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Short communication

ac impedance measurements of molten salt thermal batteries

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Abstract

Non-destructive testing of thermal batteries without activating them is a challenging proposition. Molten salt thermal batteries are activated by raising their temperature to above the melting point of the salt constituting the electrolyte. One approach that we have considered is to raise the temperature of the molten salt electrolyte to a temperature below the melting point so that the battery does not get activated yet may provide sufficient mobility of the ionic species to be able to obtain some useful ac impedance measurements. This hypothesis was put to the test for two Li(Si)/FeS_2 molten salt batteries with two electrolytes of different melting points—a standard LiCl–KCl eutectic that melts at 352 °C and a LiBr–KBr–LiCl eutectic with a melting point of 319 °C. ac impedance measurements as a function of frequency and temperature below the melting point are presented for single cells and batteries.

Keywords: Thermal batteries; Li-based molten salt batteries; Electrochemical impedance spectroscopy

1. Introduction

Thermal batteries are primary reserve batteries that employ inorganic salt electrolytes, which are non-conductive solids at ambient temperatures, and integral pyrotechnic materials scaled to supply sufficient thermal energy to melt the electrolyte [1]. A thermal battery is activated by application of an energy impulse from an external source to a built-in initiator, which ignites the pyrotechnic, melting the electrolyte, rendering it conductive, and permitting the battery to deliver high power for relatively short duration. The complete thermal battery is totally inert and non-reactive until activated. These batteries are typically used to supply power for munitions and offer excellent shelf life, on the order of 20 years.

As of now, there is no easy way of determining the condition of thermal batteries without activating them. In the present project we are investigating the feasibility of using electrochemical impedance spectroscopy (EIS) measurements to determine the state-of-health (SOH) of molten salt thermal batteries. This is done by performing EIS measurements on Li-based molten salt thermal batteries, at temperatures, well below the melting point of the eutectic electrolyte but at a temperature where sufficient ionic mobility may produce a discernible impedance response. This approach offers a potentially non-destructive means of evaluating the condition of Li-based molten salt thermal batteries without activating them.

2. ac impedance measurements and analysis of lithium-based molten salt thermal cells and batteries

ac impedance measurements have been made on Li-based molten salt thermal cells employing two different electrolytes of different melting points and on multiple cell stacks (thermal batteries). These measurements were made on both fresh cells and cells with "aged" anodes to degrade the condition of the cells.

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2.1. Single cell measurements

ac impedance measurements were made on Li(Si)/LiCl–KCl (MgO)/FeS_2 thermal cells between room temperature and 375 °C. The data were taken with the Li(Si) anode as the working electrode and the reference and counter electrodes connected to the FeS_2 cathode. Data for a dummy setup of a capacitor in parallel with a resistor in series with another resistor were also performed for before and after the cell impedance measurements to ensure a stable, calibrated, measurement system. The ac impedance measurements were made over a frequency range of 65 kHz to 0.1 Hz with 5 mV peak-to-peak ac signal amplitude. On some of the cells at temperatures below the melting point, the overload light came on regularly below 1 Hz, so that data in this frequency range can be considered suspect.

In the preliminary screening studies, impedance spectra were generated for single cells that were heated over a range of temperatures starting near ambient and extending to above the melting point. Two electrolytes were employed in the initial tests with single cells: the standard LiCl–KCl eutectic that melts at 352 °C and a low-melting LiBr–KBr–LiCl eutectic that melts at 319 °C. Flooded anodes containing 25% electrolyte were used for these tests. The catholyte was unfused and lithiated with the composition 73.5% FeS_2/25% separator/1.5% Li_2O. The MgO content of the separator used in the cells was 35% for the LiCl–KCl eutectic electrolyte and 30% for the LiBr–KBr–LiCl eutectic electrolyte.

The LiBr–KBr–LiCl eutectic melts at 319 °C and was examined as part of the impedance study because with its lower liquidus, this electrolyte generally results in longer run times in batteries. Also, this material is more ionically conducting than the LiCl–KCl eutectic. Fig. 1 shows discharge data for thermal cells incorporating the two different electrolytes. Comparable performance is observed for thermal cells using the two different electrolytes. Note that the maximum in total polarization (impedance) is much smaller with the cell with the lower-melting LiBr–KBr–LiCl electrolyte.

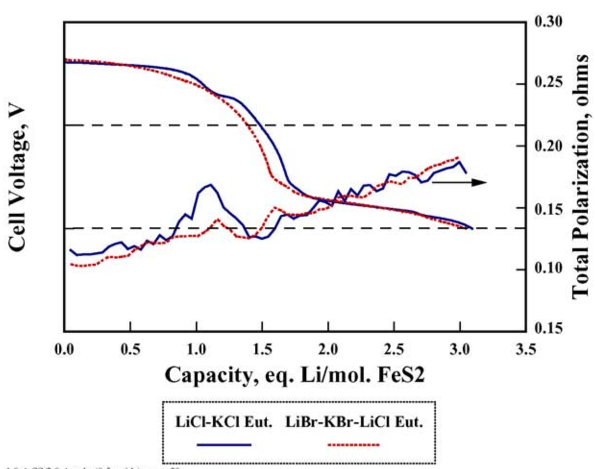

Fig. 1. Performance of Li(Si) (flooded)/FeS_2 cells at 500 °C and 125 $mA^2\,cm^{-2}$ background current density for LiCl–KCl and LiBr–KBr–LiCl electrolytes.

The magnitude and phase Bode plots of the impedance measurements as a function of temperature for the thermal batteries employing the standard LiCl–KCl eutectic that melts at 352 °C are shown in Fig. 2. A dramatic decrease in the impedance magnitude from 200 to 250 °C is observed (Fig. 2a). This is indicative of a sudden increase in ion mobility as the temperature is raised over this temperature regime (it is noteworthy that there is a much less dramatic change between 175 and 200 °C and from 250 to 275 °C.) A large change in the phase angle is also observed over the 200–250 °C temperature range (see Fig. 2b).

Fig. 3 shows similar magnitude and phase Bode plots for the thermal battery employing a low-melting LiBr–KBr–LiCl eutectic that melts at 319 °C. Again a large decrease in impedance and a large change in the phase angle are seen but at a lower temperature (150–200 °C range) than the standard LiCl–KCl eutectic, consistent with the lower melting point temperature of the electrolyte.

2.2. Aged anodes

To simulate the effect of aging of the anode, an anode was removed from the dry room and exposed to a relative humidity of 22% for two different lengths of times. The resulting weight gains of the anode from the exposure to a humid environment were measured to be 4.92 and 10.2%. These anodes were then used in cells that were tested in the same manner as

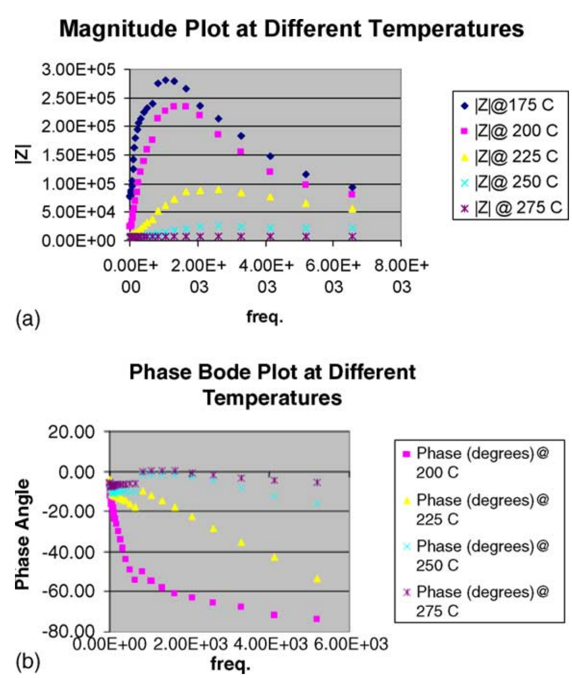

Fig. 2. (a) Bode plot of impedance magnitude for a Li(Si)/FeS_2 thermal battery employing the standard LiCl–KCl eutectic that melts at 352 °C. (b) Bode plot of impedance phase angle for a Li(Si)/FeS_2 thermal battery employing the standard LiCl–KCl eutectic that melts at 352 °C.

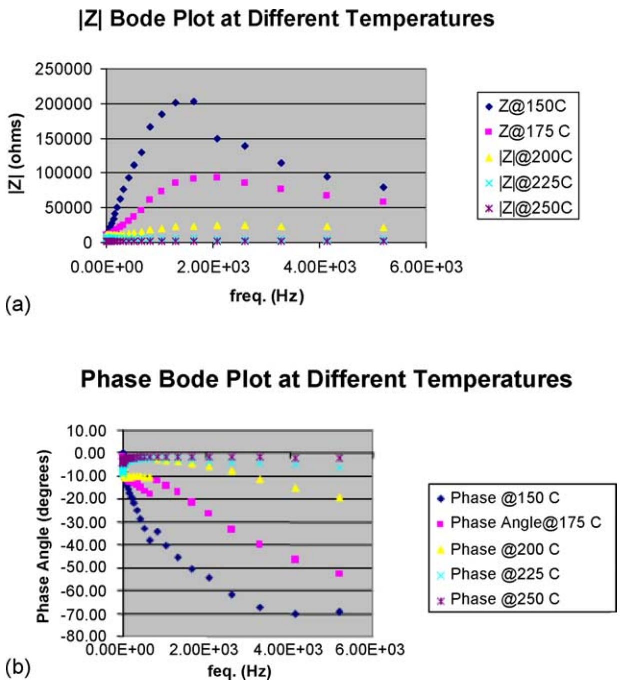

Fig. 3. (a) Bode plot of impedance magnitude for a Li(Si)/FeS_2 thermal battery employing the low-melting LiBr–KBr–LiCl eutectic. (b) Bode plot of phase angle for a Li(Si)/FeS_2 thermal battery employing the low-melting LiBr–Br–LiCl eutectic.

the control (unaged) cell. The cells were assembled in a dry room and were tested between heated platens in a glove box where the moisture and oxygen content were each <1 ppm. ac impedance measurements were made over a frequency range of 65 kHz to 0.1 Hz with a 5 mV peak-to-peak amplitude ac signal.

After the impedance measurements, the cells were then tested in the glovebox between heated platens at 500 °C at a background current density of 125 mA cm^{-2} with 0.25 s pulses of 250 mA^2 cm^{-2} applied every 30 s. This allowed the total polarization (resistance) of the cells to be determined. The cells were discharged to a cutoff voltage of 1.0 V.

The total polarization for these cells is presented in Fig. 4. The cell that contained the anode with the largest weight gain ran for about 50% shorter time than the control to a 1.0 V cut-off (Fig. 4). The cell with the anode with a 4.92% weight gain ran for an intermediate time relative to the other two cells. However, at the end of life, its capacity was actually slightly less than that of the cell with the anode with a 10.2% weight gain. The cells with aged anodes exhibited higher polarization than the control cell (Fig. 4). The loss in capacity was caused by loss of active anode materials through oxidation during the aging process. This type of behavior was expected, based on earlier similar tests of this type.

A comparison of the magnitude and phase Bode plots for the "aged" and standard electrodes over this temperature range shows an overall decrease in the impedance magnitude and phase angle is observed, particularly at the lower temperatures (see Fig. 5).

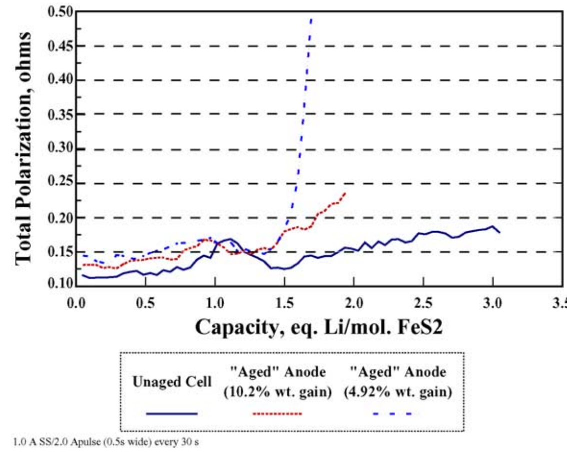

Fig. 4. Total polarization at 500 °C and a background current density of 125 mA^2 of Li(Si) (flooded)/LiCl–KCl (MgO)/FeS_2 cells made with unaged (control) and aged anodes.

For a practical application to thermal batteries deployed in missiles, etc. it would be more convenient to be able to measure the battery properties at or close to room temperature. Fig. 6 shows the magnitude and phase angle Bode plots at room temperature over frequency ranges where distinct differences in characteristics are observed between the standard electrode cell and the cell employing the "aged" electrode especially in the phase angle at 500 Hz.

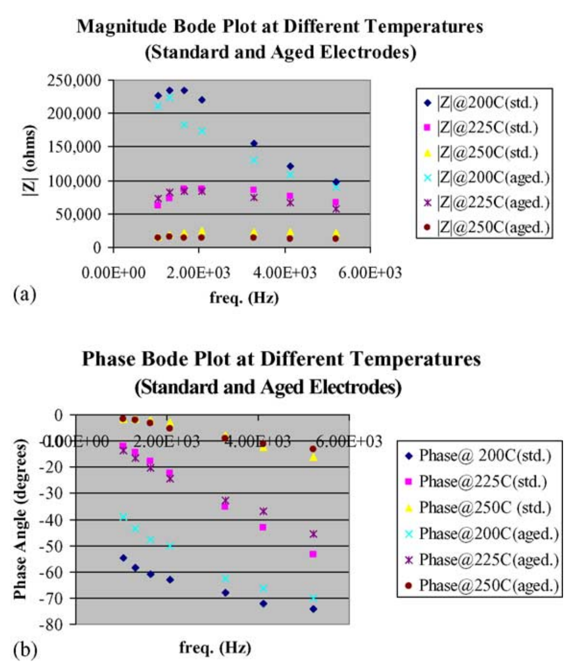

Fig. 5. (a) Bode plot of impedance magnitude for a Li(Si)/FeS_2 thermal battery employing the standard LiCl–KCl eutectic for both a standard (unaged) anode and for an "aged" (10% wt. gain) anode. (b) Bode plot of phase angle for a Li(Si)/FeS_2 thermal battery employing the standard LiCl–KCl eutectic for both a standard (unaged) anode and for an "aged" (10% wt. gain) anode.

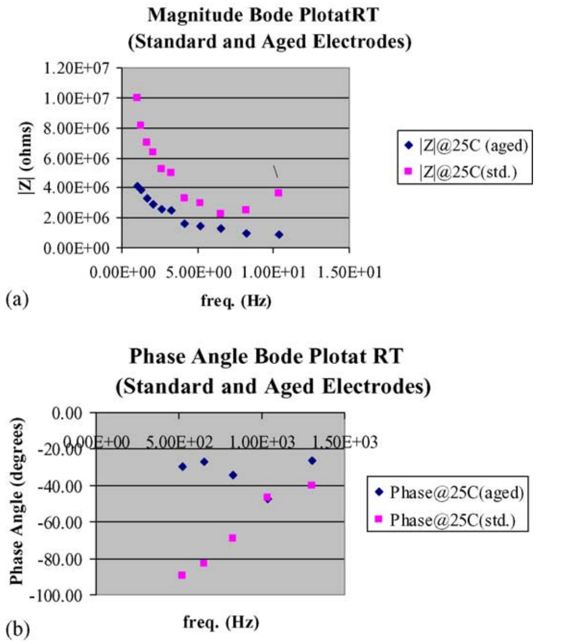

Fig. 6. (a) Low frequency, room temperature Bode plot of impedance magnitude for a Li(Si)/FeS_2 thermal battery employing the standard LiCl–KCl eutectic for both a standard (unaged) anode and for an "aged" (10% wt. gain) anode. (b) Mid-frequency, room temperature Bode plot of phase angle for a Li(Si)/FeS_2 thermal battery employing the standard LiCl–KCl eutectic for both a standard (unaged) anode and for an "aged" (10% wt. gain) anode.

2.3. Multiple cells

To determine if the impedance data for multiple cells in series would track that of a single cell, several tests were carried out on two-cell and three-cell stacks under the same conditions as for the original single cells. The Li(Si)/LiCl–KCl (MgO)/FeS_2 chemistry was used for these tests. The polarizations responses for the single, double, and triple cells are summarized in Fig. 7. The overall cell voltage per cell was higher for the double and triple cells than for the single cell. This was a direct result of the lower overall impedance on a per-cell basis of the double and triple cells.

ac impedance measurements on the two-cell stacks have also been analyzed and show some promising results. The phase plots show good monotonic variation with temperature. Both the impedance magnitude and phase angle are seen to progressively increase over a frequency range of 300–800 Hz as the temperature of the two-cell stack increases from 225 to 275 °C. This needs to be compared to two-cell stacks with aged electrodes for determining its utility for battery SOH determination.

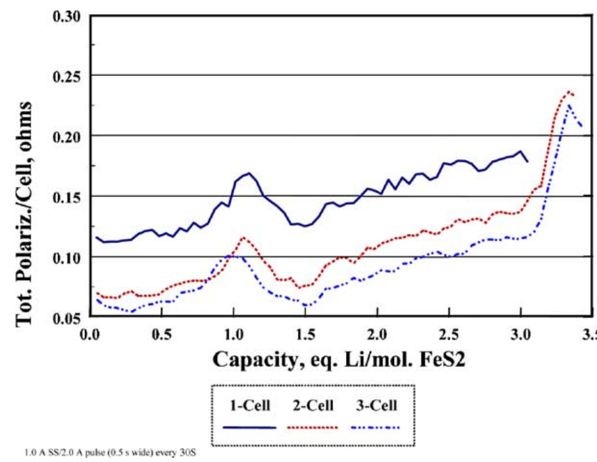

Fig. 7. Effect of number of cells on the total polarization per cell of Li(Si) (flooded)/LiCl–KCl (MgO)/FeS_2 chemistry.

3. Conclusions

We have measured ac impedance on Li-based molten salt thermal batteries with two different melting point electrolytes and have found that the impedance magnitude and phase change with temperature in a monotonic manner over specific frequency ranges at temperatures below the activation temperatures of the batteries. We have measured thermal batteries with fresh electrodes and with anodes aged to 5 and 10% weight gains. The aging of the electrodes shows up as changes in both the magnitude and phase at approx. 2 kHz at 200 °C and over a frequency range of 0–10 Hz for magnitude and 500–1000 Hz for phase at room temperature. We have studied single cells, two-cell stacks, and three-cell stacks (all with fresh electrodes) and find that the single cell stack results scale, as cells are stacked into batteries.

Acknowledgements

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