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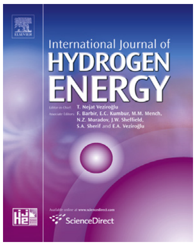

Thermal growth of NiO on interconnected Ni–P tube network for electrochemical oxidation of methanol in alkaline medium

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ABSTRACT

A novel electrocatalyst for methanol oxidation reaction in alkaline medium is elaborately fabricated by a sponge-template method involving an electroless plating of amorphous Ni–P on sponge and the following annealing process at 500 °C in air. The electrocatalyst is characterized by NiO nanoparticle/nanoflake grown on the Ni–P alloy tube. The vital annealing process aims to remove templates, crystallize Ni–P, and generate NiO nanostructures on the outside surface of Ni–P tubes, thus leading to the final structure of NiO/Ni–P composites. The tubular Ni–P framework surface is decorated with microspherical NiO (EP-M) or nanoflake NiO (EP-F), which strongly depends on the electroless plating time. For comparison, porous NiO nanoflakes are also synthesized by chemical bath deposition. The EP-M containing ~83.8 wt.% NiO and ~16.2 wt.% Ni–P has the largest BET surface area of 210.03 m^2 g^{-1} among the three samples. Moreover, the EP-M exhibits a high current density (~467 A g^{-1}) and long-term chronoamperometry stability (≥20,000 s) toward methanol oxidation in alkaline solution. The improved catalytic activity of the composite catalyst might be attributed to the strong electronic interaction between NiO and Ni–P as revealed by X-ray photoelectron spectroscopy.

Introduction

Direct methanol fuel cell (DMFC) has been recognized as a potential future power source for zero-emission vehicles and portable applications due to its undoubted advantages over analogous devices fed with hydrogen [1]. Compared with the acidic DMFCs, the alkaline DMFCs possess advantages, for example, the usability of non-noble metals as electrocatalysts, the improved kinetics in particular low anodic overvoltage for methanol oxidation, the reduced risk of corrosion of catalysts and carbons, and the reduced adsorption of CO intermediates that might limit electrocatalysis [2].

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Thus, the future development of alkaline electro-catalytic systems is a pretty active area of research [3]. The performance of an alkaline DMFC largely depends on the electrocatalytic activity of its electrode materials and the ion/electron transport rate in the electrode and at the electrode-electrolyte interface [4]. An effective way to improve the DMFC performance is to explore novel electrocatalysts with high activity and stability [5]. Some noble metals genuinely present high catalyst efficiency in methanol electro-oxidation [6–8]. However, their low utilization, high cost and decaying activity have put a barrier against their broad commercial applications. Researchers are paying great attention to explore alternative low-cost non-noble metal based anode catalysts in recent years.

Many efforts have been contributed to the synthesis of nanostructured transition metal oxides, which show attractive electrocatalytic properties. Nickel oxide has been widely studied due to their excellent electrochemcial performance in supercapacitors [9], lithium ion batteries [10], and catalysts [3,11,12]. NiO can be fabricated by precipitation [3], spray pyrolysis [12], and template method [13]. Commercially available sponges can provide unique framework for fabricating novel exciting and remarkable electrodes, in which the sponge acts as template due to its hierarchical macro-porous nature and uniform size of macro-pores [14]. However, to the best of our knowledge, using the commercially available sponge as template for fabricating NiO nanostructures is still lacking.

Herein, we designed a sponge template method to fabricate a novel NiO nanostructures, which involves an electroless plating amorphous Ni–P on sponges and the following annealing process at 500 °C in air. The final morphology of the novel catalyst is featured as NiO nanoparticle/nanoflake grown on the Ni–P alloy tube, which possesses complex and interconnected porous structure. The annealing process is vital for the formation of the novel morphology. Compositions and structures of catalysts were thoroughly investigated and compared. Significantly, we also compared their electrocatalytic properties in alkaline medium for methanol oxidation, attempting to shed some light on the correlation of structure, chemical components and catalytic performance.

Experimental section

Preparation of NiO/Ni–P composite catalysts

The NiO/Ni–P composite catalyst was elaborately fabricated by a two-step method, which involves an electroless plating of amorphous Ni–P on sponges and the following annealing process at 500 °C in air. Two samples (EP-M and EP-F) are fabricated with different electroless plating time but the same annealing process. EP-M and EP-F refer to the Ni–P/NiO catalyst samples with the electroless plating time of 5 and 15 min, respectively. Accordingly, the electroless plating samples without annealing process would be denoted as EP-M precursor and EP-F precursor. The sponge template (pore sizes 100–500 μm, ligament width 5 μm) that bought from Ledian is made up of many small cellulose fibers, which make them a highly porous and strong absorbing media with significant internal surface area. All the other reagents were bought from Shanghai Chemical Company and directly used without further purification. In a typical process, a piece of commercially available sponge with a thickness of 5 mm and area of 1×2 cm^2 was cleaned by water and ethanol several times, drying completely in a vacuum oven afterward. The sensitized solution was composed by the mixture of 4 g $SnCl_2$, 6 ml HCl (35 wt.%), and 388 ml deionized water, in which sponges were first submerged for 5 min. Then, sponges were washed by plenty of deionized water. After that, they were activated in the activated solution for 5 min, which was consisted of 0.1 g $PdCl_2$, 840 μl HCl (35 wt.%), and 390 ml deionized water. Again, sponges were washed with sufficient deionized water afterward. After sponges were sensitize and activated for 6 periods till them turned brown in color, they were transferred into the electroless plating solution, prepared by the mix of 9 g $NiSO_4$, 7.8 g CH_3COONa, 8.4 g $NaH_2PO_2 \cdot H_2O$, and 600 ml deionized water, at 80 °C for 5 min and 15 min, respectively. Subsequently, sponges were entirely washed and dried at 70 °C in a vacuum oven for 12 h. Finally, dried sponges were annealed in air at 500 °C for 3 h with a heat rate of 0.5 °C min^{-1}. In this work, we optimized the electroless plating time to maximize the specific surface area of products within controllable time, while short time degrades the robustness of Ni–P skeleton and long time eliminates their facial NiO morphology and degrades the specific surface area.

Preparation of the NiO powder catalyst for comparison

NiO was prepared by a chemical bath deposition (CBD) method, which would hereafter be denoted as CBD-NiO. The solution for CBD was prepared by mixing 240 ml of 1 M $NiSO_4$, 180 ml 0.25 M $K_2S_2O_8$, and 60 ml of aqueous ammonia (25%–28%) in a 1 L beaker at room temperature. The final product was obtained by centrifuging after CBD for 30 min, and dried at 70 °C in a vacuum oven for 12 h.

Microstructure characterization

The microstructure and morphology of the obtained samples were characterized by scanning electron microscope (SEM, Hitachi S-4800), and transmission electron microscope (TEM, JEOL JEM-2100), respectively. X-ray diffraction (XRD, RigakuD/Max-3B with Cu-K$_\alpha$ radiation) and high-resolution transmission electron microscopy (Tecnai F20) were applied to analyze the architecture and the crystalline structure of the products. X-ray photoelectron spectroscopy (XPS, AXIS UTL-TRADLD) was used to analyze the facial chemical composition and chemical state of the samples using Al (monochromatic) K$_\alpha$ radiation with $E = 1486.6$ eV. All core level spectra were referred to the C 1s peak at 284.8 eV. The specific surface area and pore diameter were determined by BET (Brunauer–Emmett–Teller) measurements using a NOVA-1000e surface area analyzer.

Electrochemical performance

About 1 mg of the as-prepared product was dispersed in 2 ml deionized water and was placed in an ultrasonic bath until the catalyst powder was thoroughly and uniformly distributed. Next, 10 μl of the above fabricated catalyst slurry was