of using non-precious metals as electrode catalysts. Its thermodynamic characteristics, such as high electromotive force (emf) of 1.64 V, high capacity of  $5.67 \text{ Ah g}^{-1}$ , and high theoretical energy conversion rate (91%) are beneficial for the portable and mobile applications [1–6].

Since the end of the last century, many investigations on anode catalysts of the DBFC have been made [7–12]. The development of cathode catalysts other than platinum has become a new area of development in the DBFC technology. It was reported that Ag [13,14] and  $\text{MnO}_2$  [15,16] exhibited good initial performance reaching close to Pt. However, these inorganic catalysts were poor in stability and were not tolerant to borohydride [13,15]. On the other hand, metallo-organic coordination compounds such as iron tetramethoxyphenyl porphyrin [17] and metal phthalocyanines [18,19] demonstrated good cell performance and excellent  $\text{BH}_4^-$  tolerance.

Polypyrrole (PPY) materials have reasonable thermal stability and also have reasonable chemical stability in air. They have

good electrochemical properties so that they can be used as electronic conductors and catalysts in electronic devices, batteries, electrochromic devices, optical switching devices, sensors, and so on. Polypyrrole is a chemical compound formed from a number of connected pyrrole ring structure which gives high electron conductivity like phthalocyanines. Furthermore, PPY with porous structure and high surface area could be employed as matrix to incorporate metallic catalysts for the reduction of oxygen [20–23]. Bashyam and Zelenay [23] developed a cobalt polypyrrole carbon (Co-PPY-C) composite which had high oxygen reduction reaction (ORR) activity without any noticeable loss of performance during operation of the PEMFC [23]. High cell performance has been achieved with the use of Co-PPY-C composite as cathode catalyst in a direct hydrazine fuel cell (DHFC) [24]. It is considered that the Co-PPY-C composite would work well as a cathode catalyst in the DBFC as in PEMFC and DHFC.

In this work, the use of Co-PPY-C composite as the cathode catalyst in a DBFC was attempted. The Co-PPY-C composite was fabricated in the laboratory and was characterized by the field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and X-ray photoemission spectroscopy (XPS). Polarization behavior, cell performance, and performance stability of the DBFC using the Co-PPY-C composite were investigated.

## 2. Experiment details

The Co-PPY-C composite catalyst was synthesized using the method described by Bashyam and Zelenay [23]. The Co-PPY was

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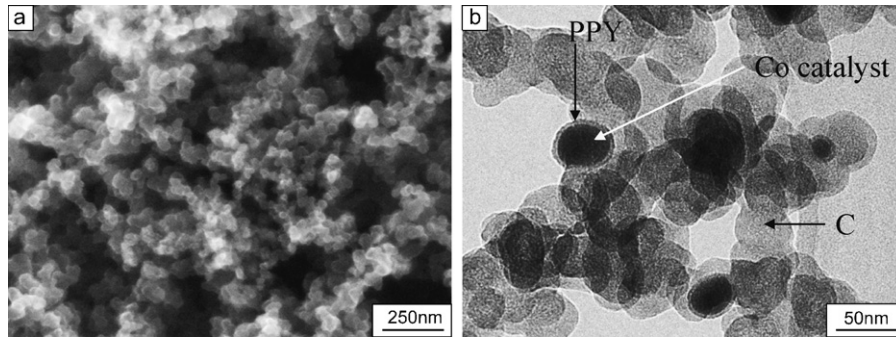


Fig. 1. FESEM (a) and TEM (b) images of the Co-PPY-C composite.

loaded on acetylene black instead of carbon black (Vulcan XC 72) as was used by Bashyam and Zeleny [23]. The morphology of the composite was characterized by the FESEM (Philips-FEI Sirion 200) and TEM (JEM-2010). The chemical valence states of Co and N were identified by the XPS (PHI-5000C ESCA system).

Test cells were assembled by using Nafion 117 membrane as the electrolyte to separate cathode from anode. The cathode was prepared by coating a cathode ink onto a piece of hydrophobic carbon cloth. The cathode catalyst ink was prepared by mixing the Co-PPY-C, de-ionized water, Nafion suspension (5 wt.%), and anhydrous ethanol in a ratio of 1:3:7:3 by weight. The hydrophobic carbon cloth was prepared by immersing the cloth in polytetrafluoroethylene (PTFE) emulsion (20 wt.%) for 3 min and then heating at 350 °C for 1 h. The catalyst layer was 0.5 mm in thickness with Co loading of 1.2 mg cm<sup>-2</sup>. Commercially available cathode with Pt loading of 1 mg cm<sup>-2</sup> (Pt 30 wt.% on Vulcan XC-72, E-Tek Co.) was used for comparison. A catalyst composite of nickel powder (INCO 210), Pd/C catalyst (10 wt.% Pd on Vulcan XC-72, E-Tek Co.), and surface-treated Zr–Ni alloy was used as anode catalyst [12]. The surface-treated Zr–Ni alloy preparation method is described in reference [25]. The anode was prepared by pasting an anode ink onto a piece of nickel foam with a catalyst loading of 10 mg cm<sup>-2</sup>. Nafion membrane was pretreated by boiling in 3% H<sub>2</sub>O<sub>2</sub> solution and de-ionized water for 1 h respectively. The test cell structure was same as described in our previous paper [2].

Alkaline NaBH<sub>4</sub> solution containing 5 wt.% of NaBH<sub>4</sub> and 10 wt.% of NaOH was used as the fuel. The fuel was replaced with fresh fuel every 12 h when investigating cell performance stability. Cell performance was measured at a fuel flow rate of 10 ml min<sup>-1</sup>, a dry O<sub>2</sub> flow rate of 150 ml min<sup>-1</sup> under ambient conditions. Calomel (Hg/Hg<sub>2</sub>Cl<sub>2</sub>) electrode was used as the reference electrode for polarization measurements.

### 3. Results and discussion

Fig. 1 shows that Co, PPY, and C is agglomerated as small granules to form a composite. It appears that the Co catalyst granules were covered with a thin film of PPY. Compared with the 1s electron binding energy of nitrogen in PPY (400.8 eV), the binding energy of nitrogen to Co-PPY was shifted to the higher value of 410.2 eV, as shown in Fig. 2, which indicated that nitrogen was not only binding with carbon in the pyrrole ring but also was binding with other elements. Furthermore, the 2p<sub>1/2</sub> and 2p<sub>3/2</sub> electron binding energies of Co clearly showed that the chemical valence of Co was +2 in Co-PPY [23,26]. Therefore, it was reasonable to consider that Co might be connected to nitrogen in the pyrrole ring to form the metallo-organic coordination compound.

Polypyrrole as a heterocyclic conjugated polymer has applications in electronics, electrochemistry, and electrocatalysis owing to its good electronic conductivity. It is considered that Co atom is linked to nitrogen atom in the pyrrole ring to form Co–N bonding without destroying the initial polymer structure of PPY. The bonded Co–N would function as an electron donor for ORR to generate active sites. As shown in Fig. 3, the cell using Co-PPY-C cathode demonstrated similar open-circuit voltage (OCV) and cell performance as with Pt/C cathode. A maximum power density of 65 mW cm<sup>-2</sup> was achieved at ambient conditions. These results indicate that the Co-PPY-C composite could not only be used for the PEMFC [23] and DHFC [24], but is also suitable as the cathode catalyst for use in DBFC.

Anode and cathode polarizations of the test cell using the Co-PPY-C cathode or the Pt/C cathode are shown in Fig. 4. It was found that the cathode using the Co-PPY-C catalyst showed similar polarization behavior as the Pt/C cathode. This result reconfirmed that the Co-PPY-C had a good activity for ORR not only in acidic medium but also in alkaline medium.

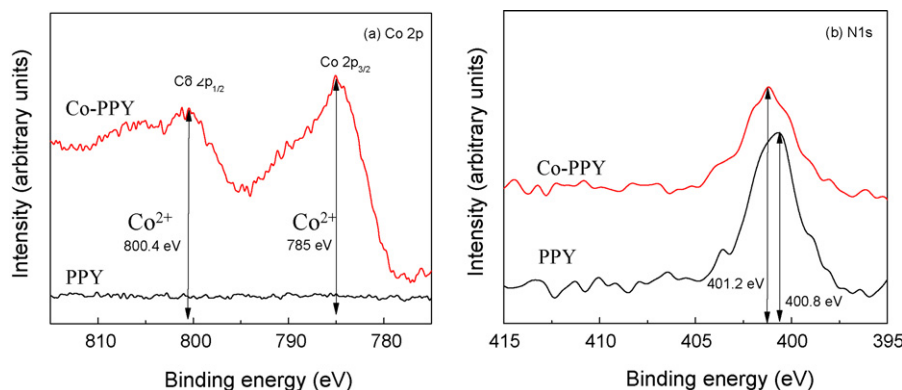


Fig. 2. Co 2p (a) and N 1s (b) core-level XPS spectra of the PPY-C and Co-PPY-C composite.

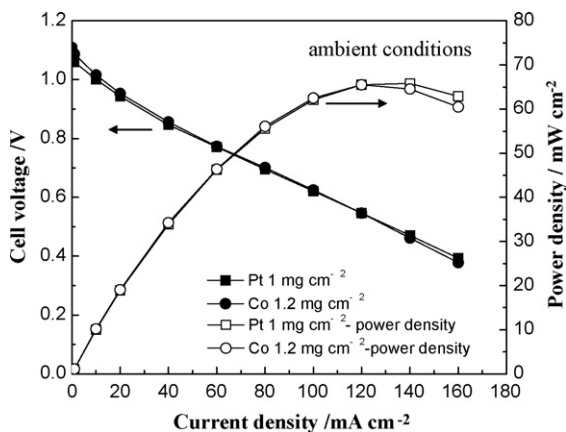


Fig. 3. Cell performances of the DBFC when using Co-PPY-C cathode and Pt/C cathode.

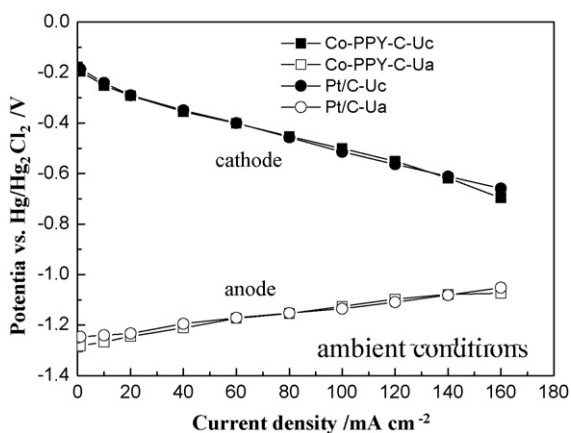


Fig. 4. Polarization curves of Co-PPY-C cathode and Pt/C cathode.

It has been reported that the cell performance decreased when Ag was used as cathode catalyst and Pt/C showed a better borohydride tolerance than that of Ag [13,14]. Fig. 5 gives the stability comparison of the DBFC when using Co-PPY-C, Pt/C, and Ag/C as the cathode catalyst. It was found that the cell performance stability improved when using Co-PPY-C as the cathode catalyst. It was considered that the thin film of PPY as shown in Fig. 1(b) had something

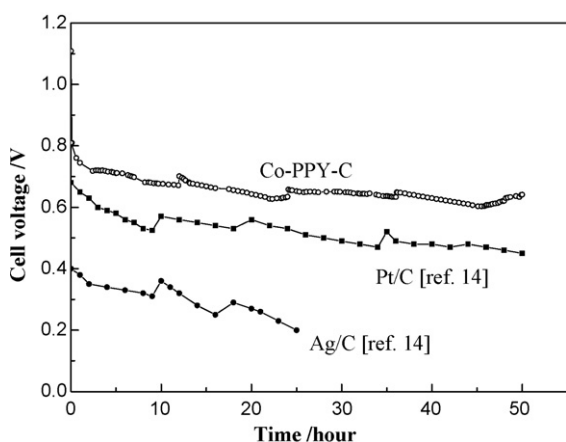


Fig. 5. Performance stability of the DBFC using Co-PPY-C cathode. Co-PPY-C: operation at current density of  $50 \text{ mA cm}^{-2}$  at ambient conditions; Pt/C and Ag/C: operation at current density of  $20 \text{ mA cm}^{-2}$  at  $25^\circ \text{C}$  [14].

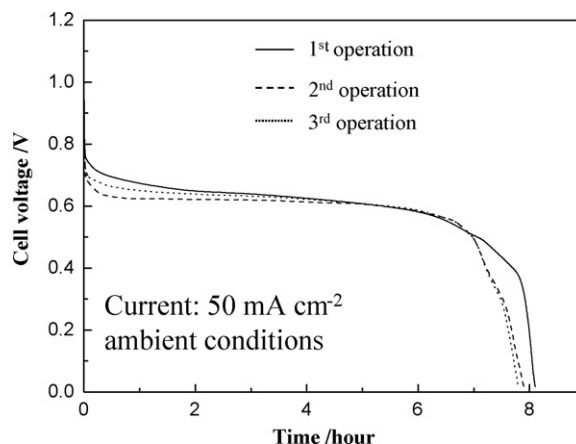


Fig. 6. Cell performance when operating discontinuously with a rest interval of 12 h.

to do with the performance stability improvement. Further detailed investigations are necessary to understand this phenomenon.

Ag cathode showed quick performance decay when operating discontinuously [13]. Fig. 6 gives the performance stability when operating the cell after a 12 h rest. The test cell did not show significant performance decay and fuel utilization was stabilized at around 45% according to the calculation by the method described in reference [27]. It was considered that the Co-PPY had such a structure that Co atom was linked to pyrrole units to form Co–N bonding without destroying the initial polymer structure (pyrrole ring) [23]. The pyrrole ring would shield Co from the attack of other compounds such as  $\text{BH}_4^-$  so that Co-PPY demonstrated little performance decay.

#### 4. Conclusions

As a cathode catalyst, Co-PPY-C composite demonstrated a good activity comparable to Pt/C for electrochemical oxygen reduction in the DBFC. The cell performance stability was improved when using Co-PPY-C as the cathode catalyst compared with the reported Ag and Pt/C catalyst. It is considered that metallo-organic coordination compounds would be potential candidates for cathode catalysts used in the DBFC. More attentions should be paid to develop non-precious metals or compounds for use as electrode catalysts for the DBFC.

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