

Forces generated by anode growth in cylindrical Li/MoS₂ cells

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Abstract

An experimental technique has been developed that provides semi-quantitative measurements of stack pressure at the core and case of cylindrical, lithium rechargeable cells. The effect of electrode expansion during phase change, and anode growth on stack pressure, can be observed. Oscillations in pressure are seen as a result of changes in the net thickness of the electrode stack during cycling. Stack pressures in the range of 500 psi are typical for cells of this type. These pressures clearly put restrictions on containment hardware and on the separators that can be used in such cells.

Introduction

A lithium metal anode can be cycled with efficiencies greater than 95% in a variety of electrolyte/cathode combinations if sufficient mechanical pressure (stack pressure) is applied normal to the anode surface [1-4]. Special laboratory cells can be constructed that provide this mechanical pressure by applying constant load over an entire flat electrode cell assembly [3, 4]. It is not practical, however, to use a constant load concept for commercial cells when the required loads are in excess of 50 psi, except for very small diameter coin cells. Instead, constant volume designs are used for commercial products such as the MOLICEL[®] [5]. A thin-wall cylindrical container is the preferred design to contain large pressures with minimal weight of hardware. The pressures required for efficient cycling of the anode can be achieved by expansion of the cathode material (such as occurs during phase transitions of some intercalation compounds) or by growth of the anode itself [3, 4].

It is useful to know how the mechanical pressure varies in such a design as a function of radius and with use. For this study, measurements of stack pressure were made at the centre (core) and container (case) of such cells. It was found that stack pressures in excess of 1000 psi could be generated prior to cell failure, and a gradient in pressure exists over the radius.

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Experimental

MOLICEL[®]-style cells were used as test vehicles. Typical construction of these cells is shown in Fig 1. There are two cathode foils consisting of powdered intercalation compound bound to aluminum foil substrates. Also used are two separator foils made from microporous polyolefin film (Celgard 2500, for example) and one anode foil which is pure lithium metal. A metal tube is used as a mandrel on which the foils are spirally wound, creating a 'jelly roll' cell. The jelly roll, in turn, is placed in a Ni-plated, mild steel can (typically 0.010 in thick wall), and a cap, containing a positive electrode feedthrough, is welded on to seal the cell top. Electrical connections are made from the negative cell case and positive feedthrough to the jelly roll via thin tabs. An organic electrolyte (typically 1 M LiAsF₆/50% PC/50% EC) is injected through a fill hole in the can. A ball bearing welded into the fill hole seals the cell and completes the assembly.

A method of measurement was developed to determine stack pressure at the core and case of these cells without significantly altering this construction. The mandrel and can both experience stress due to the jelly roll pressure. The resulting strain on this hardware could be measured using strain gauge devices. The experiment was set up as shown in Fig 2. To make case pressure measurements, strain gauges (typically Measurements Group Inc ,

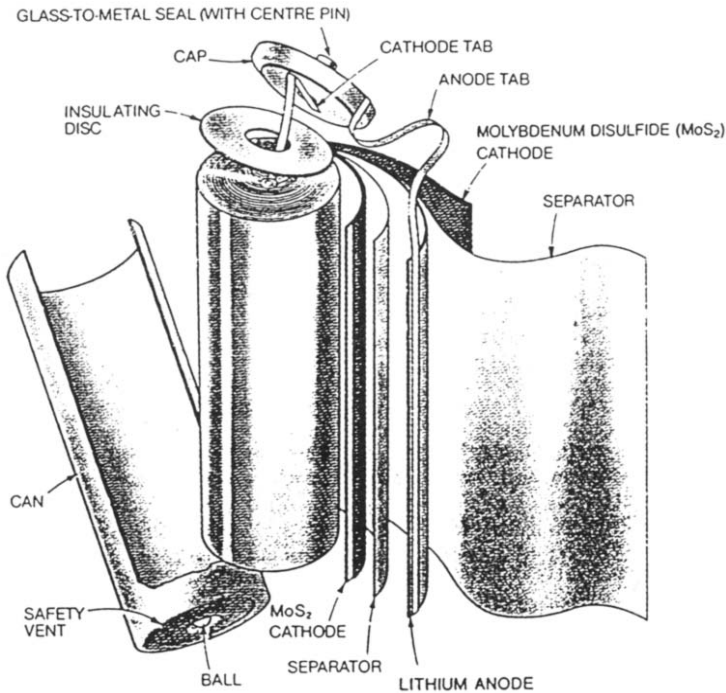


Fig 1 MOLICEL[®] construction

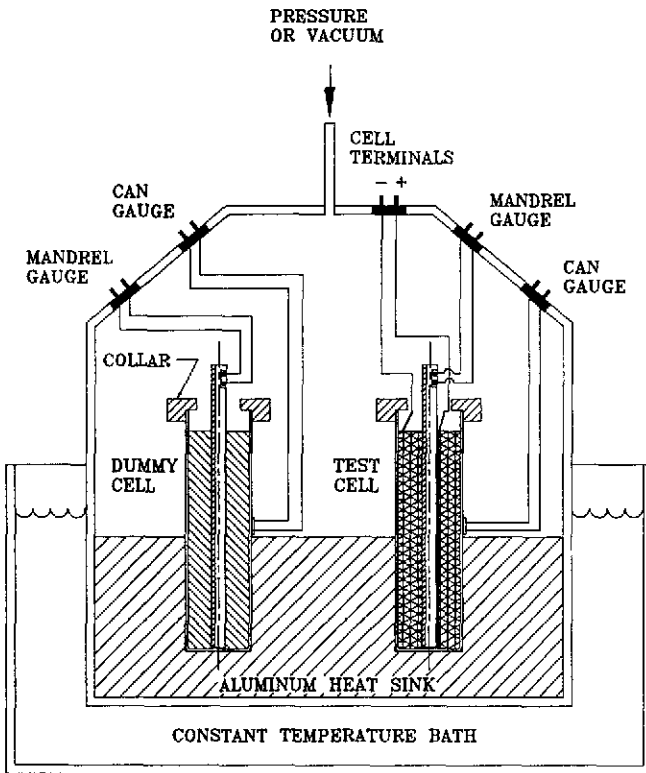


Fig 2 Experimental set-up for AA cell

model CEA-06-125UN-350) are mounted at the midpoint of empty cell cans. In order to increase sensitivity, core measurements are made using special, slit, thin-wall mandrels (typically 0.030 in. thick wall, stainless steel). A strain gauge (typically Measurements Group Inc., model CEA-09-032UW-120) is mounted above the jelly roll on this special long mandrel. Winding of the foils is accomplished by attaching them to a small mandrel inside the gauge mandrel. The winding mandrel is removed later. Care had to be taken so as not to trap material in the slit of the gauge mandrel as this would interfere with the measurements. These cells cannot be sealed in the usual way. Instead, after wetting, a collar is put over the top edge of the can to simulate the presence of a welded cap. A dummy cell complete with strain gauges is also constructed. The two cells are placed in a larger, multi-feedthrough chamber filled with inert gas. The cells sit in an aluminum heat sink inside, and the chamber is placed in a constant temperature bath ($\pm 1^\circ\text{C}$). Two bridge circuits are constructed, each having a test and corresponding dummy strain gauge as part of the legs of the bridge. (The dummy leg in the circuit was used as insurance to compensate for apparent strain changes in the test leg arising from environmental factors.) The amplified strain gauge readings and cell voltage are logged on computer.

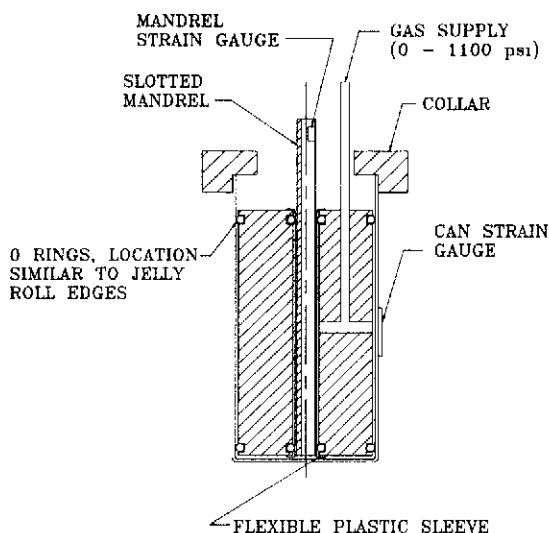


Fig 3 Calibration bladder for C cell

Calibrating the hardware was accomplished using a special gas bladder, as shown in Fig 3. Hardware was calibrated over a pressure range of 0–1100 psi and proved to be elastic (reversible), producing a linear strain gauge response. A test cell was then made using this hardware. After testing, the hardware could be recovered in many situations and rechecked to ensure that no changes occurred. It should be noted that the response of the mandrel strain gauge is fairly sensitive to its height above the jelly roll (e.g., the slope of the response curve might vary by a factor of 2 with a height variation of 0.1 in). The foils in the jelly roll may be misaligned by as much as 0.050 in. at worst. Thus errors of the order of 50% at the core might be expected. Case measurements are not as sensitive to vertical positioning of the calibration bladder and are therefore more reproducible. Multiple calibration attempts suggest an error of the order of 5% of the case reading can be expected. We are assuming, of course, that a constant pressure calibrating bladder adequately simulates the stack pressure generated by a jelly roll. This is not true at early cycle numbers, for example. Jelly rolls are not perfectly round and do not apply uniform pressure over the can wall until significant jelly-roll growth occurs. This can take quite a few cycles. Nonetheless, this method appears acceptable for semi-quantitative measurements.

Results and discussion

'C'-sized cells with MoS_2 -type cathode and 1 M LiAsF_6 /50% PC/50% EC electrolyte (A06 MOLICEL[®] chemistry) were instrumented and cycle tested. The core stack pressure measurement during the electrochemical conversion

process of $\alpha\text{-MoS}_2$ to $\beta\text{-LiMoS}_2$ is shown in Fig 4. The volume of lithium stripped during discharge is greater than the corresponding increase in volume of the lithiated cathode material [3, 6]. Thus there is a net loss of active electrode volume during conversion. However, a net increase in thickness of the electrode stack occurs as a result of generation of solid decomposition products and/or exfoliation of the cathode grains. Lithium carbonate is known to form during this conversion, but it, alone, cannot account for the increase in cathode thickness. Other solid decomposition products may also form. The relative effects of Li_2CO_3 , other solid decomposition products, and exfoliation have not been quantified. In the constant volume cell, this results in a stack pressure increase of about 200 psi at the cell core. (Heat detrimental to electrolyte stability at this voltage is generated during conversion. Therefore conversions are performed at -10°C . This heat may have had a small effect on the test strain gauge, as compensation is not applied.) The first subsequent charge/discharge cycle is shown at 25°C . As expected now, the net electrode volume increases on charge and decreases on discharge since the lithium occupies more volume as plated lithium metal than it does in intercalated MoS_2 [6]. (NB, case readings are not shown here. At early cycle numbers, the uneven stack pressure reading at the case is unreliable. However, measurements with two case-strain-gauges mounted 90° apart, have indicated that similar values of case pressure are obtained, independent of gauge location, after the cell has been cycled sufficiently.)

The stack pressures during cycling of an 'AA' cell with similar chemistry are illustrated in Fig. 5. Cycles 10–20 at $C/5$ rate are shown. The pressure oscillation as the cell cycles is clearly seen at both measurement locations

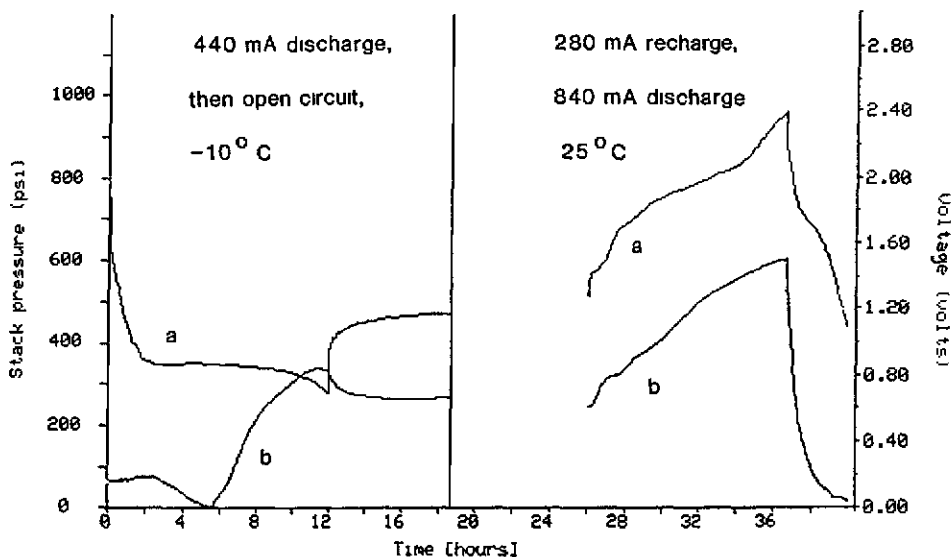


Fig 4 Core stack pressure and cell voltage during conversion of Li/MoS_2 'C' cell a, voltage, b, pressure

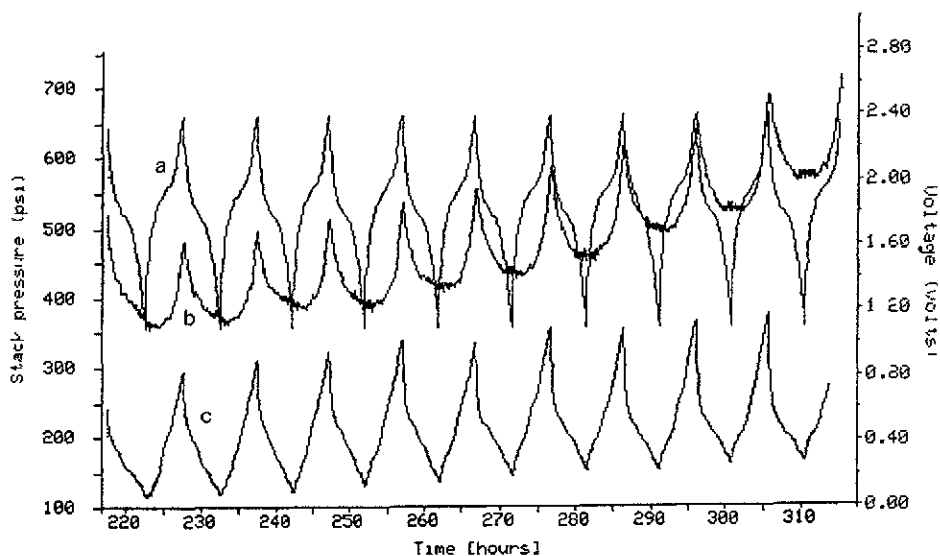


Fig 5 Stack pressure and cell voltage during cycling of Li/MoS_2 'AA' cell (C/5 rate or 120 mA at 21 °C) a, voltage, b, core pressure, c, case pressure

The stack pressure slowly increases with each cycle. Inefficient lithium plating is the mechanism behind this and takes place in other lithium-metal-based electrochemical systems [3, 4]. Even at high stack pressures, after each stripping and plating sequence, the anode is slightly thicker than before. Thus a corresponding slight increase in stack pressure is seen after every cycle. Note that the core and case pressures are not the same. A pressure gradient exists as a function of radius, maintained by frictional forces between the foils. The stack pressure already seems large at cycle 20, ranging up to 700 psi at the core and 300 psi at the case. However, the cell is still quite functional. The history of the discharge capacity with cycle number of this particular cell is shown in Fig 6. Much longer cycle life can be expected if recommended charge/discharge rates are used.

At later cycle numbers, the calibration limit of the mandrel gauges used is exceeded. Typically, the case pressure continues to rise with cycle number until pressures between 500 and 1000 psi are seen. At this point, cell failure usually occurs arising from crushing of the separator.

The pressure readings seen can be confirmed to some extent by subsequent analysis of the disassembled test cells. If cells are cycled sufficiently, the test mandrel is irreversibly deformed, confirming that pressures in excess of 1100 psi existed at the core. Also, the polyolefin separator can be used as a pressure gauge itself. The separator is the weakest cell component and it is the component that gives under load.

The separator is salvaged from the test cell and rinsed clean of cell debris in a warm bath of naphthalene and tetrahydrofuran. The physical characteristics such as thickness and permeability can then be determined.

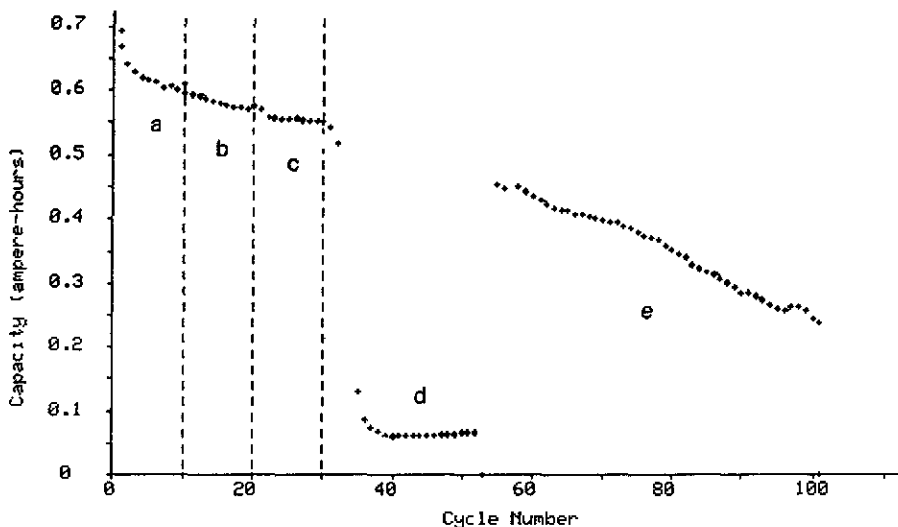


Fig 6 Capacity vs cycle number for cell shown in Fig 5 Tests at 21 °C and voltage limits of 1.1–2.4 V up to cycle 30 and 1.1–2.1 V thereafter Currents are discharge/recharge mA a, 120/60, b, 120/120, c, 180/120, d, 600/600, e, 180/120

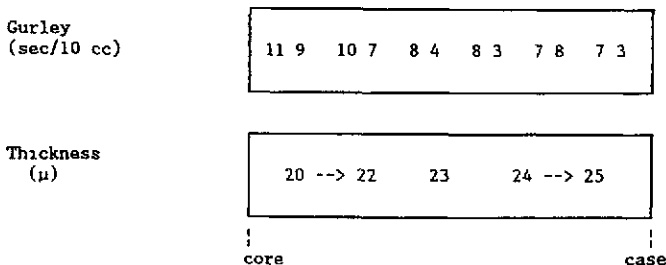


Fig 7 Resistance to air flow and thickness of Celgard 2500 taken from an A06 MOLICEL® cycled 221 times at 21 °C

again The sample readings shown in Fig 7 are from a typical well-cycled cell. The separator film used here was Celgard 2500 which is originally 25 μ m thick and has a resistance to air flow of about 7 s for 10 cm^3 (using a model 4120 Gurley densometer) Celgard 2500 is, however, a very incompressible film. Compressibility measurements on Celgard 2500 are shown in Fig. 8. Data shown are for thickness changes seen when the indicated load has been applied for several hours. A 1000 psi load effects a change of only 1 μ m in thickness over this time period. (Long term creep data are not yet available.) The separator from the test cell had been crushed up to 5 μ m at the core, suggesting pressures in excess of 1000 psi. The stack pressure gradient is clearly confirmed by the thickness and Gurley gradient seen in the test separator.

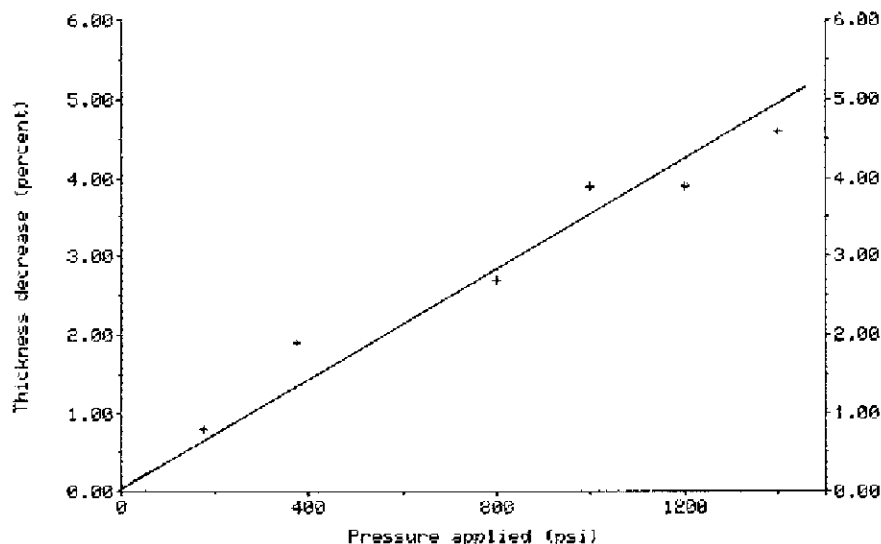


Fig. 8. Compression of Celgard 2500.

Acknowledgements

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