Electrolysis Using Composite-plated Electrodes X. Preparation of Hydrophobic Nickel and Zinc Electrodes Composite-plated with Fluorinated Pitch and Their Application in Electroreduction of Organic Compounds

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Hydrophobic electrodes were prepared by composite-plating of metals (nickel and zinc) with fine particles of fluorinated pitch as a new hydrophobic material. The electrodes were used for electroreduction of organic compounds to give current efficiencies and product selectivities higher than those obtained at electrodes unplated and composite-plated with ordinary hydrophobic materials such as poly(tetrafluoroethylene) (Teflon®) and tetrafluoroethylene oligomer which have been previously reported.

1 INTRODUCTION

It is known that metals can be composite-plated with fine particles of a variety of non-conducting materials suspended in plating baths¹⁾. The composite-plating of nickel with hydrophobic materials, such as poly(tetrafluoroethylene) (PTFE; Teflon®), tetrafluoroethylene oligomer (TFEO) and fluorocarbon ((CF)_n) affords mechanically stable plating films having hydrophobic properties²⁾.

In our previous work³⁻¹¹⁾, hydrophobic nickel, zinc and lead electrodes, i.e. Ni/PTFE, Ni/TFEO, Ni/(CF)_n, Zn/TFEO, Zn/(CF)_n, Pb/PTFE and Pb/(CF)_n, which are electrochemically stable, were prepared by the above technique and were applied in the electrolysis of a variety of organic compounds as cathodes and/or anodes. The hydrophobic electrodes were also found to suppress hydrogen and oxygen evolution in aqueous electrolytic solutions and, consequently, to increase the current efficiencies for the desired reactions by 'dissolved organic molecule-concentrating', 'emulsified organic droplet-

collecting' and 'dehydration-promoting' effects on the hydrophobic surfaces.

Recently, a production method for fluorinated pitch (FP) has been established¹²⁾. FP has received much attention as a new hydrophobic material because of its very high hydrophobicity. The aim of this work was to prepare new nickel and zinc hydrophobic electrodes composite-plated with FP and to apply them to the electroreduction of organic compounds as cathodes.

2 EXPERIMENTAL

A nickel (99.7% pure) plate (3 cm × 3 cm × 0.02 cm) was polished with alumina powder (1 μm) to give it mirror surface, washed repeatedly with acetone and water, and then was treated with 10% HCl to activate the surface. A zinc (99.99% pure) plate (2 cm × 3 cm × 0.03 cm) was also polished and then washed repeatedly with acetone and water. The plates were put between two nickel or zinc anodes (5 cm × 6 cm) in plating baths (250 cm³) which were stirred by a magnet bar.

The bath for nickel plating consisted of Ni (NH₄SO₄)₂·4H₂O (350 g dm⁻³), NiCl₂ (30 g dm⁻³), H₃BO₃ (40 g dm⁻³), FP (20 - 160 g dm⁻³) and C₈F₁₇SO₂NH(CH₂)₃(CH₃)₃NI (surfactant) (15 - 35 mg (g-FP)⁻¹). The plating was carried out at 35 - 55°C of bath temperature by passing 500 C of

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electricity at 20 - 140 mA cm⁻² of current density.

On the other hand, zinc was plated in a bath containing Zn(BF₄)₂ (350 g dm⁻³), NH₄Cl (30 g dm⁻³), NH₄BF₄ (40 g dm⁻³), FP (20 - 120 g dm⁻³) and C₈F₁₇SO₂NH(CH₂)₃(CH₃)₃NI (surfactant) (20 - 70 mg (g-FP)⁻¹) at 30 - 55°C by passing 500 - 1000 C at 20 - 70 mA cm⁻². FP (average particle size, 0.6 μm; molecular weight, 1000 - 2000; contact angle with water, 145°; density, 2.0 g cm⁻³) was supplied from Osaka Gas Co.

After plating, the plating film obtained was rinsed with water and acetone, and then dried.

The contact angle between the plated surface and a water droplet was measured using a contact angle meter (ERMA GI-1000). Corrections for gravitational deformation and evaporation of the droplet were not made, though they might cause the contact angle to be underestimated. The angle thus obtained was reproduced to within an error of ± 5% in repeated experiments. The inclusion of FP particles in the plating film was confirmed by scanning electron microscopy (SEM) (JEOL JSM-T220). The amount of the

plating film was estimated from the weight gain after plating. The film was dissolved into a nitric acid solution by dipping or anodic stripping. The amount of FP particles contained in the film was obtained by collecting them on a PTFE filtering membrane (0.2 μm). The content in volume per cent of FP in the film was indicated by conversion on the basis of densities of FP and Ni or Zn.

Cathodic polarization curves on composite-plated Ni/FP and unplated Ni electrodes (diameter, 0.6 cm) were measured in 0.5 M (M = mol dm⁻³) H₂SO₄ and 1.0 M HCl at room temperature by a steady state method⁶. A divided cell was used and the catholyte (50 cm³) was degassed with nitrogen for 30 min before the measurement.

An H-shaped divided cell equipped with various cathodes prepared by composite plating and a platinum anode (3 cm × 4 cm) was used for electroreduction of organic compounds (2.5 mmol) in catholytes (50 cm³). Ni/PTFE⁴, Ni/TFEO⁹ and Zn/TFEO¹¹) cathodes were prepared using procedures described in previous

Table 1 Influence of composite plating conditions on the contact angle of Ni/FP films with water.

Run	Composite plating conditions				Contact angle /degree
	FP /g dm ⁻³	Temp. /°C	Current density /mA cm ⁻²	surfactant /mg (g-FP) ⁻¹	
1	20	45	40	35	99
2	80	45	40	35	147
3	120	45	40	35	154
4	140	45	40	35	160
5	160	45	40	35	152
6	140	35	40	35	161
7	140	55	40	35	156
8	40	45	20	35	135
9	40	45	40	35	139
10	40	45	80	35	144
11	40	45	140	35	125
12	140	45	40	15	— ^{a)}
13	160	45	20	35	152 ^{b)}

a) No smooth surface was obtained.

b) 30 vol% FP was contained in the film.

Table 2 Influence of composite plating conditions on the contact angle of Zn/FP films with water.

Run	Composite plating conditions				Contact angle /degree
	FP /g dm ⁻³	Temp. /°C	Current density /mA cm ⁻²	surfactant /mg (g-FP) ⁻¹	
14	40	30	70	60	146
15	60	30	70	60	129
16	80	30	70	60	133
17	20	30	70	70	131
18	20	55	70	70	85
19	40	30	35	60	139
20	40	30	70	60	145
21	140	33	35	70	154 ^{a)}

a) 20 vol% FP was contained in the film.

reports. The catholytes were 0.8 M H₂SO₄/H₂O-CH₃OH(4:1) and/or 1.5 M HCl/H₂O-CH₃OH(4:1) for the reduction of aldehydes (benz-, butyl-, and n-octylaldehydes) and 0.5 M (C₂H₅)₄NBr/CH₃OH for benzyl bromides (benzyl and α -methylbenzyl bromides) and other organobromides (phenyl, n-octyl, phenethyl and 2-n-pentyl bromides). The electrolysis was carried out galvanostatically at a current density of 10 mA cm⁻² by passing 1 mol electron mol⁻¹ of charge at room temperature.

The reduction products of the aldehydes, benzyl bromides, phenyl bromide and other bromides were analyzed by gas chromatography (2 m Chromosorb 101 column, 130 - 230°C; 20 m OV-17 capillary column, 55 - 150°C; 0.75 m Chromosorb 101 column, 130°C; 2.0 m DEGS column, 50°C, respectively) thus obtained were reproduced to within a relative error of $\pm 10\%$ in repeated experiments using newly prepared electrodes.

Fig. 1 Scanning electron microscopic (SEM) photographs of the surface of composite plated (a) Ni/FP and (b) Zn/FP electrodes.

3 RESULTS AND DISCUSSION

After trial and error, certain kinds of nickel sulfamate and zinc tetrafluoroborate baths containing $C_6F_{17}SO_2NH(CH_2)_3(CH_3)_3NI$ as a surfactant were selected for composite plating nickel and zinc, respectively, as described in EXPERIMENTAL section.

Furthermore, semi-optimization for plating conditions such as the content of FP, temperature, current density and the amount of surfactant was performed. Tables 1 and 2 show influences of these conditions on the contact angle of composite plated Ni/FP and Zn/FP electrodes, respectively.

Ni/FP and Zn/FP plating films with the largest contact angles of 161° (Run 6) and 154° (Run 21), respectively, were obtained. These values are larger than 121° for Ni/PTFE⁹⁾ and 150° for Ni/TFEO and Zn/TFEO¹¹⁾. Although an Ni/TFEO film with an extremely large contact angle of 173° was reported⁹⁾, it did not seem stable enough to use as an electrode in electrolysis for a long time. In this work, Ni/FP and Zn/FP electrodes were mass-produced under conditions for Runs 13 and 21, respectively, to use them for the measurement of polarization curves and the electroreduction of organic compounds. The plating films of these Ni/FP and Zn/FP electrodes had 152° and 154° of contact angles, and contained FP in 30 and 20 vol%, respectively. Their

Fig. 2 Cathodic polarization curves on unplated Ni and composite plated Ni/FP electrodes in (a) 0.5 M H_2SO_4 and (b) 1.0 M HCl.

Table 3 Electroreduction of aldehydes (RCHO).

Run	R	Cathode	Supporting Electrolyte	Current efficiency
				/%
22	Ph	Ni	H_2SO_4	32
23	Ph	Ni/PTFE	H_2SO_4	72
24	Ph	Ni/FP	H_2SO_4	21
25	Ph	Ni	HCl	32
26	Ph	Ni/PTFE	HCl	79
27	Ph	Ni/FP	HCl	75
28	$CH_3(CH_2)_2$	Ni	HCl	0
29	$CH_3(CH_2)_2$	Ni/PTFE	HCl	18
30	$CH_3(CH_2)_2$	Ni/FP	HCl	24
31	$CH_3(CH_2)_6$	Ni	HCl	14
32	$CH_3(CH_2)_6$	Ni/PTFE	HCl	19
33	$CH_3(CH_2)_6$	Ni/FP	HCl	21

Table 4 Electroreduction of benzyl bromides (PhCH(R)Br).

Run	R	Cathode	Current efficiency /%	Selectivity for PhCH ₂ R /%
34	H	Ni	58	93
35	H	Ni/TFEO	61	97
36	H	Ni/FP	77	100
37	H	Zn	93	68
38	H	Zn/TFEO	93	90
39	H	Zn/FP	96	100
40	CH ₃	Zn	92	80
41	CH ₃	Zn/TFEO	95	88
42	CH ₃	Zn/FP	99	100

Table 5 Electroreduction of bromides (RBr) other than the benzyl bromides.

Run	R	Cathode	Current efficiency /%
43	Ph	Zn	24
44	Ph	Zn/FP	28
45	Ph(CH ₂) ₂	Zn	57
46	Ph(CH ₂) ₂	Zn/FP	74
47	CH ₃ (CH ₂) ₇	Zn	24
48	CH ₃ (CH ₂) ₇	Zn/FP	39
49	CH ₃ (CH ₂) ₂ CHCH ₃	Zn	37
50	CH ₃ (CH ₂) ₂ CHCH ₃	Zn/FP	40

surfaces were visually smooth and the SEM photographs of them are shown in Fig. 1. Since blacky and white zones in the SEM photographs correspond to the occurrence of FP and metals (Ni and Zn), respectively, FP particles seem to disperse in the film surfaces. No cross section photographs were taken because of technical difficulty in preparation of the specimens.

In previous work⁶, it was found that the hydrogen overvoltage of an Ni/PTFE cathode in an aqueous H₂SO₄ solution is lower than that of an unplated Ni one. However, the overvoltage of an Ni/FP cathode was higher than that of the unplated Ni cathode as shown Fig. 2 (a). After the polarization, the Ni/FP cathode lost its hydrophobicity. Any reason for this abnormal

phenomenon has not been clarified. On the other hand, the Ni/FP cathode exhibited normally a lower overvoltage in an aqueous HCl solution than the unplated Ni one as shown in Fig. 2 (b).

Electroreduction of aldehydes in a strongly acidic solution gives the corresponding alcohols as main products as shown in the following equation:

As shown in Table 3, the current efficiency for the reduction of benzaldehyde at the Ni/FP cathode (Run 24) in a 0.8M H₂SO₄/H₂O-CH₃OH was lower than those at unplated Ni (Run 22) and plated Ni/PTFE (Run 23) cathodes. After the electrolysis, the hydrophobicity of the Ni/FP

cathode was completely lost. However, the Ni/FP cathode (Run 27) gave an efficiency comparable to that at the Ni/PTFE cathode (Run 25) in 1.5 M HCl/H₂O-CH₃OH. Although this phenomenon was not rationalized, the HCl solution was also used in the reduction of other aliphatic aldehydes and the Ni/FP cathode gave higher efficiencies than the unplated Ni and Ni/PTFE cathodes (Run 28 - 33).

The electroreduction of benzyl bromides (PhCH(R)Br) gave a mixture of PhCH₂R and PhCH(R)CH(R)Ph as the 2- and 1- electron reduction products, respectively, in 0.5 M (C₂H₅)₄NBr/CH₃OH.

As shown in Table 4, the Ni/FP (Run 36) and Zn/FP (Runs 39 and 42) cathodes gave higher current efficiencies for the reduction and product-selectivities for the 2-electron reduction product (PhCH₂R) than the unplated Ni (Run 34) and Zn (Runs 37 and 40) cathodes, and also than the composite plated Ni/TFEO (Run 35) and Zn/TFEO (Runs 38 and 41) cathodes. It is noticeable that the cathodes composite plated with FP gave PhCH₂R in 100% selectivity. Such a high selectivity in dry CH₃OH may be rationalized as due to the radical intermediate stabilizing effect on the cathodes^{11, 13}.

The electroreduction of bromides (RBr) other than benzyl bromides in 0.5 M (C₂H₅)₄NBr/CH₃OH gave the corresponding 2-electron reduction products (RH) as sole products, regardless of the cathodes used.

The Zn/FP cathode (Runs 44, 46, 48 and 50) gave higher current efficiencies for the reduction

than the unplated Zn cathode (Runs 43, 45, 47 and 49) as shown in Table 5.

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