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Electrolysis Using Composite Plated Electrodes.[1] Preparation of a Binary Type Composite Plated Nickel Electrode with Poly(tetrafluoroethylene) and Silica Gel and Its Application in Electroreduction of Aldehydes

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A binary type composite plated nickel electrode with poly(tetrafluoroethylene) and silica gel as hydrophobic and hydrophilic components, respectively, was prepared and applied to electroreduction of aldehydes. The electrode gave higher current efficiencies for the reduction and higher selectivities for the corresponding alcohols than unplated and plated electrodes with either poly(tetrafluoroethylene) or silica gel.

It is known that metals can be composite plated with fine particles of a variety of non-conducting materials suspended in plating baths.[2] The composite plating of nickel with hydrophobic materials, such as poly(tetrafluoroethylene) (PTFE; Teflon®), tetrafluoroethylene oligomer and fluorocarbon affords mechanically stable plating films with hydrophobic properties.[3]

In our previous work,[1, 4–12] a variety of hydrophobic electrodes, which are electrochemically stable, were prepared by the above composite plating technique and applied in the electrolysis of organic compounds. The hydrophobic electrodes were also found to suppress oxygen and hydrogen evolution in aqueous electrolytic solutions and, consequently to increase the current efficiencies of the desired reactions by a 'dissolved organic molecule concentrating' effect on the hydrophobic surfaces.

Among the hydrophobic electrodes, an Ni/PTFE composite plated electrode is characterized to be an electrode which can be used as both cathode and anode in acidic and alkaline solutions, respectively. In this work, R values defined below were preliminarily estimated from a number of experimental data previously reported.

$$R = \frac{\text{Current efficiency on a composite plated Ni/PTFE electrode}}{\text{Current efficiency on an unplated Ni electrode}}$$

As result, the R values are 1 to 3 when Ni/PTFE is used as a cathode, while larger than 10 in the Ni/PTFE anode. The Ni surface of the Ni/PTFE cathode should be bare and less

hydrophilic than that of the Ni/PTFE anode because it is covered by a nickel oxide film which is more hydrophilic than Ni itself. On the other hand, most of electroorganic processes involve stoichiometrically and/or mechanistically H_2O (H^+ and OH^- species for reduction and oxidation, respectively). Hence, a suitable amount of H_2O on the surface may be required to obtain a high current efficiency, even if on the hydrophobic electrode. From this point of view, we can have the following hypothesis: If the hydrophobic Ni/PTFE cathode has hydrophilic microzones which attract H_2O but the H_2O molecules are not electrolyzed to evolve hydrogen, a higher current efficiency for the reduction of organic compounds can be expected.

In order to examine this hypothesis, a composite plated nickel cathode with PTFE and silica gel (SiO_2) as hydrophobic and hydrophilic components, respectively, was prepared and applied in the electroreduction of aldehydes as a model reaction in this work.

This is the first report of binary composite plating.

A nickel (99.7% pure) plate (3 cm x 3 cm x 0.02 cm) was polished with alumina powder (1 μm) to give it a mirror surface and then was treated with 10% HCl to activate the surface. The plate was put between two nickel anodes in a plating bath (250 cm^3) which was stirred by a magnet bar. The bath consisted of $Ni(NH_2SO_2)_2 \cdot 4H_2O$ (350 g dm^{-3}), $NiCl_2$ (30 g dm^{-3}), H_3BO_3 (40 g dm^{-3}), PTFE (0.2 μm; 40 g dm^{-3}), SiO_2 (5 μm; 40 g dm^{-3}) and $C_8F_{17}SO_2NH(CH_2)_3(CH_3)_3NI$

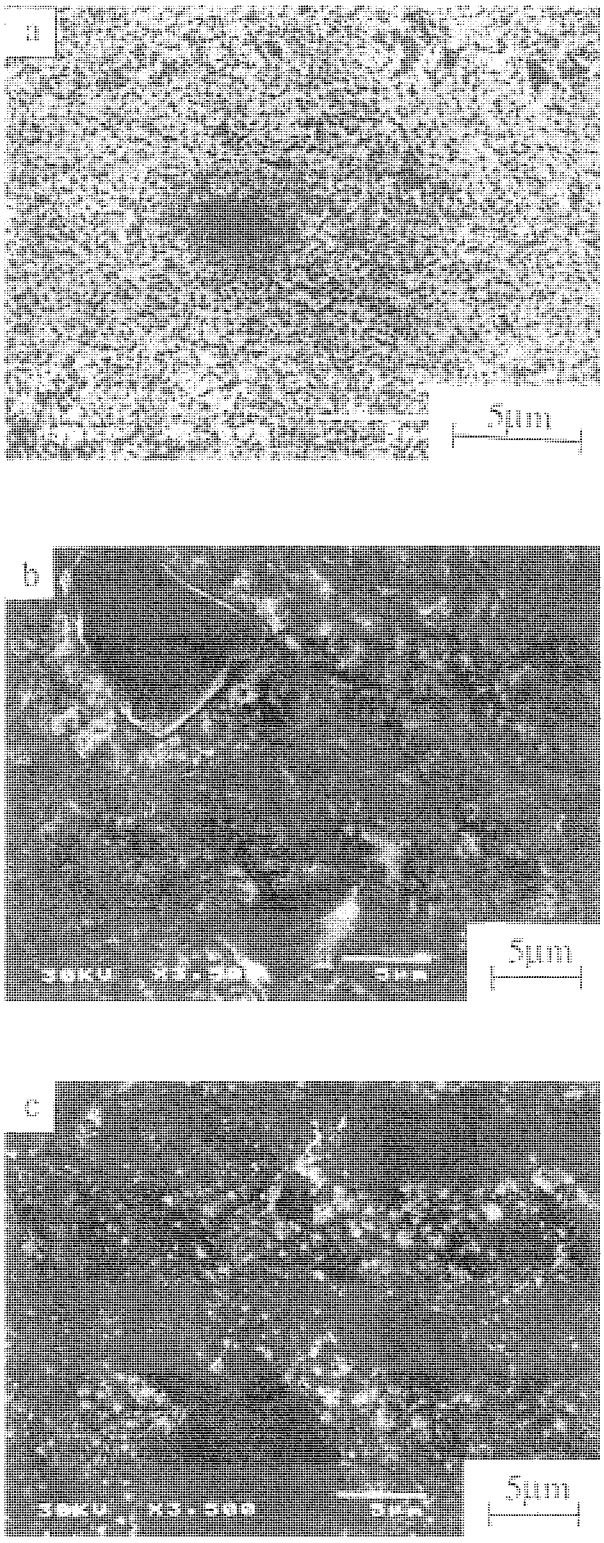

Fig. 1. Scanning electron microscopic photographs of the surface of composite plated (a) Ni/SiO_2, (b) Ni/PTFE and (c) Ni/(PTFE + SiO_2) electrodes.

(surfactant; 4 g dm^{-3}). The plating of Ni/(PTFE + SiO_2) was carried out at a current density of 20 mA cm^{-2} by passing electricity of 2000 C at 35 °C. An Ni/SiO_2 electrode was also prepared in a similar procedure without PTFE. An Ni/PTFE electrode was prepared in a procedure described in a previous report. [4]

After plating, the plating film obtained was rinsed with acetone and H_2O, and then dried. The contact angle between the plated surface and a H_2O droplet was measured using a contact angle meter (ERMA G-1). Corrections for gravitational deformation and evaporation of the droplet were not made, though they might cause the contact angle to be underestimated. The inclusion of PTFE and SiO_2 in the film was confirmed by scanning electron microscopy (JSM-T220).

An H-shaped divided cell equipped with various cathodes (3 cm x 3 cm) and a platinum anode (3 cm x 4 cm) was used for electroreduction of aldehydes. The catholyte was a 0.5 M H_2SO_4/H_2O-CH_3OH (1:1) solution. The electrolysis was carried out galvanostatically at 10 mA cm^{-2} of current density by passing 0.33 and 1.0 mol electron mol^{-1} of charge for the reduction of benzaldehyde and butylaldehyde, respectively, at room temperature. The reduction products were analyzed by methods described in previous reports. [1–9]

Figure 1 (a) shows a scanning electron microscopic photograph of the surface of an Ni/PTFE electrode. PTFE particles (0.2 μm) are clearly observed. Larger SiO_2 particles (5 μm) are also observed on a photograph for an Ni/SiO_2 electrode (Fig. 1 (b)). On the other hand, the PTFE and SiO_2 particles can be distinguished on a photograph for an Ni/(PTFE + SiO_2) from a difference in their sizes (Fig. 1 (c)).

It should be noted that the preparation of the Ni/(PTFE + SiO_2) electrode gives the first example of binary type composite plating.

In order to examine experimentally the hypothesis described above, the reduction of aldehydes (RCHO) was carried out using composite plated Ni/(PTFE + SiO_2) (contact angle with water, 114°), Ni/PTFE (146°) and Ni/SiO_2 (19°) electrodes, and an unplated Ni electrode (24°) with different hydrophobicities. The reduction gave a mixture of the corresponding 1- and 2-electron reduction products such as RCH(OH)CH(OH)R and RCH_2OH, respectively.

$$RCHO \xrightarrow{e + H^+ / 2e + 2H^+} \frac{1}{2} RCH(OH)CH(OH)R / RCH_2OH$$

Table 1 shows results of the reduction. The hydrophobic Ni/PTFE cathode (Run 3) gave a higher current efficiency for the reduction and product selectivity for RCH_2OH than the hydrophilic Ni/SiO_2 (Run 2) and unplated Ni (Run 1) cathodes. This fact has been already confirmed in previous work. [4] Interestingly, the Ni/(PTFE + SiO_2) cathode (Run 4) gave a much higher current efficiency than the Ni/PTFE one (Run 3), though the former is less hydrophobic. Similar results were also obtained in the reduction of other aldehydes (Run 5 - 12).

On the basis of the above results, it can be stated that the hypothesis was proved in this work. Further investigations on the effect of SiO_2 in the Ni/(PTFE + SiO_2) electrode on electroorganic processes are in progress.

Table 1. Electroreduction of aldehydes (RCHO)

Run	R	Cathode	Current efficiency for reduction /%	Product selectivity for RCH_2OH /%
1	C_6H_5	Ni	22	74
2	C_6H_5	Ni/SiO_2	20	89
3	C_6H_5	Ni/PTFE	51	91
4	C_6H_5	$Ni/(PTFE + SiO_2)$	67	100
5	$p\text{-}CH_3C_6H_4$	Ni	21	92
6	$p\text{-}CH_3C_6H_4$	Ni/SiO_2	25	94
7	$p\text{-}CH_3C_6H_4$	Ni/PTFE	50	100
8	$p\text{-}CH_3C_6H_4$	$Ni/(PTFE + SiO_2)$	75	100
9	$CH_3(CH_2)_2$	Ni	16	100
10	$CH_3(CH_2)_2$	Ni/SiO_2	21	100
11	$CH_3(CH_2)_2$	Ni/PTFE	30	100
12	$CH_3(CH_2)_2$	$Ni/(PTFE + SiO_2)$	63	100

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