

PRECISION CYCLING AND COULOMBIC EFFICIENCY MEASUREMENTS ON Li/MoS₂ AND Li,Al/FeS CELLS

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Summary

The use of a high precision cell and battery cycler to enhance the information obtained from constant current cycling is described. Using prototype Li/MoS₂ cells provided by Moli Energy Limited, it is shown that coulombic efficiencies measured to $\pm 0.03\%$ can be used to predict the cell's cycle life. Other measurements were used to test a percolation theory of the cell's capacity fade. Measurements of voltage relaxations during current interrupts of Li,Al/FeS cells produced by Electrofuel Inc. are described briefly.

Introduction

A cell and battery cycler capable of precise voltage measurements and parameter control has been developed, and is being used for charge/discharge cycling of Li secondary cells at the pilot-plant level of development. Selected voltammetry procedures, which are applicable to cells and batteries without significantly perturbing the on-going constant current cycling, are used to monitor variations in the cell chemistry during cycling. The measurements used are coulombic efficiencies precise to $\pm 0.03\%$, capacity/voltage derivative plots, and voltage relaxation during current interrupts. These techniques are useful adjuncts to the usual, lower accuracy cycling used to determine cell capacity fade, lifetimes, etc., and permit more rapid evaluation of prototype cell modifications designed to improve cell performance. The cycler and procedures are briefly described. Results are presented of an extensive test program on Moli Energy AA-sized 0.65 A h Li/MoS₂ secondary cells, and of preliminary work on approx. 100 A h Li,Al/FeS high temperature cells from Electrofuel Inc.

Experimental

The multi-station cycler uses a single CPU and is based upon commercially available data acquisition and system control hardware coupled to

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commercial, highly regulated d.c. power supplies for cell charging. Cells are discharged into an air-cooled resistive load with the power supply in series for current regulation. Since the power supply and the resistive load on a particular station can be sized as needed, cells of markedly different energies and power levels can be cycled simultaneously. The switching networks capable of 100 A d.c., the system control and data acquisition software, and the analysis software were developed in the laboratory. The frequent cell monitoring needed for the high precision measurements, limits the number of cycler stations to 6.

The high precision characteristics of this cycler are achieved using:

(i) 5 1/2 and 6 1/2 digit voltmeters, allowing routine measurements at 100 μV resolution and at 1 μV resolution, as needed;

(ii) current programmable power sources exhibiting 0.1% current stability or better for currents of 1 mA - 300 A;

(iii) an HP3497 scanner unit as the core of the data acquisition and control system, with IEEE 488 bussing to an HP series 200 computer. This ensures that relay contact noise is immeasurable, that data precision is not lost due to bit capacity limitations of the data bus, and that acquisition times are measured in real time within 20 ms;

(iv) time integration of cell current measurements (made during every cell monitor sequence and normally set at 15 s) to obtain cell capacities;

(v) cell temperature control of ± 0.05 $^{\circ}\text{C}$ between -20 $^{\circ}\text{C}$ and 100 $^{\circ}\text{C}$ and of ± 0.5 $^{\circ}\text{C}$ at higher temperatures.

Results and discussion

(1) Precision coulombic efficiencies

Moli Energy Limited is developing an AA-size secondary cell based upon the intercalation reaction of Li with MoS_2 . During routine, low precision, constant current cycling, pilot plant cells appeared to exhibit a coulombic efficiency (CE) exceeding 100%, the effect just being detectable in the noise ($\pm 0.5\%$) of the efficiency measurements made using a standard cycler. The precision of CE measurement using the cycler described here is limited by the cell monitoring interval of 15 s. For a discharge current of 120 mA this is equivalent to ± 0.25 mA h or $\pm 0.04\%$ in CE for the relevant cell capacities. The interval can be reduced if higher precision is needed. Unless otherwise indicated, the CEs reported below exhibit a standard error of $\pm 0.03\%$. Representative CE measurements made using the precision cycler are given in Table 1. Since the cells exhibit a small, continuous capacity fade during cycling, CEs are calculated from the ratio of the discharge capacity to the average of the preceding and following charge capacities (*i.e.*, in Table 1, for cycle 14, $\text{CE} = 2 \times 684.53 / (683.02 + 681.35)$). The effect is clear for cells cycled over 1.1 - 2.4 V (the normal operation range), the CEs being as high as 100.70% initially, and diminishing by about cycle 35 or 40 to 100.20%, where they remain for the rest of the cell's lifetime of 180 - 200 cycles.

TABLE 1

Representative precision coulombic efficiencies (CE) for Li/MoS₂ AA pilot plant cells at 25.0 °C, 60 mA charge, 120 mA discharge, 1.1 - 2.4 V limits
A numbered cycle is a charge and the subsequent discharge.

Cycle no.	Charge cap. (mA h)	Disch. cap. (mA h)	CE (%)	Cycle no.	Charge cap. (mA h)	Disch. cap. (mA h)	CE (%)
12	687.64	688.55	100.31	106	640.35	641.47	100.18
13	685.16	686.25	100.32	107	640.25	641.30	100.20
14	683.02	684.53	100.34	108	639.82	641.35	100.24
15	681.35	682.14	100.26	109	639.80	640.87	100.19
16	679.34	680.73	100.32	110	639.54	640.93	100.22
17	677.84	—	—	111	639.56	—	—

The details of cell life prediction, using these results in conjunction with percolation theory to model the ionic conductivity of the cell electrolyte, have been given by Dahn *et al.* [1]. Briefly, when the cathode potential is sufficiently close to that of metallic lithium, some of the electrolyte (LiAsF₆ dissolved in a mixture of ethylene carbonate and propylene carbonate) is reduced by lithium at the cathode. The subsequent solvent depletion, and the filling of electrode pores by the non-conducting reaction products (mostly Li₂CO₃, ethylene and propylene), reduce the effective ionic conductivity and ultimately lead to cell failure. Since this removal of lithium at the cathode interphase reduces, or effectively reduces, the amount of lithium intercalated in the cathode, it is equivalent to a partial recharging of the cell and thus gives an apparent CE above 100%. The excess discharge capacity is referred to as the primary capacity. Percolation theory qualitatively models the cell failure characteristics. For this cell chemistry, when the accumulated primary capacity reaches approximately 80% of the capacity of the secondary cell process, the effective conductivity rapidly collapses and the cell fails.

Measurements were also made of this excess CE effect as a function of charging current, cell temperature, and cycle voltage limits in order to test predictions of the theory outlined above. The CE was shown to be 100.56, 100.37, 100.22, 100.18 for discharge currents of 30, 60, 90, and 120 mA, respectively. This increase in the primary capacity with decreasing current is predicted by the theory, since residence time per cycle below the threshold cell voltage for the side reaction will increase with decreasing current.

The threshold voltage for this reaction with the electrolyte can be determined by measuring the excess CE effect as a function of the cycle voltage limits. The results of two series of such tests are shown in Fig. 1. Neglecting the brief excursions in the CE which occur immediately following each change in the voltage limits, the CE shows a well-defined trend with the lower voltage limit. No significant excess CE is observed if the cell is not cycled below 1.5 V, and the major onset voltage for the primary process is

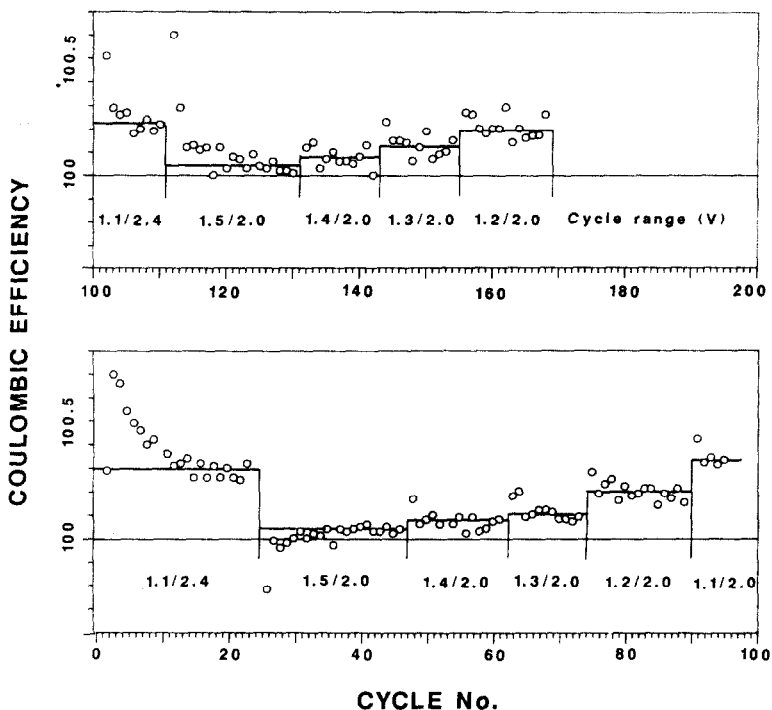


Fig. 1. Precision coulombic efficiencies (CE) for Li/MoS₂ AA prototype cells at 25.0 °C, 60 mA charge, 120 mA discharge, at various voltage limits and cycle histories. The lines indicate the mean values for each voltage cycling range.

about 1.3 V. This is consistent with the observation that a MoliCelTM cycled in the range 1.5 - 2.0 V exhibits a cycle life in excess of 1000 cycles.

The temperature dependence of the excess CE effect was also determined and showed CEs of 100.21, 100.20, 100.05, and 100.00 ± 0.06 at 55, 25, 0 and -10 °C, respectively, for cells having a history of >30 cycles. Cycling was at 60 mA charge, 120 mA discharge over 1.1 - 2.4 V, except at 55 °C where 1.1 - 2.0 V limits were used to avoid possible dendriting effects. On the basis of reaction kinetics considerations, temperature dependence of the rate of the side-reaction should yield an excess CE which increases with temperature. However, thermodynamic effects, which should cause the onset voltage for the side-reaction to be temperature dependent, will complicate the temperature variation of CE. The lack of an increase in excess CE between 25 °C and 55 °C is not wholly consistent with these concepts, although the decrease in excess CE below 25 °C is as expected from the kinetic effect alone. One should note the increase in the noise in the excess CE values at -10 °C, which presumably indicates much slower kinetics of all cell processes under these conditions. Clearly, the variation in this effect with temperature is more complex than these simple ideas would predict. The unexpected observation that the excess CE drops to near zero (within

the standard errors) at 0 °C or lower, implies an extended cycle life at this temperature. This possibility has not been fully tested.

In work not reported here in detail, this precision cycling has been used to facilitate rapid evaluation of alternative electrolyte compositions designed to eliminate this excess CE effect and, hence, to extend the cell's cycle life. In principle, this technique should be useful in studying any secondary cell for which a side-reaction occurring at the cathode is the primary mechanism of cell fade or failure.

(ii) *First derivative ($\delta C/\delta V$) curves*

The voltammetry technique of plotting $\delta x/\delta V$ versus V curves, where x is the cathode Li content or equivalent, allows one to quantify and characterize plateaux in cell voltage (V) versus x and correlate them to the cell chemistry, as determined by other procedures [2, 3]. The high precision data stored by this cyler allows the plotting of low noise, first derivative curves for these commercial prototype or pilot plant cells, as illustrated in Fig. 2. In this case the two distinct Li intercalation reactions with the MoS_2 and MoO_2 in the cathode can be easily identified by comparison with the results from laboratory button cells having single phase cathodes [2, 3]. This Figure illustrates the rapid changes in shape of the charge voltage curves which occur during the early cycles of these Li/MoS_2 , MoO_2 cells and which are attributed to particle morphology changes generated by crystal damage during the intercalation process. Corresponding changes occur in the discharge curves.

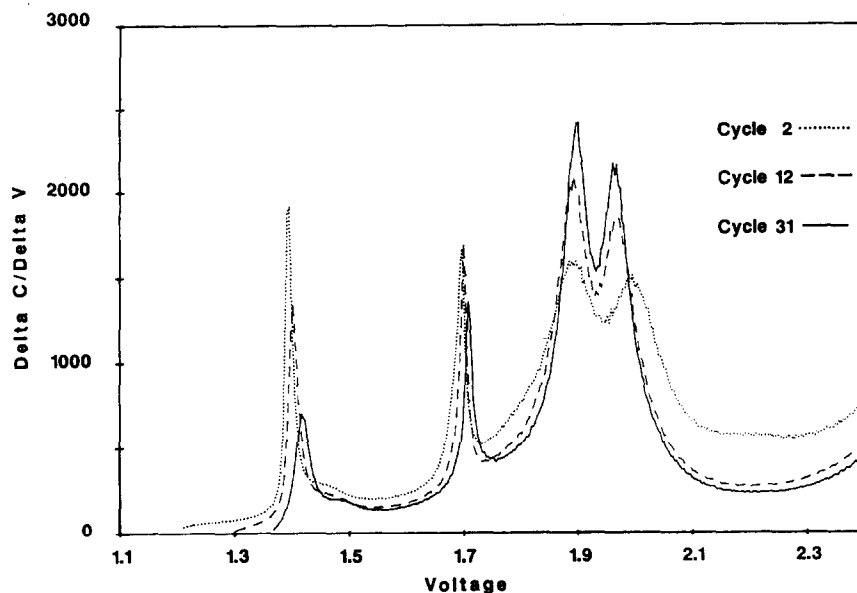


Fig. 2. $\delta C/\delta V$ vs. V plots for charging an Li/MoS_2 , MoO_2 MoliCelTM. These early cycles illustrate massive morphology changes which occur initially in this type of cell. C is cell capacity in mA h.

Particularly at higher temperatures, these cells can fail by shorting via a lithium dendrite penetrating the separator. It has been observed that during cycles prior to such failure, the precision CEs drop to about 99.98% with a scatter three times the normal. In addition, the first derivatives have shown easily observable curve shape anomalies which indicated short-lived dendritic shorts occurring above 2.2 V in charge, which burn off by 2.1 V in discharge. These techniques thereby provide early warning of incipient cell failure due to dendritic shorting.

First derivative curves have also been used to examine variations in early cycle behaviour caused by continuation of the cathode conversion process [4] from $\alpha\text{-Li}_x\text{MoS}_2$ to $\beta\text{-Li}_x\text{MoS}_2$, and to quantify impedance effects as a function of the state of charge.

(iii) Other procedures

During normal cycler operation any one station can be configured for planned current interruption. The voltage relaxation curves are measured using a 6 1/2 digit voltmeter, capable of resolving 10 μV in 3 V at a rate of 35 readings s^{-1} . Current interruptions of 120 s yield interpretable data without significantly disrupting the normal cycling. Currently, this technique is used to distinguish between purely resistive changes and variations in polarization effects as a function of construction parameters, cycle history, and state of charge. This technique has been used most extensively on the Li,Al/FeS pilot-plant cells produced by Electrofuel Inc. and operated at 10 A charge, 15 A discharge and 450 - 475 °C. For both these cells and MolicelsTM, the voltage/time (t) relaxation curves are fitted to an exponential model rather than to a $t^{1/2}$ dependence which is commonly used and expected for simple diffusion limited processes. Using a Li/NiS₂ reference electrode, installed in the prototype cell by procedures similar to those in ref. 5, preliminary current interrupt measurements appear to indicate that the major polarization process in these Li,Al/FeS cells occurs at the Li/Al electrode.

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