

Aging mechanism in Li Ion cells

Michel Broussely, Philippe Biensan, Sylvie Herreyre
SAFT
BP 1039, 86060 Poitiers, France

When studying battery aging, a difficulty is to accelerate the degradation reactions in order to quickly anticipate battery life. Temperature increase and accelerated cycling are the most usual ways, This is also true for the Li ion cells. In addition, because of the change in chemical potential of the positive electrode with the state of charge, the maximum charge voltage, or floating voltage, are also significant parameters.

Previous work ⁽¹⁾ pointed out the capacity loss on storage due to lithium corrosion from the negative electrode through the passivating layer, governed by its electronic semi-conductivity, and following an Arrhenius law with temperature. This effect is essentially independent of state of charge, as the potential of the negative electrode is almost constant. Update of the on going long term testing, continues to support this analysis and will be presented. As an example, figure 1 shows the residual capacity of $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ / graphite HE batteries (High Energy) measured at C/8 periodically during 18 months continuous floating at 3.9 or 3.8V, 40°C. These batteries are a three cell parallel assembly. No significant capacity loss, is experienced up to now, and, from previous results at higher temperature, this degradation rate is not expected to increase. In the same time a power loss on aging was experienced at high temperature, due to cell resistance increase, and attributed to the positive electrode. As it can be seen on figure 2, this effect is greatly influenced by temperature, but tends to level with time. At 40°C, or 20°C, the resistance remains unchanged after about 8 months of slight increase. Higher floating voltage would induce more power degradation. In similar experiments, physico-chemical analysis of the electrodes after cell dismantling show no evidence of materials modification in structure or composition, either in positive or negative electrodes. While the electrochemical capability of the negative carbon electrode remains intact, kinetic property of the positive is reduced, and side reactions involving the interaction with the electrolyte are anticipated, which will be discussed. The chemical nature of positive material has an influence, and specific additives may play a significant role.

From these results and additional experiments which will be described, good calendar life of these lithium ion cell design can be anticipated even at elevated temperature such as 40°C. It will be all the longer since the maximum permanent voltage is moderate, which is a definite advantage of the nickel based system, over cobalt and manganese ones

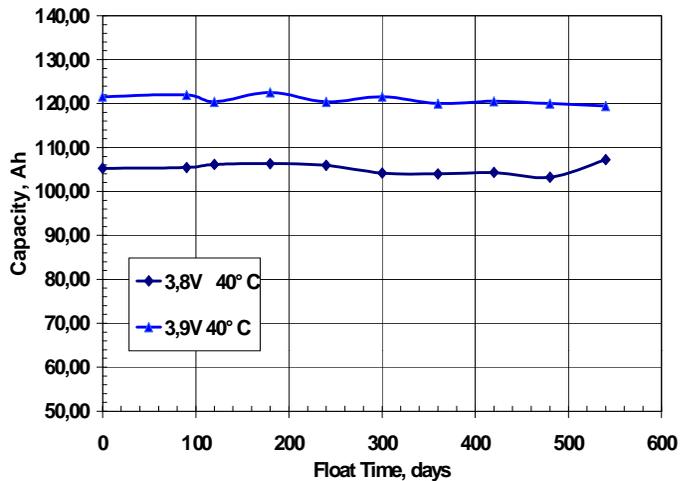


Figure 1: Capacity evolution of HE cells, LiNiMO2 / Graphite, during floating at 3.8V and 3.9V, at 40°C continuously. Residual capacity measured at C/8 @40°C.

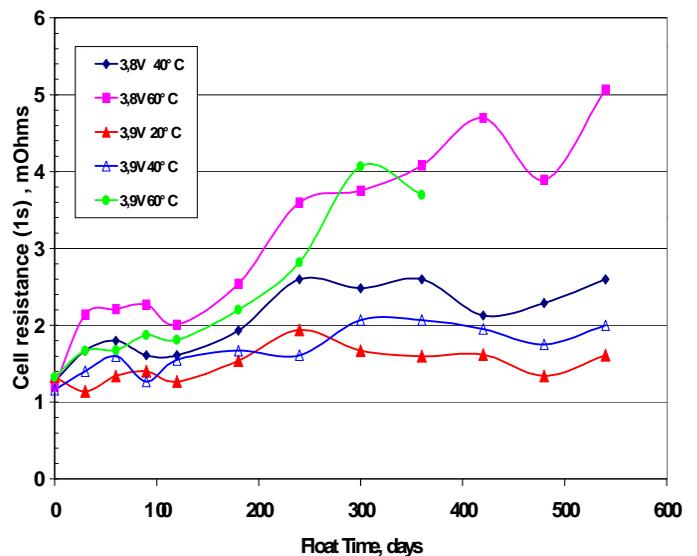


Figure 2: Resistance (1s) of HE cells LiNiMO2 / Graphite measured periodically at 20°C, after floating at 38V or 3.9V @ temperatures from 20 to 60°C.

(1): M. Broussely, S.Herreyre, P.Biensan, P. Kaszteljna, K.Nechev, R.J.Staniewicz, Proceedings IMLB10, Como, (2000), to be published in Journal of Power Sources.