

Projection of improved high rate discharge performance for homogenized cathode Li/I₂ (P2VP) batteries

C. C. STREINZ, J. SCALA, J. W. WAGNER

Corrosion and Electrochemistry Research Laboratory, Department of Materials Science and Engineering, The Johns Hopkins University, Baltimore, MA 21218, USA

P. J. MORAN

Department of Mechanical Engineering, United States Naval Academy, Annapolis, MA 21402, USA

Received 16 October 1990; revised 13 May 1991

It has been recently proposed that implementing a cathode with a homogeneous distribution of iodine and P2VP into Li/I₂ (P2VP) batteries would be a means of enhancing high rate discharge performance. A procedure for predicting high rate discharge performance gains for such cells is presented. The projected high rate discharge performance for cells with homogeneous cathodes is superior to the performance of conventional cells.

1. Introduction

Lithium iodine batteries power the vast majority of cardiac pacemakers [1]. The Li/I₂ (P2VP) battery consists of a lithium anode, a cathode mixture of iodine and polymeric poly(2-vinylpyridine) (P2VP) and a lithium iodide electrolyte layer that forms *in situ*. P2VP is added to the cathode to render the iodine conductive. For a detailed introduction to the fabrication and performance of this battery system, and implantable battery systems in general, the interested reader is referred elsewhere [2].

During discharge lithium ions diffuse through the LiI electrolyte to the cathode where they combine with reduced iodine to form additional LiI. It has been shown that for cells with pelletized cathodes LiI impedance dominates the total cell impedance for most of the discharge [3]. Initially the bulk cathode impedance is higher than the impedance of the thin LiI layer. As discharge progresses the thickness and therefore the impedance of the LiI layer increases. The impedance of the cathode decreases as its thickness and the concentration of iodine decrease until nearly end of life when it becomes depleted in iodine and the cathode impedance increases sharply. For the cells used in the present study, the cathode has a maximum conductivity at an I₂:P2VP weight ratio of 5.3:1 [4]. This occurs after approximately 90% of the discharge-capacity has been exhausted.

The poor high rate discharge behaviour of the Li/I₂ (P2VP) battery system is a well known phenomenon. For cells with pelletized cathodes, Kelly and Moran [5, 6] determined that the impedance of the LiI layer limits high rate discharge. They also demonstrated that the morphology and resistivity of the formed electrolyte are discharge rate dependent. Specifically, electrolyte layers formed at high rates are more resistive than those formed at low rates. It was

recently demonstrated that the conductivity of the formed electrolyte was dependent on the distribution of the incorporation of P2VP from the cathode into the LiI layer [7]. At low discharge rates (across constant 20 k Ω loads, approximately 40 μ A cm⁻²) P2VP was uniformly incorporated into the LiI (see Fig. 1a), resulting in an electrolyte resistivity of 1.3 \times 10⁵ Ω cm as compared to resistivity of approximately 10⁷ Ω cm for pure LiI [8, 9]. At high discharge rates (across constant 1 k Ω loads, approximately 300 μ A cm⁻²) chunks of unreacted cathode were trapped in the LiI (see Fig. 1b), resulting in a resistivity of 1.1 \times 10⁶ Ω cm. Furthermore, inhomogeneities in the cathode mixture resulted in nonuniform discharge at high discharge rates which caused chunks of unreacted cathode to become trapped into the LiI. As a result, it was proposed that implementing a homogeneous cathode would inhibit the incorporation of cathode chunks and improve the high rate discharge performance of the Li/I₂ (P2VP) battery system.

The objective of this study was to project high rate discharge performance for cells with theoretically homogeneous cathodes. Such cells would form electrolyte layers with a resistivity of approximately 10⁵ Ω cm, even when discharged at high rates, since discharge would presumably proceed uniformly across the reaction interface. This assumes that a successful cathode homogenization procedure could be developed. In order to project higher rate discharge performance, conventional cells were discharged at a low rate, where they formed LiI layers with a resistivity of 10⁵ Ω cm, and were periodically pulsed (less than five second duration) to high discharge rates. The closed circuit voltage recorded during the high rate spike was used to evaluate discharge performance at that rate. This procedure evaluated the polarization experienced during high rated discharge in the presence of a low resistivity electrolyte layer.

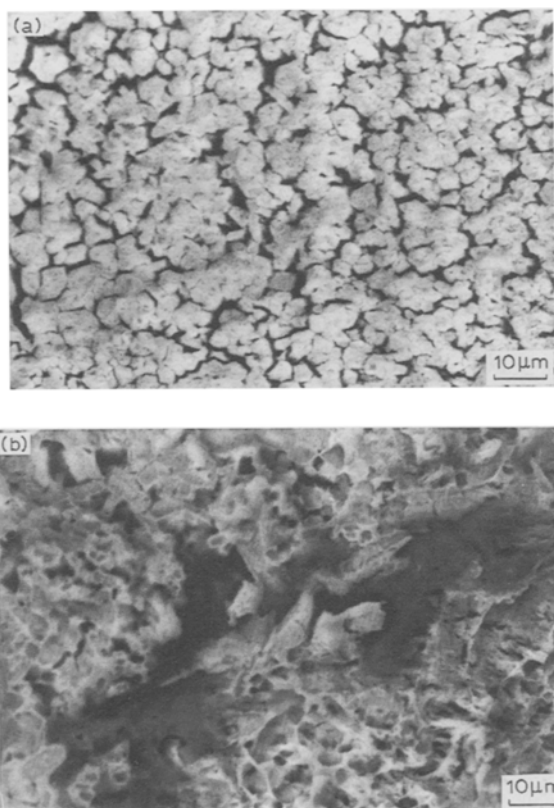


Fig. 1. Backscattered electron image of the LiI electrolyte layer for cells discharged across (a) a 20 kΩ load and (b) a 1 kΩ load. The dark areas in part (b) are chunks of unreacted cathode trapped in the LiI layer.

2. Experimental details

The cells used in this study were equivalent to the commercially available Catalyst Research S23-P15 button cell [10] except for a reduction in the nominal capacity from 120 to 74 mAh. The theoretical cell voltage is 2.8 V. The cathodes had an initial iodine : P2VP weight ratio of 19 : 1 and were pressed to a thickness of 330 μm. The average molecular weight of the P2VP polymers used in this study was 54 000 (with a polydispersity number of 1.8).

Ten cells were fully discharged across 20 kΩ loads. At 4–6 mAh intervals eight of these cells were subject to pulses of five second duration. Two cells each were pulsed across 5 kΩ, 2 kΩ, 1 kΩ and 500 Ω resistive loads. During each pulse the closed circuit voltage was recorded and plotted versus total discharged capacity to project discharge performance at that rate. Figure 2 is a schematic illustration of that procedure. The top line is the voltage/capacity behaviour of the cell discharged across 20 kΩ. The vertical lines shown at 5 mAh intervals represent the load pulses (2 kΩ in this figure). The bottom line is the voltage capacity behavior of the projected discharge compiled from the closed circuit voltages recorded during the load pulses. Since there was concern that the high rate pulses might deteriorate discharge performance of these cells, two cells were not pulsed and their performance was compared to those subject to high rate pulses. All experiments were performed at ambient temperature.

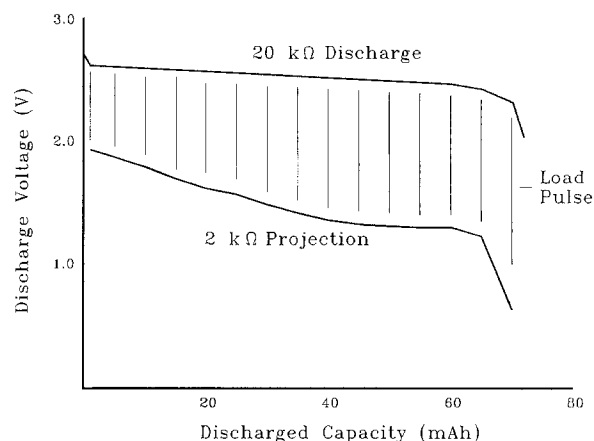


Fig. 2. Schematic illustration of the procedure for projecting high rate performance. Note that the cell is discharged across a constant 20 kΩ load and subject to a single high rate load pulse at 5 mAh intervals. The closed circuit voltages recorded for the pulses are used to project discharge performance across that load.

At 10 mAh intervals electrochemical impedance spectra were generated while the cells were potentiostatically held at their closed circuit potential. A PAR Model 388 Impedance Measurement System was utilized to generate all electrochemical impedance data. All spectra were generated over a frequency range of 100 kHz to 100 mHz. Analysis and interpretation of the impedance data utilized the equivalent circuit model developed by Kelly and Moran [6]. The parameter of interest is R'_0 , approximately the 1 kHz impedance, which is controlled predominantly by the LiI impedance is described elsewhere [3].

After discharge, cross sections of all cells were examined using backscattered electron imaging scanning electron microscopy (SEM). Sample preparation for SEM has been previously described [5]. In brief, the cell case was opened by removing the laser weldment around the periphery of the cell with a small lathe. The residual iodine was removed from the cathode by placing the cells in a continuously pumped vacuum chamber at greater than 100 kPa overnight. Prior to SEM analysis the battery pellets were cross sectioned with a razor blade.

3. Results and discussion

No morphological differences were noted between the LiI layers of any of the cells discharged normally across 20 kΩ and those subject to high rate load pulses. Both were homogeneous as shown previously in Fig. 1a. No incorporated chunks of unreacted cathode were observed such as those illustrated in Fig. 1b for cells discharged continuously at high rates.

High rate load pulsing did not adversely affect low rate discharge performance as determined by discharge voltage. Figure 3 compares the voltage capacity behaviour of two cells; one discharged continuously across 20 kΩ and the other discharged at the same rate but subject to 2 kΩ load pulses at 5 mAh intervals. It illustrates that discharge is not influenced by the small duration pulses across 2 kΩ, except for a slight

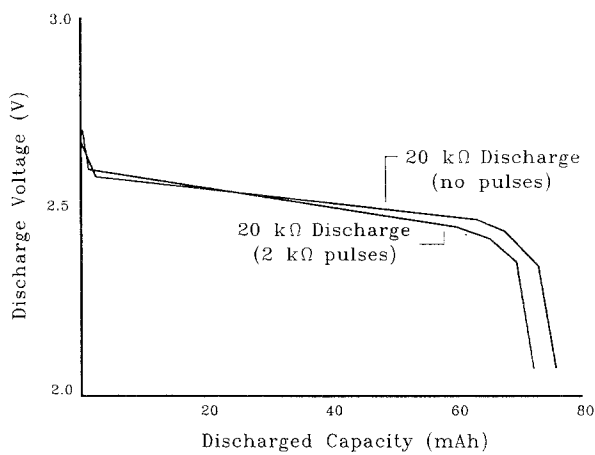


Fig. 3. Cell voltage against discharged capacity for a conventional discharge across $20\text{ k}\Omega$ and a cell load pulsed across $2\text{ k}\Omega$. Note that discharge performance is not affected by the load pulsing except for a small loss in dischargeable capacity.

decrease in dischargeable capacity. The cell pulsed across $2\text{ k}\Omega$ loses approximately 2–3 mAh of its initial 74 mAh. Except for this small loss in dischargeable capacity (less than 5%) the voltage capacity behaviour is identical. This is also true for the cells pulsed across $1\text{ k}\Omega$ and $500\ \Omega$ loads.

Further evidence supporting this method of projecting high rate discharge is given in Fig. 4 which illustrates the projected and actual discharge performance for a cell discharged across $5\text{ k}\Omega$. No significant difference in performance, as determined by discharge voltage, between the actual and projected discharges were observed. This was expected at this rate because it has been previously observed [7] that the LiI morphology and impedance are essentially identical for $20\text{ k}\Omega$ and $5\text{ k}\Omega$ discharges. This demonstrates that higher rate discharge behaviour can be accurately predicted using the periodic pulsing procedure.

Figure 5 contrasts the projected discharge performance for cells with homogenized cathodes and the actual performance for conventional cells across $2\text{ k}\Omega$ loads. Recall that Fig. 2 illustrates the procedure for projecting discharge performance. It is easily observed that the discharge performance projected for cells with

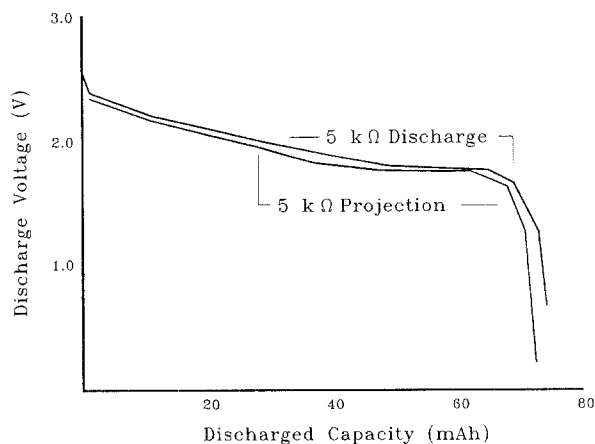


Fig. 4. Cell voltage against discharged capacity for conventional and projected discharges across $5\text{ k}\Omega$. As expected discharge performance is similar. Note that the ordinate scale ranges from 2.0 to 3.0 V.

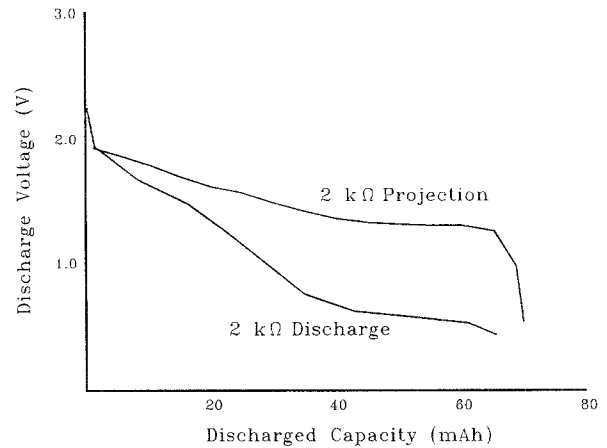


Fig. 5. Cell voltage against discharged capacity for conventional and projected discharges across $1\text{ k}\Omega$.

homogeneous cathodes is superior to that observed for conventional cells discharged across $2\text{ k}\Omega$. Early in discharge, when LiI impedance is small, performance is similar; however as discharge proceeds the LiI impedance increases more rapidly for the conventional discharge across $2\text{ k}\Omega$. As a result after 35 mAh (approximately half of discharge) the closed circuit voltage of the projected discharge was approximately twice that of the actual discharge (1.41 V compared with 0.75 V). In addition the capacity discharged above 1.5 V was increased from approximately 15 to over 35 mAh. This shows the improvements that could be realized if a cathode homogenization procedure is successfully developed.

Figure 6 contrasts the projected and actual discharge performance for cells discharged across $1\text{ k}\Omega$ resistive loads. Once again it is observed that the projected performance for cells with homogeneous cathodes is superior to that observed for conventional cells discharged across $1\text{ k}\Omega$. Early in discharge, discharge voltage was similar, however as discharge proceeded, the overpotential of the cell discharged conventionally increased considerably more rapidly than that of the projected discharge. At 35 mAh (approximately half of discharge) the projected discharge voltage was nearly 3 times the actual discharge voltage (1.02 V compared with 0.35 V) and the capacity

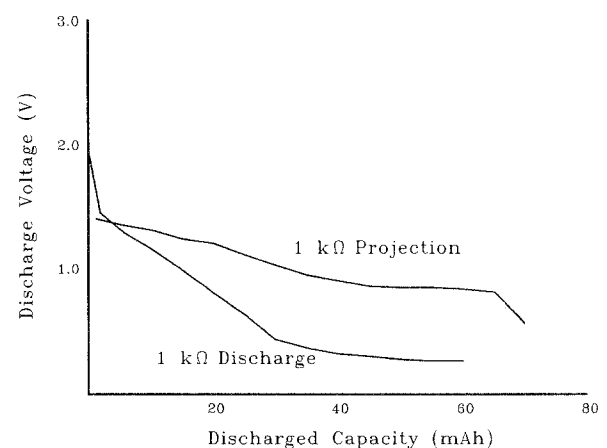


Fig. 6. Cell voltage against discharged capacity for conventional and projected discharges across $2\text{ k}\Omega$.

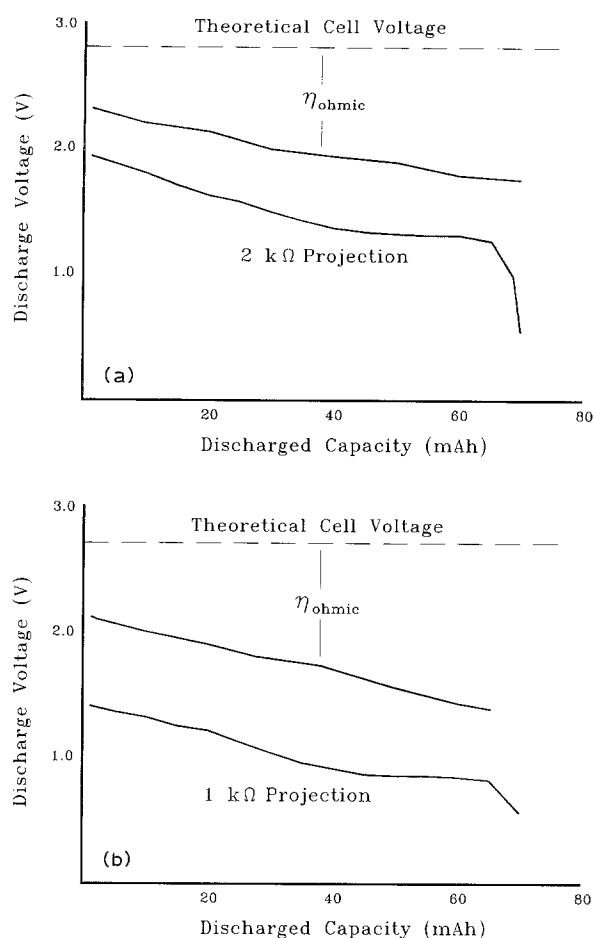


Fig. 7. Overpotential against discharged capacity for projected discharges across (a) 2 k Ω and (b) 1 k Ω loads. The ohmic contribution of the total overpotential is shown.

above one volt was increased from approximately 10 to 35 mAh.

It has also been observed that the projected performance for cells discharged across 0.5 k Ω is nearly equivalent to the actual performance of cells discharged across 2 k Ω (0.69 V compared with 0.75 V at 35 mAh) and far superior than actual performance across 1 k Ω (0.69 V compared with 0.35 V at 35 mAh). These projections show that homogenizing the cathode would enhance discharge performance considerably.

The enhancement projected is significant as described above and is further evidence that the Li/I₂ (P2VP) battery system is limited in rate by the formation of a highly resistive electrolyte layer. In fact, the projected discharges are still limited by LiI impedance even with the higher conductivity layer. Figures 7a and b illustrate this for projected discharges across 2 k Ω and 1 k Ω , respectively. The middle line in these figures represents the ohmic overpotential contributed by the sum of the electrolyte and bulk cathode impedances. The overpotential is determined by multiplying R'_Ω (as determined via EIS) by the discharge current (closed circuit voltage divided by load resistance). It can be seen that, even for the projected discharge, the ohmic overpotential is greater than one volt. This is consistent with calculations performed by the authors. It is important to realize that the ohmic overpotential is dominated by the LiI impedance except early in dis-

charge and near end of life. Therefore, it is evident that to increase the rate capabilities beyond those projected it is necessary to reduce the resistivity of the LiI layer. To date, however, the open literature reports no LiI composites with lithium ion conductivities in excess of $5 \times 10^{-5} (\Omega \text{cm})^{-1}$ at ambient temperature.

A method for forming homogeneous cathodes has been explored on a preliminary basis. Details are given elsewhere [11]. In brief the iodine and P2VP were first melted together and thoroughly mixed. The mixture was then solidified and ground into a powder that was pressed into cathode pellets. SEM analysis indicated that this method did not enhance cathode homogeneity. As a result discharge performance was not improved. It was concluded that the heat treatment that the cell was subject to after construction allowed the initially homogeneous cathode material to segregate towards its two phase equilibrium. This is consistent with the phase diagram for iodine and P2VP [12].

4. Conclusions

A method to project the high rate discharge performance for Li/I₂ (P2VP) batteries with homogenized cathodes has been presented. The procedure projects the discharge behaviour at high rates in the presence of a LiI layer formed at low rates. It was previously proposed [7] that implementing a cathode with a homogeneous distribution of iodine and P2VP would prevent the formation of a highly resistive LiI layer at high discharge rates. This study demonstrates that significant improvements in high rate discharge performance may be realized if a successful cathode homogenization procedure is developed and implemented. The method demonstrated in this study projects the magnitude of such performance improvements.

It has also been proposed that increasing the bulk diffusivity of iodine in the cathode would inhibit the incorporation of chunks of unreacted cathode into the LiI layer and hence have improved high rate discharge [7]. This has, in fact, been observed in our laboratory [12]. Cells with cathodes containing 22 000 MW P2VP (as opposed to 54 000 for the cells in the present study) exhibit superior discharge performance across 1 k Ω loads, resulting from the formation of a lower resistivity LiI layer. It is believed that this occurs because the cathode containing 22 000 MW P2VP is less viscous and hence has a higher iodine diffusivity than the cathode containing 54 000 MW P2VP. The projected voltage capacity behaviour across 1 k Ω for cells with 54 000 MW P2VP is nearly identical to the actual voltage capacity behaviour of cells containing 22 000 MW P2VP discharged across 1 k Ω .

Acknowledgements

This work was supported by the Whitaker Foundation. Catalyst Research, a division of Mine Safety and Appliances, provided the facilities necessary to manufacture the batteries used in this study. In particular the efforts of Henry Sunell and Dr Joseph

Jolsen at Catalyst Research are appreciated. EG&G Princeton Applied Research is acknowledged as a sponsor of CERL at the Johns Hopkins University. One of the authors (CCS) was supported by a National Science Foundation Creativity Fellowship in Engineering.

References

- [1] C. F. Holmes, in 'Proceedings of the Symposium on Materials and Processes for Lithium Batteries,' The Electrochemical Society, Princeton, NJ (1988).
- [2] B. B. Owens (editor), 'Batteries for Implantable Biomedical Devices,' Plenum Press, New York (1986).
- [3] C. C. Streinz, R. G. Kelly, P. J. Moran, J. J. Jolsen, J. R. Waggoner and S. Wicelinski, in 'Measurement and Compensation of Electrolyte Resistance in Electrochemical Tests,' (edited by L. Scribner and S. R. Taylor), ASTM STP 1056, Philadelphia, ASTM (1989) 202.
- [4] D. Surd, J. Jolsen, N. L. Yang and C. J. Hou, presented at the 1986 Power Sources Conference, Cherry Hill, NJ (1986).
- [5] R. G. Kelly and P. J. Moran, *J. Electrochem. Soc.* **134** (1987) 25.
- [6] *Idem, ibid.* **134** (1987) 31.
- [7] C. C. Streinz and P. J. Moran, *ibid.* **137** (1990) 2379.
- [8] C. R. Schlaiker and C. C. Liang, *ibid.* **118** (1971) 1447.
- [9] F. W. Poulsen, *Solid State Ionics* **2** (1981) 53.
- [10] A. A. Schneider, G. C. Bowser and L. H. Foxwell, U.S. Patent 4 148 975 (1979).
- [11] C. C. Streinz, Master's Essay, The Johns Hopkins University (1989).
- [12] G. M. Phillips and D. F. Untereker, in 'Power Sources for Biomedical Implantable Applications and Ambient Temperature Lithium Batteries,' (edited by B. B. Owens and N. Margalit), The Electrochemical Society Softbound Proceedings Series, Vol 80-4, Princeton, NJ (1980), p. 195.
- [13] C. C. Streinz, J. S. Steckenrider, J. W. Wagner and P. J. Moran, *J. Electrochem. Soc.* **136** (1989) 2811.