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Cathodic Reduction of Carbonyl Compounds at a Nickel-Poly(tetrafluoroethylene) Composite-plated Electrodes[1)]

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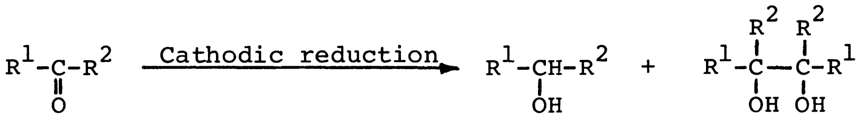
A nickel electrode composite-plated with nickel and poly(tetrafluoroethylene) was used in the cathodic reduction of carbonyl compounds to give high current efficiencies for the corresponding alcohols in aqueous sulfuric acid. This fact may indicate that this hydrophobic electrode has apparently a high hydrogen-overvoltage and consequently suppresses effectively hydrogen evolution.

Obviously it is not easy to reduce substrates having highly negative reduction potentials in high current efficiencies in aqueous acidic solutions, since considerable amount of hydrogen evolves. For efficient reduction of such substrates, therefore it is generally recommended to use (a) high hydrogen-overvoltage cathodes such as mercury, lead, and cadmium, (b) hydrogen-active cathodes such as metal blacks and Raney metals, and (c) quaternary ammonium salt supporting electrolytes. However, the high hydrogen-overvoltage cathodes and hydrogen-active ones are unfavorably used in industrial electrolytic processes, because the formers are generally poisonous and the latters are mechanically unstable. Quaternary ammonium salts suppress effectively hydrogen evolution by forming hydrophobic adsorption layers in cathode interface,[2)] but they are relatively rather expensive chemicals. Although Tari et al. reported a hydrophobic cathode which was prepared by coating a liquid film of octanethiol,[3)] it did not seem to result in any purposively satisfactory effect because of unstableness under electrolytic conditions.

In this work, it was attempted to use a nickel electrode composite-plated with nickel and poly(tetrafluoroethylene), so-called Teflon resin, as a stable hydrophobic cathode in a test reaction.

The electrode was prepared by composite-plating a nickel plate(3 x 3 cm) in a nickel sulfamate-poly(tetrafluoroethylene) dispersion bath(Metaflon FS Bath, C. Uyemura & Co. Ltd.): Current density, 20 mA cm^{-2}; amount of charge passed, 432 C; temperature, 45 °C. The electrode thus prepared seemed to have a smooth surface whose contact angle to water was 108 - 121°.

Cathodic reduction of carbonyl compounds(1) does not smoothly proceed at a low hydrogen-overvoltage cathode such as nickel in aqueous acidic solutions in general. Therefore, the reduction of a few typical carbonyl compounds(1) in aqueous sulfuric acid was examined as the test reaction using the composite-plated nickel cathode along with an unplated one for control experiments. Electrolysis was galvanostatically carried out by passing 241 C[1 F(1 F = 96480 C) mol^{-1}] of charge in a divided batch cell at room temperature. The catholyte was 50 cm^3 of 4 wt % sulfuric acid containing methanol in 20 vol % and the carbonyl compounds(1) in 50 mmol dm^{-3}. Reduction products were the corresponding alcohols(2, main product) and 1,2-diols(3, by-product), which were analyzed by GC(Silicone DC 550/100 - 200 °C for benzaldehyde and its reduction products; PEG 6000/70 - 150 °C for reduction products of acetone) and HPLC(Ultron S-C18/MeOH:0.1% H_3PO_4 = 1:1 for acetophenone and its reduction products). The unreacted carbonyl compounds(1) except for acetone were also quantitatively analyzed and consequently material balances on them were found to be in a range of 95 - 101%.



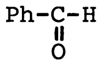
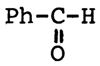
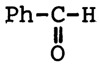
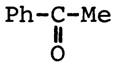
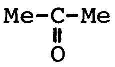
$$\underset{\textstyle 1}{R^1\text{-}\underset{\substack{\| \\ O}}{C}\text{-}R^2} \xrightarrow{\text{Cathodic reduction}} \underset{\textstyle 2}{R^1\text{-}\underset{\substack{| \\ OH}}{CH}\text{-}R^2} + \underset{\textstyle 3}{R^1\text{-}\overset{\substack{R^2 \\ |}}{\underset{\substack{| \\ OH}}{C}}\text{—}\overset{\substack{R^2 \\ |}}{\underset{\substack{| \\ OH}}{C}}\text{-}R^1}$$

1 2 3

Table 1 shows electrolytic results obtained by using comparatively the composite-plated and unplated nickel cathodes.

Current efficiency for benzyl alcohol formed in the reduction of benzaldehyde increased more than doubly at the composite-plated nickel cathode compared with that at the unplated one(Entry 1), and also any significant changes in the current efficiency were not observed when the cathodes were repeatedly used(Entry 2). A change in current density also did not cause any significant changes in the current efficiency(Entry 3). Generally, high current efficiency for the reduction of carbonyl compounds(1) can be obtained using high hydrogen-overvoltage cathodes

Table 1. Cathodic reduction of carbonyl compounds(1) at nickel-poly(tetrafluoroethylene) composite-plated and unplated nickel cathodes in aqueous sulfuric acid

Entry no.	Carbonyl compound	Current density	Current efficiency for reduction products/%			
			At composite-plated cathode		At unplated cathode	
	1	mA cm^{-2}	2	3	2	3
1	 $\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}H}$	10	72	0.0	32	0.6[a)]
2[b)]	 $\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}H}$	10	77	0.3[a)]	35	0.6[a)]
3	 $\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}H}$	5	79	0.0	41	1.5[a)]
4	 $\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}Me}$	10	46	0.0	13	0.0
5[c)]	 $\mathrm{Me{-}\underset{\underset{O}{\|}}{C}{-}Me}$	10	18	0.0	1	0.0

a) Stereochemistry(dl/meso) was not determined. b) Repeated electrolyses using the same cathodes as those used in Entry 1. c) 260 C of charge were passed through 50 cm^3 of 5 wt % sulfuric acid containing acetone in 50 vol %.

such as mercury and lead as described above, but considerable amounts of the corresponding 1,2-diols(3) are formed as by-products together with the alcohols(2, main products) particularly in the reduction of aromatic carbonyl compounds. In fact, in an investigation relating to our previous work[4)] using a flow cell it was found that the reduction of benzaldehyde gave benzyl alcohol and 1,2-diphenyl-1,2-ethanediol in 72 and 7% of current efficiencies, respectively, at a lead cathode at a relatively low flow rate such as 0.7 m min^{-1} under electrolytic conditions (catholyte, 50 vol % aqueous methanol containing sulfuric acid in 0.25 mol dm^{-3}; benzaldehyde concentration, 200 mmol dm^{-3}; current density, 20 mA cm^{-2}) essentially similar to those in Entry 1. It is noticeable that the high current efficiencies comparable to that for benzyl alcohol at the lead cathode could be achieved using the composite-plated nickel cathode while the formation of 1,2-diphenyl-1,2-ethanediol was suppressed.

Similar significant increases in current efficiency for the alcohol(2) formation at the composite-plated nickel cathode were also observed in the reduction of acetophenone and acetone(Entries 4 and 5).

Composite-plating has been well known to provide mechanically stable deposite films.[5,6] The nickel-poly(tetrafluoroethylene) composite-plated nickel cathode used in this work seemed to be electroconductive, and mechanically and electrochemically stable enough for using as a cathode in preparative electrolysis. The composite-plating can be also performed using a variety of metal ion-dispersion baths.[7,8] Therefore, composite-plated electrodes should have high potentialities to be purposively used for a variety of electrolyses. The first example was clearly shown in this work.

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