Modeling the SEI-Formation on Graphite Electrodes in LiFePO4 Batteries

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An advanced model is proposed, describing the capacity losses of C6/LiFePO4 batteries under storage and cycling conditions. These capacity losses are attributed to the growth of a Solid Electrolyte Interface (SEI) at the surface of graphite particles in the negative electrode. The model assumes the existence of an inner and outer SEI layer. The rate determining step is considered to be electron tunneling through the inner SEI layer. The inner SEI layer grows much slower than the outer SEI layer. Another contribution to the degradation process is the exfoliation of SEI near the edges of graphite particles during discharging and the formation of new SEI induced by the volumetric changes during the subsequent charging. The model has been validated by storage and cycling experiments. The simulation results show that the capacity losses are dependent on the State-of-Charge (SoC), the storage time, cycle number and graphite particle size. The model can be used to predict both the calendar and cycling life of the Li-ion batteries.

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Li-ion batteries, based on the C6/LiFePO4 chemistry, attracts nowadays much attention for application in, for example, electric vehicles due to the excellent cycling stability of the LiFePO4 electrode. The main electrochemical storage reactions of this battery type can be represented by

\[
\text{C}_6 + x\text{Li}^+ + xe^- \overset{\text{charge}}{\underset{\text{discharge}}{\rightleftharpoons}} \text{Li}_x\text{C}_6, \quad [1]
\]

\[
\text{LiFePO}_4 \overset{\text{charge}}{\underset{\text{discharge}}{\rightarrow}} \text{Li}_{1-x}\text{FePO}_4 + x\text{Li}^+ + xe^- \quad [2]
\]

During charging electrons and Li+ ions are extracted from the LiFePO4 (0 ≤ x ≤ 1) electrode and flow into the graphite electrode. The reverse reactions take place during discharging. The structure of LiFePO4 (LFP) is highly robust due to the strong bonding between the P and O atoms. LFP batteries therefore combine a good cycling stability with excellent thermal stability and long lifespan.1-5 The volume decreases only 6.8% when all Li (Δx = 1) is extracted and these small volumetric changes do not influence the structure of LiFePO4 and FePO4. Favorably, it almost fully counterbalances the volumetric changes of the graphite electrode during Li (de)insertion.

Due to these favorable properties, the capacity losses caused by the LFP cathode are generally assumed to be negligible. Furthermore, Brousseley et al. showed that the capacity of the graphite electrode can be fully recovered even after more than 1 year storage under ‘floating’ conditions at 60 °C, demonstrating that the stability of the carbon electrode is also excellent.7 However, capacity losses are still found in LFP batteries. It is generally accepted, that the formation of a Solid Electrolyte Interface (SEI) is one of the main reasons for the capacity losses of graphite-based Li-ion batteries, especially under moderate conditions during the initial stages of aging.

The SEI plays a dual-role in the performance of Li-ion batteries. On the one hand, it protects the negative electrode from solvent co-intercalation, preventing exfoliation of the graphene layers. On the other hand, it consumes cyclable lithium inside the battery, which is therefore no longer available for the energy storage process and hence leads to irreversible capacity losses. Extensive efforts have been made to study the structural and chemical composition of SEI layers.8-26

Despite the fact that a lot of studies were made to investigate the SEI by experimental methods, the understanding of the SEI formation process is still limited due to the complexity of the SEI formation reaction, which was found to be highly dependent on the composition of the electrolyte, the electrode voltage and electrode surface morphology. While modeling seems to be an efficient way to investigate the SEI formation process, only a few studies are related to the SEI growth process. For most commercial batteries very stable SEI layers are already formed as part of the manufacturing process, playing a dual role in protecting the graphite electrode. On the one hand, it insulates electrons from being in direct contact with the solvent and, on the other hand, it prevents solvent molecules passing through and, consequently, preventing exfoliation of the graphene layers.

Experimental studies demonstrate that the SEI consists of a compact inner SEI layer and a more porous outer SEI layer, which are mainly composed of inorganic Li-salts and organic Li-salts, respectively.11,12,14 The inner SEI-layer is dense and is considered to isolate the surface of the graphite electrode from being in direct contact with the electrolyte, thereby preventing solvent co-intercalation inside the graphite electrode. The inner SEI layer is, however, considered to be highly conductive for unsolvated Li+ ions. The outer SEI layer is highly porous, allowing solvated Li+ ions to pass through.27

Based on these experimental results, an advanced electron tunneling-based SEI formation model is proposed and simulated in the present contribution. The model is focusing on battery aging after formation when a relatively stable SEI has already been formed on the graphite surface during the manufacturing process. The simulation results are validated by the experimental data.

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Figure 1. Schematic representation of a C/LiFePO₄ battery, showing the formation of the inner- and outer SEI layer during charging (a) and storage under open-circuit conditions (b).

SEI Formation Mechanism

The complex morphology of the dual SEI layer is schematically represented in Fig. 1. The inner SEI layer is considered to be an insulator for electrons. Solvent reduction is assumed to take place at the interface of the inner and outer SEI layer and is facilitated by electron tunneling from the graphite electrode through the inner SEI layer to the Lowest Unoccupied Molecular Orbital (LUMO) of the solvent. The Fermi level for Lithium and LiC₆ has been reported to be −2.36 eV and −2.80 eV versus vacuum, respectively. The LUMO of ethylene carbonate (EC), one of the main solvents in LFP battery electrolytes, was reported to be −2.99 eV in the presence of Li⁺ ions. This value is more negative than the Fermi level of the graphite electrode and, consequently, EC will be reduced assuming that electrons can cross the energy barrier for electron tunneling. The electrochemical reduction of EC has, in general terms, been represented by

\[
\text{EC} + e^- \rightarrow \text{Li}^+ \text{C}_6 \quad \text{(3a)}
\]

where route (3a) is considered to be the electrochemical conversion reaction building up the inner SEI layer while route (3b) mainly contributes to the growth of the outer SEI layer. The SEI formation is initiated when the voltage of the graphite electrode drops below approximately 1.0 V vs Li/Li⁺. The SEI is formed during the activation procedure after the battery manufacturing process has been completed. During (dis)charging Li⁺ ions can easily pass the layered structure of the entire battery stack, including both SEI layers. The solvent molecules (S) present in the electrolyte can also easily pass the porous outer SEI layer but cannot penetrate the inner SEI layer. The inner SEI layer is, however, a good insulator but electrons can tunnel through it when its thickness is sufficiently small. The tunneling process is assumed to be the rate determining step, implying that solvent molecules are immediately reduced when the electrons arrive at the SEI interface. The products of these reduction reactions increase the thickness of both SEI layers but the individual rates might be significantly different as will be shown below.

When a current \( I_{ch} \) is applied to the battery (see Fig. 1a), this current is used to drive two electrochemical processes at the graphite electrode, according to

\[
I_{ch} = I_{tr} + I_{SEI}
\]

where \( I_{tr} \) represents the charge transfer current used to facilitate Li⁺ ion intercalation in the graphite electrode (Eq. 1) and \( I_{SEI} \) is the current related to the SEI formation reactions (Eq. 3). Obviously, the major
part of the current is used to drive the main electrochemical storage reaction.

It is known that the volumetric expansion/shrinkage of graphite electrodes during (dis)charging can significantly influence the SEI formation process. Due to the mechanical stress, resulting from these volumetric changes, cracks are formed in the SEI layer, inducing the formation of uncovered graphite. As a result, the solvent is directly brought in contact with pristine graphite and will immediately be reduced and new SEI products are acceleratedly formed. Therefore, these volumetric changes have a considerable influence on the increased capacity losses upon cycling.

In case of storage, no current flows through the outer circuit (see Fig. 1b). The SEI formation can, however, still occur under open-circuit conditions. When a battery is stored at a certain State-of-Charge \((x > 0)\), electrons can still tunnel through the inner layer and reduce the solvent molecules at the inner/outer SEI interface. Obviously, this reduction reaction should be counter-balanced under open-circuit conditions by an oxidation reaction as no external current is flowing. Oxidation of Lithium stored inside the graphite electrode will take place at the graphite/inner SEI layer interface, resulting in \(\text{Li}^+\) ion diffusion through the inner SEI layer. This electroless process is illustrated in Fig. 1b. As Lithium from the graphite electrode will be consumed this ultimately result in irreversible capacity losses even under open-circuit conditions. The SEI formation during storage of LFP batteries is considered to be the main cause of irreversible capacity losses.

**Model Development**

When electron tunneling is considered to be rate limiting, as discussed in Ref. 48, the tunneling current \((I_0)\) is proportional to the number of electrons reaching the surface of the graphite electrode \((dN/dt)\) and the probability \((P\text{, dimensionless})\) of electrons to tunnel through the inner SEI layer. The electron tunneling current can then be written as

\[
I_0 = P \frac{dN}{dt} e,
\]

where \(e\) is the electron charge. In the present work, the electrical double layer (dis)charging currents are excluded and the only focus is the description of the faradaic tunneling currents.

A simple rectangular energy barrier model has been adopted in the present work to describe the electron tunneling process (Fig. 2). Here \(E_f(x)\) is the Fermi level of the \(\text{LiC}_6\) electrode, which can be described by \(E_f(x) = E_f(LiC_6) - e(\psi_{LiC_6} - \psi_{LiC_6})\), in which \(\psi_{LiC_6}\) is the electrode potential of the graphite electrode at \(SoC = x\), \(\psi_{LiC_6}\) is the electrode potential, \(E_f(LiC_6)\) is the Fermi level of \(\text{LiC}_6\), \(U\) is the energy level of free electrons and \(\Delta E\) represents the energy barrier, according to \(\Delta E = U - E_f(x)\), \(I^m\) is the SEI inner layer thickness, \(U_1\) here refers to Fermi level of graphite, \(U_2\) is the LUMO of the solvents. The tunneling probability \((P)\) has been derived in Appendix as Eq. A17, i.e.

\[
P = \frac{16k_I k_2 e^{2\alpha}}{a^2(k_1 + k_2)^2(e^{2\alpha} + 1)^2 + (a^2 - k_1 k_2)^2(e^{2\alpha} - 1)^2},
\]

where

\[
k_1 = \frac{1}{h} \sqrt{2m(E_f(x) - U_1)}, \quad k_2 = \frac{1}{h} \sqrt{2m(E_f(x) - U_2)},
\]

and

\[
a = \frac{1}{h} \sqrt{2m(U - E_f(x))}.
\]

With some mild assumptions (see the more detailed derivation in the Appendix), \(P\) can be simplified as follows

\[
P = P_0 \exp \left( -\frac{2\mu^* \sqrt{2m\Delta E}}{h} \right),
\]

\[
P_0 = \frac{16k_I k_2 e^{2\alpha}}{a^2(k_1 + k_2)^2 + (a^2 - k_1 k_2)^2}.
\]

where \(E_f(x)\), the Fermi level of electrons in the graphite electrode, is a function of the electrode potential \(\psi_{LiC_6}(x)\). The equilibrium voltage (or the Electro-Motive Force (emf)) of the graphite electrode has been analyzed as a function of \(\text{SoC}(x)\) and is presented in Fig. 3. The results clearly indicate the presence of several voltage plateaus as a function of State-of-Charge. \(P_0\) in Eq. 11 is a pre-exponential coefficient, which is determined by \(E_f(x)\), \(U_1\), and \(U_2\) according to Eqs. 7-9.

The electron flux from the bulk of the graphite to the surface can be derived in line with

\[
\frac{dN}{dt} e = \frac{(6 + x)N_A \rho_C \psi_e}{4M_{e^+}} v_e A e,
\]

where the SoC ranges from \(0 < x \leq 1\), \(\rho_C\) denotes the graphite density \(\text{[g} \cdot \text{m}^{-3}]\), \(v_e\) is the Fermi velocity of electrons in the bulk of graphite \(\text{[m} \cdot \text{s}^{-1}]\), \(\Delta A\) the surface area of the graphite electrode available for electron tunneling \(\text{[m}^2\)], \(M_{e^+}\) the molar mass of graphite \(\text{[g} \cdot \text{mol}^{-1}]\), \(e\) the electronic charge, \(N_A\) the Avogadro number \(\text{[mol}^{-1}]\), the multiplier 6 in the numerator of Eq. 12 corresponds to the amount of free electrons of each graphite molecule and the multiplier 4 in the denominator stems from the assumption that the electronic velocity

![Figure 2](image-url) One-dimension rectangular barrier model for electron tunneling through the inner SEI layer. Region I corresponds to graphite surface, region II is inner SEI layer, region III corresponds to solvent side.

![Figure 3](image-url) Equilibrium potential of the graphite electrode \(\psi_{LiC_6}\) as a function of SoC, indicating the various stages of the (de)lithiation process.
vector within the graphene layers can only proceed along one of four orthogonal directions with equal probabilities (1/4).

Combining Eqs. 5, 10 and 12, the tunneling current \(I_t\) passing the graphite surface can be represented by

\[
I_t = P \frac{dN}{dt} e = \frac{(6 + x)F_{pc_{\text{c}}} v_e A P_0 e^{-\frac{2i^\alpha \sqrt{2m \Delta E}}{h}}}.
\]

The Li consumption by the SEI layer can then be expressed by

\[
dQ_{SEI}(t) = \frac{(6 + x(t))F_{pc_{\text{c}}} A v_e P_0 e^{-\frac{2i^\alpha(t) \sqrt{2m \Delta E(t)}}{h}}}{4M_{C_6}}.
\]

where \(Q_{SEI}(t)\) is the amount of Li captured in both SEI layers from time \(t \geq 0\) up to time \(t\) and \(i^\alpha_{\text{in}}(t)\) is the total thickness of the inner SEI layer at any time \(t > 0\). At \(t = 0\), \(i^\alpha_{\text{in}}\) corresponds to the thickness of initial inner SEI layer after the activation process has been completed. \(i^\alpha_{\text{in}}\) is an adjustable parameter dependent on the activation conditions and is of the order of ~2.0 nm.16,19 The total inner SEI layer thickness can, at any moment of time \(t\), be written as

\[
i^\alpha_{\text{in}}(t) = l_{\text{tot}}^\alpha + l_{\text{lin}}^\alpha(t),
\]

where \(l_{\text{lin}}^\alpha(t)\) is the increase of the inner layer thickness during storage. Using Eq. 15, Eq. 14 can be rearranged into

\[
dQ_{SEI}(t) = \frac{(6 + x(t))F_{pc_{\text{c}}} A v_e P_0 e^{-\frac{2i^\alpha(t) \sqrt{2m \Delta E(t)}}{h}}}{4M_{C_6}} \times \exp \left(-\frac{2 \left(l_{\text{lin}}^\alpha + l_{\text{lin}}^\alpha(t)\right) \sqrt{2m \Delta E(t)}}{h}\right).
\]

Assuming a homogeneous SEI layer thickness, the volume of the increased inner SEI layer can be represented by

\[
V^\alpha_{\text{in}}(t) = A \rho^\alpha l_{\text{lin}}^\alpha(t),
\]

and the corresponding mass by

\[
m^\alpha_{\text{in}}(t) = \rho^\alpha V^\alpha_{\text{in}}(t),
\]

where \(\rho^\alpha\) is the (average) gravimetric density of the inner SEI layer. Denoting \(w^\alpha_{Li}\) the average weight percentage of Li in the inner SEI layer this leads to

\[
w^\alpha_{Li} = m^\alpha_{Li} A \rho^\alpha / m^\alpha_{SEI}(t).
\]

Eqs. 18 and 19 can be rearranged, yielding

\[
l_{\text{lin}}^\alpha(t) = \frac{m^\alpha_{\text{in}}(t)}{\rho^\alpha w^\alpha_{Li}}.
\]

However, the mass of consumed lithium is connected with the number of moles of consumed lithium \((\nu^\alpha_{\text{lin}}(t))\), according to

\[
m^\alpha_{\text{in}}(t) = M_{Li} \nu^\alpha_{\text{lin}}(t),
\]

where \(M_{Li}\) is the molar mass of Li. The molar amount of consumed Li is related to the amount of Li consumed in the inner SEI layer \((Q^\alpha_{SEI}(t))\) by

\[
\nu^\alpha_{\text{lin}}(t) = Q^\alpha_{SEI}(t) / F,
\]

in which \(F\) is the Faraday constant. Combining Eqs. 21 and 22, the following expression for the mass of consumed Li is obtained

\[
m^\alpha_{\text{in}}(t) = \frac{M_{Li} Q^\alpha_{SEI}(t)}{F}.
\]

Comparing Eqs. 20 with 23, the inner SEI layer thickness can be expressed by

\[
l_{\text{lin}}^\alpha(t) = \frac{Q^\alpha_{SEI}(t) M_{Li}}{\rho^\alpha w^\alpha_{Li} F}.
\]

and the amount of charge involved to form the inner SEI layer can be represented by

\[
Q^\alpha_{SEI}(t) = \frac{A \rho^\alpha w^\alpha_{Li} F l_{\text{lin}}^\alpha(t)}{M_{Li}}.
\]

\(\delta\) is defined as the fraction of the capacity loss related to the inner SEI layer with respect to the total capacity loss consumed by both SEI layers. \(\delta\) is dependent on the aging conditions. This leads to

\[
Q^\alpha_{SEI}(t) = \delta Q_{SEI}(t).
\]

The increase of the inner SEI layer thickness as a function of time is then given by

\[
l_{\text{lin}}^\alpha(t) = \frac{\delta Q_{SEI}(t) M_{Li}}{A \rho^\alpha w^\alpha_{Li} F}.
\]

Finally, the Li consumption rate to form the SEI layer satisfies the following Ordinary Differential Equation (ODE)

\[
\frac{dQ_{SEI}(t)}{dt} = \frac{(6 + x(t))F_{pc_{\text{c}}} A v_e P_0 e^{-\frac{2i^\alpha(t) \sqrt{2m \Delta E(t)}}{h}}}{4M_{C_6}} \times \exp \left(-\frac{2 \left(l_{\text{lin}}^\alpha + l_{\text{lin}}^\alpha(t)\right) \sqrt{2m \Delta E(t)}}{h}\right).
\]

The time dependent terms \(x(t)\) and \(\Delta E(t)\) make it difficult to solve this general expression for the SEI growth analytically. In order to simplify this expression two different cases will be considered below.

**SEI formation during storage.**—In the case of storage, the capacity loss is only caused by the SEI formation, while the State-of-Charge and \(\Delta E\) are more or less constant. The SEI formation rate can then be expressed by

\[
\frac{dQ_{SEI}(t)}{dt} = \frac{(6 + x)F_{pc_{\text{c}}} A v_e P_0 e^{-\frac{2i^\alpha(t) \sqrt{2m \Delta E(t)}}{h}}}{4M_{C_6}} \times \exp \left(-\frac{2 \left(l_{\text{lin}}^\alpha + l_{\text{lin}}^\alpha(t)\right) \sqrt{2m \Delta E(t)}}{h}\right).
\]

where \(Q_{SEI}(t)\) is the amount of Li+ charge captured [C] in both SEI layers from \(t = 0\) up to \(t\) during storage. The ODE Eq. 29 is now simple and can be solved by any standard integration scheme (e.g. Euler), which leads to

\[
Q_{SEI}(t) = \frac{\rho^\alpha \sqrt{2m \Delta E(t)}}{2 \Delta E} \ln \left[1 + \frac{(6 + x)C_{\text{pc}} v_e M_{Li} P_0 \sqrt{2m \Delta E}}{2M_{Li} \rho^\alpha w^\alpha_{Li} F} t \exp \left(-\frac{2l_{\text{lin}}^\alpha \sqrt{2m \Delta E}}{h}\right)\right] \frac{M_{Li}}{A \rho^\alpha \sqrt{2m \Delta E}}.
\]

The SEI formation current can be written as

\[
I_{SEI} = \frac{dQ_{SEI}(t)}{dt} = \frac{(6 + x)F_{pc_{\text{c}}} A v_e P_0 e^{-\frac{2i^\alpha(t) \sqrt{2m \Delta E(t)}}{h}}}{4M_{C_6}} \times \exp \left(-\frac{2l_{\text{lin}}^\alpha \sqrt{2m \Delta E}}{h}\right).
\]

The derivations of Eq. 30 from Eq. 29 can be found from Appendix.
\(Q_{\text{cov}}^{\text{SEI}}(t)\); (ii) fresh SEI formed on the newly formed surface induced by the volume change expansion during (dis)charging \(Q_{\text{fr}}^{\text{SEI}}(t)\) and (iii) the peeled SEI, formed during the previous (dis)charging cycles \(Q_{\text{peel}}^{\text{SEI}}(t)\), i.e.

\[
Q_{\text{SEI}}^{\text{cov}}(t) = Q_{\text{SEI}}^{\text{cov}}(t) + Q_{\text{fr}}^{\text{SEI}}(t) + Q_{\text{peel}}^{\text{SEI}}(t).
\]

Considering the case of the inner SEI formation on the covered surface, the formation rate in each cycle is largely dependent on the thickness of the already-existing layer, which grows with cycle number. The SEI formation rate on this surface is defined by the general expression given by Eq. 30. To simplify this equation a 50\% State-of-Charge is assumed and \(\Delta E(\tau) = \Delta E(\tau) = \Delta E\), which is an unknown constant. The following expression can then be derived

\[
d\frac{dQ_{\text{cov}}^{\text{SEI}}(t)}{dt} = \frac{(6.5) F \rho_{\text{c}} A_{\text{cov}}^{\text{SEI}}}{4 M_{\text{c}}} \nu_r P_0 \\
\times \exp \left( -\frac{2 \left(t_0^{\text{in}} + t_{\text{cov}}(t)\right) \sqrt{2m \Delta E}}{h} \right),
\]

where \(Q_{\text{cov}}^{\text{SEI}}(t)\) denotes the development of capacity loss to the SEI of the covered surface, \(A_{\text{cov}}^{\text{SEI}}\) is the covered surface area of graphite, \(t\) is the operating time after the start of the experiment, \(t_0^{\text{in}}(t)\) is the inner layer thickness growth, \(t_0^{\text{in}}\) is the initial inner SEI layer thickness after activation process at \(t = 0\). The inner SEI formation rate at the covered surface can then be expressed as

\[
d\frac{dQ_{\text{SEI}}^{\text{cov}}(t)}{dt} = \frac{(6.5) F \rho_{\text{c}} A_{\text{cov}}^{\text{SEI}}}{4 M_{\text{c}}} \nu_r P_0 \\
\times \exp \left( -\frac{2 \left(t_0^{\text{in}} + \frac{3 \rho_{\text{c}} A_{\text{cov}}^{\text{SEI}} h \Delta E}{\rho_{\text{se}} w_{\text{Li}}^{\text{SEI}} F}\right) \sqrt{2m \Delta E}}{h} \right).
\]

Similar to the case of storage, the capacity loss can be calculated by integrating Eq. 34, which leads to

\[
Q_{\text{SEI}}^{\text{cov}}(t) = \frac{h A_{\text{cov}}^{\text{SEI}} w_{\text{Li}}^{\text{SEI}} \rho_{\text{se}}^{\text{SEI}} F}{2k M_{\text{Li}} \sqrt{2m \Delta E}} \ln \left[ 1 + \frac{6.5 \rho_{\text{c}} \nu_r h \Delta E \rho_{\text{se}}^{\text{SEI}} w_{\text{Li}}^{\text{SEI}}}{2 M_{\text{c}} h \rho_{\text{se}}^{\text{SEI}} w_{\text{Li}}^{\text{SEI}}} \sqrt{2m \Delta E} \right]
\times \exp \left( -\frac{2 t_0^{\text{in}} + \sqrt{2m \Delta E}}{h} \right).
\]

Figure 4. Charge and discharge curves (a), corresponding currents (b), and corresponding development of the capacity losses (c) employed for the SEI growth on fresh surface area \(Q_{\text{fr}}^{\text{SEI}}\) (green curve), by exfoliated SEI \(Q_{\text{peel}}^{\text{SEI}}\) (blue curve) and the summation \(Q_{\text{SEI}}^{\text{fr}} + Q_{\text{SEI}}^{\text{peel}}\) (red curve) during cycling.

\[
Q_{\text{SEI}}^{\text{fr}}(t) = \chi.
\]

During discharging the freshly formed SEI does not grow as it is assumed that it is exfoliated at the end of discharging, thus \(Q_{\text{fr}}^{\text{SEI}}(t^d) = 0\). At the same time the peeled SEI has increased by \(\chi\), therefore

\[
Q_{\text{SEI}}^{\text{peel}}(t^d) = i \chi.
\]

Note that for model validation using the experimental data only \(Q_{\text{fr}}^{\text{SEI}}(t^d)\) and \(Q_{\text{cov}}^{\text{SEI}}(t^d)\) are necessary, since the capacity loss is calculated according to discharge capacity. So after the discharging process in \(i^{th}\) cycle, the \(Q_{\text{SEI}}^{\text{fr}}(t^d)\) can be obtained by integrating Eq. 38 and combining the result with Eq. 37. Summary of model parameters can be found in Table 1.

Experimental

Commercial prismatic 50 Ah batteries have been electrochemically investigated. The chemical composition of the cathode is LiFePO4 and that of the anode is graphite (AG56-1). The electrochemical experiments were performed with automated cycling equipment (Maccor). The temperature of all batteries was controlled at 20 °C.

Storage experiments.— This experimental details are summarized in Fig. 5. The batteries were activated with a current of 5 A (0.1 C) for 4 cycles, then fully charged and discharged under a CCCV regime in order to find the maximum storage capacities \(Q_{\text{max}}^{\text{fr}}\) and \(Q_{\text{max}}^{\text{ch}}\). The cutoff conditions were 3.65 V until 0.1 A (1/500C) for deep-charging.
Table I. Symbols used in the paper.

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<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
<th>Value</th>
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<td>Charge of single electron</td>
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<td>$A$</td>
<td>Surface area of graphite particle which is available for electrons to tunnel</td>
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<td>$\Delta E$</td>
<td>Energy barrier between $U$ and $E_f(x)$</td>
<td>eV</td>
<td></td>
</tr>
<tr>
<td>$l_{\text{ini}}$</td>
<td>Inner SEI thickness</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>$l_{\text{ini}}(t)$</td>
<td>Total inner layer during aging or storage</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>$l_{\text{ini}}(t)^0$</td>
<td>Initial inner SEI thickness on the graphite surface after activation process</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>$l_{\text{ini}}(t)^{i}$</td>
<td>Increase of the inner layer thickness during storage</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>$l_{\text{ini}}(t)^{i+1}$</td>
<td>Inner layer thickness growth after $i$ cycles</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>$l_{\text{ini}}(t)^{j}$</td>
<td>Inner layer thickness on fresh surface in $j$th cycle</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>$\nu_e$</td>
<td>Fermi velocity of electron in the bulk of graphite</td>
<td>m \cdot \text{s}^{-1}</td>
<td></td>
</tr>
<tr>
<td>$I_j$</td>
<td>Tunneling current</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>$j_{\text{SEI}}$</td>
<td>Current density of SEI formation</td>
<td>A \cdot \text{m}^{-2}</td>
<td></td>
</tr>
<tr>
<td>$j_{\text{ch}}$</td>
<td>Charging current density</td>
<td>A \cdot \text{m}^{-2}</td>
<td></td>
</tr>
<tr>
<td>$Q_{\text{SEI}}(t)$</td>
<td>Capacity loss to SEI during storage</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>$Q_{\text{SEI}}^{\text{cov}}(t)$</td>
<td>Li consumption in the SEI of the covered inner layer surface in $i$th cycle</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>$Q_{\text{SEI}}^{\text{fr}}(t)$</td>
<td>Li consumption in the SEI formed on fresh surface in $i$th cycle</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>$Q_{\text{SEI}}^{\text{cov}}(t)$</td>
<td>Li consumption in the peeled SEI layer</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>$Q_{\text{SEI}}^{\text{fr}}(t)$</td>
<td>Total capacity loss during cycling</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>$Q_{\text{SEI}}^{\text{cov}}(t)^j$</td>
<td>Available charging capacity(the effective charging capacity)</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>$P$</td>
<td>Electron tunneling probability</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$x$</td>
<td>State of Charge (SoC)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$\delta$</td>
<td>Capacity ratio between of inner and total SEI layers</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>CE</td>
<td>Coulombic efficiency</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5. Flowchart describing the storage experiments.

and 1.6 V until 0.1 A (1/500C) for deep-discharging. Subsequently, three batteries were charged to $Q_{\text{dch}}^1 = 30\%\ Q_{\text{max}}$, $Q_{\text{dch}}^2 = 70\%\ Q_{\text{max}}$, and $Q_{\text{dch}}^3 = Q_{\text{dch}}^\text{max}$ then stored for 20 days at room temperature. The batteries were fully discharged after each 20 days and the corresponding capacities were denoted as $Q_{\text{dch}}^i$ where $i$ refers to the storage stage. The batteries were charged to the previous storage capacity $Q_{\text{dch}}^i = Q_{\text{dch}}^i$ after fully discharging in order to make sure that all batteries will continue the previous storage cycle.

Cycling experiments.— The batteries were activated using the same method as for the storage experiments. Subsequently, the batteries were cycled in the CC mode with 5 A (0.1 C). The cutoff condition was 3.65 V for charging and 1.6 V for discharging. After every 20 cycles, a regime of CCCV for deep discharging was performed. The cutoff condition was 1.6 V for CC part and 0.1 A for CV part.

Results and Discussion

Calendar aging (storage) and capacity losses induced by cycling were carried out to validate the presented model. Many factors may contribute to the capacity losses during cycling LFP batteries. However, according to Lu,\textsuperscript{35} in the acceleration stage (around the first 100 cycles), the capacity losses are mainly due to the SEI growth on the anode. The cycling current was chosen to be 0.1 C in our experiment.
and the temperature was controlled at 20°C in order to avoid severe materials decay and other factors contributing to capacity losses. Both the reversible and irreversible capacity losses in the present work are attributed to the SEI formation on anode electrode.\textsuperscript{46,49–51} The Least Squares method was used to determine the unknown parameters in the simulations. The optimized parameters are listed in Table II. Both the experimentally observed capacity losses and the simulated results are shown in Figs. 6 and 7. Fig. 6 shows the normalized capacity losses as a function of time and Fig. 7 illustrates the absolute capacity loss upon cycling and storage.

The simulation results (solid lines) are in all cases in good agreement with the experimental results (symbols) under both storage and cycling conditions. After storage at 30% SoC for more than 3000 hours the capacity decreased 0.935 Ah, which is about 2% of the initial capacity. Storage at 70% and 100% SoC increased the losses to 1.844 and 1.841 Ah, respectively, which is almost two times larger than that at 30% SoC. Under storage conditions the whole system does not change significantly. Consequently, the volumetric changes of the graphite particles can be considered negligible. The inner SEI layer will tightly adhere to the graphite surface under these conditions. Electrons can tunnel continuously through the inner SEI layer and reduce the S molecules. Consequently, new SEI will be slowly formed at the interface of the inner and outer SEI layer. The electrons for this reduction process are delivered by the oxidation of Li stored in the graphite electrode. The resulting capacity losses depend on the SoC and the total storage time.

From Fig. 7 it can be concluded that the capacity losses resulting from cycling are higher compared to those of storage, which is in agreement with experimental data reported before.\textsuperscript{45} This is caused by the volumetric changes of the graphite electrode during charging and discharging. The changes cause to form cracks in the inner SEI layer surface and partly exfoliation of this layer. New fresh surfaces ($A'fr$) are thereby generated and exposed to the electrolyte. As a result, new SEI will be formed extremely fast and lead to the extra capacity loss. The formation of $Q_{SEI}^{cov}(t)$ is a function of the cycle number $i$: $Q_{SEI}^{cov}(t) = Q_{SEI}^{fr}(t^i)$, is a constant (see Eq. 37). However, the SEI layer of most part of the covered surface area is not damaged at all and grows continuously, leading to the capacity loss $Q_{SEI}^{cov}(x,t)$. It increases as a function of cycling time and State-of-Charge, but is independent on the cycle number $i$, similar to the storage case.

The total capacity loss is the summation of $Q_{SEI}^{fr}(t)$ and $Q_{SEI}^{cov}(x,t)$. Fig. 8 shows the contribution of $Q_{SEI}^{fr}(t)$ (red line) and $Q_{SEI}^{cov}(x,t)$ during cycling at 0.1 C-rate.

| Table II. Model parameters and battery variables. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | 30%             | 70%             | 100%            | 0.1C            |
| $l_0^{/mm}$    | 2.834           | 2.834           | 2.834           | 2.834           |
| $A/m^2$        | 292.15          | 292.15          | 292.15          | 292.15          |
| $\delta$       | $6.1 \times 10^{-3}$ | $4.5 \times 10^{-3}$ | $4.5 \times 10^{-3}$ | $4.6 \times 10^{-3}$ |
| $Q_{SEI}$/Ah   | 55.179          | 54.321          | 53.165          | 53.352          |
| $\Delta V$/eV  | 2.90            | 2.8             | 2.8             | 2.81            |
| $Q_{SEI}^{fr}$/Ah | 0.935          | 1.844           | 1.841           | 1.677           |
| $Q_{SEI}^{cov}$/Ah | 0             | 0               | 0               | 1.134           |
| AMSE/Ab        | 0.0074          | 0.0057          | 0.0076          | 0.0026          |

\textsuperscript{4}$\delta$ is optimized as average value

\textsuperscript{5}optimized parameters, optimized simultaneously

\textsuperscript{6}optimized parameters, optimized independently

\textsuperscript{7}variables, calculated from literature

\textsuperscript{8}output parameters

Figure 6. Experimental (symbols) and simulated (lines) capacity losses of the graphite electrode in a 50 Ah battery upon storage at various SoC: 30% (red curve), 70% (blue curve), 100% (magenta curve) and upon cycling at 0.1 C-rate (black curve).

Figure 7. Capacity loss under storage at various SoC: 30% (red curve), 70% (blue curve), 100% (magenta curve) and upon cycling at 0.1 C-rate (black curve).

Figure 8. Simulated total capacity loss $Q_{SEI}^{cov}$ (black curve) and the contribution of the covered SEI $Q_{SEI}^{cov}$ (blue curve) and peeled SEI $Q_{SEI}^{fr}$ (red curve) during cycling at 0.1 C-rate.
The energy barrier values are calculated on data given in Ref. 38. Fig. 11 shows the normalized current consumed by the SEI formation ($Q_{SEI}$) during storage at various State-of-Charge and cycling. The SEI formation current density is 4.8 \( \mu \text{A} \cdot \text{m}^{-2} \) in the initial stages of cycling and decreases to 2.0 \( \mu \text{A} \cdot \text{m}^{-2} \) after 3000 hours. During storage the current density monotonically decreased from 4.5 \( \mu \text{A} \cdot \text{m}^{-2} \) at 100% SoC, 4.0 \( \mu \text{A} \cdot \text{m}^{-2} \) at 70% SoC and 1.6 \( \mu \text{A} \cdot \text{m}^{-2} \) at 30% SoC. From Eq. 33 a reciprocal relationship between the capacity loss and storage time is indeed predicted. The higher current density upon cycling must again be attributed to the contribution of the new surface generated by the volumetric changes. The model not only predicts the calendar life and cycle life performance of LPF batteries but can also predict the impedance increase observed upon cycling, which is caused by the peeled-off SEI particles blocking the pores of the graphite electrode. Furthermore, the present tunneling model can be coupled by taking into account electrical double layer (dis)charging effects and the electrochemical charge transfer reactions (Eqs. 1 and 2). It is generally accepted that the Coulombic Efficiency (CE) is an important factor, determining the overall performance of rechargeable batteries.

![Figure 9](image1.png)  
**Figure 9.** Simulated Inner SEI layer growth under various operating conditions: 30% (red curve), 70% (blue curve), 100% (magenta curve) and cycling at 0.1 C-rate (black curve).

![Figure 10](image2.png)  
**Figure 10.** Simulated outer SEI layer growth under various operating conditions: 30% (red curve), 70% (blue curve), 100% (magenta curve) and cycling at 0.1 C-rate (black curve).

![Figure 11](image3.png)  
**Figure 11.** Calculated current density used for SEI formation at various operating conditions: 30% (red curve), 70% (blue curve), 100% (magenta curve) and cycling at 0.1 C-rate (black curve).
batteries. CE has been generally defined as \( CE = \frac{Q_{ch}}{Q_{tot}} \) and does not get more detailed information of the origin of the system inefficiency. A modified definition of the effective Coulombic Efficiency (CE\text{eff}) is therefore proposed here

\[
CE\text{eff} = \frac{j_{ch}}{j_{SEI}} \times 100\%,
\]

which considers the efficiency of the charging process only and hence considers the fundamentals behind the inefficiency. The current used for the main electrochemical storage reaction is given by \( j_{ch} = j_{SEI} - j_{SEI} \text{eff} \).

Eq. 40 is very similar to the model proposed by Dahn.\[41\] Multiplying both sides of Eq. 40 with the charging time, the effective charging efficiency (\( Q_{ch}^{\text{eff}} \)) can be described by

\[
Q_{ch}^{\text{eff}} = Q_{ch} CE\text{eff}.
\]

As discussed before, the SEI formation current \( j_{SEI} \) decreases with increasing inner SEI layer. Since the cycling current of 0.1 C is rather low, it is reasonable that capacity loss caused by power fade is ignored. The SEI formation during discharging process is also negligible compared with the charging process. So the coulombic efficiency increases when time passes (see Fig. 12). CE can directly give capacity retention information. However, to predict the absolute values of the capacity, other parameters (e.g. cycle numbers and cycling time) are required.

Fig. 13 shows the dependence of storage capacity loss as a function of the surface area of the graphite electrode. In line with Eq. 31 a linear relationship is found. The three lines correspond to different storage times. Extrapolating the surface area to 0, the corresponding capacity loss is found to be 0 also, indicating that no capacity loss is indeed to be expected when no active surface area is exposed to the electrolyte.

Fig. 14 shows the storage capacity loss as a function of the particle size from which the graphite electrode is composed. The capacity loss decreases with increasing particle size. A reciprocal relationship is found between the capacity loss and particle size in all cases. From the model description it follows that the larger the particle size, the better the capacity retention is. However, it is well known that a larger particle size can negatively influence the mass transport properties for Li ions in the active materials. Larger particles increase the diffusion distance of Li ions and may decrease the rate capability of the battery. So the optimized particle size is a trade-off between the capacity loss and rate capability of Li-ion batteries.

**Conclusions**

An advanced electron tunneling based SEI formation model is proposed, describing the capacity losses of C6/LiFePO4 batteries under storage and cycling conditions, which can be used to predict the calendar life and cycle life performance of LPF batteries. The model assumes the existence of a compact inner and porous outer SEI layer. The rate determining step is considered to be electron tunneling through the inner SEI layer. Both SEI layers are growing at the interface of the inner and outer SEI layer. The inner SEI layer grows much slower than the outer layer. The initial thickness of the inner layer developed after activation largely determines the future degradation rate.

The capacity losses are strongly dependent on the SoC, i.e. by the electrode potential and tunneling probability. The capacity losses during cycling are larger than during storage for the same operating time due to the exfoliation of the SEI near the edges of graphite particles during (dis)charging. The capacity losses due to the peeled SEI is a function of charging time and cycling number. A relationship of \( \ln t \) between the capacity loss and aging time is found when the capacity losses are attributed to the SEI formation only.

**Figure 12.** Current density \( j_{SEI} \) of SEI formation (black line) and calculated Coulombic Efficiency (CE) upon cycling (red line).

**Figure 13.** Calculated capacity loss as a function of surface area for three different storage times: \( t_1 = 1000 \) hours (black line), \( t_2 = 2000 \) hours (blue line), \( t_3 = 3000 \) hours (red line).

**Figure 14.** Capacity loss as a function of graphite particle size for different storage times: \( t_1 = 1000 \) hours (black line), \( t_2 = 2000 \) hours (blue line), \( t_3 = 3000 \) hours (red line).
Both the particle size and particle surface area of graphite have a large influence on the capacity losses. A linear relationship between the surface area and capacity loss is observed while a reciprocal relationship between the particle size and the capacity loss is found in accordance with the model. The SEI formation currents are also discussed. It was found that those currents decline exponentially with time. A new Coulombic Efficiency definition based on SEI formation current is proposed, describing the charging efficiency.

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Appendix

1. Derivation of the tunneling probability

For a one-dimensional rectangular barrier model (see Fig. 2), the space can be divided into 3 parts: region I corresponds to graphite electrode, where we suppose \( x \leq 0 \); region II corresponds to the inner SEI, where \( 0 \leq x \leq h \); region III corresponds to the solvent side, where \( x \geq F \). The wave function of electrons in the various regions are calculated according to the stationary Schrödinger equation.

In region I, the Schrödinger equation takes the following form

\[
\frac{d^2 \psi_1}{dx^2} + \frac{2m}{\hbar^2} (E - U_1) \psi_1 = 0, \tag{A1}
\]

where \( \psi_1 \) is the electron wave function in region I. The solution of Eq. A1 yields

\[
\psi_1 = e^{ik_1x} + re^{-ik_1x}, \tag{A2}
\]

and therefore

\[
\frac{d \psi_1}{dx} = ik_1\left(e^{ik_1x} - re^{-ik_1x}\right), \tag{A3}
\]

where \( k_1 = \sqrt{\frac{2m(E-U_1)}{\hbar^2}} \) and \( r \) are constants to be determined from the boundary conditions.

Similarly, the wave function in region II can be calculated, according to

\[
\frac{d^2 \psi}{dx^2} + \frac{2m}{\hbar^2} (E - U) \psi = 0, \tag{A4}
\]

where \( \psi \) is the electron wave function in region II. Solving Eq. A4 leads to

\[
\psi = ae^{ikx} + be^{-ikx}, \tag{A5}
\]

and

\[
\frac{d \psi}{dx} = i\alpha(ae^{ikx} - be^{-ikx}), \tag{A6}
\]

where \( \alpha = \sqrt{\frac{2m(U-E)}{\hbar^2}} = i\sqrt{\frac{2m(U-E)}{\hbar^2}} \), \( a \) and \( b \) are constants.

In region III, the Schrödinger equation can be written as

\[
\frac{d^2 \psi_2}{dx^2} + \frac{2m}{\hbar^2} (E - U_2) \psi_2 = 0, \tag{A7}
\]

where \( \psi_2 \) is the electron wave function, which leads to

\[
\psi_2 = ce^{ik_2x}, \tag{A8}
\]

and

\[
\frac{d \psi_2}{dx} = ik_2ce^{ik_2x}, \tag{A9}
\]

where \( k_2 = \sqrt{\frac{2m(U-E)}{\hbar^2}} \) and \( c \) are constants.

Considering that both the wave function and its derivative are continuous, the continuity conditions must be applied at the boundary. As a result, the following system of equations holds

\[
\begin{align*}
\psi_1(x = 0) &= \psi(x = 0), \\
\psi_1(x = l) &= \psi_2(x = l), \\
\frac{d \psi_1}{dx}(x = 0) &= \frac{d \psi}{dx}(x = 0), \\
\frac{d \psi_1}{dx}(x = l) &= \frac{d \psi_2}{dx}(x = l).
\end{align*} \tag{A10}
\]

Substituting the corresponding boundary values, described by Eqs. A2, A3, A5, A6, A8 and A9, into Eq. A10 leads to the following system

\[
\begin{align*}
-a + b &= 1, \\
k_1r + ka - ab &= k_1, \\
ace^{ik_1x} + be^{-ik_1x} - e^{ik_1x} &= 0, \\
ace^{ik_1x} - abe^{-ik_1x} - ck_2e^{ik_2x} &= 0.
\end{align*} \tag{A11}
\]

This system of Eqs. A11 can be written in form of

\[
\mathbf{A} \mathbf{v} = \mathbf{Z}, \tag{A12}
\]

where

\[
\mathbf{A} = \begin{pmatrix} -1 & 1 & a & 0 \\ 0 & e^{-ik_1x} & e^{-ik_1x} & -e^{ik_1x} \\ 0 & -ae^{ik_1x} & -ae^{ik_1x} & -k_2e^{ik_2x} \end{pmatrix}, \quad \mathbf{V} = \begin{pmatrix} r \\ a \\ b \\ c \end{pmatrix}, \quad \mathbf{Z} = \begin{pmatrix} 1 \\ k_1 \end{pmatrix}.
\]

A straightforward calculation leads to

\[
c = \frac{4\alpha k_1 e^{ik_2x}}{(a(k_1 + k_2)(e^{2\alpha} + 1) - b(k_1 - k_2)^2)(e^{2\alpha} - 1)}, \tag{A13}
\]

which is known as ‘transmission coefficient’. Note that the magnitude of the complex number \( c \), given in Eq. A14 determines the amplitude of the complex function \( \psi_2 \) according to Eq. A8. However, the function of interest is not the transmission coefficient itself but rather a transmission probability, given by the equation

\[
P = \frac{k_2}{k_1}, \tag{A15}
\]

where \( \bar{c} \) is a complex conjugate of \( c \), i.e.

\[
\bar{c} = \frac{4\alpha k_1 e^{-ik_2x}}{(a(k_1 + k_2)(e^{2\alpha} + 1) - b(k_1 - k_2)^2)(e^{2\alpha} - 1)}.
\]

Straightforward multiplication leads to the tunneling probability of electrons on their Fermi level

\[
P = \frac{k_2}{k_1} \bar{c} = \frac{16\alpha k_1 k_2 e^{2\alpha}}{a^2(k_1 + k_2)^2(e^{2\alpha} + 1)^2 + (a^2 - k_1 k_2)^2(e^{2\alpha} - 1)^2}, \tag{A17}
\]

where

\[
k_1 = \frac{1}{\hbar} \sqrt{2mE}, \quad k_2 = \frac{1}{\hbar} \sqrt{2m(U - E/2)}, \quad a = \frac{1}{\hbar} \sqrt{2m(U - E/2)}, \tag{A18}
\]

and \( m \) is mass of electron, \( U_1 \) is corresponding to the graphite Fermi level, \( U_1 = -4.4eV \), \( U_2 \) is the solvent LUMO, which is determined by the state of the solvent, e.g. when 3 EC molecules combine with one Li ion, then the LUMO of each solvent is \(-2.99\ eV\).

Note that

\[
\begin{align*}
16\alpha k_1 k_2 e^{2\alpha} &= \frac{a^2(k_1 + k_2)^2(e^{2\alpha} + 1)^2 + (a^2 - k_1 k_2)^2(e^{2\alpha} - 1)^2}{a^2(k_1 + k_2)^2(1 + e^{-2\alpha})^2 + (a^2 - k_1 k_2)^2(1 - e^{-2\alpha})^2}, \tag{A21}
\end{align*}
\]

therefore

\[
P \approx \frac{16\alpha k_1 k_2 e^{2\alpha}}{a^2(k_1 + k_2)^2(1 + e^{-2\alpha})^2 + (a^2 - k_1 k_2)^2(1 - e^{-2\alpha})^2}, \tag{A22}
\]

thus

\[
P \approx P_0 e^{-2\alpha}, \tag{A23}
\]

where

\[
P_0 = \frac{16\alpha k_1 k_2 e^{2\alpha}}{a^2(k_1 + k_2)^2 + (a^2 - k_1 k_2)^2}. \tag{A24}
\]

Eq. A23 has much simpler form, widely accepted in the literature, but usually assumes \( P_0 = 1 \), which clearly violates Eq. A24. It is interesting to find out the behavior of \( P_0 \) as a function of the underlying parameters \( k_1, k_2 \) and \( a \). Eq. A24 can be rewritten in the following form

\[
P_0 = \frac{16}{k_2 + k_1 + \frac{k_2}{k_1 + \frac{a^2}{k_1}}}. \tag{A25}
\]
From Eq. A25 it can be seen that \( P_0 \) depends only on two combinations of parameters. Defining \( x = \frac{k_2}{k_1} \) and \( y = \frac{k_4}{k_3} \) will lead to

\[
P_0 = \frac{16}{x + \frac{1}{x} + y + \frac{1}{y}}
\]

[A26]

The behavior of \( P_0 \) as function of \( x \) and \( y \) is illustrated in Fig. A1.

One can see that \( P_0 \) is symmetric with respect to \( x \) and \( y \). It varies between 0 and 4, reaching the maximal value when \( x = y = 1 \), which corresponds to the symmetric case \( k_1 = k_2 = u \). That implies that using the simplified Eq. A23 with \( P_0 = 1 \) can lead to considerable errors. This error can overestimate or underestimate the real tunnelling probability.

2. Derivation of Eq. 30 from Eq. 29

\[
\frac{dQ_{SEI}^{\text{MF}}(t)}{dt} = \frac{(6 + x)F \rho_y A_B v_y P_0}{4M_{\text{Li}}} \times \exp \left( -\frac{\left( \frac{6 + x}{2} \right) \rho_y v_y \delta \cdot v_{\text{MF}} \sqrt{2m \Delta E}}{h} \right)
\]

[A27]

Moving the second term on the left side to the right side, one obtains

\[
\exp \left( \frac{2 \sqrt{Q_{SEI}^{\text{MF}}(t)} M_{\text{Li}} \sqrt{2m \Delta E}}{Ap^2 w_{\text{Li}}^2 F h} \right) = \left[ 1 + \frac{(6 + x) \rho_y v_y \delta \cdot v_{\text{MF}} P_0 \sqrt{2m \Delta E}}{2M_{\text{Li}} \rho_y v_{\text{MF}} w_{\text{Li}}^2} \times \exp \left( -\frac{2 \sqrt{Q_{SEI}^{\text{MF}}(t)} \sqrt{2m \Delta E}}{h} \right) \right].
\]

[A31]

Calculating the logarithm of both sides, results in

\[
\frac{2 \sqrt{Q_{SEI}^{\text{MF}}(t)} M_{\text{Li}} \sqrt{2m \Delta E}}{Ap^2 w_{\text{Li}}^2 F h} = \ln \left[ 1 + \frac{(6 + x) \rho_y v_y \delta \cdot v_{\text{MF}} P_0 \sqrt{2m \Delta E}}{2M_{\text{Li}} \rho_y v_{\text{MF}} w_{\text{Li}}^2} \times \exp \left( -\frac{2 \sqrt{Q_{SEI}^{\text{MF}}(t)} \sqrt{2m \Delta E}}{h} \right) \right].
\]

[A32]

Finally, the capacity loss is obtained as a function of time, according to

\[
Q_{SEI}^{\text{MF}}(t) = \frac{h A w_{\text{MF}}^2}{2M_{\text{Li}} \rho_y v_{\text{MF}} w_{\text{Li}}^2} \ln \left[ 1 + \frac{(6 + x) \rho_y v_y \delta \cdot v_{\text{MF}} P_0 \sqrt{2m \Delta E}}{2M_{\text{Li}} \rho_y v_{\text{MF}} w_{\text{Li}}^2} \times \exp \left( -\frac{2 \sqrt{Q_{SEI}^{\text{MF}}(t)} \sqrt{2m \Delta E}}{h} \right) \right].
\]

[30]

Figure A1. \( P_0 \) calculated according to Eq. A26, as function of \( x \) and \( y \).

References