



Highly porous nickel@carbon sponge as a novel type of three-dimensional anode with low cost for high catalytic performance of urea electro-oxidation in alkaline medium



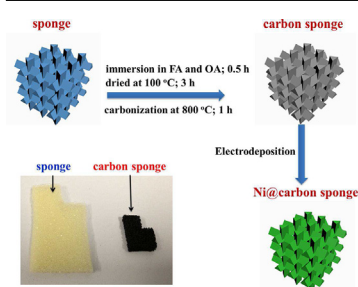
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HIGHLIGHTS

- Porous Ni@carbon sponge shows 3D open network structures with a large surface area.
- The electrode achieves an onset oxidation potential of 0.24 V (vs. Ag/AgCl).
- The electrode exhibits superior catalytic activity (290 mA cm⁻²) and stability for urea electro-oxidation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 21 November 2014

Received in revised form

6 January 2015

Accepted 26 February 2015

Available online 28 February 2015

Keywords:

Nickel
Carbon sponge
Three-dimensional anode
Urea electro-oxidation
Fuel cells

ABSTRACT

Highly porous nickel@carbon sponge electrode with low cost is synthesized via a facile sponge carbonization method coupled with a direct electrodeposition of Ni. The obtained electrodes are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The catalytic performances of urea electro-oxidation in alkaline medium are investigated by cyclic voltammetry (CV) and chronoamperometry (CA). The Ni@carbon sponge electrode exhibits three-dimensional open network structures with a large surface area. Remarkably, the Ni@carbon sponge electrode shows much higher electrocatalytic activity and lower onset oxidation potential towards urea electro-oxidation compared to a Ni/Ti flat electrode synthesized by the same procedure. The Ni@carbon sponge electrode achieves an onset oxidation potential of 0.24 V (vs. Ag/AgCl) and a peak current density of 290 mA cm⁻² in 5 mol L⁻¹ NaOH and 0.10 mol L⁻¹ urea solutions accompanied with a desirable stability. The impressive electrocatalytic activity is largely attributed to the high intrinsic electronic conductivity, superior porous network structures and rich surface Ni active species, which can largely boost the interfacial electroactive sites and charge transfer rates for urea electro-oxidation in alkaline medium, indicating promising applications in fuel cells.

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1. Introduction

In order to satisfy the increasing global demands for energy, alternative clean energy sources independent of fossil fuels, must be developed [1–8]. Urine is the most abundant waste on the earth.

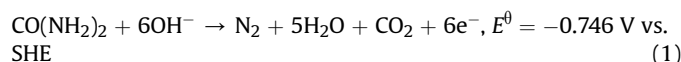
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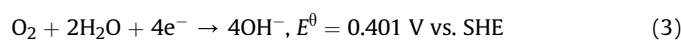
The largest constituent of human or animal urine is urea ($\text{CO}(\text{NH}_2)_2$), which is a significant organic source of H, C, O, and N. In addition, a large amount of wastewater with different concentrations of urea is produced during the industrial synthesis of urea, suggesting the availability of a considerable amount of urea in municipal wastewater [2,5–8]. Thus, urea rich wastewater has been identified as a source for sewage disposal, hydrogen production and fuel cells. Also, many related researches on the electro-oxidation of urea were reported in the literatures [1–3,5,7–14].

Tao et al. [7] successfully developed a working direct urea and urine fuel cell to generate electricity for the first time in 2010. By comparison with retrieving energy from hydrogen which is obtained by the electrolysis of urea, generating electricity from direct urea fuel cell (DUFC) is more efficient, clean and environmentally friendly. Urea as a promising alternative anode fuel has many advantages including: (1) urea is low-cost and abundantly available from industrial production and wastewater; (2) urea is liquid state and easy in safe storage and transportation; (3) the electro-oxidation of urea not only generates electricity but also purifies wastewater; (4) the products of urea electro-oxidation are benign and nontoxic nitrogen and carbonate. DUFC is composed of urea in alkaline electrolyte as the fuel and humidified oxygen as the oxidant. The theoretical open circuit voltage of DUFC is 1.147 V, which is comparable with that of $\text{H}_2\text{-O}_2$ fuel cell (1.23 V). The electrode and solution reactions of DUFC are as follows:

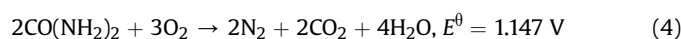
Anode:



Cathode:



Overall reaction:



Very recently, Wu et al. [9] demonstrated a DUFC with a maximum power density of 1.57 mW cm^{-2} when 0.33 M urea was used as fuel, O_2 as oxidant at 60°C . So the performance of the DUFC needs to be significantly improved in order to compete with other types of fuel cells. Highly efficient electrocatalysts play key roles for improvements of the performance of a fuel cell. Several types of electrocatalysts for urea electro-oxidation have been investigated, which include noble metals, non-noble metals, metal oxides and metal hydroxides. Previous research has shown that urea can be electrochemically oxidized using noble-metal catalysts such as Ru–TiO₂ [10], Ti–Pt [11], Ti–(Pt–Ir) [12], etc. However, the high cost of these materials has largely limited their practical applications. Therefore, the usage of inexpensive transitional metal based catalysts has caught much attention [1,2,5–9]. Above all, noble metals are unnecessary to be employed in alkaline electrolyte because alkaline medium is less corrosive than acid. Nickel is an ideal non-noble metal anode catalyst for DUFC due to its high activity with low cost [8,9]. Botte et al. [1–3,5,13] found nickel was the most favorable electrocatalyst for the electro-oxidation of urea, but planar and flat nickel electrode had a defect that the onset oxidation potential of urea reached higher than 0.35 V (vs. Ag/AgCl), which would reduce the open circuit voltage of DUFC. They also observed that the onset potential of urea electro-oxidation was nearly the same as the potential where NiOOH formed (0.39 V vs. Ag/AgCl), revealing that urea was possibly electro-oxidized on the

NiOOH. Lan et al. [8] prepared nano-sized nickel (~5 nm) as the catalyst for urea electro-oxidation. DUFC with nano-sized nickel as anode showed higher open circuit voltage (OCV) of 0.65 V and a maximum current density of 1.6 mA cm^{-2} , while that with commercial nickel (4–10 μm) only achieved 0.22 V (OCV) and 0.34 mA cm^{-2} at 20°C . Ding et al. [14] synthesized mesoporous spinel NiCo_2O_4 as the electrocatalyst for the electro-oxidation of urea. The NiCo_2O_4 electrode delivered a current density of 136 mA cm^{-2} at 0.6 V (vs. Ag/AgCl) in 1 M KOH and 0.33 M urea electrolytes and the high electrocatalytic activity was ascribed to the superior mesoporous structures. These results showed that the microstructure of electrocatalysts were quite influential on the electrochemical performance of urea oxidation in alkaline medium.

Because the performance of catalysts is mainly controlled by the electrocatalytic activity of active materials and kinetic properties in the reaction process, it is crucial to enhance the ion/electron transport rate in the electrode and at the electrode-electrolyte interface [15]. Three-dimensional (3D) porous microstructures are one of the optimal candidates due to the superior porosity [16–19] and high specific surface area which can afford easy transport pathways for both electrons and ions [20]. More importantly, porous structures are able to make the penetration of electrolytes into the whole electrode matrix simply and reduce the diffusion resistance, and further overcome the primary kinetic limits of electrochemical processes [14,21,22]. Therefore, facile and reasonable design and fabrication of highly porous 3D structures is imperative for high electrocatalytic activity towards urea electro-oxidation in alkaline medium.

In general, the most used electrodes for fuel cells are binder-enriched ones produced by the traditional slurry-coating technique. Such obtained electrodes usually suffer drawbacks of low catalyst utilization because some catalysts are unable to contact with the current collector or are inaccessible to the electrolyte. Furthermore, the existence of binder will greatly decrease the electronic conductivity of the electrode materials, reducing their electrochemical performance. To overcome these issues, preparation of electrodes via direct deposition of electrocatalysts onto a current-collecting substrate has attracted much attention [23–25]. In this study, highly porous Ni@carbon sponge electrode without binder was synthesized via a facile strategy involving a carbonization of sponge to form carbon sponge as the highly conductive skeleton and subsequent potentiostatic electrodeposition of nickel. The composite electrode had a unique 3D network structure, which provided more catalytic active sites and enabled easy access of reactants to the catalyst surfaces. The catalytic performance of Ni@carbon sponge electrode for urea electro-oxidation in alkaline medium was systematically investigated. The Ni@carbon sponge materials exhibited desirable catalytic activity, stability and tolerance towards urea electro-oxidation, indicating the great potential for future applications in fuel cells.

2. Experimental

2.1. Reagents

Acetone (CH_3COCH_3), isopropanol ($(\text{CH}_3)_2\text{CHOH}$), ethanol ($\text{C}_2\text{H}_5\text{OH}$), furfuryl alcohol ($\text{C}_5\text{H}_6\text{O}_2$), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), hydrofluoric acid (HF), nitric acid (HNO_3), nickel chloride (NiCl_2), ammonia chloride (NH_4Cl), sodium hydroxide (NaOH), urea ($\text{CO}(\text{NH}_2)_2$) and sponge (polyurethane) were obtained from Enterprise Group Chemicals Reagent Co. Ltd. China. Ti foil was purchased from Baoji Yiyuan titanium industry Co., Ltd. All chemicals are analytical grade and were used as-received without further purification. Ultra-pure water (Millipore, $18 \text{ M}\Omega \text{ cm}$) was used throughout the study.

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