

Influence of Temperature and Cycling on Electrode Degradation - Experimental and Modeling Study

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As the Li-ion battery technology expands into the automotive sector with high requirements on performance and durability, battery aging and materials degradation are increasingly important issues. Large efforts are therefore put into understanding the processes leading to capacity and power fade as the battery is used. However, the study of aging is complex since the degradation can be the combined effect of several different processes occurring in different parts of the cell [1]. There is a need for electrochemical tools able to identify changes in properties that influence the performance. In LiFePO₄/graphite cells, loss of cyclable lithium is often found to be a main mechanism in cell aging from continuous film growth on the graphite electrode [2,3], but material degradation or resistive films can also affect the capacity and impedance of the cell. Additionally, aging is affected by temperature and terms of usage, and it is therefore important to perform aging in a realistic scenario for a given application [4].

In this work, we are investigating the influence of temperature and cycling on the electrode degradation of LiFePO₄ and MCMC graphite in correlation to full cell behavior. The work is focused on a comparison of measured electrochemical impedance spectra of fresh and aged harvested electrodes coupled to a physics-based impedance model. The electrode degradation is evaluated by fitting the model to the experimental EIS data using input from capacity and SEM measurements [5,6]. This enables a detailed evaluation of changes in properties directly affecting the performance of the battery. The electrochemical measurements are performed in a three-electrode set-up using lithium as reference and counter electrodes and 1 M LiPF₆ in 1:1 ethylene carbonate (EC): diethylene carbonate (DEC). The separate measurements of each electrode are essential for a detailed EIS analysis and assignment of electrode properties as the two electrode signals overlap in the full cell.

The EIS model describes a homogenous porous electrode with electrode kinetics, ion transport in concentrated electrolyte, and diffusion in the active material. To account for possible degradation effects, the model contains a simple particle size distribution, local contact resistances between the active material and the conductive additive, resistive films on active material, current collector resistance, and capacitances on all conductive surfaces.

The electrodes were harvested from pouch cells previously aged by either storage or by a synthetic hybrid vehicle cycle at 22 and 55 °C [7]. A gradual decrease in IC capacity and increased impedance were seen at both temperatures, though more pronounced at higher temperature, until reaching end- of- life (EOL), at which point the hybrid cycle could no longer be performed.

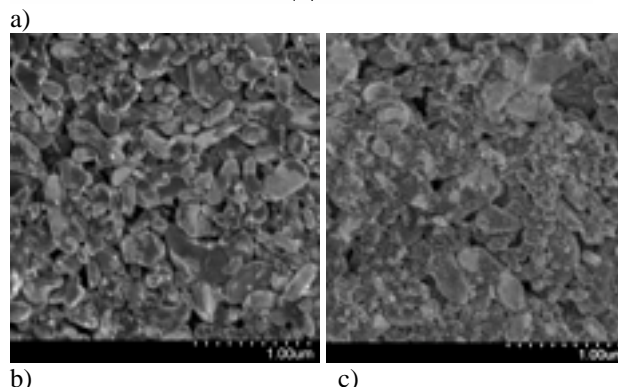
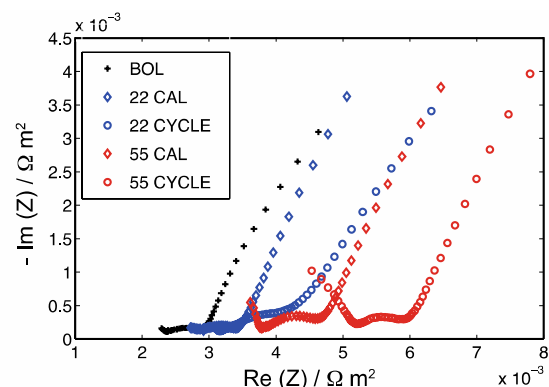


Figure 1: a) EIS spectra of LiFePO₄ measured vs lithium reference electrode for beginning- of- life (BOL), calendar (CAL) and cycle (CYCLE) aged at 22 and 55°C. b) SEM of LiFePO₄ at BOL and c) after cycle aging at 22 °C.

To further assess the causes of the full cell performance loss, the degradation on each electrode was investigated in a following step. Figure 2 displays the experimental EIS spectra of the positive electrode aged at different scenarios and temperature and example of SEM images fresh and cycle aged of LifePO₄ at 22 °C. At 22 °C the calendar aging caused negligible degradation on either positive and negative electrodes, while the LiFePO₄ was the main contributor to the impedance increase for the cycle aged cells, mainly due to impeded mass transport through the porous structure and loss of active material [5]. A decrease in porosity is also indicated by the depositions visible in the SEM image, see fig 1c. At the higher temperature, an accelerated formation of resistive films takes place on both electrodes [6]. Combining characterization of individual electrodes with detailed physical modeling is shown to be a powerful approach in the further understanding of aging in batteries.

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