



Palladium deposits spontaneously grown on nickel foam for electrocatalyzing methanol oxidation: Effect of precursors



Xiangheng Niu ^{a, b, *}, Hongli Zhao ^c, Minbo Lan ^{c, **}

^a Institute of Green Chemistry and Chemical Technology, Jiangsu University, Zhenjiang 212013, China

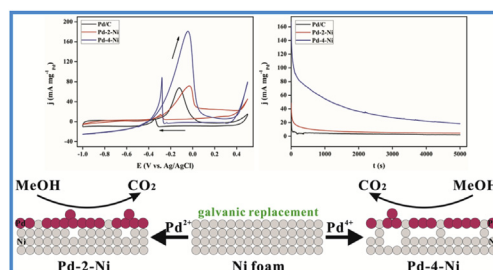
^b School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China

^c Shanghai Key Laboratory of Functional Materials Chemistry, East China University of Science and Technology, Shanghai 200237, China

HIGHLIGHTS

- Two nanosized Pd deposits were spontaneously grown on Ni foam via galvanic replacement.
- Different palladic precursors produced discrepant arrangements and coverages of Pd.
- Pd-4-Ni had more exposure of Ni atoms adjoined to Pd atoms on the catalytic interface.
- Higher catalytic activity of Pd-4-Ni toward MOR than Pd-2-Ni and Pd/C.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 27 July 2015

Received in revised form

3 November 2015

Accepted 14 December 2015

Available online 20 December 2015

Keywords:

Pd deposits

Ni foam

MOR

Electrocatalysis

Galvanic replacement

ABSTRACT

Methanol, a high-energy substance, is widely used for green fuel cells. However, the sluggish electrochemical methanol oxidation reaction (MOR) on state-of-the-art catalysts still requires for exploring high-performance and low-cost materials to further promote the reaction kinetics at low overpotentials. Here we carried out the first electrocatalytic comparison study of two Ni foam-supported Pd nano-materials (Pd-2-Ni and Pd-4-Ni, respectively), obtained through the spontaneous galvanic replacement of Ni with different palladic precursors ($[\text{PdCl}_4]^{2-}$ and $[\text{PdCl}_6]^{2-}$, respectively), toward MOR. With replacement, Pd deposits with discrepant arrangements and coverages were grown on the porous Ni support. Compared to commercial Pd/C, both Pd-2-Ni and Pd-4-Ni exhibited better mass activity and catalytic durability for MOR in alkaline media. More interestingly, different palladic precursors made a significant effect on the catalytic performance of the Ni foam-supported Pd deposits. In Pd-4-Ni, the 2:1 stoichiometric replacement of Ni with $[\text{PdCl}_6]^{2-}$ enabled the incompact arrangement of Pd structures, with more exposure of Ni atoms adjoined to Pd atoms on the catalytic interface compared to Pd-2-Ni. As a result, with the favorable Ni-neighbor-Pd regime and the higher utilization efficiency of Pd atoms, the synthesized Pd-4-Ni catalyst provided a mass activity of approximately 1.5 times higher than Pd-2-Ni toward MOR.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

With the fossil fuel depletion, increasing environmental pollution and growing energy demands across the world, fuel cells, especially direct methanol fuel cells (DMFCs), which employ

* Corresponding author.

** Corresponding author.

E-mail addresses: niuxiangheng@126.com (X. Niu), minbolan@ecust.edu.cn (M. Lan).

renewable and easy-handling methanol as the green fuel and offer a theoretical energy density of as high as 4.8 kWh L^{-1} , have attracted increasing attention and interest in recent decades [1–3]. However, much low energy density and efficiency are usually harvested in real DMFCs. One reason for this phenomenon is the sluggish electrochemical methanol oxidation reaction (MOR). Therefore, anode catalysts with high activity and favorable stability are required to promote the slow reaction kinetics. In the past few years, a variety of interesting materials, including cubic PtCu_3 nanocages [4], Pt–Pd nanoicosahedrons [5], ultrathin FePtPd nanowires [6], Pt–Zn nanocrystals [7], 3D Pt/MWCNT hybrids [8], Pt–Cu concave nanocubes with high-index facets [9], and $\text{CeO}_2/\text{rGO}/\text{Pt}$ sandwich nanostructures [10], have been explored to facilitate the MOR rate at low potentials. Although Pt-based catalysts are reported as the most effective family of anode materials for DMFCs [1,3,11–14], their state-of-the-art performance and high cost still hinder their large-scale applications. Thus, development of catalysts with lower cost and better catalytic properties to further accelerate MOR is still a matter of great significance for DMFCs.

In comparison with common Pt-based materials, the less expensive and easily available Pd is considered as a promising substitute of Pt in DMFCs, because Pd-based catalysts can exhibit high activity and good durability for MOR in alkaline media [15–18]. Theoretical and experimental results suggest that a second metal adjoined to Pd, like Au, is able to supply oxygenated species at low potentials to remove the adsorbed intermediates, thus enhancing the overall catalytic activity [19]. Apart from precious Au, other cheap and resourceful transition metals including Co [20], Ni [17,21,22] and Cu [18] have also been considered as a second metal to develop high-performance Pd-based materials for MOR. Yet, the control synthesis of Pd–X (X = inexpensive transition metals) catalysts usually demands for harsh preparation conditions and laborious manipulations [17]. More challengingly, massive and uniform production of these nanostructures for large-scale practical applications is still very hard. Therefore, seeking a facile and efficient method to fabricate Pd-based structures with favorable catalytic properties is necessary.

Here we compare, for the first time, the electrocatalytic properties of two new Pd-based materials (noted as Pd-2-Ni and Pd-4-Ni, respectively) prepared through the simple galvanic replacement reaction between commercial Ni foam and different palladic precursors ($[\text{PdCl}_4]^{2-}$ and $[\text{PdCl}_6]^{2-}$, respectively) toward MOR in an alkaline medium. With replacement, Pd deposits with different coverages and arrangements are directly grown on the porous surface. In comparison with commercial Pd/C, both Pd-2-Ni and Pd-4-Ni provide superior mass activity and catalytic stability for MOR. Among the two synthesized catalysts, thanks to the higher utilization efficiency of Pd and the more exposure of Ni atoms adjoined to Pd atoms on the catalytic interface, Pd-4-Ni exhibits much higher catalytic activity over Pd-2-Ni.

2. Experimental

2.1. Chemicals

Ni foam (99.8% in purity, 0.5 mm in thickness, 97.2% in porosity, Changsha Liyuan New Materials Co.), K_2PdCl_4 and K_2PdCl_6 (AR, Shanghai Aladdin Industrial Inc.), Pd/C (5 wt% Pd, Shanghai Aladdin Industrial Inc.), NaOH (AR, Shanghai Titanchem Co.), methanol (AR, Sinopharm Chemical Reagent Co.), ultrapure water (18.2 M Ω cm, Hitech Laboratory Water Purification Systems). All other chemicals used in this research were at least of analytical grade, and utilized directly without further purification.

2.2. Synthesis of Pd-2-Ni and Pd-4-Ni

Prior to galvanic replacement, the purchased Ni foam was pre-treated as follows: 1) firstly, the Ni foam was immersed into acetone for ultrasonic treatment for 1 h, in order to wash off possible organic residues; 2) afterwards, the Ni foam was ultrasonically treated in 1 M HCl for 1 h, aiming at cleaning up Ni oxides on the substrate surface; 3) finally, the treated Ni foam was rinsed with adequate water, and dried at room temperature for further use. In the galvanic replacement process, the Ni foam was immersed into 10 mM K_2PdCl_4 solution for reaction. To make sure that the Ni foam surface was sufficiently replaced by Pd, the replacement time was set as 12 h. After synthesis, the obtained material, noted as Pd-2-Ni, was dried at room temperature for utilization. The preparation of Pd-4-Ni was similar to that of Pd-2-Ni, except for using 10 mM K_2PdCl_6 as the precursor solution.

2.3. Characterization

The phase structure of materials was characterized by X-ray diffraction (XRD, D/MAX 2550, Japan Rigaku Co.) at room temperature with $\text{CuK}\alpha$ radiation ($\lambda = 0.154056 \text{ nm}$, 40 kV, 100 mA). Transmission electron microscopy (TEM, JEM-1400, JEOL) was used to observe the Pd deposits falling off ultrasonically from the Ni foam substrate. The surface morphology, chemical composition, and element distribution of products were observed using scanning electron microscope (SEM, S-3400, JEOL) equipped with energy dispersive spectrometer (EDS, Falcon, EDAX). The surface composition of the prepared materials was probed by X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi, Thermo Fisher Scientific). The precise contents of Ni and Pd were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, IRIS 1000, Thermo Elemental Co.)

2.4. Electrochemical measurements

Unless otherwise states, all electrochemical experiments were carried out on a CHI 440A workstation (CH Instruments Inc.) equipped with a three-electrode configuration consisting of a catalyst-modified screen-printed carbon working electrode (SPCE, with a geometric working area of 0.1256 cm^2 , and the fabrication of SPCE had been described in our previous work [23]), a Pt wire counter electrode and a KCl-saturated Ag/AgCl reference electrode. To fabricate the Pd-2-Ni (or Pd-4-Ni) modified working electrode, the synthesized Pd-2-Ni (or Pd-4-Ni) with a geometric area of 0.12 cm^2 was immobilized onto the SPCE working surface with conductive adhesive for electrochemical measurements. For comparison, the commercial Pd/C catalyst was also tested under identical conditions. To fabricate the Pd/C modified working electrode, 5.0 mg Pd/C was mixed with 50 μL 5% Nafion, 2 mL ultrapure water and 2 mL isopropanol, and then the mixture was sonicated for 30 min, and 50 μL of the suspension was drop-casted onto the SPCE working surface for full dry. All measurements were performed in stationary electrolyte solutions at room temperature, and all potentials mentioned in this work were referred to the Ag/AgCl electrode, unless special states. Electrochemical impedance spectroscopy (EIS) measurements were implemented on a CHI 660D workstation (CH Instruments Inc.) with the same electrode system.

3. Results and discussion

The Pd-2-Ni and Pd-4-Ni catalysts are obtained by simply immersing the Ni foam substrate into the K_2PdCl_4 or K_2PdCl_6 precursor solution for spontaneous reaction. Compared to the usually used methods for preparing Pd–Ni materials [17,21,22], the

Download English Version:

<https://daneshyari.com/en/article/1292332>

Download Persian Version:

<https://daneshyari.com/article/1292332>

[Daneshyari.com](https://daneshyari.com)