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Nickel phosphate as advanced promising electrochemical catalyst for the electro-oxidation of methanol

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ARTICLE INFO

Article history:

Received 4 January 2018

Received in revised form

3 April 2018

Accepted 22 April 2018

Available online xxx

Keywords:

Nickel phosphate

Methanol oxidation

Electrocatalysis

ABSTRACT

Mesoporous nickel phosphate nanotube (Meso NiPO NT) and mesoporous nickel phosphate nanosheet (Meso NiPO NS) are developed as catalysts for electrochemical methanol oxidation. Conventional mesoporous nickel phosphate which is composed of stacked nanocrystals (Meso NiPO), microporous VSB-5 and commercial nickel oxide (NiO) are used as control materials. Notably, both Meso NiPO NT (40.83 mA cm^{-2}) and Meso NiPO NS (44.97 mA cm^{-2}) exhibit much higher oxidation current density than VSB-5 (13.41 mA cm^{-2}), Meso NiPO (19.85 mA cm^{-2}) and commercial NiO (0.87 mA cm^{-2}). As for the durability test on these materials modified fluorine-doped tin dioxide transparent conductive glass (FTO) electrodes, Meso NiPO NT displays the most stable performance and still retains 91.3% electrochemical activity, which perhaps benefit from its nanotube structure and large specific surface area ($99.6 \text{ m}^2/\text{g}$). Moreover, Meso NiPO NT has higher activity and more excellent stability than many of the previously reported nickel-based materials, suggesting a potential development for direct methanol fuel cells.

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Introduction

Environmental pollution and global warming issues force people to design and develop clean energy sources to replace nonrenewable fossil fuels. Direct methanol fuel cells (DMFCs) can be a potential solution to alleviate the energy issues due to the easy handling, high energy conversion efficiency and low pollutant emission [1,2]. Up to now, platinum (Pt) based nanomaterials with high catalytic efficiency are used as anode catalysts in DMFCs. Unfortunately, the expensive price

derived from the scarcity of noble metal Pt and activity recession derived from CO intermediates poisoning are the main obstacles against broad commercialization [3–6]. Therefore, non-precious metal materials have been developed as electrocatalysts for methanol electrooxidation in recent years, but the electrocatalytic activity still needs to be further improved and perfected. The search for alkaline electrocatalytic systems with respect to methanol oxidation reaction is a pretty active area. Several main advantages of alkaline DMFCs are considered in comparison of acidic DMFCs. Firstly, the non-precious metals can be used as

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<https://doi.org/10.1016/j.ijhydene.2018.04.165>

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electrochemical catalysts [7]. For instance, several non-conducting materials such as SnO_2 [8], CeO_2 [9] and $\text{NiCu-Co}_2\text{O}_4$ [10] modified mesoporous zeolite based catalysts are used for electrochemical oxidation of methanol. Secondly, the methanol oxidation kinetics in low anodic overvoltage is enhanced. Thirdly, the risk of corrosion of catalysts and carbons is reduced. Fourthly, the adsorption of CO intermediates which might affect the electrocatalytic activity is reduced [3,11]. The electrochemical activity of electrode catalysts and the ion/electron transport rate in the electrode and at the electrode-electrolyte interface largely determine the performance of alkaline DMFCs [11]. It is essential to explore novel electrode materials with high catalytic activity and stability.

Many researches have been paid close attention to nickel-based materials such as metal Ni, Ni-alloy, nickel oxide, nickel phosphate and nickel hydroxide. Nickel phosphate is a promising transitional metal material which is used in high performance supercapacitor [12–14], electrochemistry sensor [15] and electrocatalysts [16–20]. This may be due to the following advantages of the material: low cost, earth-abundance and environmental friendliness. Although there have been several reports [19,20] on the application of methanol oxidation of nickel phosphates, the nickel phosphates materials are still need to be further developed in order to obtain better catalytic activity and stability as well as low overpotential. In the reported literature, the anodic peak current of methanol oxidation of NiPO-2/GCE is only 120 μA and the current of electro-oxidation of methanol remains 72% of the first cycle after 500 cycles [19]. The mass current density of Si-NiPO-2 is 34 $\text{mA mg}^{-1} \text{cm}^{-2}$ and the anodic current density of Si-NiPO-2 reaches a maximum at 250 cycles. It remains higher than the initial value after 750 cycles, but there is a significant decline in current density after 1000 cycles [20]. Herein, we report our effort on performance study of a series of nickel-based catalysts, mesoporous nickel phosphate nanotubes (Meso NiPO NT), mesoporous nickel phosphate nanosheet (Meso NiPO NS), microporous VSB-5, conventional mesoporous nickel phosphate (Meso NiPO) and commercial NiO. The obtained electrocatalysts are characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), field-emission scanning electron microscopy (FESEM), Raman spectroscopy, UV/vis spectra, X-ray photoelectron spectroscopy (XPS), N_2 adsorption-desorption isotherm and electrochemical measurements. The electrochemical activity and stability of Meso NiPO NT and Meso NiPO NS for methanol electro-oxidation in alkaline condition are investigated and compared with other control materials.

Experimental

Reagents

Nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) and nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were supplied from Tianjin Kemiou Chemical Reagent Co., Ltd. Ammonium dibasic phosphate ($(\text{NH}_4)_2\text{HPO}_4$) and disodium hydrogen phosphate dodecahydrate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) were purchased from Beijing chemical plant and Tianjin Chemical Reagent Six Factory, respectively. Potassium hydroxide (KOH) was obtained from

Tianjin Chemical Reagent Three Factory. Sodium dodecyl sulfate ($\text{C}_{12}\text{H}_{25}\text{NaO}_4\text{S}$) (SDS) and urea (H_2NCONH_2) were offered by Tianjin De'en Chemical Reagent Co., Ltd. Phosphoric acid (H_3PO_4) was obtained from Tianjin Kaitong Chemical Reagent Co., Ltd. All reagents were of analytical grade and required without further purification, and the ultra-pure water was used in all experiments.

Synthesis of nickel phosphate

The syntheses of materials (Meso NiPO NT, Meso NiPO NS and Meso NiPO) refer to our previous work [21]. 23.5 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added to 50 mL ultra-pure water and dissolved to obtain green clear solution firstly. And then 5.3 g $(\text{NH}_4)_2\text{HPO}_4$ was mixed with the solution and stirred for half an hour. Finally, a greenish precipitate was directly formed and then dried at 393 K for 24 h [21,22]. The product was named as mesoporous nickel phosphate nanotubes (Meso NiPO NT). The mesoporous nickel phosphate nanosheet (Meso NiPO NS) was prepared following the same synthetic steps as that for Meso NiPO NT, except that $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were used as phosphorus source and nickel source instead of $(\text{NH}_4)_2\text{HPO}_4$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, respectively. The synthesis of VSB-5 is derived from the previous report we have developed [23]. 0.1 mmol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 41 μL H_3PO_4 was mixed in a Teflon lined stainless steel vessel, and added 1.2 g urea, 0.1 g SDS, and then added 20 mL H_2O to dissolve, finally heated to 353 K for 12 h [21]. Green powder named mesoporous nickel phosphate (Meso NiPO) was obtained and washed with H_2O and ethanol.

Characterization

Morphological characteristics of the samples were captured by transmission electron microscopy (TEM) with a FEI Talosf200s. For TEM analyses, catalysts were uniformly dispersed in ethanol under ultrasonic treatment and then put a drop of the solution on a Cu grid. The morphologies and element analyses of the surface of Meso NiPO NT and Meso NiPO NS modified glassy carbon electrodes (Meso NiPO NT/GCE, Meso NiPO NS/GCE) were characterized by the field-emission scanning electron microscopy (FESEM, JSM-7610F, Japan) at accelerating voltage of 5 kV and 20 kV, respectively. Raman spectra were obtained on Renishaw inVia Laser microscopy Raman spectrometer from England. The UV/vis spectra were performed by PE Lambda 950 UV-Visible-Near Infrared spectrophotometer from America. N_2 adsorption-desorption isotherms were recorded using Autosorb-iQ-MP-C automatic physical/chemical adsorber. X-ray diffraction (XRD) analyses were recorded by X-ray D8 Advance (Bruker, Germany) diffractometer equipped with $\text{Cu-K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$). The element content (Ni, P, O) are analyzed by X-ray photoelectron spectroscopy (XPS) which was obtained on an Axis Supra (Kratos, England) spectrometer equipped with Al $\text{K}\alpha$ radiation as the exciting source.

Preparation of electrodes

The modified electrodes were prepared as follows: The bare glassy carbon electrode (GCE) was polished with 50 nm

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