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Further development of lithium/polycarbon monofluoride envelope cells

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Abstract

Lithium primary cells in a light weight plastic envelope format have been made using carbon monofluoride (CF_x) as cathode material, because previous work showed that this cathode material has the highest energy density in lithium primary batteries. Energy densities of around 650 Wh kg^{-1} were obtained in an envelope cell. Different electrolytes have been examined for high rate and low temperature performance. © 2001 Published by Elsevier Science B.V.

Keywords: Lithium primary cells; Polycarbon monofluoride

1. Introduction

Lithium/carbon monofluoride (CF_x) primary cells are known to give the highest energy density of all lithium primary cells, with a theoretical energy density of 2180 Wh kg^{-1}, cf. 1470 Wh kg^{-1} for lithium/thionyl chloride or 1005 Wh kg^{-1} for lithium/manganese dioxide [1–3]. Other cathode materials (iron disulphide, λ-manganese dioxide) for lithium primary cells and a metal-free rechargeable lithium cobalt oxide cell have been shown to have lower energy densities [4]. Polycarbon monofluoride has the further advantage that CF_x is a solid so that light weight envelope cell packaging can be used, similar to that already described [4,5] and illustrated in Fig. 1.

Lithium/carbon monofluoride primary cells are commercially available, e.g. as button cells [2,3,6], but are largely used for low rate applications, such as pagers, cameras, computer clock and memory back-up [3], gas meters [7], electronic and communications equipment. The envelope or 'pouch' construction has previously been used for lithium/manganese dioxide primary cells [8,9], so it is an established technology for primary lithium/solid cathode cells though the theoretical energy density for Li/MnO_2 is much lower. Hence, lithium/carbon monofluoride envelope cells have the potential for the highest possible energy density both on grounds of chemistry and of construction.

Previous work [10] has shown that envelope cells could be made in thickness from 0.8 mm upwards, with five-fold cells reaching 10.5 mm. Capacities were from 1.125 to 18 Ah. These cells used the EC/DEC/$LiPF_6$ electrolyte as used in lithium-ion secondary batteries. However, laboratory cells showed higher voltages on discharge with other electrolytes (e.g. EC/PC/DME/$LiBF_4$). Further studies on the effect of different electrolytes have been carried out over a range of temperatures. Energy densities up to 516 Wh kg^{-1} were achieved but 750 Wh kg^{-1} was predicted for optimised designs. This work describes the use of these better electrolytes and the optimisation of design to achieve balanced cells, with resulting higher energy density.

2. Experimental

Experimental techniques were similar to those described previously [10]. By varying the concentration and hence viscosity of the cathode mixture, the thickness of the cathode coatings could be adjusted. Cathode capacities between 10 and 17 mAh cm^{-2} were achieved.

Two electrolytes were studied in laboratory cells:

1. 1 M lithium tetrafluoroborate, $LiBF_4$, in PC:DME (1:1 w/w).
2. 1 M lithium hexafluorophosphate, $LiPF_6$, in EC:EMC (1:1) (Merck LP50).

where EC = ethylene carbonate, PC = propylene carbonate, EMC = ethyl methyl carbonate, DME = dimethoxy ethane.

In envelope cells, cathode sheets were folded around a central lithium anode so, for a balanced cell, the cathode capacity should be half the anode capacity (27.2 mAh cm^{-2}

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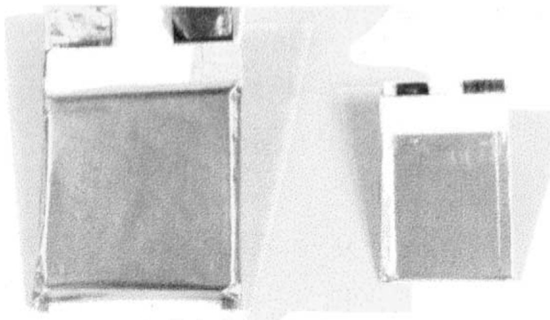

Fig. 1. Packet and envelope cells.

for 132 μm lithium foil), i.e. 13.6 mAh cm^{-2} for the cathode. The cells used a folded construction with each fold being 75 mm × 75 mm. The cells were folded successively, giving 225 cm^2 for a two-fold cell. Folded cells were put into a Surlyn bag, the electrolyte was added then the cells were evacuated and vacuum sealed. Flat packs without bulging were readily obtained. During testing, no external pressure needed to be applied. In laboratory cells, a single sheet of cathode material was used, so the lithium was in excess.

3. Discharge tests in laboratory cells

These tests studied the effects of cathode thicknesses, temperatures (−30 to +40°C), discharge rate (10–100 h) and different electrolytes in laboratory cells whose design has been described previously [5]. Previous results [4] and Fig. 2 have shown similar results in envelope and laboratory cells so laboratory cell results should be readily transferable to envelope cells, which would be used for actual battery construction.

Different cathode loadings are compared in Figs. 3 and 4. They show similar discharges for coatings of 13.6 and 17 mAh cm^{-2}.

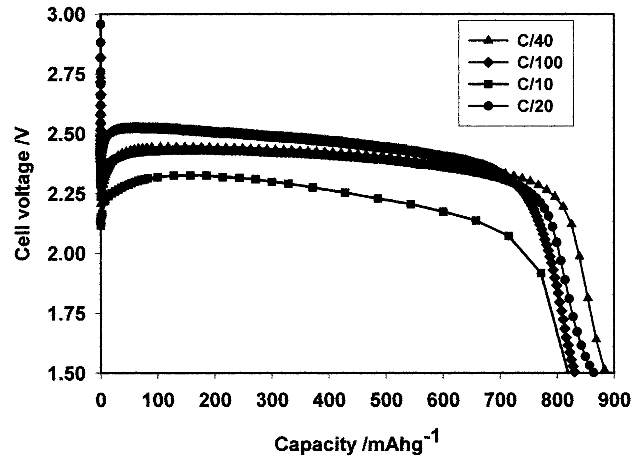

Fig. 3. Electrochemical discharges of lithium/CF_x primary laboratory cells at room temperature with PC/DME/$LiBF_4$ electrolyte for a cathode loading of 13.6 mAh cm^{-2}.

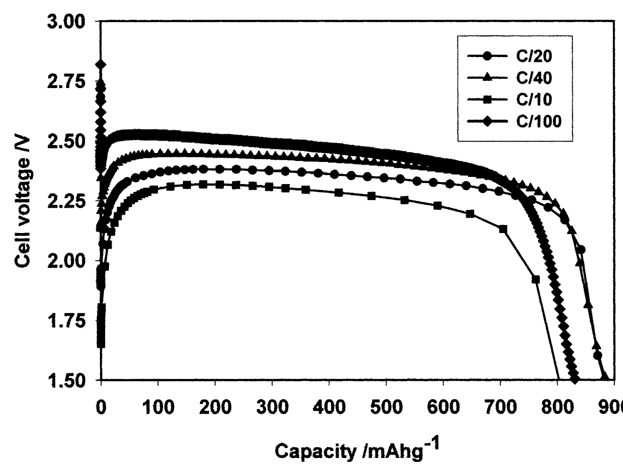

Fig. 4. Electrochemical discharges of lithium/CF_x primary laboratory cells at room temperature with PC/DME/$LiBF_4$ electrolyte for a cathode loading of 17 mAh cm^{-2}.

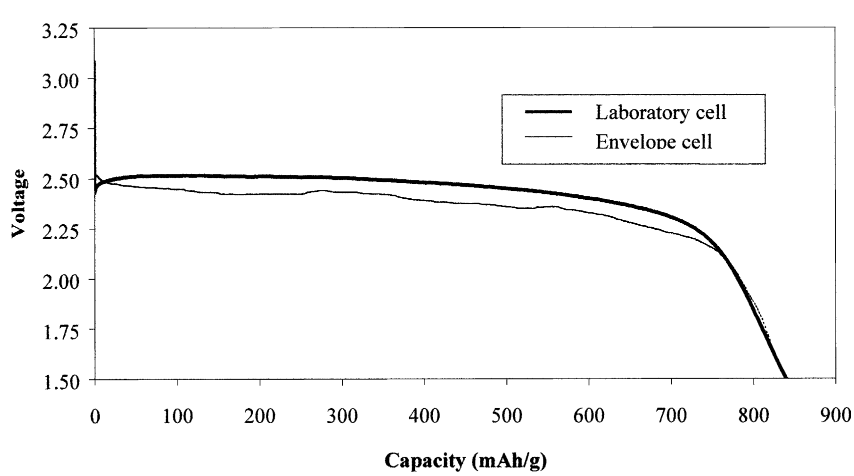

Fig. 2. Comparison of Li/CF_x primary laboratory and envelope cells discharged at 0.05 mA cm^{-2} (200 h rate).

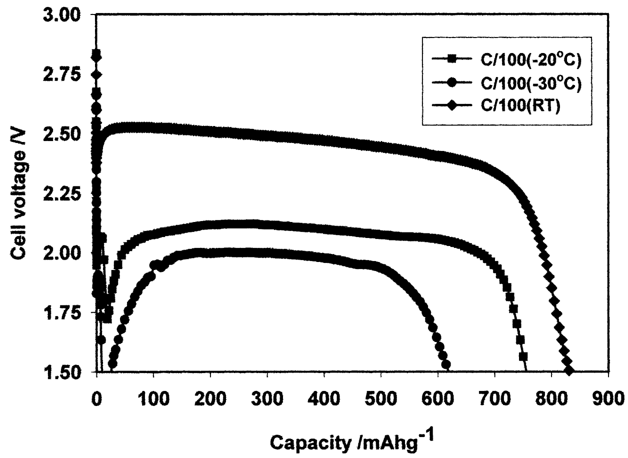

Fig. 5. Electrochemical discharges of lithium/CF_x primary laboratory cells at the 100 h rate at different temperatures.

The capacities were close to the theoretical value of 864 mAh g^{-1} showing that the cathode material was being discharged efficiently for both coating thicknesses. Good discharges were obtained at the 20, 40 and 100 h rates but slightly lower capacity and discharge voltage were found at the 10 h rate.

Figs. 5 and 6 show the effect of different temperatures at the 100 and 20 h rates, respectively. Cells could be discharged at temperatures as low as −30°C but performance was better at room temperature or +40°C.

Previous work [10] used EC/EMC/$LiPF_6$ electrolyte. Discharges using this electrolyte are illustrated in Fig. 7.

Comparison of Figs. 4, 7 and 8 shows the higher on-load voltage found when using the PC/DME/$LiBF_4$ electrolyte instead of the EC/DMC/$LiPF_6$ electrolyte used previously in [10].

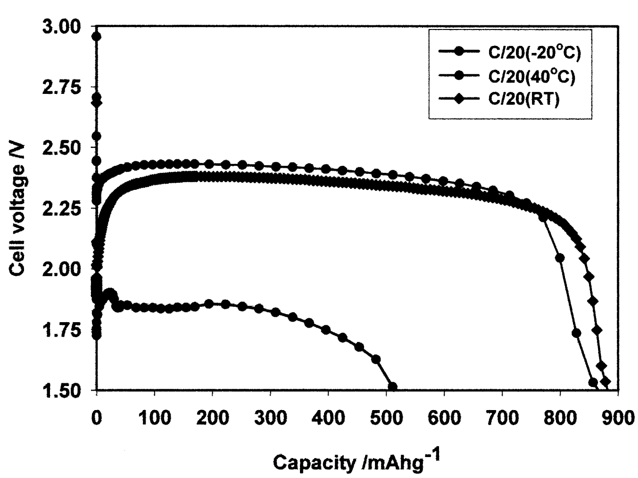

Fig. 6. Electrochemical discharges of lithium/CF_x primary laboratory cells at the 20 h rate at different temperatures.

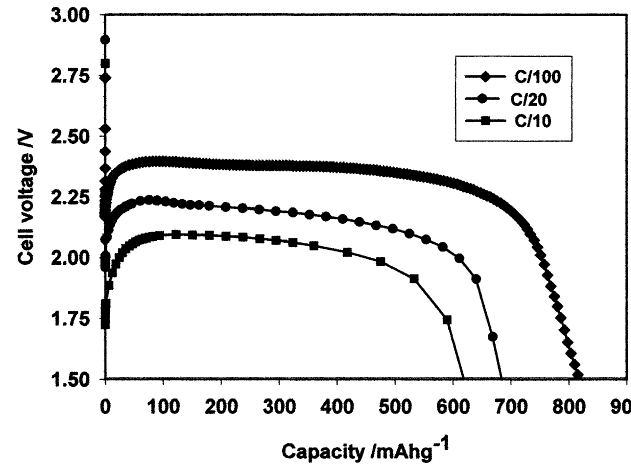

Fig. 7. Electrochemical discharges of lithium/CF_x primary laboratory cells at room temperature with EC/DMC/$LiPF_6$ electrolyte at a cathode loading of 17 mAh cm^{-2}.

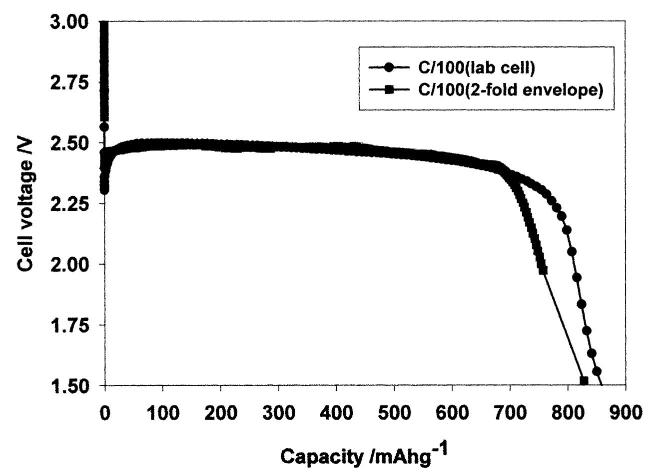

Fig. 8. Electrochemical discharge of a two-fold lithium/CF_x primary envelope cell at the 100 h rate at room temperature with 13.6 mAh cm^{-2} cathode loading and PC/DME/$LiBF_4$ electrolyte.

4. Discharge of envelope cell

A two-fold envelope cell was made as described previously [10] but with an increased cathode loading of 13.6 mAh cm^{-2} to provide a balanced design. A PC/DME/$LiBF_4$ electrolyte was used to provide higher conductivity, and hence a higher on-load voltage than the EC/DMC/$LiPF_6$ electrolyte used in the earlier work. In accordance with earlier predictions [10], this produces a higher energy density, 642 Wh kg^{-1} for a two-fold cell. Compare this value with 385 Wh kg^{-1} for the three-fold cell reported earlier. The cathode capacity was close to theoretical and the discharge was similar to a laboratory cell discharged under similar conditions.

5. Conclusions

An energy density of around 650 Wh kg^{-1} has been achieved from a lithium/polycarbon monofluoride envelope cell. This demonstrates the benefits in terms of energy of this chemical system and of the envelope cell construction. Different electrolytes have been investigated for good low temperature performance.

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