Journal of Energy Chemistry 24 (2015) 497–502

Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem

Plastic supported platinum modified nickel electrode and its high electrocatalytic activity for sodium borohydride electrooxidation

Bin Wang[a], Dongming Zhang[a], Ke Ye[a], Kui Cheng[a], Dianxue Cao[a], Guiling Wang[a,*], Xiaoli Cheng[a,b,**]

[a] Key Laboratory of Superlight Materials and Surface Technology of Ministry of Education, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, Heilongjiang, China
[b] Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education, School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, Heilongjiang, China

ARTICLE INFO

Article history:
Received 11 December 2014
Revised 25 February 2015
Accepted 9 March 2015
Available online 8 August 2015

Keywords:
Plastic
Platinum modified nickel electrode
Chemical-reducing
High electrocatalytic performance
Reduce white pollution

ABSTRACT

A novel plastic/multi-walled carbon nanotube (MWNTs)-nickel (Ni)-platinum (Pt) electrode (PMNP) is prepared by chemical-reducing Pt onto the surface of Ni film covered plastic/MWNTs (PM) substrate. The MWNTs are adhered by a piece of commercial double faced adhesive tape on the surface of plastic paper and the Ni film is prepared by a simple electrodeposition method. The morphology and phase structure of the PMNP electrode are characterized by scanning electron microscopy, transmission electron microscope and X-ray diffractometer. The catalytic activity of the PMNP electrode for $NaBH_4$ electrooxidation is investigated by means of cyclic voltammetry and chronoamperometry. The catalyst combines tightly with the plastic paper and exhibits a good stability. MWNTs serve as both conductive material and hydrogen storage material and the Ni film and Pt are employed as electrochemical catalysts. The PMNP electrode exhibits a high electrocatalytic performance and the oxidation current density reaches to 10.76 A/(mg·cm) in 0.1 mol/dm^3 $NaBH_4$ at 0 V, which is much higher than those in the previous reports. The using of waste plastic reduces the discarding of white pollution and consumption of metal resources.

1. Introduction

Nowadays, hydrogen energy has attracted much attention as an environmental friendly energy [1,2]. So the study of hydrogen storage materials (e.g. hydrogen storage alloys [3–5], carbon nanotubes [5,6], metal organic [7], hydrogen-rich compound [5,8–10]) becomes a hot topic. In recent years, fuel cells employed hydrogen contained as fuel have come to be a big plan and made tremendous progress [5,8–10].

Direct borohydride fuel cells (DBFCs) employing sodium borohydride ($NaBH_4$) directly as the fuel have caught scientists' interests due to their high power density, high open circuit voltage, low pollution, and so on [5,11–16]. $NaBH_4$ owns a high hydrogen contents (10.6 wt%) and the complete electrooxidation of $NaBH_4$ generates 8 electrons (Eq. 1) [5,11–27]. Besides, $NaBH_4$ is non-toxic and exhibits a good stability in alkaline solution and the electrooxidation of $NaBH_4$ does not release any pollutant. All of them decide $NaBH_4$ to be a promising fuel. The choice of catalysts for $NaBH_4$ electrooxidation determines the electrode performance and future.

$$BH_4^- + 8OH^- \rightarrow BO_2^- + 4H_2O + 8e^- \quad (1)$$

Hydrogen storage alloys (e.g. AB_5-type alloys [3–5]) and transition metals (e.g. Ni [17,18], Co [19], Cu [20], Zn [21]) are alternative low cost catalysts for the electrooxidation of $NaBH_4$. However, most of them suffer the drawback of lower catalytic performance compared with noble metals (e.g. Pt [22,23], Pd [24,25], Au [26], Ag [27]). So, many scientists combine base metals with noble metals to achieve a high catalytic performance and reduce the catalytic price at the same time [22,23,25,26]. Wang et al. [3] prepared Au doped AB_5-type alloy by a simple chemical reduction method for DBFCs. Our team prepared Pd doped AB_5-type alloy [4] and Pd modified three dimensional porous Ni film [25] electrodes in a similar chemical method for $NaBH_4$ electrooxidation. All of them obtained a much higher electrocatalytic performance than these pure AB_5-type alloys and Ni film.

Nowadays, people are facing the increasingly serious environmental problems. So, environmental awareness should be considered in every corner of our life. On the tradition, metal materials (e.g. Ni foam [3–5,25,28], Cu foam [29], Ti plate [24,30], Al foil [31]) are widely used as substrates of electrodes and have gotten big success due to their

* Corresponding author. Tel: +86-451-82589036; Fax: +86-451-82589036.
** Corresponding author.
E-mail addresses: wangguiling@hrbeu.edu.cn (G. Wang), chengxiaoli@hlju.edu.cn (X. Cheng).

http://dx.doi.org/10.1016/j.jechem.2015.06.002
2095-4956/

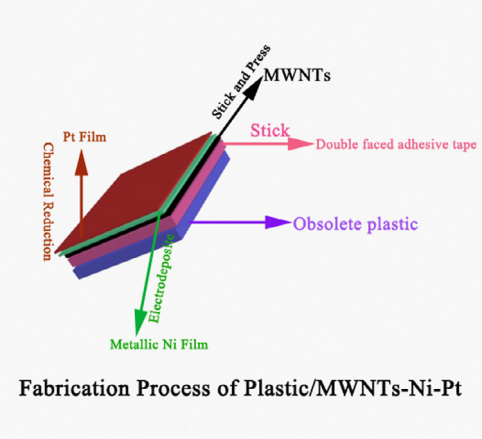

Fig. 1. Fabrication process of plastic/MWNTs–Ni–Pt (PMNP) electrode.

Fig. 2. Stability test of plastic/MWNTs in alkaline medium.

high electronic conductivity. However, the metal resources are getting more and more rare with the large consumption. In recent years, trivial materials in our dairy life have been widely employed as electrode substrates after physical or chemical procedures [18,19,32–40]. Cui et al. [32–34] employed carbon nanotubes (CNTs) modified commercial available sponge and textile as electrode substrates for wearable energy devices. Li and Hu et al. fabricated an anode consisting of a Sn thin film deposited on a hierarchical wood fiber. Cui et al. [35] and Chan et al. [36] coated CNTs/Ag and $LiCoO_2$ on the surface of common papers by a simple meyer rod coating method, respectively, and then employed them as electrode materials. Recently, our team has fabricated MWNTs modified sponge/textile and graphite modified A4 paper to serve as electrode substrates [18,19,37]. All of the sponge, textile and paper are environmental friendly and cheap.

Plastic, a kind of non-degradable chemical material, are widely used everywhere in our dairy life for more than decades of years and have caused serious environmental pollution. In this paper, we employed waste plastic paper as electrode substrate. The MWNTs are adhered by a piece of familiar double faced adhesive tape and serves as both conductive material and hydrogen storage material [5]. Ni film and Pt are used as effective catalysts for the electrooxidation of $NaBH_4$. The as-prepared plastic/MWNTs–Ni–Pt (PMNP) electrode exhibits a high electrochemical performance of 10.76 A/(mg·cm) in 0.1 mol/dm^3 $NaBH_4$ at 0 V, which is much higher than those in the previous reports.

2. Experimental

All chemicals were analytical grade and were used without further purification. Fig. 1 shows the fabrication process of the PMNP electrode. First, a piece of commercial double face adhesive tape which consists of ethoxyline resin (KunShan HeXing Yuan Electronics Co., Ltd.) sticks to the surface of a piece of obsolete plastic paper (The plastic bag of Kangshifu instant noodles). Second, the MWNTs (>50 nm in outer diameter and 10–20 μm in length, Shenzhen Nanotech Port Co. Ltd.) are uniformly adhered on the tape surface and then are pressed under a pressure of 6 MPa. The mass of the MWNTs on the plastic paper is about 3.2 mg/cm^2. Third, the plastic/MWNTs (PM) is cut into a 10 × 10 mm^2 (1.0 cm^2 planar area) sheet and then immersed in 2 mol/dm^3 NH_4Cl and 0.1 mol/dm^3 $NiCl_2$ for the electrodeposition of Ni on the PM, which was performed using the Autolab PGSTAT302 (Eco Chemie) electrochemical workstation in a conventional three electrode electrochemical cell with a saturated Ag/AgCl, KCl reference electrode and Pt foil counter electrode. The electrodeposition was carried out at a constant potential of −1.0 V for 10, 30 and 60 min. The mass of the Ni film on the PM is about 19 mg/cm^2. At last, the plastic/MWNTs–Ni (PMN) is immersed in a solution contained 1 mmol/dm^3 H_2PtCl_6 for 10, 30 and 60 s to obtain the PMNP electrode (galvanic replacement). $NaBH_4$ electrooxidation was also performed in the same three electrode electrochemical cell using a 1 cm^2 PMNP electrode. All potentials were referred to the saturated Ag/AgCl, KCl reference electrode.

The morphology of the electrodes was determined using a scanning electron microscope (SEM, JEOL JSM-6480). The structure was analyzed by a powder X-ray diffractometer (XRD, Rigaku TTR-III) equipped with Cu $K\alpha$ radiation (λ= 0.15406 nm). Pt loading was measured using an inductive coupled plasma emission spectrometer (ICP, Xseries II, Thermo Scientific). Pt in the 1.0 cm^2 electrode was first dissolved in aqua regia solution and then diluted to 1 dm^3 solution for the ICP measurement.

3. Results and discussion

Fig. 2 shows the stability test of PM in alkaline medium. Clearly, the PM has no change and the MWNTs almost do not fall off from the plastic at all after being soaked in saturated NaOH solution after 15 and 30 d, which demonstrated that the PM has a high stability.

The SEM images of PM, PMN and PMNP at different magnifications are shown in Fig. 3. At low magnification, it is obvious that the surface of the PM substrate is rough rather than complanate, which may be caused by the simple pasting and pressing process of MWNTs (Fig. 3a). However, the rough surface may be favorable to the streaming and diffusion of the fuel during the reaction process. At high magnification, it can be seen that the MWNTs distribute compactly and make up a net like structure on the PM surface (Fig. 3b). The existence of MWNTs leads to a high electronic conductivity of the PM substrate. Besides, according to the previous report, the MWNTs also can play a role of hydrogen adsorbent during the hydrolysis and electrochemical reaction process [5]. The adsorbed hydrogen may be electrooxidized further and release electrons. Fig. 3(c) and (d) shows the surface texture of PMN at low and high magnifications. Clearly, the metallic Ni exhibits a film-like structure at low magnification (Fig. 3c). Interestingly, Ni film is comprised by some Ni particles, and the diameters of which are around 100 nm. Because of the strong magnetism of metallic Ni, these small Ni particles get together and form some big aggregate (around 5 μm). The fuel may diffuse to the MWNTs layer through the gaps among the Ni particles and improve the electrochemical performance of the PMNP electrode. The Ni film not only serves as the reducer for the deposition of Pt, but also acts as the catalyst for $NaBH_4$ electrooxidation. Besides, the surface of the Ni particles is not uniform but rough, which is coincident with the coarse surface of MWNTs film (Fig. 3b) and will increase the specific surface area and improve the electrode performance for further. After doping Pt, some Pt nanoparticles uniformly distributed on the Ni surface (Fig. 3f), but the outline of the PMNP electrode (Fig. 3e) has no