Journal of Power Sources 245 (2014) 89–94

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Nickel and cobalt electrodeposited on carbon fiber cloth as the anode of direct hydrogen peroxide fuel cell

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HIGHLIGHTS

- Ni and Co supported on carbon fiber cloth is prepared by electrodeposition.
- High performance direct peroxide–peroxide fuel cells (DPPFC) are demonstrated.
- The DPPFC displays a peak power density of 21.6 mW cm^{-2} at 20 °C.

ARTICLE INFO

Article history:
Received 21 April 2013
Received in revised form
19 June 2013
Accepted 19 June 2013
Available online 28 June 2013

Keywords:
Nickel
Cobalt
Electrodeposition
Hydrogen peroxide
Electrooxidation
Fuel cell

ABSTRACT

Carbon fiber cloth (CFC) supported Ni and Co electrodes are prepared by electrodeposition (Ni/CFC and Co/CFC). Their catalytic performance for H_2O_2 electrooxidation in KOH solution is investigated and compared with Au/CFC electrode. Ni/CFC electrode exhibits higher catalytic activity than Au/CFC and Co/CFC electrodes. The performance of a direct peroxide–peroxide fuel cell (DPPFC) with Ni/CFC anode and Pd/CFC cathode is examined. The cell shows a peak power density of 21.6 mW cm^{-2} at 20 °C and 53.8 mW cm^{-2} at 50 °C. The cell performance is improved with the increase of anolyte and catholyte flow rate and operation temperature. Results indicates that the performance of DPPFC with low-cost Ni/CFC anodes is comparable with those using precious metal anodes, e.g., Au/CFC and Pd/CFC.

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1. Introduction

Hydrogen peroxide (H_2O_2) has been exploited as a carbon-free energy carrier that can be used as both fuel and oxidant in a fuel cell, namely direct peroxide–peroxide fuel cell (DPPFC) [1–10]. Recent study [6] has reported that H_2O_2 can be produced using electrical power of a photovoltaic solar cell at nearly 100% current efficiency. The produced H_2O_2 can power a DPPFC to generate electricity, thus realizing a clean and efficient way of power generation from solar energy. DPPFC is all liquid feed fuel cell operating without air. It generates power and provides O_2 at the same time. So it is a good candidate for underwater or space power sources. As the fuel of a fuel cell, H_2O_2 is carbon-free and has none of the environmental problems associated with other fuel cells such as methanol, formic acid and hydrazine [11–14]. As the oxidant of a fuel cell, H_2O_2 has faster electroreduction kinetics than O_2 [15–19].

DPPFC can be operated in one-compartment or two-compartment configuration. Yamazaki et al. [2] first reported a membraneless one-compartment DPPFC with low open circuit voltage (OCV) and low power density. Recently, Mousavi Shaegh et al. [7] significantly improved the OCV of one-compartment DPPFC to 0.6 V and the power density to 1.55 mW cm^{-2} using Ni anode and Prussian blue cathode in an acidic medium. The two-compartment DPPFC was first established by Hasegawa et al. [20]. They demonstrated that the OCV and output power density of two-compartment DPPFC is remarkably higher than that of one-compartment configuration. We [8–10] recently reported a high performance two-compartment DPPFC using carbon fiber cloth supported noble metal (Pd, Au and Pd–Au) with special structure as both the anode and cathode. The DPPFC exhibits a stable OCV of 0.9 V and a peak power density of 20.7 mW cm^{-2} at 20 °C. We [8] also found that the cathode reaction has a much larger

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http://dx.doi.org/10.1016/j.jpowsour.2013.06.115

overpotential than the anode reaction, that is, H_2O_2 electrooxidation has a faster reaction kinetics than H_2O_2 electroreduction. Therefore, non-noble metals can be used as the anode catalyst to reduce the cost of DPPFC. In this investigation, we reported two non-noble metal electrodes: carbon fiber cloth (CFC) supported Ni and Co (Ni/CFC, Co/CFC). We demonstrated that the performance of DPPFC with these non-noble metal anodes is comparable with those using noble metal anodes, e.g. Au/CFC and Pd/CFC.

2. Experimental

2.1. Reagents

$PdCl_2$ (>99.9%), $HAuCl_4$ (>99.9%), $HClO_4$, $NiCl_2$, $CoCl_2$, HBO_3, KOH, H_2SO_4 and H_2O_2 were obtained from Enterprise Group Chemicals Reagent Co. Ltd. China. Carbon fiber cloth (thickness: 0.34 mm) was purchased from Shanghai Hesen electric Co., Ltd. All chemicals are analytical grade and were used as-received without further purification. Ultrapure water (Millipore, 18 MΩ cm) was used throughout the study.

2.2. Preparation and characterization of the Ni/CFC and Co/CFC electrodes

The Ni/CFC and Co/CFC electrodes were prepared by electrodeposition of metals on carbon fiber cloth, which acts as the support of metal catalysts and the current collector of the electrode. The electrodeposition was performed by a square-wave cathodic current method in a typical three-electrode electrochemical cell controlled by computerized potentiostat (Autolab PGSTAT302, Eco Chemie). The CFC (10 mm × 10 mm × 0.34 mm) served as the working electrode, which was placed between two parallel platinum foil (10 mm × 10 mm) counter electrodes. An Ag/AgCl (3 mol L^{-1} KCl) electrode was used as the reference electrode, and all potentials in this work were referred to this reference electrode. Ni deposition was carried out in 0.1 mol L^{-1} $NiCl_2$ + 0.5 mol L^{-1} HBO_3 solution under an upper limit current of -3 mA cm^{-2} and a lower limit current of -30 mA cm^{-2} with a pulse interval of 50 s and a total cycles of 20. The Co deposition was performed in 0.1 mol L^{-1} $CoCl_2$ + 0.5 mol L^{-1} HBO_3 solution under the identical deposition parameters as the Ni deposition. The Au/CFC and Pd/CFC electrodes were also prepared for comparison using our previous reported method [8,10]. Briefly, the Au/CFC electrode was prepared using square-wave potential electrodeposition in 1.0 mmol L^{-1} $HAuCl_4$ + 0.5 mol L^{-1} H_2SO_4 solution by applying 12,000 cycles of potential pulse between 1.1 V for 50 ms and -0.5 V for 50 ms. The Pd/CFC electrode was also prepared using the square-wave potential electrodeposition in 5.0 mmol L^{-1} $PdCl_2$ + 0.1 mol L^{-1} $HClO_4$ solution by applying 120,000 cycles of potential pulse between 0.5 V for 5 ms and -0.1 V for 5 ms.

The electrode morphology was characterized by a scanning electron microscope (SEM, JEOL JSM-6480). The structure was analyzed using an X-ray diffractometer (Rigaku TTR III) with Cu Kα radiation ($\lambda = 0.1514178$ nm). The Pd loading and Au loading were measured using an inductive coupled plasma emission spectrometer (ICP, Xseries II, Thermo Scientific). Dendritic Pd and Au electrodeposited on the 1.0 cm^2 CFC substrate were first dissolved in aqua regia solution and then diluted to 1.0 L solution for the ICP measurement.

2.3. Electrochemical measurements and DPPFC tests

H_2O_2 electrooxidation was performed in a three-electrode electrochemical cell with the same configuration as that for electrodeposition, except that the two Pt foil counter electrodes were placed behind D-porosity glass frits to eliminate the effect of H_2O_2 decomposition at the counter electrode on the catalytic performance. The electrolyte for H_2O_2 electrooxidation was H_2O_2-containing KOH. The reported current densities were calculated using the geometrical area of the electrode. All solutions were made with analytical grade chemical reagents and ultra-pure water (Milli-Q 18 MΩ cm). All measurements were performed at ambient temperature (20 ± 2 °C) under N_2 atmosphere.

DPPFC with the configuration shown in Fig. 1 was fabricated using the Pd/CFC electrode as the cathode and the Ni/CFC, Co/CFC and Au/CFC electrodes as the anodes, respectively. The preparation methods of membrane electrode assembly (MEA) and the fuel cell assembling were described in our previous report [9]. Nafion-115 (DuPont, USA) membrane was used to separate the anode and cathode compartments. The Pd loading in the Pd/CFC cathode is 0.3061 mg cm^{-2} and the Au loading in the Au/CFC anode is 0.1131 mg cm^{-2} (the data obtained from ICP analysis [8,10]). The discharge performance of the DPPFC was measured using a computer-controlled E-load system (Arbin, USA).

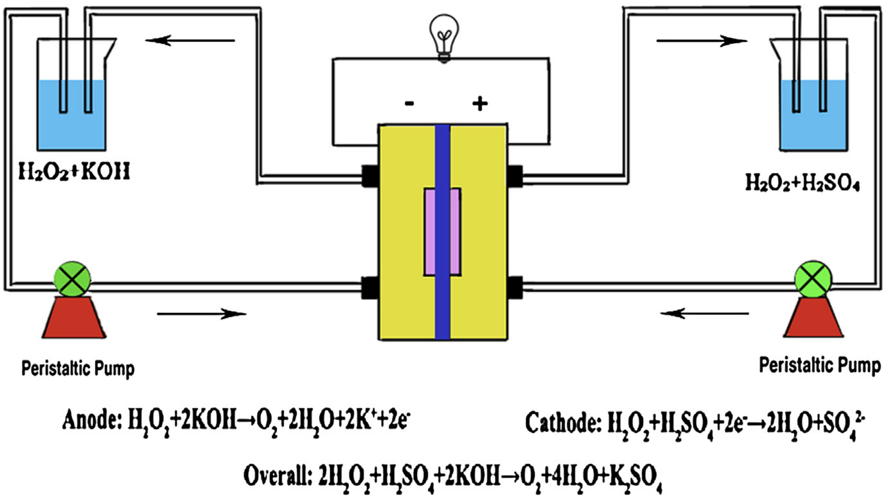

Fig. 1. A schematic representation of the direct H_2O_2–H_2O_2 fuel cell configuration.

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