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Short Communication

Catalytic Activity of Porous Pd-Ni Thin Foam towards Electrooxidation of Methanol

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Abstract: *Porous Pd-Ni thin foam was fabricated by a rapid one-step electrodeposition process within hydrogen bubble dynamic template and characterized by SEM, EDS, and cyclic voltammetry. Morphology and composition of the foam can be modified significantly by applying different deposition conditions, such as concentration ratio of Pd (II) ions to Ni (II) ions in electrolytic solution and deposition time. Electrocatalytic activities of the foam towards methanol oxidation in alkaline media were investigated, which depend mainly on Pd components and its morphology. Low nickel content can assist Pd further enhance the electrocatalytic performance, particularly the tolerance to intermediates of methanol oxidation, while high nickel content brings adverse effect. The high catalytic activity and the low cost of the Pd-Ni foams enable them to be promising electrocatalysts for the oxidation of methanol in alkaline media.*

Keywords: porous materials, palladium, nickel, hydrogen bubble template, methanol

1. INTRODUCTION

Pd-based materials have received a great deal of attention for their potential applications in catalysis, fuel cells and sensors [1,2]. Particularly they are used as electrocatalysts in direct alcohols fuel cells due to their relatively low cost and abundant in natural resources compared with Pt and especially display excellent catalytic activity even higher than Pt in alkaline media [3-5]. In these applications large specific areas and rapid reaction rates are essential.

Open porous materials not only have extremely high surface area but also allow rapid transport of the reactants, and thus are ideally suited for electrocatalysts. Recently a simple but effective technique for the materials was proposed using hydrogen bubble as template and has attracted increasing interest [6-12]. Open porous structure with self-supported porous dendritic walls can be fabricated via concurrent extremely fast metal deposition and hydrogen. So far few studies however have focused on fabricating bimetallic materials with this method and their catalytic activity. Moreover, performances of bimetallic catalyst can be further improved through a sort of synergistic effect. Considering certain nickel oxides can significantly enhance electrocatalytic activity and CO-resistance of Pd [13,14], in this paper we have prepared open porous Pd-Ni thin foams using hydrogen bubble dynamic template under different deposition conditions and measured their catalytic activity towards electrooxidation of methanol in alkaline media.

2. EXPERIMENTAL

2.1. Preparation of Pd-Ni foams

Porous Pd-Ni thin foams were synthesized by electrodeposition from an aqueous electrolyte containing 10 mM $Pd(NH_3)_4Cl_2$, 0-10 mM $NiCl_2$ and 2M NH_4Cl. All solutions were prepared from ultrapure water (≥18MΩ cm) using analytical grade chemicals. The foams were potentiostatically deposited ($E = -4$ V) on a pure palladium foil 0.2 mm thick over 10-240 s. All electrochemical measurements were performed in a conventional three electrode cell with a CHI 650A electrochemical workstation at room temperature. A Pt plate (1.0cm×1.5 cm) and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. All potentials are referred against SCE. Bulk Pd and Ni electrodes were made and prepared as already described elsewhere [15]. Current densities were normalized by geometrical area of the palladium substrate or bulk Pd and Ni electrodes.

2.2. Characterization of Pd-Ni foams

Structures and surface morphologies of the foams were observed

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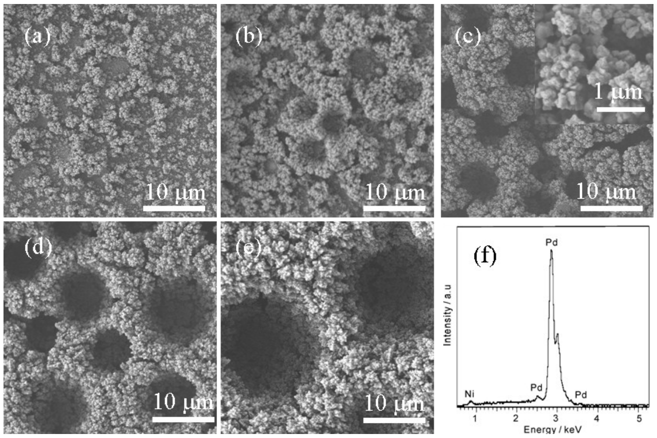

Figure 1. SEM images (a-e) and EDS spectrum (f) of the foams when deposition time was: (a) 10, (b) 30, (c) 60, (d) 120 and (e) 240 s, respectively. Electrolytic solution consists of 10 mM $Pd(NH_3)_4Cl_2$, 0.05 mM $NiCl_2$ and 2 M NH_4Cl.

by field emission scanning electron microscope (FESEM, JEOL JSM-6700F). Compositions of the foams were analyzed by INCAX-sight energy dispersive X-ray spectrometer (EDS) equipped on the FESEM.

3. RESULTS AND DISCUSSION

3.1. Surface morphology and composition of the Pd-Ni foams

Shown in Fig. 1 are some typical SEM images of the porous Pd-Ni thin foams. The insert is a magnified view taken from the wall part in Fig. 1 (c). It can be seen that three dimensional foam structures with open pores and porous walls are gradually formed. Only island deposits are formed with deposition time of 10 s and cauliflower deposits with 30 s. Porous honeycomb structures appear and become clear and distinguishable up to 60 s. The pore size, wall thickness and hole depth increased with time, because of the coalescence of the hydrogen bubbles during deposition. The pore diameters of the three foams are around 7 μm, 10 μm and 17 μm, respectively. It is noted that the pore wall are partially cracked and the crack formation becomes severe over time. It is known that palladium is an effective hydrogen-evolution catalyst. The evolution of hydrogen bubble with relatively high speed results in a smaller bubble size and so the pore size. Synchronously, hydrogen embrittlement makes the crack more severe with the growth of the foam.

EDS analysis indicates that atomic ratio of Ni/Pd does not remain constant but increases with deposition time. When times are 10, 30, 60, 120 and 240 s, respectively, the atomic ratios of Ni/Pd are 0.036, 0.052, 0.058, 0.069, and 0.086, respectively. This increase resulted probably from decrease of Pd (II) in the electrolyte during deposition. More nickel deposited onto the substrate in the latter part of the deposition, leading to a higher surface content of nickel in the foam with longer deposition time. Thus nickel content in the foam depends mainly upon initial concentration ratio of Ni (II) to Pd (II) in the electrolytic solution and secondarily upon deposition time.

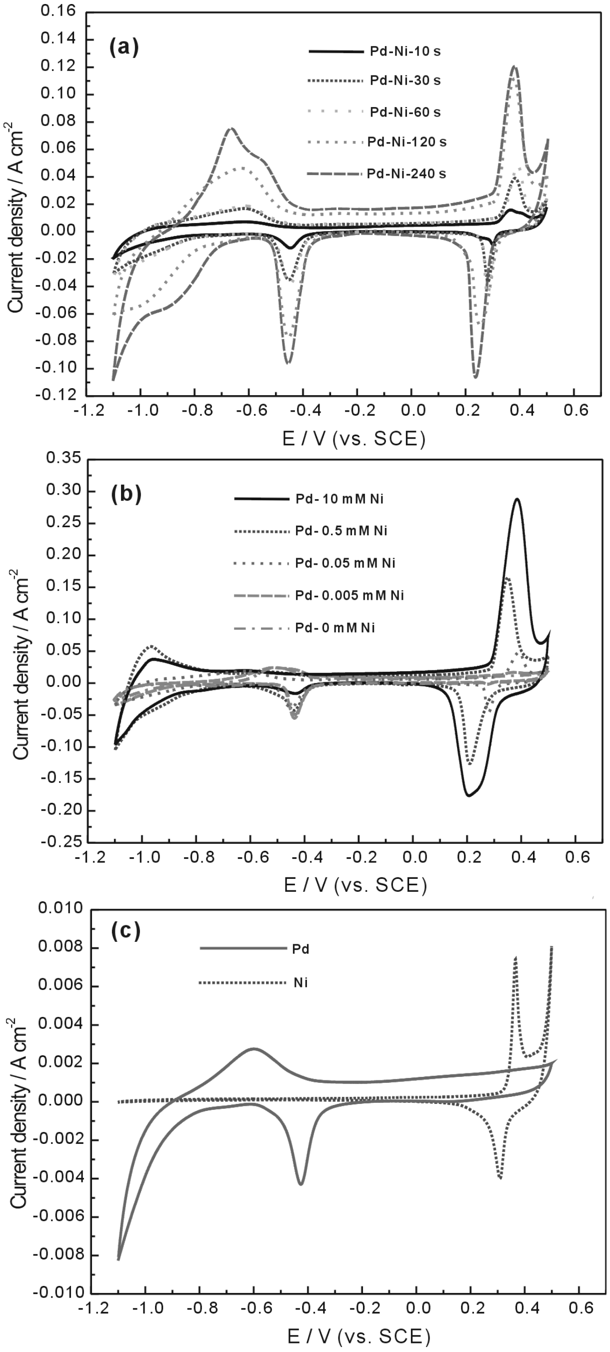

Figure 2. CVs of the foams obtained from electrolytic solutions consisting of 10 mM $Pd(NH_3)_4Cl_2$, 2M NH_4Cl and : (a) 0.05 mM $NiCl_2$ with different deposition time of 10−240 s, (b) 0-10 mM $NiCl_2$ with deposition time of 60 s in deaerated 1.0 M KOH solutions. (c) CVs of bulk Pd and Ni electrodes measured in 1.0 M KOH solutions. Scan rate: 50 mV s^{-1}.

3.2. Electrochemical properties of the Pd-Ni foams

The electrochemical behaviors of the porous Pd-Ni thin foams in 1.0 M KOH were studied, cyclic voltammograms (CVs) of which are shown in Fig. 2a and 2b. CVs of bulk Pd and Ni electrodes are also measured and shown in Fig.2c as the reference curves. CVs of the bimetallic foams reserve the essential voltammetric characteristics of individual Pd and Ni components, including the reduction peak of Pd hydroxides to Pd (−0.3 to −0.6 V) and the redox peaks (0.12 to 0.46 V) for the $Ni(OH)_2/NiOOH$ couple [15,16]. These peaks become larger and larger with growth of the foam obviously for the sake of the increase of the amount of palladium and nickel in the foam (see Fig. 2a). New electrochemical behavior in the hydrogen region however should be noted. With deposition time, a well-defined cathodic peak starting from −0.71 V gradually forms before the hydrogen evolution, which attributed to adsorbed hydrogen species at Pd site [15]. The changes in the hydrogen region may be resulted from surface morphology of the electrode and/or the so-called synergistic effect of nickel. Therefore the influence of the concentration of $NiCl_2$ in the electrolyte on the CV profiles of the foams is investigated and described in Fig. 2(b). Nickel content in the foams increased with $NiCl_2$ concentration, which manifested by accretion of the redox peaks of $Ni(OH)_2/NiOOH$ couple and shrink of the reduction peak of palladium oxide. Simultaneously the redox of hydrogen becomes stronger with nickel content, indicating positive synergistic effect of nickel on the catalytic activity of palladium. However, it should be highlighted that the higher the nickel content, the stronger the redox of hydrogen is not. The redox of hydrogen on the foam obtained from 10 mM $NiCl_2$ is less strong than that from 0.5 mM $NiCl_2$, which is obviously due to that Ni is a poor catalyst for the generation of hydrogen.

3.3. Electrooxidation of methanol on the Pd-Ni foams

The electrocatalytic performances of the porous Pd-Ni thin foams were studied in 1.0 M KOH using electrooxidation of methanol as a test reaction, CVs of which are shown in Fig. 3a and 3b with CVs on the bulk Pd and Ni electrodes also shown in Fig. 3c. The most obvious voltammetric characteristic of the methanol oxidation at the bulk Pd electrode is that the CVs recorded display a large oxidation peak (primary oxidation peak) at −0.24V in the forward anodic scan and a small oxidation peak (secondary oxidation peak) around −0.35V in the backward cathodic scan. The area ratio of the forward anodic peak (S_1) to the reverse anodic peak area (S_2), S_1/S_2, may be used to evaluate the tolerance of catalyst to carbonaceous species accumulation. The higher the S_1/S_2 ratio, the stronger the catalyst tolerance to catalyst poisons. The relative high S_1/S_2 ratio (3.73) indicates good tolerance of Pd catalyst to CO-like intermediate species formed during the electrooxidation of alcohol molecules [11]. Nickel is a poor electrocatalyst towards the oxidation of methanol and no well defined current response was detected in the potential range.

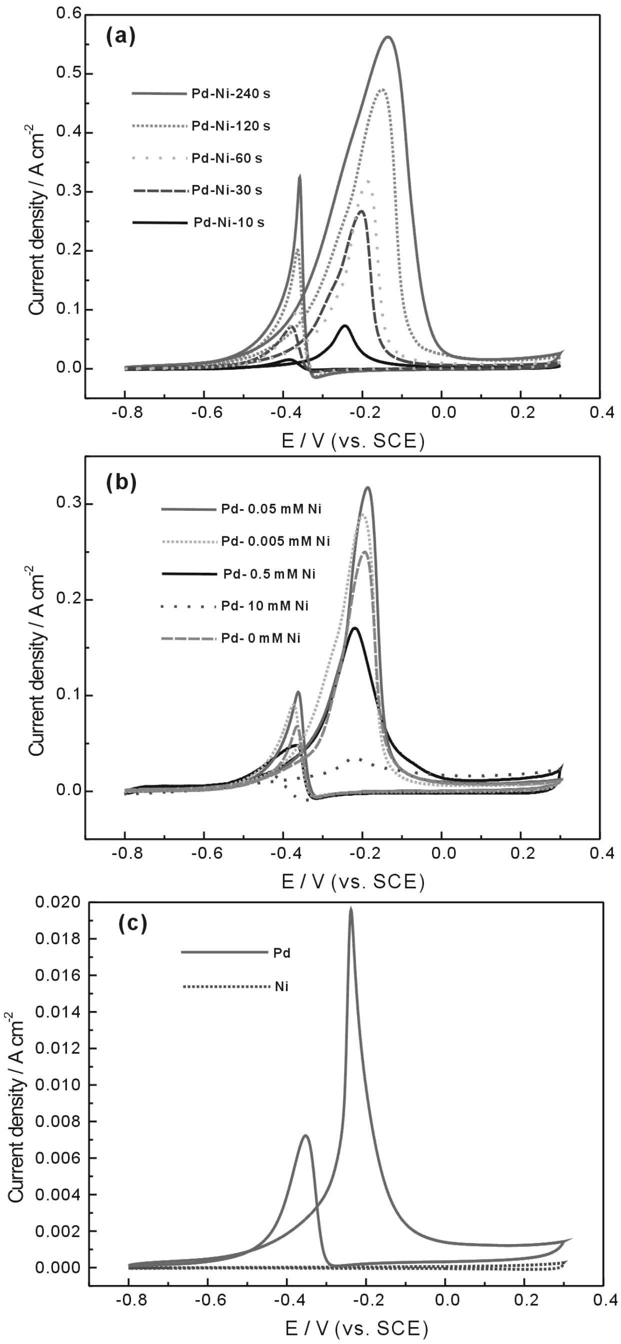

Figure 3. CVs for electrooxidation of 1.0 M CH_3OH on the foams deposited in 10 mM $Pd(NH_3)_4Cl_2$ and 2M NH_4Cl and: (a) 0.05 mM $NiCl_2$ with deposition time of 10−240 s, (b) 0-10 mM $NiCl_2$ with deposition time of 60 s. (c) CVs of bulk Pd and Ni electrodes measured in 1.0 M CH_3OH. Scan rate: 50 mV s^{-1}.

CV profiles on the foams are very similar to those on the bulk Pd electrode with three differences in the peak potentials and peak current densities, respectively. Firstly, the primary oxidation peak potential shifts positively and the shift increases with the deposition time (see Fig. 3a) but not with $NiCl_2$ concentrations (see Fig. 3b). The secondary oxidation peak potential however shifts slightly towards negative and the shifts remain constant. Thus these shifts are mainly a consequent of the changes in morphology of the electrodes and are not related to nickel component. The positive shifts may be attributed to the transport of methanol molecular in the foams being hindered with the growth of the foam. And the oxidation of the residual carbonaceous species requires no transport of the reactant and therefore the secondary oxidation peak potentials remain constant. Secondly, the current density of the two oxidation peaks on the foam is far beyond than that on bulk Pd and increases with deposition time. The high current density is because of the accumulation of deposited palladium in the foam, and on the other hand, is related to nickel component. The effect of $NiCl_2$ concentration on electrocatalytic performances of the foam is shown in Fig. 3b, in which the foams were prepared in the electrolytic solutions containing 0-10 mM $NiCl_2$ under otherwise identical conditions. With increase of $NiCl_2$ concentration, the current density showed a trend from ascent to descent, reaching the highest value in 0.05 mM $NiCl_2$ solution. Thirdly, both the areas of the two oxidation peaks on the foams increase with deposition time, much more than that on the bulk Pd, indicating that the amount of oxidized methanol significantly increased and the catalysis of the foam on methanol oxidation was promoted. The S_1/S_2 ratios for the foams are also much higher than that for the bulk Pd (3.73). And the ratio increases in the range of 10−240s, the corresponding value being 11.57, 16.52, 15.61, 22.75, and 25.14, respectively. When using electroplating solutions containing 0, 0.005, 0.05, 0.5, and 10 mM $NiCl_2$, respectively, to electrodeposit the foam, the S_1/S_2 ratios are 14.85, 15.25, 15.61, 16.09, and 3.69, respectively. These data demonstrates that the tolerance of palladium to CO-like intermediate species can be markedly enhanced by improving its morphology. Furthermore the tolerance can be enhanced by Ni component, which can be partly ascribed to a sort of synergistic effect [17]. In fact, nickel modifies the electronic states and hence the activity of palladium in the methanol oxidation process [18]. Nickel can assist palladium to oxidize the CO-like adsorbed species. However, nickel has no catalytic activity in the potential range on methanol oxidation because of surface passivation by NiO [17,18] and therefore, higher contents of nickel exhibit adverse effect. The ratio of 3.69 is obviously due to too much nickel distributed on the surface of the foam.

4. CONCLUSION

Porous Pd-Ni thin foam can be readily electrochemically deposited by a hydrogen bubble dynamic template. The surface morphology and composition of the foam can be regulated by deposition time and initial concentration ration of Pd (II) ion to Ni (II) ion in electrolytic solution. Electrocatalytic activity of the foam towards methanol oxidation depends mainly on palladium components and its morphology. Nickel components can improve further the electrocatalytic performances and tolerance to the catalyst poisons. Nickel plays a positive role in methanol oxidation on the foam in low contents but a negative role in high contents.

5. ACKNOWLEDGEMENTS

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