Battery swelling due to internal gas formation in cells can result in severe degradation of battery performance. Within a battery cell, evolved gas reduces the interfacial area between active material and electrolyte, and thus hinders the electrochemical reactions at the solid electrolyte interphase (SEI). Also, the pressure buildup due to gas generation results in mechanical stress inside the electrodes, which has been implicated in local fractures in the electrodes.

Cell swelling occurs due to gas generation resulting from the decomposition of the electrolyte and from reactions with impurities in Li-ion batteries.\(^1\)\(^2\) In Li-ion batteries, gas evolution results from complex chemical reactions in the electrolyte that are coupled with the SEI layer formation process.\(^3\) Differential electrochemical mass spectrometry (DEMS) study showed that gas generation at the anode is, in general, more significant than gas generation at the cathode.\(^4\) Gas generation is accelerated by increasing temperature.\(^5\) Cyclic voltammetry (CV) in DEMS study further showed that gas generation is continuous even after the formation of cathode\(^6\) and anode.\(^7\)

Porous electrode theory has been effective in the mathematical modeling of Li-ion batteries.\(^8\) Modeling Li-ion batteries involves the diffusion and conduction of Li ions and electrons in solid (i.e., active materials) and electrolyte phases coupled with Butler–Volmer electrochemical kinetics.\(^9\) To date, this mathematical modeling has been implemented along with side reactions to simulate capacity degradation; the corresponding porosity change results from the pore plugging of the precipitate as a result of side reaction.\(^10\)\(^11\)  

However, performance degradation stemming from gas evolution in Li-ion batteries has not been investigated via a physics-based thermoelectrochemical model. The present work is focused on modeling the gas evolution effect on performance degradation in Li-ion batteries. In this study, we have the following objectives:

1. Extend porous electrode theory to mathematically correlate gas generation with degradation of battery performance;
2. Demonstrate the effects of volume fraction changes in an inert material and electrolyte on the discharge curve and heat generation.

**Gas-Evolution Induced Volume Fraction Change**

DEMS study of both cathode and anode materials suggests that there is a constant gas accumulation over cycles\(^6\)\(^7\) and that graphite materials reveal a high mass signal near the low electrode potential \(V (0-0.5 \text{ V})\) vs \(\text{Li}/\text{Li}^+\), while cathode materials show mass signals similar to the CV cycling profile. Following this experimental observation of gas generation under cyclic voltammetry, Fig. 1 illustrates the gas generation profile in which gas evolves depending on the state of charge (SOC) within the porous electrodes adapted from the work by La Mantia and Novák.\(^7\)

Figure 2 illustrates the presumed mechanisms for swelling in a battery cell, in which the gas volume is generated by the reduction or oxidation of electrolytes and their by-products at the electrodes. Overcharge delithiation can generate oxygen at cathodes, which results in gas generation at high voltages. Early work\(^12\) suggested that the volume of gas evolved by the oxidative decomposition of electrolyte solvents at cathodes is less at anodes.

Because the Li-ion flux is higher when near the separator than the current collector, we presume that both the main and side reaction currents have similar profiles to the local current density delivered through porous electrodes. Consequently, the gas evolution is spatially nonuniform through the composite porous electrode, thus the volume of the generated gas is a function of space and time. DEMS study showed a constant accumulation of gas. Constant accumulation implies a monotonically linear increase in the amount of gas at the electrodes over cycles. Therefore, the gas generation profile can be derived easily from the mass signal and calibrated by the total amount of gas generated and the number of cycles. Dividing the generated gas volume by the overall cell volume supplies the gas volume fraction. The experimentally averaged volume fraction profile as a function of SOC can be used as a local volume fraction profile in a mathematical model of volume fraction change. In summary, for a given duration of charging/discharging with the accumulated gas volume obtained from integration of the gas profile

**Figure 1.** Schematic gas generation profile as a function of SOC.
where lithium in the electrode gas phase, illustrated in Fig. binder and conductive additive at a given time porous electrode. Here, we assume that the cell is mechanically inactive species which can be treated as inert material phases in the present model.

The overall volume fraction changes for each material phase are summarized as

\[
\frac{\partial c_i}{\partial t} + \frac{1}{\rho} \nabla \cdot (\rho \vec{J}_i) = 0
\]

[4]

\[
\frac{\partial (\rho \vec{J}_e)}{\partial t} = \nabla \cdot (\vec{D}_e \nabla c_e) + \frac{1}{F} \frac{\bar{F}}{F} \left[ J^e - J^i \right] = 0
\]

[5]

\[
\nabla \cdot \left( \kappa^{\text{eff}} \nabla \phi_e - \frac{2RT}{F} (1 - \mu) \left( 1 + \frac{d \ln f_s}{d \ln c_e} \right) \nabla \ln c_e \right) + J^i = 0
\]

[6]

\[
\text{where } \tilde{c}_e \text{ is the concentration of lithium at the SEI, and the specific interfacial surface area } a_s \text{ can be written as}
\]

\[
a_s = \frac{3\rho_{\text{active}}}{\bar{F}}
\]

[9]

where \(\rho_{\text{active}}\) is the volume fraction of the active material phase.

In Eq. 5-7, the effective transport properties are described by Bruggeman’s equation that utilizes the volume fraction of each material phase as

\[
D^{\text{eff}}_e = (\rho_{\text{active}})^{1.5} D_e
\]

[10]

\[
\kappa^{\text{eff}} = (\rho_{\text{active}})^{1.5} \kappa_e
\]

[11]

\[
\sigma^{\text{eff}} = (\rho_{\text{active}})^{1.5} \sigma_e
\]

[12]

Because gas evolution does not affect the volume fraction of the active material, the effective transport properties in the solid phase are assumed to be unchanged with gas accumulation. This implicitly assumes, however, that the structure of the electrode is not sufficiently changed such that the material architecture precludes percolation of conductive phases, a topic covered elsewhere.

Yet, following this simple assumption, the decrease in electrolyte volume fraction immediately results in a nonlinear decrease in effective Li-ion diffusion and conduction in the electrolyte. The effective transport properties in the physics-based modeling of Li-ion batteries represent the inverse of resistance. Consequently, the decrease in effective transport properties results in the increase in Li-ion battery resistance. These relations can be used to rationalize the nonlinear degradation of battery performance because a nonlinear increase in resistance is derived even under linear volume fraction changes due to the constant accumulation of gas over cycles. A schematic diagram of these relations is shown in Fig. 4.
Effect of Volume Fraction Changes on Discharging

A one-dimensional (1D) thermochemical model was used to elucidate the effect of volume fraction changes due to gas evolution. This effect can be shown by varying the C-rate. It was assumed that gas evolved by 7% of the cell volume. The parameters used here are the same as those used in previous work. The cathode is LiMnO4, and the anode is graphite. The electrolyte contains 1 M of LiPF6 in ethylene carbonate/dimethyl carbonate solvent. Figure 5 provides simulation results using a 1D thermochemical model, showing a voltage drop and an increase in heat generation of 20–30% due to the volume fraction changes.

Discussion

In addition to gas evolution, side reactions in Li-ion batteries involve Li-ion consumption, active material dissolution, and SEI layer formation. In the present work, only gas evolution is taken into account in modeling performance degradation. If Li-ion consumption or active material dissolution were considered, the volume fraction changes in active materials could also be modeled. Thus, the changes in effective transport properties in the solid phase could be combined with the changes due to gas evolution in electrolyte phases. This inclusion might correlate capacity degradation with possible degradation mechanisms in Li-ion batteries. However, to segregate the effect of gas evolution alone, we need to further investigate the implicit effect of the decrease in electrolyte volume fraction on performance degradation because it is likely to affect electrode utilization.

Conclusion

In this article, we investigated the volume fraction changes due to gas evolution in composite electrodes. Gas generation induces volume fraction changes in the electrolyte and inert material phases. The volume fraction decrease in the electrolyte phase results in a nonlinear decrease in effective transport properties, which causes a nonlinear resistance increase. Simulation results also demonstrate that resistance increase results in a voltage drop and in increased heat generation. The performance degradation simulated here is also expected to be valid for other physics-based modeling. The investigated effect of volume fraction changes can be extended and enhanced by adding other degradation mechanisms and experimental approaches.

List of Symbols

- $a_s$ surface area of active material per volume of electrode, m\(^2\)
- $c_s$ concentration of salt in the electrolyte, mol/m\(^3\)
- $e_s$ concentration of lithium in the solid electrode, mol/m\(^3\)
- $e_r$ maximum concentration of lithium in the solid electrode, mol/m\(^3\)
- $D_e$ diffusion coefficient of lithium in the electrolyte, m/s
- $D_s$ diffusion coefficient of lithium in the solid electrode particle, m/s
- $f_e$ mean molar activity coefficient of salt
- $F$ Faraday’s constant, 96,487 C/mol
- $i_k$ ionic current density in the electrolyte phase, A/m\(^2\)
- $k$ reaction rate constant
- $r$ radial position across a spherical particle, m
- $R$ universal gas constant, 8.314 J/mol K
- $R_s$ radius of a solid particle, m
- $t$ time, s
- $\lambda$ transference number of Li ion with respect to the solvent velocity
- $T$ temperature, K
- $V$ volume, m\(^3\)
- $x$ position across cell, m
- $y$ stoichiometry of lithium in the solid electrode

Greek

- $a_n$ anodic transfer coefficient
- $a_c$ cathodic transfer coefficient
- $e$ volume fraction
- $\eta$ potential difference at the SEL V
- $\kappa$ ionic conductivity of electrolyte, S/m
- $\sigma$ electronic conductivity of solid matrix, S/m
- $\phi$ electric potential, V

Superscript

- 0 solvent
- eff effective material properties accounting for porous medium

Subscript

- a anodic
- c cathodic
- $e$ electrolyte (i.e., solution phase)
- s solid phase

References


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