Battery Aging Impedance Spectroscopy and Incremental Capacity Analysis

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***Abstract*— We analize electrochemical LiFePO4 cells with impedance spectroscopy and incremental capacity analysis in order to establish a correlation with capacity fade. We found that polarization and diffusion impeances increased with aging, but at different rates depending on the aging stage. This aging stage dependence was also found in ICA analyzes, where the lithium intercalation was investigated. A correlation with capacity decrease measured with Coulomb counting was established.**

***Index Terms*—Battery, state of health, entropy, degradation, impedance spectroscopy.**

I. Introduction

BATTERIEs are widespread as electrical energy storage. Several chemistries are used such as lithium-ion, NiMH or lead acid. Li-ion are preferred in mobile applications due its high energy and power densities per unit volume. One of the main concerns is how to measure their State of Charge (SoC) and State of Health (SoH) during operation. Several experimental techniques are available, such as open circuit or cell voltage, Coulomb counting, impedance or algorism approaches [1], [2]. Two remarks have to be pointed out: SoC and SoH inferred from measurements using models because they cannot be measured directly, and battery composition completely modifies the behavior of the experimental results, which prevents to use similar models for different batteries.

Impedance spectroscopy is a reliable experimental technique that has been used for battery characterization for long [3], [4]. It provides an insight that allows discriminating time rates behavior, spatial resolution, and electrical performance when it is conveniently supported by a model. This technique stand alone is not able to predict SoC or SoH. In combination with other techniques it can be very useful. In this contribution, we investigate the relationship of SoH with impedance spectroscopy and incremental capacity analysis.

Incremental capacity analyses (ICA) consists of charge and discharge the battery at a very slow rate (C/25 or smaller), obtain the open circuit voltage, allowing the battery to rest, and relate the injected charge per unit of voltage to open circuit voltage [5].

The combination of a quasistatic measurement such as ICA and a dynamic measurement such as EIS may help to elucidate the behavior of SoH in electrochemical cells [6]. In this contribution we investigated 0.4 Ah cylindrical LiFePO4 cells. Cycling, EIS and ICA measurements were carried out in a VSP Biologic potentiostat.

II. Results and discussions

A. Impedance Spectroscopy Analyses

Impedance results for a LiFePO4 cell as a function of cycling are depicted in Fig. 1. Battery aging and cycling modifications can be clearly observed in the Nyquist diagram. The evolution of the polarization and diffusion resistances are analyzed separately in Fig. 2. We observe a significant step at the very beginning of cycling and an abrupt increase in the range of 200-300 cycles.

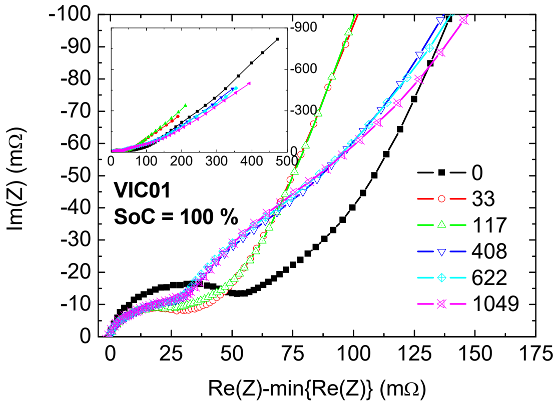

Fig. 1 - Nyquist Impedance diagram.

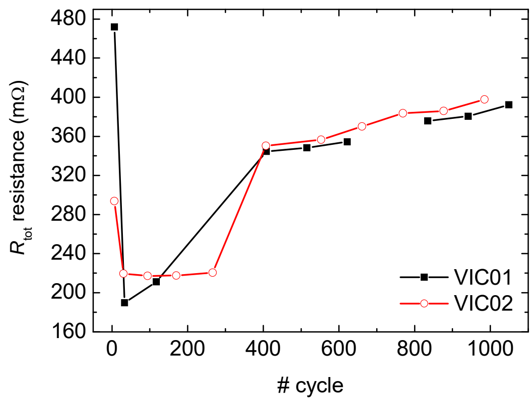

Fig. 2 - Total resistance evolution represented as the addition of polarization and diffusion resistances.

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B. Incremental Capacity Analyses

The evolution of ICA is illustrated in Figs. 3 and 4. We observe how capacity decreases with aging. The observed peaks correspond to the different stages of the graphite negative electrode. This is because LFP electrodes exhibit a unique plateau that extends to almost all the SoC range. Thus, the peaks shown in Fig 3 corresponded to lithium extraction of the graphite electrode. In particular, peaks 4 and 5 are related to the phenomena of Li^+ deintercalation at stages LiC_{12} and LiC_6, where most of the capacity is extracted.

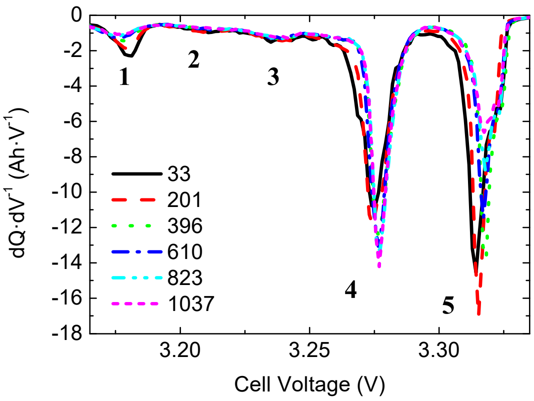

Fig. 3 - Incremental capacity analysis of a VIC cell (LFP) at different SoH at a C/25 discharge rate.

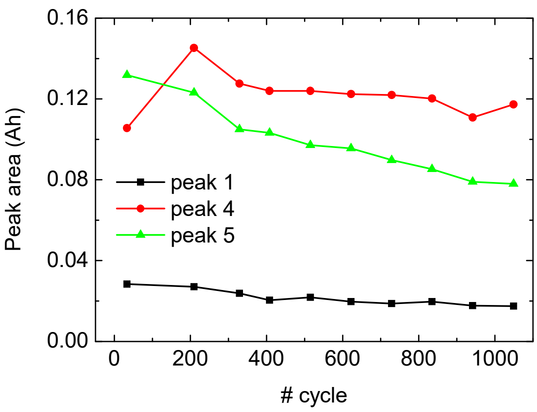

Fig. 4 - Evolution of the area of peaks obtained from ICA of a LFP cell at different SoH and at a C/25 discharge rate.

Capacity behavior shows a small increase from 0.410 Ah to 0.42 Ah during the first 30 cycles, then decrease to 0.4 Ah until 300 cycles and then the capacity decreased at a smaller rate. Thus, capacity impedance, EIS and ICA show a correlation which can be useful for battery assessment. More results and discussions connecting capacity fade, EIS and ICA will be presented, for different chemical cell compositions.

III. Conclusions

We investigated several batteries with impedance spectroscopy and ICA. A correlation between capacity fade, impedance evolution and lithium loss was found. We conclude that the combination of both techniques can be useful to discriminate different degradation mechanism occurring in the battery during aging.

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