

Effects of physical constraints on Li cyclability*

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(Received February 5, 1991, in revised form May 29, 1991)

Abstract

Mechanical pressure is shown to have a large effect on lithium plating morphology, lithium cyclability and the propensity to form dendritic shunts. *In situ* examination of lithium growth during cycling was carried out using a special force-displacement instrumented apparatus. Lithium growth is found to strongly depend on electrode stack pressure. The build up of electrode stack pressure in constant volume cells is examined in terms of cell design, component thickness and component compressibility. Methods of obtaining optimum lithium cyclability in a constant volume cell with respect to electrode stack pressure are discussed and illustrated.

Introduction

One of the main problems in rechargeable lithium batteries is the cyclability of the lithium anode. Cyclability is limited by corrosion of the lithium in the electrolyte which results in loss of electrolyte and poor electrical contact between plated lithium grains and the substrate [1, 2]. Extensive studies have been made of lithium morphology and lithium surface films especially in propylene carbonate based electrolytes. The ideal morphology of plated lithium is a dense deposit with large grains which results in a smaller total surface area, less electrochemically isolated lithium and less electrolyte decomposition. Surprisingly, there have been very few studies of the effects of mechanical pressure on lithium plating morphology and hence cyclability [3, 4]. This type of information is vital to the design of rechargeable lithium cells because the nature of the physical containment of the lithium anode determines the mechanical pressure exerted on it.

Experimental

A quantitative measurement of the thickness of the lithium deposit on cycling at different pressures was made using the special apparatus shown

*Paper presented at the 5th International Meeting on Lithium Batteries, Beijing, China, May 28-June 2, 1990

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in Fig 1 This force-displacement instrumented apparatus was also used to measure the compressibility of various cell components The apparatus consists of a flat plate cell with a plunger which by means of an external press can be made to apply a certain range of pressures normal to the electrode stack The compressed springs on the press maintain an approximately constant force for the small changes in electrode stack thickness which occur during cycling The applied pressure is measured by a pressure transducer and the

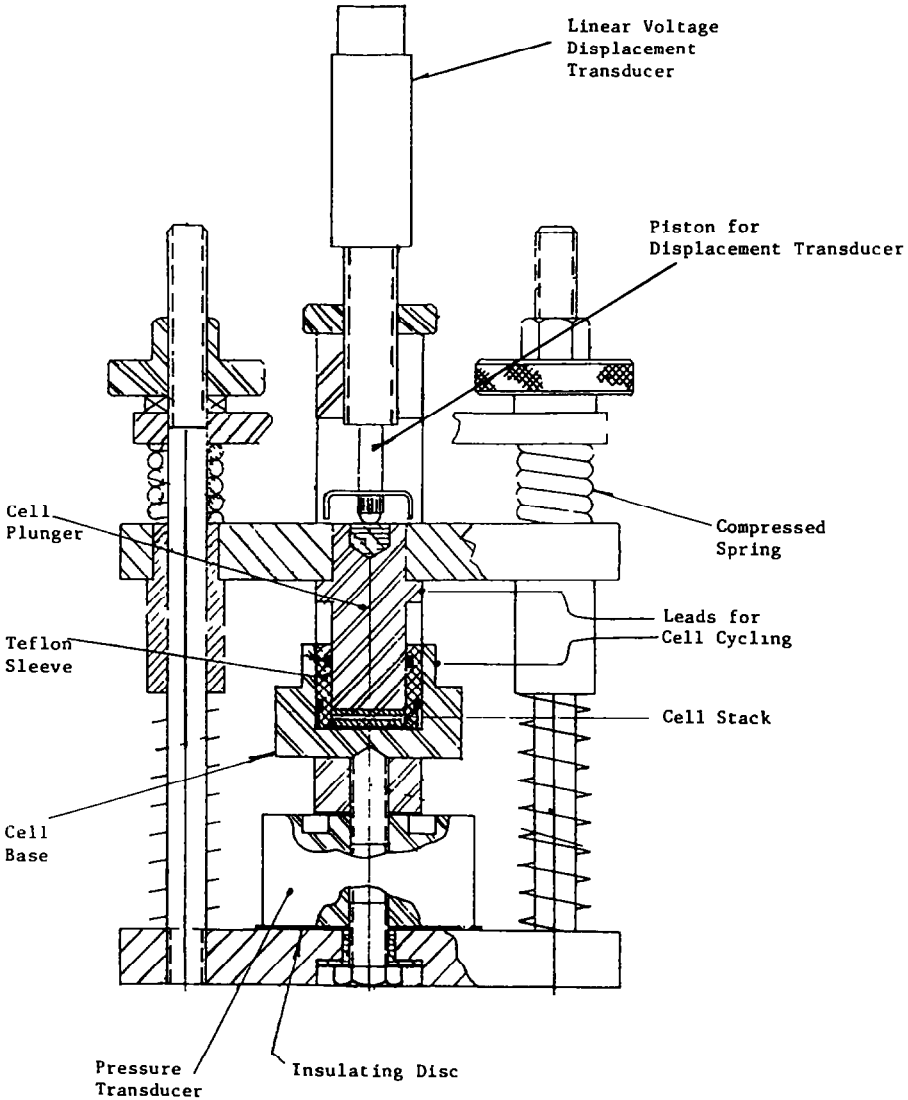


Fig 1 Force-displacement instrumented apparatus for measuring electrode thickness at constant pressure during cycling

thickness of the electrode stack is followed by a linear voltage displacement transducer. During galvanostatic cycling, the cell voltage and electrode stack thickness were stored as a function of time by a data logger. The applied pressure was monitored during cycling and did not change by more than ± 1 psi. The linear voltage transducer was calibrated regularly ($127 \mu\text{m V}^{-1}$) and the system gave a thickness sensitivity of $\pm 0.1 \mu\text{m}$.

In most cases, the electrode stack used in the force-displacement instrumented apparatus consisted of $127 \mu\text{m}$ thick Lithco lithium foil, $25 \mu\text{m}$ thick Celgard 2500 separator and either a Li_xMoS_2 or Li_xMnO_2 insertion cathode of about $121 \mu\text{m}$ thickness. The Li_xMoS_2 used in this study was obtained by chemically modifying [5] Endako Ultrapure molybdenite. The Li_xMnO_2 used was a chemical modification [6] of Chemetals EMD. Other testing was done in spirally wound AA size cells.

Electrolytes consisting of propylene carbonate (PC), ethylene carbonate (EC), LiAsF_6 (Lithco) or LiCF_3SO_3 (Aldrich) were used in the cell. The electrolyte salts were used as received and the base solvents were purified by the usual fractional distillation method. All electrolyte solutions were made in a He-filled glove box and were only considered acceptable if they had < 50 ppm H_2O .

Results and discussion

It was found that there is a very strong correlation between pressure perpendicular to the electrode surface and the number of lithium turnovers that can be obtained. Figure 2 shows the dependence of lithium turnovers

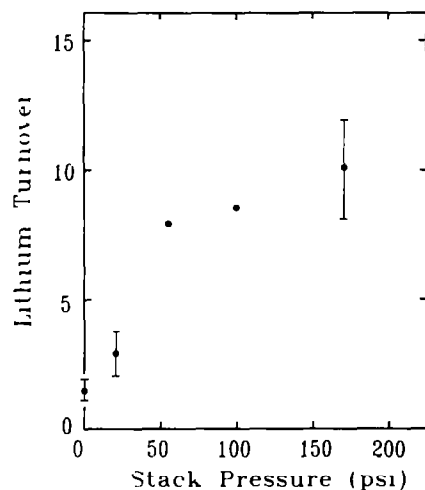


Fig 2 Dependence of Li cycling efficiency on electrode stack pressure for cycling of $\text{Li}/\text{Li}_x\text{MoS}_2$ flat plate cells containing 1 M LiAsF_6 PC. Cells were cycled at 0.35 mA/cm^2 , 2.4–1.3 V and 21°C .

as a function of stack pressure for cycling of $\text{Li}/\text{Li}_x\text{MoS}_2$ flat plate cells containing 1 M LiAsF_6 propylene carbonate. The largest increase in lithium turnovers is achieved between 0 psi (free-standing electrodes) to a critical pressure in the 60 to 80 psi range. The creep strength (60 psi for 2.2 h) [7] and tensile strength of lithium (84 psi at room temperature) [7] correspond to this critical pressure range.

Scanning electron micrographs shown in Fig. 3 indicate very different plating morphologies for lithium cycled below and above the critical pressure range. At a low stack pressure of 20 psi, a very porous lithium deposit is formed consisting of a variety of differently shaped crystals, some of them needle-like, others irregularly shaped lumps. At a higher stack pressure of 200 psi, a non-porous deposit is formed consisting of closed-packed columns extending from the uncycled lithium substrate. The effect of this latter plating morphology must be to enhance stripping of the grains near the surface of the deposit instead of the lithium substrate. This decreases the surface area of the deposit which can react with the electrolyte and hence increases the number of lithium turnovers.

Using the force-displacement instrumented apparatus it was found that little or no net electrode stack growth occurs for cycling of intercalation

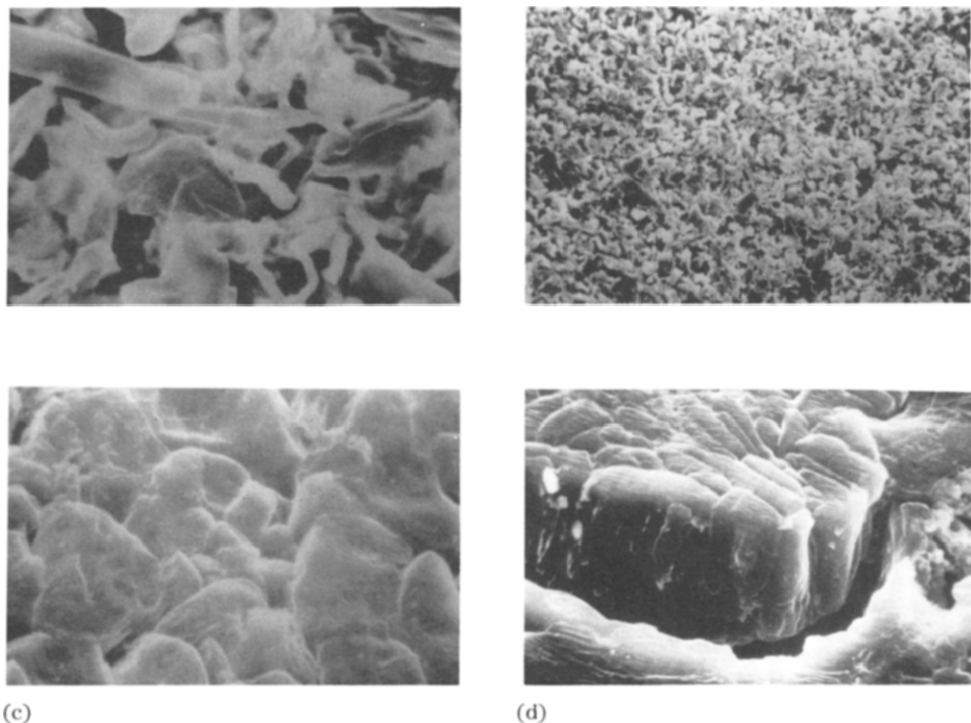


Fig. 3 SEM photographs of Li from cycled $\text{Li}/\text{Li}_x\text{MoS}_2$ flat plate cells containing 1 M LiAsF_6 PC. Cells were cycled $10\times$ at $0.30\text{ mA}/\text{cm}^2$, $2.4\text{--}1.3\text{ V}$ and $21\text{ }^\circ\text{C}$. (a) 20 psi, $7000\times$, (b) 20 psi, $1000\times$, (c) 200 psi, $8100\times$, (d) 200 psi, $2000\times$.

cathodes in the absence of lithium metal Figure 4 shows the variation in voltage and thickness for cycling of an electrode stack comprised of Li_yMnO_2 anode, microporous separator and Li_xMnO_2 cathode Disassembly of such cycled stacks and measurement of electrode thickness with a mechanical micrometer indicate the cathode thickness does not change appreciably between its fully charged and discharged states, i.e. $< 5 \mu\text{m}$ Figure 5 shows the variation in voltage and thickness for cycling of an electrode stack comprised of lithium anode, microporous separator and Li_xMnO_2 cathode Clearly, the large changes in electrode stack thickness for each cycle and the electrode stack growth with cycling can be associated with the lithium anode The observed thickness changes are smaller than those calculated for uniform stripping of the lithium and may indicate non-uniform stripping Figure 6 shows the variation in electrode stack thickness due to lithium for cycling at low (16 psi) and high (200 psi) electrode pressures The large

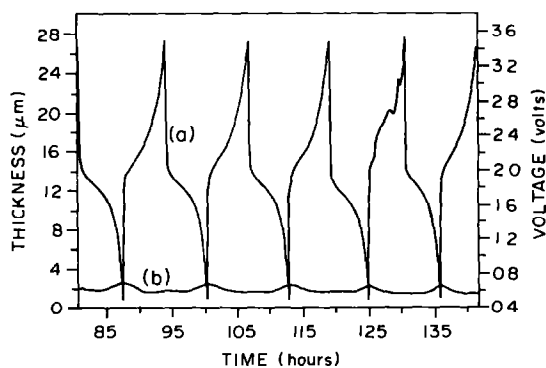


Fig 4 Thickness and voltage (2.0 V offset) of a Li_yMnO_2 (anode)/ Li_xMnO_2 (cathode) flat plate cell containing 1 M LiAsF_6 , 85 vol % PC 15 vol % EC Cell cycled at 130 psi stack pressure, 0.30 mA/cm^2 , 0.5–3.5 V and 21°C (a) Voltage, (b) thickness, initial thickness is arbitrary

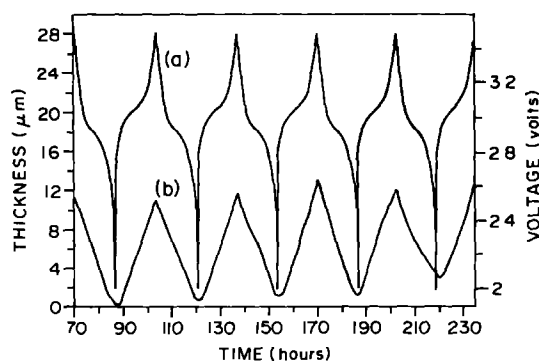


Fig 5 Thickness and voltage of a $\text{Li}/\text{Li}_x\text{MoO}_2$ flat plate cell containing 1 M LiAsF_6 , 85 vol % PC 15 vol % EC Cell cycled at 200 psi stack pressure, 0.30 mA/cm^2 , 2.0–3.5 V and 21°C (a) Voltage, (b) thickness, initial thickness is arbitrary

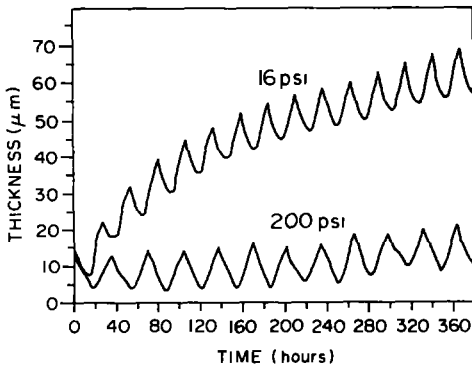


Fig 6 Thickness of $\text{Li}/\text{Li}_x\text{MnO}_2$ flat plate cells containing 1 M LiAsF_6 , 85 vol % PC 15 vol % EC cycled under two different electrode stack pressures. Initial thickness is arbitrary. Cells were cycled at $0.30 \text{ mA}/\text{cm}^2$, 2.0–3.5 V and 21°C .

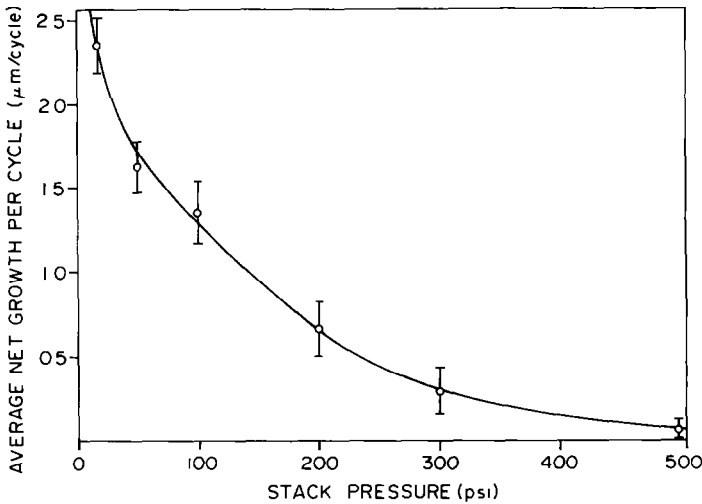


Fig 7 Plot of average net growth per cycle of $\text{Li}/\text{Li}_x\text{MnO}_2$ flat plate cells containing 1 M LiAsF_6 , 85 vol % PC 15 vol % EC cycled at different electrode stack pressures. Growth results were normalized to $3.53 \times 10^{-3} \text{ A h}/\text{cm}^2/\text{cycle}$. Cells were cycled at $0.30 \text{ mA}/\text{cm}^2$, 2.0–3.5 V and 21°C .

growth in the low pressure cell and the low growth in the high pressure cell are due to the porous and dense lithium deposits, respectively, which have been observed in the scanning electron micrographs. The average net growth per cycle (> 10 cycles) has been determined as a function of electrode pressure up to 500 psi as shown in Fig 7. It appears that there is significant net growth per cycle even above the critical pressure range of 60 to 80 psi up to about 500 psi. Using the force-displacement instrumented apparatus, it was found that in addition to pressure other factors such as cycling rates and electrolyte type also control the lithium growth during cycling [8].

The porous lithium deposits formed on cycling at low electrode pressures (< 60 psi) penetrate the $25\ \mu\text{m}$ thick separator after only a few cycles and provide an alternative path (or shunt) for the charging current. This can be seen in Fig 8 where a significant charge imbalance (excess charge) occurs after only eight cycles in the low pressure cell. The charge imbalance will often get worse with cycling until eventually all the current is being carried by the shunt with no lithium replating occurring as a parallel process. No charge imbalance occurs in higher pressure cells (100–300 psi) where dense lithium deposits are formed and there is much lower net growth of the lithium during cycling. Initial cycling at very high electrode pressures usually leads to a shunt occurring on the first recharge as is shown in Fig 9 for a cell with 500 psi electrode pressure. It is clear from this Figure that once the shunt develops there is no further electrode growth because all the current is being carried by the shunt. However, if the lithium is cycled at lower pressures initially (100–200 psi) before very high pressure is applied, no shunting occurs. These effects at very high electrode pressures where there is no apparent damage to the microporous separator are not well understood.

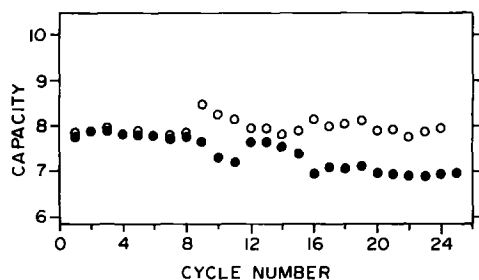


Fig 8 Plot of capacity vs cycle number for a $\text{Li}/\text{Li}_x\text{MnO}_2$ flat plate cell containing 1 M LiAsF_6 , 85 vol % PC 15 vol % EC cycled at 16 psi stack pressure, $0.30\ \text{mA}/\text{cm}^2$, 2.0–3.5 V and $21\ ^\circ\text{C}$. Plot shows data for both charge (\circ) and discharge (\bullet).

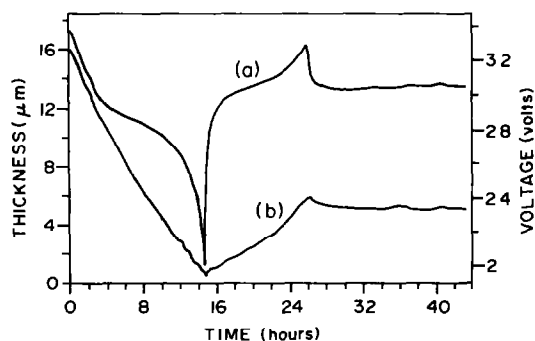


Fig 9 Thickness and voltage of a $\text{Li}/\text{Li}_x\text{MnO}_2$ flat plate cell containing 1 M LiAsF_6 , 85 vol % PC 15 vol % EC undergoing first charge/discharge cycle at 500 psi stack pressure. Cell cycled at $0.30\ \text{mA}/\text{cm}^2$, 2.0–3.5 V and $21\ ^\circ\text{C}$. (a) Voltage, (b) thickness, initial thickness is arbitrary.

With the exception of small diameter coin cells it is not practical to design commercial cells with constant mechanical pressure applied to the lithium anode. Instead, constant volume designs are used for commercial products such as that shown in Fig 10 for the MOLICEL[®] (registered trademark of Moli Energy Limited). Lithium growth during cycling will eventually build up electrode pressure to an optimum level (> 80 psi) in a constant volume cell. However, any initial porous lithium plating at low electrode pressure can adversely affect subsequent lithium cyclability and result in shunting even though optimal electrode pressures are eventually obtained. For a loose fitting electrode assembly, stack pressure can only begin to build up once the gap is filled. We have found that one to two cycles is enough for lithium growth to fill the annular gap (typically 200 μm) of a loose fitting spirally wound electrode assembly in a AA size cell. Electrode stack growth is high because both sides of the lithium are cycled and there are a large number of lithium cuts in a cell cross section. Once the gap is filled, the build up of electrode stack pressure is dependent on the lithium growth at different pressures, the compressibility of the cell components at different pressures and the number of cycles. The compressibility of the cell components at different pressures determined using the force-displacement instrumented apparatus and the calculated compressibility of different cell stack units based on these results are shown in Fig 11. These compressibility results and the lithium growth results of Fig 7 were used to determine the build up of electrode stack pressure with cycle number (one lithium turnover represents about seven cycles) for different cell stack

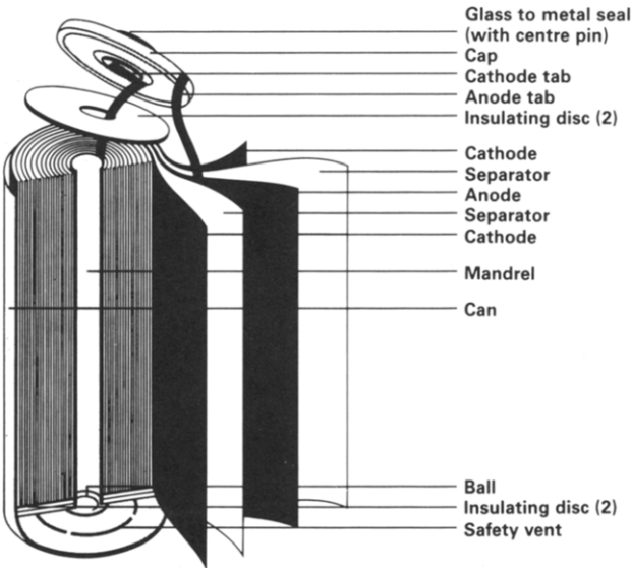


Fig 10 MOLICEL[®] cell construction showing cathode/separator/anode/separator/cathode repeating unit and outside termination area

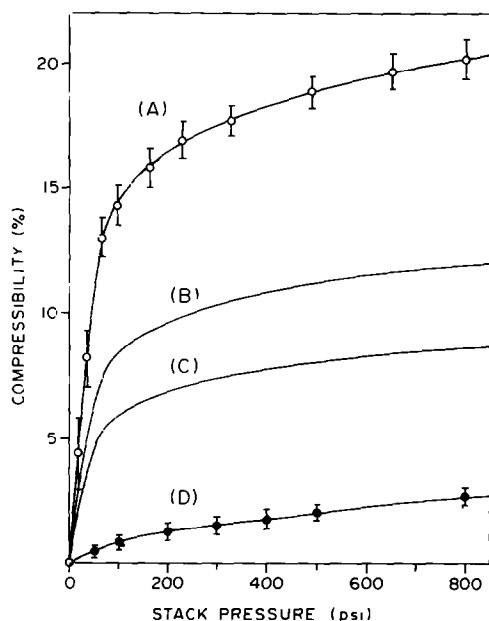


Fig 11 Plots of compressibility of different cell components and different cell stack units at different electrode stack pressures The compressibility of Li is less than 0.05% at 800 psi [7] (A) Li_xMnO_2 , (B) cell stack unit [CSLiSC] or SLiS(2C), (C) cell stack unit [SLiSC], and (D) Celgard 2500 separator S=separator, C=cathode

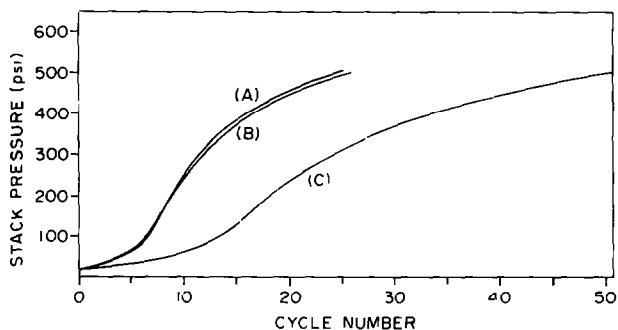


Fig 12 Plots of calculated electrode stack pressure generated during cycling of different cell stack units Growth results of Fig 7 and compressibility plots of Fig 11 were used in the calculations (A) [CSLiSC], (B) [SLiSC], (C) [SLiS(2C)] S=separator, C=cathode

units Lithium cycling was normalized to 3.53×10^{-3} A h/cm²/cycle for each Li/separator (S)/cathode (C, 2C) interface The electrode stack pressure growth results are shown in Fig 12 for an initial stack pressure of 16 psi and indicate that at least six cycles are required to achieve an optimum electrode pressure level (> 80 psi) There is little difference in the build up of electrode stack pressure for the cell stack units of [CSLiSC] and [SLiSC], but there is a large difference if the thickness of the cathode, e.g. [SLiS(2C)],

or compressibility of the cathode (not shown) is changed. Minimum compressibility and thickness of the compressible cell components, especially the cathode, are required to get the quickest build up of electrode stack pressure. Continuous build up of electrode stack pressure may eventually lead to cell failure from crushing of the separator. Electrode stack pressures much greater than 1000 psi have been observed at the core of spirally wound AA size cells with corresponding separator damage after long term cycling [9].

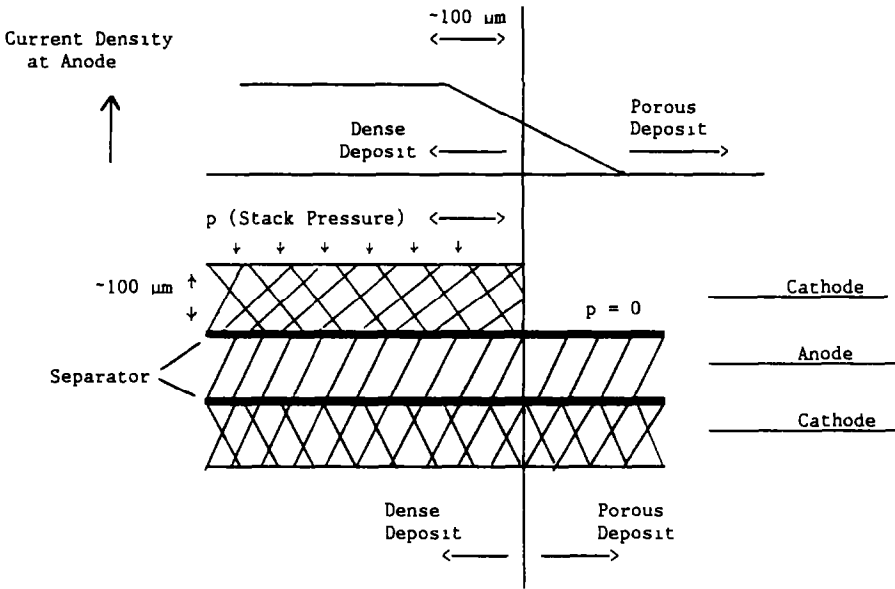


Fig 13 Model of electrode stack pressure and current density at a pressure discontinuity

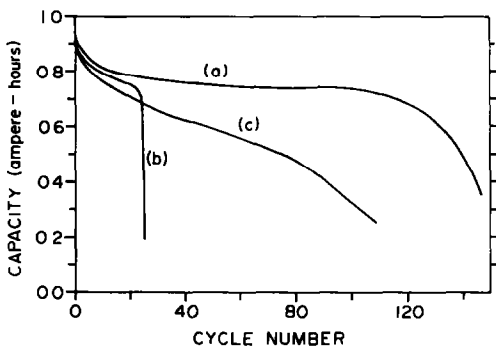


Fig 14 The effects of loose and tight fitting jelly rolls on the cycle life of AA size $\text{Li/Li}_x\text{MoS}_2$ cells containing 1 M LiCF_3SO_3 , 50 vol % PC, 50 vol % EC. Cells were cycled at 0.50 mA/cm² for discharge and 0.25 mA/cm² for charge, 2.4-1.1 V and 21 °C. (a) Tight, (b) loose, (c) loose with anode current collector.

In a practical cell, consisting of spirally wound electrode foils, the initial electrode pressure can be controlled to a certain extent by regulating the foil tensions and adjusting the fit of the electrode assembly in the cell can. Even when optimal electrode pressure is applied, lithium anode failure can occur prematurely at a pressure discontinuity such as that found in the termination region of some cells. A model of electrode stack pressure and current density at a pressure discontinuity is shown in Fig. 13. Lithium plating morphology changes from a dense deposit in the region of standard electrode stack pressure to a porous deposit in the region of low electrode stack pressure. Cell failure is due to separation of the lithium at the boundary of these two regions. Cycle life plots for spirally wound AA size Li/MoS_2 cells with different jelly roll fits are shown in Fig. 14. The very precipitous fade after only 25 cycles for the loose fit cell is a result of lithium separation in the anode tab region where there is a pressure discontinuity. The loose fit cell with anode current collector has much greater capacity fade and hence lower cycle life than the tight fit cell. The current collector prevents cell failure due to lithium separation. These results show the importance of electrode assembly fit in determining electrode stack pressure and hence the quality of plated lithium.

References

- 1 E. Peled, *J. Electrochem. Soc.*, **124** (1979) 2047
- 2 E. Peled, in J.P. Gabano (ed.), *Lithium Batteries*, Academic Press, New York, 1983, pp. 43-72
- 3 J. A. R. Stiles and K. Brandt, *Can. Patent 1 190 279* (July 1985)
- 4 B. M. L. Rao, R. W. Francis and M. A. Christopher, *J. Electrochem. Soc.*, **125** (1977) 1490
- 5 R. Haering, J. A. R. Stiles and K. Brandt, *US Patent 4 245 017* (Jan. 13, 1981)
- 6 J. R. Dahn and B. M. Way, *US Patent 4 959 282* (Sept. 25, 1990)
- 7 Foote Mineral Company, Lithium Metal, *Tech. Data Bulletin 101*
- 8 D. P. Wilkinson, D. S. Wainwright, A. Rivers-Bowerman, W. Chow and H. Blom, *In situ* study of electrode stack growth in secondary lithium cells, paper in preparation
- 9 D. Wainwright and R. Shimizu, *J. Power Sources*, **34** (1991) 31-38