

**Effect of the Initial Coulombic Efficiency of the Anode on the Over-discharge Behavior of a Li-ion Battery**

Z. Mao  
Carbon and Heavy Hydrocarbon Process Technology  
ConocoPhillips, Inc  
1000 South Pine  
Ponca City, OK 74602, USA

**INTRODUCTION**

Different graphitic materials are currently used as the anode material in Li-ion batteries by different battery manufacturers. These graphitic materials have different physical and electrochemical properties such as particle size and shape, reversible capacity and the initial irreversible capacity loss. It is generally accepted that a graphitic material with a high initial charging efficiency is desirable from the point of view of mass balance and overall energy density. For this reason, a great deal of research effort has been expended for the purpose of improving the initial charging efficiency of graphitic materials. As a result, significant progresses have been made with different physical and chemical surface treatment methods (1). As the initial charging efficiency is improved, the mass ratio of the cathode to anode materials must be balanced accordingly. As a result, the cycle life of a cell would be affected because the cycling potential windows for both the anode and the cathode are also changed. These changes also affect the behavior of a cell under abuse conditions such as overcharge and over-discharge. This communication note reports the characteristics of Li-ion cells that have different initial coulombic efficiencies under over-discharged conditions, specifically under short-circuit or discharged at 0 volt.

**EXPERIMENTAL**

Three-electrode cells were assembled using LiCoO<sub>2</sub> as the cathode material and different graphitic powders as the anode material. These graphitic materials have different initial coulombic efficiency as the anode material for Li-ion cells. The electrolyte used in the experiments was 1 M LiPF<sub>6</sub> in 40% ethylene carbonate, 30% dimethyl carbonate, and 30% diethyl carbonate mixture. The third electrode was a lithium metal.

These cells were first cycled twice under constant current condition within the cell voltage window between 2.5 and 4.15 volts. The cells were rested for 30 minutes, and subsequently discharged at a constant current to 0 volts. After that, the cells were rested for additional 30 minutes, and subsequently recharged and discharged in the same manner as the first and second cycle. Both the cell voltage and one of the electrode potentials versus the Li metal electrode were monitored during the experiments.

**RESULTS AND DISCUSSION**

Figure 1 shows the potential profiles of each electrode and cell voltage before and during discharging to 0 volts and after that. The rest potential of each electrode is the indication of the state of charge of the electrode, which depends on the mass ratio of the cathode to anode materials, and also strongly on the initial coulombic efficiencies of the electrode materials.

As shown in Fig. 1, the cell voltage rapidly drops to about 0.3 volts and then remains nearly constant before drops to 0 volt during the over-discharge. In this case, the initial coulombic efficiency of the anode material is significantly lower than that of the cathode material, consequently, when the capacity of the anode material is exhausted, the cathode still has a significant amount of capacity remaining. The over-discharge drives the carbon electrode potential to be higher than 3.5 volts, causing anodic dissolution of the copper substrate, as indicated by the plateaus near 3.5 volts in Fig. 1.

Figure 2 shows the rest potentials of each electrode and the cell voltage after the cells were over-discharged to 0 volt. It is illustrated here that the over-discharge has detrimental effect on the anode if its initial efficiency is lower than 93%. This effect reflects on the subsequent recharging efficiency and capacity

retention, as shown in Fig.3. It can be seen that the recharging coulombic efficiency increases with the initial efficiency and so does the capacity retention.

**CONCLUSIONS**

Over-discharging to 0 volt causes dissolution of copper substrate of the anode and has detrimental effect on the capacity retention. Use of graphitic materials that have a high initial coulombic efficiency can alleviate such effects.

**REFERENCES**

1. Y.P. Wu, E. Rahm, and R. Holze, *J. of Power Sources*, **114**, 228 (2003).

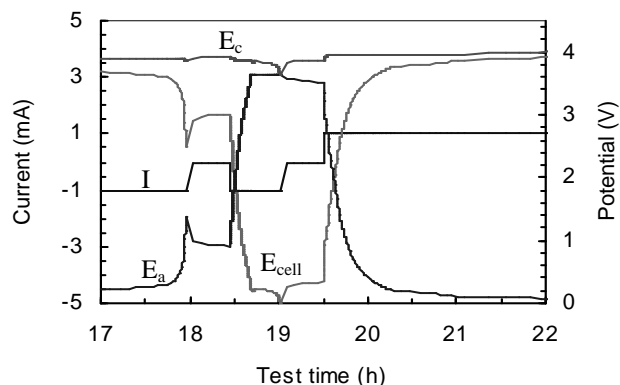


Fig. 1. Potential profiles of anode, cathode, and cell before, during, and after over-discharging to 0 volts

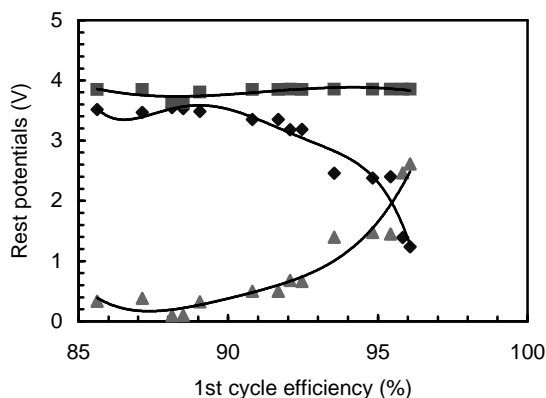


Fig. 2. The rest potentials of the anode, cathode, and the cell voltage after the cells were over-discharged to 0 volts as a function of the first cycle coulombic efficiency

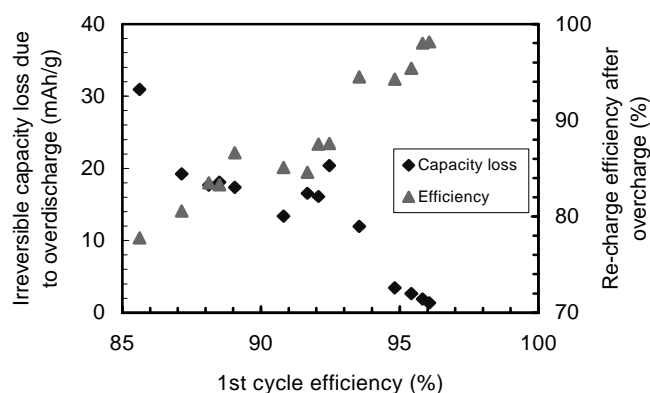


Fig. 3. The irreversible capacity loss due to over-discharging and the recharging coulombic efficiency as functions of the first cycle efficiency