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Lithium rechargeable envelope cells

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Abstract

Prototype lithium manganese oxide rechargeable cells have been made in an envelope format, which is particularly suitable for scaling up to large batteries. Materials have been tested in laboratory cells. The synthesis of lithium manganese oxide has been investigated and cathode components for cells have been fabricated. Cycling results are reported.

Keywords: Lithium secondary batteries; Manganese oxides

1. Introduction

There is widespread interest worldwide in developing high energy rechargeable batteries for high technology applications such as portable telephones and laptop computers. Lithium-ion cells are already on the market for this application but only in small sizes. Military applications need much larger size batteries. These can be made by assembling small size cylindrical size batteries into battery packs but these are inefficient in terms of size and weight; space is wasted between cylindrical cells and the weight of the metal cell cases makes batteries unnecessarily heavy. Furthermore, batteries made up of large numbers of small cells can suffer problems of cell imbalance so they need careful battery management. This paper describes the development of a flat 'envelope' cell format which can later be packaged into large batteries with good packaging efficiency. By using lightweight plastic casing for the cells, the overall battery weight will be minimised.

Commercially available lithium-ion cells use the lithium carbon/lithium cobalt oxide ($LiCoO_2$) system. While this is technically successful, their cost is high due to the high price of cobalt. We are therefore investigating lithium manganese oxide, $LiMn_2O_4$, as a longer term replacement because of the modest price and low toxicity of manganese. For the highest energy density, lithium metal would be preferable to lithium carbon, to avoid the dead weight and bulk of the carbon. Commercial lithium-metal cells have recently been announced [1]. However, it is essential to avoid plating lithium dendrites as these reduce cycle life and lead to safety

problems [2]. Some investigation into this is reported separately [3]. Initially a lithium metal/lithium manganese oxide cell is being developed; the lithium metal could later be replaced with a lithium-carbon anode, if necessary. Another possibility is a 'lithium-free' cell. Here, cells would be assembled with the lithium manganese oxide in the fully discharged state, i.e. $Li_2Mn_2O_4$, which would then be charged to plate-out lithium to form the negative electrode. This would be simpler to fabricate than lithium-ion cells, it would avoid the dead weight of carbon and would also be safer in storage than lithium-metal cells. Preliminary investigation of lithium-carbon anodes is now in progress. Work on materials development in laboratory cells and the production of prototype envelope cells is reported here.

2. Experimental

Materials were tested in laboratory cells (Fig. 1). These resemble small size, flat plate, cells. The design enables stack pressure to be applied without which lithium metal would not cycle efficiently.

The construction of envelope cells is shown in Fig. 2(a) and (b) and the cells are illustrated in Fig. 3. Two sizes were used: a 40 cm^2 active area cell weighing approximately 5 g and a 160 cm^2 cell of 20 g. The inner bag is a polyester/Surlyn material (Du Pont); the outer bag is a laminate comprising polyester, aluminum and Surlyn. Both bags are heat sealed. The current collectors in the present design are thin metal foils (copper negative, aluminum positive) so that the cells can be easily sealed. The anode, 132 μm thick lithium
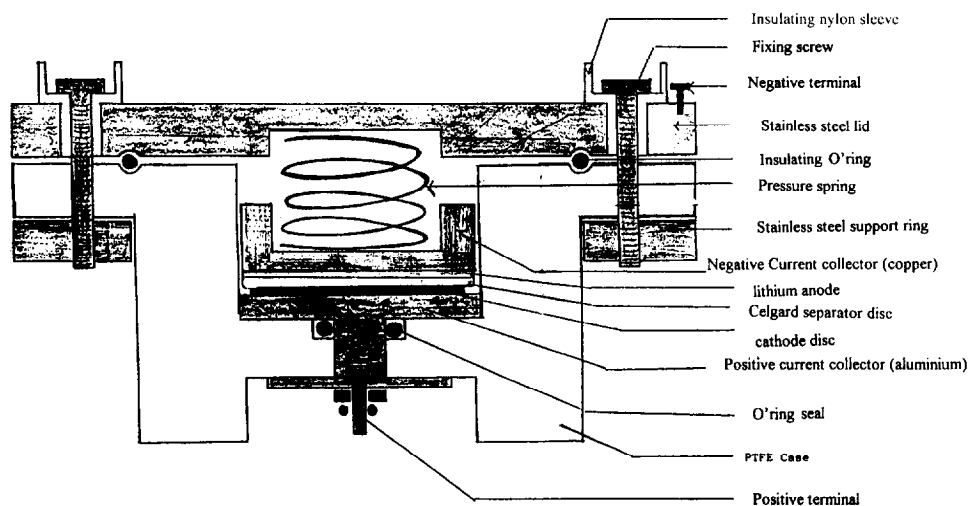
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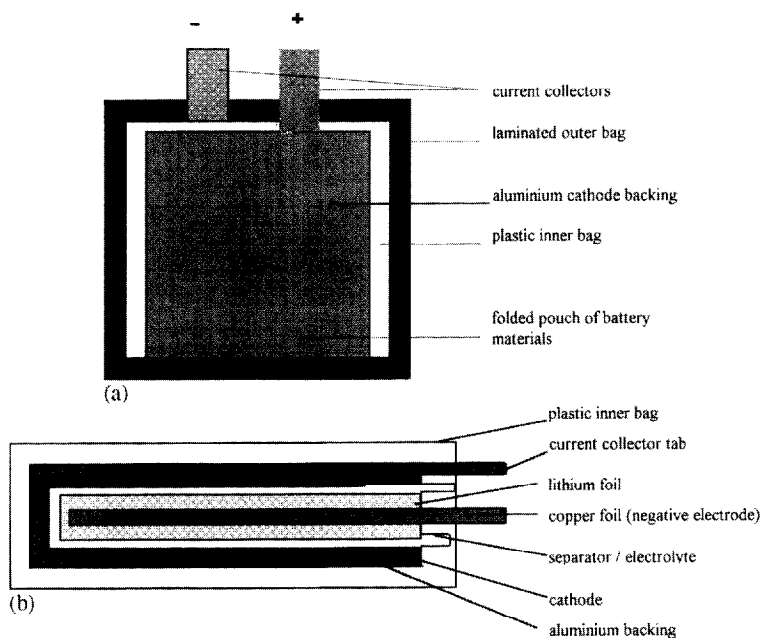Fig. 1. Construction of a laboratory cell.

Fig. 2. (a) Top view of envelope cell. (b) Cross section of envelope cell.

foil, is folded over the central copper negative current collector. The Celgard separator and the cathode sheet are then folded over it. The outer bag is formed by heat-sealing the laminate. A measured amount of electrolyte is injected into the cell which is evacuated to remove gas and heat-sealed to form the envelope package. Presently, the electrolyte used is ethylene carbonate:propylene carbonate with lithium hexafluoroarsenate. This was shown to be adequate for the Molicel lithium rechargeable system [4] but further studies are in progress to investigate electrolytes which may be more suitable at lower temperatures. Lower viscosity solvents may provide better access of the electrolyte to the cathode material, with consequently better cell cycling.

Production of the optimum phase of lithium manganese oxide is difficult, due to the large number of different phases possible [5]. Furthermore, scale-up of synthesis is difficult [6]. Moreover it is difficult to characterise lithium manga-

nese oxide by analytical techniques [7]. Lithium manganese oxide was made by the solid state synthesis reaction of manganese carbonate with lithium carbonate in flowing oxygen. The synthesis temperatures were: 425, 480, 520, 560, 585 and 615°C. The mixture was heated for 24 h, then the product was ground and heated again for another 24 h. Lithium manganese oxide was the major product, but traces of manganese oxide Mn_2O_3 were found [7]. Most of the envelope cells used commercially manufactured $LiMn_2O_4$ as this was available in large batches.

For production of cells, as opposed to laboratory cell testing of cathode materials, it is necessary to make coatings of lithium manganese oxide onto a current collector of aluminum foil. Coatings have been prepared using both doctor blade and meter bar coaters (RK Print Coat). The lithium manganese oxide was mixed with conductive carbon additives and a dissolved binder to form a slurry. The thickness
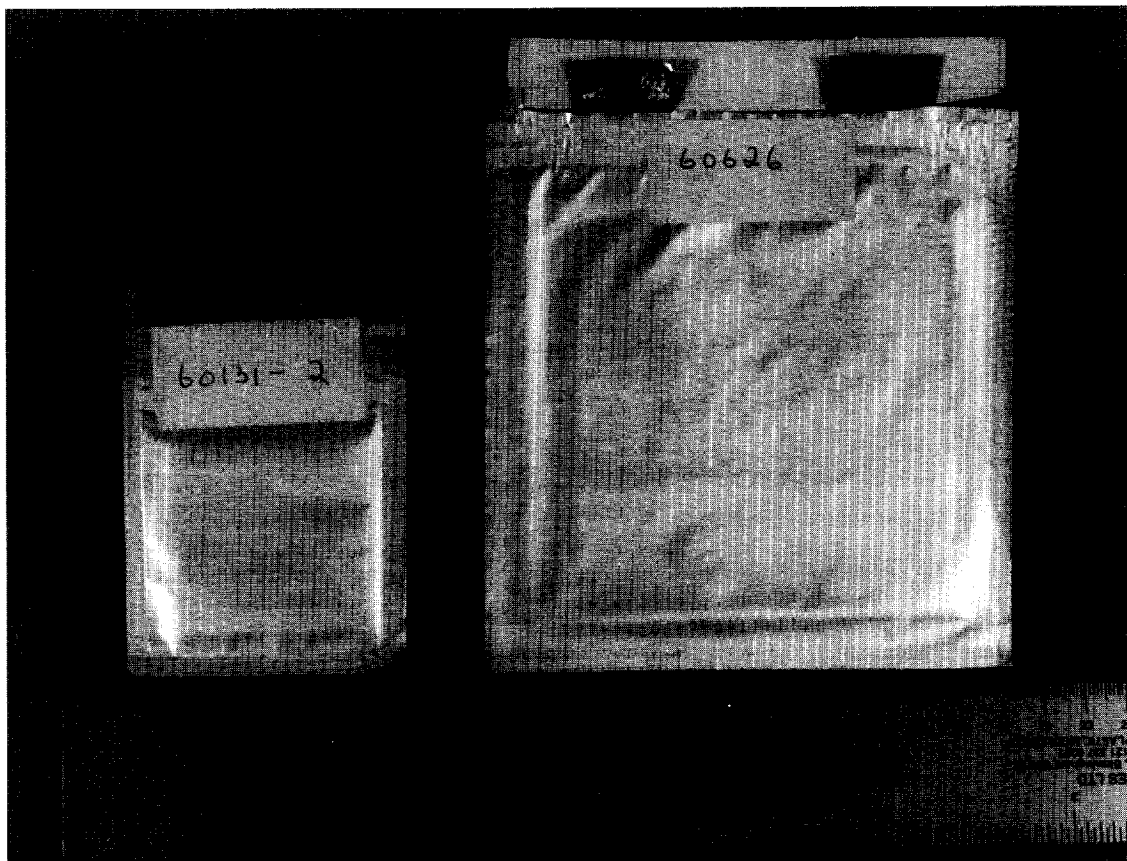
Fig. 3. Photograph of envelope cells.

of the dry coating is usually about 200–250 μm. Various carbons and binders have been investigated. Rolling of coatings is beneficial for promoting adherence, which is necessary as coatings need to withstand folding and flexing during battery manufacturing. Hot pressing has been tested but cold rolling is generally satisfactory, particularly if the binder is prone to melt on heating. A PVB (polyvinylbutyral, Hoechst):carbon:LiMn₂O₄ composition was initially used as it produced adequate adherence for use in laboratory cells. However, improvements were needed for use in batteries. In order to address this, along with the need to increase cathode capacity, cathode composition was investigated further. This involved use of different types and mixes of carbon along with a study of alternative binders. Some coatings were heated on a hot bed at 130°C which seemed to have a beneficial effect on adherence. Recent cathodes coated at DERA have also been cold rolled. This also improves adherence, although further work is needed here to assess the effect on cycling performance. PVDF (polyvinylidene fluoride, Elf Atochem) and mixtures of carbons produced the best results in terms of adherence.

Where possible, laboratory and envelope cells were cycled under the same conditions. Current densities on charge and discharge were usually 0.5–0.8 mA cm⁻², although some of the large envelope cells were tested at lower rates. This corresponded to charging times of 4–10 h, though most of the charge was absorbed in 2–3 h. Charging was at constant

voltage with the above current limits and discharge was at constant current. The voltage range was generally 2.2–3.5 for nominally 3 V cells; some tests have also been carried out at higher voltages (3.7–4.3) to provide a 4 V cell.

3. Results

3.1. Comparison of laboratory and envelope cells

Charge and discharge capacities of a laboratory lithium metal/lithium manganese oxide cell are plotted in Fig. 4. The cell showed good cycling efficiency (charge/discharge balance). It is possible to cycle cells over 150 times. 'Lithium-free' cells have also been investigated briefly (Fig. 5). Here, a normal lithium-metal cell was given a few cycles, ending with discharge. The lithium metal was then removed and the rest of the cell was reassembled. Cycling was then resumed, beginning with a charge to plate lithium on to the negative current collector. On cycling, capacity faded faster than for complete lithium-metal cells, indicating that some of the lithium was being lost on cycling so some lithium excess is needed. However, the capacity decline on each cycle was small so only a small amount of lithium excess would be needed to replenish the losses.

Most work on envelope cells has used the smaller size. Their discharge capacities in mAh cm⁻² are shown in Fig. 6.
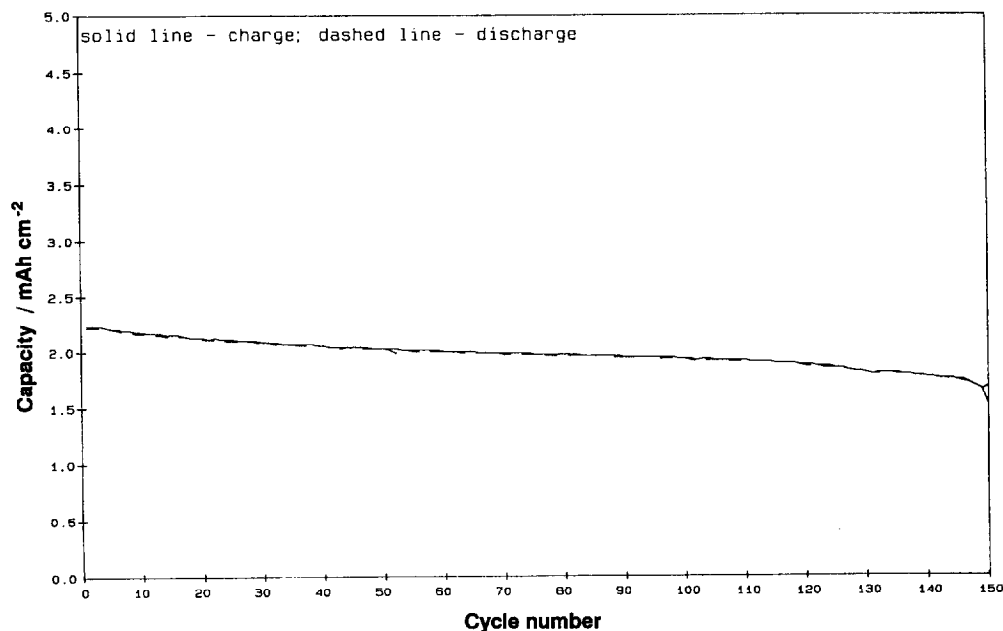
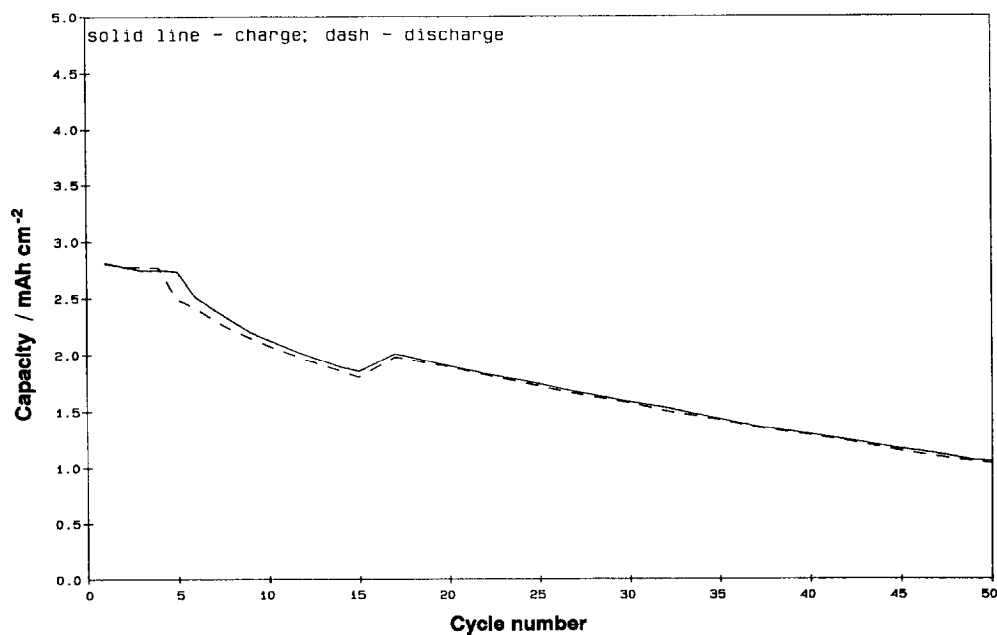Fig. 4. Charge/discharge capacity of laboratory cells.

Fig. 5. Lithium-free cell.

The values are comparable to those obtained with laboratory cells. External pressure was applied to one cell by means of a G-clamp and 1.7 kg weight placed on top of the cell. Consequently, it showed slower capacity fade than the other two cells which were not clamped.

3.2. Comparison of materials

Different batches of lithium manganese oxide are compared in Fig. 7. All batches were tested in laboratory cells. Of the batches prepared in-house, best results were obtained with material made at the lowest temperature, 425°C. Commercial material is also shown. The 425°C material gave the

best performance overall in terms of capacity and cycle life so this was used for further work. The capacity of the higher temperature materials was probably limited by their larger particle size [7].

Three different binders were compared in terms of cathode coating adherence and cycling performance in laboratory cells. These were PVB, Primacor and PVDF. The cells using PVB generally cycled with the highest capacity. However, their adherence was insufficient for use in a battery. Better adherence was obtained with Primacor but the cathode slurry coated unevenly. PVDF gave the best cathode adherence and most uniform coatings. These cathodes were sufficiently robust for use in battery production. However, as the binders
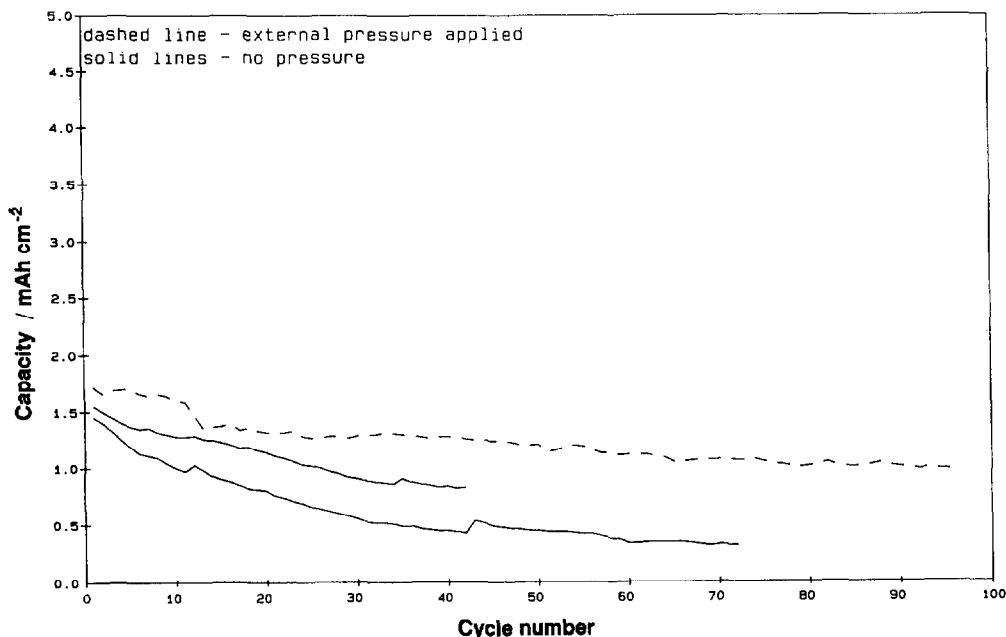
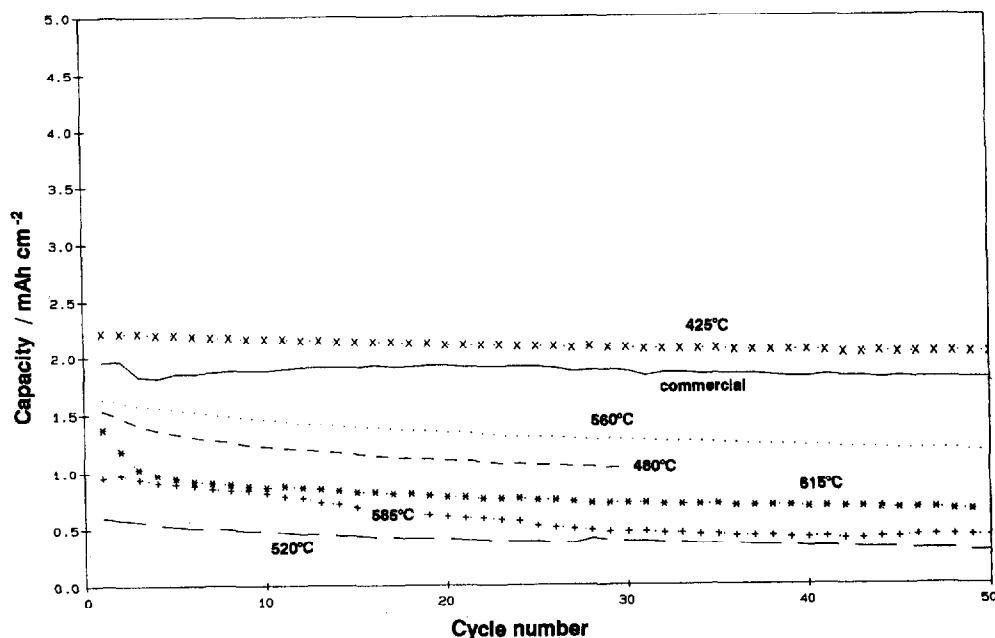Fig. 6. Discharge capacities of small size envelope cells.

Fig. 7. Comparison of different batches of lithium manganese oxide.

are intrinsically insulating, this improvement came at the expense of capacity. The binder lowered cathode porosity reducing the cyclability of the cell. Therefore, further work is needed to optimise the cathode binder content and obtain an acceptable compromise between capacity and cathode adherence.

In conjunction with the binder studies, different cathode carbon compositions have been investigated briefly. Initially, all the cathode carbon was a carbon black. Being bulky, though, it needed a high binder content to produce adherent coatings. Graphite was therefore added. Cells with all the carbon as graphite would only pass very low currents ($C/20$ rate) and capacities were very low. Mixtures of carbon black

and graphite are now used. As with the binder, further optimisation is necessary.

3.3. Comparison of large and small size envelope cells

The engineering process used to make envelope cells was successfully scaled up to produce a four-fold increase in active cell area. All of the smaller cells were cycled on the lower voltage plateau of lithium manganese oxide. Some of the larger cells were also tested at the higher voltages. These gave starting capacities comparable to the smaller cells and laboratory cells but they faded rapidly. The cells cycled in the lower voltage range had longer cycle life but low capacity.

The generally poorer performance seen with the larger cells is probably attributable to the differences in materials used and the need for further optimisation.

3.4. Demonstration of envelope cells

In addition to laboratory tests, a number of demonstrations were carried out to show the envelope cells powering a variety of different equipments. The larger cells successfully drove a portable battery-operated fan, designed for an AA-size alkaline cell. The peak current measured was 800 mA, the average value being 300 mA. This is considerably higher than the currents used in cycling tests. The smaller size cells performed particularly well in driving d.c. motors which required similar currents to the fan. All these cells had been used extensively in cycling tests and had been left to stand for several months. Two cells with OCVs of around 2.98 V were connected in series to power a 6 V motor. A single cell was used to drive a 3 V motor. The measured currents were 300–360 mA. The cells also lit 40 mA LED bulbs, including four bulbs connected in parallel.

4. Conclusions

Lithium rechargeable battery materials developed by DERA have been fabricated into envelope cells. These cells are lightweight and could be packed efficiently into a large battery. They are capable of operating motors and fans requiring currents of up to several hundred milliamperes.

Small envelope cells have been cycled with comparable capacity to laboratory cells. External pressure improved cycle life.

Cathodes have been made which are sufficiently mechanically robust and flexible to be made into a battery though binder and carbon content may need to be optimised for the best performance. Further work on cathode material synthesis is in progress to obtain optimum capacity and cycle life.

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