INVESTIGATION OF LITHIUM INTERCALATION MATERIALS WITH ORGANIC SOLVENTS AND MOLTEN SALTS AS ELECTROLYTES AT TEMPERATURES BETWEEN 60 AND 175 °C

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Summary

Lithium intercalation in TiS_2 and vanadium oxides (V_2O_5, V_2O_4, V_2O_3) has been investigated in two kinds of electrolytes: (i) molten chloroaluminates (butylpyridinium chloride–$AlCl_3$–LiCl) at 60 °C, and $LiAlCl_4$–LiCl (saturated) at 175 °C; and (ii) dimethylsulfone ($DMSO_2$) + $LiClO_4$ or $LiAsF_6$ at 130 - 150 °C. The intercalation process has been studied by cyclic voltammetry, galvanostatic discharge/charge and open-circuit voltage measurements.

In chloroaluminates, TiS_2 appears to be stable in both media, with a one-step intercalation at 0.40 V (60 °C) or 0.65 V (175 °C) (*versus* Al reference). V_2O_5 can only be cycled at a low temperature (60 °C) and two steps are observed at ~1 V and 0.45 V.

In $DMSO_2$, V_2O_5 intercalates ~2.5 Li^+ per unit V_2O_5, with four steps, as observed in propylene carbonate (PC).

OCV measurements at different intercalation steps indicate that the effect of temperature increases the kinetics of the processes.

A comparison of the OCV variations with Li^+ concentration in $DMSO_2$ and PC suggests that the intercalation process differs in both solvents. The difference can be correlated with changes in the Li^+ solvation effects of the solvents.

Introduction

Lithium intercalation materials for reversible lithium batteries have been widely investigated both in liquid electrolytes at ambient temperature (<100 °C) [1] and in molten salts of the alkaline chloride type at high

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temperature (>300 °C) [2]. However, little is known about liquid electrolytes in the temperature range 100 - 200 °C.

In this study, two kinds of electrolytes have been investigated with lithium intercalation materials: (i) "Low temperature" molten salts of the chloroaluminate type at ≈ 60 °C (a mixture of 31.2 mol% butylpyridinium chloride (BpCl), 55.5 mol% $AlCl_3$ and 13.3 mol% LiCl) and at 175 °C ($AlCl_3$ saturated with LiCl); and (ii) "High temperature" organic electrolytes formed by solutions of lithium salts ($LiClO_4$ or $LiAsF_6$) in molten dimethylsulfone. Both classes of electrolyte have been recently shown to be compatible with lithium intercalation materials [3, 4]. The solvents allow a study to be made not only of the temperature effect on the kinetics of the intercalation process, but also of the solvation effect on Li^+ ions [5, 6].

Experimental

Electrolytes. The method of preparing the molten chloroaluminates has been reported previously [6]. Dimethylsulfone, $DMSO_2$ (Janssen), was recrystallized once in water and then twice in absolute methanol. The material was dried at 90 °C for 48 h and then sublimated under reduced pressure (2 mm-Hg) at 100 °C.

Propylene carbonate, PC (Carlo Erba), was purified by distillation under reduced pressure at 70 °C.

Anhydrous lithium perchlorate (Fluka) was dried under vacuum at 190 °C for 12 h.

Electrodes. The reference electrode used in the chloroaluminate studies was an aluminium wire electrode dipped in the molten electrolyte and buffered with the Cl^- ions of the solution (system Al/Al(III) [7]).

In $DMSO_2$, the reference electrode was a lithium wire in a 0.1 or 1 mol kg^{-1} $LiClO_4$ solution and was housed in a separate compartment.

The working electrodes were aluminium or platinum grids (1 cm^2) on which the cathodic material was pressed under a pressure of 1 ton cm^{-2}. This material comprised vanadium oxide or titanium sulfide particles (overall diameter 20 μm) mixed with graphite powder (Koch-Light, purity 99.99%) at 50 - 90 wt.%. The V_2O_5 (K and K lab.), V_2O_4, V_2O_3 (Alfa-Ventron) and TiS_2 (Cerac) were dried at 120 °C under vacuum for 4 h and stored in a dry atmosphere.

Cells. The design of the cells used for galvanostatic and voltammetric measurements has been described previously [8]. The cells were assembled in a moisture-free, argon atmosphere.

The variation in the open-circuit voltage (OCV) as a function of the intercalation ratio x was obtained by constant-current increments of 50 μA cm^{-2} for 3 - 15 min. Equilibrium was considered to have been reached when the variation of the electrode potential was <1 mV over 1 h.

Potentiometric measurements in $DMSO_2$ and PC were taken with two working electrodes ($Li_x V_2O_5$ and Li) in the same cell, the potential of each one being measured against the same lithium reference electrode.

The electrochemical cells were thermostatically controlled to within ±1 °C.

Results and discussion

Lithium intercalation in molten chloroaluminates

The intercalation of Li^+ ions in TiS_2 was examined in $BpCl-AlCl_3-LiCl$ at 60 °C and $LiAlCl_4-LiCl$ (saturated) at 175 °C both by galvanostatic charge/discharge cycles and by cyclic voltammetry.

The galvanostatic charge/discharge curves exhibited a pattern similar to that obtained in organic or molten chloride electrolytes (Fig. 1(a)). A plateau was observed at low potential values (versus Al reference), i.e., at 0.40 V in $BpCl-AlCl_3-LiCl$, and at 0.65 V in $AlCl_3-LiCl$. The faradaic capacity was 0.8 - 1 Faraday per mole of TiS_2. The end of the voltage plateau was not well defined because of the aluminium reduction phenomenon. The second and subsequent cycles were found to be reversible.

The cyclic voltammogram in the low-temperature solution (Fig. 1(b)) confirmed the reversibility of the intercalation process in the potential range 0.2 - 0.4 V, indicating that TiS_2 behaves in chloroaluminates in the same manner as in other molten salt electrolytes [2].

The intercalation of Li^+ ions in the vanadium pentoxide usually exhibits four steps in lithium-compatible electrolytes. As this compound is not very stable in molten chloroaluminates, the intercalation process can be observed only at low temperature and therefore has been studied in $BpCl-AlCl_3-LiCl$ at 60 °C.

The galvanostatic charge/discharge curves exhibit the first two intercalation steps (corresponding to $x < 1$ Li^+ per V_2O_5 unit) between 1.3 and 0.6 V, and a well-defined plateau at ≈ 0.4 V. The two steps could not be distinguished from each other, even at very low current densities (Fig. 2(a)).

The cyclic voltammogram showed three reduction peaks at 1.1, 0.6 and 0.35 V, and corresponding oxidation peaks at 1.5, 0.90 and 0.65 V (Fig 2(b)). Comparison with equivalent studies in organic electrolytes indicates that the first peak corresponds to $x < 1$ and the third peak to $1 < x < 2$; peak 2 has not been identified.

The stability of the material was investigated by determination of the vanadium dissolved in the electrolyte: no trace of vanadium was observed after 10 cycles but a slow dissolution could be detected after several days.
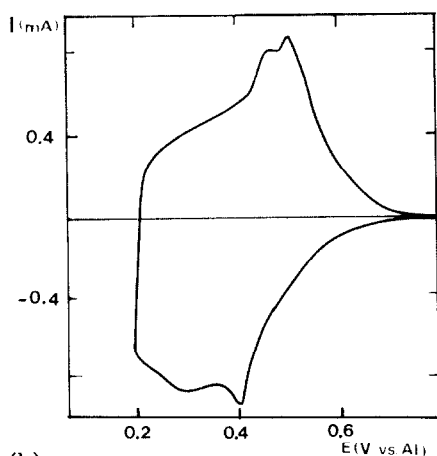
Another vanadium oxide, V_2O_4, yielded a poor Li^+ capacity (Fig. 2(a)) and was not sufficiently stable to be cycled in molten chloroaluminates.

Lithium intercalation in dimethylsulfone

It has been reported that lithium-compatible electrolytes made from $DMSO_2$ and lithium salts (e.g., $LiClO_4$, $LiAsF_6$, $LiAlCl_4$) are good candidates
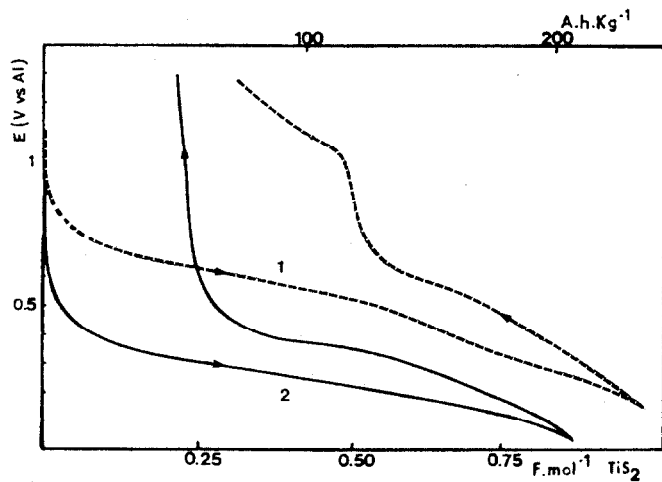
Fig. 1. TiS$_2$ in molten chloroaluminates (reference electrode: Al/Al(III)). (a) Galvano-static discharge/charge at 0.5 mA cm^{-2} (1) LiAlCl$_4$–LiCl (saturated) at 175 °C; (2) AlCl$_3$–BpCl–LiCl at 60 °C. (b) Cyclic voltammetry in AlCl$_3$ (0.555): BpCl (0.312): LiCl (0.133) at 60 °C (0.1 mV s^{-1}).

for lithium intercalation at 150 °C [3, 9]. The behaviour of titanium sulfide in these electrolytes is the same as that observed in low-temperature organic electrolytes, and the galvanostatic charge/discharge curves exhibit a potential plateau at $x = 2.2$ V (*versus* Li reference) [9].

The voltammetric behaviour of V$_2$O$_5$ showed two reversible and very well defined steps between 3.1 V and 3.5 V, and two other steps between 2 V and 2.3 V [3]. Data from galvanostatic curves (Fig. 3) agreed with that from cyclic voltammograms: the first two steps were observed at 3.4 V and 3.2 V (for $x < 0.8$), and the following two appeared at 2.25 V and 2.1 V.
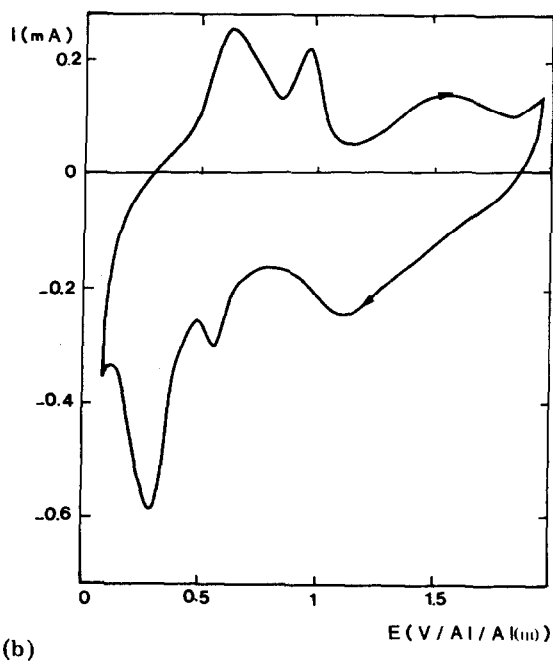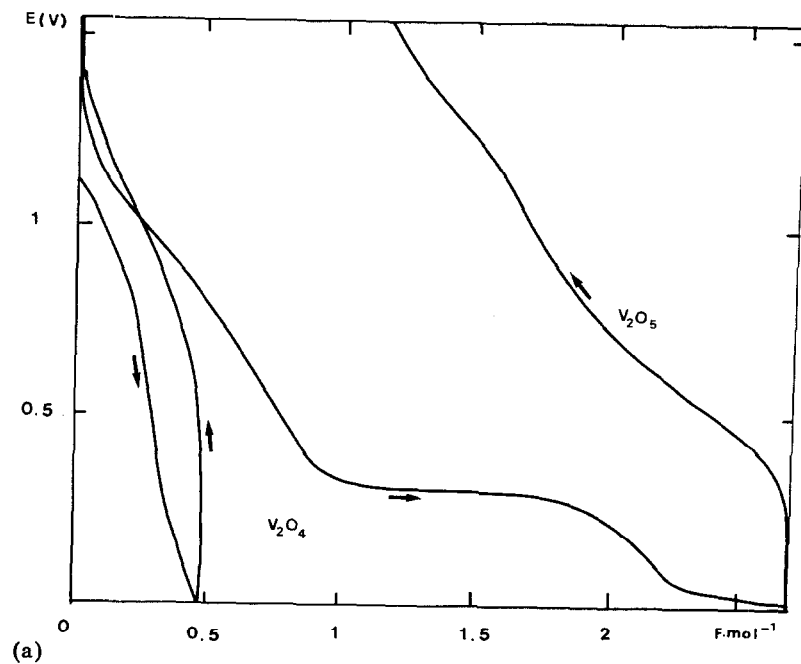
(a)

(b)

Fig. 2. Vanadium oxides in molten $AlCl_3$ (0.555): BpCl (0.312): LiCl (0.133) at 60 °C (reference electrode: Al/Al(III)). (a) V_2O_5 and V_2O_4 galvanostatic discharge/charge at 0.5 mA cm^{-2}; (b) cyclic voltammetry of V_2O_5 (0.1 mV s^{-1}).
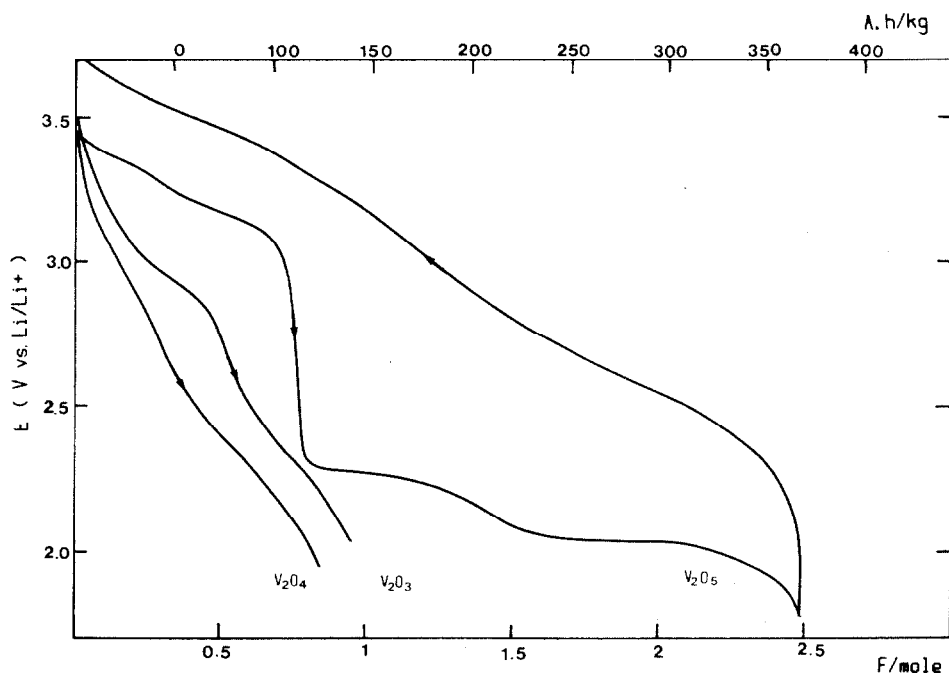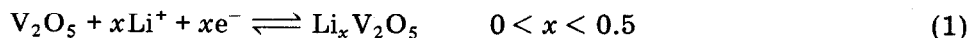
Fig. 3. Galvanostatic discharge/charge curves of vanadium oxides in $DMSO_2 + 1$ mol kg^{-1} $LiClO_4$ at 150 °C and 1 mA cm^{-2} (reference electrode: 1 mol kg^{-1} Li^+/Li).

Vanadium trioxide, V_2O_3, exhibited ill-defined plateaux at 2.9 V and 2.4 V (Fig. 3) with a total capacity lower than 1 Faraday per mole of V_2O_3.

Charge/discharge curves of V_2O_4 in $DMSO_2$ did not allow a better analysis than in molten chloroaluminates.

A more precise study of the first two reversible intercalation steps in V_2O_5 can be undertaken by analysis of the charge/discharge phenomenon with current increments and open-circuit voltage (OCV) measurements (Fig. 4). The quasi-superposition of the discharge and charge curves indicates that, under these conditions, an equilibrium can be reached. The temperature effect on the kinetics of intercalation allows the equilibrium potential to be obtained within 30 min for each increment of current in the interval $0 < x < 1$.

It has been confirmed that in both solvents, PC and molten $DMSO_2$, the $V_2O_5/Li_xV_2O_5$ system ($0 < x < 0.5$) behaves as a reversible and Nernstian system. The potential dependence of the $V_2O_5/Li_{0.15}V_2O_5$ and Li^+/Li redox systems as a function of Li^+ concentration in the electrolyte was compared in PC and $DMSO_2$. $V_2O_5/Li_{0.15}V_2O_5$ electrodes were prepared according to the intercalation reaction:

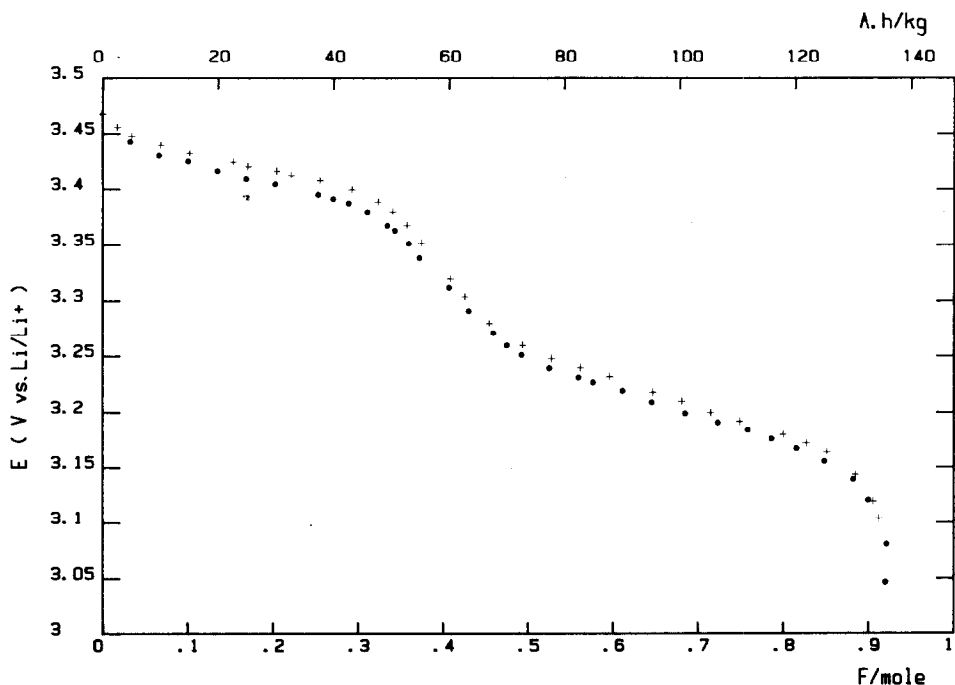$$V_2O_5 + xLi^+ + xe^- \rightleftharpoons Li_xV_2O_5 \qquad 0 < x < 0.5 \qquad (1)$$

Fig. 4. Galvanostatic discharge/charge of V_2O_5 in $DMSO_2$ + 1 mol kg^{-1} LiClO$_4$ for $0 < x < 1$ at 130 °C and 50 μA cm^{-2} (reference electrode:1 mol kg^{-1} Li$^+$/Li).

Experimental results are reported in Fig. 5. In each solvent, the same linear variation of E *versus* log/Li$^+$(s) was found for both the Li$^+$/Li and the V_2O_5/Li$_{0.15}V_2O_5$ redox systems, as expected from the Nernst's relation:

$$E = \text{cste} + \frac{RT}{F} \ln[\text{Li}^+]_s \qquad (2)$$

where (s) refers to Li$^+$ ions in solution.

The discrepancies observed between the theoretical and the experimental slopes are due to the absence of a supporting electrolyte, since the Li$^+$/Li system is known to be reversible in $DMSO_2$ and PC under the corresponding conditions [3]. The V_2O_5/Li$_x$V$_2$O$_5$ system is found to behave like the Li$^+$/Li system, *i.e.*, as a reversible and Nernstian system.

Nevertheless, when OCV measurements, reported as a function of x $(0 < x < 0.5)$, are performed and compared in $DMSO_2$ at 130 °C and in PC at 60 °C, a significant difference appeared between the two sets of results. A classical voltage plateau, corresponding to a two-phase region already described by Dickens *et al.* [10], was found in PC, whereas the experimental OCV plots were seen to be strongly dependent on x in molten $DMSO_2$ (Fig. 6). This difference cannot be attributed to the effect of the temperature; it has been shown, for example, that Li$^+$ intercalation in TiS$_2$ proceeds in the same way in organic electrolytes at ambient temperature and in molten

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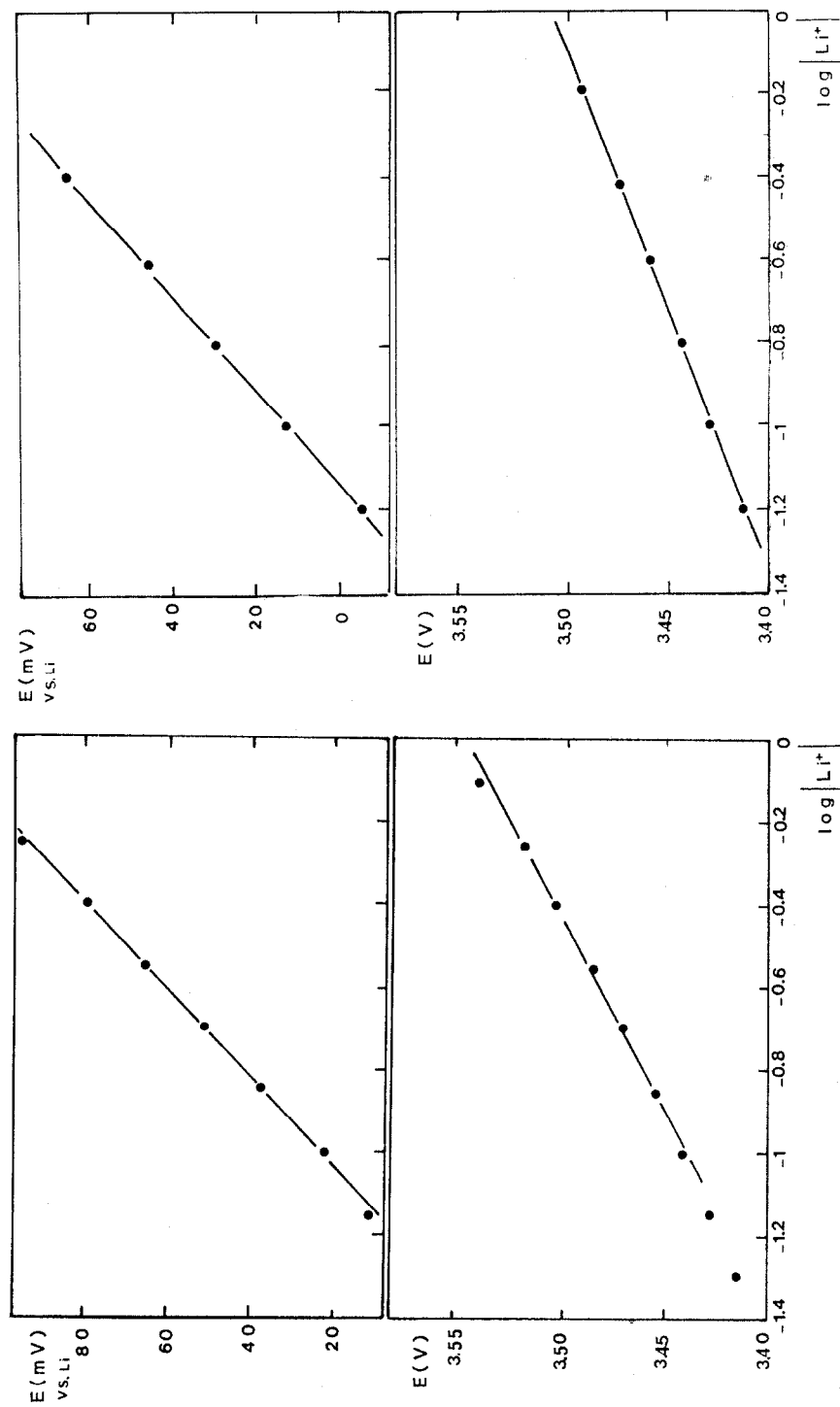
(a)

(b)

Fig. 5. Variation of potential of lithium electrode and $Li_{0.15}V_2O_5$ electrode as function of Li^+ concentration in electrolyte (a): PC at 60 °C; (b) molten $DMSO_2$ at 130 °C. Potential variations of both electrodes were simultaneously recorded in same cell vs. same reference electrode.
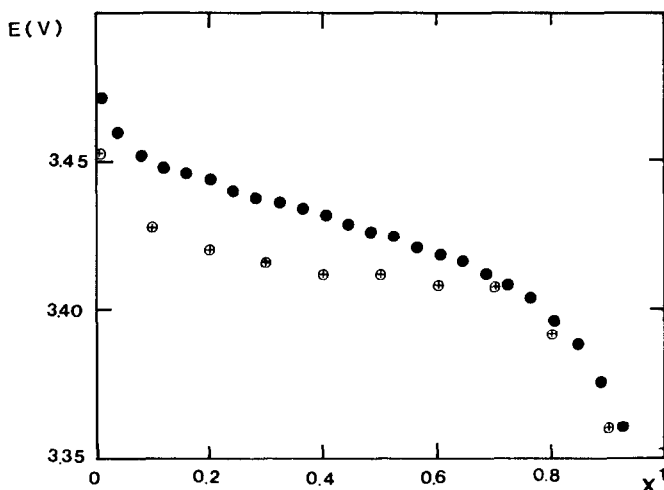
Fig. 6. Open-circuit voltage of cells Li/mol kg^{-1} LiClO$_4$, DMSO$_2$, V$_2$O$_5$ (●) and Li/1 M LiClO$_4$, PC/V$_2$O$_5$ (⊕) as a function of X during discharge of V$_2$O$_5$. X = (moles Li discharged/mole V$_2$O$_5$)/total faradaic yield for discharge process.

chlorides at 300 °C. Therefore, the discrepancy in behaviour is associated with an intercalation process that is different from that observed in "classical" electrolytes. Research is in progress to examine whether these differences are connected with lithium solvation and solvent intercalation effects.

Acknowledgements

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