Capacity Fade of Li-ion Cells at Elevated Temperatures Cycled Using Pulse and DC Charging Protocols

Branko N. Popov, Ramadass Premanand, Bala S. Haran, Anand Durairajan, Soto Herie, and Ralph E. White
Department of Chemical Engineering
University of South Carolina, Columbia, SC

Introduction

Capacity fading during cycling at ambient and elevated temperatures is one of the immediate problems facing Li-ion batteries.[1-5] The increase in the internal impedance of the battery upon cycling has been shown to be the most dominant effect in case of $LiCoO_2$ based Li-ion cells.

Our recent studies have shown that pulse charging can be used to prevent capacity fade in lithium ion batteries. Pulse current prevents the reduction to metallic lithium and oxidation of the electrolyte under overcharging conditions. Objectives of this study were to evaluate the capacity fade mechanism $LiCoO_2$ based Li-ion cells at elevated temperatures. The Sony US18650S batteries were charged using direct and pulse charging protocols. Impedance spectroscopy is used as a tool to characterize the internal resistances that are believed to contribute to the capacity fade of Li-ion cells.

Experimental

Sony US18650S cells were charged using two different protocols. In case of DC charging, the cell was charged at a constant current of 1A until the potential reached 4.2 V. Subsequently the voltage was held constant at 4.2 V to complete charging. In case of pulse charging, the cell was charged using pulse current charging protocol developed in our laboratories.

Solartron SI 1255 HF Frequency Response Analyzer and Potentiostat/Galvanostat Model 273A were used for the electrochemical characterization of Sony US18650S cells. Charge-discharge studies were carried out in the potential range of 2.0–4.2 V. The cells were left on open circuit for 1 h and after the potential stabilized, impedance studies were performed. The cell was stable during the experiments and its voltage changed less than 1 mV. EIS measurements were done on the cells at both charged and discharged states. The impedance data generally covered a frequency range of 0.002 to 5000 Hz. A sinusoidal ac voltage signal varying by +/- 5mV was applied.

The following studies were done to understand the processes occurring at individual electrodes of the cell. The can of cycled Sony US18650S cells was carefully opened at fully discharged state in a glove box filled with ultra pure argon. Next, pellet electrodes were made from the positive and negative electrodes of Sony US18650S cell and were used as working electrodes in the T-cell. Pure lithium metal was used as the counter and reference electrode. Separator taken from the Sony US18650S battery was used as a separator in the T-cell. The diameter of the pellet electrodes was 1.20 cm. 1 M $LiPF_6$ was used as the electrolyte in a 1:1:3 mixture of propylene carbonate (PC), ethylene carbonate (EC), and dimethyl carbonate (DMC). EIS studies were done on the T-cells to understand the influence of positive and negative electrode on total impedance of the cell. Impedance was measured at both charged and discharged states. The frequencies of the AC signal ranged from 10 kHz to 5 mHz.

Results and Discussion

The influence of temperature and two types of charging protocols namely DC charging and pulse charging on capacity fade has been studied. After 800 cycles, the discharge capacity of DC charged $LiCoO_2$ cell dropped to 840 mAh from 1200 mAh, a large capacity loss occurring after extended cycling. Pulse charged battery shows lesser capacity fade with a capacity of 1100 mAh after 800 cycles. CVs of $LiCoO_2$ and carbon electrodes indicate an increase in the interfacial resistance with cycling. It is also seen that $LiCoO_2$ deteriorates more severely than the carbon electrode. To confirm these results impedance spectroscopy was used to determine the interfacial impedance as well as the internal ohmic resistance at different charge/discharge cycles of the battery. The total cell resistance varies significantly with SOC, with resistance being higher at the discharge state. It is also seen that the impedance of the positive electrode dominates the total cell resistance.

Data from these studies for both DC and pulse charged batteries cycled at elevated temperatures (50 and up to 65^{o}C) will be presented.

Acknowledgment

Financial support provided by DOE Division of Chemical Sciences, Office of Basic Energy Sciences G. M. DE-FG02-96ER 146598 and National Reconnaissance Office is acknowledged gratefully.

References

1. M. J. Isaacson, M. E. Daman and R. P. Hollandsworth, *Proceedings of the 32nd International Society Energy Conversion Engineering Conference*, Vol.2, 31 (1997).
2. V. Ganesh Kumar, N. Munichanctaiah and A. K. Shukla, *J. Appl. Electrochem*., **27**, 43 (1997).
3. Ping Yu, James Ritter, Ralph E. White and B. N. Popov, *J. Power Sources,* **91**, 107 (2000).
4. D. Zhang, B. S. Haran, A. Durairajan, R. E. White and B. N. Popov, *J. Power Sources*, **91**, 122 (2000).
5. B. N. Popov, B. S. Haran, A. Durairajan, R. E. White and R. Cope, Abstract No. 111, The Electrochemical Society Meeting, Toronto May 14-18 2000.

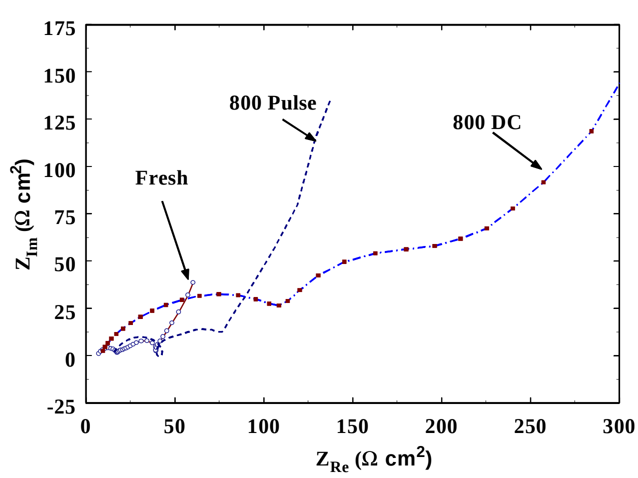

Fig. 1. Change of Impedance of carbon electrode with cycling.