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Electrooxidation of methanol in alkaline solution on composite electrodes

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The electrooxidation of methanol in an alkaline electrolyte has been studied on nickel foam-based composite electrodes. The aim of this work was to establish the electrochemical usefulness of electrodes in alkaline fuel cells. Nickel foam, exhibiting electrocatalytic activity, was modified by covering it with a polyaniline (PANI) film, followed by the electrodeposition of platinum particles on the PANI matrix (Ni | PANI | Pt). For comparison, platinum was also deposited directly on the surface of the nickel substrate. The results show that Ni | PANI | Pt electrodes exhibit the highest electrocatalytic activity for methanol oxidation in the reaction occurring in the potential range of NiOOH formation.

Key words: *methanol oxidation; nickel, platinum; polyaniline; electrocatalysis*

1. Introduction

Large energy consumption and a global increase in ecological awareness have created a strong demand for new, efficient and ecological sources of energy. An attractive alternative to the combustion of fossil fuels is the fuel cell [1, 2]. At present, extensive works are being carried out in many laboratories on new types of electrode materials involving electronically conducting polymers (ECP) [3–6] which offer wide possibilities for practical application as electrodes in alkaline fuel cells. Platinum and other noble metal microparticles dispersed on materials with high surface area are of considerable interest in catalysis [4–10]. It has been proved that such electrodes exhibit electrocatalytic behaviour toward the electrooxidation of various organic substances which may be used as fuels, e.g., methanol [11]. Although the process of anodic methanol oxidation has been intensively studied over many years, the mechanism of the reaction is still under discussion [12–18]. The process, occurring with a platinum catalyst, is described by the overall reaction [13]:

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$$CH_3OH + H_2O = CO_2 + 6H^+_{aq} + 6e^- \qquad (1)$$

The fact that the overall process involves six electrons per methanol molecule to produce carbon dioxide makes methanol a promising fuel for direct fuel cells. The reaction in Eq. (1) is favoured in alkaline solution due to generation of hydrogen ions. There are many mechanisms proposed for methanol oxidation in an alkaline medium. One path is the following process [14]:

$$Pt + OH^- \longleftrightarrow Pt\text{–}(OH)_{ads} + e^- \qquad (2)$$

$$2Pt + CH_3OH \longleftrightarrow PtH + Pt\text{–}(CH_3O)_{ads} \qquad (3)$$

$$Pt\text{–}(CH_3O)_{ads} + Pt\text{–}(OH)_{ads} \longrightarrow Pt_2\text{–}(CH_2O)_{ads} + H_2O \qquad (4)$$

$$Pt_2\text{–}(CH_2O)_{ads} + Pt\text{–}(OH)_{ads} \longrightarrow Pt_3\text{–}(CHO)_{ads} + H_2O \qquad (5)$$

$$Pt_3\text{–}(CHO)_{ad} + Pt\text{–}(OH)_{ads} \longrightarrow Pt_2\text{–}(CO)_{ads} + 2Pt + H_2O \qquad (6)$$

$$Pt_2\text{–}(CO)_{ads} + Pt\text{–}(OH)_{ads} \longrightarrow Pt\text{–}(COOH)_{ads} + 2Pt \qquad (7)$$

$$Pt\text{–}(COOH)_{ads} + Pt\text{–}(OH)_{ads} \longrightarrow 2Pt + CO_2\uparrow + H_2O \qquad (8)$$

Various intermediates formed during the main reaction [15] result in poisoning the electrode surface [15, 16]. It is generally accepted that the most poisoning species are adsorbed CO molecules [17]. The most important reasons for using microcrystalline platinum dispersed onto a polymer matrix are: (a) a catalyst exhibits higher tolerance toward poisoning by intermediate species occurring in the oxidation process (mainly by absorbed CO), (b) electrodes containing fine platinum particles are cheaper than bare platinum [19]. Numerous publications have been devoted to examining the electrocatalytic properties of platinum particles deposited onto ECP films (mainly on polyaniline, polypyrrole, and polythiophene), and it has been reported that such electrodes exhibit even higher catalytic activity for methanol oxidation than bare platinum [5, 6]. El-Shafei [20] examined methanol oxidation on a nickel | glassy carbon composite electrode, whereas Rahim et al. [21] have studied this reaction on a nickel | graphite composite electrode. The results reported in both publications led to the conclusion that methanol is oxidized with the participation of trivalent nickel, after nickel anodically oxidizes to NiOOH. Skowroński and Ważny [22] have shown that methanol is oxidized on a nickel foam electrode in 6 M KOH via a NiOOH layer formed on the electrode surface in the potential range 0.4–0.5 V vs. the Hg | HgO electrode.

The aim of this work was to make an attempt to prepare new composite electrodes for methanol oxidation in an alkaline electrolyte based on nickel foam, which is both lightweight and highly porous (above 95%), and to estimate the electrochemical activity of these electrodes.

2. Experimental

Electrochemical measurements were performed using a potentiostat-galvanostat PGSTAT 30 Autolab (Eco Chemie B.V.). All experiments were carried out in a three-electrode system. The working electrodes were: (a) a nickel | polyaniline electrode (Ni | PANI), (b) a nickel | polyaniline | platinum electrode (Ni | PANI | Pt), and (c) a nickel | platinum electrode (Ni | Pt). Nickel foam with a thickness of 1.6 mm, density 500 g/m^2, and porosity higher than 95% (produced by Nitech) was modified to prepare these electrodes. The geometrical area of all the electrodes was 1 cm^2. The counter electrode was the nickel-sintered electrode filled with cadmium hydroxide. The Hg | HgO | 6 M KOH system was employed as the reference electrode (E = 0.098 V vs. NEW). The electrolyte was a 6 M KOH solution, either with or without CH_3OH (0.1 M). The catalytic activity of all the composite electrodes in methanol oxidation was measured by cyclic voltammetry (CV) in the potential range 0.1–0.7 V at a scan rate of 50 mV/s.

Using the CV technique, the nickel foam electrode (density 500 g/m^2, thickness 1.6 mm, geometric surface 1 cm^2) was coated with polyaniline film in a freshly prepared solution of 0.1 M H_2SO_4 + 0.1 M aniline, purged with argon to remove oxygen. For each electrode, 50 oxidation/reduction cycles were made in the potential range –0.66–0.37 V vs. Hg | Hg_2SO_4 | 1 M H_2SO_4 (E = +0.674 V vs. NEW) at a scan rate of 10 mV/s. A lead sheet (containing 0.6% of Ca and 1% of Sn) was used as a counter electrode. Platinum microparticles were dispersed on the PANI film by the galvanostatic reduction of chloroplatinic acid (0.03%) in 0.1 M H_2SO_4 for 2 h using a cathodic current of 1 mA/cm^2. All measurements were performed at a temperature of 20 °C.

3. Results and discussion

Nickel | PANI electrode. The nickel | polyaniline (Ni | PANI) electrode was prepared by electrodepositing a polyaniline film on the porous surface of nickel foam. As can be seen in Fig. 1a, the nickel foam corroded in the acid solution admixed with aniline during a few cycles until a PANI film of sufficient thickness covering the electrode protected it effectively. After about the first ten cycles, the PANI film thickened systematically along with an increase in anodic peaks (Fig. 1b). The electrochemical activity of the Ni | PANI electrode for methanol oxidation was estimated in a 6 M KOH solution containing 0.1 M CH_3OH. As can be seen from Fig. 2 (solid line), the Ni | PANI electrode exhibits a total lack of electrochemical activity. Instead of an anodic peak, a steep and linear rise of current, a typical resistor-like characteristic, is observed. On the contrary, this electrode is active in a KOH solution free of CH_3OH, for which a distinct anodic peak noted at a potential of about 450 mV corresponds to the oxidation reaction $\beta\text{-Ni(OH)}_2 \rightarrow (\beta,\gamma)\text{-NiOOH}$ [21, 22] (Fig. 3, solid line).

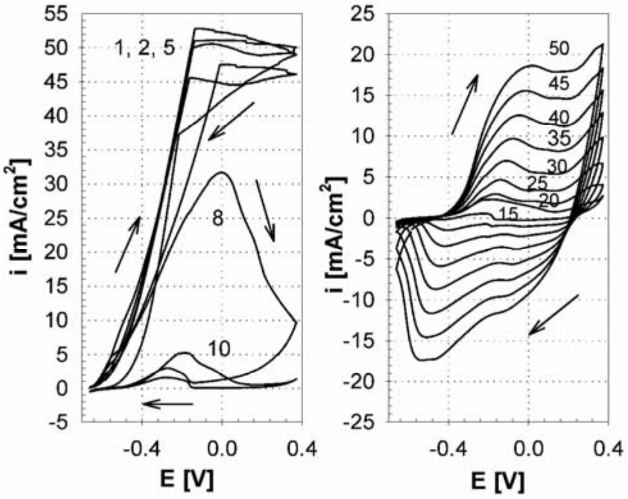

Fig. 1. Cyclic voltammograms illustrating the formation of polyaniline on the nickel foam electrode in a 0.1 M aniline | 0.1 M H_2SO_4 solution: a) cycles 1–10, b) cycles 15–50. Scan rate: 10 mV/s. Potential range: –0.66–0.37 V vs. Hg | Hg_2SO_4 | 1 M H_2SO_4

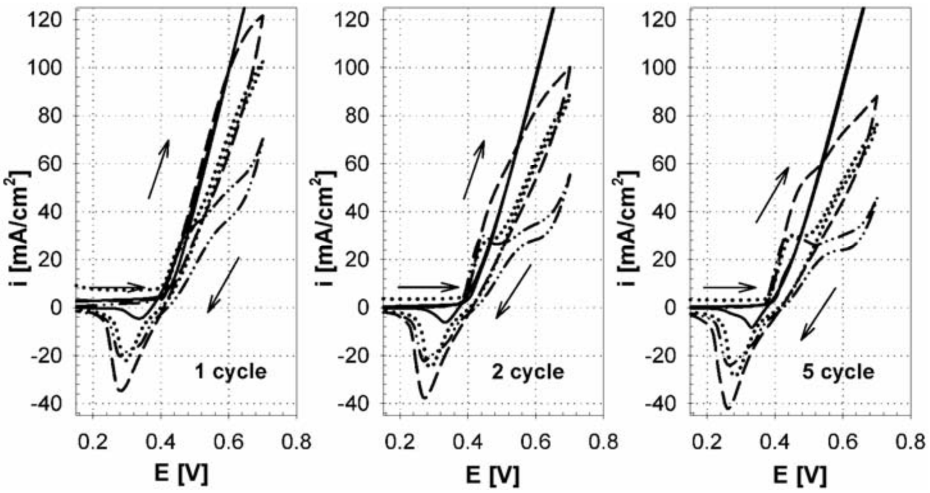

Fig. 2. Cyclic voltammograms of methanol oxidation in a 0.1 M CH_3OH | 6 M KOH solution on a nickel foam electrode (- ·· -), Ni | PANI electrode (──), Ni | PANI | Pt electrode (----), and Ni | Pt electrode (····); potential range: 0–0.70 V, scan rate: 50 mV/s

From this comparison, one can assume that the Ni | PANI electrode surface is blocked by passive products of methanol oxidation in the CH_3OH/KOH solution. The different behaviour of the electrode, depending on whether or not methanol is present in the KOH solution suggests that the PANI film is partially permeable to hydroxyl ions and that it is too dense to allow the penetration of methanol or/and the product of methanol oxidation to the nickel foam surface. From these results, one can infer that the Ni | PANI electrode can be used as a catalyst carrier, but not as a self-contained catalyst in the reaction of methanol oxidation. Taking this into account, in the following experiments the PANI film was used as an organic substrate for the platinum catalyst.

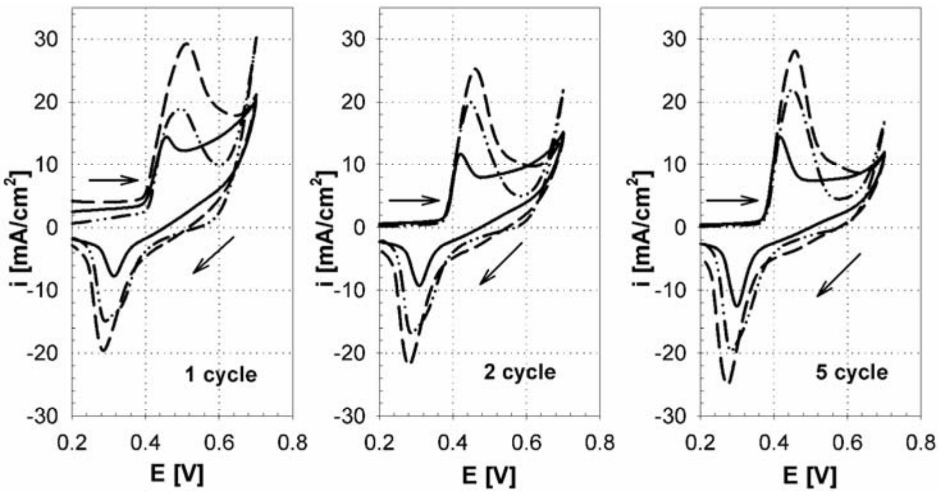

Fig. 3. Cyclic voltammograms recorded in 6 M KOH for
a nickel foam electrode (- ·· -), Ni | PANI electrode (—), Ni | PANI | Pt electrode (----),
and Ni | Pt electrode (····); potential range: 0–0.70 V, scan rate: 50 mV/s

Nickel | PANI | platinum electrode. The deposition of platinum particles on a freshly prepared polyaniline film was carried out using the CV technique. The obtained three-component electrode (Ni | PANI | Pt) was examined in a CH_3OH/KOH solution (Fig. 2, dashed line) and the recorded CV curves were compared to those obtained in a pure KOH solution (Fig. 3, dashed line). From comparing these figures, it is clear that after the Pt particles are dispersed on the PANI film, the catalytic activity of the Ni | PANI | Pt electrode, expressed by an anodic peak positioned in the potential range of the Ni(II) → Ni(III) transformation, is considerably higher in a methanol-containing electrolyte than in a pure KOH solution. The increase in anodic charge can simply be related to methanol oxidation. The reactivation of the Ni | PANI electrode towards methanol oxidation due to incorporating Pt particles into the PANI matrix may be accounted for by changes in the morphology of the polymeric layer covering the Ni substrate, and by the formation of some connections between the Ni surface and PANI layer. In this way, the Pt catalyst dispersed in the polymer lattice acts as both a catalyst for methanol oxidation and a promotor of the Ni(II) → Ni(III) oxidation reaction. Such an explanation is consistent with CV curves for different types of electrodes (Fig. 2). The contribution of the polyaniline matrix to increasing the electrochemical activity is substantiated by the fact that methanol oxidizes less effectively on the Ni | Pt electrode (Figs. 2 and 4).

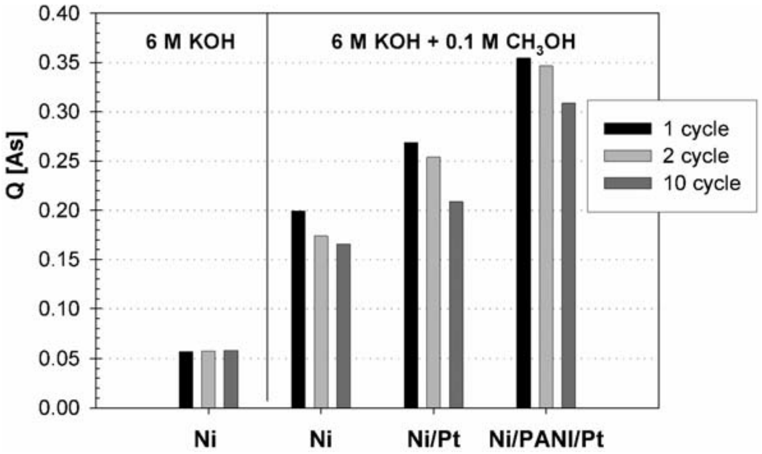

Fig. 4. Effectiveness of various electrodes in methanol oxidation estimated by comparing anodic charges calculated from CV curves recorded in a solution of 0.1 M CH_3OH | 6 M KOH (Fig. 2) and 6 M KOH (Fig. 3). Potential range: 0.38–0.60 V

Nickel | platinum electrode. The influence of platinum on the activity of nickel foam electrodes towards methanol oxidation is illustrated on the CV curves in Figure 2 (dotted line). It is clearly seen from this figure that after platinum is deposited the anodic peak attributed to methanol oxidation increases in intensity and is shifted by about 100 mV, compared to that of uncovered nickel foam. This result shows that the presence of platinum particles modifies the mechanism of the reaction $\beta\text{-Ni(OH)}_2 \rightarrow (\beta,\gamma)\text{-NiOOH}$ in such a way that the formation of Ni(III) ions becomes easier. This phenomenon remains to be examined in the future.

4. Conclusions

Nickel foam can be successfully modified to prepare a new type of electrode material for methanol electrooxidation in alkaline solution. Based on the differences in the anodic charge of the current peaks recorded in a CH_3OH/KOH solution (Fig. 2), the catalytic activities of the examined electrodes can be concluded to decrease in the order: Ni | PANI | Pt > Ni | Pt > nickel foam (Fig. 4). As can be seen from Fig. 4, the activity of the Ni | PANI | Pt electrode is about 30% higher compared to the Ni | Pt electrode, and about 75% higher compared to the unmodified nickel foam electrode. It was clearly shown that the activity of the unmodified electrode can be improved after coating the nickel surface with platinum. It is likely that the presence of Pt particles makes the $Ni(OH)_2 \rightarrow NiOOH$ reaction more effective and, as a consequence, more active NiOOH species can take part direct methanol oxidation. The best results were obtained for a sandwich-like electrode consisting of three layers - Ni | PANI | Pt. It is assumed that the polyaniline interlayer enhances the dispersion of platinum and brings about the formation of Ni-Pt sites, which facilitate charge transfer for oxidizing methanol. The Ni | PANI | Pt electrode seems to be a promising catalyst for methanol oxidation, for which high current densities can be reached in practical fuel cells (it exceeds 100 mA/cm^2 in Fig. 2). Figure 4 shows that the anodic charge associated with methanol oxidation decreases on cycling. In the future, three possibilities should be taken into account to elucidate this phenomenon: (a) an exhaustion of methanol at the electrode/electrolyte interface, (b) changes in the chemical composition and structure of nickel oxide, (c) the role of organic poisoning intermediates formed during methanol oxidation.

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