Calendar life studies of lithium-ion batteries

Background

Lithium ion batteries are currently used in a wide range of applications. NASA uses high capacity lithium-ions batteries for its space mission. The battery should ensure long life and less self-discharge capacity loss in order to be used in long-term space missions. We, at the University of South Carolina are studying the calendar life performance of pouch Li-ion batteries. It is critical to determine the capacity loss due to self-discharge and to analyze the contributions to the self-discharge phenomena.

Problem Definition

Lithium Batteries exhibit self-discharge phenomena even at moderate oxidation levels due to electrolyte decomposition, and spontaneous Li^+ reinsertion due to instability of de-lithiated cathodes. Self discharge is predominantly due to loses occurring at the negative electrode and is governed by the electronic conductivity of the SEI layer. Moreover, aging of Li-ion cells depends upon the storage temperature as well. The objective of the work is to study the storage characteristics of lithium ion batteries. The effects of temperature, end of charge voltage (EOCV) with trickle charge and EOCV without trickle charge are to be evaluated on stored Li-ion cells in a stretch of two years. The batteries were tested under two different temperatures (5 ^{0}C and 35 ^{0}C), two different end-of-charge voltages (4.0 V and 4.2 V) and two different types of charging conditions (float and open).

Self-Discharge Phenomena in Lithium-ion batteries

The major factors contributing to the self-discharge in a lithium-ion battery are listed here:

- External electron leakage resulting from the poor isolating properties of the battery seals or gasket or from external finite resistance between the leads (external conductors, humidity...).
- Electrode/electrolyte reactions such as, anode corrosion or cathode reduction by the electrolyte or impurities.
- Partial dissolution of the electrode's active material.
- Electrode passivation by decomposition products Electrode mechanical disintegration or isolation from current collectors.
- Internal pressure built up and electrolyte leakage.

The solvent in the electrolyte has a tendency to oxidize and form an electron-ion-solvent complex. Self-discharge can also be explained as the tendency of the electron-ion-solvent complex to dissociate or recombine that determines the reversible or irreversible self-discharge. The main location of the side reactions (e.g., electron-ion-solvent complex formation as above) is the interface between the active material and the electrolyte. The most commonly adopted picture for the passivating film formed over the surface of the electrode material at the alongside of the electrolyte is called the SEI (Solid-Electrolyte-Interphase). Temperature plays a dominant role in determining the self-discharge losses. The usual way of analyzing the temperature influence is to assume that the side reactions rates follow an Arrhenius law through a coefficient linked to an

'activation-energy'. The difficulty comes from the fact that a self-discharge may result from several side reactions, each with their own activation energy and rate constant.
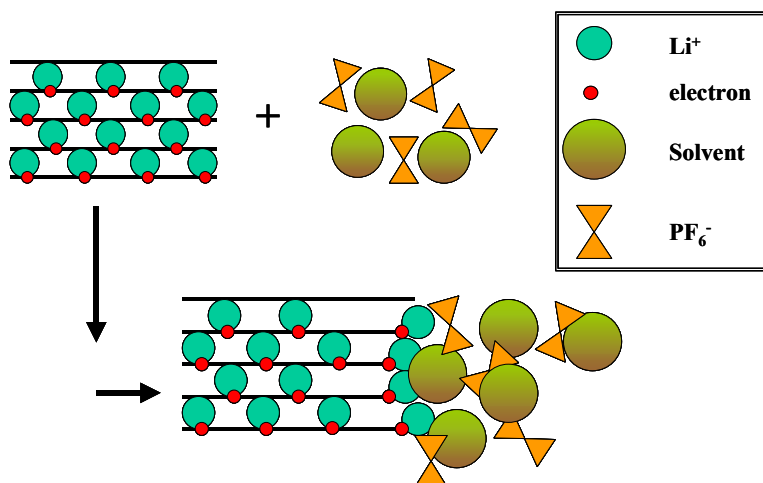

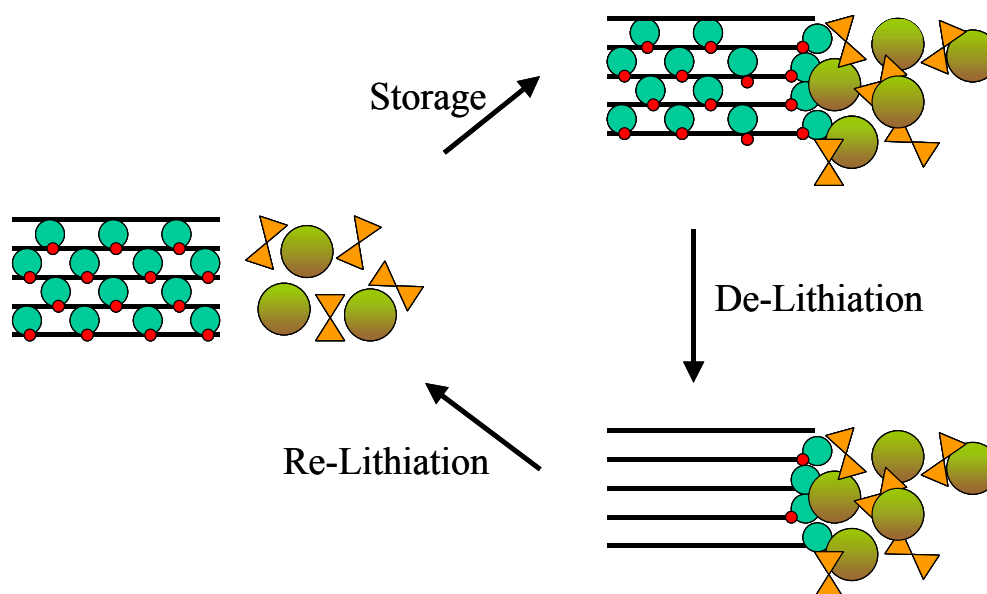Fig-1 Mechanism of the electron-ion-solvent complex formation

Fig-2 Schematic representation of the mechanism of the reversible capacity loss

In our experiments the storage studies were done at two different temperatures 5^0 C and 35^0 C with and without trickle charge (float) at two different voltages 4.2 V and 4.0 V. A capacity measurement experiment was done at every 1-month interval at 25 ^{0}C. During the capacity measurement tests, the cells were discharged at C/2 rate from their existing state of charge to 3.0 V to measure their residual capacity. The cells are then charged back to 4.2 V at C/5 rate with a taper to 50 mA. A second discharge to 3.0 V at the same rate will give the measure of the actual capacity of the cell. Impedance experiments were done at 100 % state of charge for all the cells during the capacity measurement tests. After the completion of the capacity measurement tests, all the cells

were restored to their original test conditions. The following data were analyzed every month

$$\text{Irreversible capacity loss (\%)} = \frac{\text{Initial Capacity - Actual Capacity}}{\text{Initial Capacity}} \times 100$$

$$\text{Total capacity loss (\%)} = \frac{\text{Initial Capacity - Residual Capacity}}{\text{Initial Capacity}} \times 100$$

$$\text{Reversible cap loss (\%)} = \text{Total Cap Loss(\%) - Irreversible Cap loss (\%)}$$

The total irreversible capacity loses in seven months of storage experiments for case is given in Fig-3.
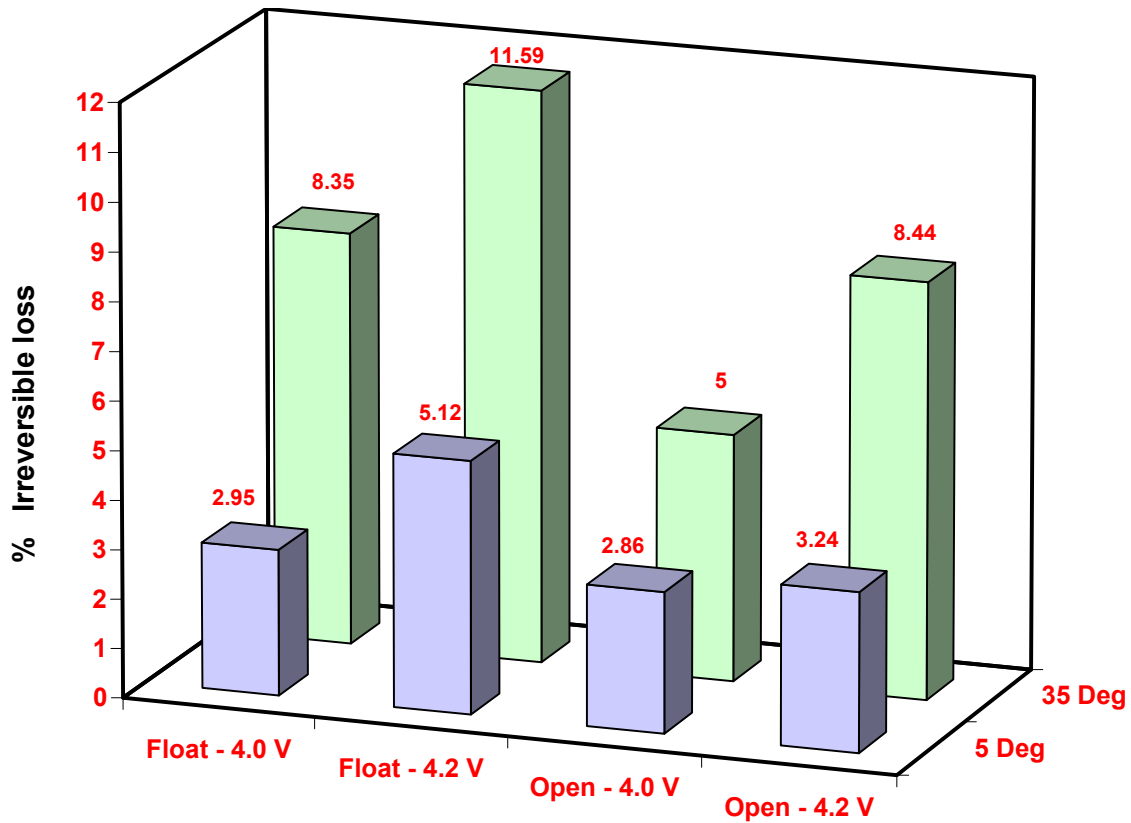

Fig-3 showing the irreversible capacity loss in 7 months of storage