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Electrooxidation of methanol on NiMn alloy modified graphite electrode

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ABSTRACT

Nickel and nickel–manganese alloy modified graphite electrodes (G/Ni and G/NiMn) prepared by galvanostatic deposition were examined for their redox process and electrocatalytic activities towards the oxidation of methanol in alkaline solutions. The methods of cyclic voltammetery (CV), chronoamperometry (CA) and impedance spectroscopy (EIS) were employed. In CV studies, in the presence of methanol NiMn alloy modified electrode shows a significantly higher response for methanol oxidation. The peak current of the oxidation of nickel hydroxide increase is followed by a decrease in the corresponding cathodic current in presence of methanol. The anodic peak currents show linear dependency upon the square root of scan rate. This behavior is the characteristic of a diffusion controlled process. Under the CA regime the reaction followed a Cottrellian behavior and the diffusion coefficient of methanol was found to be 4×10^{-6} cm^2 s^{-1}. A mechanism based on the electro-chemical generation of Ni^{3+} active sites and their subsequent consumptions by methanol have been discussed and the corresponding rate law under the control of charge transfer has been developed and kinetic parameters have been derived. The charge transfer resistance accessible both theoretically and through the EIS have been used as criteria for derivation of the rate constant.

1. Introduction

Investigation of electrooxidation processes of alcohols is critical in attaining a better understanding of the direct alcohol fuel cell (DAFC). Methanol is one of the interesting future fuels for fuel cell application. Compared with other cells, the direct methanol fuel cell (DMFC) has several advantages such as high efficiency, very low polluting emissions, a potentially renewable fuel source, fast and convenient refueling, simple operation and ease of fuel storage and distribution. The low operating temperature of a DMFC (typically <95 °C) allows for easy start up and rapid response to changes in the load or operating conditions [1–3]. However, compared to the hydrogen based fuel cells, DMFC still remains to be further developed. One of the problems still unsolved is the slow kinetics of methanol electrooxidation [4]. Considerable efforts have been directed towards the study of methanol electrooxidation at high pH. The use of alkaline solutions in a fuel cell has many advantages such as increasing its efficiency [5,6], a wider selection of possible electrode materials, almost no sensitivity to surface structures [7] and negligible poisoning effects in alkaline solutions [8,9].

In the electrochemical oxidation of methanol, the electrode material is clearly an important factor where a highly efficient electrocatalyst is needed. As described previously [10–15], a considerable increase in power density and fuel utilization was obtained by optimizing different components of fuel cells. Different electrode materials based on Pt and Pt-binary electrodes were commonly used as a catalyst for the electrochemical oxidation of methanol. As catalysis is a surface effect, the catalyst needs to have the highest possible surface area. Carbon is a common choice for supporting electrocatalyst particles in DAFCs because of its large surface area, high electrical conductivity, and porous structure [16–19]. Meanwhile carbon is electrocatalytically inactive and serves only as a mechanical support. Therefore, carbon-supported electrocatalysts [16], such as Pt–Ru and Pt–Ru–P/carbon nanocomposites [17], Pt/Ni and Pt/Ru/Ni alloy nanoparticles [20] are generally used as catalyst. Ni has commonly been used as an electrocatalyst for both anodic and cathodic reactions in organic synthesis and water electrolysis [21–24]. Ni based electrodes have lower poisoning effect than Pt based electrode and also are cheap. One of the very important uses of nickel as a catalyst is for the oxidation of alcohols. Several studies of the electro-oxidation of alcohols on Ni have been reported [25,26]. Taraszewska and Roslonek [27] found that $Ni(OH)_2$ modified glassy carbon electrode acts as an effective catalyst for the oxidation of methanol. Most oxidizable organic compounds were found to oxidize at the same potential and this potential coincided exactly with that at which the surface of the nickel anode becomes oxidized [26–30]. Van Effen and Evans [31] found that the oxidation of ethanol on Ni in KOH

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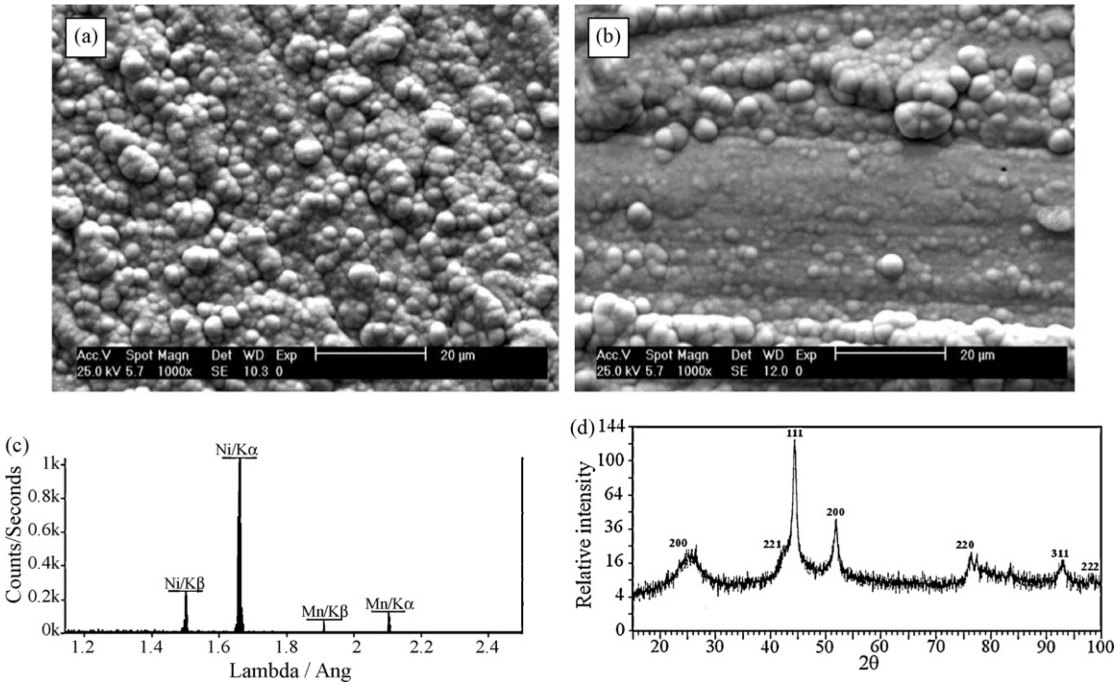

Fig. 1. Metallograph of electrode surface after electrodeposition of (a) Ni and (b) NiMn alloy from a solution composed of 0.22 M $NiSO_4 \cdot 6H_2O$ + 0.4 M $C_6H_5Na_3O_7 \cdot 2H_2O$ + 0.22 M $(NH_4)_2SO_4$ for Ni deposition at the current density of 7 mA cm^{-2} and for 300 s and addition of 0.2 M $MnSO_4 \cdot 5H_2O$ for NiMn alloy deposition. (c) WDX results of the chemical composition of NiMn alloy at the surface. (d) X-ray diffractogram (XRD) of electrodeposited NiMn alloy, in the range $10^\circ < 2\theta < 100^\circ$.

solution involved the formation of a higher valent nickel oxide, which acts as a chemical oxidizing agent. This fact was confirmed by both cyclic voltammetry and impedance spectroscopy [32].

The study of alloy electrodes is motivated primarily from the anticipation of a synergistic electrocatalytic benefit from the combined properties of the components of alloys. Furthermore, the use of preanodized alloy electrodes offered the advantages of ease of preparation and long-term stability in comparison with thermally prepared and electrolytically deposited mixed-oxide film electrodes. Kuwana and co-workers investigated the alloy electrodes in their studies of carbohydrate reaction at Ni-based alloys containing high percentages of Cu and Cr [33,34]. One promising characteristic of such alloy electrodes is the resistance to corrosion in the alkaline media. However, semiconductive oxide films, e.g. Cu_2O and NiO, if formed might cause a slowly increasing ohmic drop at the electrode surface as the thickness of these oxide films increase with time [35,36]. The addition of small amounts of alloying elements to Cu has been demonstrated to provide increased electrocatalytic activity in comparison to the pure Cu electrode. For example, the presence of 5% Mn to Cu, denoted as Mn_5Cu_{95}, shows a much improved electrochemical activity for the oxidation of glucose in alkaline media in comparison to that of the pure Cu electrode [37].

The purpose of the present work is to study the electrochemical oxidation of methanol on a nickel–manganese alloy modified graphite electrode in a solution of 1 M NaOH aiming at the elucidation of the mechanism, derivation of the kinetic parameters of the process and the usefulness of the electrocatalytic process.

2. Experimental

Sodium hydroxide, nickel sulfate, manganese sulfate, sodium citrate, ammonium sulfate and methanol used in this work were Merck product of analytical grade and were used without further purification. Electrochemical studies were carried out in a conventional three electrode cell powered by an electrochemical system comprising of EG&G model 273 potentiostat/galvanostat and Solartron model 1255 frequency response analyser. The system is run by a PC through M270 and M398 commercial software via a GPIB interface. Fitting of experimental impedance spectroscopy data to the proposed equivalent circuit was done by means of home written least square software based on the Marquardt method for the optimization of functions and Macdonald weighting for the real and imaginary parts of the impedance [38,39].

A dual Ag–AgCl saturated KCl, a Pt wire and a graphite (G) disk electrode were used as the reference, counter and working electrodes, respectively. All studies were carried out at 298 ± 2 K. The G disk electrode was polished with 0.05 mm alumina powder on a polishing microcloth and rinsed thoroughly with distilled water prior to modification.

Films of nickel were formed on the graphite surface by galvanostatic deposition from a solution composed of 0.22 M $NiSO_4 \cdot 6H_2O$ + 0.4 M $C_6H_5Na_3O_7 \cdot 2H_2O$ + 0.22 M $(NH_4)_2SO_4$ where a current density of 7 mA cm^{-2} for 300 s was employed. Addition of $MnSO_4 \cdot 5H_2O$ to achieve the concentration of 0.2 M in the previous solution and applying the same condition was used for NiMn deposition. Working electrode was placed in the middle of the cell and electrolyte was stirred with magnetic stirrer during electrodeposition. The surface morphology and chemical composition of the deposit was evaluated by Leica Cambridge S360 SEM equipped with wavelength dispersive X-ray (WDX). Structural investigation was conducted by X-ray diffraction (XRD) method using a Philips (Xpert) diffractometer and Cu Kα radiation.

3. Results and discussion

The micrographs presented in Fig. 1a and b display the morphology of the electrodeposited Ni and NiMn alloy obtained by SEM. Mirror finished surfaces are observed for the electrodeposited Ni and NiMn alloy although the surfaces are rough under micrometer scale. The films are fairly compact with virtually no pores and cavities. The result of chemical composition analysis obtained by WDX revealed that the composite contains 91% Ni and 9% Mn. The compositions are given in weight percents (Fig. 1c).