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Preparation of catalytic anodes for methanol oxidation by spontaneous deposition of Pd onto porous Ni or porous Co

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ABSTRACT

Spontaneous deposition of Pd onto porous electrodeposits of either Ni or Co yields active anodes for the oxidation of methanol and ethanol in basic aqueous media. These electrodes may sustain steady-state currents of the order of 0.25 A cm^{-2}. Their peak current per unit Pd mass is about 100 A g^{-1}.

1. Introduction

Catalysis of methanol oxidation is a hot topic due to its relevance in the operation of direct methanol fuel cells. Most investigations were focussed on acid media. However, the interest in alkaline direct alcohol fuel cells has recently increased [1,2], in spite of the tendency of basic aqueous media to become polluted by CO_2 and acid oxidation intermediates. An advantage of basic media is that less expensive electrode materials can be used: Pd, at present about 4 times cheaper than Pt, although almost inert in acid media [3], is an active catalyst for the oxidation of methanol [4,5] and other alcohols [1,2] in basic media. Many groups are investigating ways to minimize the Pd loading in the electrodes. A common approach is using variously prepared Pd nanoparticles [5–8]. An alternative approach is the deposition of Pd (or Pd alloyed with non-noble metals) onto substrates with large effective surface area; for instance, Miao et al. [9] supported Ni–Pd catalysts, formed by an electroless process, onto silicon microchannel plates. In the present communication we report on the preparation and performance of electrodes produced by spontaneous deposition of Pd onto porous layers of either Ni or Co. Porous Ni was deposited according to Marozzi and Chialvo [10]; porous Co was deposited from basic sulphate solutions previously used by Jovic et al. [11] to produce Co powders. Pd deposits were then formed onto these porous substrates via a spontaneous deposition process in which Pd^{2+} ions displaced Ni or Co.

2. Experimental

2.1. Electrode preparation

Anodes for the oxidation of alcohols were prepared by a two-step procedure involving: (i) the electrodeposition onto Ni rotating disc electrodes (0.317 cm^2 area) of either porous Ni layers in 0.2 M $NiCl_2$ + 2 M NH_4Cl aqueous solution, pH 4.5, at −1 A cm^{-2} [10], or porous Co layers in 0.1 M $CoSO_4$ + 1.0 M $(NH_4)_2SO_4$ + 0.7 M NH_4OH aqueous solution, pH 11, at −0.05 A cm^{-2} [11], and then (ii) the spontaneous deposition of Pd by immersion of these layers in acid, deaerated $PdCl_2$ solutions. The main experimental variables were the deposition charge in step (i), the $PdCl_2$ concentration and the duration of the immersion in step (ii). The pH of the $PdCl_2$ solutions was either 1 or 2, i.e. it was in a range where no hydrolysis of Pd^{2+} chloride complexes to give PdO is expected and where minor amounts of Ni or Co oxides, possibly formed by atmospheric oxidation of porous electrodeposits, should be readily dissolved.

2.2. Electrode characterization

SEM images were obtained with a FEI Quanta 200 FEG ESEM instrument. Electrochemical experiments were carried out with an Autolab PGSTAT 302N, in a three-electrode cell with a Pt wire counter electrode (ca. 10 cm^2 area) and an Hg|HgO|1 M KOH reference

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electrode to which potentials are referred. The electrodes were submitted to cyclic voltammetry in 1 M KOH, to monitor the Pd deposition. The catalytic activity of the electrodes was studied by recording cyclic voltammograms (typically at 10 mV s^{-1}) and pseudo-steady-state curves (each potential imposed for 4 min) in deaerated KOH + methanol or KOH + ethanol solutions. All experiments were performed at 25 °C. The mass of deposited Pd was estimated by analyzing, with an UV–Visible spectrophotometer, the solutions used for spontaneous deposition and measuring the variation in their Pd^{2+} concentration [12]. This method was preferred to measuring the electrode weight variation, which is the result of both Pd deposition and Ni dissolution, the latter process being partially coupled with H^{+} reduction that takes place as a side reaction.

3. Results and discussion

3.1. Voltammetries in 1 M KOH

Fig. 1, curve a, shows a voltammogram recorded with a porous Ni electrode (deposition charge 60 C cm^{-2}): the redox system centred at ca. 0.45 V is due to the NiO/NiOOH couple [13]; the associated redox charge is ca. 20 times higher than that measured with a polished Ni electrode of the same geometric area. Curves b and c show, after immersion of the porous Ni electrode in an acid PdCl$_2$ solution, the appearance of an oxidation current at E > −0.4 V and of a cathodic peak at ca. −0.29 V, due to PdO reduction [14]. The size of this peak increases with the immersion time in the PdCl$_2$ solution. The peak current density measured after a 3-hour immersion is ca. 55 times higher than that measured with a polished Pd electrode. The size of the peaks due to the NiO/NiOOH redox system also increases with the immersion time, because Ni corrosion promoted by Pd^{2+} (and H^{+}) reduction tends to further enhance the porous Ni surface area, and the Pd deposits do not entirely coat the Ni surface (see SEM images below). Similar phenomena were observed in the spontaneous deposition of either Ru or Ir [15].

3.2. SEM characterization

SEM images of as-deposited porous Ni (a, a′) and Pd-modified Ni layers (b, b′, c, c′) are compared in Fig. 2. The Pd-modified electrodes retain the typical morphology of porous Ni deposits, consisting of rounded columnar dendrites, grown perpendicularly to the electrode surface [16]. The growth of spiky Pd microcrystals onto Ni, more evident after the longer immersion, is not homogeneous: the protruding parts of the Ni layer are more heavily decorated by Pd crystals than the recessed ones. These images and the persistence of the NiO/NiOOH redox system in the voltammograms (Fig. 1) suggest that the reactions of Ni oxidation and Pd reduction involved in the deposition process are preferentially localized in different areas.

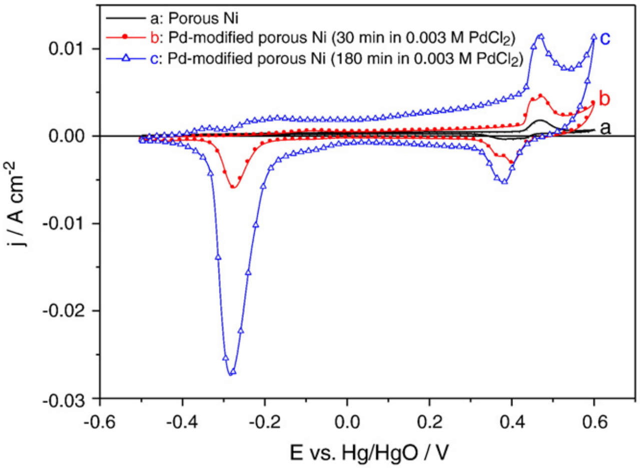

Fig. 1. Cyclic voltammograms recorded with porous Ni (a) and Pd-modified porous Ni electrodes (b,c) in 1 M KOH. Sweep rate: 10 mV s^{-1}. The 4th cycle is shown.

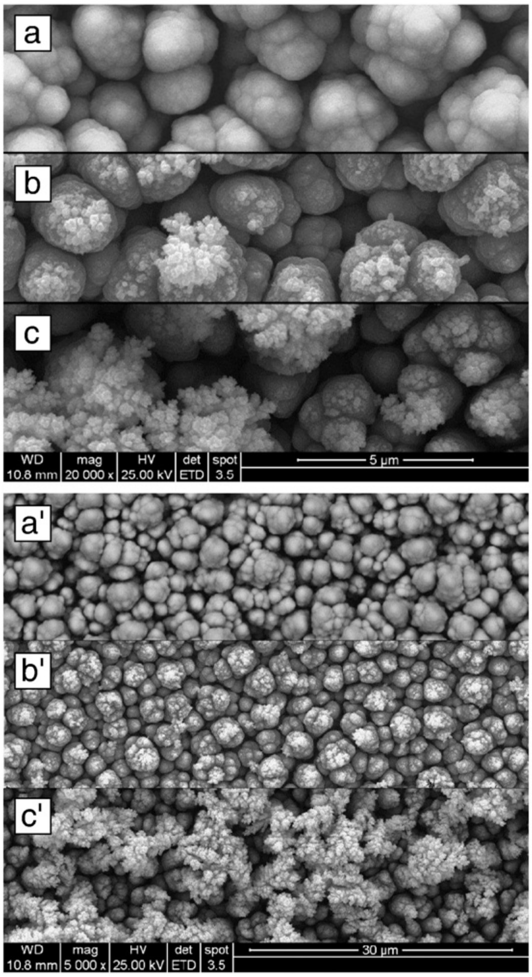

Fig. 2. SEM images of porous Ni layers, as-deposited (a, a′) or modified by immersion in 0.01 M PdCl$_2$, pH 2, for 10 min (b, b′) or 30 min (c, c′).

3.3. Methanol (and ethanol) oxidation

The voltammetric curves obtained with a Pd-modified porous Ni electrode in either methanol or ethanol solution are shown in Fig. 3, curves a and b, respectively. Their shape is the one currently observed with Pd electrodes [5]: during the scan towards positive potentials an oxidation current flows (from −0.5 V onward for methanol, from −0.6 V onward for ethanol) a current peak is observed (at 0.07 V for methanol, at −0.08 V for ethanol) followed by passivation due to electrode poisoning [17] and/or Pd surface oxidation [18]; during the reverse sweep the electrode undergoes a sharp depassivation. The peak current (j_P) is about twice higher for methanol than for ethanol, in agreement with Ref. [7]. The peak currents are ca. 500 times higher than those measured, under the same conditions, at a polished Pd electrode and comparable to the j_P value of 0.35 A cm^{-2} measured by Miao et al. [9] in 2 M KOH + 1 M CH_3OH, at 50 mV s^{-1}, i.e. with twice higher methanol and KOH concentrations, and a higher sweep rate. The oxidation current of either alcohol measured with an unmodified porous Ni electrode is negligible in the same potential range. Curve c in Fig. 3 shows that the performance of a Pd-modified porous Co electrode is comparable, in methanol oxidation, to that of Pd-modified porous Ni.