Batteries for Transportation

An overview of degradation phenomena that determine the lifetime of lithium ion batteries

Mark Verbrugge
General Motors R&D Center

Outline

- GM HEV, pHEV, and EREV plans
- Chemical degradation (better understood)
  - Negative electrode
  - Positive electrode
  - SEI (solid electrolyte interface)
- Life models
- Solid mechanics (stress distribution)
- Summary of combined chemical and mechanical degradation
Global Energy Concerns (for every nation state)

- Energy security
  - Secure
- Environmental health
  - Clean
- Economic competitiveness
  - Affordable

Sustainability & National Security

To some extent, we can reduce demand, but the ultimate solution will come out of advancements in science and technology.
Advanced Propulsion Technology Strategy

- Improved Vehicle Fuel Economy and Emissions
- Displace Petroleum
- Hydrogen Fuel Cell Vehicles
- Extended Range Electric Vehicles
- Hybrid Electric Vehicles (including Plug-In HEV)
- IC Engine and Transmission Improvements

Energy Diversity

- Petroleum (Conventional & Alternative Sources)
- Bio Fuels (Ethanol E85, Bio-diesel)
- Electricity (Conventional & Alternative Sources)
- Hydrogen
### GM Hybrid and Electric Programs

**Lithium ion post 2010**

<table>
<thead>
<tr>
<th>Year</th>
<th>Model</th>
<th>Type</th>
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<tbody>
<tr>
<td>2001</td>
<td>Saturn VUE Green Line</td>
<td>GM-Allison Hybrid Bus</td>
</tr>
<tr>
<td>2002</td>
<td>Saturn AURA Green Line</td>
<td>GM/Allison Hybrid Bus</td>
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<tr>
<td>2003</td>
<td>Saturn AURA Green Line</td>
<td>GM/Allison Hybrid Bus</td>
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<tr>
<td>2004</td>
<td>Chevrolet Malibu Hybrid</td>
<td>GM/Allison Hybrid Bus</td>
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<tr>
<td>2005</td>
<td>Shanghai GM Buick LaCrosse Eco-Hybrid</td>
<td>GM/Allison Hybrid Bus</td>
</tr>
<tr>
<td>2006</td>
<td>Tahoe/Yukon</td>
<td>GM-Allison Hybrid Bus</td>
</tr>
<tr>
<td>2007</td>
<td>Escalade</td>
<td>GM-Allison Hybrid Bus</td>
</tr>
<tr>
<td>2008</td>
<td>Silverado/Sierra</td>
<td>GM-Allison Hybrid Bus</td>
</tr>
<tr>
<td>2009</td>
<td>Saturn VUE Green Line 2-Mode</td>
<td>GM-Allison Hybrid Bus</td>
</tr>
<tr>
<td></td>
<td>VUE PHEV</td>
<td>GM-Allison Hybrid Bus</td>
</tr>
</tbody>
</table>

- **GM-Allison Hybrid**
- **GM Hybrid**
- **RWD 2-Mode Hybrid**
- **FWD 2-Mode Hybrid**
- **E-REV**
## Comparison of GM’s requirements to USABC specs

### Requirements of End of Life Energy Storage Systems for PHEVs

<table>
<thead>
<tr>
<th>Characteristics at EOL (End of Life)</th>
<th>High Power/Energy Ratio Battery</th>
<th>GM 2-Mode PHEV</th>
<th>High Energy/Power Ratio Battery</th>
<th>EFLEX EREV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference Equivalent Electric Range</td>
<td>miles</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Peak Pulse Discharge Power - 2 Sec / 10 Sec</td>
<td>kW</td>
<td>50 / 45</td>
<td>50/45</td>
<td>46 / 38</td>
</tr>
<tr>
<td>Peak Regen Pulse Power (10 sec)</td>
<td>kW</td>
<td>30</td>
<td>27</td>
<td>25</td>
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<tr>
<td>Available Energy for CD (Charge Depleting) Mode, 10 kW Rate</td>
<td>kWh</td>
<td>3.4</td>
<td>3.5</td>
<td>11.6</td>
</tr>
<tr>
<td>Available Energy for CS (Charge Sustaining) Mode</td>
<td>kWh</td>
<td>0.5</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>Minimum Round-trip Energy Efficiency (USABC HEV Cycle)</td>
<td>%</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Cold cranking power at -30°C, 2 sec - 3 Pulses</td>
<td>kW</td>
<td>7</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>CD Life / Discharge Throughput</td>
<td>Cycles/MWh</td>
<td>5,000 / 17</td>
<td>5,000 / 58</td>
<td>4700 / 54</td>
</tr>
<tr>
<td>CS HEV Cycle Life, 50 Wh Profile</td>
<td>Cycles</td>
<td>300,000</td>
<td>300,000</td>
<td>300,000</td>
</tr>
<tr>
<td>Calendar Life, 35°C</td>
<td>year</td>
<td>15</td>
<td>10</td>
<td>15</td>
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<tr>
<td>Maximum System Weight</td>
<td>kg</td>
<td>60</td>
<td>90</td>
<td>120</td>
</tr>
<tr>
<td>Maximum System Volume</td>
<td>Liter</td>
<td>40</td>
<td>TBD</td>
<td>80</td>
</tr>
<tr>
<td>Maximum Operating Voltage</td>
<td>Vdc</td>
<td>400</td>
<td>420</td>
<td>400</td>
</tr>
<tr>
<td>Minimum Operating Voltage</td>
<td>Vdc</td>
<td>&gt;0.55 x Vmax</td>
<td>170</td>
<td>&gt;0.55 x Vmax</td>
</tr>
<tr>
<td>Maximum Self-discharge</td>
<td>Wh/day</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>System Recharge Rate at 30°C</td>
<td>kW</td>
<td>1.4 (120V/15A)</td>
<td>1.4</td>
<td>1.4 (120V/15A)</td>
</tr>
<tr>
<td>Unassisted Operating &amp; Charging Temperature Range</td>
<td>°C</td>
<td>-30 to +52</td>
<td>-30 to +52</td>
<td>-30 to +52</td>
</tr>
<tr>
<td>Survival Temperature Range</td>
<td>°C</td>
<td>-46 to +66</td>
<td>-46 to +66</td>
<td>-46 to +66</td>
</tr>
<tr>
<td>Maximum System Production Price @ 100k units/yr</td>
<td>$</td>
<td>$1,700</td>
<td>$3,400</td>
<td></td>
</tr>
</tbody>
</table>

**EFLEX EREV requires 2.5 times the power of USABC requirements**
Specific Discharge Ragone Plot of Li-Ion Plug-In Hybrid Batteries at 25°C

- LiC₆
- LiMO₂
- LiMPO₄

**Post 1995, Lithium ion**

- Hitsachi #1
- NLE L3-10 #NE4
- JCS VL27M #SM0
- Kokam #J007
- PEVE NiMH #RM4

**Post 1990, NiMH**

- NLE L3-10 #NE5
- JCS VL27M #SM1
- PEVE NiMH #RM6

**Post 1900, PbA, NiCd**

- A123 #152
- A123 #172

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Specific Discharge Power (Watts/kg) vs. Specific Discharge Energy (Watt-hours/kg)
Electrode microstructure

- Porous electrodes (~100 μm thick) composed of host particles (~1 to 5 μm diameter) are used to
  1. increase the surface area for reaction
  2. reduce lithium diffusion resistance

**Anode charge reaction**

1. Lithium ion is reduced at the electrode surface:
   \[ \text{Li}^+ + \text{e}^- \rightarrow \text{Li}^0 \]

2. Lithium diffuses *rapidly* into host electrode through vacancies
   - Opposite reactions takes place at cathode particle surfaces
     \[ \text{Li}^+ + \text{e}^- \rightarrow \text{Li}^0 \]
Lithium Intercalation of Carbon-Fiber Microelectrodes

Mark W. Verbrugge* and Brian J. Koch*

General Motors Research and Development Center, Physical Chemistry Department, Warren, Michigan 48090-9055, USA

Fig. 2. Micrograph of fibers heat-treated for 4 h at 2000°C.

Fig. 3. Characteristic cyclic voltammogram. Data for 300 cycles are plotted.

- Ability of lamellar compounds of carbon to insert various species was well known by the later half of the 1800s (Schauffäütl, 1841…Sony, 1992)
- Single fiber electrode: phenomena associated with the fabrication of a porous electrode do not obfuscate the subsequent characterization…use the Scientific Method to isolate critical characteristics
- Extremely stable lithiated carbon anode and Li reference (there is still confusion around the stability of carbon lithiation!)
Lithium ion challenges: durability focus

- **Cost**
  - Can we size pack closer to end-of-life requirements?
  - Can we reduce materials & processes costs?

- **Life**
  - How do electrodes fail?
  - Can we develop an accelerated life test?

- **Temperature tolerance**
  - Can we improve low temperature power?
  - Why is battery life shorter at higher temperatures?
Durability…terminologies, *bathtub curves*

- **Chemical degradation**
  - Critical role of SEI (solid electrolyte interface) to impede deleterious degradation reactions within lithium ion cells
  - Calendar life determined by chemical degradation

- **Mechanical degradation**
  - Cyclic expansion and contraction of insertion or alloy materials leads to fatigue, cracking, and structural changes
  - Cyclic life issues are affected by mechanical degradation and chemical degradation

![Today's focus graph]

**Number of Failures**

- Early (infant mortality) failures
- Useful life (durability)
- Wear out failures

**Time in service**
Electrode potentials

- By changing an electrode voltage, new electrolytes can be employed with improved stability.
- For traction applications, conventional lithium ion cells still dominate...lower utilization for improved durability & abuse tolerance.
Negative electrode
Mathematical modeling of high-power-density insertion electrodes for lithium ion batteries

Mark W. Verbrugge\textsuperscript{a,*}, Daniel R. Baker\textsuperscript{b}, Brian J. Koch\textsuperscript{c}

\textsuperscript{a}General Motors Research and Development Center, Warren, MI 48090-9055, USA
\textsuperscript{b}General Motors Fuel Cell Propulsion Center, Warren, MI 48090-9055, USA
\textsuperscript{c}General Motors Advanced Technology Vehicles, 1996 Technology Drive, Troy, MI 4807-7083, USA

\[ \text{Li}^+ + \square + e^- \rightarrow \text{Li} \]

- Solvent reduction at \(~0.8\text{V vs Li}\) on first cycle
- Then \(~100\%\) Coulombic efficiency
- Next slide for more detail
Formation of the SEI...solvent reduction
(ethylene carbonate)

\[
2\text{Li}^+ + 2\text{e}^- + \text{Li}^+ + 2\text{e}^- = \text{Li} \\
V_{\text{cell}} \sim \mu_{\text{Li}} \sim \ln(SOC) \\
(\text{Calendar life influence})
\]

- For computed IR spectra of surface species in an EC electrolyte, see S. Matsuta, T. Asada, and K. Kitaura. J. Electrochem. Soc. 147(2000)1695-1702...dimers found to be lowest energy
- Experimental FTIR data indicates predominance of \([\text{Li(OCOOCH}_2\text{)}_2]\) for EC and EC+DEC systems with 1M LiPF\(_6\), see C. R. Yang, Y. Y. Wang, C. C. Wan, J. Power Sources, 72(1998)66.
In situ TEM study of the interface carbon/electrolyte

M. Dollé, S. Grugeon, B. Beaudoin, L. Dupont, J-M. Tarascon

Laboratoire de Réactivité et de Chimie des Solides, UPRES A 6007, UPJV, 33 rue Saint-Leu, 80039 Amiens Cedex, France

The electrolyte used was LiPF$_6$ (1 M) in EC:DMC (1:1, w/w).
Electrochemical SPM investigation of the solid electrolyte interphase film formed on HOPG electrodes

D. Alliata a,1, R. Kötz a,*, P. Novák a, H. Siegenthaler b

a Laboratory for Electrochemistry, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland
b Department for Chemistry and Biochemistry, University of Bern, CH-3112 Bern, Switzerland

Fig. 1. CV curves recorded at 5 mV s⁻¹ on HOPG in 1 M LiClO₄ in EC:DMC

SEI grows to at least 20 nm in thickness upon cycling
Phenomenologically modeling the formation and evolution of the solid electrolyte interface on the graphite electrode for lithium-ion batteries

Jian Yan\textsuperscript{a,b,*}, Bao-Jia Xia\textsuperscript{a}, Yu-Chang Su\textsuperscript{b}, Xiao-Zhong Zhou\textsuperscript{b}, Jian Zhang\textsuperscript{a}, Xi-Gui Zhang\textsuperscript{a}

\textsuperscript{a} Laboratory for Nano Sciences and Technologies, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, PR China
\textsuperscript{b} School of Materials Science and Technology, Central South University, Changsha 410083, PR China

As a result, the constituents of the surface films nearest to the graphite surface will eventually be transformed to consist almost entirely of Li$_2$O and LiF in a mature SEI film.
A Mathematical Model for the Lithium-Ion Negative Electrode Solid Electrolyte Interphase

John Christensen and John Newman
Department of Chemical Engineering, University of California, Berkeley, California 94720, USA

Resistance of the inner inorganic layer is modeled

Resistance of the outer organic layer is ignored
Positive electrode
Electrochemical oxidation of propylene carbonate (containing various salts) on aluminium electrodes

Kiyoshi Kanamura, Takashi Okagawa, Zen-ichiro Takehara
Division of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-01, Japan
Received 28 July 1995; accepted 11 September 1995

Petr Novák* and Wolf Viestich
Institute of Physical Chemistry, University of Bonn, D-5300 Bonn 1, Germany

PC oxidizes on Pt above 2.1 V vs Li (forms lithium adducts).
CO₂ observed above 4.2 V on LiNiO₂, above 4.8 V on LiCoO₂, LiMn₂O₄
Review of selected electrode–solution interactions which determine the performance of Li and Li ion batteries

Doron Aurbach*

Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel

Surface film formation on cathode materials
Option I: Nucleophilic reactions

- Growth of passive film on the positive electrode surface
- Li adducts (SEI) at low potentials (low SOC)
  - Similar to SEI formation on carbon
  - CO₂ evolution at high potentials (over-charge)
- High SOC, less Li, and oxygens can release
Review of selected electrode–solution interactions which determine the performance of Li and Li ion batteries

Doron Aurbach*

Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel


Surface film formation on cathode materials

Option II: Exchange reactions, formation of inactive mass

- Growth of passive film on the LMO surface
- Dissolved Mn$^{2+}$ transports to the negative electrode and breaks down the SEI

- This problem can also occur with Fe dissolution within iron phosphate cells
### Summary: role of surface layers on + and −

<table>
<thead>
<tr>
<th>Electrochemical reaction</th>
<th>V</th>
<th>Conventional lithium ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NiOOH} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{Ni(OH)}_2 + \text{OH} )</td>
<td>1.35</td>
<td>~1.35 V</td>
</tr>
<tr>
<td>( \text{Li}_{1-x}\text{MO}_2 + x\text{Li}^+ + xe^- \rightarrow \text{LiMO}_2 ) (M: Ni, Co, Mn)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>( \text{FePO}_4 + \text{Li}^+ + \text{e}^- \rightarrow \text{LiFePO}_4 )</td>
<td>0.4</td>
<td>~1.2 V</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{e}^- \rightarrow 0.5\text{H}_2 )</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>( \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} )</td>
<td>~3.3</td>
<td></td>
</tr>
<tr>
<td>( -1.5\text{Li}_4\text{Ti}<em>5\text{O}</em>{12} + 3\text{Li}^+ + 3\text{e}^- \rightarrow \text{Li}_7\text{Ti}<em>5\text{O}</em>{12} )</td>
<td>~3.3</td>
<td></td>
</tr>
</tbody>
</table>

- **Solvent oxidation on Pt** ~2.1 V vs Li
  - \( \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} \)
- **Solvent reduction on negative** ~0.8 V vs Li
  - \( -2.9\text{C}_6 + \text{Li}^+ + \text{e}^- \rightarrow \text{LiC}_6 \)
  - \( -3\text{Li}^+ + \text{e}^- \rightarrow \text{Li} \)

- **Lithium ion conventional stability window** ~4 V

- **Lithium ion conversion** ~1.3 V

- **Underscores the importance of the SEI**
  - Disruption of the SEI (e.g., due to dilation, crack propagation, etc.) is deleterious to cell life...even low reaction rates are a problem
    - Loss of Li
    - Gas generation
Life modeling (cell)
An accelerated calendar and cycle life study of Li-ion cells


*Electrochemical Technology Program, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA
bIdaho National Engineering and Environmental Laboratory, Idaho Falls, ID 83415, USA
cSandia National Laboratories, Albuquerque, NM 87185, USA

<table>
<thead>
<tr>
<th>Test/group</th>
<th>Time to 20% power fade (weeks)</th>
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<tbody>
<tr>
<td>40% SOC calendar life</td>
<td>387.21</td>
</tr>
<tr>
<td>60% SOC/A calendar life</td>
<td>127.64</td>
</tr>
<tr>
<td>60% SOC/B calendar life</td>
<td>39.37</td>
</tr>
<tr>
<td>80% SOC calendar life</td>
<td>11.33</td>
</tr>
<tr>
<td>60% SOC, 3% ΔSOC cycle life</td>
<td>6.91</td>
</tr>
<tr>
<td>60% SOC, 6% ΔSOC cycle life</td>
<td>0.99</td>
</tr>
<tr>
<td>80% SOC, 3% ΔSOC cycle life</td>
<td>38.72</td>
</tr>
<tr>
<td>80% SOC, 6% ΔSOC cycle life</td>
<td>1.94</td>
</tr>
</tbody>
</table>

Table 9
Calculated times to 20% power loss

The data were fit by the general equation

\[ Q = A \exp \left( -\frac{E_a}{RT} \right) t^z \]

where \( Q \) is the ASI or power, \( A \) the pre-exponential factor, \( E_a \) the activation energy in J, \( R \) the gas constant, \( T \) the absolute temperature, \( t \) the time, and \( z \) the exponent of time. For simple diffusion control or layer growth, \( z = 1/2 \). This
Aging mechanism in Li ion cells and calendar life predictions

M. Broussely, S. Herreyre, P. Biensan, P. Kasztejna, K. Nechev, R.J. Staniewicz

SAFT BP 1039, 86960 Poitiers, France
SAFT, 111 Blvd A. Daney, 33074 Bordeaux, France
SAFT America, 107 Beaver court, Cockeysville, MD, USA

The most commonly adopted picture is that the interface layer is considered as a solid electrolyte interphase (SEI) being a good ionic but poor electronic conductor, as proposed by Peled [4].

\[
\frac{dx}{dt} = kX = \frac{k\chi s}{e}
\]

where \(x\) is the number of moles of Li being reacting, \(\chi\) the specific conductivity, \(s\) the interface area and \(e\) is the layer thickness.

\[
t = e^{\left[(4661/T) - 14\right]x^2} + e^{\left[(4437/T) - 11.6\right]x}
\]

The "5 Ah" prismatic cell used a stainless steel can and was configured as can negative. The chemistry was LiCoO₂/EC-DEC-DMC 1 M LiPF₆ + VC additive/synthetic graphite.
Main aging mechanisms in Li ion batteries

M. Broussely, Ph. Biensan, F. Bonhomme, Ph. Blanchard, S. Herreyre, K. Nechev, R.J. Staniewicz

Saft, BP 1039, 86060 Pattiers, France
Saft 111 Blvd. A. Daney, 33000 Bordeaux, France
Saft America, 107 Beaver Court, Cockeysville, MD, USA

Extrapolation of Li loss vs time

Both cells use the LiNi_xCo_yAl_zO_2/graphite + PC/EC/DMC 1 M LiPF_6 chemistry.

Fig. 8. Storage time on float (3.9 V) at 60 and 40 °C vs. lithium loss. Saft "Industrial" Li ion Ni-based cells.
Simulation of capacity fade in lithium-ion batteries

R. Spotnitz

Battery Design Co., 2277 DeLucchi Dr., Pleasanton, CA 94588, USA

(1) Capacity loss on storage has reversible and irreversible components.
(2) Capacity loss on storage or cycling increases with increasing temperature.
(3) Capacity loss on storage increases with increasing cell voltage.
(4) Cycling causes capacity loss at a greater rate than storage.
(5) Capacity loss can correlate with cell impedance.

5.3. Irreversible and irreversible capacity loss due to SEI growth and dissolution

\[
t = - \left( \frac{R_{f,0} - R_b}{R_b^2 D} \right) \left[ 1 - \exp \left( - \frac{R_b N_{\text{loss}} D}{R_{f,0}} \right) \right] + \frac{N_{\text{loss}}}{R_b}
\]
Development of First Principles Capacity Fade Model for Li-Ion Cells

P. Ramadass,* Bala Haran,** Parthasarathy M. Gomadam,* Ralph White,*** and Branko N. Popov,**z

Department of Chemical Engineering, University of South Carolina, Columbia, South Carolina 29208, USA

\[ S + 2\text{Li}^+ + 2e^- \rightarrow \text{P} \]

S: Solvent (EC)
P: Products

- **Butler-Volmer equation for solvent reduction**
- **Film-growth model for SEI resistance...**
- **Lithium loss model for capacity loss...**
- **Note:** This is treats chemical degradation
  - No influence due to expansion and contraction of the host material

Figure 5. Variation of film resistance during charging for (solid line) cycle 40 and (dotted lines) variation of film resistance with cycle number.
A generalized cycle life model of rechargeable Li-ion batteries

Gang Ning, Ralph E. White, Branko N. Popov

Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208, USA

Resistance of the outer organic layer is modeled

Resistance of the inner inorganic layer is ignored

\[ EC + 2e^- + 2Li^+ \rightarrow LiCH_2CH_2OCO_2Li \downarrow \]

\[ j_{para} = -j_{para}^0 \exp \left( \frac{\alpha_c F}{RT} \eta \right) \]

\[ \eta = \phi_s - \phi_e - U_{para} - jR_f \]

\[ \frac{\partial \delta_f}{\partial t} = -\frac{j_{para}}{\rho \times F} \]

\[ R_s |_{N} = \frac{\delta_f |_{N}}{\kappa} \]

\[ Q_s = \int_{t=0}^{t=t_{para}} j_{para} a_{s,n} \, dt \]
Multimodal Physics-Based Aging Model for Life Prediction of Li-Ion Batteries

M. Safari, a M. Morcrette, a A. Teyssot, b and C. Delacourt a,*

aLaboratoire de Réactivité et Chimie des Solides, Université de Picardie Jules Verne, 80039 Amiens Cedex, France
bRenault Research Department, 78288 Guyancourt, France

Resistance of the outer organic layer is modeled

Resistance of the inner inorganic layer is ignored

Figure 1. (Color online) Physical picture for SEI growth at the anode particle surface.
Governing equations

\[ i_{\text{int}} = Fk_{\text{MP}} \sqrt{c_e(t, \max - c_e)}^{1 - \beta} \exp \left[ -\exp \left( \frac{(1 - \beta) F}{RT} \left( \Phi_1 - U - \frac{\delta}{\kappa_{\text{SEI}}}i \right) \right) \right] \]

\[ -\exp \left[ -\frac{F}{RT} \left( \Phi_1 - U - \frac{\delta}{\kappa_{\text{SEI}}}i \right) \right] \]

\[ \frac{\partial c_L}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( D_{\text{Li}} r^2 \frac{\partial c_{\text{Li}}}{\partial r} \right) \]

\[ i_s = -Fk_{\text{f}, \text{EC}} \exp \left[ -\frac{F}{RT} \left( \Phi_1 - \frac{\delta}{\kappa_{\text{SEI}}}i \right) \right] \]

\[ i = i_{\text{int}} + i_s \]

\[ i_s = i_{\text{int}} + i_s \]

\[ \frac{\partial c_{\text{EC}}}{\partial t} = D_{\text{EC}} \frac{\partial^2 c_{\text{EC}}}{\partial r^2} - \frac{d \partial c_{\text{EC}}}{dt} \frac{\partial \delta}{\partial r} \]

\[ \frac{\partial \delta}{\partial t} = \frac{i_{\text{int}}}{2F} \frac{M_{\text{SEI}}}{\rho_{\text{SEI}}} \]

\[ \frac{\partial c_{\text{Li}}}{\partial r} \bigg|_{r=0} = 0 \]

\[ \frac{\partial c_{\text{Li}}}{\partial r} \bigg|_{r=R} = -\frac{i_{\text{int}}}{FD_{\text{Li}}} \]

\[ -D_{\text{EC}} \frac{\partial c_{\text{EC}}}{\partial r} \bigg|_{r=R} + \nu c_{\text{EC}} \bigg|_{r=R} = \frac{i_s}{F} \]

\[ c_{\text{EC}} \bigg|_{r=R+1} = \frac{\delta}{\kappa_{\text{SEI}}} c_{\text{EC}} \bigg|_{r=R} \]

\[ \square \text{ Electrochemical degradation model} \]
On the importance of coulombic efficiency $\eta_i$

$$\text{Li}^+ + e^- + \frac{1}{2} \text{LiCH}_2\text{CH}_2\text{OCO}_2\text{Li} \rightarrow \frac{1}{2} \text{LiCH}_2\text{CH}_2\text{OCO}_2\text{Li}$$

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$(\text{Ah}_0)\eta_i$</td>
</tr>
<tr>
<td>2</td>
<td>$[(\text{Ah}_0) \eta_i, \eta_i]$</td>
</tr>
<tr>
<td>3</td>
<td>$[(\text{Ah}_0) \eta_i, \eta_i, \eta_i]$</td>
</tr>
<tr>
<td>...</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>$(\text{Ah}_0)(\eta_i)^N$</td>
</tr>
</tbody>
</table>

For $N = 5000$ cycles and a 12/16 or 75% capacity retention, the current efficiency per cycle must be such that $$(\text{Ah}_0(\eta_i)^N)/\text{Ah}_0 > 0.75$$, or $\eta_i > (0.75)^{(1/5000)}$, hence $\eta_i > 0.99994$.

- This is why very low rates of lithium-consuming reactions can lead to premature cell failure. The rates can be so low that they are not measureable in terms of seeing current maxima associated with solvent reduction, for example.
Second emphasis: mechanical degradation leading to wear out
Capacity fading of lithiated graphite electrodes studied by a combination of electroanalytical methods, Raman spectroscopy and SEM

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SEM images of the surface of the KS-15 composite pristine electrode (a) and the same electrode after 140 intercalation–deintercalation cycles at 25 °C (b and c).

During cycling, graphite particles crack into smaller pieces that are less oriented than the original platelets, with the possible filling of the cracks thus formed by the reduction products of the electrolyte solution. In addition, the average crystalline size (estimated by Raman spectroscopy) decreases as cycling progresses.
In this study, the deterioration mechanism of lithium-ion batteries using 
commercial LiNiCoO$_2$ as the positive electrode was examined. The 
particles were formed in particles with cracks that cause the increase in 
resistance at positive electrode. The electronic conduction, due to 
volume change, causes the increase in resistance. In order to verify this mechanism, 
Fig. 9. Morphology of positive particle: (a) state of discharge, (b) state of charge.

“This result indicates volume change causes the increase in resistance.”
Cracking causing cyclic instability of LiFePO₄ cathode material

Deyu Wang, Xiaodong Wu, Zhaoxiang Wang, Liquan Chen*

| Cycles | 0’ 0 | 10 30 | 60 60_p1 | 60_p2 |

LiFePO₄ possesses an olivine structure with three-dimensional network. The lattice constants of LiFePO₄ are $a = 10.33 \text{ Å}$, $b = 6.01 \text{ Å}$, $c = 4.69 \text{ Å}$, $V = 291.2 \text{ Å}^3$ and the lattice constants of FePO₄ are $a = 9.81 \text{ Å}$, $b = 5.79 \text{ Å}$, $c = 4.78 \text{ Å}$, $V = 271.5 \text{ Å}$, respectively [11]. The volume change of this phase transformation is 6.77%. The volume change is Li-extraction/insertion. The formation of cracks will lead to increased polarization of electrode and poor electric contact between active particles and conductive additives or aluminum foil current collector. This should be one of the
**Wöhler S-N curve**
(1870...railroad axles)

*Ultimate goal:* Determine the endurance limit (cycle life) for insertion electrodes by comprehending the periodic stress.
Direct analogy to the lower cycle-life fatigue…stress amplitude is replaced by ΔSOC
- Temperature & chemical degradation

Model result (next slide): maximum stress is proportional to the maximum difference in SOC, or ΔSOC

What about self-healing ("steel-like") electrodes?

A mathematical model that calculates volume expansion and contraction and concentration and stress profiles during lithium insertion into and extraction from a spherical particle of electrode material has been developed.

Fig. 5 Simulated normal stress profiles in the particle, as a function of dimensionless radial position, at the end of lithium insertion. Positive values indicate tensile stresses, while negative values correspond to compression. The solid curves include the effect of pressure-driven diffusion, while the dashed curves neglect it. The parameters used in the simulation are listed in Table 1.
Surface Mechanics. \( \sigma_{\theta}^{\text{surf}} \equiv \sigma_{\theta\theta}^{\text{surf}} = \sigma_{\phi\phi}^{\text{surf}} = \tau^0 + K^s \varepsilon_{\theta} \), where \( K^s \) is known as the “surface modulus.” For mechanical equilibrium,

\[
\sigma_r (r \to R) = -\frac{2\sigma_{\theta}^{\text{surf}}}{R} \quad \text{NEW for insertion electrode modeling (Conventional condition recovered for large radius } R)
\]

Solid Mechanics

\[
\varepsilon_r = \frac{1}{E} \left( \sigma_r - 2\nu \sigma_{\theta} \right) + \frac{1}{3} \Omega C
\]

\[
\varepsilon_{\theta} = \frac{1}{E} \left[ (1-\nu)\sigma_{\theta} - \nu \sigma_r \right] + \frac{1}{3} \Omega C
\]

\[
\varepsilon_r = \frac{du}{dr} \quad \text{and} \quad \varepsilon_{\theta} = \frac{u}{r}.
\]

\[
\frac{d\sigma_r}{dr} + 2\frac{\sigma_r - \sigma_{\theta}}{r} = 0
\]

\[
\frac{d^2u}{dr^2} + \frac{2}{r} \frac{du}{dr} - \frac{2u}{r^2} = \left( \frac{1+\nu}{1-\nu} \right) \Omega \frac{dC}{dr}
\]

Intercalate (lithium) transport

\[
\tau = \frac{Dt}{R^2}, \ x = \frac{r}{R}, \ \text{and} \ y = \frac{C(t,r) - C_0}{C_R - C_0} = \frac{\Theta(t,r) - \Theta_0}{\Theta_R - \Theta_0}
\]

\[
\frac{\partial y}{\partial \tau} = \frac{\partial^2 y}{\partial x^2} + \frac{2}{x} \frac{\partial y}{\partial x}
\]

\[
y(0, x) = 0
\]

\[
y(t,1) = 1
\]

\[
\frac{\partial y}{\partial x} \Bigg|_{x=0} = 0
\]

This equation system can be solved analytically.

**Mathematical details**

Potential step, $\Theta_0 \rightarrow \Theta_R$

For the stress functions, the transient terms are proportional to $\Delta SOC (\Delta SOC \propto \text{stress})$
Surface Mechanics. \[ \sigma_{\theta}^{surf} \equiv \sigma_{\theta\theta}^{surf} = \sigma_{\phi\phi}^{surf} = \tau^0 + K_s \varepsilon_{\theta} \quad \sigma_r(r \to R) = -\frac{2\sigma_{\theta}^{surf}}{R} \]

- Charge (lithiation) of negative (carbon) electrode
- Influence of surface mechanics is quite significant
  - Radial stress transformed from tensile to compressive
  - Similar influence on tangential (circumferential) stress
- Note: it is more challenging to make electrodes with smaller particles…enhanced stability comes with a cost
**What’s wrong with cracks?**

Overall qualitative degradation model...

1. **SEI focused**

   - Expanded view of surface
   - SEI forms on newly exposed surfaces (cracks)
   - \([\text{Li-S}] + R \cdot H \cdot O \rightarrow \text{SEI} + \text{gasses} + \ldots\)
   - \([\text{Li-S}] + \text{Li} + \text{C} \rightarrow S + \text{LiCO}_3 \downarrow + H_2 C = \text{CH}_2 \uparrow\)

2. **Electrode isolation and loss of active material when cracks join**

   - No firm experimental confirmation to date, but consistent with observations

**Increased disorder.**  
\(d_{002}\) peak-width at half max amplitude increases with time for lithiated carbon

**1. Loss of Li:** SEI formation and loss of Li seen in full cell experiments

HRL project for observations
Next steps & open questions on life modeling

- Crack initiation and propagation within a particle
  - A difficult problem even in the absence of electrochemical phenomena
  - (Griffith) Flaw distributions within electrode particles?
  - Primary particles, potentially with grains, and secondary particles (agglomerates)
  - Incorporate the influence of chemical degradation processes
  - How does temperature come into play?
    - Mechanical deformation of particles is not likely to be affected appreciably by the limited temperature fluctuations
    - Chemical reactions rates are substantially thermally activated

- Scale up from individual particles to porous electrodes
  - Comprehend influence of particle geometry as well as temperature and SOC on physicochemical parameters

- Construct relevant accelerated life tests
Looking forward: nano-structures for improved performance with lower cost materials
Geometric and electronic studies of Li$_{15}$Si$_4$ for silicon anode

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For the reaction of Li/Si electrochemical cell:

\[ \text{Si} + x\text{Li} \rightarrow \text{Li}_x\text{Si} \]

\[ V(x) \text{ can be obtained by following formula:} \]

\[ V(x) = -\frac{E_{\text{total}}(\text{Li}_x\text{Si}) - E_{\text{total}}(\text{Si}) - xE_{\text{total}}(\text{Li})}{x} \]

Fig. 1. (a) Primitive cell of Li$_{15}$Si$_4$ and (b) atomic configuration around a Si atom. The Li atoms labeled with the same number indicate same distance with Si atom.
Nanostructured Si–C composite anodes for lithium-ion batteries

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Fig. 3(b) shows a TEM photo of nano Si–C composite powders. It clearly demonstrates that Si powders are surrounded by amorphous carbon. Spot EDX (energy dispersive X-ray) analysis confirmed that the spherical black crystals in Fig. 3(b) are Si. Therefore, nanocrystalline Si particles are uniformly embedded in amorphous carbon matrix through the carbon aerogel synthesis process.
Li$_2$MnO$_3$-stabilized LiMO$_2$ (M = Mn, Ni, Co) electrodes for lithium-ion batteries†

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A strategy used to design high capacity (>200 mAh g$^{-1}$), Li$_2$MnO$_3$-stabilized LiMO$_2$ (M = Mn, Ni, Co) electrodes for lithium-ion batteries is discussed. The advantages of the Li$_2$MnO$_3$ component and its influence on the structural stability and electrochemical properties of these layered $x$Li$_2$MnO$_3$$(1-x)$LiMO$_2$ electrodes are highlighted. Structural, chemical, electrochemical and thermal properties of $x$Li$_2$MnO$_3$$(1-x)$LiMO$_2$ electrodes are considered in the context of other commercially exploited electrode systems, such as LiCoO$_2$, LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$, Li$_{1+x}$Mn$_{2-x}$O$_4$ and LiFePO$_4$. 
Summary

1. Recognize the importance of the SEI/protective layers

2. Calendar life
   - Large particles are desired for low surface area (and lower cost manufacturing)

3. Cycle life
   - Small particles are desired to reduce mechanical deformation and surface cracking (and reduce transport & charge-transfer resistance)

Life is a balancing act