

## TESTING TECHNIQUES FOR MATERIALS USED IN LITHIUM BATTERIES

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### Summary

Accelerated techniques for materials testing are described. Direct resistance heating of electrodes and current-collectors has been conducted in molten electrolyte media with the object of accelerating the onset of failure. A multi-cell tester has been used for the simultaneous evaluation of large numbers of electrodes, this involves the periodic measurement of cell voltage. The test cycle includes direct resistance heating and polarity reversal. Open-circuit voltage measurements and responses to heat-pulse doses correlate to the mechanical properties and the corrosion behaviour of the materials under test.

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### Introduction

Lithium cells are known for their high performance: lithium offers a high energy content of about  $1 \text{ kW kg}^{-1}$ , as well as a superior shelf life which may reach about 10 years. Lithium cells are widely used in missile and aircraft applications, but the selection of materials for lithium cells is a difficult task. The object of the studies reported here is to introduce simple and effective techniques for testing various materials relevant to lithium cells and other energy conversion systems.

### Experimental

Accelerated electrotechniques assist the selection of materials used in batteries and other applications involving aggressive media [1]. Both environmental and operating conditions, such as the working temperature and the temperature gradient experienced during cell performance, may vary over a wide range.

Heating of selected materials at high temperature ( $1000 \text{ }^\circ\text{C}$ ) for short periods (up to 2 min) was used as an accelerated test for the oxidation/corrosion of materials in contact with air or aggressive chemicals. The material contacting lithium salt is affected by high temperature diffusion and is exposed to severe corrosion.

The experimental set-up included a fast heating facility that resulted in oxidation and/or other types of corrosion, particularly when aggressive chemicals were used. Pre-coating of materials before heating with chemicals accelerated material failure. Thermal shocks and chemical attack occurred when the hot part of the metal was quenched in aqueous or non-aqueous solutions. Such solutions are commonly chosen to simulate the electrolyte composition employed in lithium cells.

The progress of material failure was monitored by electrochemical and thermal techniques [2 - 5]. Heat-pulse monitoring of material corrosion is a simple, non-destructive technique [2, 6]. Electrode potential and open-circuit voltage (OCV) measurements are very well known techniques for materials evaluation [7].

## Results and discussion

The variation in thermal response for a copper wire which was first electroheated and then either quenched in a saturated solution of lithium chloride, or left to cool in air, is given in Fig. 1. A thermocouple (or thermistor) was used to measure the signal, which was recorded on a chart recorder over a range of 1 mV. The measured response to a heat pulse dose (measure-

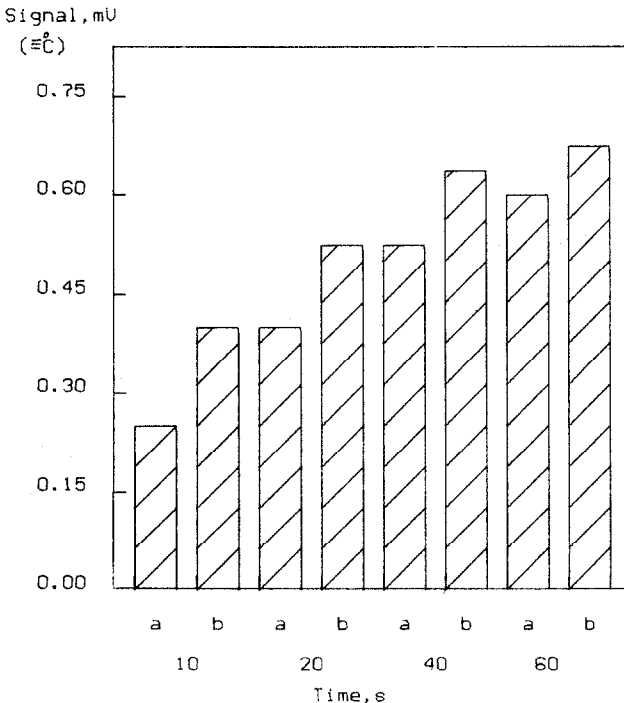


Fig. 1. Monitoring corrosion by heat-pulse response: (a) air cooled to room temperature; (b) quenched in LiCl saturated solution.

ments were conducted one month later) shows that there is a significant difference between the rates of heat dissipation in wires subjected to the above two treatments. This behaviour is attributed to variation in the characteristics of the surface layer formed on the wire. Further details on this new monitoring technique are available elsewhere [2, 6].

The voltage (mV) signal is an indication of the response of the material to the heat pulse. If either microcracks or multi-phase/air inclusions lie in the path of heat, then the transient heat transfer will be affected and, consequently, also the measured mV signal. Such defects are known to influence both the behaviour and the corrosion rate of materials. The signal from a reference material is used as a benchmark for detecting defective materials.

Figure 2 presents data obtained from rapidly heated samples when monitored by the heat-pulse technique. It can be seen that the thermal response depends on the identity of the sample. The exposure of a sample to a high temperature, followed by air cooling to ambient temperature, also affects the open-circuit voltage (Fig. 3). The cell used in these studies was a lithium button cell electrolyte and the electrodes of the tested materials, Ni, was used as reference electrode. OCV is an important property in materials testing as it gives direct evidence of contamination of either the electrode and/or the electrolyte. The measured value is a mixed potential and is

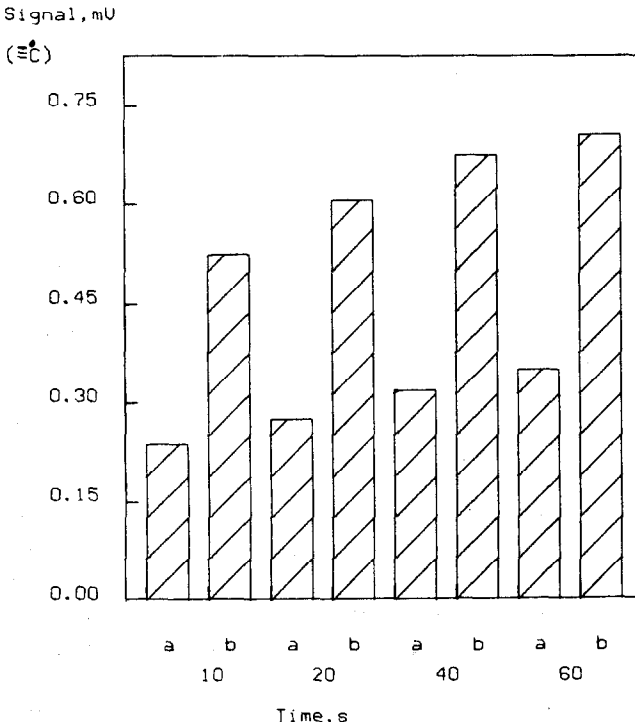


Fig. 2. Effect of sample type on heat-pulse response: (a) brass (Cu-30Zn); (b) galvanized steel. Samples preheated at 1000 °C for 2 min.

OCV,

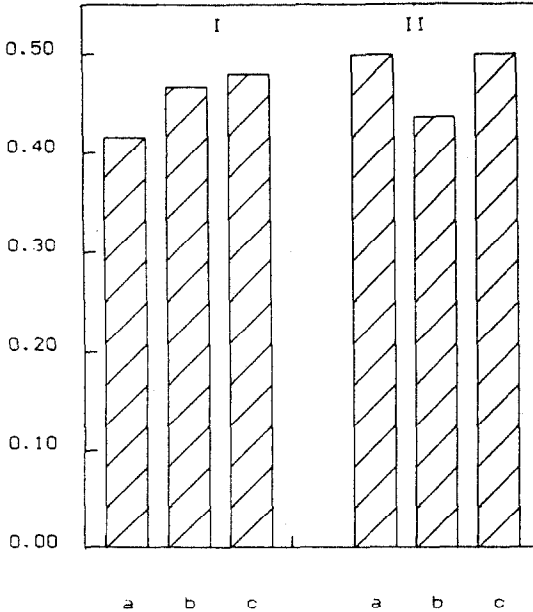
 $U(\text{Li}/\text{LiCl})$ 

Fig. 3. Electrochemical characteristics of various materials: (I) Fast heated at 1000 °C, 2 min, air cooled, (II) as received (no heat treatment). (a) Phosphatized steel; (b) mild steel; (c) stainless steel (304).

dependent on the metallurgical condition of the electrode material. Comparison of the OCVs of test and reference materials will give immediate evidence of the electrode condition whether from the reference standard material or not. This method is of prime interest for quality control of materials in battery manufacture.

Severe corrosion is noticed when a lithium salt (LiCl) is placed in contact with heated samples as, for example, has been demonstrated by the microstructure of a tested specimen of steel.

Relative values of mechanical test results show that the hardness and ductility are significantly altered by rapid heat treatment. Phase transformation occurs at high temperatures or during subsequent cooling of the specimen (*i.e.*, quenching in liquid or cooling in air). Such transformations have been found [7] to change the mechanical and electrochemical properties of materials.

Conventional tensile tests are of major use particularly when the sample has been subjected to attack from an aggressive chemical such as LiCl. More details are given elsewhere [6].

## Conclusions

Non-destructive testing, such as heat-pulse monitoring of materials, can be used to compare the performance of various metals in aggressive environments. Corrosion and/or mechanical properties correlate to the thermal response to heat-pulse testing of such materials.

Electrode potential measurement correlates to material substrate thermal history, e.g., materials exposed to 1000 °C for 2 min and then air cooled are different from those not subjected to heat treatment.

## Acknowledgements

The financial support of CanReactor Material, Inc. (Box 189, Mississauga, Ontario, L5M 2B8, Canada), is acknowledged. Partial finance from Kuwait University (EDC 017) and the assistance of Dr M. R. Reda, Dr T. Al-Sahhaf and Dr J. Al-Hajji is appreciated.

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