Modeling Volume Change in Dual Insertion Electrodes

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A mathematical model is presented that incorporates the dimensional and porosity changes in porous electrodes caused by volume changes in the active material during intercalation. Porosity and dimensional changes in an electrode can significantly affect the resistance of the battery during cycling. In addition, volume changes generate stresses in the electrode, which can lead to premature failure of the battery. Here, material conservation equations are coupled with the mechanical properties of porous electrodes to link dimensional and porosity changes to stresses and the resulting resistances that occur during the intercalation processes. Several different battery casings are examined in order to generate summary figures to aid in battery design. The associated stress, strain, porosity and resistance is predicted and discussed in relation to battery performance.

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Significant strides have been made to improve the range, cost, and fueling times of electric vehicles through the improvement of the design and control of cells, and several automobile manufacturers are releasing battery powered vehicles with price points that target the general public.1–10 New chemistries, such as lithium ion, have also been examined in order to increase the energy densities of these batteries in order to increase the range of battery powered vehicles, and decrease the volume displacement of these batteries in the vehicle powertrain. However, because these new chemistries result in more energy in a smaller volume, safety problems may arise.11 Therefore, it is critical to be able to predict the performance of new battery systems in order to improve safety and reliability, while also continuing to increase the energy density, which in turn decreases the weight and volume requirement of battery systems in alternative energy passenger vehicles.

Due to the recent commercial and government sector success of high energy density batteries, high performance electrode materials, separators, electrolytes, and new cell and stack designs are being actively developed to further improve cell capacity, charging and discharge rates, safety, cycle life, and shelf life. The most widely used anode material (graphite) in Lithium-ion batteries undergoes a volume change (10%) during lithiation and delithiation cycles.12 However, high capacity anode materials, such as silicon and its alloys, undergo even higher volume changes ranging from 100% to 270%.13–15 Other battery chemistries, such as Li-Sn alloy intercalation cathodes, have seen volume changes as high as 350% as observed by Yang et al.16 The volume changes seen in these new battery electrode materials induce a significant amount of stress in the electrodes during battery operation.12,17–19 These volume changes and high stresses may result in the fracturing of active particles within the electrodes, and induces bulk stresses at the cell and stack level. A moderate amount of bulk stress in lithium-ion cells may be beneficial to cell operation, however, excessive stresses cause reduced cell performance and cell damage. Recently, electrode stresses have been connected to the capacity fade in lithium-ion pouch cells.20

In order to accurately predict the behavior of electrochemical devices, it is necessary to develop sophisticated models that take into consideration transport processes, electrochemical phenomena, mechanical stresses, and structural deformations (i.e. strain) on the operation of an electrochemical system. There are many models in the literature that can predict the electrochemical performance of devices with porous electrodes (e.g. voltage vs time) under a variety of operating (e.g. current) and design (e.g. electrode thickness) conditions.10–21 In many of these models, the dimensions of the porous electrode are often assumed constant and any volume changes in the active material result in only porosity changes.21–23 Gomadam and Weidner developed a model to allow both porosity and dimensional changes to occur. However, they assume an a priori split between these two. In order to predict the fraction of volume change that goes into porosity change, the prediction of the stresses in the porous electrode must be coupled to the material balances. Recently, models have been developed that couple volume expansion of the active material and stresses during intercalation and deintercalation of a single porous electrode.24–28 They reveal the importance that a change in volume plays in the generation of stresses and strains, and how this may be linked to experimentally observed failure in the active material.22–31

The model developed here accounts for the stresses that build up in porous electrodes due to volume change in the active material through the application of porus rock mechanics to porous electrode theory. In previous models, a single electrode expanding against a casing with varying rigidity was examined in order to derive analytical expressions that governed the volume change in a single electrode. However, battery cells are composed of two electrodes which are required for operation, a positive electrode and a negative electrode. The presence of two electrodes affect the overall stress and strain observed in the system and show a deviation from the single electrode predictions seen earlier and are illustrated by the simulations shown here for the stress, strain, and porosity variations that can exist in a battery comprised of two porous electrodes and a compliant separator, enclosed in a semi-rigid casing. Uniform reaction rates throughout the porous electrodes are assumed in order to initially predict the interactions between the two electrodes without considering non-uniformities, which is valid for low discharge and charge rates. This addition of a second porous electrode that can compress and contract during the expansion of the other electrode more accurately accounts for the total dimensional changes of the battery. This enables us to examine the effects of relative thickness of the electrodes, relative active material expansion of the electrodes during cycling, and the tradeoff between stress and

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volume expansion in the system that can assist in realizing the benefits of these novel electrode materials, while accounting for the large volume changes that are associated with their use.

**Model Equations**

Figure 1 illustrates the setup considered in this work. For illustrative purposes, the positive electrode is assumed to have an active material volume expansion during intercalation that is significantly larger than the active material volume expansion seen in the negative electrode during intercalation and deintercalation. This is similar to what would be seen in a single electrode study if coupling a high expansion electrode material with a reference such as lithium, where the high expanding electrode is the positive electrode, and the reference is the negative electrode. In Figure 1 it is assumed that the separator is incompressible with fixed dimensions, and it is also assumed that there is no free space or gap between the electrodes, casing, and separator, but that a head space exists to allow for the inflow and outflow of electrolyte.

During discharge, charged particles intercalate from the negative electrode, resulting in a contraction of the negative electrode due to a decrease in the volume of the active material, into the positive electrode, resulting in an expansion of the positive electrode due to an increase in the volume of the active material. The opposite is true during charging.

As given previously, the relationship governing the volume change in porous electrodes is obtained from an overall material balance on the solid active material and is seen below:

\[
\frac{\partial (1 - \varepsilon)}{\partial t} + \nabla \cdot [(1 - \varepsilon) \mathbf{u}] = -\frac{s\Delta \hat{V}}{nF} \frac{\partial \varepsilon}{\partial t}
\]  

[1]

The term on the right side of the equal sign is the volume change due to intercalating the reacting species into the active material. This volume change can cause either a change in porosity (the first term on the left side of the equal sign) or dimensional changes (second term) expressed by the velocities of the control volume. Assuming one dimensional expansion, and uniform porosity across the length of each electrode, the velocity vectors can be replaced by the dimensional strain of the electrode, resulting in a simplified version of Equation 1:

\[
\frac{\partial (1 - \varepsilon)}{\partial t} + (1 - \varepsilon) \frac{\partial \varepsilon}{\partial t} = -\frac{s\Delta \hat{V}}{nF} \tau
\]  

[2]

Here, we assume low rates for charging and discharging, and therefore \( j = I/V \). If the battery electrodes are anisotropic, unequal expansion in different directions can be included and applied to a more general material balance. Porous rock mechanic theory can be applied in these cases as well.

Taking into consideration rock mechanics, the compressibility of the two electrode system is treated as a continuum of fractions of the solid phase and pores and can be defined as:

\[
C_E = -\frac{1}{\rho} \frac{dV}{d\sigma}
\]  

[3]

The volume of the electrode under consideration as a function of strain can be derived from the definition of strain similar to what is seen in solid mechanics, assuming equal expansion in all directions, or uniform expansion in one direction:

\[
V = V_0 (1 + \psi)
\]  

[4]

When solving Equations 3 and 4 simultaneously with the appropriate boundary conditions, the mechanical strain can be solved as a function of electrode compressibility and stress and illustrates the change in dimensions due to stress on the electrodes:

\[
\psi = e^{-C_E \sigma} - 1
\]  

[5]

If no volume was added to the electrode due to intercalation, this equation would govern the strain of the electrode due to an applied pressure. However, similar to heating in rock mechanics, the electrode expands with the addition of intercalate, and is therefore also a function of the intercalation of ions into the matrix:

\[
\psi = \left[ \frac{\Delta \hat{V}}{V_0} \right] \tau
\]  

[6]

The expansion as a function of state of charge is known for certain substances, and in this instance, could be a function of the state of intercalation, and Equation 6 would still be valid. This model is assumed to be galvanostatic, and \( \tau \) is defined accordingly:

\[
\tau = \frac{tI}{Q_{\text{max}}}
\]  

[7]

With the system defined here, as seen in Figure 1, the porous positive electrode is assumed to expand during discharge and contract during charge. Therefore, \( \tau \) refers both to the state of intercalation of charged species into the positive electrode, as well as the state of discharge of the system. \( 1 - \tau \) therefore is equal to the state of charge of the battery. The strain of the positive electrode is then defined by combining Equations 5 and 6 as follows:

\[
\psi_+ = \psi_m + \psi_i = e^{-C_E \sigma} - 1 + \left[ \frac{\Delta \hat{V}}{V_0} \right] \tau
\]  

[8]

The strain of the negative electrode is then defined as:

\[
\psi_- = \psi_m + \psi_i = e^{-C_E \sigma} - 1 + \left[ \frac{\Delta \hat{V}}{V_0} \right] (1 - \tau)
\]  

[9]

The strain of each electrode can then be used to determine the overall strain inside the battery. Here, we assume that the strain develops in one direction, and the following equation is reduced to consider initial thicknesses, however, initial volumes could be used instead of initial thicknesses if strain in three dimensions is considered:

\[
\Psi_{\text{battery}} = \frac{(\psi_+ + 1) L_+^0 + (\psi_{\text{sep}} + 1) L_{\text{sep}}^0 + (\psi_- + 1) L_-^0}{L_+^0 + L_{\text{sep}}^0 + L_-^0} = 1
\]  

[10]

An equivalent volumetric strain can be defined for the space enclosed by the casing. It is termed casing strain and is equivalent to the total strain of the combined electrodes. For small deformations in the absence of free space, the casing strain can be assumed to be proportional to the electrode strain, and in turn the bulk stress. When free space exists inside the battery casing, the casing strain and total electrode strain are not equal, rather, the casing strain is equal to zero while the total electrode strain varies, up until the point at which the expansion and contraction of either or both electrodes fills the free space. The casing strain is therefore written as follows and is equal to the strain of the electrode system when no free space is present:

\[
\Psi_{\text{battery}} = \psi_i = C_E \sigma
\]  

[11]
Table I. List of Parameters used with Equations 8, 9, and 10 for Figures 2–8.

| Parameter | Figure 2 | Figure 3 | Figure 4 | Figure 5 | Figure 6 | Figure 7 | Figure 8 |
|-----------|----------|----------|----------|----------|----------|----------|----------|
| $C/C_0$   | 2, 10    | 2, 10    | 2, 10    | Infinite (Strain = 0) | Function of Strain | Infinite (Strain = 0) | Function of Strain |
| $\Delta V/\Delta V^0_{\text{sep}}$ | 1        | 1        | 1        | 1        | 1        | 1        | 1        |
| $L_0$     | $6.8 \times 10^{-5}$ m | $6.8 \times 10^{-5}$ m | $6.8 \times 10^{-5}$ m | $6.8 \times 10^{-5}$ m | $6.8 \times 10^{-5}$ m | $6.8 \times 10^{-5}$ m | $6.8 \times 10^{-5}$ m |
| $L_{0\text{sep}}$ | Varies | Varies | Varies | Varies | Varies | Varies | Varies |
| $L_0^b$   | $5 \times 10^{-5}$ m | $5 \times 10^{-5}$ m | $5 \times 10^{-5}$ m | $5 \times 10^{-5}$ m | $5 \times 10^{-5}$ m | $5 \times 10^{-5}$ m | $5 \times 10^{-5}$ m |
| $\phi$    | 0.5      | 0.5      | 0.5      | 0.5      | 0.5      | 0.5      | 0.5      |
| $\tau$    | 0-1      | 0-1      | 0-1      | 1        | 1        | 1        | 1        |

The casing strain as defined here is not the mechanical strain of the casing, rather $C/C_0$ is an equivalent compressibility of the casing and represents the ratio of incremental volume strain of the casing to incremental internal pressure inside the casing. When $\psi_+$ is positive during expansion, the actual mechanical strain in the casing or separator can have a negative component in the thickness direction and a positive membrane strain component.

Combining Equations 10 and 11 allows the dimensionless hydrostatic stress of the dual electrode system to be solved for as a function of the state of intercalation of the expanding electrode in the battery, similar to what is seen for a single electrode. Once the hydrostatic stress is known, the strain of each individual electrode can be predicted by substituting in the hydrostatic stress. Combining the material balance seen in Equation 2 with boundary conditions as seen in previous work\textsuperscript{17} a solution for porosity of each electrode as a function of the order of high expansion electrode materials such as silicon or tin, and is useful for comparison to previous work.\textsuperscript{17} If $\frac{\Delta V}{\Delta V^0_{\text{sep}}}$ was set higher, then the stress and strain would have higher magnitudes than currently shown. The contracting single electrode particle expansion was chosen in Figures 2–4 to illustrate the addition of a secondary electrode and focus on the compression of the secondary electrode, rather than the contraction due to the removal of charged species. Also, many materials that are available to be coupled to high expanding electrode materials undergo qualitatively smaller volume changes during lithiation and delithiation. The initial expanding electrode thickness, $L_0$, was chosen based on previous work,\textsuperscript{17} and is irrelevant for the mechanical studies seen here, but significant when considering the single particle expansion, $[\frac{\Delta V}{\Delta V^0_{\text{sep}}}]$, was chosen to be 1 because it is on the order of high expansion electrode materials such as silicon or tin, and is useful for comparison to previous work.\textsuperscript{17} If $[\frac{\Delta V}{\Delta V^0_{\text{sep}}}]$ was set lower, higher, then the stress and strain would have higher magnitudes than currently shown. The contracting single electrode particle expansion was chosen in Figures 2–4 to illustrate the addition of a secondary electrode and focus on the compression of the secondary electrode, rather than the contraction due to the removal of charged species. Also, many materials that are available to be coupled to high expanding electrode materials undergo qualitatively smaller volume changes during lithiation and delithiation. The initial expanding electrode thickness, $L_0$, was chosen based on previous work,\textsuperscript{17} and is irrelevant for the mechanical studies seen here, but significant when considering the

![Figure 2](image1.png) Stress generation from single electrode model seen Ref. 17 (dotted lines) compared to stress generation from the two electrode model developed in this work (solid lines). State of intercalation for two electrode model based on the state of intercalation for the expanding electrode.

![Figure 3](image2.png) Strain development from single electrode model seen in Ref. 17 (dotted lines) compared to strain development in the expanding electrode from the two electrode model in this work (solid lines).
effect of conductivity and diffusion when examining higher rates in future work. The initial contracting electrode thickness was chosen based on previous work, and was varied relative to the initial expanding electrode thickness in order to show the effect of different length ratios in Figures 5–7. The separator thickness was taken from previous work to aid in comparison, and would be varied in a real system in order to more closely match the capacities of each electrode, but does not have an effect on the stress and strain generated in the system based on the rock mechanics treatment, and was therefore not varied in this work. Lastly, the state of intercalation was chosen for comparison to previous work for Figures 2–4, and set at 1 for the remaining figures due to this state illustrating the highest stress and strain in the system.

Results and Discussion

Figures 2–4 show the stress, strain and porosity changes in the expanding electrode as a function of state of charge (solid lines). For comparison, these three figures show the results from our previous work (dashed lines), where there is only one electrode (i.e., no corresponding contracting second electrode).

Figure 2 shows the increase in stress, $\sigma$, as the charged species are inserted into the matrix of the expanding electrode. This is due to the increase in volume in the active material expanding against the contracting electrode and/or the cell casing. When comparing the stress increase between a single electrode system and a dual electrode system, it can be seen for identical $C_{E}/C_{C}$ values, the presence of a secondary electrode results in the relieving of some of the stress observed in the single electrode system. This is due to the compression of the secondary electrode (negative electrode in Figure 1) allowing for higher volume change in the expanding electrode. Decreasing the $C_{E}/C_{C}$ value is also seen to have a similar effect on the overall stress generation, with lower $C_{E}/C_{C}$ values representing more compliant casings and therefore resulting in lower stress generation when compared to higher $C_{E}/C_{C}$ values representing an increase in casing rigidity (decrease in casing compressibility). This combination of secondary electrode selection and casing rigidity selection can have a significant effect on the stress in the system. As seen here, increasing the casing compressibility and adding a secondary electrode serves to decrease the final hydrostatic stress in the system from $\sim$174 MPa to $\sim$44 MPa.

Figure 3 illustrates the strain development, $\phi$, as a function of state of intercalation in a two electrode system compared to the strain development predicted in a single electrode system in earlier works. As seen in the dual electrode system represented by the solid lines, as particles are inserted into the active material of the expanding electrode, volume change occurs resulting in an increase in the strain of the ex-

Figure 5. Dimensionless stress as a function of the electrode compressibility ratio. $L_{E}^0$ and $L_{C}^0$ represent the initial length of the expanding and contracting electrode respectively.

Figure 6. Dimensionless stress as a function of the final casing strain. $L_{E}^0$ and $L_{C}^0$ represent the initial length of the expanding and contracting electrode respectively.

Figure 7. Dimensionless stress as a function of the single particle expansion ratio. $L_{E}^0$ and $L_{C}^0$ represent the initial length of the expanding and contracting electrode respectively. $\bullet$ represents lithium intercalation from an electrode similar to a LiCoO$_2$ electrode into a graphite/silicon composite electrode while $\blacksquare$ represents the case of intercalation from a LiCoO$_2$ electrode into a graphite electrode.
panding electrode. This is coupled to the contraction and compression of a secondary electrode. When compared to a single electrode system with identical \( \frac{C_{CE}}{C_{CC}} \) value, the strain the expanding electrode can be seen to increase more rapidly than its single electrode counterpart. This is due to the presence and compression of a secondary electrode as seen in Figure 1 which serves to allow for an increase in the volume expansion of the expanding electrode. When decreasing the casing rigidity (decrease in \( \frac{C_{CE}}{C_{CC}} \)), the strain in the expanding electrode increases more rapidly due to the shift in volume changes from porosity changes toward dimensional changes associated with the decrease in stress as seen in the earlier figure. These strain changes are also significant considerations when designing a battery pack. With the advent of newer electrode materials that undergo significant volume change, vehicle manufacturers want to take advantage of the increased energy density while still minimizing the volume used in the vehicle for battery pack storage. Therefore, the strain of each electrode, and the corresponding strain of the entire system must be considered and modeled in order to aid in the design of battery packs. If the strain in the cell is too large, this could cause degradation of the battery pack components over time, resulting in loss of electrical contact to the cell, or cracking of the battery pack casing. Significant strain could also result in the rupture of the cell packaging and leakage of the electrolyte and other cell components.

Figure 4 illustrates the porosity changes, \( s \), in the expanding electrode in a dual electrode system as a function of intercalation compared to the porosity changes in a single electrode system modeled in earlier work.\(^{17}\) Seen here, as the state of intercalation of the system increases, the porosity is seen to decrease in the expanding electrode. This is due to an increase in the stress in the system as seen earlier in Figure 2 resulting in forcing volume changes to go into porosity changes. When comparing a dual electrode system and a single electrode system with identical \( \frac{C_{CE}}{C_{CC}} \); it can be seen that the porosity does not decrease as rapidly in the dual electrode system. This is due to lower stresses in the dual electrode system tied with higher strain in the expanding electrode resulting in volume changes going toward dimensional changes and relieving the volume changes going toward porosity changes. When increasing the \( \frac{C_{CE}}{C_{CC}} \), the casing is more rigid, resulting in more volume changes going toward porosity changes, and in turn a lower porosity at the end of intercalation. The porosity changes are also an important parameter to consider when designing a cell and battery pack, because if the overall porosity is too low, or if porosity changes during use are too large, high rate charge or discharge can be inhibited, resulting in loss of available range or a decrease in performance.

As discussed, many different parameters must be considered when designing a cell and a battery pack. Stresses and strains in an individual cell can cause degradation within the cell, but can also result in material degradation in the battery housing and the battery pack. During design phases for production vehicles and battery packs, modeling predictions are heavily used in order to meet vehicle design deadlines and minimize the amount of testing necessary to obtain model parameters for vehicle simulation. To this end, Equation 12 offers the ability to determine material characteristics based on rock mechanics principles in order to meet battery cell and pack design constraints.

Figure 5 illustrates the effect of the electrode compressibility ratio \( \frac{C_{CE}}{C_{CC}} \) on the overall dimensionless stress, \( \bar{\sigma} \), observed in the system for an expanding electrode undergoing significant volume change during insertion of lithium constrained by a rigid casing or a set maximum strain as would be typical in a battery pack, as well as the ratio between the initial electrode lengths, \( \frac{L_{CE}}{L_{CC}} \). Here, the compressibility of the expanding electrode was set as the reference for the dimensionless stress, i.e. \( \bar{\sigma} = \sigma \cdot C_{CC} \). The effect of initial length ratios between the expanding and contracting electrodes is also considered. Here, as \( \frac{C_{CE}}{C_{CC}} \) is increased (the rigidity of the contracting electrode is increased compared to the rigidity of the expanding electrode), the stress in the system at the final state of intercalation is predicted to increase. This stress increase is due to the restriction of volume expansion in the cell, resulting in more volume change being forced into porosity changes compared to dimensional changes. As the length ratio is increased, as would be typical if changing the volume of either electrode in order to match capacities, or trying to cycle over a small state of charge for performance reasons, the stress in the system is also observed to increase at the final state of intercalation across all electrode compressibility ratios. This length ratio may need to be varied in order to match the capacities of the electrode materials under consideration in order to realize the full capacity of both electrodes, or may be varied in order to cycle over a small state of charge in one electrode in order to minimize lithium plating or other physics resulting in capacity loss. Here, if one desires to maximize the dimensional change of the expanding electrode during intercalation in order to utilize the high capacity offered by that material, a cell with a very compressible secondary electrode would be desired in order to relieve stresses in the system, regardless of the ratio of initial electrode lengths. Looking at Figure 1, this would mean that the positive electrode is expanding into a compressible negative electrode with a shift of the separator to the right as the negative electrode decreases in dimension. However, if the secondary electrode needed to be very rigid and the overall volume available for the individual cell was restricted due to battery pack design constraints, one could easily predict the increase in stress and determine if it fell within the allowed stress in the battery pack.

These stress variations can also have a significant effect on the overall design of an electric vehicle from a materials standpoint. For example, when designing battery packs, one must keep moderate stress on the batteries in the pack to keep them from working loose during use, causing degradation of the electrical contacts and failure of the battery pack. Significant generated stresses by each cell can result in cracking of the battery pack material, or irreversible compression of the spacers and heat transfer devices, resulting in pack failure or runaway thermal conditions.

Figure 6 illustrates the dimensionless stress, \( \bar{\sigma} \), as a function of the final casing strain, \( \psi_{c} \), and initial electrode length ratio, \( \frac{L_{CE}}{L_{CC}} \). As the allowed casing strain is increased (an increase in the dimensions of the cell seen in Figure 1), corresponding to the allowed casing expansion in the battery pack, the stress in the system decreases. This is due to a shift in volume changes toward dimensional changes in the expanding electrode (positive electrode in Figure 1) away from volume changes going toward porosity changes. When considering a case with \( \frac{L_{CE}}{L_{CC}} = 1 \), the maximum stress that could be reached with a very rigid enclosure or very limited pack space is 1.1. For the same system, ensuring that there was enough volume to allow the cells in the battery pack to expand by 28% would minimize the stresses in the cell and on the cell’s surroundings. As seen here, significant weighting in initial length toward the high expanding electrode (\( \frac{C_{CE}}{C_{CC}} = 4 \)) would still only realize a maximum overall strain of 0.7 (70%) expansion from the initial state. Modeling this stress and strain tradeoff is integral in the initial design stages of battery modules and battery packs in order to minimize degradation in the cell and degradation of the battery pack materials.

Figure 7 illustrates the dimensionless stress, \( \bar{\sigma} \), as a function of the single particle expansion ratio between the contracting electrode and the expanding electrode, \( \frac{\Delta V_{CE}}{\Delta V_{CC}} \), as well as the ratio between the expanding electrode initial length, \( L_{CE}^{0} \), and the contracting electrode initial length, \( L_{CC}^{0} \). The circle represents the case of lithium intercalation from an electrode similar to a LiCoO\(_2\) electrode into a graphite/silicon composite electrode while a square represents the case of lithium intercalation from a LiCoO\(_2\) electrode into a graphite electrode. As the single particle expansion ratio increases, a decrease in the predicted stress is observed. This is due to a more rapid contraction of the secondary electrode (negative electrode in Figure 1) compared to the dimensional change of the expanding electrode (positive electrode in Figure 1), resulting in a minimization of the generated stresses. An increase in the initial electrode length ratio also sees an increase in
the stress at the final state of intercalation. Seen here are two repre-
sentative cases illustrating the practicality of this prediction. For the
case of lithium intercalation from an electrode similar to a LiCoO2
electrode into a graphite/silicon composite electrode, it is assumed
that the composite electrode is undergoing an assumed expansion of
100% observed in the composite electrode active material and an
assumed active material expansion of 3% in the positive electrode.
Also, the expanding electrode is 2/3 of the initial length of the con-
tracting electrode. In Figure 7 it can be seen that these conditions
predict a dimensionless stress of 0.48. When considering the case of
intercalation from a LiCoO2 electrode into a graphite electrode,
represented by a square in Figure 7, it can be seen that for the sin-
gle particle expansion ratio of 0.3 for this system, the dimensionless
stress is predicted to be 0.83. A figure such as this could be generated
for any chemistry and could be used to determine the mix of chem-
istry in a particular electrode in order to meet stress targets in the
system.

Taking the previous 3 figures and Equation 12 into consideration
allows for the user to determine the stress, \( \sigma \), in the cell as a function of
a variety of material properties such as casing and electrode compress-
ibilities, initial internal component thicknesses, and the total allowed
volume expansion in the system. Once the dimensionless stress is
known, the porosity can easily be determined for either electrode in the
system.

Conclusions

A modeling approach has been extended to a two electrode system
to predict the dimensional and porosity changes caused by volume
change in the active material during intercalation and make a compar-
ison to a single electrode system. Stress-strain relationships that were
obtained from examining the similarities between thermal rock expa-
ansion and electrode expansion due to intercalation were used to link
the stress to material balances. The model equations were then used
to generate summary figures illustrating considerations that must be
examined when working with electrode materials that undergo signif-
icient expansion. This approach can be integrated into a more complex
battery model based on porous electrode theory in order to accurately
account for volume change effects. The work seen here can aid in
the design and realization of batteries for use in alternative energy
vehicles.

List of Symbols

- \( C_C \): Casing compressibility, 1/GPa
- \( C_E \): Electrode compressibility, 1/GPa
- \( F \): Faraday’s constant, 96485 C/mol
- \( \dot{j} \): Current density, A/cm²
- \( L \): Length or thickness, cm
- \( n \): Electrons transferred in the reaction
- \( Q_{\text{max}} \): Capacity, mAh
- \( \bar{s} \): Stoichiometric coefficient
- \( t \): Time, s
- \( u \): Electrode velocity, cm/s
- \( V \): Molar volume, cm³/mol
- \( \dot{V} \): Electrode volume, cm³
- \( \dot{V}_0 \): Initial electrode volume, cm³

Greek

- \( \varepsilon \): Porosity
- \( \bar{\delta} \): Dimensionless length
- \( \psi \): Volumetric strain
- \( \sigma \): Stress, GPa
- \( \tau \): State of charge or intercalation

Subscripts and Superscripts

- 0: Initial
- +: Expanding electrode
- -: Contracting electrode
- c: Casing
- sep: Separator

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