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Carbon-supported Pt–Co nanoparticles as anode catalyst for direct borohydride-hydrogen peroxide fuel cell: Electrocatalysis and fuel cell performance

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ABSTRACT

Carbon-supported Pt–Co nanoparticle catalysts (Pt–Co/C) with a mean crystallite size of approximate 2 nm are prepared by a modified $NaBH_4$ reduction method in aqueous solution at room temperature and employed as anode catalyst for direct borohydride-hydrogen peroxide fuel cell (DBHFC). The physical and electrochemical properties are investigated by transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), chronoamperometry (CA) and fuel cell test. The results show that Pt–Co/C catalyst presents more excellent performance as DBHFC anode catalyst compared with Pt/C catalyst, especially, $Pt_{67}Co_{33}/C$ catalyst presents the highest catalytic activity for BH_4^- electrooxidation among all as-prepared catalysts. The single DBHFC using $Pt_{67}Co_{33}/C$ as anode catalyst and Pt/C as cathode catalyst obtains the maximum power density as high as 79.7 mW cm^{-2} at 25 °C.

1. Introduction

The proton exchange membrane fuel cells (PEMFCs) have attracted intense attention as power sources for electric vehicles or residences because of their high energy conversion efficiency and environmental friendliness [1–3]. However, there still exist some problems for transportation and storage of hydrogen. In 1960s, $NaBH_4$ was first tested as a fuel for fuel cells [4]. Since then, $NaBH_4$ has been considered to be an attractive hydrogen sources for fuel cell because it not only contains a hydrogen content of 10.6 wt.% and a capacity of 5.7 Ah g^{-1}, which are much higher than other hydrogen storage compounds, but also is non-toxic, easy to store and transport and relatively stable in alkaline solution. In addition,

the CO poisoning is not an issue for the direct borohydride fuel cell (DBFC) which uses $NaBH_4$ aqueous solution as fuel, because carbon is absence in the fuel of $NaBH_4$.

In the past decade, DBFC has been intensively studied [5–21]. The anode reaction of DBFC is a direct borohydride oxidation reaction in alkaline medium, according to the following eight-electron process [5,12–15]:
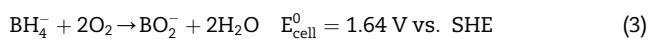
$$BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^- \quad E^0_{anode} = -1.24 \text{ V vs. SHE} \quad (1)$$
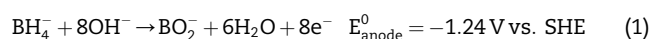
The cathode reaction with oxygen as the oxidant is according to Eq. (2):

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad E^0_{cathode} = 0.40 \text{ V vs. SHE} \quad (2)$$

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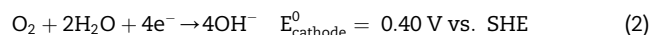
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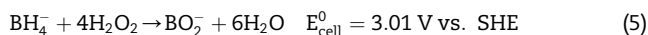The overall fuel cell reaction is:

$$BH_4^- + 2O_2 \rightarrow BO_2^- + 2H_2O \quad E_{cell}^0 = 1.64 \text{ V vs. SHE} \tag{3}$$

However, when hydrogen peroxide in acid electrolyte substituted for oxygen is used as the oxidant at the cathode, the direct borohydride-hydrogen peroxide fuel cell (DBHFC) can yield a theoretical cell voltage as high as 3.01 V and present a higher energy density [17–20].

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad E_{cathode}^0 = 1.77 \text{ V vs. SHE} \tag{4}$$
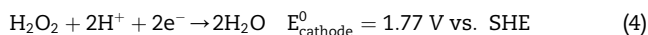
The over cell reaction is as follows:

$$BH_4^- + 4H_2O_2 \rightarrow BO_2^- + 6H_2O \quad E_{cell}^0 = 3.01 \text{ V vs. SHE} \tag{5}$$

Moreover, DBHFC have many other advantages than DBFC in both theoretical and practical aspects [17–20]. However, the successful commercialization of DBHFC depends largely on the anode electrocatalyst. In present, almost all low-temperature fuel cells use carbon-supported Pt as their anode electrocatalyst, and the high cost of the precious metals inhibit the commercialization of DBHFC. Many investigations have shown that alloying Pt with 3d transition metals such as Co [21–28], Fe [25,29,30] and Ni [25,28,31] is an efficient route to not only enhance the catalytic activity but also decrease the cost of the Pt catalyst. Pt–Co/C has been used as an electrocatalyst for oxygen reduction reaction (ORR) [21–24] as well as anode electrocatalyst for the oxidation of methanol [26,27]. Tegou et al. [28] studied the electrochemical oxidation of borohydride by means of voltammetry on the bimetallic Pt(Ni)/GC and Pt(Co)/GC RDEs (prepared by spontaneous galvanic replacement of Ni and Co electrodeposits upon their immersion in a chloroplatinic acid) and found that the cyclic voltammetry of bimetallic Pt(Ni)/GC and Pt(Co)/GC was similar to that of pure Pt, except that the oxidation currents at low overpotentials is higher than that of Pt. To the author's knowledge, there is little information available in literature about carbon-supported Pt–Co nanoparticles as anode catalyst for DBFC. In our previous studies, Au–Co/C as anode electrocatalyst for DBHFC have been well studied [32]. It has been found that the Au–Co/C catalysts exhibit much higher catalytic activity and stability for the direct electrooxidation of BH_4^- than Au/C catalyst. In this paper, a series of Pt–Co/C catalysts were prepared by a modified NaBH$_4$ reduction method in aqueous solution at room temperature and the electrocatalytic activities for BH_4^- electrooxidation on Pt–Co/C catalysts were studied by means of CV and CA. Moreover, the performances of the DBHFCs using Pt–Co/C as anode catalysts and Pt/C as cathode catalyst were studied in detail by single fuel cell test.

2. Experimental methods

All chemical reagents were of analytical grade: sodium borohydride (Alfa-Aesar, 98%), hexachloroplatinicacid (Sigma–Aldrich), cobaltous chloride (Sigma–Aldrich), Polyvinylpyrrolidone (Sigma–Aldrich), Vulcan XC-72R carbon black (Cabot Corp., 240 m^2 g^{-1}) and Nafion solution (Dupont, 5%).

2.1. Catalysts preparation

Pt–Co/C and Pt/C catalysts were prepared using a modified NaBH$_4$ reduction method. H$_2$PtCl$_6$·6H$_2$O and CoCl$_2$·6H$_2$O were used as precursors of Pt–Co bimetallic catalysts. Vulcan XC-72R carbon black and NaBH$_4$ were used as support and reducing agent, respectively. Polyvinylpyrrolidone (PVP) was used as stabilizing agent to prevent nanoparticles from aggregating in the solution. A brief description of the preparation method is as follow: the required amounts of H$_2$PtCl$_6$, CoCl$_2$, carbon and PVP were added to 100 ml deionized (DI) water under vigorous stirring, and then it was kept stirring for 30 min. The pH of the mixed solution was adjusted to 10 by adding 3 M NaOH solution, and 1 ml of 1 M NaBH$_4$ was added dropwise. After an additional 24 h stirring, the resulting catalyst was filtered and washed with deionized water until no Cl$^-$ was detected, finally dried for 12 h at 80 °C in vacuum to obtain Pt–Co/C catalysts. The atomic ratios of Pt/Co contained in the impregnation solutions were 100:0, 75:25, 67:33 and 50:50, and the corresponding four catalysts were denoted as Pt/C, Pt$_{75}$Co$_{25}$/C, Pt$_{67}$Co$_{33}$/C and Pt$_{50}$Co$_{50}$/C, respectively. The loading of metals in all four catalysts is 20 wt.%.

2.2. Catalysts characterization

2.2.1. Physical characterization
The structure and morphology of Pt–Co/C catalysts were examined by TEM (JEM-3010, JEOL) operated at 300 kV. For TEM analyses, samples were prepared by adding one or two drops of the suspension, which was made by ultrasonically dispersing the catalyst in ethanol, onto the carbon-coated copper grid and drying it in air at room temperature.

Crystal structure identification of Pt–Co/C catalysts was carried out using an X-ray diffractometer (D/MAX-3C) which was employed with Cu Kα radiation ($\lambda = 1.54056$ Å) and a graphite monochromator at 50 kV, 100 mA to obtain XRD patterns of the samples. The 2θ angular regions between 20° and 90° were explored at a scan rate of 4° min^{-1}. The average crystallite sizes for the Pt–Co/C catalysts were evaluated according to the full width at half maximum (FWHM) and the angular position of the Pt (220) peak.

The surface chemical state and bonding of the as-prepared catalysts were analyzed by XPS (K-Alpha 1063, Thermo Fisher Scientific) using XPSPEAK software to deconvolute the narrow scan spectra of Pt and Co.

2.2.2. Electrochemical characterization
The electrocatalytic activities of the as-prepared catalysts were measured by CV and CA experiments by means of a CHI660A Electrochemistry Workstation and a typical three-electrode one-compartment electrolysis cell. The cell was composed of a Pt–Co/C or Pt/C working electrode, a Ni foam mesh counter electrode (3 cm × 5 cm) and an Ag/AgCl, KCl$_{std}$ reference electrode. In this study, CV test was conducted at 20 mV s^{-1} with potential ranging from −1.2 to 0.6 V (vs. Ag/AgCl, KCl$_{std}$) and CA test was from −1.2 to −0.2 V (vs. Ag/AgCl, KCl$_{std}$).

The working electrode was prepared as follows: 10 mg Pt–Co/C or Pt/C catalyst was dispersed by ultrasonic for 2 h in 1 ml solution composed of 0.25 ml 5% Nafion solution and