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ORIGINAL PAPER

# NiCoFe/C cathode electrocatalysts for direct ethanol fuel cells

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**Abstract** A direct ethanol fuel cell (DEFC), which is less prone to ethanol crossover, is reported. The cell consists of PtRu/C catalyst as the anode, Nafion® 117 membrane, and Ni–Co–Fe (NCF) composite catalyst as the cathode. The NCF catalyst was synthesized by mixing Ni, Co, and Fe complexes into a polymer matrix (melamine-formaldehyde resins), followed by heating the mixture at 800 °C under inert atmosphere. TEM and EDX experiments suggest that the NCF catalyst has alloy structures of Ni, Co and Fe. The catalytic activity of the NCF catalyst for the oxygen reduction reaction (ORR) was compared with that of commercially available Pt/C (CAP) catalyst at different ethanol concentrations. The decrease in open circuit voltage ($V_{oc}$) of the DEFC equipped with the NCF catalysts was less than that of CAP catalyst at higher ethanol concentrations. The NCF catalyst was less prone to ethanol oxidation at cathode even when ethanol crossover occurred through the Nafion®117 film, which prevents voltage drop at the cathode. However, the CAP catalyst did oxidize ethanol at the cathode and caused a decrease in voltage at higher ethanol concentrations.

**Keywords** Oxygen reduction · Direct ethanol fuel cells · Ethanol crossover · Ni–Co–Fe

## 1 Introduction

Direct methanol fuel cells (DMFCs) are promising power sources, especially for portable electronics applications, including mobile phones, laptop computers and small auxiliary power units [1]. In the recent past, ethanol has attracted special interest as a renewable resource, because it is easily produced in large quantities from biomass [2]. Moreover, ethanol provides excellent energy density (8.0 kWh $kg^{-1}$), comparable to that of gasoline (10 – 11 kWh $kg^{-1}$) [3].

Recent work has focused on the development of new electrocatalysts for direct ethanol fuel cells (DEFCs) to improve the catalytic activity of the ethanol oxidation [4–6] and oxygen reduction reactions [7–10]. In addition, new proton conductive films to reduce the ethanol crossover have been focused on [11, 12]. Lower performance of DEFC compared to that of DMFC can be attributed to the lower catalytic activity of ethanol oxidation than that of methanol oxidation [13, 14]. Another crucial problem for the DEFC is the decrease in open circuit voltage caused by ethanol crossover. The decrease in the open circuit voltage can be prevented by blocking the ethanol crossover using a selective proton exchange membrane having capability to prevent the permeation of ethanol [15, 16]. Another solution against the voltage drop associated with the ethanol crossover is to use the cathode catalyst (oxygen reduction catalyst) which can efficiently reduce oxygen [17, 18], without oxidizing the crossover-ethanol. Such fuel cells have been realized as bio-fuel cells, where enzymes are used as catalysts causing the selective reactions [19–21]. However, these bio-fuel cells lack long term stability. Carbon supported platinum (Pt/C) is commonly used as the electrocatalysts for the oxygen reduction reaction (ORR) in DEFC due to its high catalytic activity and high chemical stability. The Pt/C catalyst decreases the open circuit voltage when high concentrated ethanol is used as the fuel, because the ethanol crossovers through the Nafion® 117 membrane

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from the anode to the cathode, and is oxidized by the Pt/C catalyst on the cathode.

It has been reported that Ni–Co–Fe catalyst has the ability to reduce oxygen [22]. In the course of the study on the composite catalyst for the direct ethanol fuel cell, we found that a Ni–Co–Fe composite catalyst reduces oxygen, without oxidizing the ethanol. This prompted us to evaluate the efficiency of this catalyst as a suitable cathode catalyst (a reduction catalyst for oxygen).

In this paper, the effect of Ni–Co–Fe (NCF) composite catalysts on ethanol crossover is discussed in order to improve DEFC performance.

## 2 Experimental

### 2.1 Materials

Nickel(II) acetate tetrahydrate, cobalt(II) acetate tetrahydrate and iron(II) acetylacetonate, melamine, formaldehyde and Nafion® solution (5 wt%) were purchased from Aldrich. Carbon particles (Vulcan XC-72R) were obtained from Cabot Corporation. PtRu/C electrocatalyst (Pt:Ru:C = 30:24:46 wt%) was purchased from Tanaka Kikinzoku Group. Carbon paper (TPG-H-120) was purchased from Toray Industries. A counter electrode (cathode) consisting of Pt/C (TEC10E50E) was purchased from Tanaka Kikinnzoku Group. Other solvents used in this experiment were commercially available and were used without further purification.

### 2.2 Synthesis of catalyst

Ni–Co–Fe electrocatalyst (NCF) was prepared using the method reported previously by Bianchini and Witherspoon [22, 23]. About 0.3 M of formaldehyde, 0.1 M of melamine, and 0.5 g of NaOH were mixed at room temperature and the mixture was heated at 60 °C for 10 min. Then 0.5 g of Nickel(II) acetate tetrahydrate, 0.5 g of cobalt (II) acetate tetrahydrate, 0.5 g of iron (II) acetylacetonate, 5 g of carbon black (Vulcan XC-72R), 0.5 g of concentrated HCl aq. solution and 40 mL of water, were added to the mixture under stirring. The mixture was mechanically stirred for 20 h at 90 °C to give gel like composite material. The gel was heated in a tubular furnace at 800 °C under inert atmosphere for 1 h. The pyrolyzed, metal-doped copolymer has been reported to be a metal-doped heterocarbon/nitrogen complex [23]. It has been reported that the gel material is a melamine resin, which was prepared by the reaction of melamine and formaldehyde in the presence of NaOH and the metal compounds are entrapped in the polymeric gel. The melamine resins prevent the metal from aggregation during the pyrolysis of the gel compounds. The gel was pyrolyzed in an inert atmosphere to provide the carbon particles on which metal particles were highly dispersed. Schematic procedures for NCF catalyst preparation are shown in Fig. 1.

### 2.3 Physicochemical characterization

The morphology of NCF catalyst was observed by transmission electron microscopy (TEM, H-9000NAR, Hitachi High-technologies). The particle size and the composition were estimated by EDAX (SS550, Shimatsu).

### 2.4 Preparation of the membrane electrode assembly (MEA)

The anode catalyst paste (PtRu/C paste) was prepared by mixing 0.2 g of PtRu/C (commercially available, see material section), and 1 g of Nafion solution (5 wt%). The anode catalyst layer was made by printing the PtRu/C paste on carbon paper using 0.05 mm thickness films as the spacer, followed by drying in air at room temperature for 30 min. The cathode catalyst paste (NCF paste) was prepared by mixing 0.2 g of NCF and 1 g of Nafion® solution (5 wt%). The cathode catalyst layer was prepared by printing the NCF paste on the carbon paper by using 0.05 mm thickness film as the spacer, followed by drying in air at room temperature for 30 min. The supported catalyst on the carbon paper was about 1.6 mg cm$^{-2}$ which includes Vulcan carbon. A Nafion® 117 membrane was pretreated by boiling with 3 wt% $H_2O_2$ solution for 1 h, followed by rinsing with deionized water at 100 °C for 1 h. The film was again treated with 0.5 M $H_2SO_4$ in water at 100 °C for 1 h, followed by rinsing with deionized water at 100 °C for 1 h [12, 16]. The membrane-electrode assembly (MEA) was prepared by sandwiching the Nafion® 117

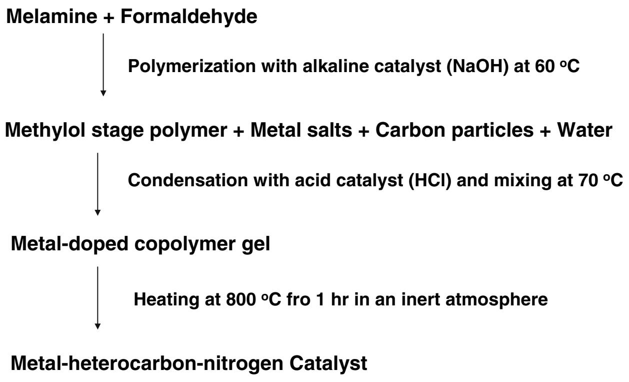

**Fig. 1** Preparation procedure of NCF catalyst

membrane between the cathode and the anode electrodes by hot pressing at 100 kg $cm^{-2}$ and 130 °C for 5 min [24].

### 2.5 Cyclic voltametric (C–V) experiments

Cyclic voltametry (C–V) was carried out employing a potentiostat/galvanostat (Hokuto Denko, Model HSV-100) coupled to a personal computer and a three-electrode test cell at room temperature. The working electrode was a thin layer of Nafion® solution (5 wt%) impregnated catalyst composite on the carbon paper. An aqueous solution containing 0.5 M $H_2SO_4$ and 1 M ethanol was used as the electrolyte. A saturated calomel electrode (SCE) was used as reference electrode and a platinum wire as counter electrode [22, 25, 26].

### 2.6 Single fuel cell test

Single DEFC test were performed using an MEA with an active area of 2.2 cm × 2.2 cm. The outer frame of the DEFC cell was purchased from ElectroChem (EFC05). The flow fields consisting of machined two-pass serpentine grooves on the graphite block were identical for both anode and cathode. The MEA was inserted into the compartment. Ethanol aqueous solution was supplied through the anode compartment by a peristaltic pump (Masterflex, Model 7518–00) at a flow rate of 1.0 mL $min^{-1}$. The flow of nonpreheated dry air was supplied at 2 atm and controlled by a pressure controller (AS ONE, Compact Air Pump): the cell temperature was controlled by a digital temperature controller (Iuchi, Model T-550). The polarization curves were obtained at 40 °C in a fuel cell testing system using a dc electronic load apparatus (Fujitsu Access, Model EUL-150αXL).

## 3 Results and discussion

Figure 2 shows the TEM images of NCF catalyst treated at 800 °C. The size of these nano-particles was not uniform and varied from 10 nm to 200 nm. Figure 3 shows the EDX pattern of one crystal of the NCF catalyst after heating at 800 °C for 1 h in inert atmosphere. One crystal had Debye-Scherrer rings and contained Fe, Co and Ni atoms, suggesting that the nano-particle is a crystal alloy of Fe, Co and Ni. We did not analyze the composition; it was assumed to be similar to the feed concentration of the precursor metal complex.

Figure 4 exhibits C–V curves for these Pt/C and NCF electrodes measured in 0.5 M $H_2SO_4$ and 1 M ethanol [27]. It has been reported that ethanol oxidation occurs at 0.75 V/SCE [27]. The C–V curve for the Pt/C increased at around 0.5 V and had a shoulder at 0.85 V. Similar results have been observed by Liu et al. [27]. It can be seen that the ethanol electro-oxidation current for the NCF electrode is lower than that of the Pt/C electrode. This suggests that the NCF electrode has lower susceptibility to ethanol oxidation than the Pt/C electrode. This prompted us to evaluate this NCF catalyst for oxygen reduction (cathode). If the NCF catalyst in the cathode is less susceptible to ethanol oxidation than the Pt/C catalysts, we can expect to prevent Voc decrease caused by ethanol crossover.

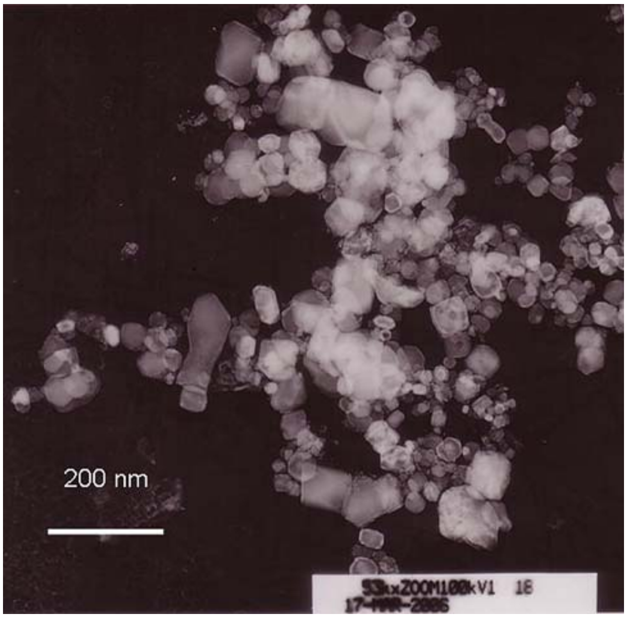

**Fig. 2** TEM image of NCF catalyst synthesized by heat treatment at 800 °C

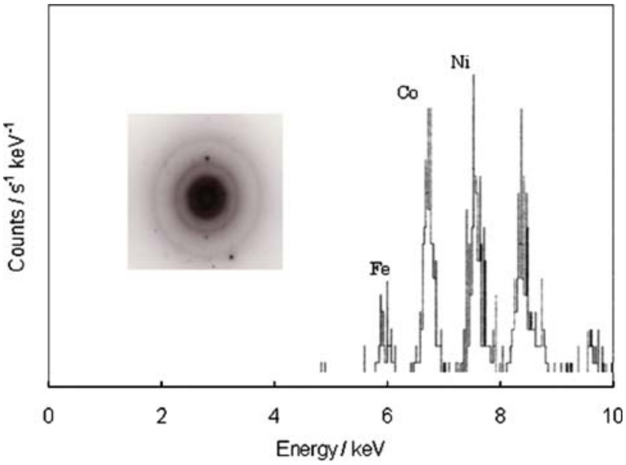

**Fig. 3** EDX composition analysis and EDX ring pattern of NCF catalyst heat-treated at 800 °C

Figure 5 shows the fuel cell performance for the cell consisting of PtRu/C (anode)/Nafion®/Pt/C (cathode)

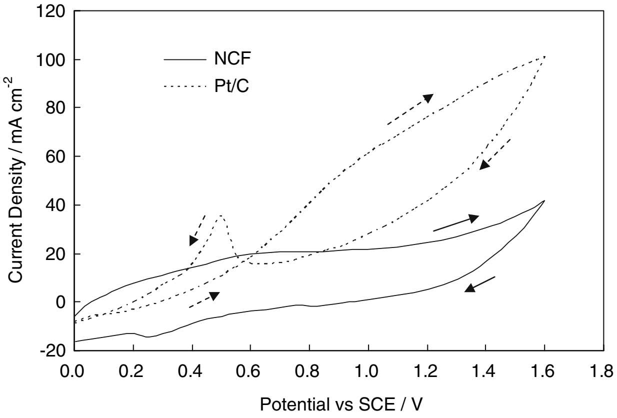

**Fig. 4** Cyclic voltammogram of NCF/C and Pt/C electrode 0.5 M $H_2SO_4$ + 1 M $C_2H_5OH$ electrolyte in water at room temperature. The potential sweep rate was 50 mV $s^{-1}$

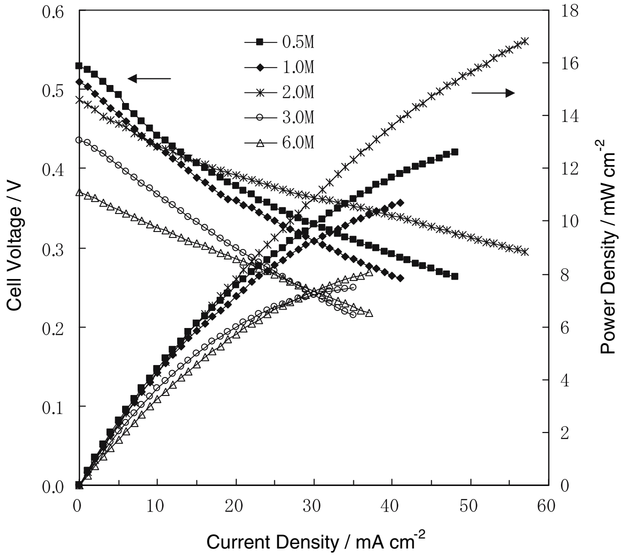

**Fig. 5** DEFC performance of cell 1 operated at different ethanol concentrations. Cell operated at 40 °C; anode: PtRu/C; cathode: Pt/C; electrolyte: Nafion® 117 membrane. Detail: see experimental section

(Cell1). The ethanol concentration was changed from 0.5 M to 6.0 M. The open circuit voltage ($V_{oc}$) decreases with increase in ethanol concentration. A similar phenomenon of $V_{oc}$ decrease with increase in alcohol concentration has also been reported to be caused by methanol crossover for a DMFC [1]. Figure 5 also contains curves showing the relationship between current density and power density. The best performance was obtained with 2.0 M ethanol solution.

Figure 6 shows the performance of a cell consisting of PtRu/C (anode)/Nafion®/NCF (cathode) (Cell 2). The ethanol concentration was also varied from 0.5 to 6.0 M. The open circuit voltage ($V_{oc}$) did not change and was about 0.52 V even when the ethanol concentration was varied from 2.0 to 5.0 M. The $V_{oc}$ decreased to 0.48 V when the ethanol concentration increased to 6.0 M. Thus the results clearly reveal that cell 2 is less prone to ethanol crossover. The best results were obtained when the ethanol concentration was 4.0 M, which is much higher than that for Cell 1 (2.0 M). Figure 7 summarizes the relationship between $V_{oc}$ and ethanol concentration for cell 1 (conventional cell) and cell 2 (new cell). Figure 7 shows that the magnitude of Voc for cell 1 with the Pt/C electrode decreases gradually over the entire range of concentration. On the other hand, surprisingly, Cell 2 with the NCF electrode shows a different trend with change in ethanol concentration. The $V_{oc}$ for Cell 2 gradually increases up to 0.56 V at 3.0 M ethanol concentration and thereafter shows a decrease in Voc up to 0.48 V at 6.0 M ethanol concentration. Figure 7 therefore clearly shows the difference between cell 1 and cell 2, and suggests that cell 2 is less

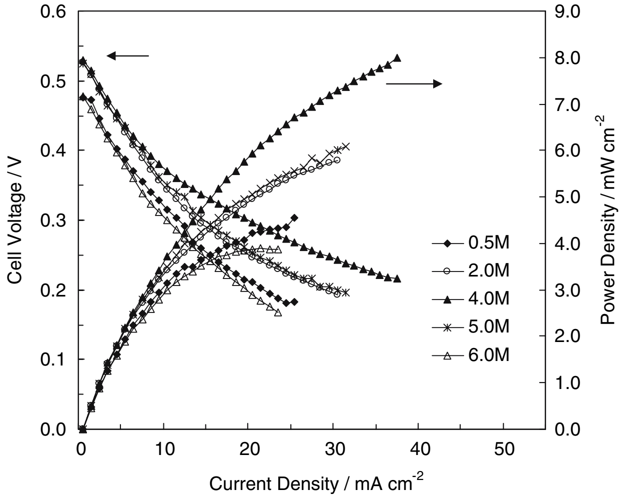

**Fig. 6** DEFC performance of cell 2 operated at different ethanol concentrations. Cell operated at 40 °C; anode: PtRu/C; cathode: NCF; electrolyte: Nafion® 117 membrane. Detail: see experimental section

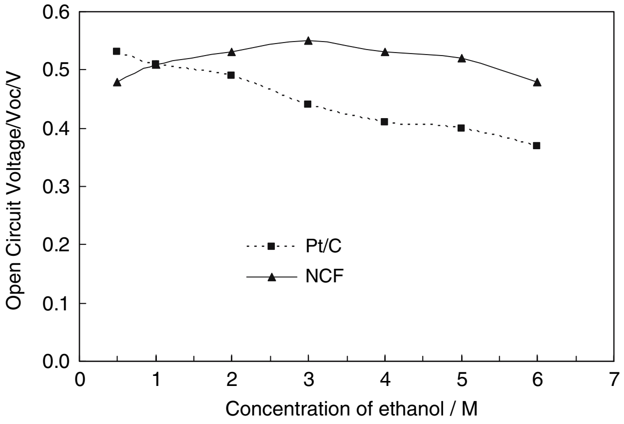

**Fig. 7** $V_{oc}$ of cell 1 and cell 2 at various ethanol concentrations Cell1: PtRu/C (anode)/Nafion® 117/Pt/C (cathode), Cell2: PtRu/C (anode)/Nafion® 117/NCF/C (cathode)

sensitive to ethanol crossover. Since both have similar ethanol crossover, the difference in cell performance may be attributable to the cathode taken for the cell construction. When ethanol crosses from the anode side to the cathode side through Nafion® 117, the Pt/C cathode in cell 1 oxidizes ethanol, which decreases $V_{oc}$. However, the NCF cathode in cell 2 does not react with the ethanol, even when ethanol reaches the cathode by crossover from the anode.

## 4 Conclusion

The Cell 2 consisting of PtRu/C(anode)/Nafion® 117/NCF(cathode) composition was less sensitive to ethanol crossover. It has been clearly demonstrated experimentally that the NCF catalyst is capable of selectively reducing oxygen without oxidation of ethanol deriving from the anode. This is in contrast with the commonly used conventional cathode catalyst (Pt/C). The conventional Pt/C cathode reduces oxygen and oxidizes ethanol from the anode side. Thus the NCF composite catalyst has potential as cathode catalyst in DEFCs as it is less prone to ethanol crossover.

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