Thermal Stability of Lithium Ion (Li-ion) Batteries

The calendar life and cycle life of Li-ion batteries are sensitive to the environmental temperature. An examination of commercial 18650 cell specifications reveal that all cells do not behave in the same manner. Typically, a Li-ion cells shows two types of capacity loss on storage at elevated temperature; a reversible capacity loss and an irreversible capacity loss. Interestingly, the values of each of these capacity fades are manufacturer dependent suggesting that they are both construction and material dependent. Similarly, the capacity fade rate on charge/discharge cycling of 18650 Li-ion cells can also vary from manufacturer to manufacturer. Our recent studies of Li-ion cells with reference electrodes have provided insight into the origin of these capacity losses

The traditional view has been that Li-ion battery degradation is largely due to thermal decomposition of the electrolyte. However, our recent investigations have shown that this is not correct. In this context we studied the thermal stability of lithium-ion battery electrolytes composed of $LiPF_6$ in a mixture of organic carbonate solvents. The generation of PF_5 via the thermal dissociation of $LiPF_6$ and its conversion to POF_3 in presence of moisture or alcohol impurities leading to an autocatalytic decomposition reaction is the primary source of thermal decomposition. It was found that the addition of low concentrations (3 –12 %) of Lewis basic additives provides a dramatic increase in the thermal stability of the electrolyte. The increased stability is linked to the formation of base: PF_5 complexes which reversibly sequester PF_5 preventing the decomposition of the electrolyte. Lewis bases investigated include pyridine, hexamethoxycyclotriphospazene (HMOPA), and hexamethylphosphoramine (HMPA). We hae found that our results can serve as a valuable model for stabilizing organic electrolytes against thermal decomposition initiated by Lewis acids. WE have also found that $LiPF_6$ solutions in mixed organic carbonates do not decompose when stored at 85°C in the presence of charged or discharged cathodes such as lithium cobalt oxide and lithium nickel-cobalt oxide. The cathodes stabilize the electrolytes apparently scavenging the impurities that catalyze the reaction. Thus, homogeneous chemical reactions in the electrolyte solution do not appear to be the ultimate cause of Li-ion cell thermal degradation. The most significant contribution to the cell's capacity and power fade upon storage seem to come from chemical reactions at the electrode-solution interfaces.

The question arises whether an accelerated test, either cycling or storage of Li ion cells at elevated temperature, can be used to predict life at room temperature. This author has formed some definite opinion on this from studies both commercial and custom made li-ion batteries. It is first of all useful to examine the theory behind accelerated tests.

The accelerated test is usually based on the Arrhenius relationship and relies upon the assumption that the logarithm of rate of capacity fade, K, is proportional to the inverse of temperature, T (in Kelvin).

$K = A \cdot e^{-E/RT}$ (1)

$$\log K = \log A - \frac{E}{2.303RT} \quad (2)$$

Here, A is a proportionality constant, E is the activation energy for the capacity fade reaction and R is the gas constant, 1.987. According to equation 2, a plot of logarithm of capacity fade rate versus 1/T will give a straight line from which the activation energy can be determined which then can be used to determine the life at an unknown temperature. It should be noted the fade reaction mechanism is assumed to remain the same over this temperature range

First of all we can show that that for an activation of energy of ~15 kCal/mole, the life of a cell would double for a 10 degree decrease in temperature. For this we differentiate equation 2 with respect to temperature and integrate between two temperature limits, giving

Log $\dfrac{K_2}{K_1}$ = $\dfrac{E\ (T_2\text{-}T_1)}{2.303\ R\ (T_1T_2)}$ (3)

It can be shown that the value of E, the activation energy, determines whether the Li-ion battery capacity fade will double, triple, or follow some other order, for every 10 degree rise in temperature. We can put in some numbers into equation (3) to see this outcome.

For the two temperatures of 40 and 50 °C with an activation energy, E, of 15 k Cal (15,000 Cal) /mole the fade rate will approximately double when going from 40 to 50 oC. (Note temperature is in Kelvin). Thus,

Log $\dfrac{K_{50}}{K_{40}}$ = $\dfrac{15{,}000\ (323\text{-}313)}{2.303 \times 1.987\ (323 \times 313)}$

= $\dfrac{150{,}000}{462635}$ = 0.32

Therefore, $\dfrac{K_{50}}{K_{40}}$ = $10^{0.32}$ = 2.1

That is the fade rate at 50 °C will be about 2.1 times faster than that at 40 °C for an E of 15,000 Cal /mole or conversely the life at 40 °C will be about twice as long as the life at 50 oC. If the activation energy is higher than 15 kCal/mole, the fade rate will increase more than twice from 40 to 50 °C or the life at 40 °C will be more than twice that at 50 °C. It is clear that a very good understanding of the relevant capacity fade reactions and their kinetics are needed for a comprehensive understanding of the thermal stability of Li-ion cells.

References:

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