Analysis of the Deposit Layer from Electrolyte Side Reaction on the Anode of the Pouch Type Lithium Ion Polymer Batteries: The Effect of State of Charge and Charge Rate

Victor A. Agubra [a,*], Jeffrey W. Fergus [a], Rujian Fu [b], Song-yul Choe [b]

[a] Materials Research and Education Center, 275 Wilmore Laboratories, Auburn University, Auburn, AL 36849, USA
[b] Department of Mechanical Engineering, 1418 Wiggins Auburn University, Auburn, AL 36849, USA

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ABSTRACT

The formation of the solid electrolyte interface (SEI) layer on the surface of the anode electrode of a lithium ion battery prevents further electrolyte decomposition reaction. However, at certain battery operating conditions, the SEI breakdown leading to more electrolyte decomposition reactions that form several species on the anode electrode surface. This paper focuses on the effect of battery potential and charge rate on the decomposition side reaction on the anode electrode of a lithium ion polymer battery, as a result of the breakdown of the SEI layer. The results from this study indicate that raising the state of charge (SOC) increases the rate of the electrolyte decomposition side reaction that resulted in formation of a thick deposit layer at the electrolyte/electrolyte interface. This deposit layer contains lithium that can no longer participate in the reversible electrochemical reaction. In addition, at high cycling potential and charge rates the amount of lithium in the graphite after complete cell discharge increased due to the entrapment of lithium in the graphite. The amount of irreversible capacity loss for the batteries cycled at high potential and current correlates with the amount of trapped lithium in the graphite and the growth of the deposit layer thickness at the electrode/electrolyte interface.

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1. Introduction

The high energy/power density and excellent cycle life of the lithium-ion battery (LIB) compared to other batteries chemistries, e.g. lead acid and nickel-cadmium, have positioned it as the preferred portable energy source for most consumer appliances and in the automotive industry for electric vehicles (EV) and hybrid electric vehicles (HEV). However, several reported battery failures during its operation have raised several safety concerns for the LIBs, thus hampering its large scale application. The performance of the lithium-ion battery depends on the development of materials for the various battery components [1–3]. The degradation of these components during operation adversely affects the energy delivery of the LIB. Mechanisms such as loss of accessible lithium ions, degradation of electrodes, binder, current collectors, and decomposition of the electrolyte have been reported to contribute to battery capacity fade [4–7].

A robust SEI layer will prevent further electrolyte solvent reduction on the carbon electrode. However, at elevated temperature, the metastable species $ROCO_2Li$ within the SEI layer decomposes into more stable compounds $–Li_2CO_3$ and LiF, which distort the SEI layer and create a porous SEI structure that exposes the graphite surface to more electrolyte decomposition reaction [8,9]. The distortion of the SEI layer leads to the formation of additional deposit layers on top of the SEI. These side reactions tend to consume recyclable lithium ions [9]. In addition, the surface layer formed on the anode could clog the pores on the carbon anode electrode and may limit the accessibility of lithium ions to the anode surface [10,11], which can lead to an increased in the charge transfer/Ohmic resistance and overall impedance of the battery [12–15]. This surface layer affects the electrochemical reaction on the surface of the anode and thus impacts on the reversible capacity of the LIB.

This paper presents a quantitative and qualitative analysis of the effect of the state of charge (SOC) and charge rate on the growth of the deposit layer at the anode electrode/electrolyte interface. In this work the deposition due to solvent reduction was observed only at the graphite electrode - reaction on the cathode was considered negligible. Understanding how the battery charging protocol influences the formation of the deposit layer is critical to effectively controlling/limiting these operational parameters to extend the operational lifetime of the lithium ion battery.

2. Experimental

2.1. Battery Chemistry

The batteries used in this study were large format pouch type-lithium ion polymer batteries from battery manufacturer LGChem with a Li(Mn,Ni,Co)O_2 cathode and the anode material made of carbon with polyvinylidene fluoride (PVDF) as the binding material. The current collectors of the anode and cathode electrodes are copper and aluminum, respectively. The electrolyte is an inorganic salt, $LiPF_6$, with co-solvents of ethylene carbonate (EC), and dimethyl carbonate (DMC). The nominal capacity of each battery is 15.7 Ah with an operating voltage level of 2.5 to 4.15 V.

2.2. Cycling Test

The charge/discharge cycles were performed using an in-house designed test station comprised of a programmable charging system, a programmable electronic load system and a data acquisition system that are computer controlled using LabVIEW^{TM}. The testing system allowed for the input of various charging conditions, such as C-rate and state of charge (SOC). The battery fixture was located in an environmental chamber to allow for control of the external temperature at 25 °C ± 2 °C.

The batteries were charged by a constant current-constant voltage (CC-CV) charging protocol at room temperature (25 °C ± 2 °C). In each cycle, the batteries were discharged with a constant current until the terminal voltage decreased to the voltage corresponding to the desired lower SOC (e.g. 25% = 3.13 V) and then charged with a constant current up to the voltage corresponding to the upper SOC (e.g. 3.78 V) followed by a constant voltage (CV) charge. After every 20 cycles, a 1 C (15.7 A)

Table 1
Test matrix used to carry out the electrochemical aging experiment, each battery was cycled at SOCs set within 65% capacity band of the battery.

State of Charge	Equivalent cycling Voltage (V)	C-rate/Current (A)	Other Conditions
25–90%	3.13–3.78	4C/62.8	25 °C @
5–70%	2.63–2.94		600 cycles
25–90%	3.13–3.78	3C/47.1	
5–70%	2.63–2.94		
25–90%	3.13–3.78	2C/31.4	
5–70%	2.63–2.94		

discharge-resting-charge profile was applied to the battery to measure its capacity. The capacity (Q_{max}) was calculated by integrating the current when the cell is being discharged from 100% to 0% SOC (i.e. 4.15 V to 2.5 V) using 1 C current (15.7 A) at room temperature. The Q_{max} data for each battery was recorded every 20 cycles. The battery was rested for 10 minutes before and after the Q_{max} measurement. The pre-test terminal voltages for the desired SOC were determined by coulomb counting and then adjusted by capacity. Table 1 summarizes the test matrix used in cycling the batteries.

2.3. Electrochemical impedance spectroscopy (EIS)

A Gamry electrochemical impedance spectroscopy (EIS) framework in galvanostatic mode was used to apply different frequencies (1 mHz to 1 kHz) of small AC excitation current (1 A) to battery and voltage responses were collected at 25 °C. A bipolar power supply was used to amplify the signal from EIS signal board. The measured impedances of the batteries were fit using the equivalent circuit model (Fig. 3a insert) was used to extract resistances, the SEI
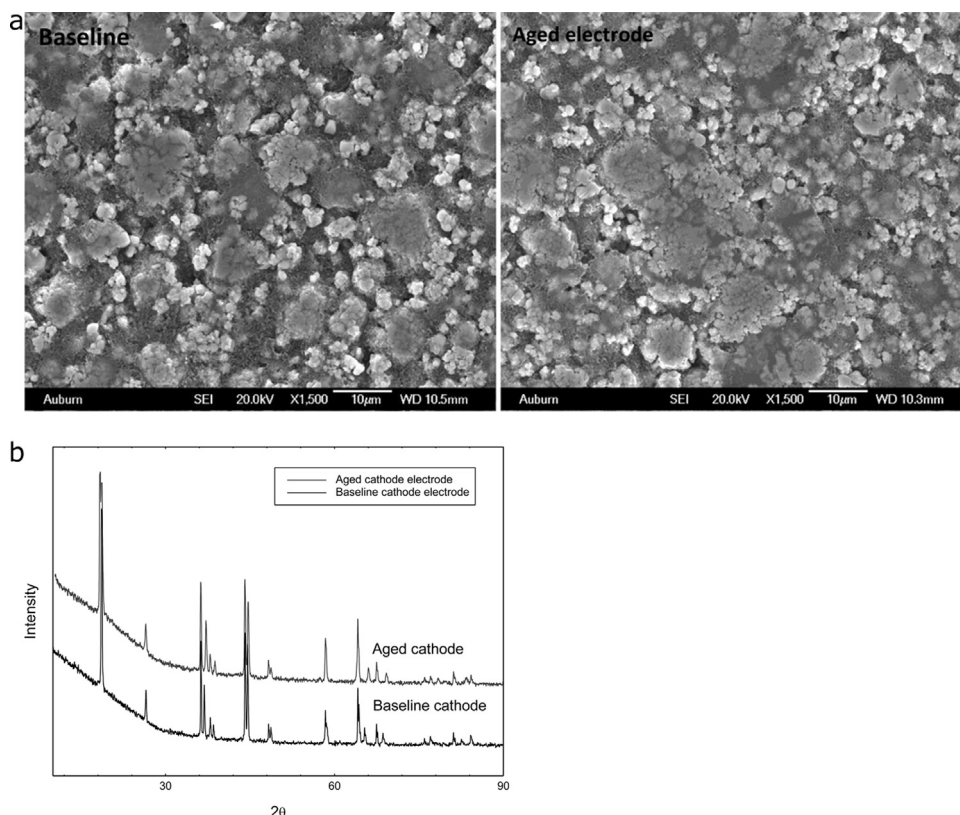

Fig. 1. (a) SEM micrograph showing the similarity of surface morphology of the baseline cathode and aged cathode electrode after cycling 600 cycle at 25–90% SCO and 4 C charge rate, (b) XRD spectra of baseline and aged cathode electrode showing no new phases formed aged aging the cell at 25–90% SOC and 4 C charge rate.