



Gas-Evolution Induced Volume Fraction Changes and Their Effect on the Performance Degradation of Li-Ion Batteries

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Li-ion batteries swell due to gas evolution that results from decomposition of the electrolyte and from reaction with impurities. To study dimensional changes in Li battery cells, we derive a model for gas-evolution induced volume fraction changes in both electrolyte and inert material phases in composite Li-ion electrodes. The nonlinear increase in cell resistance is explained using volume fraction changes within the context of physics-based modeling. The simulation results given here are also used to map the effects of volume fraction changes on the discharge curve and on heat generation.

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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.¹⁻³ In Li-ion batteries, gas evolution results from complex chemical reactions in the electrolyte that are coupled with the SEI layer formation process.⁴ Differential electrochemical mass spectrometry (DEMS) study showed that gas generation at the anode is, in general, more significant than gas generation at the cathode.⁵ Gas generation is accelerated by increasing temperature.⁶ Cyclic voltammetry (CV) in DEMS study further showed that gas generation is continuous even after the formation of cathode⁶ 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 V) vs Li/Li^+ , while cathode materials show mass signals similar to the CV cycling profile. Following this experimental ob-

servation 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 work³ 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

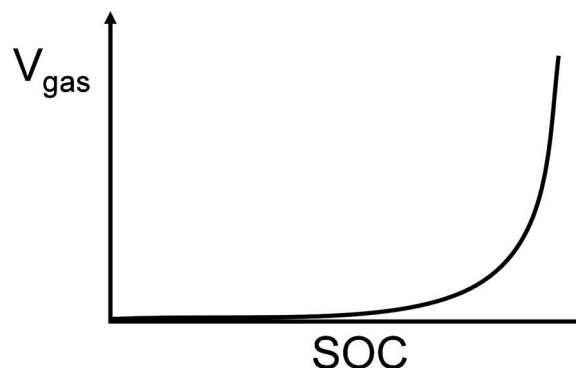


Figure 1. Schematic gas generation profile as a function of SOC.

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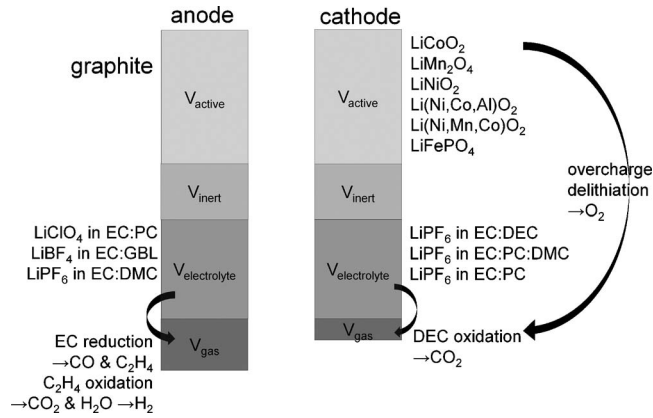


Figure 2. Cell swelling and gas generation mechanisms; materials commonly used for anodes, cathodes, and electrolytes in Li battery cells are shown.

$$\Delta \varepsilon_{\text{gas}}(x) = \frac{\Delta V_{\text{gas}}[y(x)]}{V_{\text{cell}}} \rightarrow \varepsilon_{\text{gas}}(x, t + \Delta t) = \varepsilon_{\text{gas}}(x, t) + \int_t^{t+\Delta t} \Delta \varepsilon_{\text{gas}} dt \quad [1]$$

where $y = c_s/c_T$ is the local state of charge (i.e., stoichiometry of lithium in the electrode), ε_{gas} is the volume fraction of the evolved gas phase, ΔV_{gas} is the volume of the evolved gas as shown in Fig. 1, and V_{cell} is the volume of the battery cell.

Because the DEMS studies further identified accumulated gases as CO₂ and H₂,^{5,6} the gas phase is assumed to be composed of inactive species which can be treated as inert material phases in the porous electrode. Here, we assume that the cell is mechanically fixed. Thus, the electrolyte volume is displaced from the electrode in proportion to the volume of generated gas; we compensate for its loss with a proportional decrease in active material volume. After Δt at a given time t , the electrolyte volume fraction within the porous electrode is thus presumed to be reduced as

$$\varepsilon_e(x, t + \Delta t) = \varepsilon_e(x, t) - \Delta \varepsilon_{\text{gas}}(x, t) \quad [2]$$

and the inert material volume increases by

$$\varepsilon_{\text{inert}}(x, t + \Delta t) = \varepsilon_{\text{inert}}(x, t) + \Delta \varepsilon_{\text{gas}}(x, t) \quad [3]$$

where $\varepsilon_{\text{inert}}$ is the volume fraction of inert material phase (e.g., binder and conductive additive).

The overall volume fraction changes for each material phase are illustrated in Fig. 3. Due to gas evolution, the inert material volume

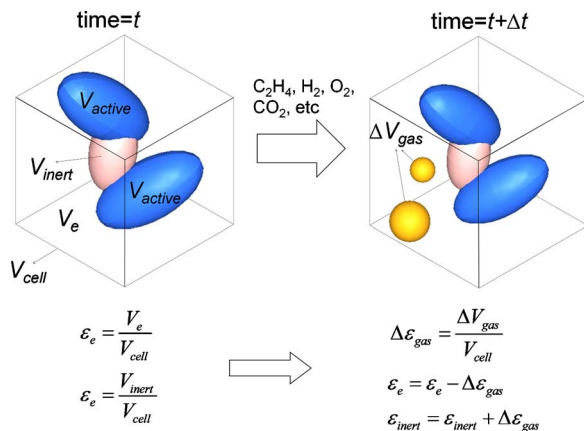


Figure 3. (Color online) A schematic diagram of gas-induced volume fraction changes in composite electrodes, along with terminology used in the present model.

fraction increases while the electrolyte volume fraction decreases. Therefore, gas evolution during battery cycling results in the decrease in electrolyte volume fraction and the increase in inert material volume fraction.

Resistance Changes in Li-Ion Batteries

The volume fraction changes in composite electrodes can affect five terms in the mathematical modeling of Li-ion batteries. The governing equations in this mathematical model describe the diffusion and conduction of Li ions and electrons in solid and liquid phases as a result of volume averaging theory, which can be summarized as

$$\frac{\partial c_s}{\partial t} + \frac{1}{r^2} \nabla \cdot (r^2 D_s \nabla c_s) = 0 \quad [4]$$

$$\frac{\partial (\varepsilon_e c_e)}{\partial t} = \nabla \cdot (D_e^{\text{eff}} \nabla c_e) + \frac{1-t_+^0}{F} J^{\text{Li}} - \frac{\mathbf{i}_e \cdot \nabla t_+^0}{F} = 0 \quad [5]$$

$$\nabla \cdot (\sigma^{\text{eff}} \nabla \phi_s) - J^{\text{Li}} = 0 \quad [6]$$

and

$$\nabla \cdot \left\{ \kappa^{\text{eff}} \left[\nabla \phi_e - \frac{2RT}{F} (1-t_+^0) \left(1 + \frac{d \ln f_{\pm}}{d \ln c_e} \right) \nabla \ln c_e \right] \right\} + J^{\text{Li}} = 0 \quad [7]$$

In Eq. 4-7, local Li-ion flux (i.e., J^{Li}) is governed by Butler-Volmer kinetics, i.e.

$$J^{\text{Li}} = a_s k (\bar{c}_{\text{se}})^{\alpha_c} (c_T - \bar{c}_{\text{se}})^{\alpha_a} (c_e)^{\alpha_a} \left[\exp\left(\frac{\alpha_a F}{RT} \eta\right) - \exp\left(-\frac{\alpha_c F}{RT} \eta\right) \right] \quad [8]$$

where \bar{c}_{se} is the concentration of lithium at the SEI, and the specific interfacial surface area a_s can be written as

$$a_s = \frac{3\varepsilon_{\text{active}}}{R_s} \quad [9]$$

where $\varepsilon_{\text{active}}$ 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

$$D_e^{\text{eff}} = (\varepsilon_e)^{1.5} D_e \quad [10]$$

$$\kappa^{\text{eff}} = (\varepsilon_e)^{1.5} \kappa_e \quad [11]$$

and

$$\sigma^{\text{eff}} = (\varepsilon_{\text{active}})^{1.5} \sigma_s \quad [12]$$

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.^{12,13}

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.

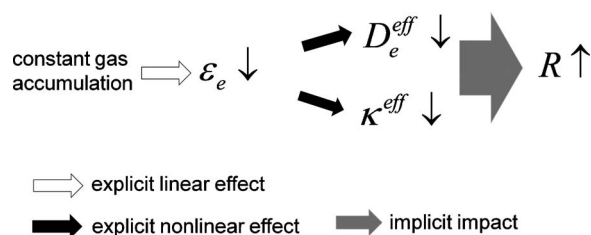


Figure 4. Resistance degradation due to volume fraction changes induced by gas evolution.

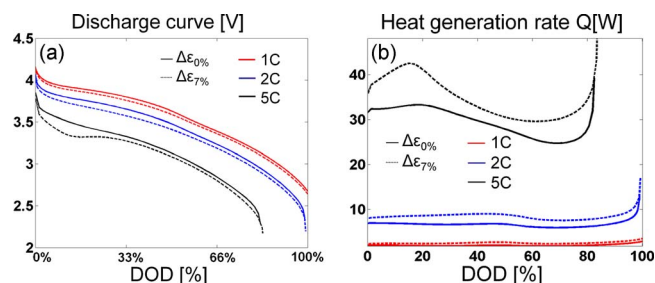


Figure 5. (Color online) Galvanostatic discharging simulation of thermo-electrochemical model: (a) Discharge curve and (b) heat generation.

Effect of Volume Fraction Changes on Discharging

A one-dimensional (1D) thermo-electrochemical model¹⁴ 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.¹⁴ The cathode is LiMn_2O_4 and the anode is graphite. The electrolyte contains 1 M of LiPF_6 in ethylene carbonate:dimethyl carbonate solvent. Figure 5 provides simulation results using a 1D thermo-electrochemical 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 consumptions, 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.

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List of Symbols

a_s	surface area of active material per volume of electrode, m^{-1}
c_c	concentration of salt in the electrolyte, mol/m^3
c_s	concentration of lithium in the solid electrode, mol/m^3
c_T	maximum concentration of lithium in the solid electrode, mol/m^3
D_c	diffusion coefficient of lithium in the electrolyte, m^2/s
D_s	diffusion coefficient of lithium in the solid electrode particle, m^2/s
f_{\pm}	mean molar activity coefficient of salt
F	Faraday's constant, 96,487 C/mol
i_c	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, 8.3143 J/mol K
R_s	radius of a solid particle, m
t	time, s
t_+^0	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

α_a	anodic transfer coefficient
α_c	cathodic transfer coefficient
ε	volume fraction
η	potential difference at the SEI, V
κ	ionic conductivity of electrolyte, S/m
σ	electronic conductivity of solid matrix, S/m
ϕ	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

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