

Electrochemical behaviour of some transition metal oxides in molten dimethylsulphone at 150° C

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Received 2 March 1985; revised 3 June 1985

In view of the possible application in non-aqueous lithium cells operating at relatively high temperatures, molten dimethylsulphone (DMSO₂) has been used as the electrolyte solvent in lithium cells at 150° C. The stability of lithium in molten DMSO₂ has been found to be good as compared with that observed in organic solvents such as propylene carbonate, thus indicating that the Li⁺/Li system can be used as a suitable reference electrode in this medium.

The electrochemical behaviour of some transition metal oxides has been investigated in LiClO₄ solutions in molten DMSO₂. The results obtained from voltammetric and chronopotentiometric measurements have shown a satisfactory behaviour for all the cathodic materials tested. Moreover, electrochemical insertion of Li⁺ ions into the crystal lattice of these oxides is a very fast process. Thus molten DMSO₂ appears to be a very interesting organic solvent usable in high energy density non-aqueous lithium cells.

1. Introduction

Owing to its physical and chemical properties, dimethylsulphone (DMSO₂) is a promising solvent for use in the field of high energy density non-aqueous cells. It is an organic solvent with melting and boiling points of 108–109° C [1] and 240° C [2], respectively. Furthermore, DMSO₂ is an inert solvent which readily dissolves many inorganic salts. Thermal decomposition occurs at about 500° C, producing methane, ethane and sulphur dioxide [3].

The first electrochemical research on DMSO₂ concerned the stability constants of lead and cadmium nitrate complexes measured polarographically at 125° C [4]. Other studies concerning the stability constants of transition metal complexes with halide anions [5] and thiourea and thiocyanates anions [6] have also been performed. Electrochemical investigations in molten DMSO₂ have been significantly extended by Tremillon and co-workers [7–11].

In spite of numerous advantageous characteristics, particularly a high thermal and chemical [12] stability, a weak solvation effect on ions [4, 5, 9, 13–15] and an enhancement of chemical

and electrochemical kinetics, the utilization of molten DMSO₂ as a solvent in primary cells operating at relatively high temperature has not yet been practiced.

The present paper reports the electrochemical study of the Li⁺/Li system in DMSO₂ at 150° C and the electrochemical behaviour of some well-known transition metal oxides [16–18] in 1 mol kg⁻¹ LiClO₄/DMSO₂ at 150° C.

2. Experimental details

2.1. Materials

Dimethylsulphone (Aldrich, purity 98%) was dissolved in boiling water, filtered and recrystallized. The material was then recrystallized twice from absolute methanol, air dried at 90° C for 48 h and dried again *in vacuo* at 30° C for 12 h. The solvent was then stored in an argon-filled glove box. Under these conditions the water concentration did not exceed 5×10^{-3} mol kg⁻¹ [4]. Anhydrous lithium perchlorate (Fluka) was dried under dynamic vacuum at 120° C for 8 h. The solid was then dried under vacuum at 190° C for 6 h and preserved from moisture by keeping

in an argon-filled glove box. Other inorganic salts such as NaClO_4 and NBu_4ClO_4 were treated according to a similar procedure. The metal oxides tested during the present work were dried at 120°C *in vacuo* for 6 h. Manganese dioxides (γ and β) were supplied by 'La Société Saft', and other metal oxides by Prolabo and K.K. Laboratories.

2.2. Apparatus

The reference electrode generally used was formed by the Li^+/Li redox system and consisted of a lithium wire in contact with a 1 mol kg^{-1} lithium perchlorate solution in molten DMSO_2 . The equilibrium potential of such an electrode was stable over the period required for any of the experiments described below.

The electrochemical study was carried out with electrodes of area 1 cm^2 and thickness about 0.1 mm containing small quantities of cathodic material ($\cong 2\text{--}3\text{ mg}$) mixed with 90 wt % graphite (Koch Light, purity 99.99%). The mixture containing the active material was pressed onto a platinum grid. The auxiliary electrode consisted of a lithium rod facing the working electrode. The electrochemical cell used in our investigations is fully described elsewhere [19]. The cell was thermostated with silicon oil whose temperature ($150^\circ\text{C} \pm 0.1^\circ\text{C}$) and circulation were controlled by a Tamson thermostat. The conductivity of a 1 mol kg^{-1} LiClO_4 solution in molten DMSO_2 at 150°C is $\cong 2/3 \times 10^{-2}\ \Omega^{-1}\text{ cm}^{-1}$. Such a value is about ten times higher than that achieved for a 1 M LiClO_4 solution in bidistilled propylene carbonate at ambient temperature ($5 \times 10^{-3}\ \Omega^{-1}\text{ cm}^{-1}$).

The density of DMSO_2 may be calculated from the following relationship established by Smith *et al.* [13]: $\rho = 1.258 - 1.16 \times 10^{-3}(T - 273)\text{ g cm}^{-3}$; hence, at 150°C , $\rho = 1.08\text{ g cm}^{-3}$. Faradaic yields are expressed as the number of Faradays per mole of oxide.

3. Results and discussion

3.1. Electrochemical study of the Li^+/Li system

The potential, reached after a few tens of seconds, of a lithium electrode in contact with a

solution of Li^+ ions in molten DMSO_2 was measured as a function of Li^+ ion concentration. The experiment consisted of potential measurement between two lithium wires; in order to hold one wire at constant potential, a lithium wire was immersed in a 0.1 mol kg^{-1} lithium perchlorate solution contained in a separate compartment. A fine porosity frit was used to prevent the diffusion of Li^+ ions. A second lithium wire, extending into a solution containing the various Li^+ concentrations acted as the working electrode.

For a reversible Li^+/Li system, the expected dependence of the equilibrium potential (E) on the Li^+ ion concentration should be in agreement with the Nernst equation [1] at 150°C :

$$E = E_{\text{Li}^+/\text{Li}}^\circ + 0.083 \log [\text{Li}^+] \quad (1)$$

A linear variation of equilibrium potential versus $\log [\text{Li}^+]$ was found, as shown in Fig. 1a. Nevertheless, the experimental value of the slope ($104\text{ mV per log } [\text{Li}^+]$ unit) is not in accordance with the theoretical value given in Equation 1. Indeed, under these conditions the experimental data include junction potential measurements which are also dependent on Li^+ concentration.

In order to avoid such a phenomenon, further measurements were performed in the presence of a 1 mol kg^{-1} NBu_4ClO_4 solution in both compartments. Thus we again found a linear dependence of the equilibrium potential versus $\log [\text{Li}^+]$ when $10^{-2} \leq [\text{Li}^+] \leq 5 \times 10^{-1}\text{ mol kg}^{-1}$ (Fig. 1b). The experimental slope of the straight line reported in Fig. 1b is $82\text{ mV per log } [\text{Li}^+]$ unit. Agreement with Equation 1 is seen to be well within experimental error except at Li^+ concentrations higher than $5 \times 10^{-1}\text{ mol kg}^{-1}$, where variations of ionic strength are not negligible. Therefore the Li/Li^+ system was used as reference electrode for all the experiments described below, although such a system has never been used as reference electrode in molten DMSO_2 before [4–11, 20–22].

3.2. Electroactivity ranges

At 150°C the potential range of molten DMSO_2 extends from 0.2 to 5 V versus a Li/Li^+ 1 mol kg^{-1} reference electrode (Fig. 2) with a stationary platinum microelectrode (8×10^{-2}

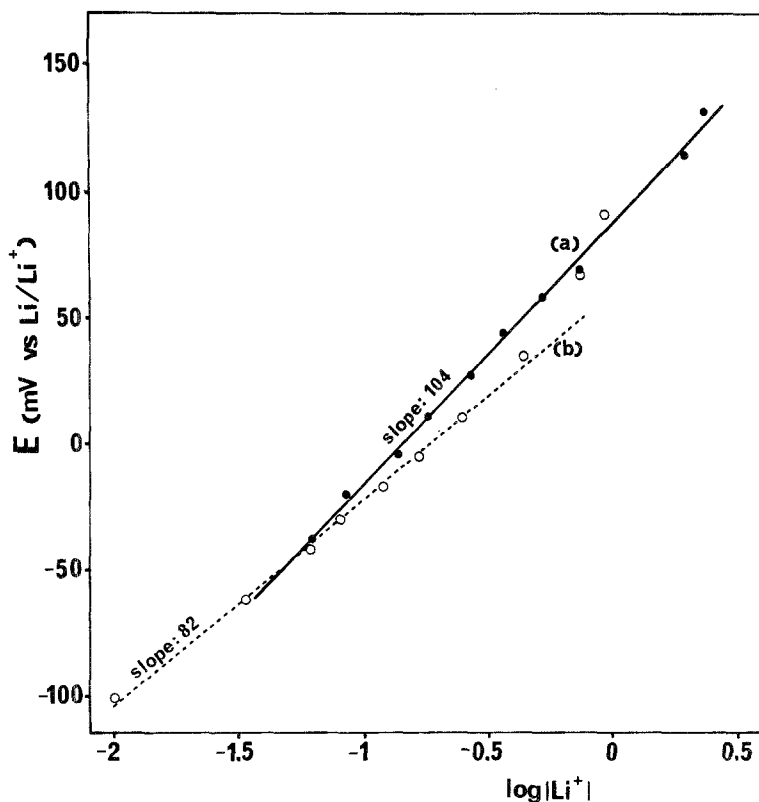


Fig. 1. Potential variation of a lithium electrode with $\log \text{Li}^+$. (a) Without NBu_4ClO_4 ; (b) with $1 \text{ mol kg}^{-1} \text{NBu}_4\text{ClO}_4$.

cm^2 area). The limiting reaction which prevails for both anodic and cathodic sweeps is probably the electrochemical decomposition of the solvent [7].

Absence of oxygen is assured by vigorous argon bubbling for 30 min before each measurement. During measurements, an argon atmo-

sphere is maintained over the solution to prevent a subsequent redissolution of oxygen. When concentration of residual water becomes too high, its reduction occurs close to 1.8 V with formation of a black deposit corresponding to LiOH precipitation [7].

The electroactivity range exhibited with a 1 cm^2 graphite-loaded platinum electrode is less than that obtained with a 1 cm^2 platinum electrode. Indeed, the increased surface area makes the water reduction easier. However, such a fact does not restrict the present study since the materials are mainly investigated between 2 and 4 V.

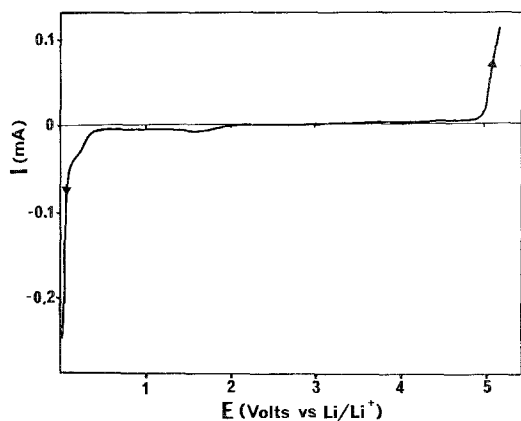


Fig. 2. Potential range obtained with a platinum electrode ($8 \times 10^{-2} \text{ cm}^2$) in $1 \text{ mol kg}^{-1} \text{LiClO}_4$; 150°C , 60 mV mn^{-1} .

3.3. Electrochemical behaviour of some transition metal oxides

3.3.1. Vanadium pentoxide. Typical discharge-charge curves of V_2O_5 at a current density of 1 mA cm^{-2} are shown in Fig. 3. Three main reduction steps appear as mentioned by other authors [23–25]. A total balance of around 2.45 Faraday per mole of active material is obtained,

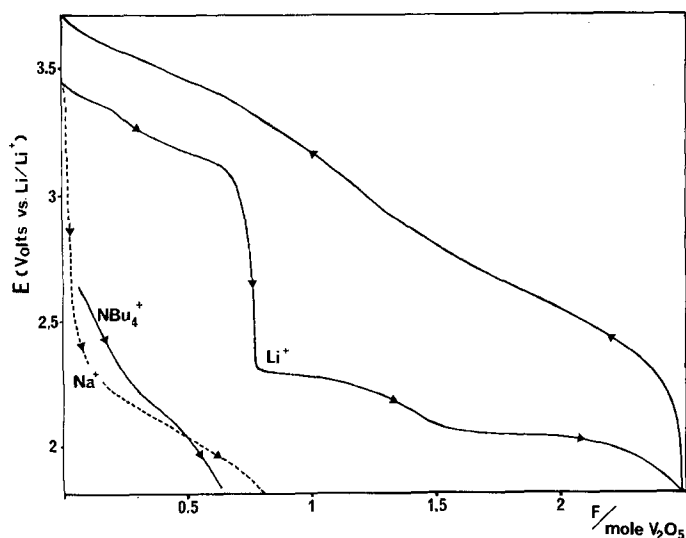
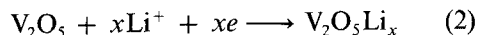


Fig. 3. Discharge-charge curves of V_2O_5 in $1 \text{ mol kg}^{-1} \text{ MClO}_4$ solution in molten DMSO_2 at 1 mA , 150°C , $M^+ = \text{Li}^+$, Na^+ , NBU_4^+ .

in good agreement with reported results achieved in other non-aqueous media.

The first reduction step is subdivided into two steps of similar magnitude, since the voltage shifts from a plateau of about 3.4 V to a plateau of 3.2 V with a faradaic yield of about $0.8 \text{ F}/V_2O_5$. These processes are generally accepted to correspond to a reversible insertion of Li^+ ions into the crystal lattice as described by Equation 2 [26, 27]:



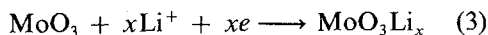
The further electroreduction of V_2O_5 occurs in two steps around 2.25 V and 2.05 V with faradaic yields of 0.7 and $1 \text{ F}/V_2O_5$, respectively (Fig. 3).

We have established that all the reduction processes are dependent on the ionic radius of the cation contained in the electrolyte (Fig. 3). This result confirms that all the reduction steps are kinetically determined by the insertion of cationic species into the crystal frame work [25].

The voltammetric curves clearly point to four processes for V_2O_5 reduction [25] (Fig. 4a). The oxidation curves performed after the two first cathodic steps show that the electrochemical processes are quite reversible. When the oxidation is performed after the third reduction process (at 2.25 V) the amounts of electricity required for the reduction and recovered in the oxidation are still practically identical, although this third process appears less than the first two (Fig. 4b). All the oxidation processes are very

attenuated and practically irreversible after cathodic scanning has been performed beyond the last reduction process (Fig. 4a). These results suggest that in molten DMSO_2 the V_2O_5 crystal lattice undergoes a sudden and irreversible transformation after further Li^+ ion insertion as mentioned by several authors using other media [25–28].

3.3.2. Molybdenum trioxide MoO_3 . As in the case of V_2O_5 , electrochemical reduction of MoO_3 requires an insertion process of Li^+ ions into the host lattice of the oxide according to Equation 3 [26, 29, 30].



Several authors have shown that electrochemical reduction of MoO_3 in organic solvents occurs in two steps [30–33]. A discharge curve of MoO_3 (1 mA , 150°C) in molten DMSO_2 is reported in Fig. 5. Again, two steps appear (2.7 V and 2.3 V) with faradaic yields of about 0.5 and 1 Faraday per mole of oxide respectively, i.e. with a total balance of $1.5 \text{ F}/\text{MoO}_3$. No well-defined oxidation process can be ascribed to the first reduction step (Fig. 6b) and the discharge-charge curves (Fig. 5) indicate that the recovered capacity in reoxidation practically corresponds to the faradaic yield involved in the second reduction process only, i.e. about 1 Faraday per mole of oxide.

As has already been shown [30], and in accord-

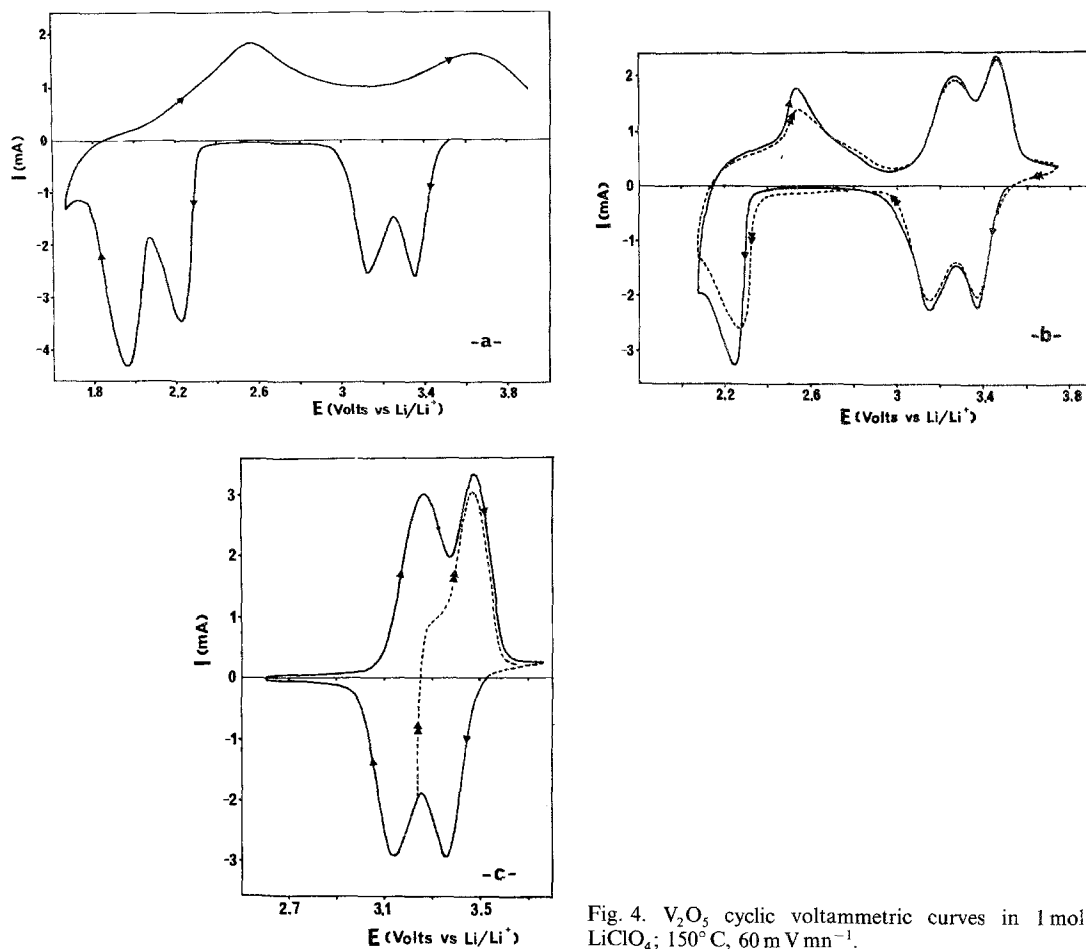


Fig. 4. V_2O_5 cyclic voltammetric curves in 1 mol kg^{-1} $LiClO_4$; $150^\circ C$, 60 m V min^{-1} .

ance with our results, the first reduction step of MoO_3 should lead to a material whose crystal structure differs from that of the initial solid. It can be suggested that a new distribution of the octahedral MO_6 groups occurs [30]. Such a phenomenon may make insertion of Li^+ ions easier [30]; this could explain why the second step was practically reversible. In contrast, the Li^+ ions intercalated during the first reduction step remain inside the initial layered structure of MoO_3 . Therefore no significant oxidation process is allowed.

3.3.3. Manganese dioxide. Two kinds of manganese dioxide were studied here: electrolytic MnO_2 whose crystal structure is γMnO_2 and a chemically prepared MnO_2 , i.e. βMnO_2 .

3.3.3.1. γMnO_2 . Fig. 7 shows a chronopotentiogram (1 mA cm^{-2} , $150^\circ C$) for electrochemical

reduction of γMnO_2 in molten $DMSO_2$ at $150^\circ C$. Two reduction steps appear around 3.2 V and 2.8 V with faradaic yields of about 0.15 F/MnO_2 and 0.35 F/MnO_2 , respectively, i.e. with a total balance of about 0.5 Faraday per mole of MnO_2 . The existence of these two steps is confirmed by the cyclic voltammetric curves reported in Fig. 8. The electrochemical reoxidation is equally subdivided into two steps as shown in Fig. 8a and b. From the second cycle it can be seen that the reduction processes give rise to more defined curves. From a quantitative point of view it has been established that the faradaic yield recovered during the charge process is similar to that achieved for the discharge (Fig. 7).

3.3.3.2. βMnO_2 . Only one reduction step of βMnO_2 appears [34, 35] at 2.8 V , i.e. at the same voltage plateau as the second step in the γMnO_2

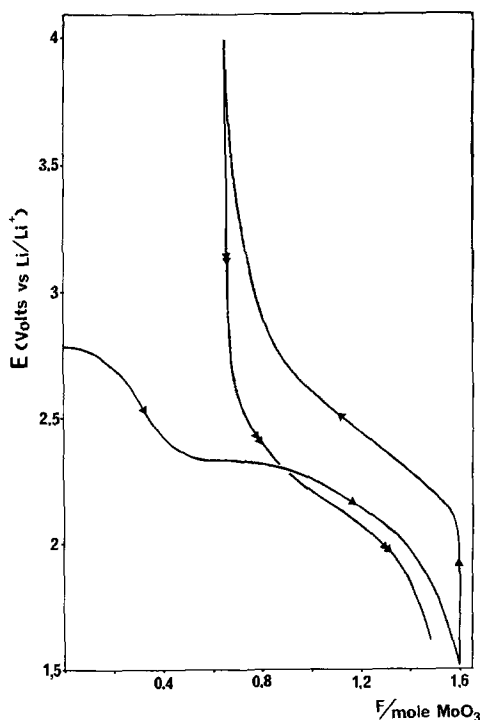


Fig. 5. Discharge-charge curves of MoO_3 in 1 mol kg^{-1} LiClO_4 solution in molten DMSO_2 at 1 mA , 150°C .

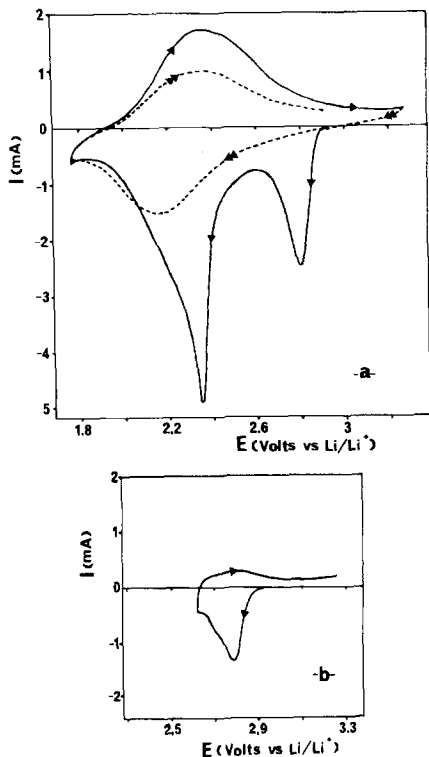


Fig. 6. MoO_3 cyclic voltammograms at 150°C , 60 mV min^{-1} .

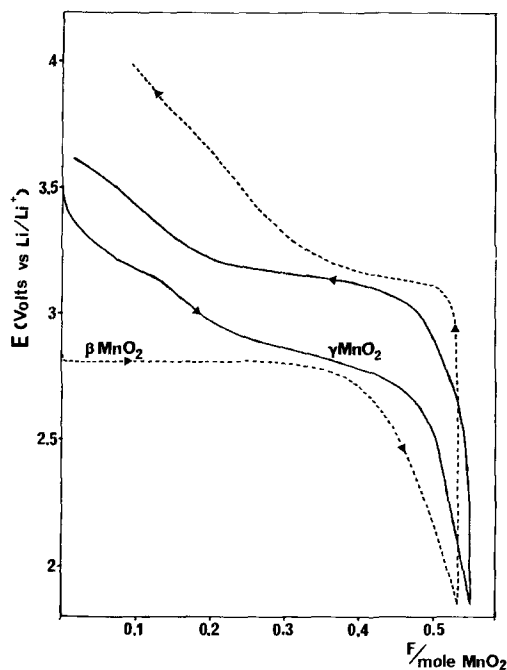
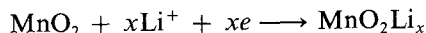


Fig. 7. Discharge-charge curves of γMnO_2 and βMnO_2 at 1 mA ; 1 mol kg^{-1} LiClO_4 , 150°C .

reduction (Fig. 7). This reduction performed under 1 mA at 150°C in molten DMSO_2 required the exchange of 0.5 Faraday per mole of oxide MnO_2 .

The capacity recovered during the charge process is about the same as that measured in the discharge. Cyclic voltammograms presented in Fig. 9 confirm the presence of only one reduction step corresponding to an oxidation process occurring at 3.4 V . From the second cycle it can be seen that the reduction processes give rise to more defined curves and remain unchanged for at least a few cycles (Fig. 9).

Investigations conducted into the discharge mechanism of MnO_2 in other media have established that an expansion of the crystal lattice occurs as the discharge proceeds, while Li^+ ions are introduced into the crystal lattice according to [35]:



We have clearly shown that the electrochemical reduction of γMnO_2 in molten DMSO_2 occurs in two steps, as already demonstrated in propylene carbonate [30]. The two steps observed during the reduction of γMnO_2 and the

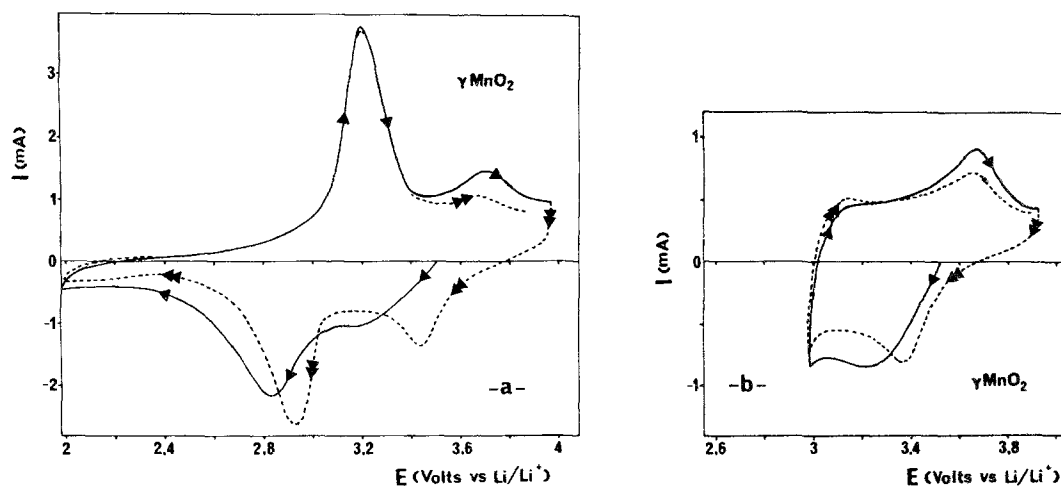


Fig. 8. γMnO_2 cyclic voltammetric curves at 150°C, 60 mV min^{-1} , 1 mol kg^{-1} LiClO_4 .

one for βMnO_2 reduction can be explained in terms of crystallographic data.

The differences between the various kinds of manganese dioxide correlate with the type and the size of cavities provided by arrangement of single or multiple octahedral (MnO_6) chains joined along their lengths by sharing corners [36]. The rutile structure of the β form only has longitudinal cavities which are smaller than those contained in the ramsdellite structure [36], whereas both types of cavities exist in the γMnO_2 crystal lattice. The ability to insert Li^+ ions into the oxide framework probably correlates with the size of the cavities in the host lattice. The larger the cavities, the easier the insertion of Li^+ ions. Therefore by taking this assumption into account, we can suggest that the processes

observed during γMnO_2 reduction correspond to the intercalation of Li^+ ions in both types of cavity. So both 2.8 V voltage plateaux in the reduction of γ and βMnO_2 may be associated with the insertion of Li^+ ions into the small cavities of the host lattice.

4. Conclusion

The results reported in the present work have proved that molten DMSO_2 can be used as a solvent in lithium cells. The Li^+/Li system is a very suitable reference electrode for such a medium. In comparison with performances achieved in other media, all the cathodic materials tested have exhibited a satisfactory electrochemical behaviour. Moreover, LiClO_4 solutions in molten DMSO_2 have been found to have acceptable compatibility with lithium, at least during the period required for any of the previous experiments. Under these experimental conditions the potential range extends from 1.8 V to 5 V in the presence of graphite. The obvious conclusion to be drawn from this work is that molten DMSO_2 offers interesting features required in the field of high energy density non-aqueous lithium cells operating at relatively high temperature.

References

- [1] Beilstein Handbuch der Organische Chemie, I (1941) 277; I (1958) 1217.

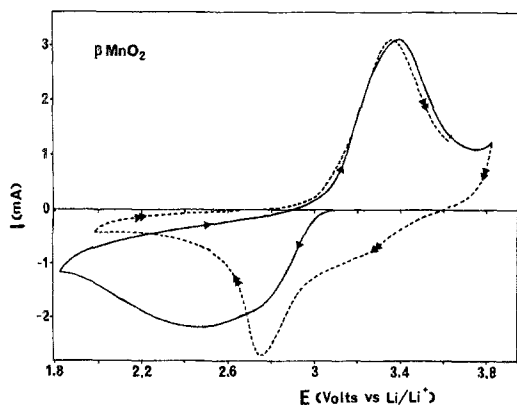


Fig. 9. βMnO_2 cyclic voltammetric curves at 150°C; 60 mV min^{-1} , 1 mol kg^{-1} LiClO_4 .

- [2] H. L. Clever and E. F. Westrum, Jr, *J. Phys. Chem.* **74** (1970) 1309.
- [3] W. K. Busfield and K. J. Ivin, *Trans. Faraday Soc.* **57** (1961) 1044.
- [4] C. Auerbach and D. K. McGuire, *J. Inorg. Nucl. Chem.* **28** (1966) 2659.
- [5] C. H. Liu, L. Newman and J. Harson, *Inorg. Chem.* **7** (1968) 1868.
- [6] J. Hennion, J. Nicole and G. Tridot, *C.R. Acad. Sci., Ser. C.* **278** (1974) 235.
- [7] B. Bry and B. Tremillon, *J. Electroanal. Chem.* **30** (1971) 457.
- [8] *Idem, ibid.* **46** (1973) 71.
- [9] B. Bry, Thèse de Doctorat d'Etat, Paris (1976).
- [10] J. C. Moscardo, Thèse de Doctorat de 3ème cycle, Paris (1976).
- [11] M. Machtinger, M. J. Vuaille and B. Tremillon, *J. Electroanal. Chem.* **83** (1977) 273.
- [12] R. Sowada, *Z. Chem.* **8** (1968) 361.
- [13] G. P. Smith, C. H. Liu and T. R. Griffiths, *J. Amer. Chem. Soc.* **86** (1964) 4796.
- [14] C. H. Liu, J. C. Harson and G. P. Smith, *Inorg. Chem.* **7** (1968) 2244.
- [15] B. Bry and B. Tremillon, *J. Chem. Res.* (1979) 156.
- [16] G. Eichinger and J. O. Besenhard, *J. Electroanal. Chem.* **72** (1976) 1.
- [17] M. S. Whittingham, *J. Electrochem. Soc.* **123** (1976) 315.
- [18] G. Pistoia, *J. Power Sources* **9** (1983) 307.
- [19] R. Messina, M. Broussely, G. Gerbier and J. Perichon, *J. Appl. Electrochem.* **8** (1978) 87.
- [20] P. G. Varlashkin and J. R. Peterson, *J. Less Comm. Metals* **94** (1983) 333.
- [21] J. L. Pison Garces, P. Sanchez Batanero and R. Gallego Andreu, *Bull. Soc. Chim. France* **I** (1983) 9.
- [22] *Idem, ibid.* **I** (1984) 106.
- [23] A. N. Dey, *Thin Solid Films* **43** (1977) 131.
- [24] M. Lang, J. R. Backland and E. C. Weidner, Proceedings 26th Power Sources Symposium, Atlantic City (1974) Paper 37.
- [25] A. Tranchant, R. Messina and J. Perichon, *J. Electroanal. Chem.* **113** (1980) 225.
- [26] M. S. Whittingham, *J. Electrochem. Soc.* **122** (1975) 713.
- [27] *Idem, ibid.* **123** (1976) 315.
- [28] C. R. Walk and J. S. Gore, *ibid.* **122** (1975) 686.
- [29] A. L. Rotinyan, S. V. Shishkina, K. I. Tikhonov and L. A. Sokolov, *Elektrokhimiya* **11** (1975) 1493 (English translation p. 1396).
- [30] A. Tranchant, Thèse de Doctorat de 3ème cycle, Paris (1980).
- [31] A. N. Dey, Electrochemistry Society Meeting, Boston (1973) paper 132.
- [32] N. Margalit, *J. Electrochem. Soc.* **121** (1974) 1460.
- [33] F. W. Dampier, Proceedings 14th National Meeting Electrochemistry Society, Miami Beach, Florida (1972) paper 4.
- [34] H. Ikeda, T. Saito and H. Tamura, Meeting Electrochemistry Society, Japan (1974) paper 21.
- [35] H. Ikeda, 'Lithium Batteries' (edited by J. P. Gabano) Academic Press, New York (1983) p. 169.
- [36] A. F. Wells, 'Structural Inorganic Chemistry', 4th edn, Clarendon Press, Oxford (1975), p. 459.