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Cobaltocene Electrode Films Prepared by Electropolymerization of $[Co(C_5H_4CCl{=}CHCHO)_2]PF_6$

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A new cobalticinium salt $[Co(C_5H_4CCl{=}CHCHO)_2]PF_6$ gives electroactive films on electrode surfaces by electroreduction in n-Bu_4NI-MeCN and the formed films act as a one-way charge-carrier for the redox reactions of solution species.

Charge-transport properties of electroactive thin films are of considerable recent interest.[1-3] As for cobaltocene electrode films, only two reports are available, where cobalticinium redox polymers were confined onto electrodes by dip coating,[4] and by silanization.[2] Electropolymerization method is useful for the preparation of uniform and pinhole-free electrode films and easily utilized to many electrode materials. We present here the first example of cobaltocene electrode films prepared by electrochemical polymerization and their selective charge-transport properties for the reaction of redox solutes.

A new cobalticinium salt $[Co(C_5H_4CCl{=}CHCHO)_2]PF_6$ (**1**) was synthesized by the reaction of $[Co(C_5H_4COCH_3)_2]I_3$ with $POCl_3$-*N*,*N*-dimethylformamide, followed by treatment with NH_4PF_6.[5] Electroactive electrode films were formed on glassy carbon (GC) and indium tin oxide (ITO) coated glass electrodes by repeated potential scan between -0.4 and -1.9 V *vs*. Ag/Ag^+ (10 mol m^{-3} $AgClO_4$ in MeCN) in the solution of **1** in n-Bu_4NI-MeCN (Fig. 1(a)). The electrode thus treated showed a cyclic voltammogram of the redox reaction in a solution with only supporting electrolyte and its formal potential was -1.34 V *vs*. Ag/Ag^+ (Fig. 1(b)). The coverage of electroactive sites on the electrode, Γ, was proportional to the thickness of the film and the redox site concentration in the film in the oxidized state was estimated at 2.3×10^{-3} mol cm^{-3}. The film is quite stable in air and in both aqueous and acetonitrile solutions. The films formed on ITO electrodes were brownish-yellow and exhibited an absorption band at 410 nm.

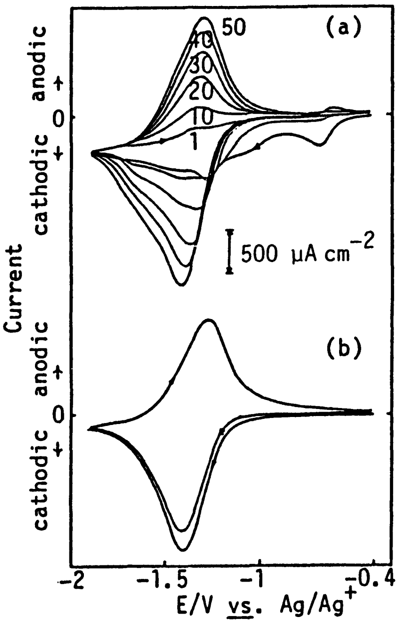

Fig. 1. (a) Cyclic voltammograms for **1** (1.0 mol m^{-3}) at a GC electrode in 0.1 mol dm^{-3} n-Bu_4NI-MeCN at 100 mV s^{-1}. Numbers in the figure refer to those of the cyclic scans. (b) Cyclic voltammetry of the above electrode at 100 mV s^{-1}, in 0.1 mol dm^{-3} n-Bu_4NI-MeCN. $\Gamma = 6.0 \times 10^{-8}$ mol cm^{-2}.

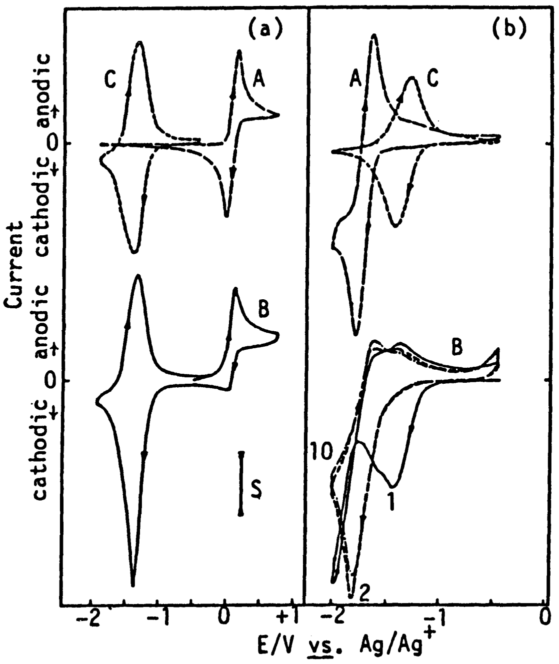

Fig. 2. Cyclic voltammograms of 8.0 mol m^{-3} ferrocene in 0.1 mol dm^{-3} n-Bu_4NClO_4-MeCN (a) and of 9.3 mol m^{-3} p-nitroaniline in 0.1 mol dm^{-3} n-Bu_4NI-MeCN (b) at 100 mV s^{-1}. Curve A: at a bare electrode. Curve B: at a cobaltocene polymer coated electrode. Curve C: cyclic voltammogram of the cobaltocene polymer in an electrolyte solution without redox species. Numbers in the figure refer to those of the cyclic scans. S = 2 mA cm^{-2} for curve A of (a), 500 μA cm^{-2} for the other curves of (a), and 1 mA cm^{-2} for the curves of (b).

The charge-transport properties of the cobaltocene polymer on GC electrodes were examined by cyclic voltammetry in solutions of ferrocene and p-nitroaniline whose formal potentials are more and less positive, respectively, than that of the polymer (Fig. 2). The oxidation peak of ferrocene at the coated electrode appears at the same potential as that at the uncoated one, while the rereduction peak is observed at the cathodic wave of the film. This is due to the fact that the reduction of ferricinium ion is mediated by the reduction of cobalticinium sites in the film. On the other hand, the reduction peak of p-nitroaniline at the coated electrode is observed at the same potential as that at the uncoated one, but the reoxidation wave appears slightly. In this case, a steady-state cyclic voltammogram was not obtained and the redox waves of the film became small with the increase of scan number. The film on ITO electrodes showed no considerable decrease of the absorption at 410 nm by the consecutive potential scan in the solution of p-nitroaniline. This suggests that the disappearance of the film's redox wave is due to the change in the surface state of the film.

Above results imply that in the oxidized state, Co(III), the film conducts current for oxidation of the redox couples and in the reduced state, Co(II), for reduction of the couples. This diode-like characteristics have recently been found for poly[1,1'-bis(chloromethyl)ferrocene] film.$^{3)}$ The charge-transport selectivity of the cobaltocene electrode film for the redox species in solution is much different from the ferrocene film because of the difference in redox potential and electronic state of the redox sites between those films.

References

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5) ^{1}H-NMR (CD_3COCD_3), δ 10.22 (d, 2H, J 6 Hz), 7.07 (d, 2H), 6.09 (m, 4H) and 6.34 (m, 4H). IR (KBr disk), ν(C=O); 1685 cm^{-1}, ν(C=C); 1615 cm^{-1}. Elemental analysis. Found: C, 37.42; H, 2.36; Cl, 13.45%. Calcd: C, 37.60; H, 2.37; Cl, 13.87%.

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