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In situ growth of polymer electrolytes on lithium ion electrode surfaces

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Polyacrylonitrile (PAN) films were grown on glassy carbon, nickel foam and MnO_2 substrates by cathodic electropolymerisation of acrylonitrile in acetonitrile with tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. The electronic barrier properties of the films were confirmed by impedance spectroscopy of carbon |PAN| Hg cells while the ionic resistance of the films varied from 200 $k\Omega\ cm^2$ in the dry state to 1.4 $\Omega\ cm^2$ when plasticised with 1 M $LiPF_6$ in propylene carbonate. A galvanic cell was prepared by successive electrodepositions of MnO_2 and PAN on a carbon substrate, using liquid lithium amalgam as the top contact. The cell showed a stable open circuit potential and behaved normally under the galvanostatic intermittent titration technique (GITT).

1. Introduction

One can imagine many possible applications for the electrodeposition of a solid polymer electrolyte onto an electrode surface. The first one that springs to mind is the formation of planar cells on electronic circuits, where electrodeposition should have several advantages, for example automatic alignment so that the polymer completely covers the electrode surface without affecting the remainder of the device, avoidance of pinholes, and conformity with surface undulations with a film of uniform thickness. The latter concept can be extended to the conformal coating of porous electrodes with a thin layer so that a second electrode can be infused to form a 3D battery or supercapacitor structure [1,2]. Other possible applications include electrochromic displays and dye sensitised solar cells [3,4].

Electropolymerisation is well established as a method of bulk synthesis, and also the electrodeposition of vinyl polymers as thin layers on metals has been employed extensively for corrosion protection of metals [5]. The latter requires polymers that are impermeable to ions, although electronic conductivity is acceptable in that application [6]. Our requirement here is exclusively ionic conduction, as observed in polymer electrolytes [7] or in polymer electrolyte interfaces which form naturally between some non-aqueous electrolytes and strongly reducing electrode materials [8].

Porous polyacrylonitrile (PAN) has been shown to be an effective separator [9] for absorption of liquid electrolytes and also a solid polymer electrolyte by addition of a suitable plasticizer containing a lithium salt [10]. Therefore in this work we have investigated the ionic conductivity of electrodeposited poly(acrylonitrile) (PAN) films under conditions that allow the incorporation of ions into the layer, and demonstrated the formation of simple electrochemical cells by successive electrodepositions of one electrode and the electrolyte followed by ink deposition of the top electrode.

2. Experimental

Acetonitrile (ACN) and acrylonitrile (AN, Aldrich) were distilled over CaH_2 at ambient pressure and tetrabutylammonium perchlorate (TBAP, Aldrich) was dried under vacuum at 120 °C prior to use. Experimental cells were prepared using a standard three-electrode setup with a silver wire reference electrode immersed in ACN containing 0.05 M TBAP and 0.01 M $AgNO_3$. Vitreous carbon working electrodes ($\varnothing = 3$ mm) (VC) were polished with 1 μm alumina and dried at 80 °C. Electrochemical experiments were carried out using a variable multichannel potentiostat (VMP2, Princeton Applied Research; Bio-Logic – Science Instruments). Stainless steel foil working electrodes were used for film mass measurements using an A&D GR-202 10 g sensitivity balance.

PAN was deposited by cyclic voltammetry from a solution of 2 M acrylonitrile in acetonitrile with 0.05 M TBAP as supporting electrolyte over 5 or more cycles between −0.5 and −3.5 V vs. Ag/Ag^+ (+0.8 V vs. SHE). AC impedance spectroscopy was performed on films of PAN on VC electrodes. A mercury ‘soft contact’ was used as the counter/reference electrode in a two electrode configuration. Impedance experiments were performed with a peak to peak amplitude of 20 mV over the frequency range

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200 kHz–0.1 Hz. The samples were dried under vacuum 1 h at 60°, measured dry, after addition of a drop of DMF to give a soft but firm consistency, and after soaking in 1 M $LiPF_6$ in 1:1 by weight ethylene carbonate and dimethyl carbonate (EC:DMC).

Manganese dioxide was electrodeposited as a 2.5 cm^2 film, about 1 μm thick, onto stainless steel electrodes via electroreduction from an aqueous solution of $KMnO_4$ and KOH (0.01 and 0.6 M, respectively). The MnO_2 films were rinsed repeatedly in distilled water and dried (100 °C 12 h). PAN was electrodeposited onto the MnO_2 films using the method described above. The PAN coated MnO_2 films were dried under vacuum (12 h 60 °C) and transferred to an argon filled glove box (<0.1% H_2O, O_2; Unilab from MBraun). Once in the glove box the MnO_2 |PAN| films were soaked in lithium battery electrolyte (1 M $LiPF_6$ in EC:DMC 1:1 by weight) for 1 h.

The stainless steel |MnO_2| PAN electrode was assembled into a cell using a liquid lithium (<5 at.%) amalgam 'soft contact' negative electrode (area ∼0.3 cm^2) as shown in Fig. 3a. After measuring the open circuit potential, the cell potential was discharged galvanostatically to 1.5 V then charged galvanostatically to 3.5 V vs. Li/Hg at approximately C/30 (with 5 h relaxations after discharge/charge). The galvanostatic intermittent titration technique (GITT) experiment involved applying a charge or discharge current pulse (3.6 $\mu A\ cm^{-2}$, *C*/10, for 60 s) followed by an open circuit relaxation (30 min) and repeating numerous times over the desired potential range.

3. Results and discussion

Vitreous carbon electrodes subjected to several potential cycles as shown in Fig. 1 were coated with a thin translucent film, yellow in colour. The voltammogram of the pure acetonitrile (dashed line) shows no significant redox activity up to the negative stability limit at −3.2 V vs. Ag/$AgNO_3$ (0.01 M), where we observe decomposition of the solvent limited by an uncompensated electrolyte resistance of about 20 $\Omega\ cm^2$. The solid lines show the result for the same electrolyte solution with freshly distilled acrylonitrile added at a 2 M concentration. On all cycles the cathodic reaction begins at −3.0 V and ends at −2.75 V on the anodic scan, suggesting an initiation or nucleation step, e.g., radical formation. Subsequent steps display decreasing gradients due to the added resistance of a thickening surface layer. Post deposition mass measurement (with stainless steel foil electrodes) showed some degree of control of film thickness from 2 μm after 10 cycles to 30 μm after 30. This corresponded to between 0.5 and 2.5 electrons per monomer deposited on the electrode surface. This value contrasts with a typical value of around two for the Faradaic deposition of polyaromatics such as polythiophene [11]. A much lower value would be predicted by the standard models of vinyl polymerisation, e.g. [12–14] where polymerisation is initiated by single electron transfer then propagated, linking several monomers before a random termination. In the present case, our charge to mass ratio reflects some loss of material by dissolution and the uninhibited current at high overpotentials suggests the formation of a highly conducting or porous film.

Fig. 1b shows a low resolution SEM of PAN grown on a nickel foam substrate by the same method as above as a coherent film with no visible pinholes. Higher magnification showed a grainy structure with grain sizes between 100 nm and 1 μm. The films were brittle when dry and could easily be scraped off as a powder for analysis. The IR spectrum showed a strong CN band at 2250 cm^{-1} as observed by Mertens et al. [13].

The real axis intercept in the impedance of the brittle, dry sample shows an ionic resistance of 200 $k\Omega\ cm^2$, Fig. 2a. The 45° line is characteristic of diffusion into the electrodes and any electronic conductance is outside the measurement range. Addition of 1 M $LiPF_6$:PC reduced the ionic resistance to 8.4 and 1.4 $\Omega\ cm^2$, respectively (Fig. 2b) as the film became progressively softer. The barrier property of the film was confirmed by a blocking interfacial capacitance in series with the film resistance. The conductance therefore varied from 10^{-5} to 1 S cm^{-2} depending on the amount of plasticiser and the thickness.

Replacing the carbon and mercury with active electrodes lithium amalgam and manganese dioxide as in the diagram of Fig. 3a gives a lithium ion cell with the following formal description:

$$\mathrm{Li(Hg)|LiPF_6(PAN)|MnO_2}$$

$$\text{Anode}: \mathrm{Li}_x\mathrm{Hg} \rightarrow \mathrm{Li}_{x-\delta}\mathrm{Hg} + \delta\mathrm{Li}^+ + \delta\mathrm{e}^- \quad E_{\mathrm{Hg}} = \frac{-\mu_{\mathrm{Li}}(\mathrm{Hg})}{F}$$

$$\text{Cathode}: \mathrm{Li}_x\mathrm{MnO}_2 + \delta\mathrm{Li}^+ + \delta\mathrm{e}^- \rightarrow \mathrm{Li}_{x+\delta}\mathrm{MnO}_2$$
$$E_{\mathrm{MnO}_2} = \frac{-\mu_{\mathrm{Li}}(\mathrm{MnO}_2)}{F}$$

The open circuit potential of the cell at equilibrium is thus written:

$$E_{eq} = \frac{-(\mu_{\mathrm{Li}}(\mathrm{MnO}_2) - \mu_{\mathrm{Li}}(\mathrm{Hg}))}{F} \tag{1}$$

On connecting the external circuit a continuous current of Li^+ should pass from the Hg anode and insert into the cathode, provided the potential between the manganese dioxide and mercury is less than the equilibrium potential, E_{eq}. The particular design used here incorporates a cathode of much lower capacity for lithium than that available from the anode. Therefore we can regard $\mu_{Li}(Hg)$ as approximately constant, so the electrode becomes a good reference electrode as well as a counter electrode, as would metallic lithium,

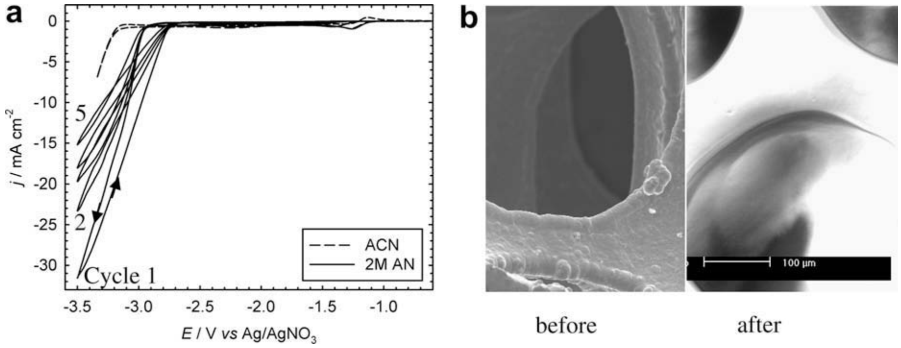

Fig. 1. (a) Voltammograms for pure acetonitrile (ACN - - -) at 50 mV s^{-1} and 2 M acrylonitrile (AN—) at 100 mV s^{-1} in ACN, each containing 0.05 M TBAP as a supporting electrolyte on a 3 mm diameter vitreous carbon disc electrode. The AN traces indicate several cycles of polymer deposition. (b) SEM of nickel foam before and after coating with PAN.