Irreversible Charge-transport through Films of Electropolymerized 1,1'-Bis(chloromethyl)ferrocene

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Electroactive polymer films, prepared by electroreduction of 1,1'-bis(chloromethyl)ferrocene (BCMF) at a glassy carbon electrode in acetonitrile, act as a selective charge-transport mediator for the reduction of redox couples in the ferrocene state and for the oxidation of the couples in the ferricinium state.

Electron-transfer reactions of redox species in solution at electropolymerized electroactive films and charge-transport through the films have received much recent attention.[1—5] We report here the new preparation of electrochemically polymerized ferrocene coatings on electrode surfaces and their unusual selectivity for the charge-transfer in redox reactions between the solution species and the electrode substrate.

When the potential of a glassy carbon electrode in a 2 mM solution of 1,1'-bis(chloromethyl)ferrocene (BCMF) in 0.1 M Bu_4NClO_4–MeCN was swept from 0.0 to 1.0 V *vs.* Ag/AgCl and scanned repeatedly between 1.0 and −2.5 V, the electrochemical waves for the $BCMF^+/BCMF$ couples at 0.75 V and for the reduction of BCMF at −2.25 V observed in the first scan decreased gradually in size, and new anodic and cathodic peaks at *ca.* 0.5 V appeared in the second scan and increased in the following scans [see Figure 1(a)]. The electrode, after several tens of scans, showed a cyclic voltammogram of the redox reaction ($E_c^{\circ\prime}$ 0.525 V *vs.* Ag/AgCl) in a clean electrolyte solution as shown in Figure 1(b). The maximum apparent coverage of ferrocene sites in the poly-BCMF, PBCMF, film formed in 2 mM solution of BCMF was 5×10^{-9} mol cm^{-2}.

With slow scan rates (≤ 0.2 V s^{-1}) in 0.1 M Bu_4NClO_4–MeCN, the peak-to-peak separation, ΔE_p, of PBCMF remained constant at values of 30 mV and the peak currents, i_{pa} and i_{pc}, varied linearly with scan-rate, as expected for the reaction of surface localized material. The PBCMF-coated electrode also showed stable reversible cyclic voltammograms in water, and the potentials and slope of the voltammetric peaks of PBCMF were a function of the dissolved electrolyte; for example, ΔE_p 40, 90, 55, and 75 mV and $E_c^{\circ\prime}$ 0.31, 0.47, 0.17, and 0.40 V *vs.* Ag/AgCl in 1 M $NaBF_4$, 0.5 M Na_2SO_4, 1 M $HClO_4$, and 0.5 M H_2SO_4, respectively.

The charge-transport ability of PBCMF was examined in solutions of the redox species, 2,6-dichloro-*p*-benzoquinone (DCBQ) with a formal potential $E_s^{\circ\prime}$ less positive than the $PBCMF^+/PBCMF$ potential $E_c^{\circ\prime}$, and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) with $E_s^{\circ\prime}$ more positive than $E_c^{\circ\prime}$. Figure 2(a) and (b) shows the cyclic voltammograms of DCBQ and DDQ, respectively, at naked (curve A) and PBCMF-coated (curve B) glassy carbon electrodes in Bu_4NClO_4–MeCN. Curve C is a voltammogram of PBCMF in clean electrolyte solution and curve D represents the difference (B − C), equivalent to the voltammogram for the reaction of electroactive solutes only.

At the PBCMF-coated electrode, the reduction peak of DCBQ is observed at the same potential as at the uncoated electrode, but the oxidation peak of $DCBQ^{\cdot-}$ shifts in the positive direction to the negative limit of the anodic wave of PBCMF as shown in Figure 2(a). In contrast with this, the oxidation peak of $DDQ^{\cdot-}$ is observed at the same potential as at the uncoated electrode, but the reduction peak of DDQ is

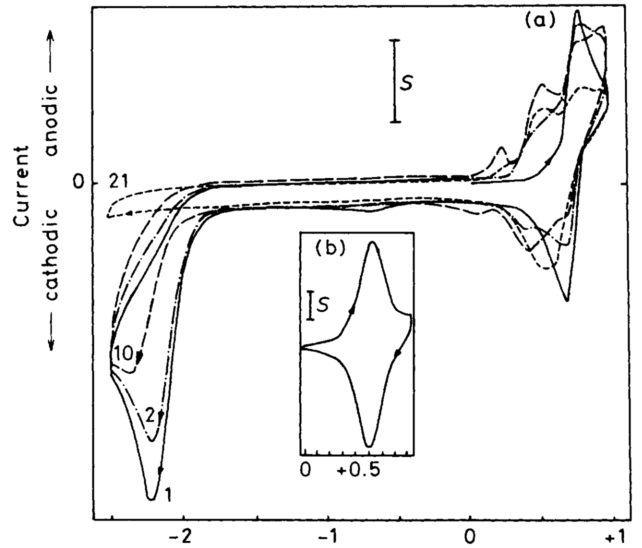

Figure 1. (a) Cyclic voltammograms for the reduction of 2 mM BCMF at a glassy carbon electrode in 0.1 M Bu_4NClO_4–MeCN at 200 mV s^{-1}. 1, 2, 10, 21; First, second, tenth, and twenty-first scan, respectively. $S = 500$ μA cm^{-2}. (b) Cyclic voltammetry of the above electrode at 200 mV s^{-1}, in clean 0.1 M Bu_4NClO_4–MeCN. $\Gamma = 3.2 \times 10^{-9}$ mol cm^{-2}. $S = 100$ μA cm^{-2}.

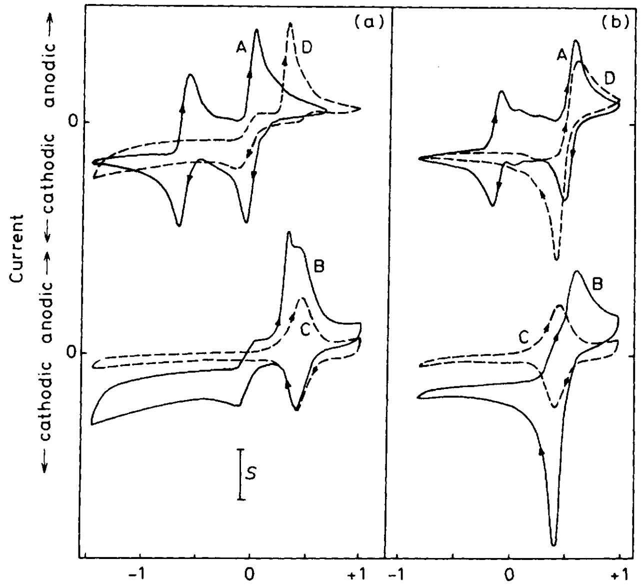

Figure 2. Cyclic voltammograms of 2 mM DCBQ (a) and DDQ (b) in 0.1 M Bu_4NClO_4–MeCN at 200 mV s^{-1}. Curve A: at naked glassy carbon electrode. Curve B: at PBCMF-coated electrode. Curve C: cyclic voltammogram of the PBCMF in clean 0.1 M Bu_4NClO_4–MeCN. Curve D: the difference (B − C). $S = 400$ μA cm^{-2} for curve A and 200 μA cm^{-2} for curves B, C, and D.

overlapped with the PBCMF$^+$ reduction peak as shown in Figure 2(b). These inhibition effects of PBCMF for the oxidation of redox species in the ferrocene state and for the reduction in the ferricinium state were also observed with other redox species like anthracene, nitrobenzenes, quinones, and ferrocyanide.

The above results imply that the reducing and oxidising states of PBCMF are selective mediators for positive and negative charge transport, respectively, from the solutes to the electrode substrate. This can be explained by the assumption that charge-transfer reactions occur between PBCMF or PBCMF$^+$ and the solutes in the oxidising or reducing states, respectively, and the produced hole or electron, respectively, on the PBCMF film acts as a charge-carrier. It is noteworthy that PBCMF changed into an electroinactive but conductive polymer film by repeated potential scans between 0.9 and −1.8 V *vs.* Ag/AgCl in tetramethyl-*p*-benzoquinone solution in 0.1 M Bu_4NClO_4–MeCN. The film thus formed exhibited a u.v. absorption band at 258 nm characteristic of PBCMF and an additional band at 300 nm suggestive of charge-transfer complex formation.

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