

On the Coupling Between Stress and Voltage in Lithium Ion Pouch Cells

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ABSTRACT

This paper studies the coupling between stress and open circuit voltage in a commercial lithium-ion pouch cell. This coupling is characterized through measurements of a coupling factor, which is defined as the rate of change in voltage with respect to applied mechanical stress. Based on a simple thermodynamic model, this coupling factor is expected to be related to the expansion characteristics of the pouch cell during charging. The expansion characteristics of the pouch cell are compared with measurements of the coupling factors at different states of charge, and are found to be in agreement with the simple thermodynamic model. This work opens the door for the development of mechanical force sensors based on intercalation materials.

Keywords: load cell, force sensor, lithium-ion battery, intercalation material, mechanical stress coupling

1. INTRODUCTION

Lithium-ion batteries are complex electrochemomechanical systems owing to the coupling between electrochemistry and mechanics exhibited by their constituent electrode materials. Typically, electrode materials will expand with increasing lithium concentration, which has been the subject of many studies on the electrochemomechanical coupling in common electrode materials such as graphite and silicon,¹⁻⁸ as well as composite electrodes comprised of these materials.⁹⁻¹² The expansion/contraction characteristics of the anode and cathode comprising a pouch cell are generally imbalanced such that net cell expansion occurs during charging. This net expansion of pouch cells has been the subject of numerous studies of lithium-ion batteries¹³⁻¹⁷.

The expansion of pouch cells during charging has been exploited in previous work in which lithium-ion cells are used as actuators.¹⁸ This previous work was followed up by a study of actuators fabricated from intercalation materials,¹⁹ which benefited from a strong coupling between electrochemistry and mechanics (i.e. relatively small voltages can produce very large stresses). In this present work, we examine the reverse scenario: the use of lithium-ion pouch cells as mechanical stress sensors. The use of intercalation materials as a stress sensor has a few interesting potential benefits. Intercalation load cells could be passive, not requiring a power source to produce a signal. Load cells made of silicon could be manufactured into intricate shapes and patterns by taking advantage of silicon fabrication techniques. Because intercalation load cells do not require deformation to produce a signal, they could be fabricated into extremely thin form factors which could exhibit near-zero deflection.

However, the use of intercalation materials as stress sensors is expected to be disadvantaged by the relatively weak coupling between mechanics and electrochemistry (i.e. large stresses produce small voltages). In this present work, the coupling of an entire pouch cell system is measured. The coupling is measured simply as the ratio of the voltage increase to applied stress when a pouch cell is subjected to a uniaxial stress ramp. While the definition of an electromechanical coupling factor is novel for battery systems, similar usage of coupling factors are common in electromechanical energy conversion applications.²⁰ The measurements presented here are similar to previous work studying the stress-potential coupling in silicon, using intercalation to produce mechanical stress within a thin film of silicon.⁷ The previously measured coupling exhibited by the electrode material is necessarily related to the coupling exhibited by the full pouch cell that is measured in this current work. However, while the pouch cell coupling is related to the fundamental materials properties, the pouch cell coupling is also dependent on the geometry and construction of the system.

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2. EXPERIMENTAL

2.1 Pouch cells

The pouch cells used in this study are commercially available 240 mAh pouch cells (lithium cobalt oxide / graphite) obtained from Tenergy. The actual capacities of the cells range from 230 to 240 mAh when measured at C/20, owing to capacity fade during storage. The dimensions of the cell with packaging are 1.8cm wide, 1.7cm long, and 5.3mm thick. These are the dimensions used in calculating stress and strain in this work. The double-sided anode is 140 μm thick, the double-sided cathode is 120 μm thick, and the separator is 14 μm thick. The electrodes are wound in a prismatic jelly roll configuration such that the entire stack consists of 17 layers of the electrode sandwich.

2.2 Expansion measurements

Expansion measurements of the cell are made using an electromechanical compression testing machine (Instron 5969) using spherically seated platens for good alignment. Expansion is measured by compressing the pouch cell with 0.5 MPa of stress and measuring the displacement of the compression tester platens using an LDVT while the cell is charged. Because the cell contains many polymeric components (binder, separator, and packaging), it exhibits a high degree of creep deformation under the applied load.²¹⁻²³ Because the rate of deformation due to creep decays over time, the load is held on the cell for 72 hours before any expansion measurements are made to allow creep deformation to decay to a level that is negligible relative to the expansion of the cell during charging. Subsequently, the cell is charged while a 0.5 MPa stress is maintained such that the platens are displaced as the cell expands during charging. The expansion measurements presented here are made using a cell that is charged at a C/20 rate.

2.3 Coupling factor measurements

To measure the coupling factor, the voltage change of a cell in response to an applied stack stress is measured. The voltage changes with applied stress are small (on the order of 100 μV) and cannot be resolved for a single cell. This is because the cell voltage is roughly 4 orders of magnitude higher than the voltage change, and the voltage resolution of a potentiostat scales with the absolute magnitude of the voltage being measured. However, if two cells with the same voltage are arranged into a cell couple as shown in Fig. 1 such that the voltage between them is close to 0mV, then small changes in the working cell voltage during compression are able to be resolved. As shown in Fig. 1, the cell couple is created by connecting the negative terminals of two cells of the same state of charge (SOC). In this work, all coupling factor measurements are made by compressing the "working cell" of the cell couple, and measuring the increase of the working cell voltage relative to the reference cell, labelled ΔV in Fig. 1.

To vary the SOC of the cell couples for the SOC-dependent coupling factor measurements, two cells comprising a cell couple are first connected in parallel to ensure that both cells are at the same voltage, and then charged using a battery cycler (Maccor). The parallel-connected cells are charged to a specific SOC by first fully discharging the cell to 2.7V and then charging by a specific amount of charge. The parallel-connected cells are allowed to rest until there is no noticeable voltage relaxation in the cells. The cells are then connected into the cell couple configuration shown in Fig. 1. Prior to making the coupling factor measurements, it is confirmed that no noticeable voltage changes with time can be observed in the cell couple. The working cell of the cell couple is then compressed in an electromechanical compression testing machine at a constant stress rate of 15 MPa/min to a maximum stress of 15 MPa. No internal shorting due to separator deformation is observed at these stress levels. The voltage of the cell couple (nominally 0mV), is monitored during compression using a potentiostat (Solartron 1287).

3. THERMODYNAMIC MODEL

The voltage change of a pouch cell under compression can be understood from a simple thermodynamic analysis. We start by considering two identical pouch cells, A and B, which expand by $d\delta$ when charged with a small quantity of charge dq . For cell A, which is unloaded, the open circuit voltage is V , which is a measure of the difference in chemical potential of a lithium ion between the two battery electrodes. Now consider an identical

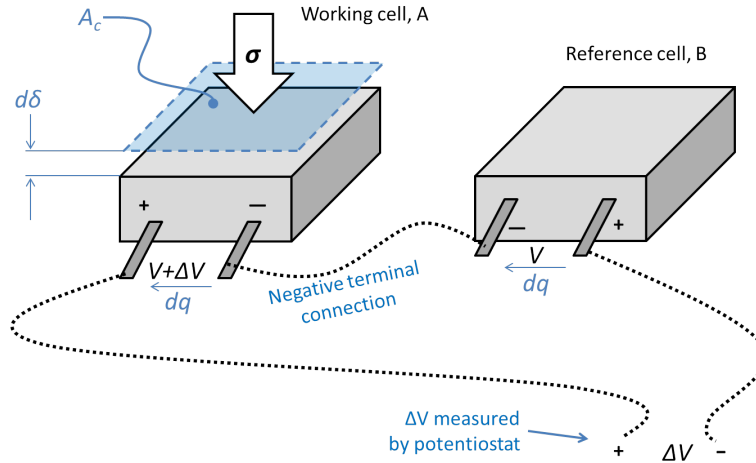


Figure 1. Schematic of the experimental setup showing how the negative terminal of the working cell is connected to the positive terminal of the reference cell to form a cell couple. The voltage of the cell couple is nominally 0mV. The load is applied to the working cell.

cell B which is placed under a uniaxial stress σ applied over the area A_c of the cell's flat face. Charging cell B with a small amount of charge dq requires additional energy because the system does mechanical work against pressure σ , equivalent to $\sigma A_c d\delta$. Because additional work must be done when this charge is passed, the charge must be passed through a voltage higher than that required in cell A. This increase in voltage is ΔV .

Equating the increase in electrical energy required to move charge dq across the voltage to the mechanical work produced by expanding $d\delta$ against load σA_c gives

$$\Delta V dq = \sigma A_c d\delta \quad (1)$$

Rearranging Eq. (1) gives an expression for the voltage change due to an applied stress.

$$\Delta V = \sigma A_c \frac{d\delta}{dq} = k\sigma \quad (2)$$

Eq. (2) predicts a linear relationship between voltage increase and applied load, with the constant of proportionality defined as the coupling factor k . The coupling factor is dependent on the expansion characteristics of the cell electrode materials with lithiation as well as the cell geometry. For a cell that expands during charging, the cell voltage is expected to increase with the application of a compressive load. The coupling factor has units of mV/MPa which is also equivalent to mm^3/C . Note that this analysis ignores the effects of the applied stress on the internal energy of the system and on the mechanics of the system, both of which can affect the voltage change.

4. RESULTS AND DISCUSSION

4.1 Cell expansion measurements

As described in the previous thermodynamic analysis, the coupling factor of the cell is expected to be related to the expansion characteristics of the cell during charge/discharge. To this end, the expansion of the cells during charge/discharge is measured and plotted in Fig. 2a. The expansion profile shown in Fig. 2a shows 3 distinct regions characteristic of graphite staging, which is similar to previous expansion measurements of pouch cells employing graphite anodes.^{13,17} The expansion of the cell during charging is also partly attributed to expansion of the lithium cobalt oxide cathode, which expands as it is delithiated.¹⁹ The contribution of the lithium cobalt

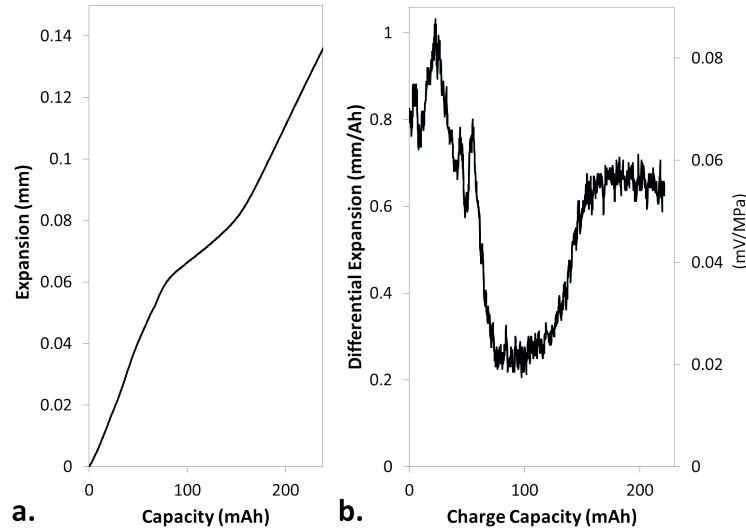


Figure 2. Expansion (a) of a cell charged at a rate of $C/20$ and the corresponding differential expansion $\left(\frac{d\delta}{dq}\right)$ curve (b).

oxide expansion to the overall cell expansion is responsible for the upward slope of the center region of the expansion curve, which is not observed in cells containing only a graphite electrode.

While at a glance these three regions appear to be linear with charge, differentiating the expansion-capacity curve with respect to capacity uncovers detailed features as shown in Fig. 2b. This curve is the $\frac{d\delta}{dq}$ term in Eq. (2) and is expected to be proportionate to the coupling factor based on simple thermodynamic arguments used in deriving Eq. (2). The variations in the differential expansion curve are reminiscent of the variations in the more well known differential voltage curves for a LCO/C cell, which is shown for this cell in Fig. 3. This suggests that the variations are intimately related to the materials properties of the electrode materials, making differential expansion analysis a potentially useful technique for fundamental materials study.

4.2 Coupling factor measurements

A typical plot of the voltage change of a cell couple as a function of the applied stress is shown in Fig. 4. The plot shows that the voltage of a cell increases as it is compressed, which is consistent with thermodynamic arguments. This voltage increase is generally linear such that the slope can be used to measure the coupling factor k . In some cases the curve has a slight concavity. In these scenarios the slope is taken to be the linear portion of the curve between 10 and 15 MPa. The differences in slope between the top and bottom of a curve are all less than 10%.

Voltage-stress curves are plotted in Fig. 4 with the lines corresponding to sequential load cycles conducted on the same cell. The curves are labelled 1 through 5, representing the order in which each curve was produced. In general, the first few voltage-stress measurements tend to produce different values, likely owing to changes in the mechanical structure of the pouch cell.²¹ However, after multiple compression tests (generally after 4), the voltage-stress curves become reproducible. The slope of the reproducible voltage-stress curve is taken to be the coupling factor of the cell.

The coupling factor of the cell is expected to have a SOC dependence owing to the non-linear nature of the expansion characteristics of the electrode materials seen in Fig. 2. The SOC-dependence of the coupling factor is shown in Fig. 5, which shows coupling factor measurements of cells charged to 8 different charge states. The plot of coupling factor versus charge state is in agreement with the differential expansion measurements shown in Fig. 2a, which is underlain in Fig. 5.

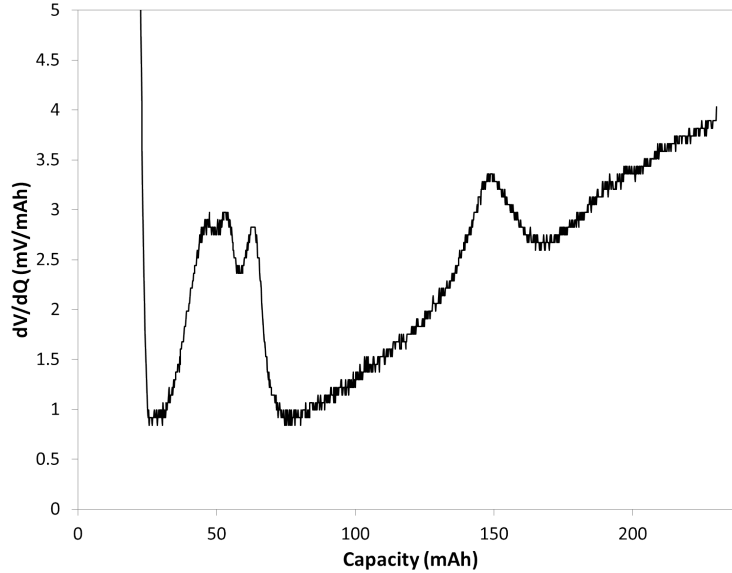


Figure 3. Differential voltage $\left(\frac{dV}{dQ}\right)$ data for a cell charged at C/20.

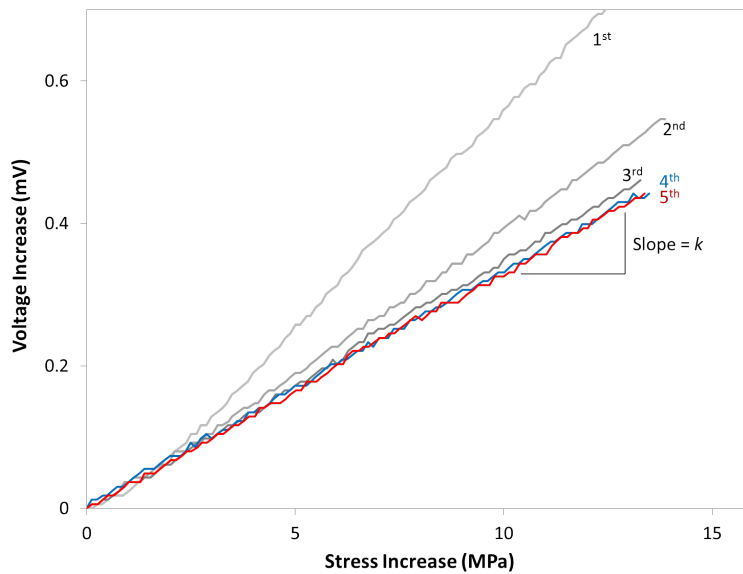


Figure 4. Voltage change as a function of applied stress of a compressed cell couple. Multiple compression tests (labelled 1 through 5) are conducted on a single couple. The voltage-stress response becomes repeatable after 4 compression cycles.

The underlain differential expansion curve in Fig. 5 has been scaled by the cross sectional area of the cell to satisfy the definition of coupling factor presented in Fig. (2). Prior to scaling, the units of the differential expansion curve are converted from mm/mAh to mm/C, the latter being equivalent to mV/N. The slight quantitative deviation between the expected coupling factor based on cell expansion measurements and the measured coupling factor may be due to the underlying assumptions used in deriving the simple thermodynamic model of Eq. (2). As discussed previously, this model does not account for changes to the internal energies of the system as a result of applied load nor does it account for changes to the mechanics of the system, both of which can affect coupling factor. The measurements of coupling factor may also be dependent on the loading rate, as a result of

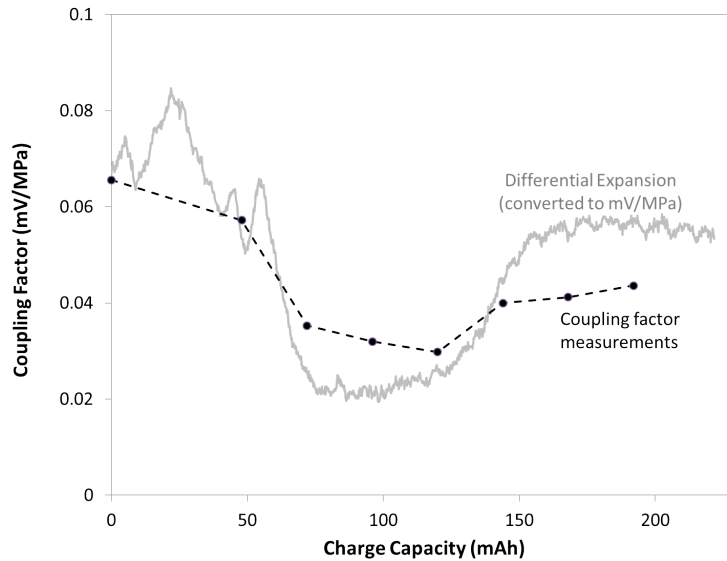


Figure 5. **Coupling factor k as a function of SOC.** The coupling factor as calculated by differential expansion measurements according to Eq. (2) is underlain in grey.

the non-ideal viscoelastic mechanical properties of the pouch cell. Similarly, the expansion measurements may also be dependent on the charging rate of the cell, which would effect the uniformity of the lithium concentration within the individual electrode particles.

It is also difficult to relate the pouch cell coupling factor to the fundamental stress-potential coupling of the materials. One major difficulty is due to the non-ideal geometry of the pouch cell. Because of the wound structure, the stress state within the pouch cell is not uniform under uniaxial compression. Also, the wound faces of the cell are not compressed in the same manner as the flat faces of the cell, such that the cell operates at a mixed potential as the voltage of the flat faces increases with stress while the wound faces remains the same. The non-ideal geometry of the electrode particles also serves to cause deviation of the coupling factor. This is because uniaxial compression of spherical or irregular particle shapes results in complex stress-states within the particle. Thus the calculation of coupling factor is not straightforward. Furthermore, both graphite and lithium cobalt oxide exhibit anisotropic expansion properties, such that the orientation of the crystals is important in determining the coupling factor. Any deviation from non-uniaxial stress which arises from the non-ideal particle shapes and non-ideal geometric configuration of the wound pouch cell would result in changes to the coupling factor.

5. CONCLUSIONS

This work demonstrates that intercalation materials can be used as mechanical force sensors through measurements of the voltage change of commercial pouch cells in response to applied mechanical stresses. The ratio of the voltage change to applied stress is defined as the coupling factor, for which is expected to be related to the expansion characteristics of the cell during charging. The thermodynamic model is found to be in general quantitative agreement with experiment. While coupling here is relatively weak ($k < 0.07$ mV/MPa), larger coupling factors are expected for more highly optimized systems. For example, a much stronger coupling factor is expected if the anisotropy of the materials is exploited such that all expansion occurs in the direction of applied load. Higher expansion materials such as silicon have been shown to have much stronger coupling factors as well (0.1 mV/MPa for Silicon⁷). Finally, a pouch cell represents a very poor load cell configuration. One could envision a practical intercalation load cell to have a highly optimized structure to be resistant to deformation (e.g. no polymeric components) and to allow for loads in the desired measurement range to produce large stresses on the intercalation materials, thereby increasing the voltage output.

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