

## A novel rechargeable lithium composite cathode system

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### Abstract

A new type of rechargeable lithium cell is under development which consists of the lithium salt of a sulfur oxy-acid and a transition metal oxide. The selection, composition and thermal history of the starting oxides and the incorporation of the lithium salt are crucial factors which govern cell performance. A high energy has been demonstrated and shown to be commensurate with the higher ratio of lithium to metal oxide which can be intercalated and deintercalated in comparison with state-of-the-art cathode systems based on cobalt, nickel and manganese oxides. A model of the cell chemistry changes which take place on cycling is proposed and discussed.

*Keywords:* Lithium secondary batteries; Sulfur; Transition metal oxides

### 1. Introduction

The demand for rechargeable batteries having substantially higher energy density than lead–acid or alkaline–nickel oxide systems is indicative of a wide and profitable market opportunity. Hand-portable electronic devices particularly mobile telephones, video camcorders and laptop computers have, over the past five years, shown rapid growth in the market and need a rechargeable power pack. There is, however, an outstanding and urgent need for rechargeable power in electric vehicles where the unit size of battery is very much larger and the existing electrochemical systems are grossly inadequate. It is generally accepted that energy densities of more than  $100 \text{ Wh kg}^{-1}$  cannot be realised with rechargeable aqueous electrolyte systems and that lithium based systems are the most likely to emerge as the next generation of sealed rechargeable power sources.

Whereas primary lithium batteries have been developed over the past 25 years having energy densities up to  $500 \text{ Wh kg}^{-1}$ , no commercially available rechargeable lithium system has yet demonstrated an energy density of more than  $150 \text{ Wh kg}^{-1}$  at a typical 4 h rate of discharge. The lithium-ion system developed by Sony is the most successful lithium rechargeable battery currently available in capacities up to around 10 Ah. Their first application was in video camcorders and more recently they are being used in portable computers and mobile phones. The raw material cost is however high, the major constituent of the cathode being lithium cobalt oxide  $\text{LiCoO}_2$ .

Over the past four years, research at Lexcel Technology Ltd. has been directed towards the development of lithium rechargeable systems having potentially higher energy density but using relatively low cost, ecologically acceptable, raw materials. For electric vehicle motive power, the cost of a commercially acceptable battery unit must be sufficiently low in order to be competitive with internal combustion engine vehicles and have a life in the region of 1000 cycles or more. For the manufacture of large, high energy density, high rate cells it is considered essential to assemble the units in the uncharged state in order to obviate the risk of a short-circuit being formed on processing. Since this implies the absence of lithium metal as a thin foil or composite intercalate, a substantial cost saving is thereby achieved. In the investigations described below, lithium metal was used as the negative electrode. In later studies lithium metal was absent, the lithium compound or complex being present only in the positive electrode.

The tetravalent sulfur compounds  $\text{SO}_2$  and  $\text{SOCl}_2$  are the key constituents in the high energy density lithium primary systems bearing their respective names. However they constitute a major part of the electrolyte in contact with lithium metal and the corrosive effect on the latter tends to rule out their use in rechargeable systems. By using the insoluble compound lithium sulfite  $\text{Li}_2\text{SO}_3$  as precursor together with a transition metal oxide in an oxidation state lower than its maximum, a totally solid cathode is obtained. Under the appropriate charge/discharge cycling conditions, a solid compound or complex persists as active cathode material.

## 2. Experimental

Active materials for cathodes, comprising lithium sulfite and transition metal oxides, were prepared by ball milling the constituents for 5–6 h in the presence of an inert solvent. In order to obtain fine particle size, the transition metal oxides were precipitated from their soluble salts using an alkali solution. After solvent removal, the composite material was dried in a vacuum oven at 130°C. The effect of heating the composite material at temperatures up to 400°C was also investigated.

The cathode compositions used had at least 75% by weight of transition metal oxide/lithium sulfite; up to 20% Super S carbon (MMM Sedema) and/or Timcal KS44 graphite and 5% PVDF powder as binder. Discs 25 mm diameter and approximately 0.3 mm thick were prepared by pressing the mix under a load of 15 tonnes. Celgard 3501 was used as separator and, where appropriate, a disc of lithium foil 132  $\mu\text{m}$  thick as anode. Various electrolyte compositions were used containing  $\text{LiAsF}_6$  and  $\text{LiBF}_4$  dissolved in mixtures of diethyl carbonate and ethylene carbonate.

All charge/discharge cycling tests were carried out using cells of the design shown in Fig. 1. This is similar to that described previously [1], the advantage being that inter-electrode pressure can be accurately controlled from the regulator in line with a cylinder of dry nitrogen. The main body of the cell (A) is constructed from PTFE and has an accurately machined 25 mm bore. The negative electrode (B) consists of pure copper having a rubber O-ring to ensure a tight fit in the PTFE body. This has a flexible connection to the end-cap (C), which is made of stainless steel and is fitted with a miniature brass valve to enable pneumatic pressurisation. The positive electrode (D) is made from an aluminum alloy and fitted with two PTFE valves to facilitate vacuum filling of electrolyte. The cell is made both vacuum and pressure tight by the six threaded rods which compress the end-plates (C and D) against the body (A) using O-ring seals (E).

Cycling tests were carried out using equipment automatically programmed to switch at set voltage and time events between charge and discharge modes. All charge and discharge tests were carried out at constant current, the voltage

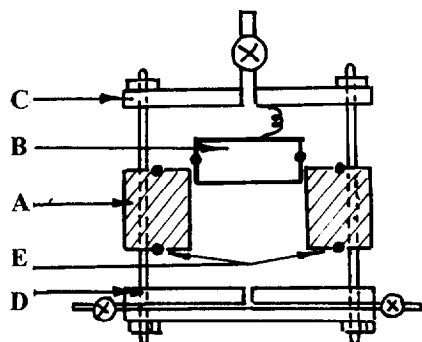


Fig. 1. Design of the experimental cell. A, PTFE block, 25 mm bore; B, negative electrode; C, stainless steel end-cap; D, positive electrode; E, O-ring seals.

limits being 4.3 maximum on charge and 2.7 minimum on discharge. The current densities used ranged between 0.1 and 1.0  $\text{mA cm}^{-2}$  of the electrode area.

## 3. Results and discussion

### 3.1. Ratio of metal oxide to lithium sulfite

An investigation into the relative proportions of the constituents of the composite cathode which would give the optimum performance was carried out using the test cells described in Fig. 1. The atomic ratios of lithium to transition metal were varied from 2:1 to 2:3. The ball milled mixtures were dried for 8 h at 160°C under vacuum and then made up into cathode discs as already described. Lithium metal was used as anode. Test cells were charged at 0.2  $\text{mA cm}^{-2}$  to 4.3 V and discharged at 0.3  $\text{mA cm}^{-2}$  to 2.7 V. The discharge capacities obtained on the first cycle are given in Table 1.

The above results show that a 1:1 ratio of lithium to transition metal in the composite cathode gives the highest capacity. This was found to be applicable for a number of oxides provided they were not in their maximum oxidation state for stable compound formation.

### 3.2. Thermal stability of lithium sulfite

As the compound of a strong base and a fairly weak acid, lithium sulfite is known to decompose with loss of  $\text{SO}_2$  when heated to over 455°C [2]. In order to determine its thermal stability, a sample was tested in a Stanton thermal analyser. Fig. 2 shows the traces obtained, verifying that there is no weight loss up to 400°C. The process of heating lithium sulfite mixed with a transition metal oxide up to this temperature can therefore be undertaken without fear of decomposition and loss of sulfur dioxide.

### 3.3. Effect of heating the composite cathode

In order to further explore the nature and operation of the cathode, mixtures having two different ratios of lithium to transition metal were prepared and heated to temperatures up to 400°C under a nitrogen atmosphere. Ratios of 1:1 and 0.8:1 were chosen and subjected to three different temperatures for a period of 24 h. The discharge capacities obtained, again on the first discharge cycle, are shown in Table 2.

Table 1  
Discharge capacities obtained during the first cycle

Li:M <sub>T</sub> atomic ratio	Capacity of complex ( $\text{mAh g}^{-1}$ )
2.0	80–94
1.5	122–130
1.0	175–182
0.8	150–157
0.67	116–128

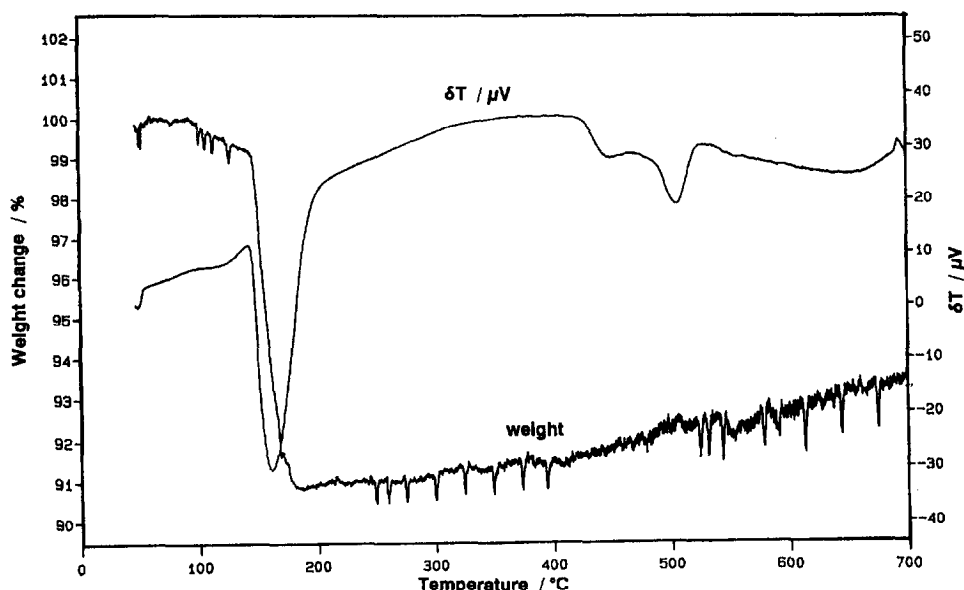


Fig. 2. Thermal analysis of lithium sulfite.

Table 2

Discharge capacities obtained during the first cycle, after heating to various temperatures between 200 and 400°C

Li:M <sub>T</sub> atomic ratio	Temperature (°C)	Capacity of complex (mAh g <sup>-1</sup> )
1	200	182–189
1	300	187–193
1	400	180–188
0.8	200	158–164
0.8	300	163–170
0.8	400	160–168

Some improvement in capacity is evident when the composite material is heated between 300 and 400°C. It was not considered desirable to heat at higher temperatures as the onset of softening in the lithium sulfite near the melting point

would probably result in an increase in particle size, with possible segregation.

### 3.4. Cycling performance

Performance during charge/discharge cycling was studied using material having a 1:1 ratio of lithium to transition metal oxide M<sub>T</sub> which had been heated for 24 h at 300°C.

Fig. 3 shows the results obtained at 21°C on the first and tenth cycles, the current densities being 0.45 mA cm<sup>-2</sup> on charge and 0.60 mA cm<sup>-2</sup> on discharge. Lithium metal was used as anode and the electrolyte was 0.5 M LiAsF<sub>6</sub> + 0.5 M LiBF<sub>4</sub> in a 2:1 volume ratio of diethyl carbonate and ethylene carbonate. The coulombic efficiency on discharge was more than 95% of the charge applied.

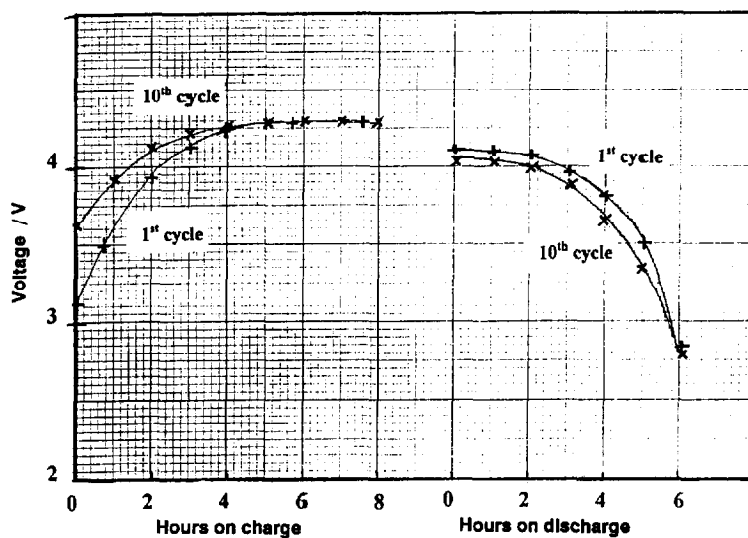


Fig. 3. Voltage/time characteristics during the first and tenth cycle. Li to M<sub>T</sub> ratio: 1:1, current densities were 0.45 mA cm<sup>-2</sup> for charge and 0.6 mA cm<sup>-2</sup> for discharge.

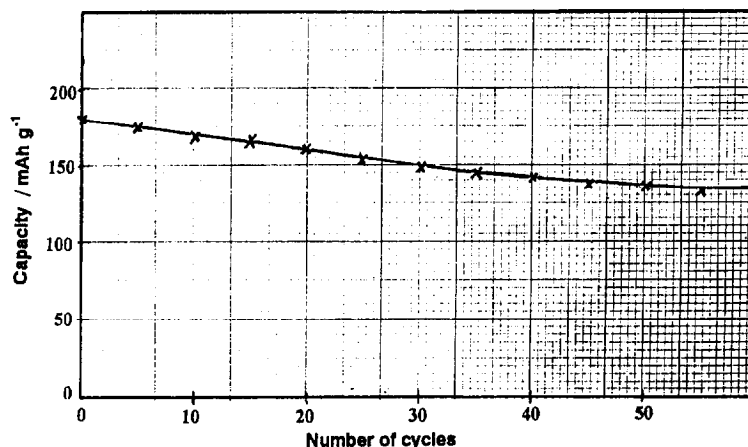


Fig. 4. Variation in capacity with cycle number. Same criteria as Fig. 3.

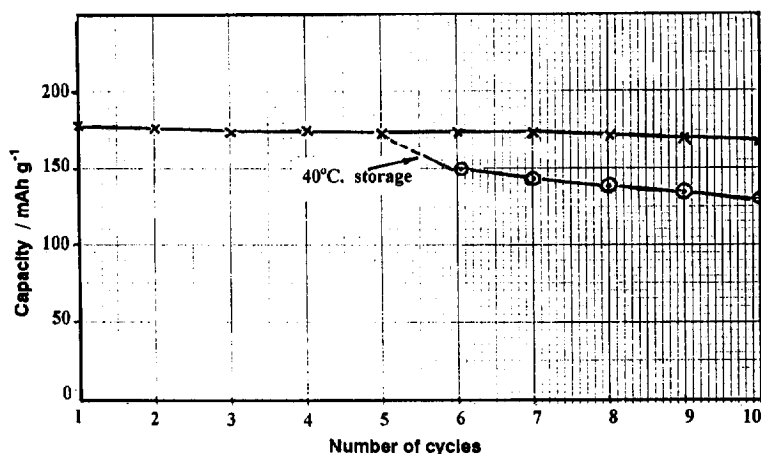


Fig. 5. Effect of storage at 40°C for four weeks between cycles 5 and 6. Otherwise, same criteria as Fig. 3.

Fig. 4 shows a plot of capacity of the same cells for up to 60 charge/discharge cycles. The capacity is seen to fall gradually on cycling, the difference between the first and sixtieth cycles amounting to around 26%. This deterioration is due in part to electrolyte reactivity at the lithium anode as well as irreversible reactions at the cathode which collectively lead to increased cell impedance.

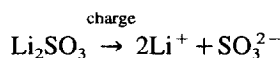
### 3.5. Effect of storage temperature on capacity

Cells from the same batch as tested above (Section 3.4) were subjected to five charge/discharge cycles at 21°C and then stored at 40°C for four weeks before cycling was resumed. Fig. 5 shows the capacities observed up to ten cycles, i.e. before and after 40°C storage. The higher temperature exposure results in a capacity loss after the tenth cycle of some 18% over and above that obtained under constant room temperature conditions.

## 4. Model of cell chemistry

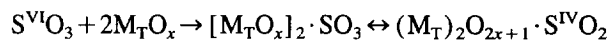
The electrolytic formation of lithium metal from lithium sulfite by charging the composite cathode is a key step in the

successful operation of this novel system. For utilisation in batteries, electrochemical changes which take place in the cathode must occur at a sufficiently high rate. The latter is dependent on adequate electronic conductivity in the transition metal oxide. The initial process is:



On charge, lithium metal is deposited at the anode and sulfur trioxide, initially formed by oxidation of the sulfite ion, will instantly react to further oxidise the transition metal oxide.

This may be represented as:



The oxidation state of sulfur, although momentarily increasing from four to six on discharge of sulfite ion, would not persist as such in the 'complex' and the charged cathode is best regarded as an  $\text{SO}_3$  adduct rather than a sulfite.

On discharge, lithium will intercalate into the complex, react with the  $\text{SO}_3$  and effectively lower the oxidation state of the transition metal. The mechanism proposed is similar to that described by Okada et al. [3] in the intercalation of lithium into ferric sulfate. On discharge of the latter versus a lithium anode, two lithium ions intercalate into the sulfate

lattice. On charge there is an electrolytic split of lithium sulfate in which lithium metal is plated out and iron is oxidised from the ferrous to the ferric state.

## 5. Conclusions

A rechargeable cathode based on an intimate mixture of lithium sulfite and a transition metal oxide has been demonstrated. An energy density approaching  $200 \text{ mAh g}^{-1}$  was obtained with optimised formulations. Heat treatment of an intimate mixture of cathode material at temperatures up to  $400^\circ\text{C}$  was shown to have a beneficial effect on performance.

At this stage of the development, using lithium metal as anode, cycle life evaluation has not extended beyond 60

cycles. Further work using an intercalate anode material will be directed towards achieving much longer cycle life. Hermetically packaged cells having an intercalate anode are confidently expected to have energy densities in excess of  $150 \text{ Wh kg}^{-1}$ . The results of further detailed studies on the structure of these new cathode materials in relation to performance should enable energy densities of  $200 \text{ Wh kg}^{-1}$  to be a realistic target.

## References

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