A SOL–GEL ROUTE TO COMPOSITE POSITIVE ELECTRODES FOR LITHIUM CELLS WITH POLYMER ELECTROLYTES

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Summary

Vanadium oxides prepared via the sol–gel technique have been shown to exhibit high capacities as positive electrodes in polymeric electrolyte–lithium cells. One of the main advantages of the sol–gel technique is the facility to place additives into a dilute gel mixture which may then be frozen into the resulting oxide structure. By using this method, novel composites have been prepared by incorporating ionically and electronically conducting polymers into the vanadium oxide matrix.

1. Introduction

In recent years, all-solid-state lithium cells based on polymeric electro-lytes, for example poly(ethylene oxide) (PEO), have been extensively studied as potential high energy rechargeable battery systems [1 - 3]. Lithium insertion compounds such as transition metal oxides, for example V_6O_{13}, function as positive electrodes in cells of this type. In order to obtain a battery with a high specific power the transport of both lithium ions and electrons into the insertion electrode material should be fast. The overall rate of discharge will be controlled by the slower of these two processes. Some insertion electrode materials exhibit high electronic con-ductivities which are maintained during discharge. However, most com-pounds have poor electronic conductivities or electronic conductivities which decrease on discharge, for example V_6O_{13} [4]. The ionic conductivity of lithium in transition metal oxides is generally lower than that in the polymeric electrolyte. For example, the ionic conductivity of V_6O_{13} varies from 10^{-4} to 10^{-6} S cm^{-1} for $x = 0 - 0.17$ [5] at 120 °C compared with 10^{-4} S cm^{-1} for PEO–LiCF$_3$SO$_3$ ([EO units]:[Li] = 8:1) at 120 °C. As a result there is a build up of lithium inside the surface of the insertion electrode material during cell discharge. This, in turn, creates a negative over-

voltage which acts to depress cell voltage and reduce the available capacity in the insertion electrode material.

To overcome these problems, insertion electrode materials are often mixed with ionic and electronic conductors to form composite electrode structures with improved discharge kinetics [1 - 3]. In the case of polymeric electrolyte cells, small particles of the oxide are mixed with polymer electrolyte and acetylene black. One of the main problems with this type of composite structure is the loss in capacity which occurs to varying degrees depending on cycling conditions. This loss has been attributed to changes in the macrostructure of the composite electrode due to the breaking up and expansion and contraction of V_6O_{13} particles on insertion and extraction of lithium [6]. This is believed to result in a reduced surface area of contact, and isolation of V_6O_{13} particles from the ionic and electronic conducting pathways.

For maximum operational efficiency, the ionic and electronic conductors must form two sets of interconnected networks, each maintaining contact with its respective bulk phase and the insertion oxide material in such a way as to minimise the number of voids and isolated particles. Therefore, the ideal structure for an insertion electrode oxide material would be in a composite structure in which the oxide was microdispersed in, and in intimate contact with, an ionically and electronically conducting medium. This would provide redox centres directly upon the ionic and electronic conducting pathways. A completely homogeneous material of this type would not be expected to lose capacity as a result of macroscopic changes in the electrode structure.

The sol–gel method of preparing materials has emerged as a powerful technique in recent years [7]. Sol–gel processes have been exploited in making a wide range of glass ceramics and oxides of practical importance. An interesting feature of the sol–gel reaction is that composites can be made on a molecular scale by dipersing oligomeric or polymeric species in the colloidal sol–gel solution; on drying, these species can become fixed within the sol–gel matrix. Materials made in this way should reflect a combination of the properties of the sol–gel oxide and the incorporated polymeric components.

The aim of this work was to prepare transition metal oxide composites with ionic and electronic conductors via a sol–gel process. A single 'mixed' conducting polymer combining both high electronic and ionic conductivities would have been ideally suited to this purpose; such polymers were synthesised by the addition of oligoether side chains to electronically conducting poly(pyrrole) [8], but their insolubility prevented incorporation into a sol–gel solution. In the experiments reported here, it was necessary to add both the ionically (in this case Li^+-doped PEO) and the electronically (in this case poly(pyrrole) and acetylene black) conducting additives separately to the sol–gel matrix. The properties of composites formed in this way are described in this paper.

2. Experimental

2.1. Materials and preparation

Vanadium oxide sols were prepared by the hydrolysis of vanadyl triisopropoxide, $VO(OC_3H_7)_3$ (ex Alpha Ventron Chemicals). $VO(OC_3H_7)_3$ (2 cm^3) was poured into distilled water (50 cm^3) in a 100 ml beaker. A red gel was immediately formed on contact of the two solutions. The gel was dispersed by vigorous stirring with a magnetic follower to produce a homogeneous dark red solution. Polymer electrolyte–complex solutions were prepared by dissolving PEO (MW 5×10^6, ex Aldrich) and lithium trifluoromethanesulphonate (ex Aldrich) in an appropriate solvent to form 2% (wt./vol.) solutions of PEO–LiCF$_3$SO$_3$ ([EO units]:[Li] = 8.1). Solutions were prepared in both acetonitrile (H.P.L.C. grade, ex B.D.H.) and distilled water. Poly(pyrrole) colloidal solutions (2% in distilled water) were prepared after the method of Armes et al. [9] by the oxidation of pyrrole with FeCl$_3$ in the presence of poly(vinyl acetate) (96% hydrolysed, ex Aldrich).

By careful manipulation of addition and mixing procedures, it was possible to disperse, uniformly, both PEO and colloidal poly(pyrrole) in the vanadium oxide sol. The preparation procedures were as follows.

(i) Vanadium oxide/PEO. Colloidal vanadium oxide solution (50 cm^3) was added to an aqueous 2% PEO–LiCF$_3$SO$_3$ solution (11 cm^3) dropwise and with vigorous stirring to produce a uniform viscous solution.

(ii) Vanadium oxide/PEO/poly(pyrrole). 2% colloidal poly(pyrrole) (5 cm^3) was added dropwise with stirring to an aqueous 2% PEO–LiCF$_3$SO$_3$ solution. Colloidal vanadium oxide solution was added to the resulting solution in the same manner as outlined above.

Vanadium oxide and composite films were produced from the above solutions by casting onto poly(ethylene) substrates. After evaporation of water, dark red, free-standing films (of approximate thickness 50 - 60 μm) could be peeled from the substrate. The films were further dried at 120 °C under vacuum (<1 Torr) for 24 h.

In an additional series of experiments, composites were prepared by ball-milling Shawinagan acetylene black (0.06 g) into both colloidal vanadium oxide solution (50 cm^3) and colloidal vanadium oxide/PEO solution (50 cm^3). The resulting dispersions were cast and dried in the same manner as reported above to form free-standing composite films.

2.2. Materials characterisation

X-ray diffractograms of the films produced were taken using a Phillips PW1840 X-ray diffractometer (Cu Kα radiation). Optical micrographs were taken (using an Olympus BH2 microscope) of the vanadium oxide sol and composite solutions cast directly onto microscope slides to produce thin (optically transparent) films of approximately 5 μm thickness, Electron micrographs of the films were taken on a JEOL JSM-35 electron microscope with a Phillips 9100 EDAX attachment. Transmission electron micrographs were taken on composite samples by casting directly onto TEM stubs

to produce extremely thin films. Electron diffraction patterns of these samples were also measured. Electronic conductivities of the films were measured by the Van der Pauw method using a Jandel commercial 4-point probe apparatus.

2.3. Electrochemical characterisation

In order to assess the performance of the films as positive electrode materials in lithium–polymeric electrolyte batteries, small scale 'sandwich' type cells were constructed. The cells consisted of lithium foil (100 μm, ex Lithco) cut into 1.5 cm^2 discs, polymer electrolyte (PEO–LiCF$_3$SO$_3$, [EO units]:[Li] = 8:1, 2 × 50 μm discs of area 2 cm^2 prepared by casting a 2% solution of the polymer complex in acetonitrile), and discs of area 1.5 cm^2 of the vanadium oxide and composite films, prepared as outlined above, as the positive electrode. The cells were assembled in an argon-filled glove box (H$_2$O < 10 ppm); the components were placed into specially designed (water and air tight) cell holders and squeezed together under spring pressure (0.20 - 0.25 kg cm^{-2}). Constant current, cell cycling measurements were made using an in-house-built, computer-controlled, constant current supply and data logger.

3. Results and discussion

3.1. Vanadium oxide gels

Optical and scanning electron micrographs of vanadium oxide gels showed uniform featureless films (and are therefore not shown here). Transmission electron micrographs (Fig. 1(a)) show that the vanadium oxide gels have a structure which consists of intertangled, ribbon-like fibres of approximately 10 nm thickness. This structure is very similar to that reported for vanadium oxide xerogels prepared by the polycondensation of decavanadic acid [10] and hydrolysis of vanadium alkoxide in an ethanol solution [11]. The structure of gels of this type has been extensively studied by Livage et al. [10, 12 - 14] and found to consist of fibres with a structure closely related to the lamellar structure of orthorhombic V$_2$O$_5$. A broad but weak X-ray diffraction pattern (Fig. 2) was obtained for the vanadium oxide gel; the d-spacings of the peaks were about the same as those reported by Livage [14], who deduced that the peaks arose as a result of stacking of the ribbons along a direction perpendicular to the surface of the substrate.

Conductivity measurements (4-point method) are shown in Table 1 for both vanadium oxide and the composite materials before, and after, drying. The values obtained were in the same range as those reported by previous workers [14]. The conductivity of the vanadium oxide sample was found to decrease after the drying step at 120 °C. It should be noted that the measurement technique does not distinguish between ionic and electronic conductivities. Therefore, water may play a significant role in the conduction process, particularly for the samples dried at room temperature.
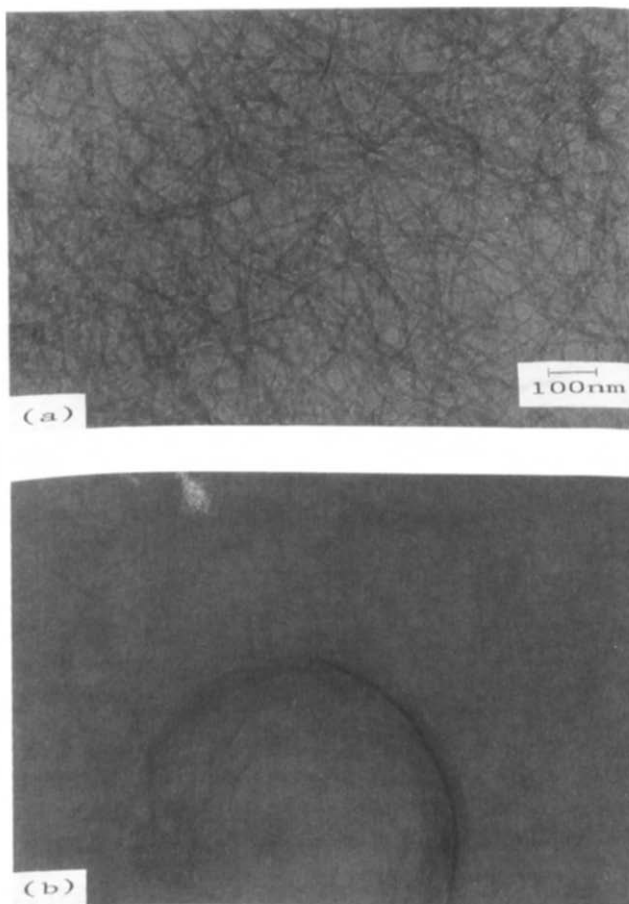
Fig. 1. Transmission electron micrographs of (a) vanadium oxide gel and (b) vanadium oxide/PEO composite gel.

In fact, vanadium oxide gels have already been identified as solid state proton conductors [14].

A slow (0.033 mA cm^{-2}, approximately $C/50$) discharge curve for a vanadium oxide film is shown in Fig. 3; the smooth curve, corresponding to single phase behaviour, is consistent with its amorphous structure. The constant current cycling behaviour (0.333 mA cm^{-2}, approximately $C/5$, discharge current, 0.083 mA cm^{-2} charge current) is summarised in Table 2. The capacity achieved from the amorphous vanadium oxide gel (0.79 Li: V_2O_5) was lower than that reported by West $et\ al.$ [15] who obtained 1.1 Li:V_2O_5 (in a vanadium oxide xerogel prepared by polycondensation of decavanadic acid, evaluated in a similar all-solid-state cell construction to that reported here using identical voltage limits). The difference in results was probably due to the higher current densities used here (0.33 mA cm^{-2}, compared to 0.05 mA cm^{-2} used by West).
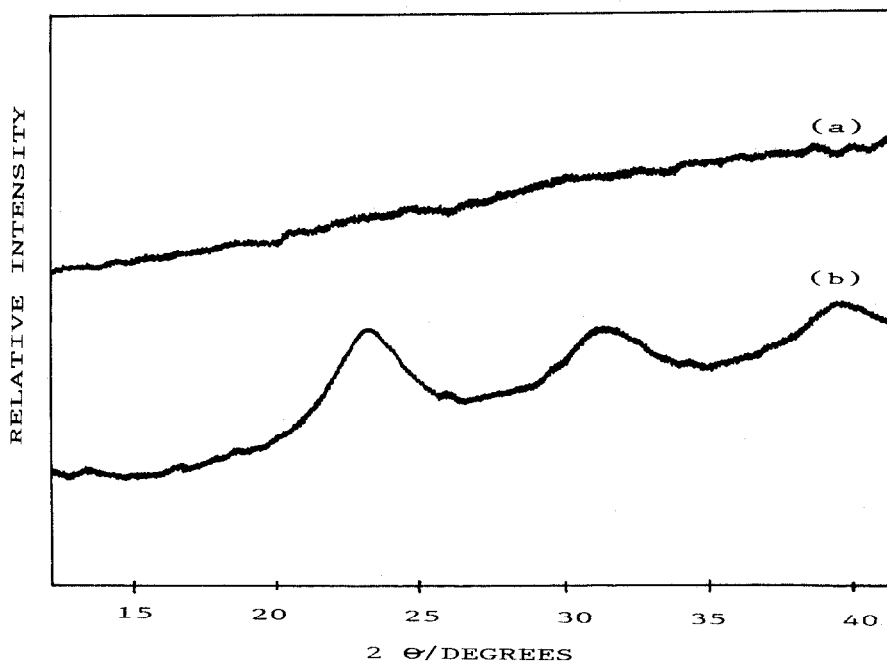
Fig. 2. X-ray diffraction patterns of (a) vanadium oxide/PEO composite film compared to (b) vanadium oxide film.

TABLE 1

Conductivities (measured on 4-point probe) of amorphous vanadium oxide (AV_2O_5) and composites with PEO, acetylene black (C) and poly(pyrrole) (PPy)

Sample	Conductivity (S cm^{-1} × 10^{-8})	
	Prior to drying	After drying at 120 °C
AV_2O_5	44.2	2.95
AV_2O_5/PEO	1.92	0.034
AV_2O_5/C	147.0	29.5
AV_2O_5/PEO/C	1.97	0.085
AV_2O_5/PEO/PPy	86.5	0.031

3.2. Vanadium oxide/PEO composite gels

Optical and scanning electron micrographs of vanadium oxide/PEO composite gels again showed uniform homogeneous films. EDAX elemental mapping of vanadium *versus* sulphur (contained in the PEO dopant compound, $LiCF_3SO_3$) showed an even distribution of both elements throughout the sample giving evidence of an even distribution of vanadium oxide and PEO on a micron scale. Transmission electron micrographs (Fig. 1(b)) showed that the vanadium oxide gels maintained a similar microstructure in
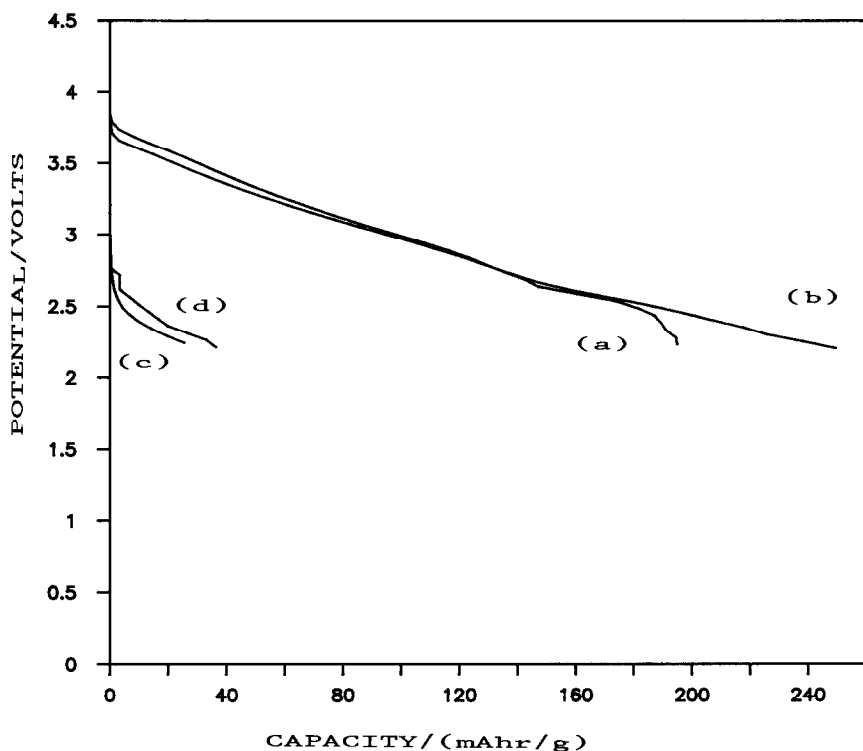
Fig. 3. Variation of cell capacities of vanadium oxide and composite cells for a 0.033 mA cm^{-2} discharge; (a) vanadium oxide, (b) vanadium oxide/acetylene black, (c) vanadium oxide/PEO and (d) vanadium oxide/PEO/acetylene black.

TABLE 2

Summary of cell cycling data for vanadium oxide (AV_2O_5) and composites, with PEO and acetylene black (C)

Material	OCV initial (V)	OCV 24 h (V)	Cycling capacity (mA h g^{-1}) (3.5 - 2.2 V, 0.33 mA cm^{-2} discharge)		
			Cycle 1	Cycle 10	Cycle 25
V_2O_5	3.937	3.839	116 (0.79)[a]	102 (0.69)	81 (0.55)
V_2O_5/PEO	3.319	3.160	7 (0.05)	11 (0.07)	12 (0.08)
V_2O_5/C	3.833	3.819	185 (1.26)	160 (1.08)	120 (0.81)
V_2O_5/C/PEO	3.371	3.196	14 (0.10)	16 (0.11)	16 (0.11)

[a] Results in brackets denote the number of Li per vanadium oxide formula unit (assumed to be V_2O_5).

the presence of PEO. However, the pictures were less clear and it was thus more difficult to distinguish clearly. The presence of small bubble-like features of approximately 500 nm diameter was also noted. These were

probably due to the formation of crystalline PEO spherulites. Both X-ray (Fig. 2) and electron diffraction (Fig. 4) patterns showed the vanadium oxide films to be more amorphous in character in the presence of PEO.

These results suggested that the desired uniform microcomposite structure had been obtained. However, constant current cycling measurements (Table 2, Fig. 3) showed that the vanadium oxide/PEO composite had a disappointingly low capacity, in comparison to vanadium oxide alone, under the cycling conditions used. The results may be explained with reference to the electronic conductivity measurements shown in Table 1. Vanadium oxide composites containing PEO had a conductivity reduced by two orders of magnitude when compared to vanadium oxide alone. This result, together with the microscopic characterisation results described above, suggests that vanadium oxide particles become isolated from one another due to the presence of PEO. Interparticle electron transport must
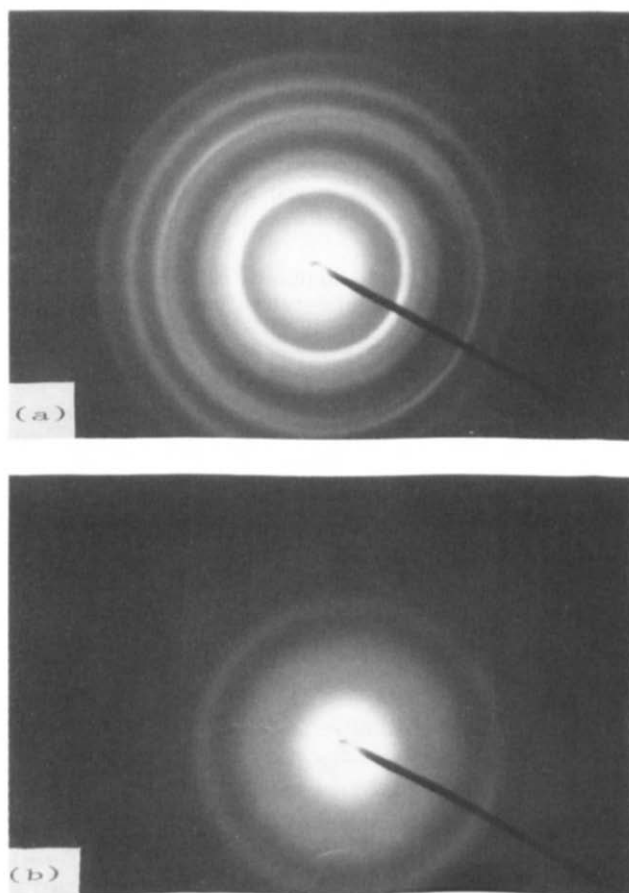

Fig. 4. Electron diffraction patterns of (a) vanadium oxide gel and (b) vanadium oxide/PEO gels for selected areas from Fig. 1.

then occur via a greater tunnelling distance from one vanadium oxide particle, through PEO, to another vanadium oxide particle. This would explain the large conductivity decrease observed. The low capacities achieved during cell cycling may then be explained by the lower electronic conductivity resulting in higher overpotentials on discharge in the vanadium oxide/ PEO composite in comparison to vanadium oxide alone.

3.3. Vanadium oxide/PEO/poly(pyrrole) composites

In vanadium oxide/PEO composites containing poly(pyrrole), a homogeneous film was again seen in optical and scanning electron micrographs. An attempt was made to monitor the poly(pyrrole) distribution by elemental mapping of chlorine (incorporated in the dopant anion) by EDAX. However, the concentration of chlorine was too low to be accurately monitored. The transmission electron micrographs obtained were similar to that illustrated in Fig. 1(b): no additional features directly attributable to poly-(pyrrole) could be observed.

The effect of incorporation of poly(pyrrole) into a vanadium oxide/ PEO composite was a slightly enhanced conductivity in samples dried at room temperature (Table 1); however, after drying at 120 °C, this improvement disappeared. A poly(pyrrole) film, cast from colloidal solution and dried in the same manner, was also found to decrease in conductivity, in this case from 10^{-2} to 10^{-5} S cm^{-1}, after drying at 120 °C. The decrease may have been due to either degradation of poly(pyrrole) or loss of water. Although no poly(pyrrole) could be detected in the composite by TEM, other workers have reported that the polymer consists of spheres of approximately 100 nm diameter [9]; these spheres would not be expected to form a continuous electron conducting 'percolation' pathway through the vanadium oxide/PEO structure unless incorporated at very high concentrations. Electron transport would, therefore, again have to be via a tunnelling mechanism through PEO. Since no improvement in electronic conductivity was obtained, no attempts were made to evaluate the cycling capacity of this particular composite.

3.4. Composites with acetylene black

A more ideal electronically conducting component would consist of long fibres which could be expected to form a continuous electron conducting pathway through the composite structure. No suitable, soluble, conducting polymer of this type is currently available; however, acetylene black, which is used as the electronically conducting component of ball-milled oxide/PEO composite films, does have a suitable structure. When acetylene black was incorporated into vanadium oxide solutions by ball-milling, the resulting films exhibited an enhanced conductivity by one order of magnitude (Table 1).

Constant current cycling measurements on these films (Table 2, Fig. 3) showed an enhanced capacity compared with that of vanadium oxide alone. A similar capacity (1.26 Li:V_2O_5) was achieved to that of West *et al.* [15]

despite using a higher current density. This indicates enhanced kinetics, as a result of the addition of the acetylene black, due to an improved electronic conductivity. In the experiments of West *et al.* reversible cycling of 1.1 Li:V_2O_5 could be obtained over 20 or more cycles with greater than 99% cycling efficiency. However, in these experiments a decline in capacity with cycle number was observed. This may have been due to the presence of some residual water, since the oxides in this study were dried at 120 °C, whereas the oxide of West *et al.* was dried at 230 °C.

In the case of addition of acetylene black to a vanadium oxide/PEO composite, only a small enhancement in electronic conductivity (Table 1) was obtained. Consequently, low cell cycling capacity was achieved (Table 2, Fig. 3). These results may be explained with reference to the optical micrographs shown in Fig. 5. In the case of the vanadium oxide/acetylene black composite, a continuous network of acetylene black fibres was formed.
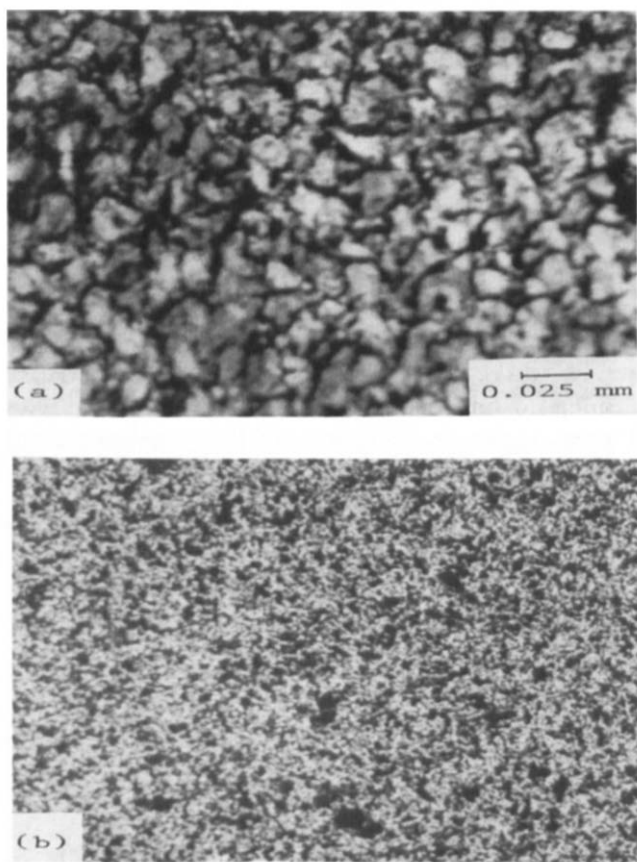
Fig. 5. Optical micrographs of (a) vanadium oxide/acetylene black ball-milled composite and (b) vanadium oxide/PEO/acetylene black ball-milled composite.

However, for the vanadium oxide/PEO/acetylene black composite, the acetylene black was dispersed as discrete aggregate particles of approximately 10 μm diameter. No continuous, electronically conducting pathway was formed and therefore there was only a slight improvement in conductivity of the sample.

The morphology change of the acetylene black in the presence of PEO is not understood — although the effect is similar to the flocculation of long chain colloidal molecules in media of high ionic strength. A method is required for producing a long chain electronic conductor which is not affected by the presence of ionic conductors, such as PEO, before the microcomposite electrode concept can be fully evaluated. There have been many advances in the improvement of the solubility and processibility of electronically conducting polymers over the past year [16] and it is now possible to achieve limited solubility in several ways; therefore a suitable polymer may soon become available.

Conclusions

Sol–gel has been demonstrated as a suitable technique for preparing composite structures with ion and electron conducting polymers; the electronic conductivity was the limiting factor in the cycling rate. It has not been possible to prepare the proposed microcomposite electrode structure. The major problem was to find an appropriate soluble electronic conductor: the only solution-processible form of poly(pyrrole) available was a colloidal latex solution that, as a result of its structure, did not form a continuous electronically conducting pathway. Acetylene black, which has an appropriate structure, could be used to enhance the capacity of vanadium oxide gels but in the presence of PEO it did not form a continuous conducting pathway. The critical step for further development is therefore the preparation of a polymer which is compatible with sol–gel processing technology, possesses moieties conducive to high electronic and ionic conductivity and forms into a structure in which both conducting pathways form percolating networks.

Acknowledgements

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