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Stress evolution and capacity fade in constrained lithium-ion pouch cells

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HIGHLIGHTS

- Stack stress is a dynamic quantity that evolves during electrochemical cycling.
- The initial applied stack pressure determines how stress evolves during cycling.
- Small stack stresses prevent layer delamination, benefiting long term performance.
- Higher stress causes higher rates of capacity fade through cycleable lithium loss.
- Stack stress leads to localized separator deformation and chemical degradation.

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ABSTRACT

The effects of mechanical stress on lithium-ion battery life are investigated by monitoring the stack pressure and capacity of constrained commercial lithium-ion pouch cells during cycling. Stack stress is found to be a dynamic quantity, fluctuating with charge/discharge and gradually increasing irreversibly over long times with cycling. Variations in initial stack pressure, an important controllable manufacturing parameter, are shown to produce different stress evolution characteristics over the lifetime of the cells. Cells manufactured with higher levels of stack pressure are found to exhibit shorter cycle lives, although small amounts of stack pressure lead to increased capacity retention over unconstrained cells. Postmortem analysis of these cells suggests a coupling between mechanics and electrochemistry in which higher levels of mechanical stress lead to higher rates of chemical degradation, while layer delamination is responsible for the capacity fade in unconstrained cells. Localized separator deformation resulting in nonuniform lithium transport is also observed in all cells.

1. Introduction

Lithium-ion batteries are finding application in many large scale technologies such as electric vehicles, aerospace, and grid level storage. For such applications it is necessary to develop batteries with long cycle and calendar lives as battery replacement is impractically expensive. To this end there have been many studies investigating the various competing aging mechanisms that occur in lithium-ion batteries such as SEI growth, electrode material loss, and separator pore closure [1–3]. These aging studies consider a wide range of parameters (e.g. state of charge, depth of discharge, charge/discharge rate, charge variability, and temperature) to better understand the effects of different operating/environmental conditions on aging [4,5]. One important parameter that has been neglected in the literature is the effect of compressive stack pressure on lithium-ion battery aging.

Compressive stack pressure is present in all lithium-ion batteries and is used to maintain intimate contact between battery components as well as to prevent layer delamination and deformation during operation. This stack pressure is applied during manufacturing when the electrode stack is placed into a rigid constraint and is typically in the range of 0.1–1 MPa. Examples of rigid constraints are the rigid housings placed over pouch cells in design applications or the canisters of cylinder or prismatic cells. While the initial application of this stack stress is controlled during battery manufacturing, this stress is a dynamic quantity that varies over the lifetime of the cell. During operation the compressive stress at the stack level within the cell fluctuates owing to expansion of the electrodes within a constrained environment. The issue

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of mechanical stress becomes increasingly important as higher capacity materials with higher volumetric expansions (e.g. silicon) are incorporated into battery electrodes. Other competing mechanisms such as SEI growth [6], binder swelling [7], and viscoelastic creep [2] further complicate prediction of stack level stress evolution in batteries.

Typical studies on mechanical stress evolution in lithium-ion cells focus on stress arising within individual electrode particles or within the plane of the composite electrodes [7–9]. These particle level and composite electrode level stresses have been linked to capacity fade through particle exfoliation and SEI growth mechanisms. Previous work has also suggested links between stack level mechanical stress and capacity fade [2,3], but no publications have explicitly investigated stack level stress in lithium-ion cells and its effects on capacity fade. To date there has been only a limited number of studies on the subject of stack level stress: a few experimental measurements of stack level stress evolution [10,11] and thickness changes [12] during cycling, as well as well as numerical simulations of stress induced in the separator by electrode expansion [13].

This paper focuses on measuring the stack level stress evolution in constrained commercial pouch cells and its effect on rate of capacity fade. It is shown that the level of initial stack pressure can strongly influence the stress evolution and capacity fade characteristics of cells, with higher stress levels showing higher rates of capacity fade. A postmortem analysis of the cycled cells indicates that loss of cycleable lithium is the main failure mechanism, with higher stressed cells exhibiting higher rates of capacity fade. These results suggest an important coupling between mechanical stress and chemical degradation, possibly through inhomogeneous electrode utilization due to transport restriction from separator deformation [3].

2. Experimental

Commercial 500 mAh pouch cells with nominal dimensions of 25 mm × 35 mm × 6.5 mm are used in this study. The active materials are lithium cobalt oxide and graphite and the electrolyte is $LiPF_6$ in organic solvent. These cells are initially discharged at a C/2 rate until reaching a 2.7 V cutoff before being placed into the constraint fixture shown schematically in Fig. 1. Subsequent charging results in stress build up due to electrode expansion.

The constraint fixture consists of a pouch cell in series with an amplified load cell. An aluminum plate is placed between the pouch cell and load cell to distribute the mechanical load evenly along the flat face of the pouch cell. The load cell and pouch cell assembly is then clamped down between two aluminum plates held together with nuts and bolts. Prior to tightening the nuts, a controlled load is applied with a compression testing machine according to the initial load prescribed in Table 1. After the initial load is applied the nuts

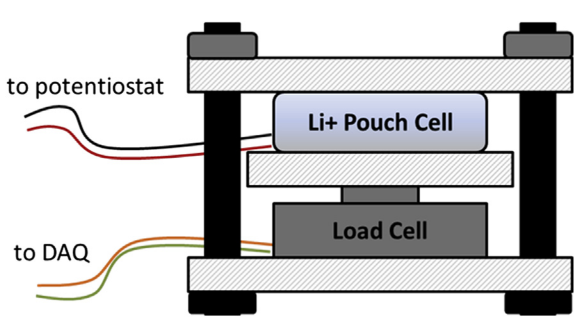

Fig. 1. Schematic of the constraint fixture used to maintain and measure compressive stack stress.

Table 1
Summary of cell stack pressures in MPa. Initial is the stack pressure applied before stress relaxation occurs. Min and Max correspond to the minimum and maximum stresses experienced by the cells after stress relaxation.

Stack pressure	Initial	Min	Max
Unconstrained	–	–	–
Low	0.05	0	0.5
Medium	0.5	0.2	1.5
High	5	1	3

are gently secured in position and thread-locking adhesive is applied to prevent the nuts from loosening during the cycling portion of the test. The constraint fixture with pouch cell is removed from the compression tester for electrochemical cycling.

The pouch cells are cycled using a C/2 CCCV scheme between 4.2 V and 2.7 V with a C/50 cutoff. The cells are cycled at room temperature, although precise temperature control is not used. Mechanical and electrical data is collected every 10 min. After cycling, the pouch cells are disassembled in an argon atmosphere containing less than 0.1 ppm water vapor and oxygen. Coin cells are fabricated using electrodes harvested from the pouch cells. These electrodes have the active material removed from one side to expose the current collector for good electrical connection. The area of the negative electrode in each cell is slightly larger than the area of the positive electrode to prevent misalignment. The graphite anodes half cells are cycled between 0.01 V and 1.3 V, and the lithium cobalt oxide half cells are cycled between 2.8 and 4.3 versus lithium.

3. Results and discussion

3.1. Mechanical stress evolution

Typical plots of compressive stack stress as a function of time for cells held at different stack pressures are shown in Fig. 2 for early times and in Fig. 3 for the entire duration of the cycling test. To understand these stress evolution plots of the constrained pouch cells it is necessary to first understand the constant thickness nature of the rigid constraint. The constraint shown in Fig. 1 constrains the pouch cell to maintain a constant thickness such that stress, not thickness, is free to evolve. Stress changes therefore correspond to the cell thickness changes that would occur in the

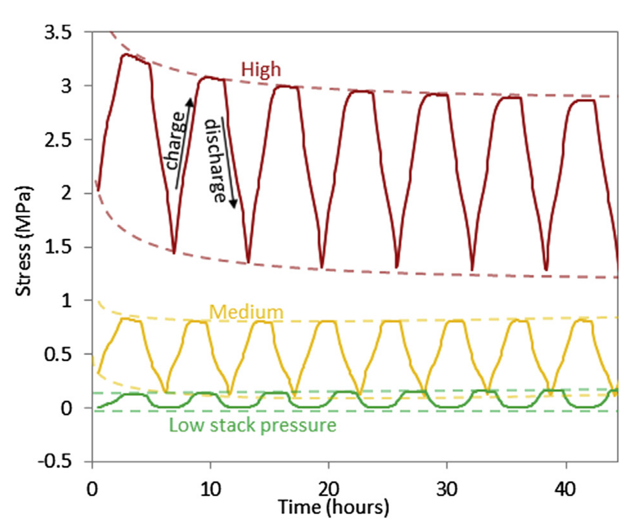

Fig. 2. Stack stress evolution at early times. The high and medium stack pressure cells exhibit stress relaxation spanning time scales on the order of days.