# PULSE DISCHARGE CHARACTERISTICS OF SOLID-STATE LITHIUM BATTERIES

A. HOOPER, R. J. POWELL, T. J. MARSHALL and R. J. NEAT*

*The Applied Electrochemistry Centre, The Harwell Laboratory, Oxfordshire OX11 0RA (U.K.)*

(Received September 15, 1988)

## Summary

A preliminary evaluation of an all-solid-state, polymer electrolyte-based, rechargeable lithium battery technology has been undertaken, in terms of its performance under pulsed-discharge conditions. Studies have concentrated on the lithium/poly(ethylene oxide)—lithium perchlorate/ $V_6O_{13}$ system, operating at 120 °C for pulse lengths of 10 ms to 20 s.

For pulses in excess of one second duration, high initial currents, equivalent to an approximate 40C discharge rate, have been observed [*e.g.* 1.5 A from a 40 mA h cell]. High peak currents can be sustained for tens of pulses of a few seconds duration and high cumulative cathode utilisations obtained. Good cell to cell reproducibility is found and the capability to pulse-charge cells has also been demonstrated.

For pulses of 10 ms duration, the cells exhibit a rapid response and recovery, together with a high current capability, long pulse life and reasonable cathode utilisation. Nine thousand pulses of greater than 1 A [average 1.3 A] were obtained from a 110 mA h cell, with a cumulative cathode utilisation of 25%.

A $PEO_{12}LiClO_4$ electrolyte composition is found to be optimum for operation at 120 °C, in terms of both the type and the proportion of lithium salt used. The use of a novel electrolyte has also allowed the preliminary demonstration of high-rate performance at room temperature.

## Introduction

Rechargeable lithium batteries, using ion-conducting polymer electrolytes, offer a breakthrough in battery technology [1, 2]. They will be easy to fabricate, rugged and safe. Practical gravimetric and volumetric energy densities in excess of 200 W h/kg and 250 W h/litre can be projected

---

*Author to whom correspondence should be addressed.

for large, bipolar-configured, systems with equivalent continuous power output ratings of up to the $C$ (one hour) discharge rate. Combined with the ability, via the advent of improved polymer electrolytes, to operate down to at least room temperature, these features make the technology appropriate to a very wide range of applications, from consumer electronics to vehicle traction.

To date, however, applications requiring higher rate operation have generally been ruled out, since the continuous power capability of the technology is restricted by a current-limiting effect in the electrolyte [3] as well as, possibly, the kinetics of the battery electrodes. Nevertheless, short-circuit tests, which show the above characteristic to be a useful safety feature, have indicated that high currents can be achieved over short periods and this opens up the possibility of high power pulsed operation.

Here, we report on an initial investigation of the pulsed operation of cells operating at 120 °C and comprising lithium metal anodes, $V_6O_{13}$-based composite cathodes and electrolytes of poly(ethylene oxide) complexed with either lithium perchlorate or lithium trifluoromethanesulphonate. This elevated temperature technology is more mature than room temperature options currently emerging and may actually be more appropriate for high power systems. These will be subject to high internal heat generation and will require a wide range of thermal stability. The operating temperature is not so high, however, as to pose severe problems with either thermal management or corrosion, for example. Since the option of a 'room temperature' system does, however, also have positive features, a few experiments have been carried out on cells containing a novel polymer electrolyte developed at Harwell.

## Experimental

### Materials

$V_6O_{13}$ was prepared by the thermal decomposition of ammonium metavanadate in an argon atmosphere. Composite cathodes were fabricated by the casting of slurries of mixtures of the $V_6O_{13}$, acetylene black and polymer electrolyte in solution, onto nickel foil current collectors. The cathode composition was 45 vol.% $V_6O_{13}$/5 vol.% acetylene black/50 vol.% poly(ethylene oxide):lithium salt. Electrolyte membranes were also cast from solution and lithium foil (Lithco. Inc.), typically 150 $\mu$m thick, was used for anodes. Experimental cells were produced in a flat-plate design, typically 40 cm$^2$ in area, via a warm vacuum laminating technique. Encapsulation was either within o-ring sealed metal cell cases or within heat-sealed flexible pouches. Component storage and cell fabrication was performed within a 1 - 2% relative humidity dry-room facility.

### Techniques

Two experimental techniques, fixed potential and fixed load resistance, were used to cover a range of pulse lengths from 10 ms to 20 s.

For the potentiostatic measurements, a Solartron 1286 Electrochemical Interface [ECI] was used to impose fixed voltage levels at the cell terminals. For discharge, this was typically set at 1.7 V and, for charge, 3.25 V. These values represent the voltage limits generally used for standard galvanostatic cyclic tests. Pulse lengths from 3 to 20 s were used and discrete current measurements were facilitated via an associated microcomputer. In some cases, the applied discharge potential was automatically set at one half of the cell open circuit voltage. This represents the maximum power situation. Complementary a.c. impedance measurements were also carried out on some cells using a Solartron 1254 Frequency Response Analyzer with the 1286 ECI.

Fixed resistance discharges for periods in the range between 10 ms and 1 s were carried out using a Gould PG52B pulse generator in association with a V-MOS FET device (International Rectifier 'HEXFET' Part No. IRF-730), acting as a switch. Data acquisition and storage was carried out using a Hitachi VC-6050 digital storage oscilloscope and hard copy output was via a Philips PM8141 X-Y recorder. The FET switch approach was found to be superior to the use of relays because of 'bounce' limitations in the latter but did necessitate the use of bifilar-wound load resistors. Measurements indicated a total additional circuit resistance of approximately 0.5 ohm. The a.c. impedance measurements on cells were used to aid the choice of load resistor; for maximum power $R_{load} = R_{cell}$.

## Results

Figure 1 shows some typical first, 20 s potentiostatic, pulses at 1.7 V for a series of lithium perchlorate-based electrolyte cells at 120 °C. The capacities of the cells are approximately 40 mA h and the peak currents of
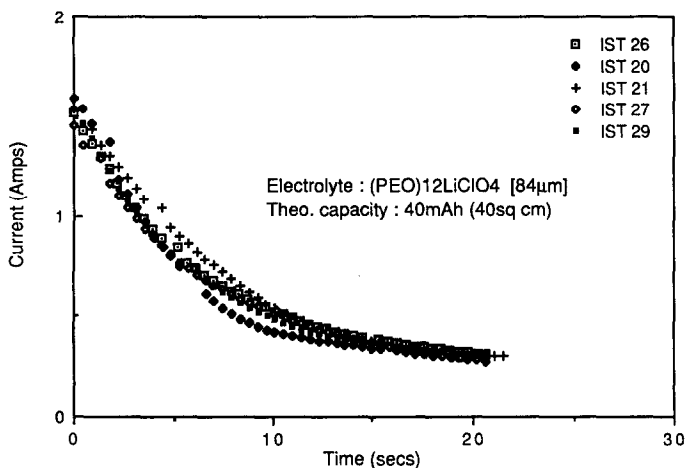


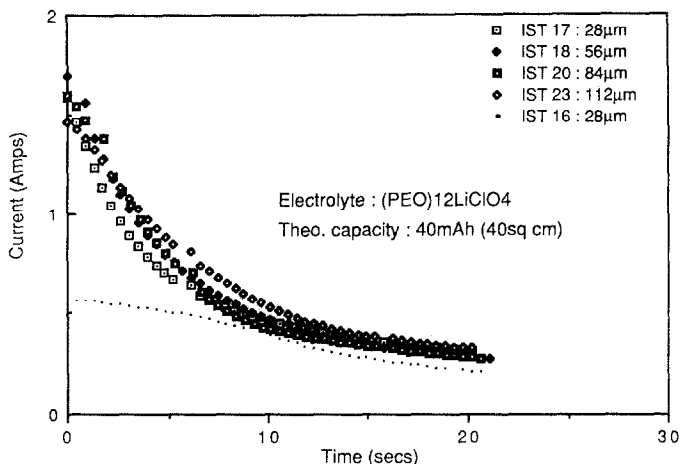Fig. 1. Initial 1.7 V potentiostatic pulses at 120 °C.

Fig. 2. The effect of electrolyte thickness variation.

1.5 A represent an equivalent discharge rate of around $40C$. Clearly this is not sustained over the full length of the pulses but even the final, and levelling out, current values represent an approximate $8C$ rate. Good performance reproducibility is observed for these cells, which contain an 84 $\mu$m thickness of electrolyte.

In fact, cell performance does not appear to be a strong function of the electrolyte film thickness, at least between 28 and 112 $\mu$m, as shown in Fig. 2. This indicates that the primary rate-limiting factor in these cells is not the electrolyte membrane resistance. From a practical point of view, however, it was found that cells containing thin electrolyte membranes (e.g. IST 16 and IST 17) gave rise to variable performance due, presumably, to mechanical limitations and difficulties during cell fabrication.

The continued imposition of 20 s pulses, with rest intervals of a few minutes leads to a relatively rapid performance degradation. By the 10th pulse the peak current has decreased by about a factor of four. Figure 3 illustrates, however, that by this stage almost 50% of the maximum theoretical capacity of the cell has already been extracted. This is based on a limited cathode capacity and assuming lithiation of $Li_8V_6O_{13}$. Good cell to cell reproducibility is again found as illustrated by the upper two curves.

Because the open circuit voltage of a $Li/V_6O_{13}$ cell is a function of its state of charge (Fig. 4), it is not surprising to find a fall-off in the attainable peak current with pulse number for a fixed applied potential. A better test is to look at the maximum power situation at each point by setting the load potential to one half of the value of the cell open circuit voltage. As shown in Fig. 5a, higher peak currents are indeed attained under this regime, although the capacity associated with each pulse falls more steeply than for the fixed, 1.7 V, situation (Fig. 5b). The application of voltage levels less than 1.7 V may also lead to problems associated with the over-
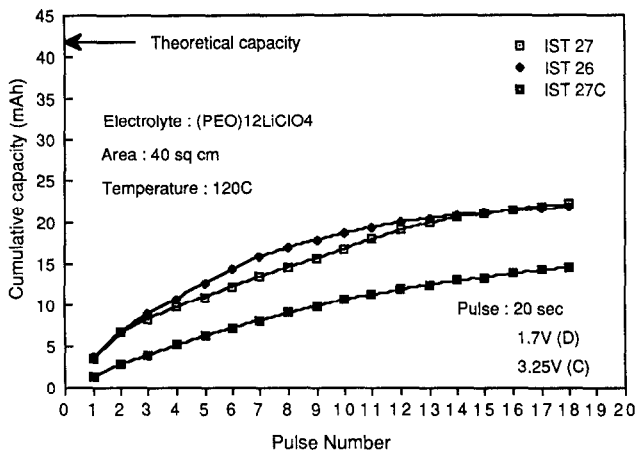
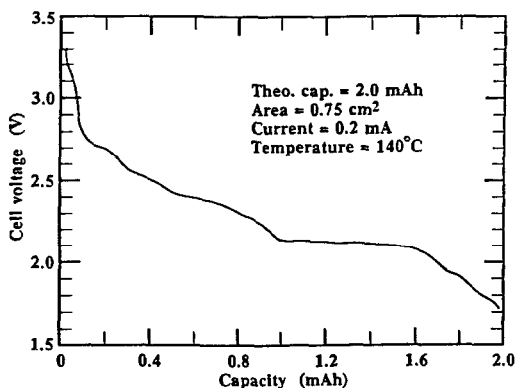Fig. 3. Cumulative capacities on discharge and charge.



Fig. 4. Example of a 'high temperature' cell discharge curve.

discharge of the $V_6O_{13}$ cathode and thus deleteriously affect any subsequent cell recharge capability.

The lower curve (IST 27C) in Fig. 3 shows the results of a subsequent equivalent charging experiment. It is clear, even from this relatively crude and non-optimised experiment, that rapid charging can also be achieved although the efficiency may be inferior to the discharge situation. The magnitude of the peak currents attainable per pulse can be increased, for the fixed 1.7 V discharge, by reducing the pulse length. This is already apparent even for pulses which are still of a few seconds duration, as shown in Fig. 6. For 3 s pulses, currents in excess of 1 A and 0.75 A were maintained over 10 and 25 pulses, respectively, for a 44 mA h cell. The shapes of the curves in Figs. 6 and 5a are similar to the form of the discharge curve illustrated in Fig. 4, which indicates a correlation between performance and state of charge. However, although the relative lengths of individual regions of the curves are reasonably consistent with the estimated capacity withdrawal
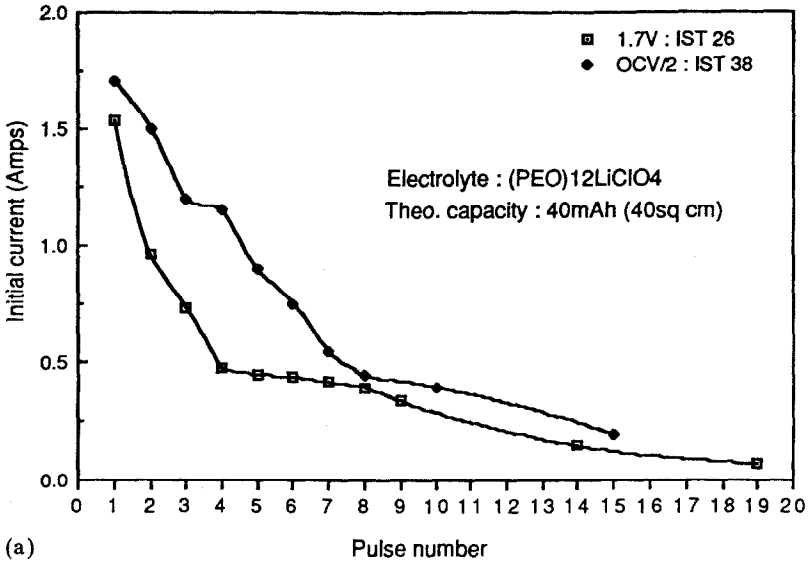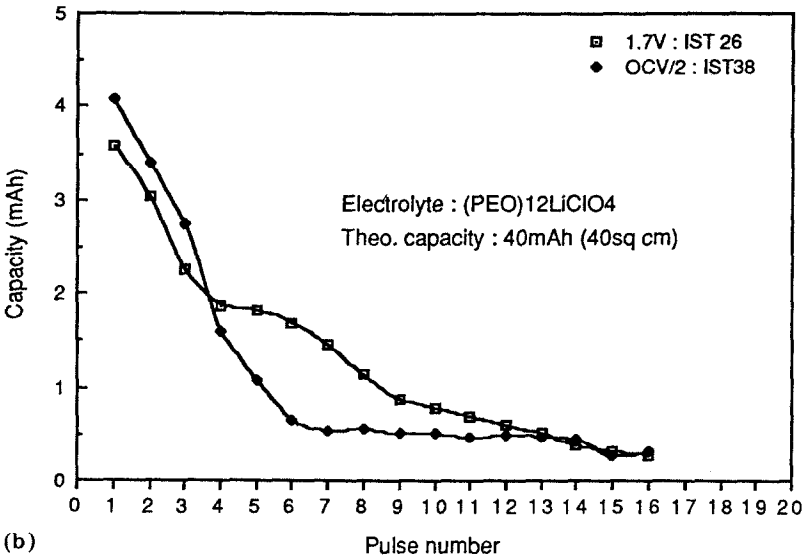
Fig. 5. The effect of voltage limit on (a) the peak current and (b) the capacity of potentiostatic pulses.

(compare, for example, IST 66 and 68 in Fig. 6), there is a clear decline in the magnitude of the currents associated with the long plateaux regions as the pulse length is increased. This suggests that the loss of current capability is not only a function of the state of charge and the associated value of the cell open circuit voltage prior to discharge, but also of the pulse-history of the cell.
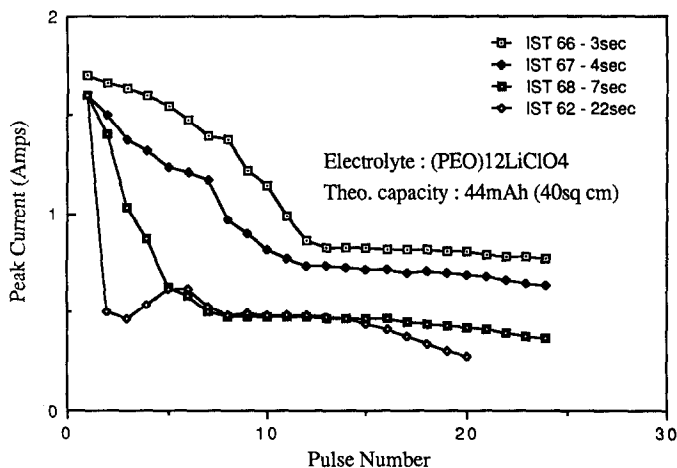
Fig. 6. Peak current *vs.* pulse number as a function of pulse length.

The continued beneficial effects of further reducing the pulse length are illustrated in Fig. 7. Here, a sequence of 10 ms discharge pulses has been applied to a 110 mA h capacity cell with alternate 'rest' periods of 90 ms. The load resistance was 1.5 ohm (including circuit contributions) and the lithium perchlorate-based cell was again maintained at a temperature of 120 °C. The choice of a one ohm load resistor was determined by the aim of achieving a maximum power situation and the measured a.c. impedance of a number of cells, which was found to be approximately equal to, or just less than, this value. However, as can be seen from the Figure, the additional 0.5 ohm circuit resistance leads to a less than maximum power situation. Nine thousand pulses were achieved before the load voltage reached an imposed cut-off value of 1.7 V. The final current level was still 1.1 A (10$C$ rate), with an average value of around 1.3 A. The cumulative capacity of 25 mA h represented roughly 23% of the nominal value and was extracted in a total 'ON' time of 90 s and an overall time of 15 min. As can be seen from Fig. 7, the response and recovery times of the cell are both rapid and it should be possible to reduce the 'OFF' time of the cell considerably so as to increase its effective overall rate capability. Based on already achieved nominal energy densities of around 100 W h/kg for 1 A h cells, a 25% utilisation and consideration of 'ON' time only, these data correspond to a power density of approximately 1 kW/kg. This figure already compares well with the few hundred W/kg previously quoted for the pulsed operation of bipolar-designed conventional chemistries such as Pb–acid [4, 5] and Ni–Cd [6]. In addition, for larger batteries based on the solid-state technology, also of bipolar design and using optimised components, further improvements can be confidently expected. Even if the many tens of kW/kg reported for high temperature systems such as lithium alloy/molten salt/iron sulphide cells operating at 500 °C [7] are not achieved, in many applications the overall advantages to be gained from the lower temperature solid-state technology
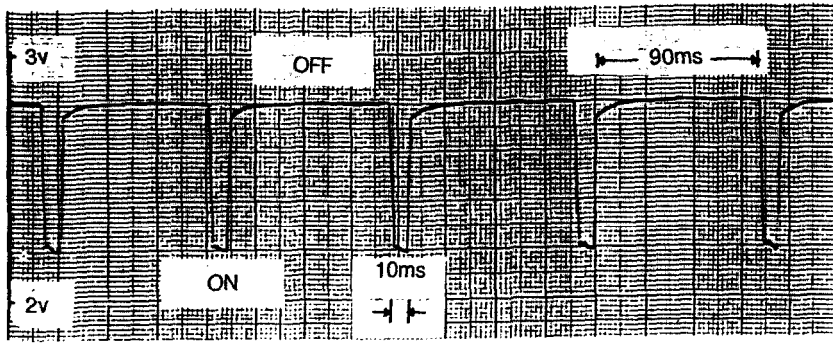
(a)
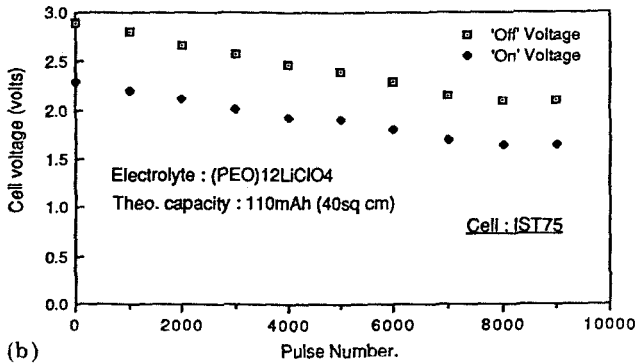


(b)
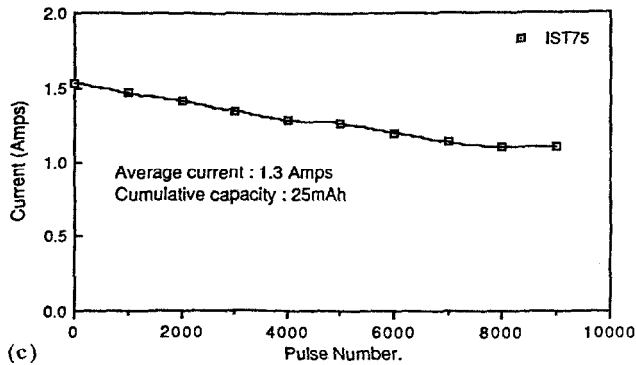


(c)

Fig. 7. 1.5 ohm load discharge at 120 °C: (a) initial pulse train; (b) cell voltage *vs.* pulse number and (c) cell current *vs.* pulse number.

in terms of, for example, corrosion, mechanical stability and safety will more than compensate for a reduced electrical performance.

Figure 8 shows both the peak current and the capacity of the first and second, 20 s potentiostatic (1.7 V), pulses of a 40 mA h $(PEO)_{12}LiClO_4$ electrolyte-based cell as a function of temperature. The data confirm 120 °C as the optimum operating temperature for this type of cell. The poorer performance at lower temperature is related primarily to a decreasing elec-
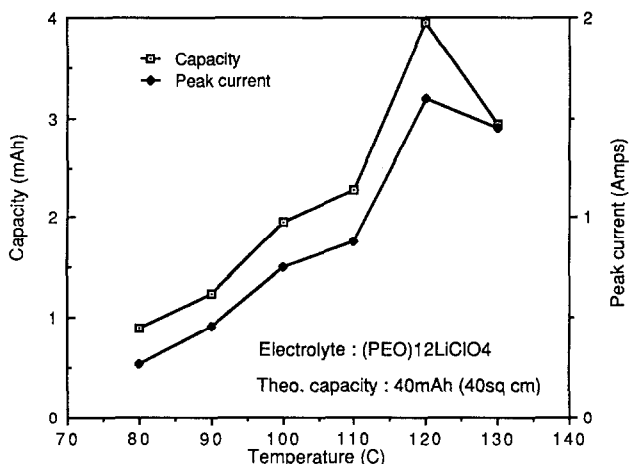
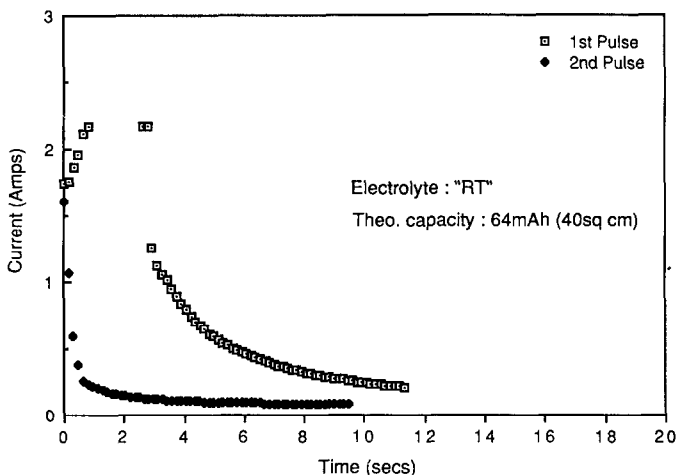Fig. 8. The temperature characteristics of the 'high temperature' system.



Fig. 9. 1.7 V potentiostatic pulses at 25 °C using an improved electrolyte.

trolyte conductance, whilst above 120 °C problems may arise because of the poor mechanical properties of the electrolyte.

If, however, the standard electrolyte is substituted by a material developed at Harwell for lower temperature operation, then good performance can also be achieved at room temperature for a $V_6O_{13}$-based composite cathode cell. In a preliminary experiment (Fig. 9) a first pulse peak current in excess of 2 A was achieved for a 64 mA h cell. An obvious difference between the performance of this cell and the high temperature versions described above is the significant time delay prior to the attainment of the peak current after the imposition of the 1.7 V potential. This effect may be similar in origin to the well-known voltage delay found in some primary

lithium battery systems. It is not apparent for the second pulse where again a high peak current is attained. However, the capacity of this second pulse is very low.

The original choice of $(PEO)_{12}LiClO_4$ as the preferred electrolyte composition for high temperature cells was based on earlier measurements of a.c. conductivity. However, other factors, such as ionic transport numbers and reactivity with lithium will also affect the rate at which lithium ions can be transported within a cell and, hence, its high rate, pulsed, performance. Consequently, a study has been carried out of variations in lithium perchlorate concentrations and alternative salts; $LiCF_3SO_3$, $LiAsF_6$ and $LiI$.

The cells were subjected to both potentiostatic and constant resistance discharge regimes at 120 °C. In the former case, a sequence of twenty, 20 s and 1.7 V, pulses were applied with a 40 s rest period between each and the cell performance was based on the total achieved capacity. For the constant resistance discharge, the figure of merit was the number of 10 ms 'ON'/90 ms 'OFF' pulses than could be sustained to a cut-off load voltage of 1.7 V.

The results are shown in Fig. 10 and confirm the choice of the $(PEO)_{12}$-$LiClO_4$ electrolyte as the optimum composition.
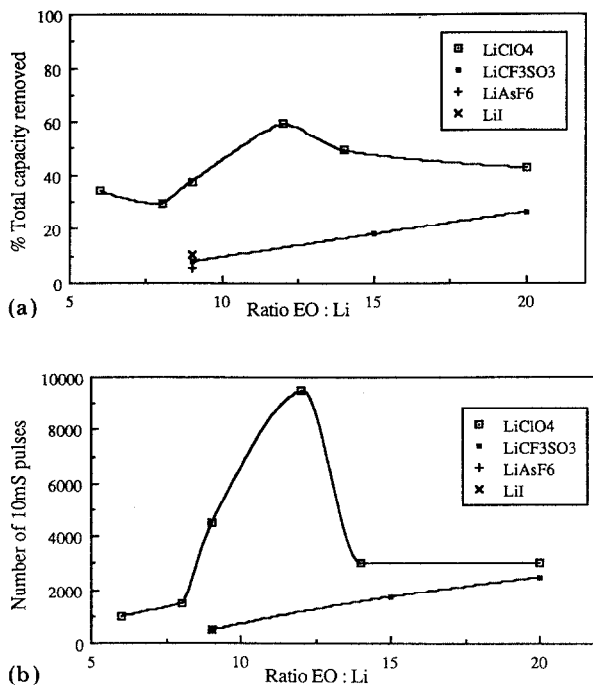


Fig. 10. The effect of salt content on (a) the 1.7 V and (b) 10 ms pulse, performance.

## Conclusion

The results of this work have demonstrated conclusively that, when operated in a pulsed-mode, the polymer electrolyte-based all-solid-state lithium battery technology can exhibit high power density, as well as high energy density characteristics. This is a new observation, which adds to the existing list of attractive features for the technology and now makes it a viable prospect for a wider range of applications than previously envisaged.

Notable results, in addition to the ability to draw large, short duration, currents include pulse recharge capability, rapid response and recovery times, good associated capacity utilisations, good cell to cell reproducibility and operation demonstrated both at elevated and normal ambient temperatures.

## Acknowledgement

## References

1 (a) A. Hooper, in C. A. C. Sequeira and A. Hooper (eds.), *Solid-State Batteries,* NATO ASI Series, Martinus Nijhoff, Dordrecht, 1985, p. 399; (b) B. C. Tofield, p. 423.

2 A. Hooper, A. Belanger and M. Gauthier, Polymer electrolyte lithium batteries, in R. G. Linford (ed.), *Electrochemical Science and Technology of Polymers,* Vol. 2, Elsevier Applied Science, Barking, U.K., in press.

3 S. Atlung, K. West and T. Jacobsen, *J. Electrochem. Soc., 126* (1979) 1311.

4 R. E. Biddick and R. D. Nelson, *Proc. Intersoc. Energy Convers. Eng. Conf.,* (1968) 47.

5 H. P. Silverman, N. R. Garner, R. R. Sayano, R. E. Biddick and E. T. Seo, *Proc. Intersoc. Energy Convers. Eng. Conf.,* (1972) 119.

6 H. N. Seiger, A. E. Lyall and S. Charlip, *Proc. Intersoc. Energy Convers. Eng. Conf.,* (1966) 271.

7 L. Redey, *Proc. Intersoc. Energy Convers. Eng. Conf.,* (1987) 1091.