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Carbon-encapsulated nickel-iron nanoparticles supported on nickel foam as a catalyst electrode for urea electrolysis

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ABSTRACT

A cyanide-bridged bimetallic coordination polymer, nickel hexacyanoferrate, could be pyrolyzed to form carbon-encapsulated nickel-iron (CE-NiFe) nanoparticles. The formation of nitrogen-doped spherical carbon shell with ordered mesoporous structure prevented the structural damage of catalyst cores and allowed the migration and diffusion of electrolyte into the hollow carbon spheres. An ultra-thin layer of CE-NiFe nanoparticles could be tightly attached to the three-dimensional macroporous nickel foam (NF) by electrophoretic deposition. The CE-NiFe nanoparticles could lower the onset potential and increase the current density in anodic urea electrolysis and cathodic hydrogen production as compared with bare NF. Macroporous NF substrate was very useful for the urea electrolysis and hydrogen production, which allowed for fast transport of electron, electrolyte, and gas products. The superior electrocatalytic ability of CE-NiFe/NF electrode in urea oxidation and water reduction made it favorable for versatile applications such as water treatment, hydrogen generation, and fuel cells.

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1. Introduction

Water pollution by various harmful contaminants such as urine has become one of the most serious environmental problems [1]. Electrochemical remediation of urea-rich wastewater has attracted much research interest in recent years because it allows for purifying the wastewater while also producing hydrogen gas as a fuel [2,3]. Noble metal catalysts have been developed for efficient urea electrolysis [4–6]. However, the expensive noble metals limit their potential application in large-scale removal of urea. Thus, many attempts have been made to research the low-cost catalysts alternative to the noble metal catalysts for urea electrolysis. More recently, nickel and nickel-containing oxides/hydroxides have been characterized as the promising catalysts for urea electrolysis, offering the low-cost catalyst materials for cost-sensitive application [7–13]. In alkaline electrolytes, the redox transition between nickel hydroxide (Ni^{2+}) and nickel oxyhydroxide (Ni^{3+}) at the catalyst layer of anode results in the catalytic oxidation of urea [14,15]. The classic electrochemical-catalytic mechanism, referred to as the EC' mechanism, can be expressed by the following two reactions at the anode [2].

$$6Ni(OH)_2 + 6OH^- \rightarrow 6NiOOH + 6H_2O + 6e^- \qquad (1)$$

$$6NiOOH + CO(NH_2)_2 + H_2O \rightarrow 6Ni(OH)_2 + CO_2 + N_2 \qquad (2)$$

Water can be electrochemically reduced at the catalyst layer of cathode, generating hydrogen gas through the following reaction [2]:

$$6H_2O + 6e^- \rightarrow 3H_2 + 6OH^- \qquad (3)$$

Several factors affect the electrocatalytic performance of nickel-based catalysts towards urea electrolysis, including electrolyte composition, catalyst composition, structure, and morphology [8,9,16–27]. One of the most straightforward methods in improving the electrocatalytic performance of nickel-based anodes is to incorporate foreign metals into nickel, forming the multi-metal catalysts [28]. Incorporation of cobalt or zinc into nickel reduces the onset potential of urea electrolysis and decreases the oxygen evolution reaction (OER) [7,23]. Rhodium-nickel catalysts can reduce surface blockage and increase the stability of catalyst, leading to an enhancement in oxidation current density compared to nickel catalyst [29]. One-dimensional (1D) catalysts such as nickel and nickel-cobalt nanowires show greater electrocatalytic ability and current efficiency than the bulk catalysts due to a significant decrease in overpotential during urea electrolysis [8,21]. Mesoporous materials such as nickel cobaltites turn out to help the urea electrolysis on account of their huge surface area and large mesopore volume [30]. Incorporation of catalyst and

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carbon nanofibers distinctly enhances the electrocatalytic activity of nickel towards urea electrolysis [20,25].

The urea electrolysis takes place at the interface between catalyst and electrolyte. Thus, the catalyst layer on electrode acts a particular role in enhancing the catalytic activity of electrode. Formation of a unique catalyst layer on three-dimensional (3D) porous substrates such as nickel foam (NF), graphene, and carbon sponge shows impressive electrocatalytic activity owing to their high electronic conductivity, unique porous structure, and large active species, which can promote the charge-transfer rate for urea electrolysis [12,24,27,31]. Previous study has shown that NF is a superior skeletal material to support the catalyst layer because it exhibits stable electrochemical properties in alkaline electrolyte and open porous structure with high electrical conductivity for easy transport of electrolyte, electron, and gas products [31]. In addition, NF cathode facilitates high volumetric generation of hydrogen in microbial electrolysis cells [32]. In the present study, we propose a novel configuration of catalyst electrode, carbon-encapsulated nickel-iron alloy (CE-NiFe) nanoparticles on 3D macroporous NF (denoted as CE-NiFe/NF), as a bifunctional catalyst for enhanced urea electrolysis and hydrogen production. As illustrated in Fig. 1, mesoporous carbon shell allows the migration and diffusion of electrolyte into the core region of CE-NiFe to participate the electrocatalytic reaction. The large open space in NF substrate facilitates the transport of electrolyte and allows gaseous products to diffuse back into the bulk electrolyte. 3D NF affords a highly conducting network to connect the CE-NiFe nanoparticles for fast conduction of electrons and large open channels for exclusion of gas products, lowering the charge-transfer resistances of urea electrolysis and hydrogen evolution. Thus, this electrode configuration, CE-NiFe/NF, is able to improve the transport of electron, electrolyte, and gas for application in efficient urea electrolysis and hydrogen production.

2. Experimental

CE-NiFe powder was prepared through thermal pyrolysis of nickel hexacyanoferrate (NiHCF) precursor under an argon atmosphere. NiHCF precursor was synthesized by dropwise adding 50 ml of nickel nitrate solution ($0.04\,\mathrm{mol\,l^{-1}}$) into 50 ml of potassium hexacyanoferrate (III) solution ($0.02\,\mathrm{mol\,l^{-1}}$) at 343 K while stirring [33,34]. After completion of the dropwise addition, the reaction temperature was naturally cooled down to room temperature. Thereafter, the stirring was further continued for 6 h at room temperature. The colloidal solution was centrifuged and rinsed with de-ionized (DI) water several times to obtain NiHCF nanoparticles. CE-NiFe sample was obtained through thermal pyrolysis of NiHCF powder at 773 K for 5 h in a quartz tube furnace under flowing argon [35]. CE-NiFe material was etched in 1 M hydrochloric acid for 1 h to remove the unencapsulated NiFe particles, forming the NiFe@carbon core-shell structure. The acid-treated powder was washed with DI water until neutralized, and then dried overnight at 333 K in air. CE-NiFe nanoparticles were attached onto NF (2 cm × 2 cm) with 1.7 mm thick and 100 ppi (pores per inch) to form CE-NiFe/NF electrode by EPD (electrophoretic deposition) method. In typical, EPD process was performed using a Keithley 2400 source meter (Keithley Instruments) in a colloidal suspension (50 ml) containing CE-NiFe (20 mg), isopropyl alcohol solvent, and a small amount of nickel nitrate ($0.6 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$) as charging agent. A potential difference of -20 V was applied between the working (NF) and Pt counter (2 cm × 2 cm) electrodes equipped in the EPD cell with a separation of 1 cm. After EPD, the NF with attached CE-NiFe nanoparticles was rinsed with DI water and then heat-treated at 423 K in a hot air oven for 1 h. The amount of CE-NiFe nanoparticles on NF could be varied by tuning the EPD time, which was determined by subtracting the amount of NF substrate from the CE-NiFe/NF electrode using an electronic microbalance (Mettler, XS105DU). The NiFe alloy without carbon encapsulation was obtained by calcining the NiHCF powder at 773 K in air for 5 h and then heat-treated at 773 K in a reducing atmosphere containing 95% argon and 5% hydrogen for another 5 h.

Crystal structure and internal microstructure of CE-NiFe powder were identified using an X-ray diffractometer (Bruker D8 Advance) and transmission electron microscopy (TEM, Jeol JEM-1400), respectively. Surface morphology of CE-NiFe/NF electrode was observed by a scanning electron microscopy (SEM, Auriga). Pore size distribution and surface area of CE-NiFe nanoparticles were analyzed using Barrett-Joyner-Halenda (BJH) and Brunauer-Emmett-Teller (BET) techniques, respectively, through nitrogen adsorption/desorption (Micromeritics, ASAP 2020). The electrochemical oxidation of urea and reduction of water were characterized using cyclic voltammetry in a three-compartment electrolytic cell with 1 M KOH solution containing urea ($0.33\,\mathrm{mol\,l^{-1}}$). NF (or CE-NiFe/NF) electrode, platinum sheet (2 cm × 2 cm), and saturated calomel electrode (SCE) were used as the working, counter, and reference electrodes, respectively. The working electrode (2 cm × 2 cm) was placed approximately parallel to the counter electrode with a separation of about 1 cm. Cyclic voltammetry was carried out under a scan rate of $5\,\mathrm{mV\,s^{-1}}$ over a potential range of 0.00–0.60 V and 0.00 to -1.50 V *vs.* SCE for urea electrolysis and hydrogen evolution, respectively. Potential-step chronoamperometry for urea electrolysis was measured at 0.45 V *vs.* SCE for 1000 s. To investigate the current efficiency in various

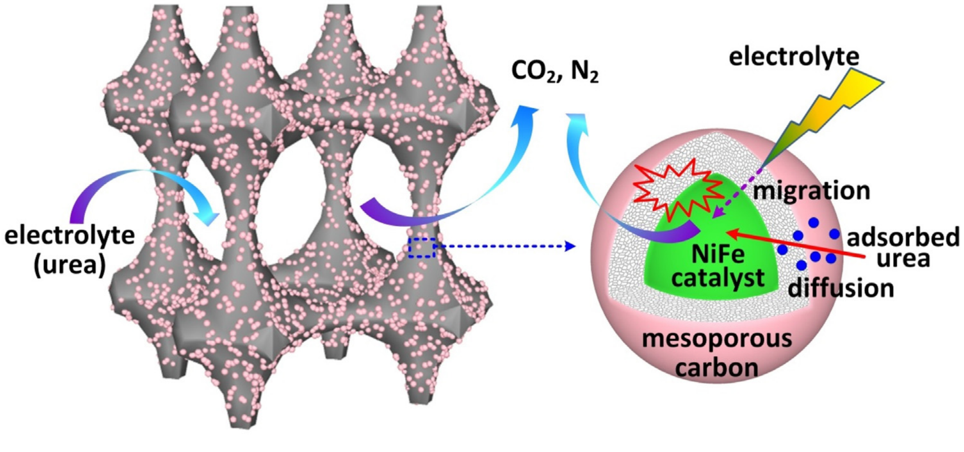

Fig. 1. Schematic illustration of enhanced urea electrolysis in CE-NiFe/NF electrode.

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