Electro-oxidation of methanol on mesoporous nickel phosphate modified GCE

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ABSTRACT

The electro-oxidation of methanol on mesoporous nickel phosphate NiPO-2, in comparison with that on zeolitic nickel phosphate VSB-5, was investigated by cyclic voltammetry (CV) in alkaline medium. The mesoporous nickel phosphate modified GCE (NiPO-2/GCE) showed relatively high activity and stability. The positive correlation between the scan rates and the anodic currents implied a single diffusion-controlled kinetic process. The CV and SWV currents of NiPO-2/GCE varied with the concentration of methanol. The sensitivity of NiPO-2/GCE reached 1 μM methanol, showing its potential use in developing sensors for the methanol determination.

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1. Introduction

The direct methanol fuel cell (DMFC) has been of great interest, due to its higher volumetric energy density and better transportation convenience of methanol as compared to hydrogen fuel cell [1]. In the field, many efforts have been made to improve the efficiency of the anode electro-catalysts. Precious metals, especially Pt and Pt-based alloys, are widely studied as anode catalyst due to their high catalytic activity for methanol electro-oxidation [2,3]. However, Pt-based catalyst can be easily poisoned by even trace of CO which is inevitable owing to the decomposition of methanol [4]. Many researches have been focused on the non-noble metals or their complexes [5–7] for substitution of precious metals. Among these materials, metal Ni [8–10], Ni-alloy [11–13] and Ni-complexes (such as Ni(OH)2 and NiO) [14–17] exhibit good electro-chemical activity and are regarded as good candidates.

A zeolitic nickel phosphate VSB-5 with a pore size of −1.0 nm, first reported by Cuillou et al. [18], showed high activity and high selectivity in the epoxidation of cyclic olefins [19]. Lately, we have reported several mesoporous nickel phosphates (NiPO-1, NiPO-2 and NiPO-3) [20,21]. These materials are composed of hollow nanotubes of different lengths. Their structures are constructed by rows of nanotubes which array to form a lamellar arrangement. The nanotubes of NiPO-1 and NiPO-3 are as long as 200–400 nm and 400–600 nm in length respectively, while NiPO-2 appears as short nanotubes which are around 10 nm.

The high activities of these materials in the epoxidation of cyclic olefins were also verified [20]. Porous nickel phosphates combine the advantages of redox catalytic property of nickel with large surface area and open diffusion accesses. Accordingly, their performance in electro-catalytic oxidation is expectable. In the present work, porous nickel phosphates NiPO-2 and VSB-5 were employed to fabricate modified glassy carbon electrodes (GCE) and their catalytic performance on the electro-oxidation of methanol was evaluated in alkaline medium.

2. Experimental

2.1. Reagents and materials

Nafion (5 wt.% ethanol solution) was purchased from Alfa Aesar, and diluted to 0.1 wt.% with doubly distilled water in use. Sodium hydroxide and methanol were analytical reagent, obtained from Beijing Chemical Co. Hexadecyltrimethyl ammonium bromide (CTAB), tetramethy lammonium hydroxide (TMAOH), H3PO4 (85%) and Ni(NO3)2·6H2O were products of Tianjin Kernel Chemical Co. in analytical grade. All stock solutions used in this work were prepared with deionized water resistivity not less than 18.2 MΩ cm.

2.2. Synthesis of materials

The nanotubular mesoporous nickel phosphate NiPO-2 was synthesized by sol–gel method using CTAB as surfactant in the presence of TMAOH. A starting gel of molar composition 1.0 H3PO4:0.7 Ni(NO3)2:1.0 CTAB:2.1 TMAOH:150 H2O was prepared at 333 K (pH=8–10) and kept at 373 K for 24 h, followed by filtering, washing and drying at
373 K for 12 h, to obtain an as-synthesized sample (as-NiPO-2). The template-free NiPO-2 was obtained by extracting as-NiPO-2 twice with a 0.1 M CH3COONa–EtOH solution at 351 K for 2 h to removed surfactant, followed by washing and drying the resulting sample at 343 K for 12 h. The VSB-5 was synthesized by the same method as described in reference [19]. The Ni(OH)2 and NiO were prepared by the same procedures as describe in reference [15].

2.3. Characterization

Nitrogen adsorption and desorption measurements were carried out at 77 K on a Micromeritics ASAP 2010 analyzer. Prior to the measurements, NiPO-2 sample was outgassed at 373 K for over 4 h, VSB-5 sample at 573 K for over 4 h. The specific surface area was calculated using the BET (Brunauer, Emmett, and Teller) equation. Pore size distribution of NiPO-2 was calculated by the BJH (Barrett, Joyner, and Halender) method using the adsorption branches of the isotherms.

2.4. Preparation of modified GCE

The glassy carbon electrode (GCE, 3 mm diameter, Tianjin Aida, Inc.) was polished with 70 nm Al2O3 power, rinsed twice by deionized water and ethanol respectively, and then dried at room temperature. 5 mg material (NiPO-2, as-NiPO-2, VSB-5, Ni(OH)2 or NiO) was dispersed in 1 ml of 0.1 wt.% nafion solution. Then the mixtures were dropped on the pre-treated GCE to fabricate modified GCEs which are nominated as NiPO-2/GCE, as-NiPO-2/GCE, VSB-5/GCE, Ni(OH)2/GCE and NiO/GCE, respectively. Then the modified GCEs were dried under infrared light. A parent GCE sample was used for comparison in the measurements.

2.5. Electrochemical measurements

Electrochemical measurements were performed with a CHI660D electrochemical workstation (CHI, Shanghai) using a three-electrode setup at 298 K. GCE or modified GCEs acted as working electrode. Saturated calomel electrode (SCE) was used as reference electrode, and platinum wire as counter electrode.

3. Results and discussion

The XRD pattern and TEM image (not shown) of the as-NiPO-2 coincided with reference [20]. After the template was removed by extraction, nitrogen adsorption revealed two groups of pores in the structure of NiPO-2 (2.7 nm and 3.5 nm), with a BET surface area of 273.5 m² g⁻¹ and a pore volume of 0.28 cm³ g⁻¹. The XRD pattern of the VSB-5 showed in accordance with that reported in the literature [19]. Its measured BET surface area and pore volume are 257 m² g⁻¹ and 0.18 cm³ g⁻¹, respectively.

The steady-state cyclic voltammograms (CVs) of the parent GCE and modified GCEs in 0.1 M NaOH solution recorded at a potential scan rate of 50 mV s⁻¹ are depicted in Fig. 1(A) and (B). The cyclic voltammetric behavior of the parent GCE shows no significant response for the methanol oxidation. However, well resolved and defined voltammetric signals for methanol oxidation can be observed on NiPO-2/GCE. In the absence of methanol in the electrolyte, there are a pair of redox currents at +0.45 V (vs. SCE) and +0.37 V (vs. SCE) which can be defined as the redox couple of Ni²⁺/Ni³⁺ [8,22]. In the presence of methanol, NiPO-2/GCE gives an intensive anodic peak at +0.65 V (vs. SCE), showing relatively higher electro-oxidation activity than those of Ni(OH)₂/GCE and NiO/GCE (shown in the inset of Fig. 1(A)). We suppose that the good performance of NiPO-2/GCE should profit from the open porous channel and the easy access of active Ni. The electro-oxidation of methanol on the NiPO-2/GCE might take place as described in references [8,22–24]: first, methanol diffused into the pores of NiPO-2 and then was absorbed on the surface. Second, the redox transition of Ni(II) species to Ni(III) species took place. Third, methanol was oxidized by the Ni(III) species toward intermediate or final products. Last, Ni(III) species were re-generated by the power source.

In contrast, as-NiPO-2/GCE exhibits poor activity (Fig. 1(B)), which should be attributed to the small surface area due to the pore blocking by template. It is noticeable that the VSB-5/GCE gives a much weaker anodic current at +0.6 V (vs. SCE) when compared with that of NiPO-2/GCE, though they have nearly the same BET surface area. This might be explained by the easier diffusion of the reactant molecules in the larger space in the mesopores of NiPO-2. The CVs of NiPO-2/GCE on 500 cycles were also measured. Obviously, the current density of electro-oxidation of methanol remains a substantial level (28% of the first cycle) even after 500 cycles, implying a better electro-stability than that of NiO [15].

CVs for methanol electro-oxidation on NiPO-2/GCE at different scan rates are depicted in Fig. 2, from which the relationship between peak current versus the square root of the scan rate can be drawn (shown in the inset). The anodic peak currents increase with increasing scan rate ranging from 5 mV s⁻¹ to 100 mV s⁻¹. The linear growth of the anodic current with the square root of the scan rate indicates that the electro-chemical behavior of NiPO-2/GCE for methanol oxidation is a diffusion-controlled process [25–27]. Not like most other catalysts [24], NiPO-2/GCE maintains the linear growth even at high scan rate of 100 mV s⁻¹. This might be explained by the benefit of the large
pore size for the diffusion of reactant molecules from solution to the surface redox sites of NiPO-2. Fig. 3 represents the CVs and square wave voltammograms (SWVs) of NiPO-2/GCE in 0.1 M NaOH solution in the presence of various concentrations of methanol. The CVs current and the anodic voltage of Ni$^{2+}$/Ni$^{3+}$ increase with increasing methanol concentration, indicating a dependence of methanol peak current on methanol concentration. The SWV currents at +0.47 V (vs. SCE) increase linearly with the increase of the methanol concentration in the range of 1–10 and 10–70 μM, respectively (shown in the inset of Fig. 3(B)). It is noticeable that the sensitivity of NiPO-2/GCE reaches the detection limit of 1 μM at a signal-to-noise ratio of 3. The high sensitivity also implies a potential use of NiPO-2/GCE as sensor material for the determination of methanol in many fields.

4. Conclusions

Porous nickel phosphate modified GCE were employed as electrocatalysts for the oxidation of methanol in alkaline medium. The mesoporous NiPO-2 modified GCE (NiPO-2/GCE) exhibited better electrochemical activity and stability than that of NiO/GCE. The methanol electro-oxidation of NiPO-2/GCE was a diffusion-controlled process in the range of scan rate from 5 mV s$^{-1}$ to 100 mV s$^{-1}$. The benefit of the large pore space of NiPO-2 for better diffusion of reactant molecules is suggested to explain its unique electro-chemical behavior. The CVs and SWVs on NiPO-2/GCE in the presence of various concentrations of methanol were also investigated. The NiPO-2/GCE showed high sensitivity to the determination of methanol. In our present work, a potential prospect of the porous nickel-contained materials as electro-chemical catalyst has been revealed, though their activity is still much lower than that of Pt-base catalysts. For improving their performance, further research on optimizing the reaction conditions, applying active support electrodes and preparing the materials in film or composite, is in progress.

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