V_2O_5-BASED GLASSES AS CATHODES FOR LITHIUM BATTERIES

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Summary

The electronic conductivities of glasses in the TeO_2–V_2O_5 and TeO_2–V_2O_5–MoO_3 systems have been determined in the 20 - 200 °C temperature range to give simple Arrhenius relationships. Chemical and electrochemical lithium intercalations have been performed showing that V_2O_5-based glasses are suitable positive electrode materials for lithium batteries.

Introduction

The growing interest in new solid state, high density batteries has led to research into electrochemical cells with alkali metal negative electrodes. In such cells, the positive electrode materials must present a high oxidizing power compared with the redox couple involved at the anode (Li/Li^+ for lithium batteries). Since these electrode materials have to provide the transition between the ionic conductivity in the electrolyte and the electronic conductivity in the current collector, they have to exhibit both electronic and ionic conductivity, and the electrochemical reaction has to be able to delocalize itself throughout the whole material. For that reason, the electrode material must have a large non-stoichiometric domain for the involved ionic species.

Such compounds can be described as rigid host structures for mobile alkali ions with their compensating electrons and can be regarded as intercalation compounds. The most widely studied materials among these intercalation compounds are *crystallized* solids such as transition metal oxides [1, 2] or sulphides [3, 4]. Intercalation studies on some of these crystallized materials have shown that they may become *amorphous* after many intercalation/de-intercalation cycles. On the other hand, some promising new compounds (MoS_3 or $MoSeS_3$) can only be obtained in the amorphous state [5, 6]. Much interest is, therefore, now focussed on new amorphous electrode materials and particularly on conductive glasses.

Transition-metal-ion-containing glasses are known to be electronic conductors [7]. They are, in fact, electronic semiconductors and are able to accept alkali or silver ions in their structure. Associated with appropriate network formers, they may be relatively easy to synthesize with promising electrochemical properties.

The following relates to results obtained for glasses in the TeO_2–V_2O_5 binary system and in the TeO_2–V_2O_5–MoO_3 ternary system.

Experimental

The different compositions are prepared by dry mixing the appropriate amounts of the different oxide powders. Each mixture is then placed in a vacuum-sealed quartz tube which is heated in an oven at 900 °C for two hours. The melts are then rapidly quenched in cold water. To eliminate the mechanical stresses resulting from the quenching the samples are annealed for several hours at a temperature of about 180 °C.

The glass transition temperatures, T_g, are determined by differential thermal analysis and the amorphousness of the samples is checked by X-ray diffraction measurements. The glass density is determined by the liquid displacement method and the concentration in lithium after chemical lithiation is determined by flame spectroscopy analysis.

Conductivity measurements

The massive glass samples are sliced into cylindrical pellets. Platinum paint (Degussa M 308A) is deposited on the pellet faces to form the electrodes. The resistance of the sample is measured by a 4192A Hewlett-Packard impedance meter in the frequency range 5 Hz - 13 MHz. For all TeO_2–V_2O_5 samples, the characteristic impedance diagrams are slightly decentred semi-circles, indicating that the samples are homogeneous and single-phased.

In the temperature range studied (20 - 200 °C), Arrhenius plots of the conductivity are straight lines (Fig. 1) leading to a simple relationship of the form:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \tag{1}$$

where all parameters have their usual meaning. This expression corresponds to a simplified equation given for the electronic conductivity in semiconducting glasses derived from the small polaron theory [8]. For non-crystalline compounds, with acceptor levels (ions in the higher valency state) and donor levels (ions in the lower valency state), the conductivity can be expressed by [9]:

$$\sigma = \frac{c(1-c)e^2\nu_0}{kTR} \exp(-2\alpha R) \exp\left(-\frac{W_p + W_d}{2kT}\right) \tag{2}$$

ν_0 is a frequency term, c the site occupancy ratio, *i.e.*, the ratio between the number of sites at the lowest valency and the total number of sites, and R is the average distance between two adjacent sites. The $\exp(-2\alpha R)$ term describes the overlap of the wave function, W_p is the polaron binding energy and W_d is a disorder energy term.
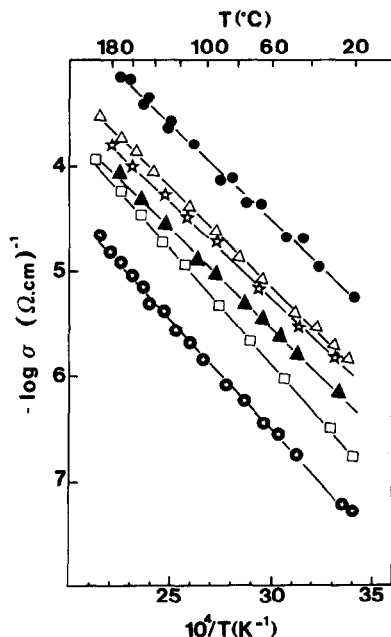
Fig. 1. Arrhenius plots of the conductivity for glasses in the yV$_2$O$_5$–$(1-y)$TeO$_2$ system ($\square$, 0.2; ⬤, 0.33; ▲, 0.4; ☆, 0.5; △, 0.6; ●, 0.7).

Experimental results show that the conductivity increases while activation energy decreases with the V$_2$O$_5$ content. These results are consistent with those published by Dhawan *et al.* for the same system [10].

Assuming a random distribution in the vitreous matrix, the average distance between two vanadium atoms, R, can be calculated from the glass density and the chemical composition by the following equations as proposed by Hirashima [11]:

$$R = \left(\frac{M_m}{2x\rho N}\right)^{1/3} \tag{3}$$

where M_m is the molar mass of the sample, ρ the glass density, x the molar concentration in V$_2$O$_5$ and N is Avogadro's number. The results presented in Table 1 show a decrease of the mean spacing with increasing V$_2$O$_5$ content and decreasing density.

The isothermal conductivity variations *versus* composition for glasses containing the two transition metal oxides, *i.e.*, V$_2$O$_5$ and MoO$_3$, are presented in Fig. 2. These results show that a conductivity maximum is obtained for a composition for which the activation energy presents a minimum (Fig. 3). No simple explanations can be given for these variations. Comparing these variations with the glass transition temperature variations (Fig. 4) in the ternary system, note the similar evolution of these parameters with composition, indicating a probable correlation between conductivity and transition temperature.

TABLE 1

Compositions, glassy transition temperatures, densities, average distances, chemical lithium intercalation ratios, conductivities and activation energies for the different samples

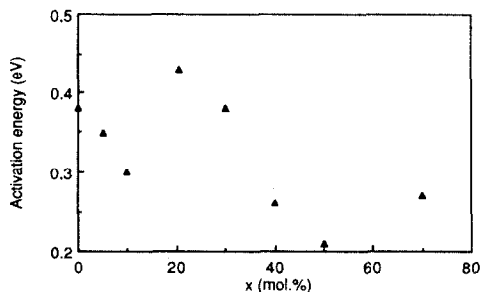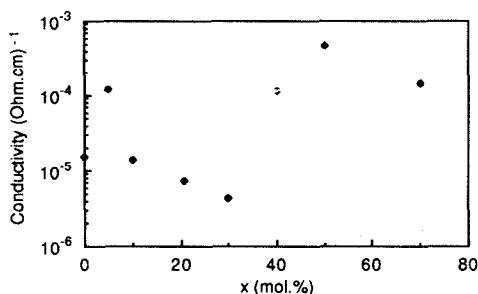| Nominal V_2O_5 (mol%)	70	60	50	40	33	20
Actual V_2O_5 (mol%)	68.72	61.26	49.77	—	32.17	—
T_g (°C)	218	223	228	245	259	273
ρ (g cm^{-3})	3.45	3.68	4.07	4.25	4.32	4.69
R (nm)	0.392	0.402	0.411	0.435	0.460	0.526
Li/V ratio	1.08	2.59	3.42	—	1.85	—
σ_0 (Ω cm)$^{-1}$	91.2	3.75	1.63	1.37	0.62	4.57
E_a (eV)	0.364	0.380	0.362	0.370	0.417	0.433

Fig. 2. Isothermal conductivity variations as a function of the molar content in MoO_3 for glasses $xMoO_3-(1-x)[0.6V_2O_5-0.4TeO_2]$ ($T = 80$ °C).

Fig. 3. Activation energy variations as a function of the molar content in MoO_3 for glasses $xMoO_3-(1-x)[0.6V_2O_5-0.4TeO_2]$.
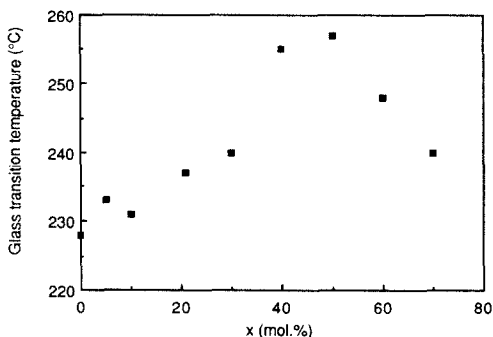

Fig. 4. Glass transition temperature variations as a function of the molar content in MoO_3 for glasses $xMoO_3-(1-x)[0.6V_2O_5-0.4TeO_2]$.

Chemical lithiation

To check the ability of lithium to intercalate in glasses of the $TeO_2-V_2O_5$ system, chemical lithiations with n-BuLi have been performed on vitreous samples in the composition range 33 - 70 mol.% in V_2O_5. All

experiments were carried out under inert atmosphere (argon with less than 1 vpm in O_2, H_2O, N_2). The samples (0.5 - 1 g) are crushed to a powder and placed in a Pyrex tube with cyclohexane. An excess of n-BuLi (1.6 M in cyclohexane) is then slowly added. The volume of reagent is calculated taking into account a possible reduction of vanadium (+V) to vanadium (+II). The tube is firmly closed by a Teflon cork and shaken once a day. The reaction is evidenced by the change in color of the glass powder which turns from brown-yellow to a dark color while the solution becomes orange-red. After three weeks, the compound is vacuum dried to remove the solvent and any remaining n-BuLi. X-ray diffraction analysis has been carried out before and after the reaction in order to check the amorphousness of the lithiated sample. The results are presented in Table 1.

The Li/V ratio, y, has been determined by flame spectroscopy on $Li_x–V_2O_5–TeO_2$ samples. Some results seem to be very large and an over-estimation can come from the remaining lithium after lithiation. Nevertheless, intercalation ratios around 3 have been obtained by electrochemical titration.

The increase in intercalation ratio with decreasing V_2O_5 content may be the result of structural considerations. X-ray diffraction studies by Dimitriev [12] show a change of structural units in $TeO_2–V_2O_5$ glasses with composition. For a low content in TeO_2, the structural units are TeO_3, VO_5. By contrast, for high contents in TeO_2, the units are TeO_4, VO_5, which seem more favourable to the lithium intercalation.

Electrochemical studies

Electrochemical studies have been carried out for the $TeO_2–V_2O_5$ and the ternary system. Solid state cells were formed with pure lithium as the negative electrode and $POE–LiClO_4$ as the Li^+ conductor solid electrolyte. Considering the low electronic conductivity of the glasses, the cathodes were composite electrodes [13] made of a mixture of glass powder ($0.4TeO_2–0.6V_2O_5$), graphite, and a small quantity of polymer electrolyte.

The open circuit voltage curve was obtained as a function of the Li/V ratio (*i.e.*, the number of intercalated lithium atoms per vanadium atom) by the galvanic intermittent titration technique [14]. The electrochemical cell is discharged by pulsing small quantities of direct current and the voltage is recorded when equilibrium is reached, *i.e.*, when the cell voltage variations are less than 1 mV per hour.

The resulting titration curve is presented in Fig. 5. The voltage decreases continuously from a voltage of 3.6 V, showing a break in the slope for a value of the Li/V ratio around 0.6. After this break, the slope is almost constant. The discharge was stopped when the voltage reached 1.5 V. The corresponding Li/V ratio is then 2.75.

A titration curve presenting a break in the slope was also found by Pagnier *et al.* [15] for a similar cell with a $P_2O_5–V_2O_5$ composite electrode. These authors have interpreted this phenomenon in terms of adjacent non-stoichiometry domains as proposed by Armand [16]. Other studies made
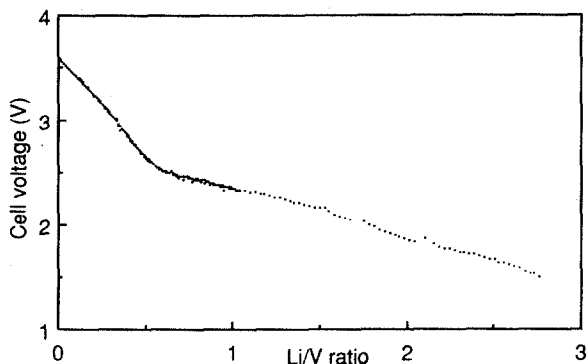
Fig. 5. Open circuit voltage variations as a function of the lithium intercalation ratio for $TeO_2–V_2O_5$ glass. $T = 80$ °C. Discharge rates: Li/V < 1:ΔLi/V = 5.6 × 10^{-3}; Li/V > 1:ΔLi/V = 2.8 × 10^{-2}.

on vitreous V_2O_5 using the same cell-making technology, show the same break in the voltage profile. Under such conditions, it could not be attributed to the presence of tellurium dioxide in the glass.

However, the absence of plateaux after the break and the regular decrease of the voltage shows that no major structural changes occur. The specific energy density calculated from this curve is 1336 W h kg^{-1} (for active material, i.e., $0.4TeO_2–0.6V_2O_5$). Our results are consistent with those given by Sakurai and Yamaki [17] for a cell with a $V_2O_5–P_2O_5$ electrode and a liquid electrolyte: 900 W h kg^{-1} at 1.5 V cut-off voltage and Li/V ratio of 3.

The determination of the lithium diffusion coefficient can be carried out using Fick diffusion equations in the case of a galvanic study. According to the hypotheses proposed by Weppner and Huggins [14, 18], the interfacial concentration in lithium can be approximated by the following expression for small values of time (i.e., $t \ll L^2/D$, where L is the length of the electrode and D the diffusion coefficient):

$$C(0, t) = C_0 + \frac{2I_0\sqrt{t}}{zFS\sqrt{\pi D}} \tag{4}$$

In this expression I_0 is the current intensity, S the electrode surface and F the Faraday constant. Replacing the unmeasurable concentration by the molar fraction of the intercalated ion, y, then $C_0 = y/V_m$, with V_m the molar volume of the electrode. Then differentiating eqn. (4) with respect to the square root of time, the diffusion coefficient can be expressed by:

$$D = \frac{4}{\pi}\left(\frac{I_0V_m}{zFS}\right)^2\left(\frac{dE}{dy} \Big/ \frac{dE}{d\sqrt{t}}\right)^2 \tag{5}$$

All terms in this expression are known or can be experimentally measured. dE/dy is the slope of the coulometric titration curve and $dE/d\sqrt{t}$ the slope of the voltage drop, during the intermittent discharge step, as a

TABLE 2

Li/V ratios, lithium diffusion coefficients and corresponding voltages

Li/V ratio	0.005	0.5	0.9
Li diffusion coefficient ($cm^2 s^{-1}$)	3.14×10^{-11}	1.62×10^{-11}	4.1×10^{-13}
Voltage (V)	3.60	2.65	2.33

function of the square root of time. We have calculated the lithium diffusion coefficient at 80 °C for three different values of the intercalation ratio. The results are presented in Table 2. These values are very similar to the values proposed by Jourdaine [19] for lithium diffusion coefficients in thin films of vapour deposited P_2O_5–V_2O_5 glasses.

The lithium diffusion coefficient in glasses $0.5MoO_3$–$0.3V_2O_5$–$0.2TeO_2$ has been determined using Atlung's abacus [20]. This author has calculated the theoretical concentration profiles of the intercalated species during galvanostatic discharges. Depending on the average grain size of the active material, he deduced the faradic efficiency as a function of the time of the discharge and of the intercalated ion diffusion coefficient. These results can be plotted on abacus giving the discharge depth as a function of the a-dimensional term $\tau D/a^2$ where τ is the discharge duration and a the particle's average size. The discharge depth is deduced from the curves presented in Fig. 6, showing the voltage drop as a function of time when the cells are discharged under constant current. A simple reading of the abacus gives the $\tau D/a^2$ value for the experiment and therefore allows the determination of the diffusion coefficient. The values obtained by this method are around 5×10^{-11} $cm^2 s^{-1}$. Note that this is a quick method giving only the order of magnitude of the diffusion coefficient.
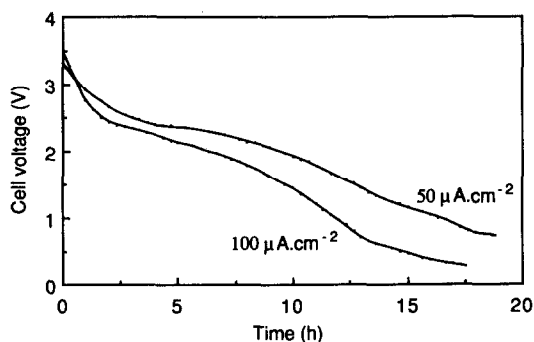

Fig. 6. Galvanostatic discharges on $0.5MoO_3$–$0.5[0.6V_2O_5$–$0.4TeO_2]$-based cells (current densities: 50 μA cm^{-2} and 100 μA cm^{-2}).

Conclusion

V_2O_5-based glasses are good candidates for cathode materials in lithium batteries. Nevertheless, the very poor electronic conductivity of these glasses requires the use of an electronic conductor such as graphite to form composite electrodes, thereby decreasing the specific density energy.

Considering the low conductivity, and the relatively good diffusion coefficient (for a low Li intercalation ratio), the question arises as to which is the limiting step in the intercalation process: Li^+ diffusion or the electronic displacement.

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