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Conduction and electrooptical properties of vanadium-containing polymer electrolyte networks from sol–gel methods with modified poly(ethylene glycol)s and poly(tetramethylene oxide)

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Poly(ethylene glycol) (PEG) and poly(tetramethylene oxide) (PTMO) were functionalised using ethyl acetoacetate to obtain organic molecules with dicarbonyl groups appended. These polymers were reacted with vanadium isopropoxide to prepare vanadium-based *ormocers*, using a sol–gel method. Low frequency electrical conductivities of the lithiated hybrid coatings were studied by impedance spectroscopy. Both polyethers performed as good polymer electrolytes using $LiN(SO_2CF_3)_2$ at $[Li^+/O]=0.05$. The conductivities were shown to be dependent on the composition of the initial sols as well as on the type of starting polymers. The dependence of alkali ion coordination by polyethers $[-(CH_2)_m-O-]$ ($m=2$–4) is discussed. A two-step colour change was observed upon applying ±2 V to the solid-state electrochromic window with a response time of <2 min being observed.

Vanadium oxides have been of considerable interest in recent years owing to the diverse areas in which they have been applied such as semiconductive coatings,[1] anti-static coatings,[2] electrochromic films[3,4] and lithium batteries.[5,6] Over the same period the development of sol–gel processing has offered a convenient approach to the preparation of inorganic glass and ceramic networks.[7] One of its most useful features is the low processing temperature allowing incorporation of organics into the oxide network. This provides a route to hybrid or composite materials.

Poly(ethylene oxide) (PEO) has long been known for its ability to solvate Li^+ ions leading to solid electrolytes[8] and may be conveniently incorporated into the metal oxide. The combination of the vanadium oxide network with PEO should give rise to mixed conductor composites having ionic conductivity in the PEO–salt system and electronic conductivity *via* the metallic oxide. This paper reports studies of the electrical conductivity of such composites. The composites were made by reacting a vanadium alkoxide precursor with modified polymers based on poly(ethylene glycol), PEG, of molar masses 200 and 600 having dicarbonyl groups appended (FPEG 200 and FPEG600). In addition similar networks were created using modified poly(tetramethylene oxide) of molar mass 650 (FPTMO650) in order to compare the electrical behaviour of a less ionophilic environment with that of the ethoxide system. A preliminary result on the study of an all-solid-state electrochromic window based on the FPEG600–V_2O_5 composite coating is also reported.

Experimental

Vanadium isopropoxide, VIP (Aldrich), was used as received. In order to react vanadium with the organic molecules, these polymers were functionalized with ethyl acetoacetate. The preparation of functionalized polymers has been previously reported.[9] This consists of an ester-interchange reaction between 2 mol ethyl acetoacetate and 1 mol polymer. The starting polymers were poly(ethylene glycol 600 and 200) and poly(tetramethylene oxide 650) which were used as received from Aldrich. The ester-interchange reaction gives rise to functionalized PEG and PTMO (FPEG600, FPEG200 and FPTMO650) with dicarbonyl groups appended having the following formula:

$$CH_3COCH_2CO_2[-(CH_2)_m-O]_nCOCH_2COCH_3$$

where $m=4$ for FPTMO650 and $m=2$ for FPEG600 and FPEG200. Acetonitrile and chloroform were used as solvents for FPEG-based and FPTMO polymers, respectively.

Sols were prepared by dissolving a known amount of functionalized polymer in the solvent, to which VIP was added slowly followed by magnetic stirring overnight at room temperature in a sealed bottle. The concentration of functionalized polymer in the sols was constant at 25 wt.%. The modification ratio, r, defined as the molar ratio of VIP to difunctionalized polymer, was varied between 1 and 3:

$$r=[\text{VIP}]/[\text{FPEG or FPTMO}]$$

The lithium salt in the polymer electrolyte was $LiN(SO_2CF_3)_2$. The 'salt content' x is given by:

$$x=[Li^+]/[\text{ether oxygen}]$$

The values of x were 0, 0.05, 0.1 and 0.2. After adding the lithium salt the mixture was agitated for at least 2 h. Indium tin oxide (ITO) coated glasses were used as electrodes for measuring the conductivity. ITO glass slides were ultrasonically cleaned in an acetone–methanol (1 : 1 w/w) solution and subsequently washed with distilled water prior to being dried in an oven at 100 °C. A spacer with a thickness of *ca.* 60 µm was used to separate the two electrodes. The sols were deposited onto the surface of ITO and were left in air for one day to hydrolyse and condense. The films were then heated at 100 °C in an electric furnace for 45 min after which they were kept in a vacuum desiccator for 24 h. Low frequency conductivity was measured by impedance spectroscopy using a Solartron 1250 Frequency Response Analyser (FRA) connected to a 1286 Electrochemical Interface (ECI) controlled by a model ST 520 Atari microcomputer. The impedance was measured under vacuum from 20 to 70 °C over a frequency range 10–64000 Hz with an amplitude of 2 V. The low frequency impedances of bulk samples were obtained from the impedance plots and hence the conductivities were calculated.

An all-solid-state electrochromic window was assembled to study the electrochromism of hybrid coatings based on FPEG600. A cell was fabricated from several layers as follows:

$$\text{Glass}|\text{ITO}|TiO_2–CeO_2|\text{FPEG600}–V_2O_5|$$

$$\text{PEO}–LiN(SO_2CF_3)_2|\text{ITO}|\text{Glass}$$

Small pieces of ITO glass (2 × 2 cm) were cut and cleaned according to the method described previously. The polymeric electrolyte for electrochromic cells was prepared by dissolving the lithium salt in a PEO(5×10^6)–acetonitrile solution. The viscous solution of electrolyte was then poured onto an ITO glass in a dry box and was left for 24 h to dry at room temperature. Samples were then placed in a vacuum dessicator for 48 h. The hybrid layer was deposited by dip-coating of the ITO glass into the sol (modification ratio = 2) at a withdrawal speed of 2 mm s^{-1}. This layer was then heat-treated in an oven at 100 °C for 45 min. Films were stored in a vacuum dessicator for 24 h. A thin layer of TiO_2–CeO_2 was deposited onto the ITO according to the method described elsewhere.[10] This layer was charged up to 25 mC cm^{-2} using a liquid cell containing 0.05 M $LiClO_4$ in propylene carbonate and lithium ribbon. The assembly of the electrochromic cells was performed in a dry box by pressing the layers together. The cell was then sealed by epoxy resin. The optical density of the complete transmissive device was measured *in situ* between 400 and 800 nm using a Perkin Elmer 330 spectrophotometer at ±2 V.

Results and discussion

Following addition of VIP to the solutions of functionalised polymers a slightly reddish colour developed and the solution became warm to touch suggesting that an exothermic reaction had occurred. FTIR analysis[9] showed that vanadium had chelated to the functionalised polymers through the enol form of the dicarbonyl functional groups. The hybrid sols were stable for up to 6 months in sealed bottles. The hybrid coatings turned green after heat treatment indicating the existence of some V^{IV} species. These gel coatings were shown to be amorphous by X-ray diffraction at the processing temperature. The integrity of the gel films was shown to be dependent on the composition of the sols. IR analysis[11] indicated that V–O–V groups are always present so that the most primitive cross-link is likely to have the structure shown in Fig. 1.

At modification ratios $r\leqslant1$ the films were ‘sticky’. Since 1 mol of functionalised polymer contains two diketo groups, at modification ratio $r\leqslant1$ each polymer molecule must, on average, have at least one unreacted diketo terminus and the formation of a cross-linked network is not fulfilled. At $r\geqslant2$ all diketo termini, on average, may react. However, it was apparent from TEM[11] that particles ⩽100 nm were present. These would provide polyfunctional cross-links for extensive network formation but some unreacted functional groups, including free molecules, must be present. Solvent extraction using dichloromethane[11] also showed that as the modification ratio increased gels showed lower weight loss indicating that a more crosslinked network is obtained.

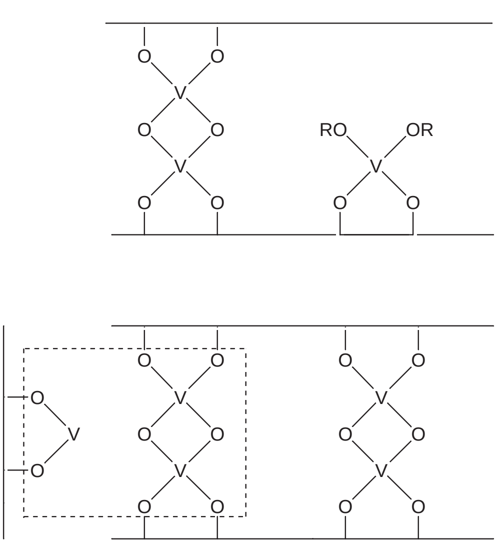


Fig. 1 Schematic diagrams of hybrid networks at different modification ratios r : (a) $r<2$ and (b) $\geqslant2$.

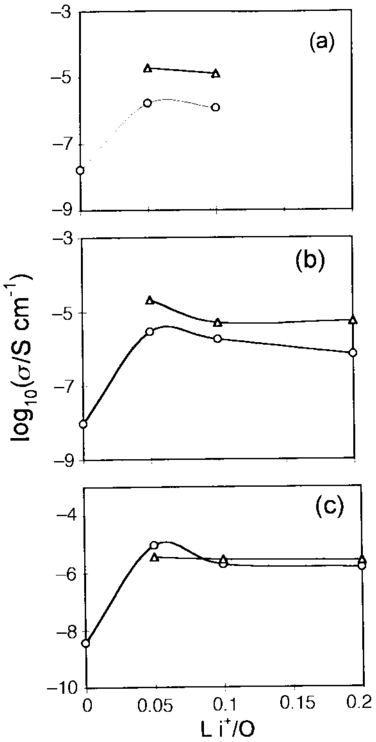


Fig. 2 Conductivities of lithiated hybrid gels at different $x=Li^+/O$ for (a) FPTMO650-based gels, (b) FPEG600-based gels and (c) FPEG200 based gels. (—△— $r=0$, —○— $r=3$).

Conductivity studies

The lithium salt, $LiN(SO_2CF_3)_2$, used to study the conductivities of hybrid films could be dissolved in FPEG600 and FPEG200 at all $x\leqslant0.2$. FPTMO650, however, was unable to dissolve the lithium salt at $x=0.2$ but clear isotropic mixtures were obtained for $x\leqslant0.1$.

Fig. 2 shows plots of $\log_{10}(\sigma/S\ cm^{-1})$ *vs.* x at 20 °C for each of the three systems having $r=0$ (liquid) and $r=3$ (gel network). The conductivities of all samples were found to be maximum at $x=0.05$ irrespective of the modification ratio. The conductivities of the gel films without lithium salt were 2–3 orders of magnitude lower than those of the lithiated samples.

The observation of a maximum in conductivity at a relatively low concentration of salt, $x=0.05$, is in accord with general observations on PEO–$LiClO_4$ polymer electrolytes.[12] Much of the salt mainly exists as ion pairs or higher clusters that hinder segmental motion of the polymeric backbone; mobility under the influence of the field may require them to dissociate. At concentrations of salt below the optimum the carrier number is low whereas at higher concentrations of salt the tendency to aggregation is greater.

Fig. 3 shows how the conductivity of the three systems varies with the modification ratio. It is seen that the conductivity of the gels films based on FPTMO650 and FPEG600 decreased as the modification ratio increased. At the modification ratio $r=0$ the samples are liquid-like but as the molar ratio of vanadium to diketo function was increased the samples became more rigid. A decrease in ionic conductivity of the gel films is anticipated as a result of the higher degree of cross-links within the network lowering the mobility of ions and polymer segments. This trend is clearly observed for the FPTMO650 and FPEG600 systems. However, a *reverse* effect

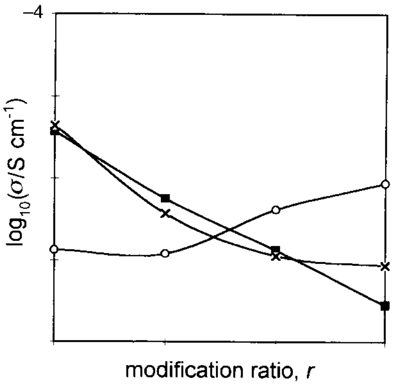
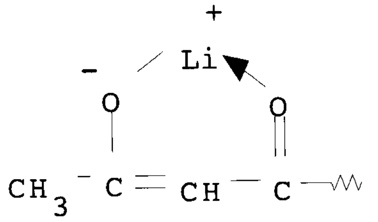


Fig. 3 Conductivities of hybrid gels at different modification ratios with constant salt content ($x = 0.05$). (—■— FPTMO650, —×— FPEG600, —○— FPEG200).

is seen for the gel films based on FPEG200. As the modification ratio increases there is a rise in conductivity.

At $r = 0$ the conductivity of lithiated FPEG200 is significantly lower than that of FPTMO650 and FPEG600. Since all systems are liquids at $r = 0$, the lower conductivity of the more fluid FPEG200 is surprising. However, this perhaps arises from a stronger association of Li^+ with the diketo termini than with the ether links. The diketo functionalities are present at a factor of three greater concentration in the short chain polymer than in the other two systems. The carbonyl functions should be readily polarised by the lithium ion.



$CH_3{-}C(O^-){=}CH{-}C(=O){-}$ ··· Li^+

As a consequence Li^+ will be less labile than in its association with the ether residues. However, with the introduction of vanadium crosslinks the systems become rigid and whilst FPEG600 and FPTMO650 decrease in conductivity, as mentioned above, the increase in conductivity in the FPEG200 system suggests an enhancement to the conduction process not explained by the ionic conductivity alone.

Vanadium exists in two valence states in the gels and conduction can take place by electron transfer from low to high valence states. One can expect that when the concentration of vanadium is increased (higher modification ratio) a more cross-linked network is formed in which vanadium particles are closer together. When the distances between these particles are smaller, as in the case of FPEG200 composites, the contribution of electronic conduction could be greater. Thus, the overall conductivity increases with increasing modification ratio in this case. For a constant modification ratio, the concentration of vanadium oxide and the contribution of electronic conductivity in FPEG200 gels are higher than those of FPTMO650 and FPEG600.

Fig. 4 shows the dependence of $\log_{10}(\sigma/\mathrm{S\,cm^{-1}})$ vs. $1/T$ for the three different gels at constant lithium salt concentration ($x = 0.05$) and at several modification ratios. It is clearly seen that the plots are not linear and so the conduction mechanism does not follow the simple Arrhenius type. In amorphous polymer electrolyte systems the temperature dependence can usually be described by the Vogel–Tamman–Fulcher (VTF) equation based on free volume theory $\{\sigma = AT^{-1/2}\exp[B/(T - T_0)]\}$ where T_0 is a reference temperature associated with the glass transition temperature (T_0 is usually ca. 50 °C lower than T_g, i.e. $T_0 = T_g - 50$); E_a is the activation energy and $B = -E_a/R$.

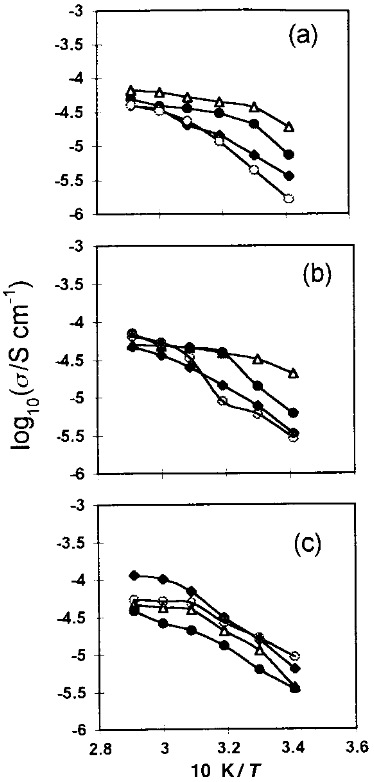


Fig. 4 Temperature dependence of conductivities of (a) FPTMO650-based gels, (b) FPEG600-based gels and (c) FPEG200-based gels (—△— $r = 0$, —●— $r = 1$, —◆— $r = 2$, —○— $r = 3$).

The smooth curvature of some of the conductivity plots in Fig. 4(a) and (b) for the FPTMO650 and FPEG600 systems suggest that the VTF form of equation may be fitted to that data. In these cases, this would suggest that conduction is considerably affected by the segmental motion of polymer chains since the polymer segmental motion at a given temperature is primarily controlled by the temperature interval above T_0. In Fig. 4(a) and (b) the room temperature conductivity of FPTMO650- and FPEG600-based gels having a modification ratio $r = 0$ is higher than those of other samples and the conductivities decrease with r as shown in Fig. 3. However, the plots in Fig. 4(b) for $r = 1$ and 3 are not smooth curves. A similar change in gradient to that in the case of $r = 1$, in the region 40–60 °C for PEG400 polyester networks, has been remarked upon by Hu and Wright[13] and also Lee and Wright[14] who observed endotherms in networks in this region. These changes in gradients are clearly unrelated to PEO melting such as may be observed in salt-deficient PEO complexes since PEG600 melts at ca. 20 °C, and may perhaps be attributed to the break up of local ion–polymer aggregates. The step in the plot for $r = 3$, however, in Fig. 4(b) is not so readily explained on this basis. The most highly cross-linked system giving the lowest conductivity at room temperature has the highest conductivity at 70 °C. It seems likely that in this case electronic mobility between vanadium oxide particles is enhanced at 40–50 °C. Such mixed processes may also be invoked to explain the sequence of $\log_{10}(\sigma/\mathrm{S\,cm^{-1}})$ vs. $1/T$ with respect to vanadium content for the PEG200 system in Fig. 4(c). It is noticeable that in the impedance plots for these systems capacitive arcs observed for the FPEG600 and FPTMO650 systems at frequencies ⩽64000 Hz are absent for FPEG200 systems (see Fig. 5). This is consistent with a greater electronic contribution to the conduction of the the latter.

It is of interest that the FPTMO650–$LiN(SO_2CF_3)_2$ system is an effective polymer electrolyte performing as well as the

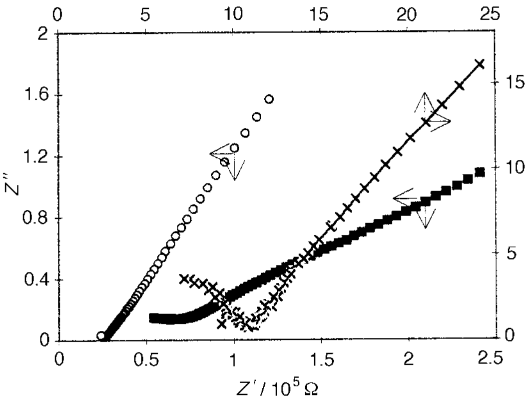
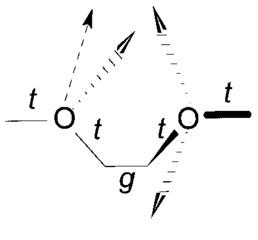
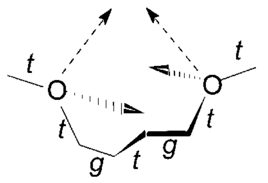


Fig. 5 Impedance plots of lithiated hybrid gels ($r=3$, $x=0.05$) at 20 °C (—■— FPTMO650-based gels, —×— FPEG600-based gels, —○— FPEG200-based gels).

PEG-based systems in these studies. The possibility of using PTMO as a polymer electrolyte has also been suggested by Furtado *et al.*[15] The latter group also proposed a crystalline complex with stoichiometry [Li^+/ether oxygen] $=0.25$ although in the present work the maximum salt concentration was $x=0.05$ before the $LiN(SO_2CF_3)_2$ salt was observed to precipitate under the optical microscope. It is well known that in PEO-based electrolytes the alkali metal salts are dissolved by association with adjacent ether oxygens in *trans–gauche–trans* (*tgt*) conformations about O–C, C–C and C–O bonds, respectively.



In PTMO, however, a plausible structure with similarly converging oxygen 'lone pairs' can only be constructed with *tgtgt* conformations of the $CH_2CH_2CH_2CH_2$ segment (arrows indicate directions of 'lone pair' electrons).



Even with a lower proportion of the flexible C–O bonds, ion mobility might be expected to be comparable to that of PEO as the T_g and T_m of the pure high molecular weight polymers suggest. Published T_g values for high molecular weight PEO and PTMO are 232 and 189 K, respectively[16] and corresponding melting temperatures are *ca.* 65 °C for PEO and 43–60 °C for PTMO.

The origins of poor salt solubility and conductivity in the 'intermediate' poly(trimethyleneoxide) system are an interesting subject for further investigation.[17,18]

Electrochromic studies

To study the electrochromic behaviour of the hybrid films, FPEG600-based coatings made from the sol containing 25 wt.% polymer at modification ratio $r=2$ were constructed. A cell with the configuration glass|ITO|$Li_x(TiO_2–CeO_2)$| $PEO_8–LiN(SO_2CF_3)_2$|FPEG600–V_2O_5 ($r=2$)|ITO|glass was set up. A reversible colour change was observed upon applying ±2 V to the cell. When +2 V was applied to the ion storage layer the cell turned from green to bluish-grey; by reversing the potential the cell changed from bluish-grey to yellow according to the following reversible process:

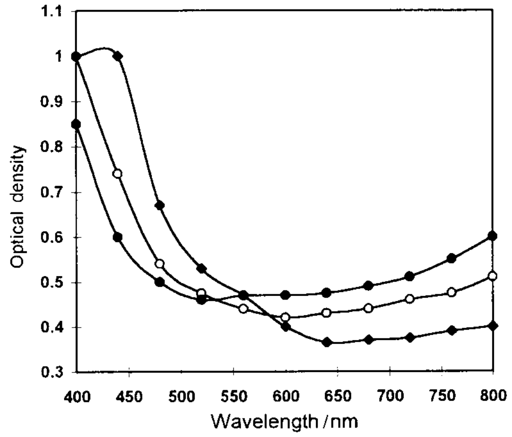


Fig. 6 Optical density *versus* wavelength of a transmissive electrochromic cell glass|ITO|$TiO_2–CeO_2$|FPEG600–V_2O_5 coating|PEO–LiN-$(SO_2CF_3)_2$|ITO|glass at various potentials across the cell with respect to the ion storage layer (—○— 0 V, —◆— −2 V, —●— +2 V).

$$x\,Li^+ + x\,e^- + V_2O_5 \leftrightarrow Li_xV_2O_5$$

yellow–green bluish-grey

The net result of the Li^+ ion insertion is the reduction of vanadium from a valency of 5 to 4. When the current is reversed and a positive potential is applied to the electrode coated with the ion storage layer, Li^+ ions move towards to the negative side. This causes the vanadium ions to be oxidised to V^V which is responsible for the yellow colouration.

The colour change observed for the hybrid coatings is consistent with the observations of Nagase *et al.*[19] and Shimizu *et al.*[20] who reported a two step colour change, yellow–green to bluish grey, in a liquid electrochromic cell based on a vanadium pentoxide film. (Nabavi *et al.*[3] reported that their cell showed a one-step electrochromism from yellow to green and *vice versa*. The difference in these observations may be attributed to the different 'starting' valences of vanadium. The V_2O_5 film, which was prepared from $VO(OAm^t)_3$ (Am^t = *tert*-amyl) by Nabavi *et al.*, has less tendency to be reduced, owing to incomplete hydrolysis, and the vanadium mainly exists in a valency of 5. Electrochemical reduction of the film and insertion of Li^+ produces blue V^{IV} species and changes the colour of the film to green. However, the vanadium pentoxide film prepared by Nagase *et al.* had been prepared from VIP, so that the vanadium had valences of both 5 and 4). The response time of the cell was <2 min. Fig. 6 shows the variation of optical density with wavelength observed for this cell.

Although the optical densities of electrochromic cells prepared in this study were not measured under open-circuit conditions, it was noted that the colours remain stable for *ca.* one day after which they tend to fade. This duration is comparable with the results of Shimizu *et al.*[20] who reported that the short-term memory effect of their open circuit cell was *ca.* 50 h.

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