Catalysis at Redox Modified Electrodes based on Polysiloxanes

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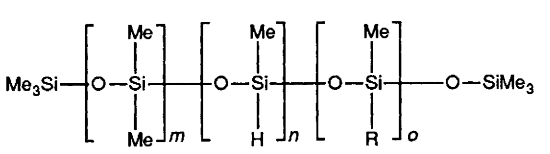
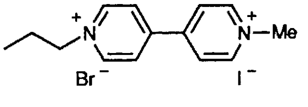
Remarkably high catalytic currents and turnover numbers are found for electrochemical reactions at electrodes coated with thin films of polysiloxanes bearing redox centres, *e.g.* viologens, or nitroxides.

The catalysis, or overpotential reduction, of electrochemical reactions is one of the primary goals in the application of chemically modified electrodes.[1] The performance of modified electrodes depends on the efficiency of the catalyst/substrate system in rate and turnovers, on the electron diffusion rate within redox polymers, and on the diffusional access of catalytic sites in the film for substrate molecules. An optimum film thickness is predicted by theory for a given case.[2] In this communication we report two cases of extraordinarily high catalytic currents and turnover numbers with *very*



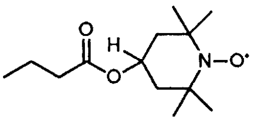
(1a) R = H, $m = 0$, $n + o = 60$
(1b) R = H, $m = 45$, $n + o = 5$

(1c) R =



$m = 0$, $n = 56$, $o = 4$

(1d) R =



$m = 45$, $n = 0$, $o = 5$

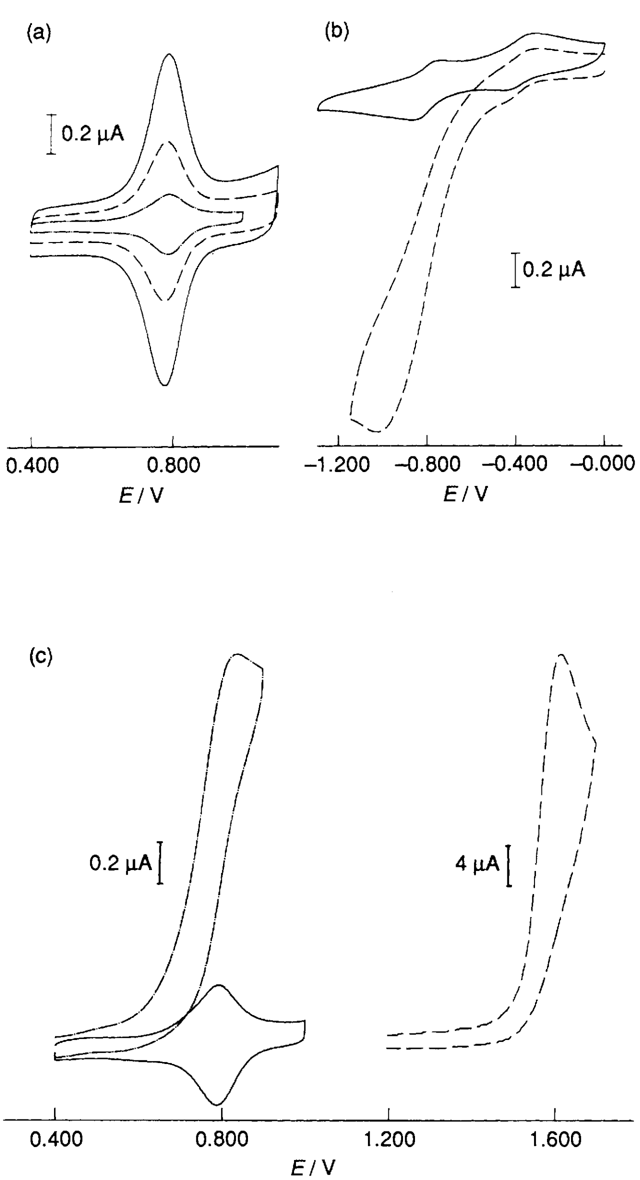


Figure 1. Cyclic voltammograms of polysiloxane-coated 0.01 cm^2 Pt disk electrodes in acetonitrile–0.1 M Bu_4NClO_4. (a) (**1d**), $\Gamma = 9.6 \times 10^{-10}$ mol cm^{-2} in pure solvent–electrolyte, scan rates 20, 50, 100 mV s^{-1}. (b) (**1c**), $\Gamma = 5.9 \times 10^{-9}$ mol cm^{-2} in pure electrolyte and (dashed line) with 1×10^{-3} M 1,2-dibromo-1,2-diphenylethane added, scan rate 100 mV s^{-1}. (c) (**1d**), $\Gamma = 9.6 \times 10^{-10}$ mol cm^{-2} in pure electrolyte and with 1×10^{-2} M *p*-methoxybenzyl alcohol and 2×10^{-2} M lutidine added, scan rate 20 mV s^{-1}; the peak at + 1.6 V (dashed line) corresponds to the uncatalysed oxidation at bare Pt. All potentials given in volts *vs.* Ag/AgCl reference.

thin polysiloxane films as a matrix for binding redox catalysts. This type of surface modification has been applied for silica[3] and, recently, also for platinum.[4] Siloxane-based electrode coatings with viologen moieties (viologen = 4,4′-bipyridinium) as constituents of the polymer chain, and their use in the mediated reduction of some outer-sphere oxidants, have been described previously.[5]

Allylmethylviologen and 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-yl but-3-enoate, respectively, were coupled to the oligohydrosiloxanes (**1a**) or (**1b**) by Pt-catalysed hydrosilylation in refluxing toluene or acetonitrile until the desired conversion of Si–H groups had been achieved.[6] The amount of redox centres in the resulting polymers (**1c**) and (**1d**) was determined by elemental analysis, and ^{1}H NMR spectroscopy for (**1c**), and also by EPR spectroscopy for (**1d**).

Polymer films on Pt or glassy carbon disk electrodes were obtained by spin coating with dilute dimethyl sulphoxide (DMSO) (**1c**) or CH_2Cl_2 (**1d**) solutions of the polymers and drying in air. In cyclic voltammetry, polymer (**1d**) with electrically neutral redox centres shows highly symmetric peaks with peak separations $>$ 5 mV and an exact linear growth of peak current with scan rate (Figure 1a). The ionic polymer (**1c**), on the other hand, shows a diffusion-like response (Figure 1b). Although the oligomers are slightly soluble in acetonitrile, the films are not dissolved in the electrolyte, perhaps indicating cross-linking and surface binding *via* residual Si–H bonds by traces of moisture.

There is practically no loss of electroactivity of either type of film on repeated cycling of the potential across the redox signals even after many hundreds of cycles, nor after storage in normal atmosphere for several weeks.

The catalytic activity of the viologen electrode was tested in the reduction of *meso*-1,2-dibromo-1,2-diphenylethane in acetonitrile[7] (Figure 1b). The catalytic current corresponds to 7 average turnovers of single redox sites in the forward voltammetric sweep. The reduction of the substrate at an uncoated electrode occurs at −2.1 V.

Similar high catalytic currents and turnovers are observed for the oxidation of *p*-methoxybenzyl alcohol[8] at the nitroxide polymer (Figure 1c). At the same electrode, a constant current of 5 μA (0.01 cm^2 electrode) is maintained at an electrode potential of 0.9 V in a stirred solution of 1 M *p*-methoxybenzyl alcohol and 2 M lutidine in acetonitrile with tetrabutylammonium perchlorate electrolyte. After 30 min, more than 60% of the original electroactivity of the polymer film is preserved. The charge balance corresponds to a conversion of 0.1 μmol of substrate, or over 10000 average catalyst turnovers. These data compare favourably with previous results using the same or similar catalyst–substrate combinations with other polymer matrices.[7,8]

We point out that, in our case, the film thickness is estimated as hardly more than 0.1 nm and the amount of catalyst corresponds to about one molecular monolayer.

In summary, redox-modified polysiloxanes on electrode surfaces films are easily prepared, show good chemical and electrochemical stability, and allow for high turnover numbers in electrocatalytic reactions. Work to scale up the process with large-area electrodes is in progress.

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