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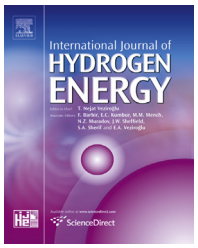

A novel, effective and low cost electrocatalyst for direct methanol fuel cells applications

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ABSTRACT

Electrocatalytic oxidation of methanol in alkaline solution on a NiCd/C catalyst chemically modified by a leaching process of Zn was investigated. Scanning electron microscopy (SEM), X-ray florescence spectroscopy (XRF) and atomic force microscopy (AFM) were used for coating characterization. The electrochemical properties and behaviors and also kinetic values of alkaline leached NiCdZn/C catalyst were characterized using cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS). The electrocatalytic activity of the alkaline leached NiCdZn/C catalyst toward methanol oxidation is shown to strongly depend on the porous and larger structure of coating and increasing of electrocatalytic active sites. The prepared catalyst in the present work is the most promising system for use in direct methanol fuel cells.

Introduction

Direct liquid fuel cells are to be very attractive devices by researchers, and it is showing as alternative candidates of clean power sources. These systems have many advantages such as storage conditions are easy; they have high-energy density (6.1 kW h kg^{-1} for methanol, 10.5 kW h kg^{-1} for gasoline [1,2]), low environmental pollution and these devices are portable, chemical energy convert to electric energy directly [3,4]. It is known the slow anode reaction kinetics on the direct liquid fuel cell, the great efforts to researchers to develop new and cheap electrocatalysts.

Pt-based catalysts are often studied the oxidation of methanol due to the high catalytic efficiency [5–7]. But Pt-based catalysts have some disadvantages such as high cost and CO-poisoning. Catalytic efficiency decreases significantly during the oxidation process and exhibits instability. To this end, the most promising candidates on anode reaction are nickel and nickel-based catalysts [8–10]. These materials showed that exhibited high catalytic efficiency, low CO-poisoning and high catalytic stability [11].

One of the most important issues is that catalysts have large surface area. Alkaline leaching of Zn from the binary and ternary deposits promotes the catalysts surface. This chemical route (leaching of Zn) is used to prepare very effective catalysts in hydrogen evolution [12–16]. Alkaline leaching procedure is yielding a high porous and crack catalytic surface.

Various carbon materials such as carbon nanotubes [17,18], glassy carbon [11], graphite [8], carbon ceramic [19–22] and carbon nanofibers [23] are used as a catalyst support. In

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addition graphite is used in real fuel cell as current collector and flow field plate. Although lots of studies have been reported toward the methanol oxidation for preparing effective catalysts, alkaline leaching of procedure is not used to prepare the catalysts for the oxidation of methanol, exception of a few studies [24].

Recently, we studied the methanol oxidation reaction (MOR) activity of nickel-promoted Cd coating and reported that this coating had a good electrocatalytic activity and good time stability [25]. Another our study showed that the oxidation of methanol increased on the alkaline leached NiZn and NiZn–Ru deposits [26]. In this study, we further developed these studies. We have prepared NiCdZn ternary coating on the graphite substrate and then more active Zn was leached from the deposit to produce a porous and electrocatalytic surface suitable for use in direct methanol fuel cell (DMFC).

Experimental

Graphite rod (electrical resistance is 4.8–5.6 Ω) is used as a working electrode (C) for about 5 cm length of graphite substrate. Polyester block was covered all graphite surfaces. Only measurement area is open to the atmosphere, and this surface is 0.283 cm^2. Sand papers (320–1000 grain size) are used to polish the surface of working electrode. After the polishing the surface, working electrode was washed with distilled water and immersed the bath solution. The electrochemical experiments were conducted by the CHI660C electrochemical analyzer (CHI instruments Co.). Auxiliary electrode and reference electrode were used as Pt wire (with 2 cm^2 surface area) and Ag/AgCl electrode, respectively. Electrodeposition process is performed galvanostaticly (80 mA cm^{-2}) at room temperature and under stirring conditions. Small nickel block and Ag/AgCl electrode were used as counter electrode and reference electrode, respectively, during the deposition. Bath solution is composing 30% $NiSO_4 \cdot 6H_2O$, 1.00% $NiCl_2 \cdot 6H_2O$, 0.274% $CdSO_4 \cdot 8/3H_2O$, 0.00787% $CdCl_2$, 0.159% $ZnSO_4 \cdot 7H_2O$ and 1.25% H_3BO_3 (wt%). 1 M NaOH solution is used to leaching of Zn from the deposit for several hours as a first step. Then the coating (NiCdZn) is immersed in 30% NaOH solution to obtain the porous surface as the second step. Leaching of Zn from the deposit is providing the large surface area.

We investigated impacts of scan rate, temperature and methanol concentration on the methanol oxidation. Scan rates are between 25, 50, 75, 100 and 250 mV s^{-1}, temperatures are 25, 35, 45 and 50 °C in 1 M KOH + 1 M methanol solution and methanol concentrations are 1.0, 0.75, 0.50, 0.25 and 0.10 M in 1 M KOH. In order to determine the stability of this coating, we performed chronoamperometry technique in 1 M KOH + 1 M methanol solution at 0.50 V (vs. Ag/AgCl) for 3600 s. EIS measurements were carried out in the frequency range of 100 kHz to 0.003 Hz. Potential amplitude is 0.005 V. Nuve BS 302 type thermostat was used to control the solution temperature.

SEM and XRF analysis were determined the changing in the surface modifications. Mean roughness of coating is measured by AFM. All chemicals were of analytical grade from Merck and Sigma and were used without further purification.

Results and discussion

Surface characterization

Fig. 1(a) indicates the SEM images of NiCdZn/C surface before the leaching process. Nanoparticles of coating spread over the surface homogeneously. Coating closed the surface like in the form of cover. Various sizes of particles can be seen clearly on the electrode surface. This modification depends on the deposition of current density, composition of bath solution and deposition time. After exposing with NaOH solution (Fig. 1(b)), surface structure is more and more improved. Surface structure transformed crystalline grains, and these structures are dispersed uniformly on the substrate. Particle sizes are bigger than that of one. Some cracks can be seen at the surface. Chemical compositions of metals in the coating was determined with XRF. The surface compositions are 9.4% Ni, 88.5% Cd, 2.1% Zn before and 14.7% Ni, 83.8% Cd, 1.5% Zn after leaching of Zn from the deposits, respectively. All amounts of Zn are not removed from the surface. Mean roughness of NiCdZn layer is measured with AFM. Related diagrams are seen in Fig. 2. Hill-like structures are seen at the surface. According to cross sectional analysis (Fig. 2c) from the AFM, mean roughness of this layer is measured as 538.80 nm. We measured mean roughness of NiCd layer was 486.51 [25]. Chialvo et al. [27] reported that hemispherical particles were obtained on the Pt/Ru electrode and the mean value of the diameter of the hemispheres was obtained as 80 nm from the analysis of the height profiles. Munichandraiah et al. [28] believed that electrochemical nucleation of a metal on a foreign substrate takes place on high-energy surface sites such as crystal edges, kinks, steps, corners, and defects. They reported that, Pd modified electrode posses dendritic structure and this structure was improved the electrochemical process. According to literature, it is inferred that the surface structure plays an important role in the methanol oxidation reaction.

Electro-oxidation of methanol on NiCdZn/C

CV curves were recorded in the potential range of hydrogen and oxygen evolution. Fig. 3 shows the CV of NiCdZn/C electrocatalyst in 1 M KOH solution without and with 1 M methanol at 298 K. It can be seen from Fig. 3 without methanol that two peaks can be appeared. First, one is seen at −0.885 V (Ag/AgCl) and second one is seen 0.624 V (Ag/AgCl). These peaks are related to transitions of Ni/Ni(II) and Ni(II)/Ni(III), respectively [25–31]. It is observed that α-Ni(II) transforms β-Ni(II) in the potential ranges of −0.80 to 0.40 V (Ag/AgCl) [32]. α-Ni(II) transforms to Ni(III) with forward scan but with methanol, methanol behaves like reducing agent and it transforms to β-Ni(II), a crystalline form with more resistance to oxidation [33–36]. In the backward scan, Ni(III)/Ni(II) transition is seen at 0.248 V (Ag/AgCl). The CV of NiCdZn/C electrocatalyst in an alkaline solution with methanol is seen in Fig. 3. In the forward scan, there is a peak at −0.945 V (Ag/AgCl). The value of current density is 295.5 mA cm^{-2} at this potential. In these potential regions, it can be seen from Fig. 3 that oxidation of alcohols on electrocatalysts and peak current is found to be significantly high. Other one peak in the backward scan, a relatively high