ON THE USE OF ROCKING CHAIR CONFIGURATIONS FOR CYCLABLE LITHIUM ORGANIC ELECTROLYTE BATTERIES

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Summary

The characteristics of concentration cells based on two electrodes having different lithium activity have been evaluated by examining the performance of various systems. The results indicate that with the selection of appropriate electrode materials, lithium 'rocking chair' cells having high voltage and good discharge and cycling behaviour can be developed.

Introduction

Lithium organic electrolyte batteries are of current interest as high-energy, secondary power sources. Being capable of operating at room temperature, these batteries appear an almost ideal means of storage for discontinuous energy sources such as solar, wind and tide.

In the field of secondary lithium batteries, considerable attention has been devoted to systems based on topochemical reactions. Typical examples are the Li/TiS_2 and the Li/V_2O_5 cells. These cells, however, suffer from limited rechargeability, mainly due to the poor cyclability of the lithium electrode. As evidenced by Brummer and co-workers [1], lithium is unavoidably passivated by any organic electrolyte. This results in irregular lithium deposits which, during cycling, assume a progressively dendritic morphology. The cell internal resistance increases accordingly and the cycling efficiency rapidly declines.

Such a process may not be too severe under shallow cycling conditions but becomes massive under deep regimes and/or upon long storage times [2]. A possible solution to this problem could be found with the replacement of the lithium electrode with another lithium-based electrode having less tendency to being passivated or attacked by the organic electrolyte than the pure metal.

To ascertain the feasibility of this concept, we have developed [3, 2, 4] cells of the type

$$LiWO_2/LiClO_4-PC/TiS_2 \qquad OCV = 2.1 \text{ V} \qquad (1)$$

$$LiWO_2/LiClO_4-PC/WO_3 \qquad OCV = 2.5 \text{ V} \qquad (2)$$

$$LiWO_2/LiClO_4-PC/NbS_2 \qquad OCV = 2.0 \ V \qquad (3)$$

using a fully intercalated $LiWO_2$ electrode as negative and a non-intercalated compound as positive electrode in a typical organic electrolyte, *i.e.*, a solution of lithium perchlorate, $LiClO_4$, in propylene carbonate (PC).

These cells have a reasonably high open circuit voltage (OCV), and are characterized by reactions which imply the reversible transport of lithium from one electrode to the other. Therefore, cells of this type have been quite appropriately referred to as having a 'rocking chair' configuration [5].

Cells (1) - (3) have shown good rechargeability and no indication of deterioration upon cycling [3, 2, 4]. However, because of slow Li diffusion in the two intercalated electrodes, cycling is limited to low regimes. This disadvantage, together with the low energy density values, limits the practical importance of cells of this type.

On the other hand, rocking chair lithium cells have a high intrinsic interest and this has stimulated us to carry out further study on improved electrode materials, with the aim of evaluating the true possibility of application of these types of cell.

Experimental

Propylene carbonate (PC), a reagent grade Merck product, was further purified by fractional distillation under reduced pressure. Lithium perchlorate, $LiClO_4$, an Alfa product, was vacuum dried at 150 °C.

Iron oxide, Fe_2O_3, and vanadium pentoxide, V_2O_5, reagent grade products, were used as received. The preparation of titanium sulphide, TiS_2, has been described elsewhere [2].

The lithium cells, assembled in a controlled-atmosphere glove box, consisted of a Li disk and a pellet of positive material, separated by three glass fiber separators soaked with the $LiClO_4-PC$ electrolyte solution. The positive pellet was generally obtained by compressing the powdered selected electrode material onto an inert metallic support. The overall cells, having a surface of 1.2 cm^2 and a volume of about 0.3 cm^3, were housed in a Teflon container employing Ni terminals.

For the three-electrode polarization cells, a similar configuration was used. The Li working and reference electrodes were prepared by cutting the lithium disk into two parts which were electrically separated by a Teflon spacer.

The $Li_x Fe_2O_3$ electrodes were prepared electrochemically by passing a known quantity of charge in an Li/Fe_2O_3 cell. The rocking chair cells were then obtained by replacing the Li disk with the pellet of the desired positive material, *i.e.*, TiS_2 and V_2O_5, respectively.

The cycling tests were carried out automatically with the aid of electronic polarity-reversing timers inserted between the galvanostat and the cell. The polarization curves were obtained at various sweep rates with a galvanostat driven by a function generator.

Lithium diffusion coefficients were obtained using the current-pulse technique and related equations developed by Basu and Worrell [6]. Current pulses were applied to the $Li_x V_2 O_5$ electrode and the voltage recovery (*vs.* Li) was followed with a fast $x-t$ recorder which was calibrated with a high-input impedance electrometer. The data were then analyzed for the diffusion coefficient with the aid of an HP-85 computer system.

Results and discussion

For the realization of high-voltage, high-energy lithium rocking chair cells, negative electrodes with high lithium activity and low weight must be selected. Furthermore, these electrodes should have a small voltage variation during discharge (to ensure high operational voltage of the cell) and fast lithium kinetics (to ensure high cycling rates).

Considering these requirements, we have focussed our attention on metal oxides which seem to offer the promise of fulfilling the above conditions, having fast and reversible reactions with lithium over small voltage ranges [7, 8]. In particular, we have selected the $Li/Fe_2 O_3$ system and examined its electrochemical properties in order to establish the feasibility of using $Li_x Fe_2 O_3$ electrodes in lithium rocking chair cells.

Effectively, very few electrochemical data are available for the $Li/Fe_2 O_3$ system. Ohzuku *et al.* [9] have reported a 0.5 mA cm^{-2} discharge curve of the $Li/Fe_2 O_3$ couple in the $LiClO_4-PC$ organic electrolyte. This curve shows a single plateau which has been interpreted by the authors in terms of the following mechanism

$$2Li + Fe_2 O_3 \rightarrow 2FeO + Li_2 O. \tag{4}$$

Godshall *et al.* [10, 7], in a thermodynamic study of the $Li-Fe-O$ ternary system at 400 °C, indicated that lithium could react with $Fe_2 O_3$, giving $Li_2 O$ and metallic Fe, through intermediate formation of various phases such as $LiFe_5 O_8$, $LiFeO_2$ and $Li_5 FeO_4$. The overall reaction, according to Godshall *et al.*, is

$$6Li + Fe_2 O_3 \rightarrow 3Li_2 O + Fe. \tag{5}$$

We have extended the investigation of the $Li/Fe_2 O_3$ system by examining the behaviour of cells of the type

$$Li/LiClO_4-PC/Fe_2 O_3. \tag{6}$$

A typical discharge curve is shown in Fig. 1. This curve reveals various plateaux and indicates a process involving six lithium equivalents per mole of $Fe_2 O_3$. These results seem to be explainable on the basis of reaction (5), in agreement with the conclusions of Godshall *et al.* [10, 7].

However, further attempts to confirm this interpretation have not been successful. For instance, X-ray analysis of the discharged products of cell (6) did not provide useful information in this respect. In fact, X-ray powder
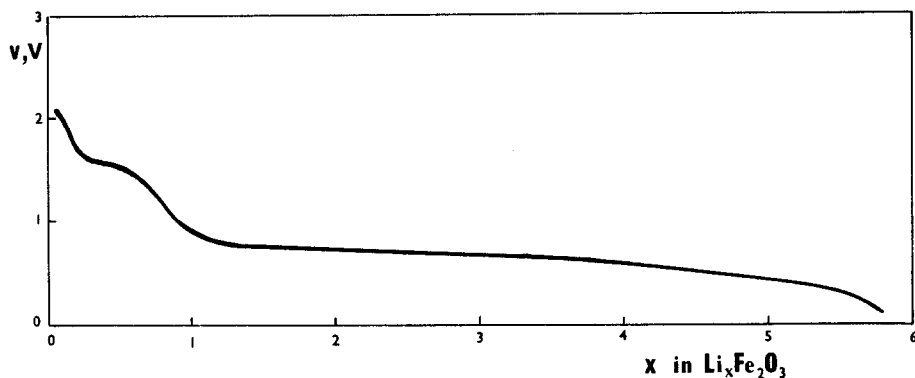
Fig. 1. Discharge behaviour at 1 mA cm^{-2} constant current density of the Li/LiClO$_4$-PC/ Fe$_2$O$_3$ cell at 25 °C.

diffraction patterns of the cathodic mass, determined at various stages of discharge, did not give any indication of new phases. In the first stage of discharge (*i.e.*, up to the reaction of one Li equivalent per Fe$_2$O$_3$ mole) a displacement of the Fe$_2$O$_3$ peaks was observed while, as the reaction proceeded, essentially peak-free spectra were obtained.

Further study is certainly necessary for the thorough elucidation of the mechanism of discharge of cells of type (6). In the present work, which is mainly directed towards the evaluation of the electrode performance, we shall refer to a generic reaction involving 6 Li equivalents per mole of Fe$_2$O$_3$, and which may be schematically represented as

$$x\text{Li} + \text{Fe}_2\text{O}_3 \rightarrow \text{Li}_x\text{Fe}_2\text{O}_3. \tag{7}$$

The typical discharge curve of cell (6) reported in Fig. 1 indicates that the Li$_x$Fe$_2$O$_3$ electrode may indeed be advantageously used as the negative in a lithium rocking chair cell, being able to sustain high rates with small changes in voltage even for large variations in lithium content. Furthermore, the electrode also has a very good reversibility, as ascertained by X-ray and cycling polarization analyses.

X-ray spectra of the cathodic mass of cell (6) as a function of state of charge are shown in Fig. 2. Figure 2(a) shows the spectrum after the discharge of 1 equivalent of Li (*i.e.*, schematically corresponding to the formation of Li$_1$Fe$_2$O$_3$). Figure 2(b) is the spectrum after the discharge of 4 equivalents of Li (*i.e.*, schematically corresponding to the formation of Li$_4$Fe$_2$O$_3$). Figure 2(c) is the spectrum recorded after recharging back to Li$_1$Fe$_2$O$_3$. The similarity between spectra (a) and (c) indicates that cell (6) is rechargeable, thereby confirming the reversibility of the Li$_x$Fe$_2$O$_3$ electrode.

The latter has been further controlled by cyclic polarization studies. Figure 3 reports galvanostatic anodic and cathodic polarization cycles of the Li$_x$Fe$_2$O$_3$ electrode over the entire discharge range, *i.e.*, up to 6 Li per Fe$_2$O$_3$. It may be noticed that the electrode reversibility, indicated by the
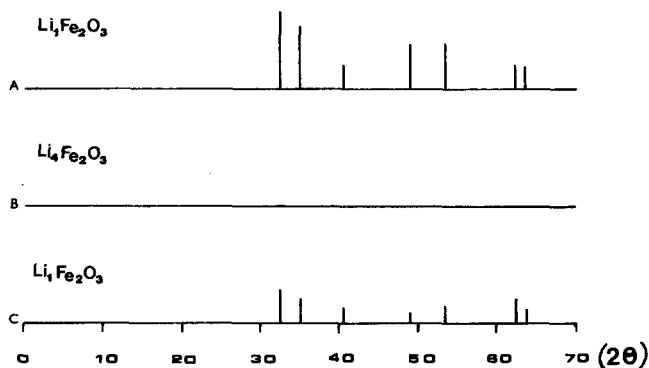
Fig. 2. X-ray diffraction powder patterns (Cu Kα) of the cathodic mass of the cell Li/ Li$_x$Fe$_2$O$_3$, as a function of state of charge. (a) Li$_1$Fe$_2$O$_3$ (first discharge); (b) Li$_4$Fe$_2$O$_3$ (first discharge); (c) Li$_1$Fe$_2$O$_3$ (after charging from (b)).
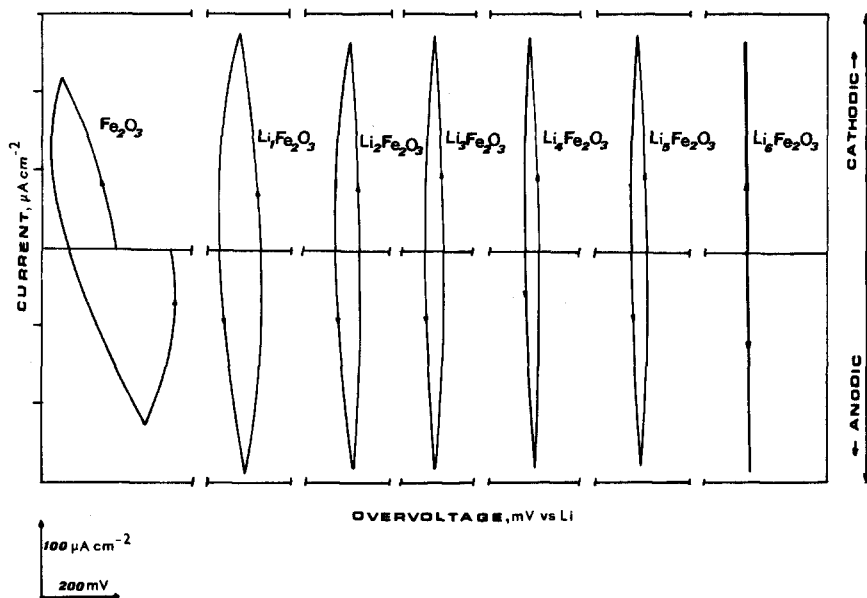

Fig. 3. Cathodic and anodic polarization cycles of the Li$_x$Fe$_2$O$_3$ electrode at various Li contents and at 8 μA s^{-1} scanning rate (T = 25 °C.)

lack of hysteresis between anodic and cathodic cycles, increases as the lithium content increases, reaching optimized conditions between 4 and 6 Li equivalents.

This is finally confirmed by the results of shallow cycling of cell (6) for various values of x in Li$_x$Fe$_2$O$_3$. These results are shown in Fig. 4 for values of x between 0.5 and 5.5. Again, optimum behaviour (in terms of charge–discharge profiles) is obtained for cycles involving concentration ranges between 4 and 6 Li per Fe$_2$O$_3$.

Having established high reversibility together with good kinetics (for $4 \leqslant x \leqslant 6$), Li$_xFe_2O_3$ may be considered as a promising negative electrode
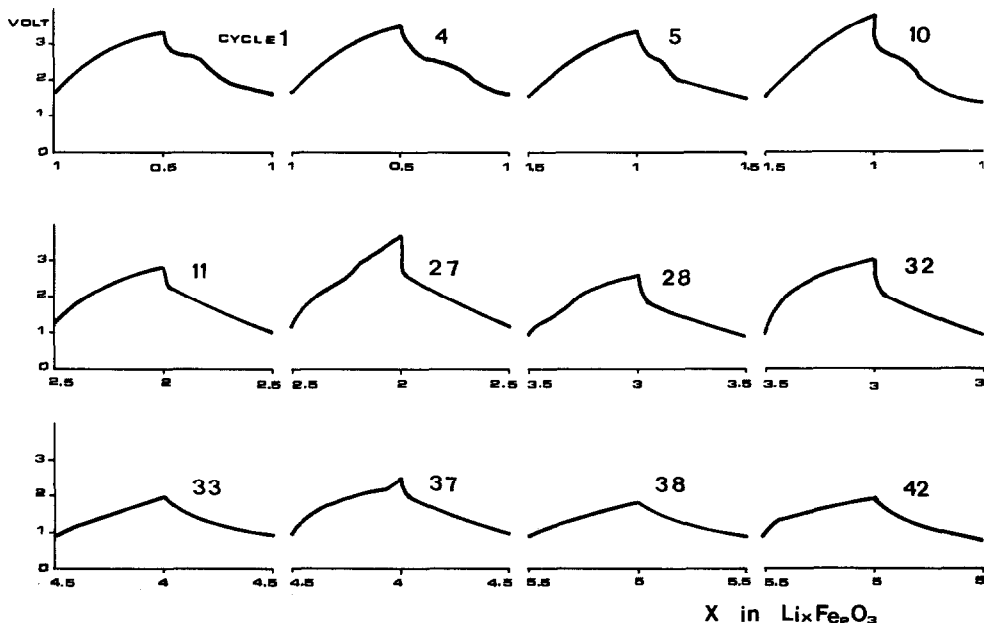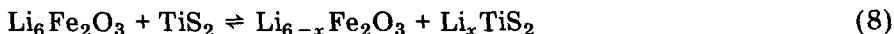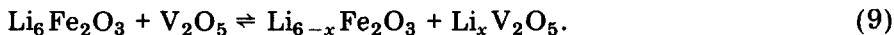
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Fig. 4. Shallow cycling test (0.25 mA cm^{-2}) of the Li/LiClO$_4$–PC/Li$_x$Fe$_2$O$_3$ cell, around various Li concentrations and at 25 °C.

in lithium rocking chair cells. Various positive electrodes may be coupled with this electrode to form high voltage systems. Among these we have considered two 'classical' insertion compounds such as TiS$_2$ and V$_2$O$_5$.

For rocking chair cells of the Li$_6$Fe$_2$O$_3$/TiS$_2$ and Li$_6$Fe$_2$O$_3$/V$_2$O$_5$ type, respectively, the discharge processes may be written as

$$Li_6 Fe_2 O_3 + TiS_2 \rightleftharpoons Li_{6-x} Fe_2 O_3 + Li_x TiS_2 \tag{8}$$

and

$$Li_6 Fe_2 O_3 + V_2 O_5 \rightleftharpoons Li_{6-x} Fe_2 O_3 + Li_x V_2 O_5. \tag{9}$$

The thermodynamic ranges of potential of the three electrodes Li$_x$Fe$_2$O$_3$, Li$_x$TiS$_2$ and Li$_x$V$_2$O$_5$ for the exchange of 1 Li equivalent, are reported in Fig. 5(A). On the basis of these potential ranges it is possible to evaluate the theoretical voltage range of Li$_6$Fe$_2$O$_3$/TiS$_2$ and Li$_6$Fe$_2$O$_3$/V$_2$O$_5$ rocking chair cells as a function of the number of Li equivalents transferred. This is shown in Fig. 5(B) for equimolar quantities of reactants.

From the above considerations, the theoretical energy density values may also be evaluated. They are, at 25 °C, 140 W h kg^{-1} for the Li$_6$Fe$_2$O$_3$/TiS$_2$ system and 180 W h kg^{-1} for the Li$_6$Fe$_2$O$_3$/V$_2$O$_5$ system. These values are of practical interest and thus justify the selection of the above electrode systems.

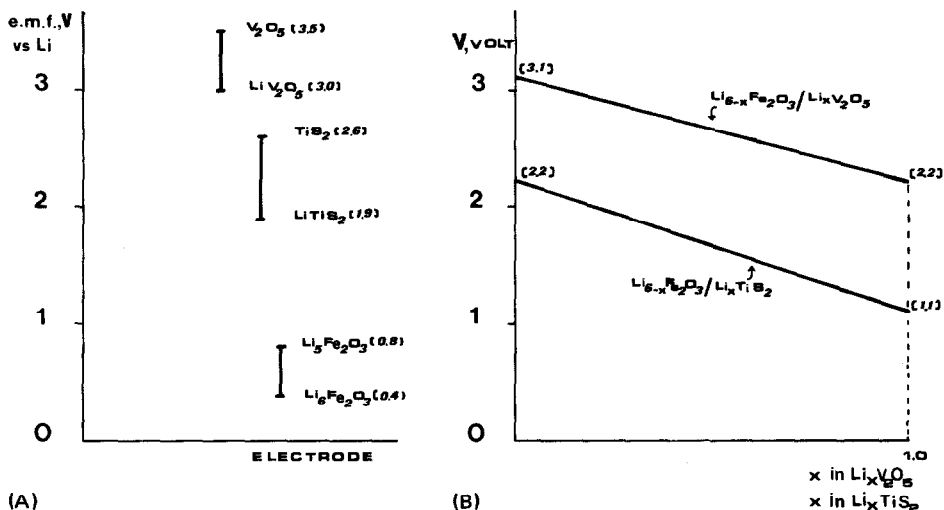The theoretical evaluations are confirmed by experimental results. In fact, a cell of the type

Fig. 5. Potential ranges of (A) the $Li_xFe_2O_3$, Li_xTiS_2 and $Li_xV_2O_5$ electrodes; (B) the related lithium rocking chair cells at 25 °C.

$$Li_6Fe_2O_3/LiClO_4\text{--}PC/TiS_2 \qquad\qquad\qquad (10)$$

shows an OCV of 2.2 V at room temperature, which is in excellent agreement with the value of Fig. 5(B). Typical performance of the cell, in terms of discharge and cycling behaviour, is shown in Fig. 6. The results indicate that cell (10) is indeed capable of sustaining high rates as well as deep cycling regimes. This good performance is consistent with the high reversibility of
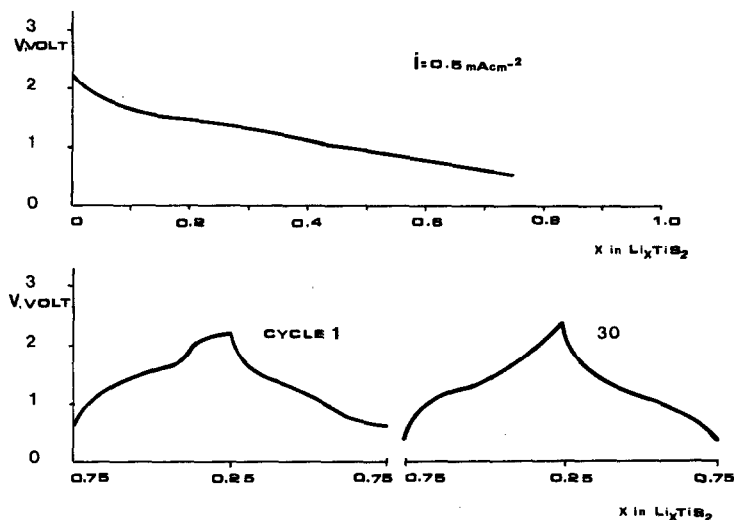

Fig. 6. Discharge and cycling behaviour of the $Li_xFe_2O_3/TiS_2$ cell at 0.5 mA cm^{-2} and at 25 °C.

both the $Li_x Fe_2 O_3$ (Figs. 2 and 3) and the $Li_x TiS_2$ [2] electrodes, as well as with the relatively fast diffusion of Li in TiS_2, which is between 10^{-8} and 10^{-9} cm^2 s^{-1} [6, 11, 12].

The above described results were sufficiently encouraging to extend the study to rocking chair cells using $V_2 O_5$ as the positive electrode. The available data on reversibility and lithium diffusivity for the $Li_x V_2 O_5$ electrode are rather scarce. It therefore appeared to us to be important to examine in further detail the properties of this electrode before proceeding to the evaluation of its behaviour in lithium rocking chair cells.

Galvanostatic anodic and cathodic cycles for the $Li_x V_2 O_5$ electrode at two sweep rates, and for various lithium contents up to 1 equivalent per $V_2 O_5$ mole are reported in Fig. 7. Within this limit the reversibility is effectively high. However, the results of Fig. 7 also show that the cycling behaviour is somewhat dependent on the lithium content as well as on the scanning rate of the polarization sweeps, reaching the optimum condition for compositions around $Li_{0.5} V_2 O_5$ and for fast scanning rates.

This type of behaviour has often been observed for insertion-type electrodes such as $Li_x V_2 O_5$, and it has been interpretated by assuming a difference in bonding energies at various stages of intercalation as well as kinetics controlled by lithium diffusion in the host matrix [2, 4].

No diffusion data for lithium in vanadium pentoxide over the entire composition range are so far available. We have therefore attempted to measure the Li diffusion coefficient in $Li_x V_2 O_5$ by submitting cells of the type
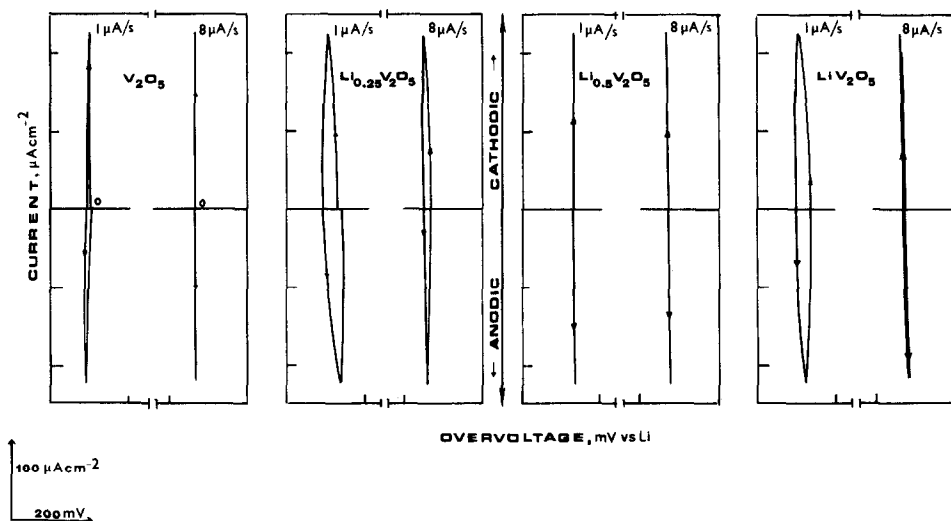
$$Li/LiClO_4-PC/Li_x V_2 O_5 \tag{11}$$

Fig. 7. Cathodic and anodic polarization cycles of the $Li_x V_2 O_5$ electrode at various lithium contents and at (a) 1 μA s^{-1} and (b) 8 μA s^{-1} scanning rates. (T = 25 °C.)

to constant current pulses of various magnitudes and duration. From the voltage recovery, ΔE, after the pulse, it is possible to determine the diffusion coefficient, D, by the formula [6]

$$\Delta E = m\nu i\tau / [FA(\pi Dt)^{1/2}] \tag{12}$$

where ν is the molar volume of V_2O_5 (54.21 cm^3), i is the current density of the pulse, τ the duration of the pulse, A is the electrode surface area (1.2 cm^2 geometrical value), and m is the slope of the e.m.f.–composition curve of cell (11).

The latter has been determined in this work and resulted in agreement with that reported by other authors [13].

The dependence of D on lithium composition for the $Li_x V_2O_5$ electrode is shown in Fig. 8, from which it is seen that the diffusion of lithium reaches maximum values for x around 0.5, in agreement with the polarization data (Fig. 7). It should be pointed out that the determination of diffusion coefficients by the above method may involve an error due to the intrinsic difficulty in defining accurately the active surface of the polycrystalline electrode [14]. Under these circumstances, the present values of the diffusion coefficient of Li in polycrystalline V_2O_5 are comparable with those observed for other electrode compounds such as TiS_2 and NbS_2, which are generally regarded as constituting optimized insertion electrodes.

Vanadium pentoxide may, then, be considered for use in lithium rocking chair systems, and, in fact, the cell
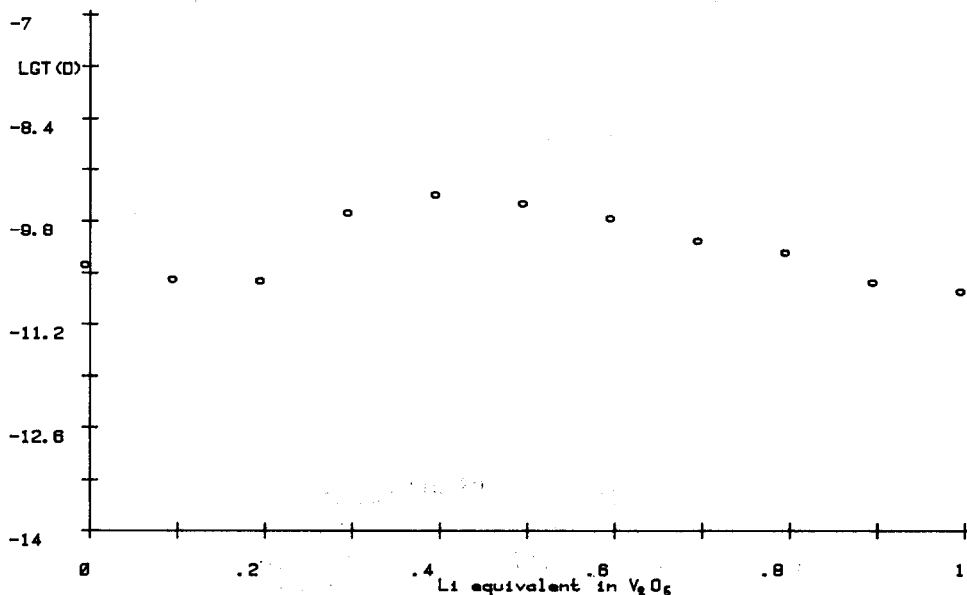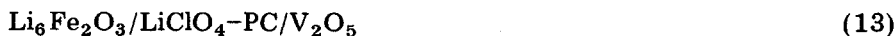
$$Li_6 Fe_2O_3 / LiClO_4 – PC / V_2O_5 \tag{13}$$

Fig. 8. Lithium diffusion coefficient in $Li_x V_2O_5$ at various Li contents and at 25 °C.
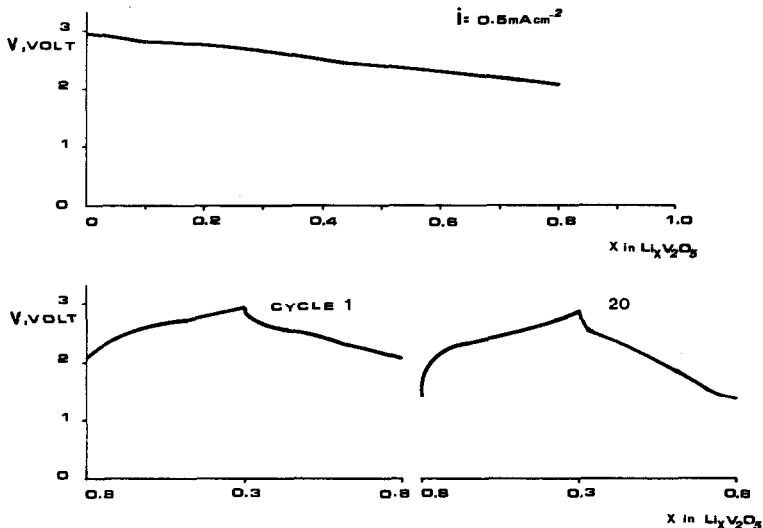
Fig. 9. Discharge and cycling behaviour of the $Li_xFe_2O_3/V_2O_5$ cell at 0.5 mA cm^{-2} and at 25 °C.

has an OCV of 3.0 V, which again is in good agreement with the value evaluated in Fig. 5(B).

Typical discharge and cycling behaviour is illustrated in Fig. 9. This behaviour is very promising, and suggests that the $Li_6Fe_2O_3/V_2O_5$ rocking chair cell may be comparable, in terms of high-rate discharge and deep cycling characteristics, with more established lithium organic electrolyte cells using metal anodes.

Conclusion

In conclusion, the results described demonstrate that with the selection of appropriate electrode materials, lithium rocking chair batteries having reasonably high voltage and good discharge and cycling characteristics can, indeed, be constructed. Of the two systems studied, $Li_6Fe_2O_3/V_2O_5$ appears more interesting because of the higher cell voltage and lower polarization during cycling. Furthermore, V_2O_5 is more easily obtainable in the pure state than TiS_2.

Acknowledgements

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