

Degradation Mechanism of $\text{LiMn}_2\text{O}_4/\text{graphite}$ Li-ion cells

K. Amine, J. Liu, S. H kang, A. Kahaian, I. Belharouak, D. Vissers, G. Henriksen
Argonne National Laboratory, 9700 South Cass Ave.,
Argonne, IL 60439, USA

Introduction:

Lithium manganese oxide spinel (LMOS) has many advantages over lithium nickel cobalt oxide in terms of cost (because of Mn abundance), improved cell safety (due to the superior stability of Mn^{4+} to Ni^{4+} in the fully charged state), and environmental friendliness. At room temperature, LMOS/graphite Li-ion cells have been shown to exhibit excellent cycle life and good rate capabilities [1]. However, these batteries showed poor electrochemical performance, such as short cycle life and poor storage performance at elevated temperatures, because of manganese dissolution in the electrolyte, which delays wide acceptance of this battery system by battery manufacturers.

In this work, we investigated the degradation mechanism of LMOS/graphite Li-ion cells at elevated temperatures. Experimental results regarding the galvanostatic cycling of LMOS versus various anodes (such as lithium metal, graphite, and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel) and AC impedance measurements using reference electrode equipped cells (RE) are reported in this article.

Experimental

The reference electrode cell used to investigate the role of each electrode to the cell performance was Li-Sn alloy thin film deposited on the tip of a 25- μm thick Cu wire. Experimental details of the RE cell construction are described elsewhere [2]. The RE cell was galvanostatically cycled at 55°C; after 25 cycles, the impedances developed in the RE cell were measured between the cathode and the RE, the anode and the RE, and the cathode and the anode in the frequency range 10 mHz-100 KHz.

Results and discussions

Figure 1 shows the galvanostatic cycling results of SLMOS/graphite cells cycled at room temperature (RT) and at 55°C. The SLMOS/graphite cells exhibited good cycling performance at room temperature [Fig. 1(a)]; with a capacity retention after 100 cycles of 88%. However, when cycling the cell at 55°C [Fig. 1(b)], a dramatic decrease in the capacity took place with only 50% of capacity retention after 100 cycles. In this case the amount of manganese dissolved in the electrolyte after storage at 55°C for 4 weeks was 5 ppm only. The small amount of manganese ion dissolved could not account for a large capacity drop in a full cell. To investigate the contribution of each electrode to the cell degradation, we performed an AC impedance measurement with the RE cell, the results of which are given in Fig. 2. The AC impedance was measured after one formation cycle at RT [Fig. 3(a)] and after 25 cycles at 55°C [Fig. 3(b)]; the open-circuit voltage at which the impedance was measured was 3.91 V and 3.95 V, respectively. At the initial stage of cycling, the impedance of the negative electrode was much smaller than that of the positive electrode, as is seen in Fig. 2(a). The positive impedance represents the bulk of the overall impedance of the cell (denoted as “Full” in Fig. 2). After cycling at 55°C, however, the impedance of the negative electrode is significantly increased, so that it overwhelms the impedance of the positive electrode.

From the results in Figs. 1-2, it appears that the degradation of the LMOS/graphite cells occurs as follows: Step I, disproportionation and dissolution of the Mn ions from the spinel powder into the electrolyte; Step II, migration of the dissolved Mn ions to the graphite anode; Step III, reduction of the Mn ions on the anode surface due to the chemical activity of the graphite; and Step IV, increase of charge-transfer impedance at the graphite/electrolyte interface due to a possible catalytic effect of Mn metal at the surface of carbon resulting in surface film formation at the anode.

To investigate the impact of the surface reactivity at the surface of carbon caused by the reduction of dissolved Mn- ions, we selected $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel (LTOS) as an alternative anode to graphite. Unlike carbon, this material cycles at a potential of 1.5V at which the Mn-ions are reduced and remained in the electrolyte solution. In this case, the cell cycled very well with no capacity loss after 100 cycles at 55°C.

To address the stability problem of the spinel, we investigated the impact of a stabilized spinel combined with the new lithium bis(oxalato)borate, $\text{LiB}(\text{C}_2\text{O}_4)_2$ (“LiBOB”) salt. Better cycling and aging performance were obtained in this case.

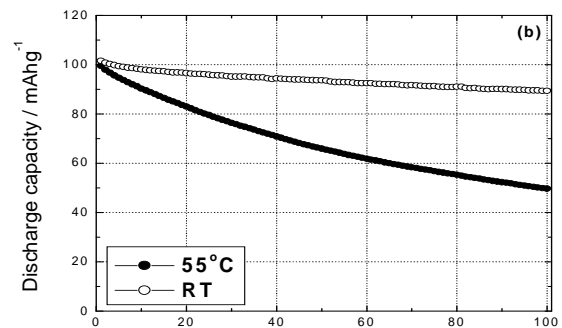


Figure 1. Variation of Cycle Number discharge capacity against cycle number of (a) SLMOS/Li and (b) SLMOS/graphite cells cycled at room temperature (RT, open circles) and at 55°C (solid circles).

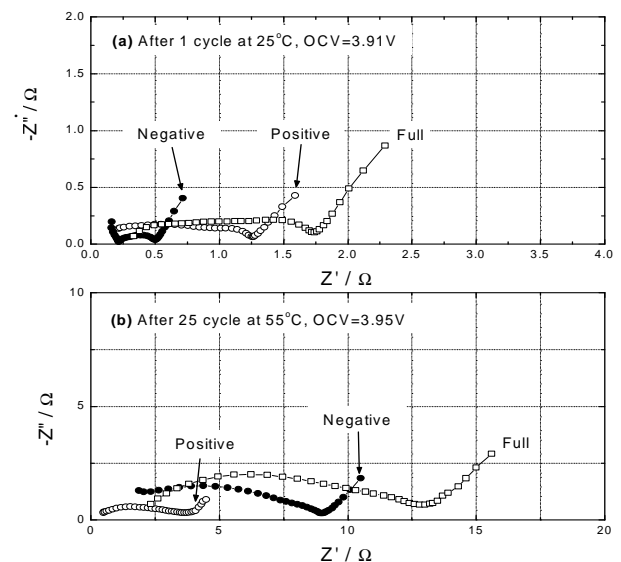


Figure 2. Impedance of graphite/SLMOS cells with Li-Sn alloy reference electrode (RE). (a) After 1 cycle at 25°C (b) after 25 cycles at 55°C.

References:

D. Abraham, J. Liu, C. H. Chen, Y. E.Hyung, M. Stoll, , K. Amine, and G. Henriksen, *J. Power Sources* **119-121**, 511 (2003).

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