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Enhancement of direct urea-hydrogen peroxide fuel cell performance by three-dimensional porous nickel-cobalt anode

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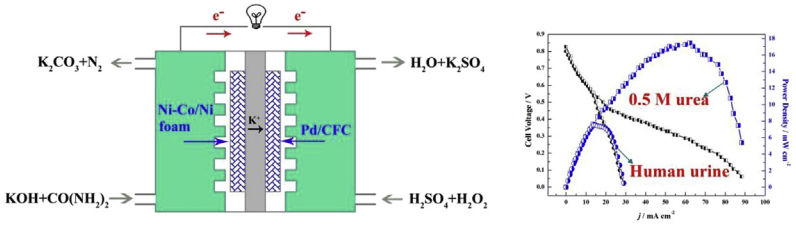
HIGHLIGHTS

- The 3D porous Ni-Co/Ni foam anode is prepared using hydrogen bubble template.
- The DUHPFC performance is greatly enhanced by the Ni-Co/Ni foam anode.
- The effects of KOH, urea concentration, flow rate and temperature are investigated.
- DUHPFC fed with human urine as the fuel shows excellent performance.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel three-dimensional (3D) porous nickel-cobalt (Ni-Co) film on nickel foam is successfully prepared and further used as an efficient anode for direct urea-hydrogen peroxide fuel cell (DUHPFC). By varying the cobalt/nickel mole ratios into 0%, 20%, 50%, 80% and 100%, the optimized Ni-Co/Ni foam anode with a ratio of 80% is obtained in terms of the best cell performance among five anodes. Effects of the KOH and urea concentrations, the flow rate and operation temperature on the fuel cell performance are investigated. Results show DUHPFC with the 3D Ni-Co/Ni foam anode exhibits a higher performance than those reported direct urea fuel cells. The cell gives an open circuit voltage of 0.83 V and a peak power density as high as 17.4 and 31.5 mW cm^{-2} at 20 °C and 70 °C, respectively, when operating on 7.0 mol L^{-1} KOH and 0.5 mol L^{-1} urea as the fuel at a flow rate of 15 mL min^{-1}. Besides, when the human urine is directly fed as the fuel, direct urine-hydrogen peroxide fuel cell reaches a maximum power density of 7.5 mW cm^{-2} with an open circuit voltage of 0.80 V at 20 °C, showing a good application prospect in wastewater treatment.

1. Introduction

Direct urea fuel cell (DUFC), composed of urea electro-oxidation at the anode and oxidant (oxygen, air or hydrogen peroxide) electro-reduction at the cathode, has attracted much attention recently [1–5]. Compared with other types of fuel cells, urea used as the fuel has many advantages: (1) urea is cheap and in solid-

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state, thus, easy to transport and preserve; (2) the products of urea electro-oxidation are harmless nitrogen and carbonate (Eq. (1)); (3) the anolyte can be directly fed with urine or factory urea-rich wastewater, which can further purify the urea-rich sewage accompanied by generating electricity; therefore the products of nitrates from biodegradation can be thoroughly avoided [6,7]; (4) The energy density of urea is 16.9 MJ L^{-1}, much higher than that of liquid H_2 (10.1 MJ L^{-1}), compressed H_2 (700 bar, 5.6 MJ L^{-1}) or NH_4OH(28%, 1.17 MJ L^{-1}) [1,8,9]. (5) As reported by Abraham et al. [4] and Cinti et al. [5], urea can be directly used as a hydrogen carrier in high-temperature solid oxide fuel cell with the characteristics of being neither flammable nor toxic. When H_2O_2 is used as the oxidant, the theoretical cell voltage of direct urea-hydrogen peroxide fuel cell (DUHPFC) reaches up to 2.509 V (Eq. (3)), higher than other types of fuel cells. The reactions are illustrated as below:

$$\text{Anode}: \quad CO(NH_2)_2 + 8KOH \rightleftarrows N_2 + 6H_2O + K_2CO_3 + 6K^+ + 6e^-, E^\theta = -0.746 \text{ V vs. SHE} \tag{1}$$

$$\text{Cathode}: \quad 3H_2O_2 + 3H_2SO_4 + 6e^- \rightleftarrows 6H_2O + 3SO_4^{2-}, \ E^\theta = 1.763 \text{ V vs. SHE} \tag{2}$$

$$\text{Overall reaction: } CO(NH_2)_2 + 3H_2O_2 + 3H_2SO_4 + 8KOH \rightarrow K_2CO_3 + 3K_2SO_4 + N_2 + 12H_2O, E^\theta = 2.509 \text{ V} \tag{3}$$

Tao and co-workers [1] have compared the performances of direct urea fuel cell (DUFC) with different anodes and cathodes in 2010. The open cell voltage (OCV) and peak power density of DUFC containing Ni/C anode catalyst and MnO_2/C cathode catalyst reached ~0.46 V and ~0.27 mW cm^{-2} respectively, meaning the feasibility of direct urea fuel cell. After that, the same group [2] prepared nano-sized nickel with primary particle size of 2–3 nm as the anode catalyst for direct urea fuel cell. Compared with the poor performance of commercial nickel powder, the OCV of nano-sized nickel was up to ~0.6 V with peak power density as high as 1.5 mW cm^{-2} at 20 °C, indicating the significant role of anode catalyst. Although much effort was made on studying DUFC, the relatively low OCV and peak power density hinder itself as a competitive fuel cell when compared with other kinds of fuel cells.

Nickel-based catalyst was found to be the most efficient catalyst for urea electro-oxidation in alkaline solution [10]. According to the former reports, no matter what Ni-based materials (Watts nickel deposits [11], Ni nanowire arrays [12], $Ni(OH)_2$ [13,14], ordered mesoporous NiO [15], Ni-WC/MWNTs [16], etc.) were used as the catalysts, the electrochemical oxidation mechanism of urea on a nickel-based catalyst in alkaline medium can be explained as an electrochemical-chemical (E-C) mechanism [12]: $Ni(OH)_2$ spontaneously formed in alkaline medium was first electrochemically oxidized to NiOOH as the potential swept to the positive direction, and then urea was chemically oxidized by NiOOH. Clearly seen, the formation of NiOOH is a key role for urea electro-oxidation. However, the onset oxidation potential of NiOOH formed from $Ni(OH)_2$ was as high as ca. 0.25 V (vs. Ag/AgCl) in 5.0 mol L^{-1} KOH, which further results in a limited cell operation voltage. Recently, it has been found that the introduction of cobalt in Ni-based catalysts electrode not only affected the morphology and structure, but also the electro-catalytic activity [3,7,17–21]. The change can be mainly ascribed to the following reasons: (1) the addition of cobalt increased the charge-acceptance of Ni-based electrode and pushed the $Ni(OH)_2$/NiOOH peak to more negative potential; (2) the addition of Co increased the conductivity of Ni-based electrode; (3) Co allowed Ni to reach a higher oxidation state and small molecules electro-oxidation can be facilitated by the higher oxidation state of Ni. With the intention of lowering the oxidation overpotential for urea electro-oxidation, Botte et al. [7] synthesized a series of Nickel-Cobalt bimetallic hydroxide electrodes with different Ni/Co composition ratios. A significant reduction in the overpotential (150 mV) was observed with the Nickel-Cobalt bimetallic hydroxide electrode (ca. 43% Co content) when compared to a nickel hydroxide electrode.

In this work, we attempt to fabricate a binary anode catalyst and utilize H_2O_2 as the oxidant in order to improve the cell performance. Five porous Ni-Co microparticle anodes differing in morphology, structure, deposits mass, active surface area and electrochemical signals were electro-deposited on nickel foam by using hydrogen bubble as a dynamic template with different cobalt/nickel mole ratios. The performance of direct urea-hydrogen peroxide fuel cell (DUHPFC) using these five Ni-Co electrodes were investigated. Effects of the KOH and urea concentrations, the flow rate and the operation temperature on the cell performance were discussed. Besides, the cell performance directly fed with human urine as the anolyte was also tested. Finally, the stability of DUHPFC at low and high temperatures was evaluated by the long term and short term test, respectively. Results showed that DUHPFC with the as-prepared 3D porous Ni-Co/Ni foam anodes demonstrated a significantly higher performance than those reported in the previous literature.

2. Experimental

2.1. Preparation and characterization of Ni-Co/Ni foam anodes

The Ni-Co/Ni foam anodes were prepared by electro-depositing a porous Ni-Co film on Ni foam using hydrogen bubble as a dynamic template. The deposition was performed in a two-electrode electrochemical cell with nickel foam working electrode and platinum foil counter electrode in 2.0 mol L^{-1} NH_4Cl, 0.1 mol L^{-1} $NiCl_2$ and $CoCl_2$ aqueous solution. The Ni-Co/Ni foam electrode was obtained by applying a constant current of - 4.0 A cm^{-2} for 60 s via a DC power supply (Keysight, E3644A). Prior to the electrodeposition, the nickel foam was sonicated in acetone for 20 min and soaked in 6.0 mol L^{-1} HCl for 15 min successively. Five anodes with various Co mole ratios (0%, 20%, 50%, 80% and 100%) in the deposition solutions were separately fabricated, labeled as Ni 10, Ni 8, Ni 5, Ni 2 and Ni 0. Ni-Co/Ni foam anode was activated in 5.0 mol L^{-1} KOH using the three-electrode electrochemical cell with the as-prepared Ni-Co/Ni foam working electrode, platinum counter electrode and saturated Ag/AgCl reference electrode respectively. The reported current densities were normalized by geometrical area of the electrode. The active surface area of the Ni-Co/Ni foam anode was estimated by measuring the electrochemical capacitance of the film-electrolyte interface in the double-layer regime of the voltammograms. Using 5.0 mol L^{-1} KOH as the electrolyte, the electrode was potentiostatically cycled, typically between −0.35 V and −0.25 V, at scan rates between 0.3 V s^{-1} and 0.8 V s^{-1} until the measured voltammograms was stabilized. The positive and negative capacitance currents at the center of the potential window were averaged and plotted against the scan rate to extract the measured capacitance. The active surface areas were obtained by using a specific capacitance of 60 μF cm^{-2}. The electrode morphology and structure were respectively characterized by a scanning electron microscope (SEM, JEOL JSM-6480) equipped with an energy dispersive X-ray spectrometer (EDX) and X-ray diffractometer (Rigaku TTR III) with Cu Kα radiation (λ = 0.1514178 nm). The cobalt content was measured using an inductive coupled plasma emission spectrometer (ICP,