Battery Design

Mechanisms for Impedance Rise in Lithium-Ion Cells

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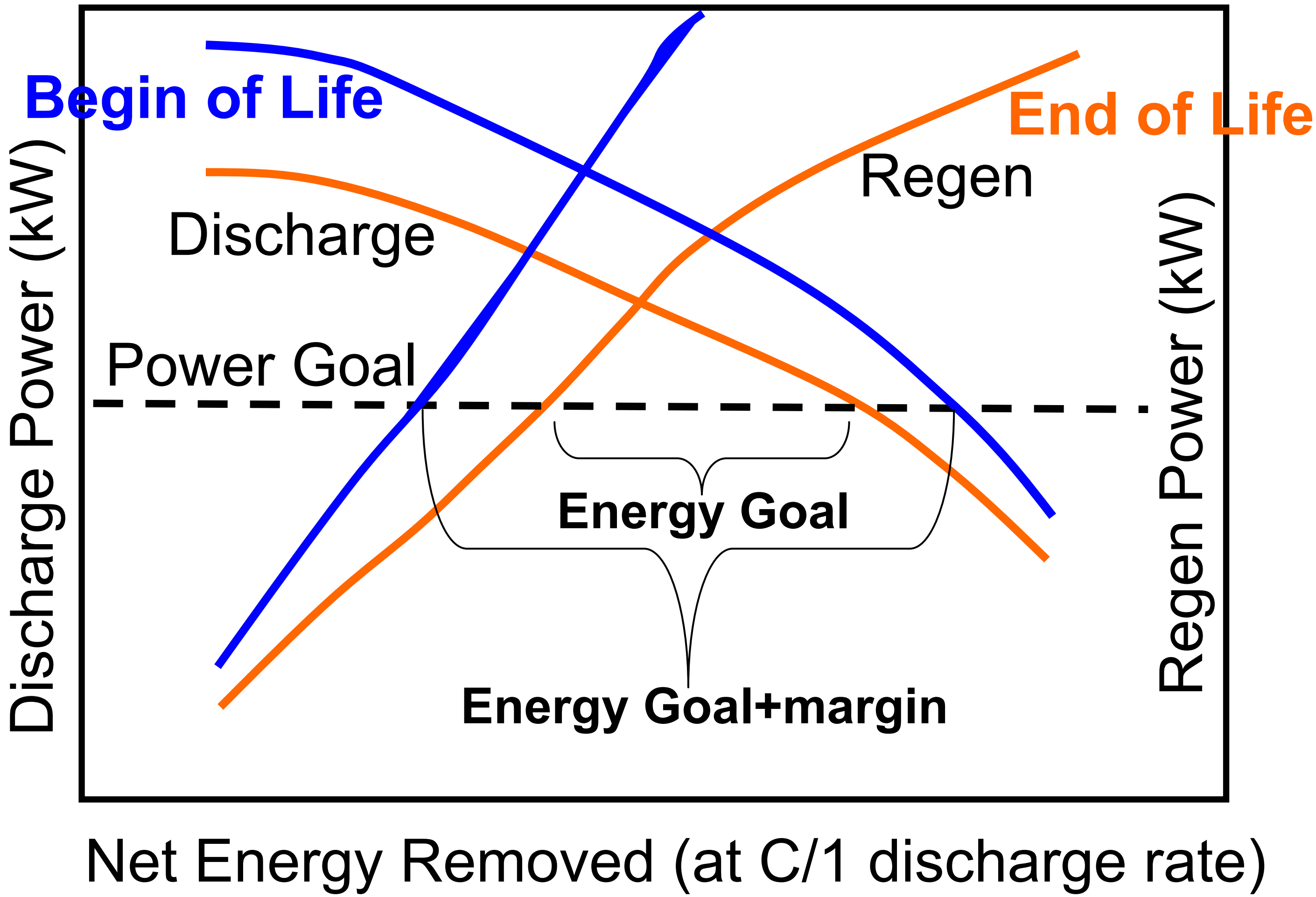
LLIBTA 2006 – Baltimore, MD

Overview

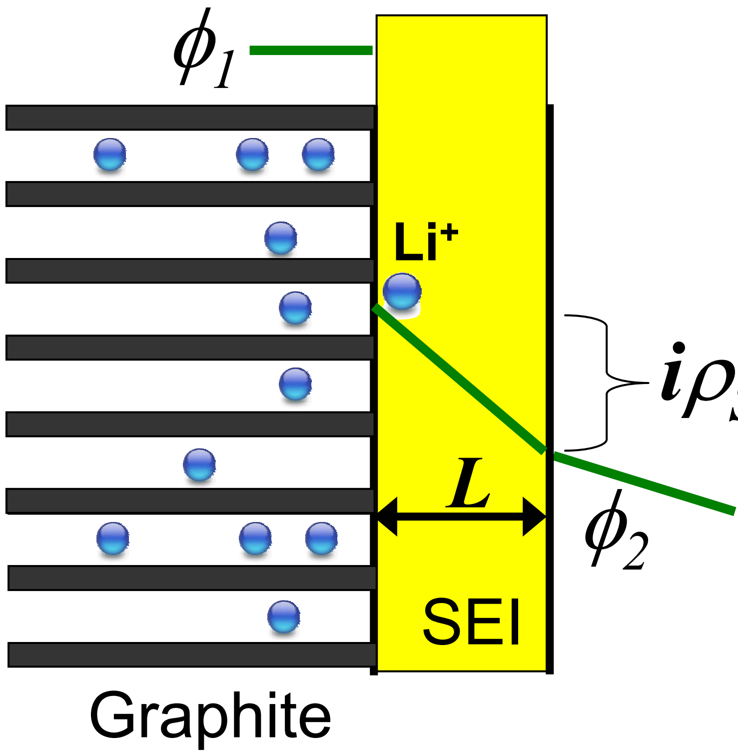
- Need to Estimate Battery Life
- Anode Mechanisms
- Cathode Mechanisms
- Electrolyte Decomposition
- Cell Chemistry
- Conclusions

Goal: 10-15 Year Battery Life



Solid Electrolyte Interface (SEI) Resistor Model

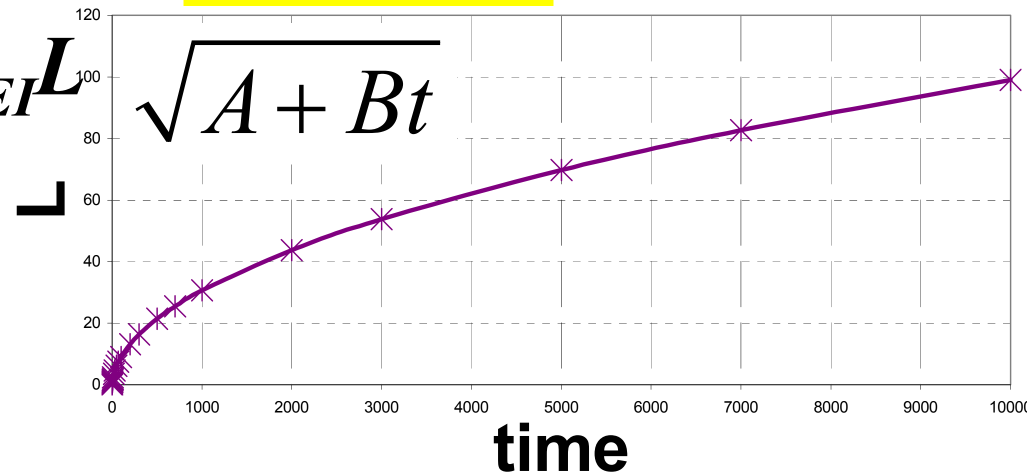
Lithium ion conductor that acts as resistive film, increasing potential drop across electrode/electrolyte interface.



Rate of SEI formation

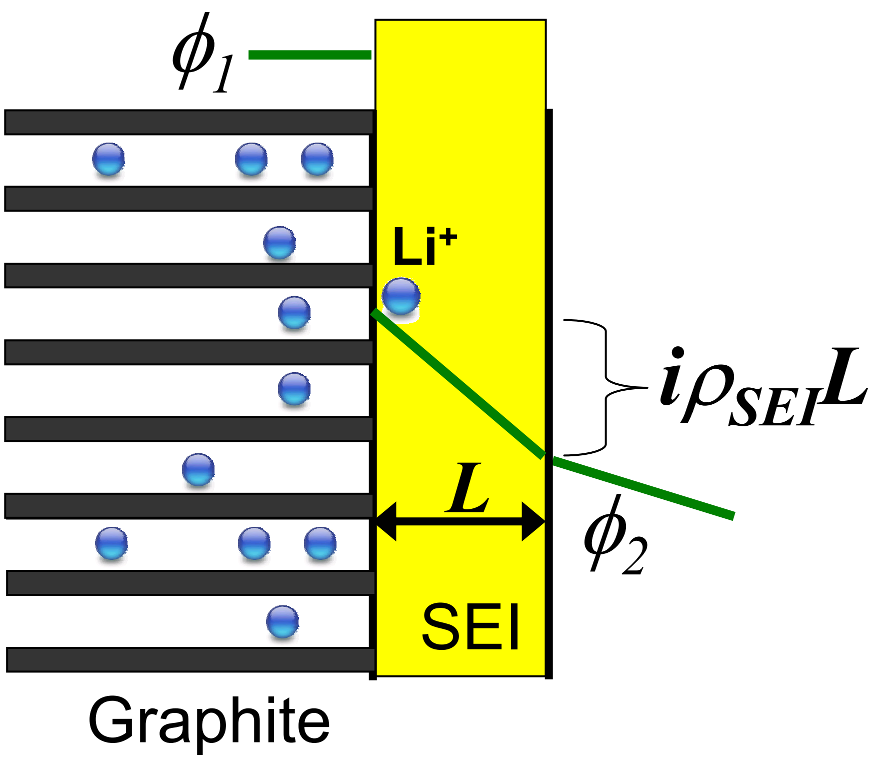
$$\frac{dL}{dt} = \frac{k}{L}$$

M. Broussely et al. *J. Power Src.*. 97-98 (2001) 13.



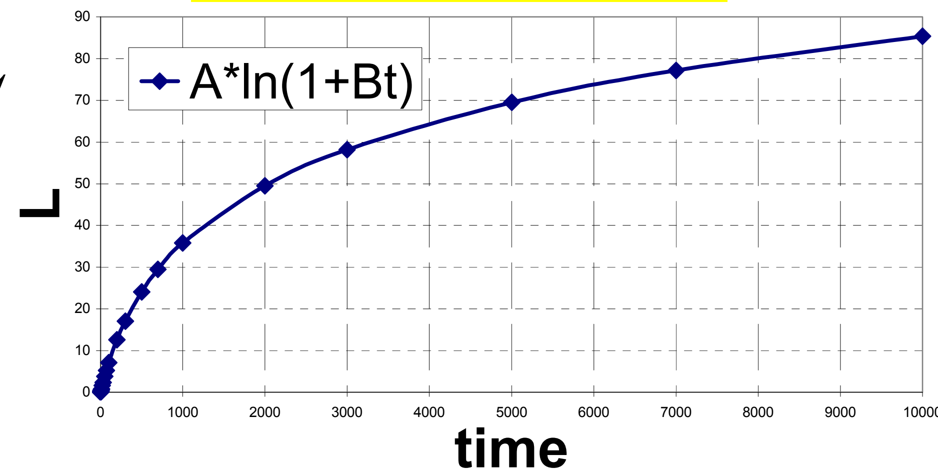
Solid Electrolyte Interface (SEI) Electron Tunneling Model

Lithium ion conductor that acts as resistive film, increasing potential drop across electrode/electrolyte interface.



Rate of SEI formation

$$\frac{dL}{dt} = k_o e^{-fL}$$



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Comparison of SEI Growth Models

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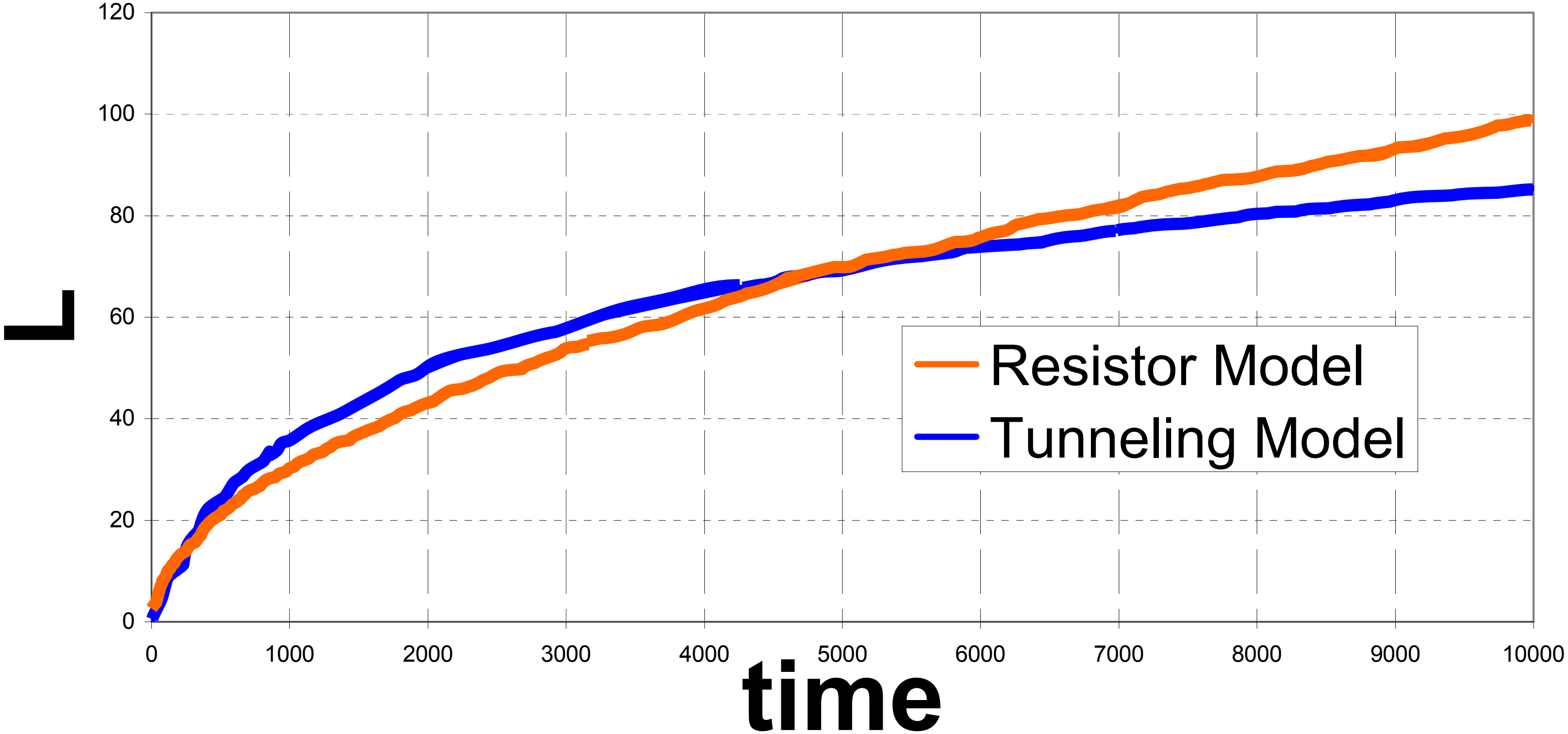
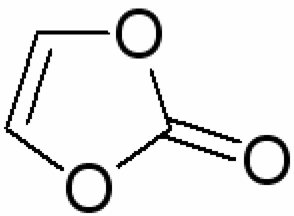


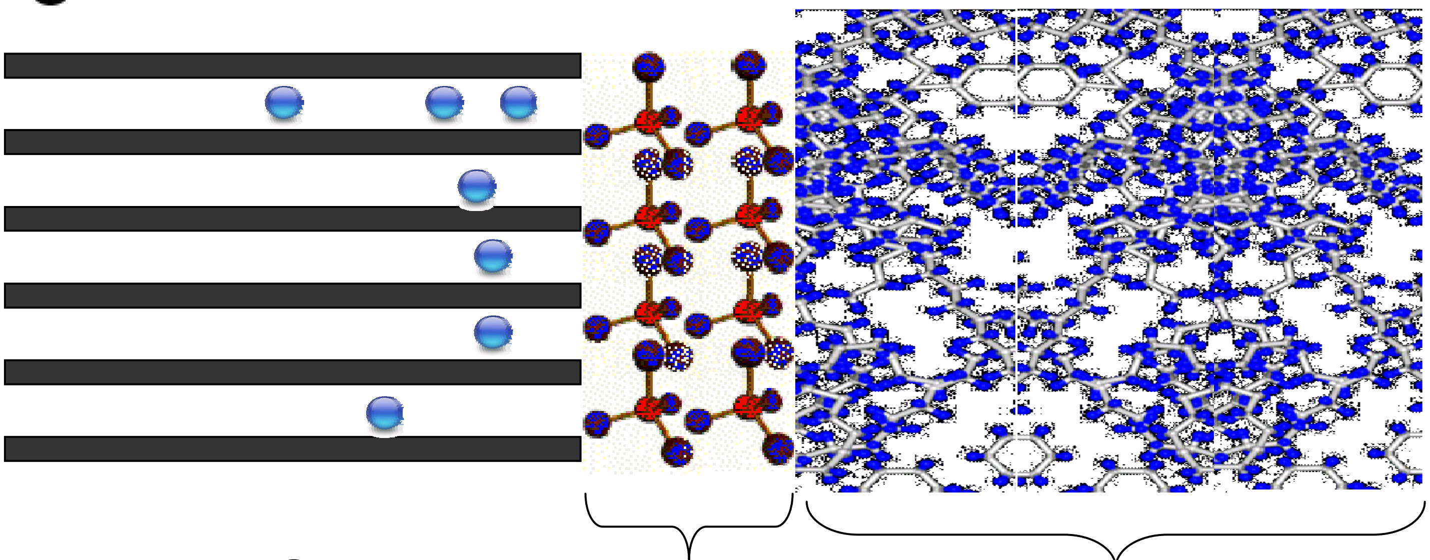
Tunneling model and resistor model can give nearly equivalent fits to data over limited periods of time

Schematic of SEI at Graphite

Vinylene carbonate



$$+ 2e^- \rightarrow Li_2CO_3 + -(\overset{H}{C}=\overset{H}{C}-O)- \Big\} R_f$$



Crystalline solid ion conductor

Polymeric film

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Acid attack of SEI

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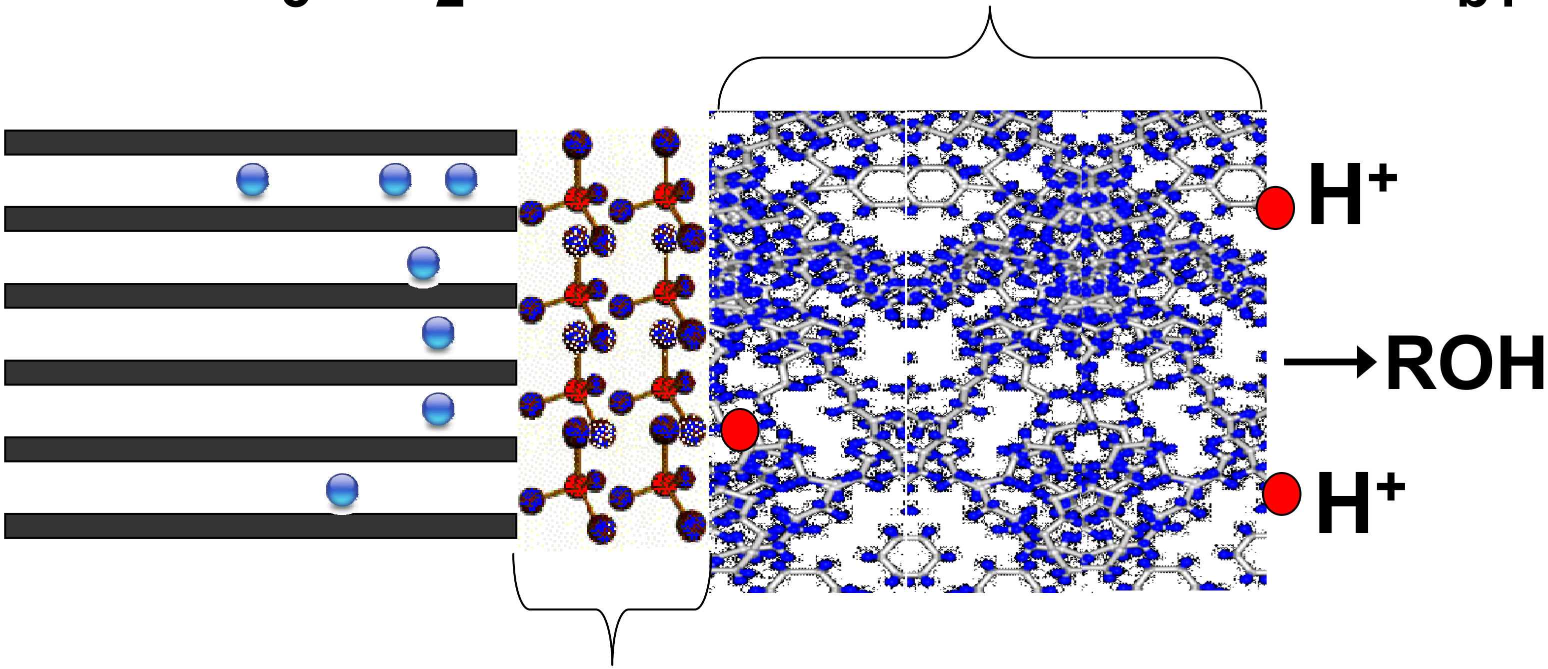
$$CH_3CH_2OLi + H^+ \rightarrow ROH + Li^+ : R_{b1}$$

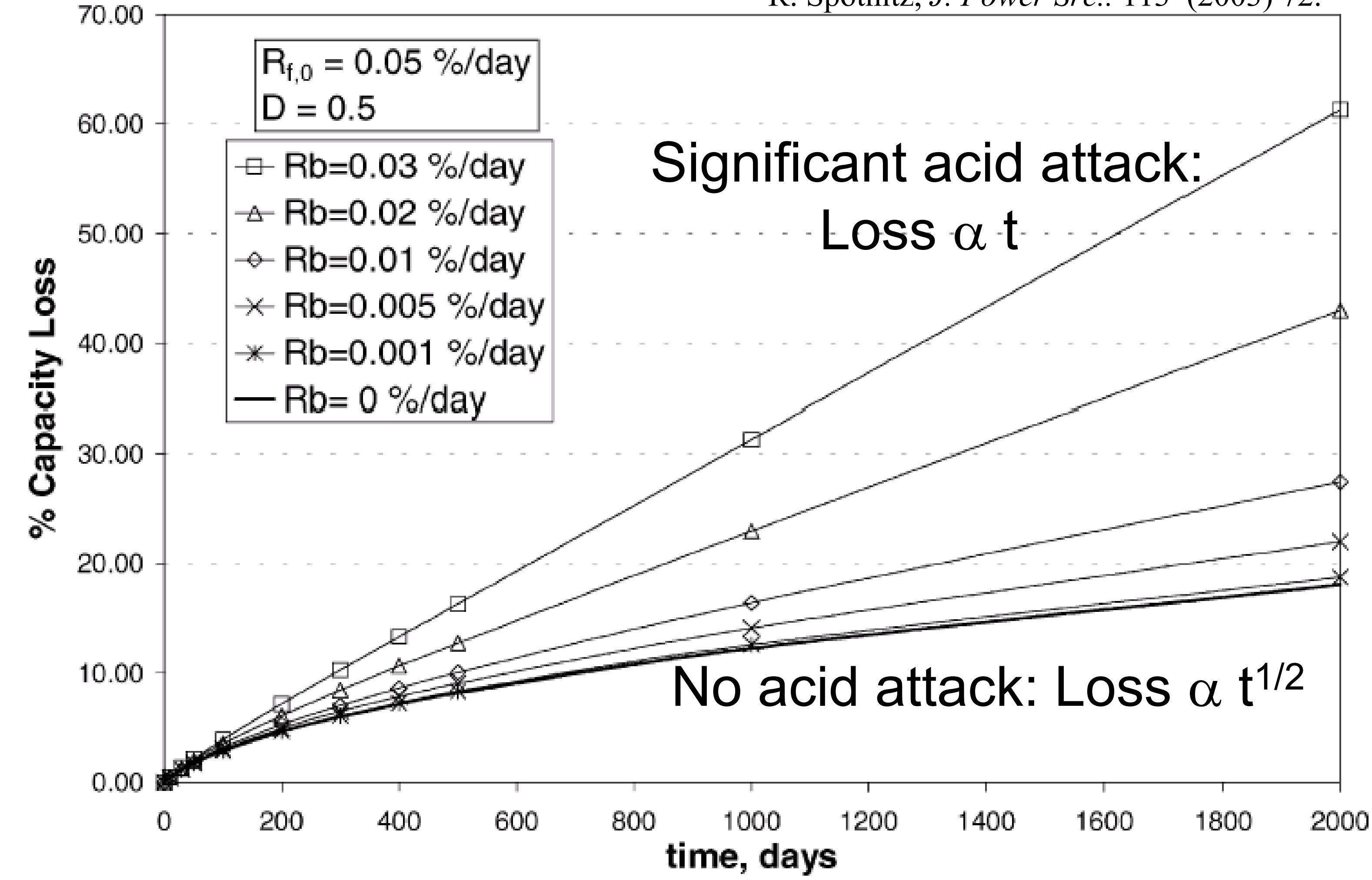


$$Li_2CO_3 + H^+ \rightarrow LiHCO_3 + Li^+ : R_{b2}$$

$$LiHCO_3 + H^+ \rightarrow H_2O + CO_2 + Li^+ : R_{b3}$$

Simulation of Acid Attack - Acid destroys SEI layer

R. Spotnitz, *J. Power Src.*. 113 (2003) 72.



Simulation of Acid Attack - Acid destroys SEI layer

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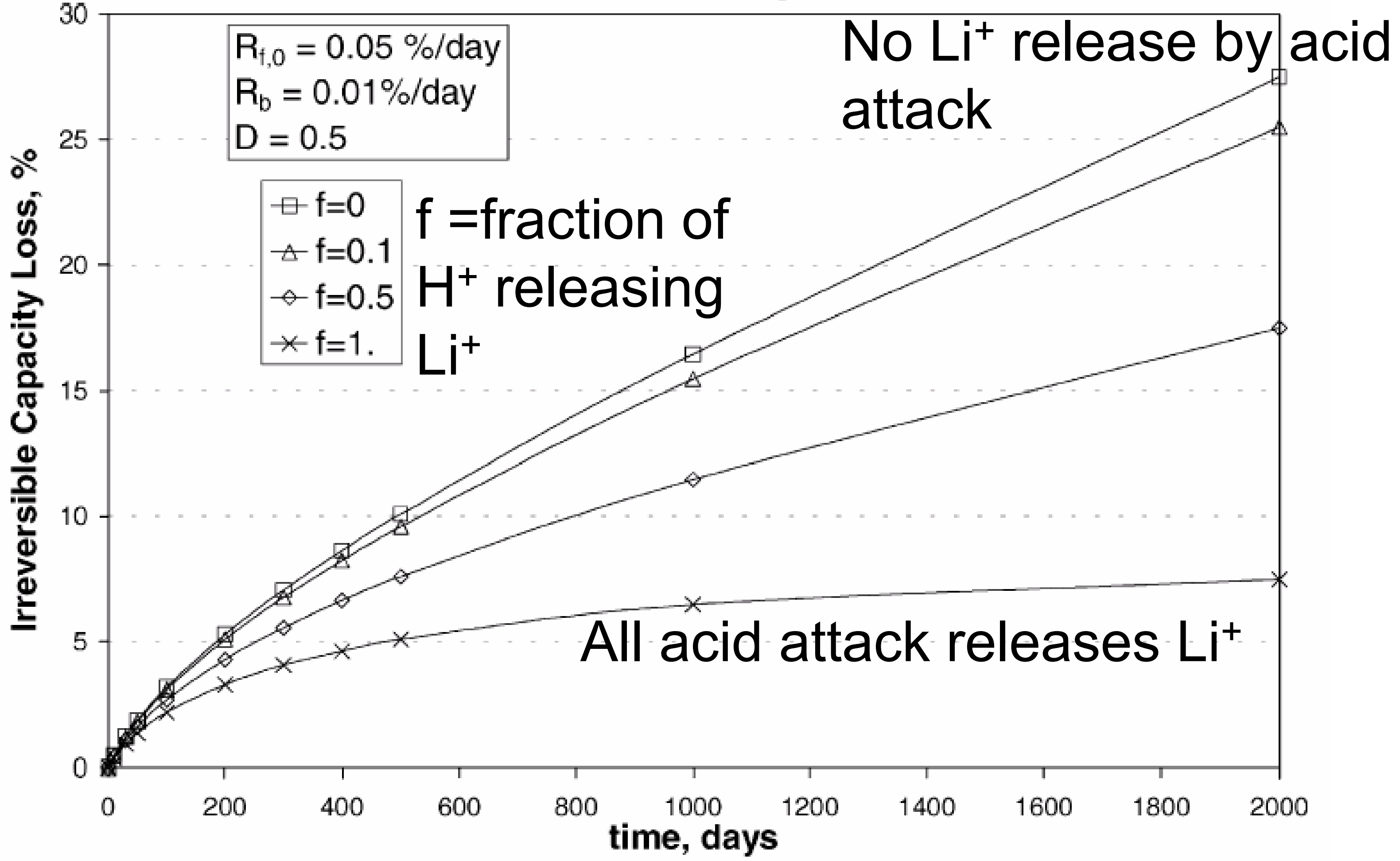
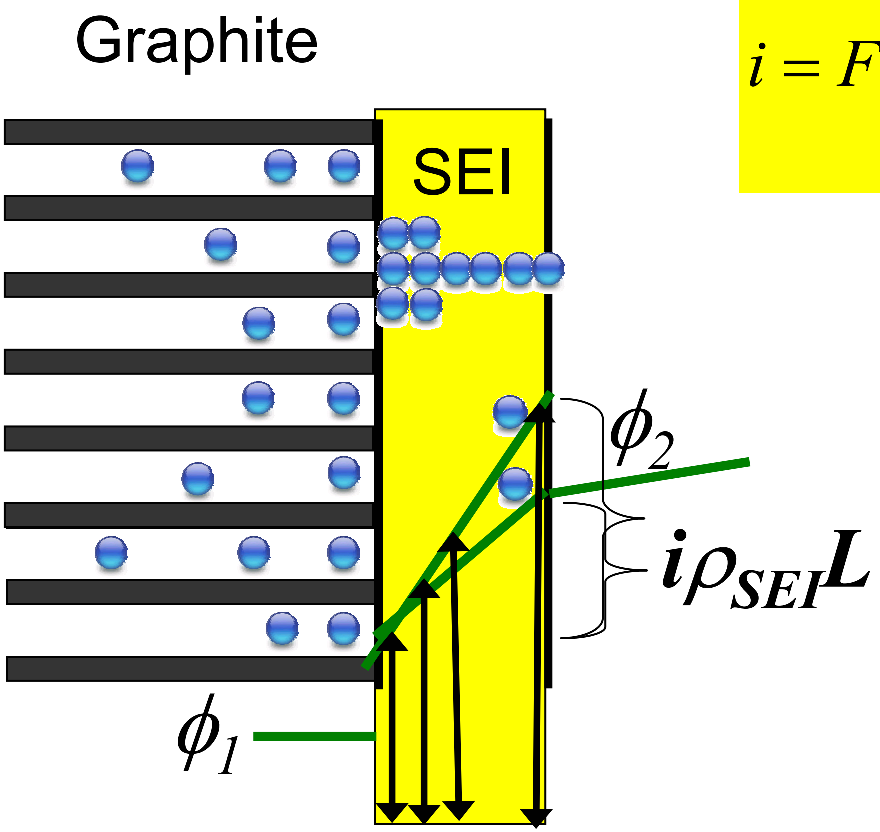
R. Spotnitz, *J. Power Src.*. 113 (2003) 72.



Lithium Deposition at Negative



$$Li^{+} + e^{-} + C_6 \rightarrow LiC_6$$

$$i = Fk_n \exp\left[\frac{-F\left(\phi_1 - \phi_2 - \phi_{eq} - i\rho_{SEI}L\right)}{RT}\right]$$

$$Li^{+} + e^{-} \rightarrow Li^{0}$$

$$i_{Li} = Fk_{Li} \exp\left[\frac{-F\left(\phi_1 - \phi_2 - \phi_{eq,Li}\right)}{RT}\right]$$

Side Reactions at Positive

$$ROH \rightarrow RO + H^{+} + e^{-}$$

Electro-oxidation of organics produces acid.

$$LiMO_2 \rightarrow Li_{(1-x)}MO_{2-x} + \frac{x}{2}Li_2O + \frac{x}{4}O_2$$

Oxygen-deficient oxide has much lower Li^{+} diffusivity.

D. Dees, E. Gunen, D. Abraham, A. Jansen, J. Prakash, *J. Electrochem. Soc.* 152(7) A11409 (2005)

$$OGP \rightleftarrows OGP_{ads}$$

Organofluorophosphate adsorbs on positive forming a resistive film.

M. Kerlau, J. A. Reimer, E. J. Carins, *J. Electrochem. Soc.* 152(8) A1629 (2005)

Phase Transition at Positive

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Surface phase acts as diffusion barrier for lithium ions.

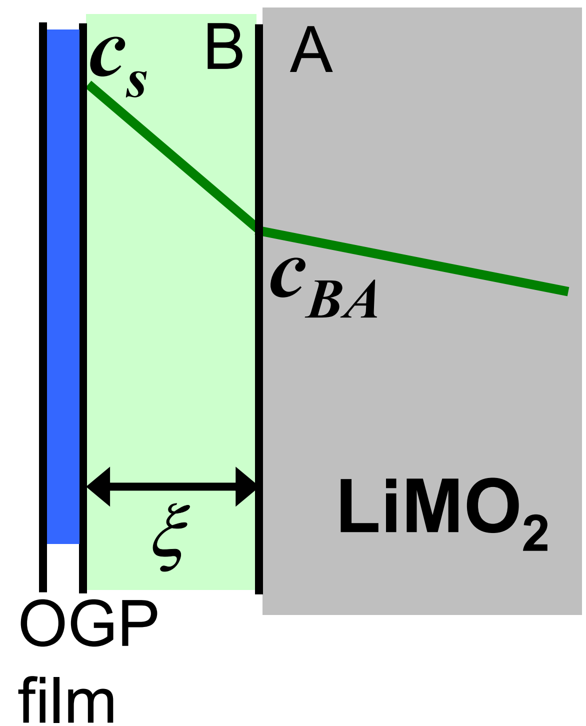
Rate of Phase Growth

$$\frac{d\xi}{dt} = \frac{k_{AB}}{g}\exp\left[-f\,\xi\right]$$

Solid-Phase Li^+ Diffusion

$$i = -FD\frac{\left(c_s - c_{BA}\right)}{\xi}$$

Li^+ Concn. Profile



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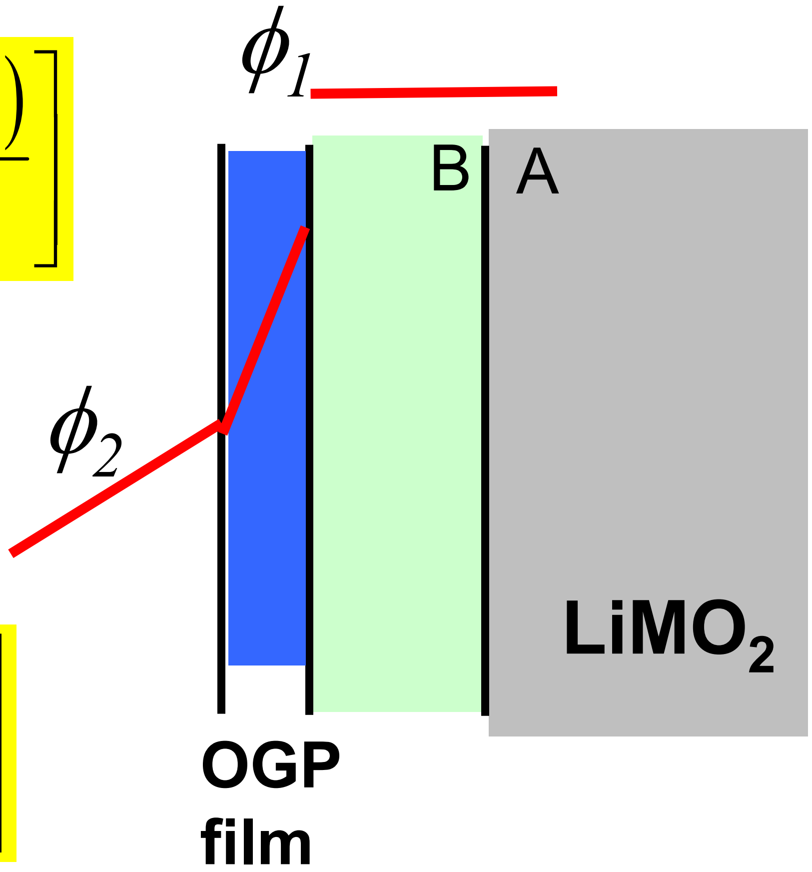
Acid Generation at Positive

$$LiMO_2 \rightarrow MO_2 + Li^+ + e^-$$

$$i_{Li^+} = Fk_p \exp\left[\frac{F\left(\phi_1 - \phi_2 - \phi_{eq} - i\rho_f L_p\right)}{RT}\right]$$

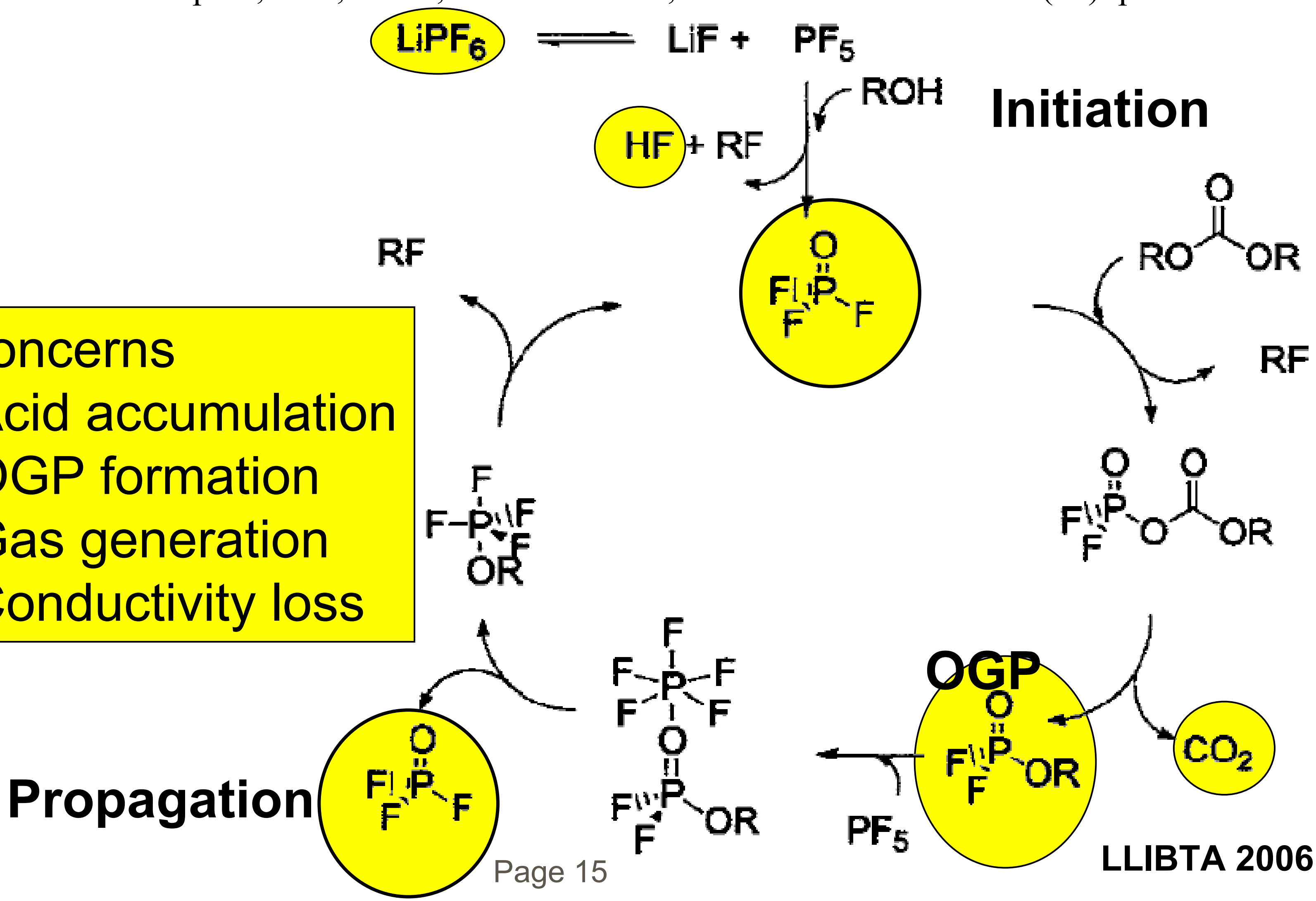
$$ROH \rightarrow RO + H^+ + e^-$$

$$i_{H^+} = Fk_{H^+} \exp\left[\frac{F\left(\phi_1 - \phi_2 - \phi_{eq,H^+} - i\rho_f L_p\right)}{RT}\right]$$



Mechanism of Diethyl Carbonate Decomposition by LiPF6

Campion, C.L., W. Li, and B.L. Lucht, *J. Echem. Soc*. 2005. 152(12): p. A2327.



Concerns
- Acid accumulation
- OGP formation
- Gas generation
- Conductivity loss

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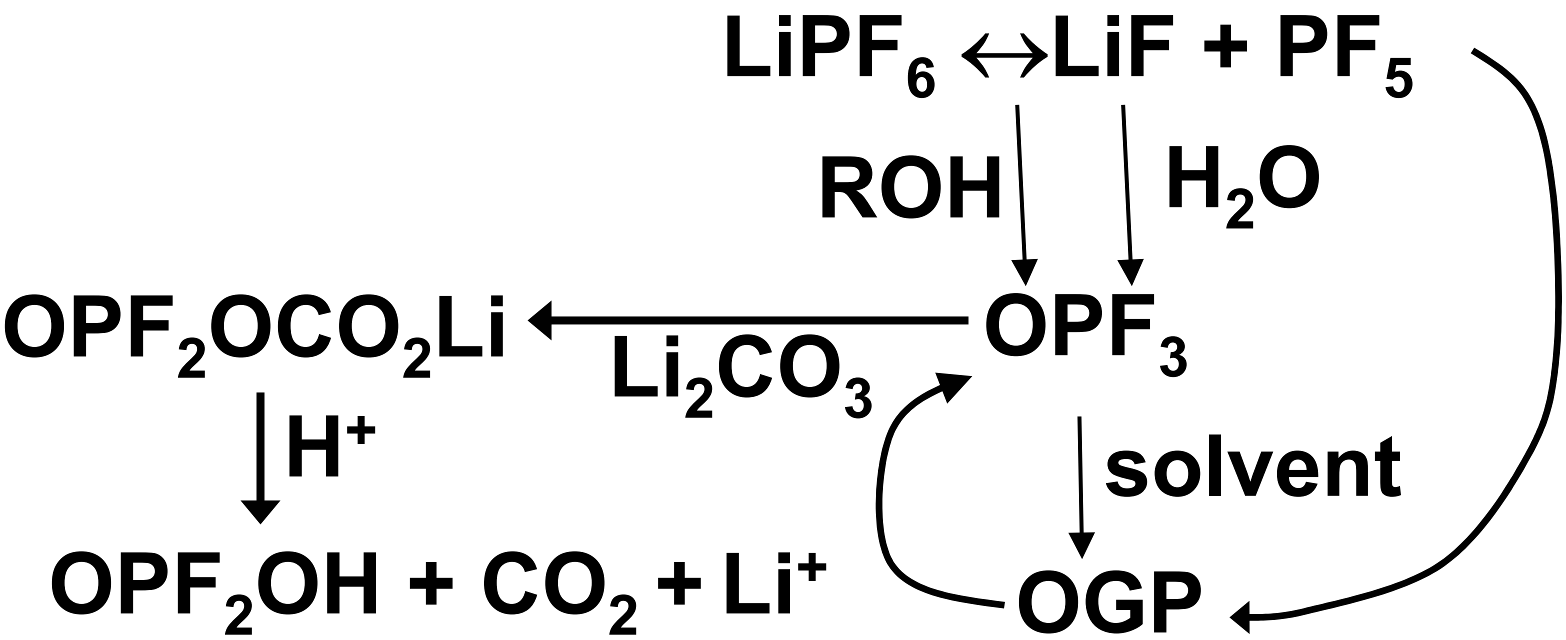
Does Li_2CO_3 inhibit $LiPF_6$ Decomposition?

$$OPF_3 + Li_2CO_3 \rightarrow OPF_2OCO_2Li + Li^+ + F^-$$



Electrolyte Decomposition at 80°C – Effect of EtOH Addition

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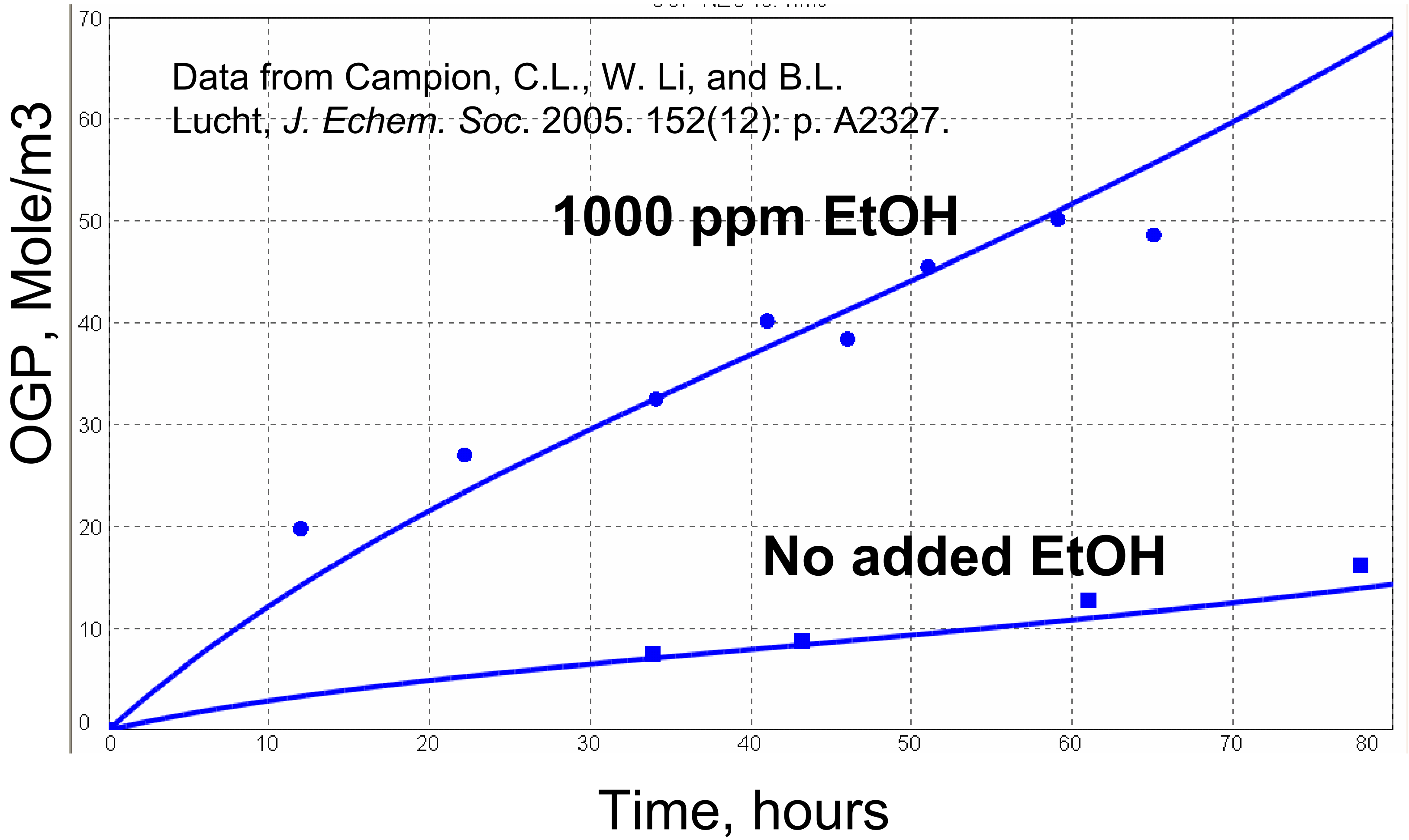
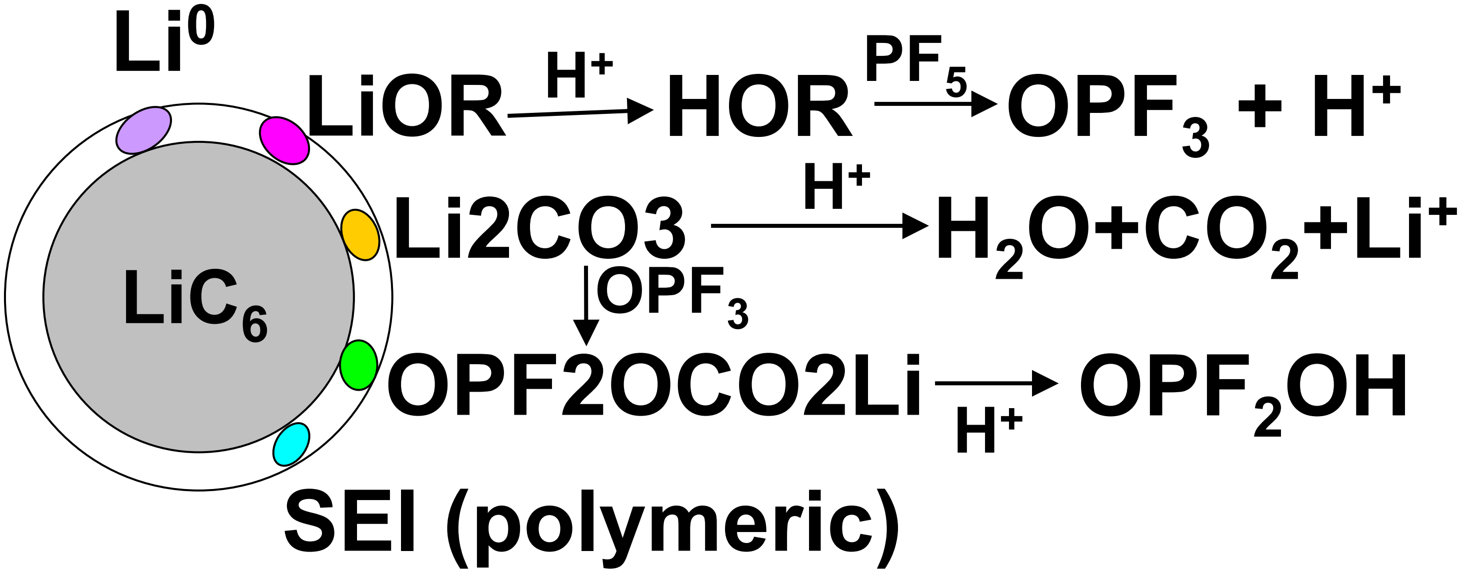
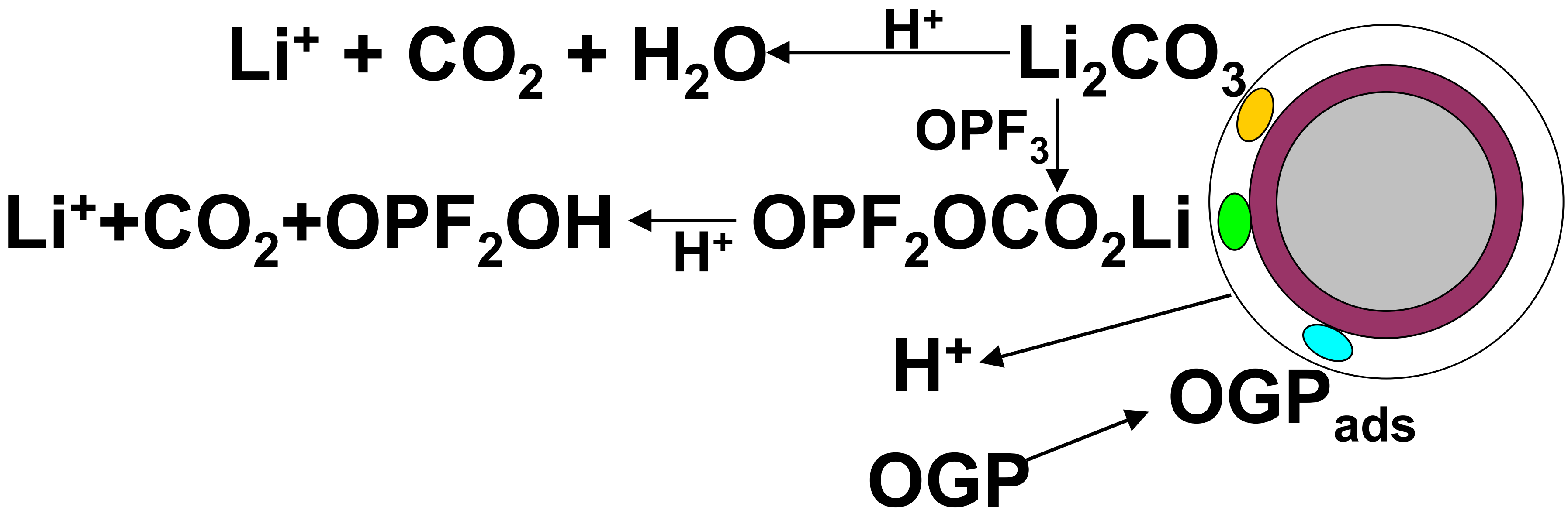


Negative Chemistry



Concerns
- SEI resistance
- Li loss

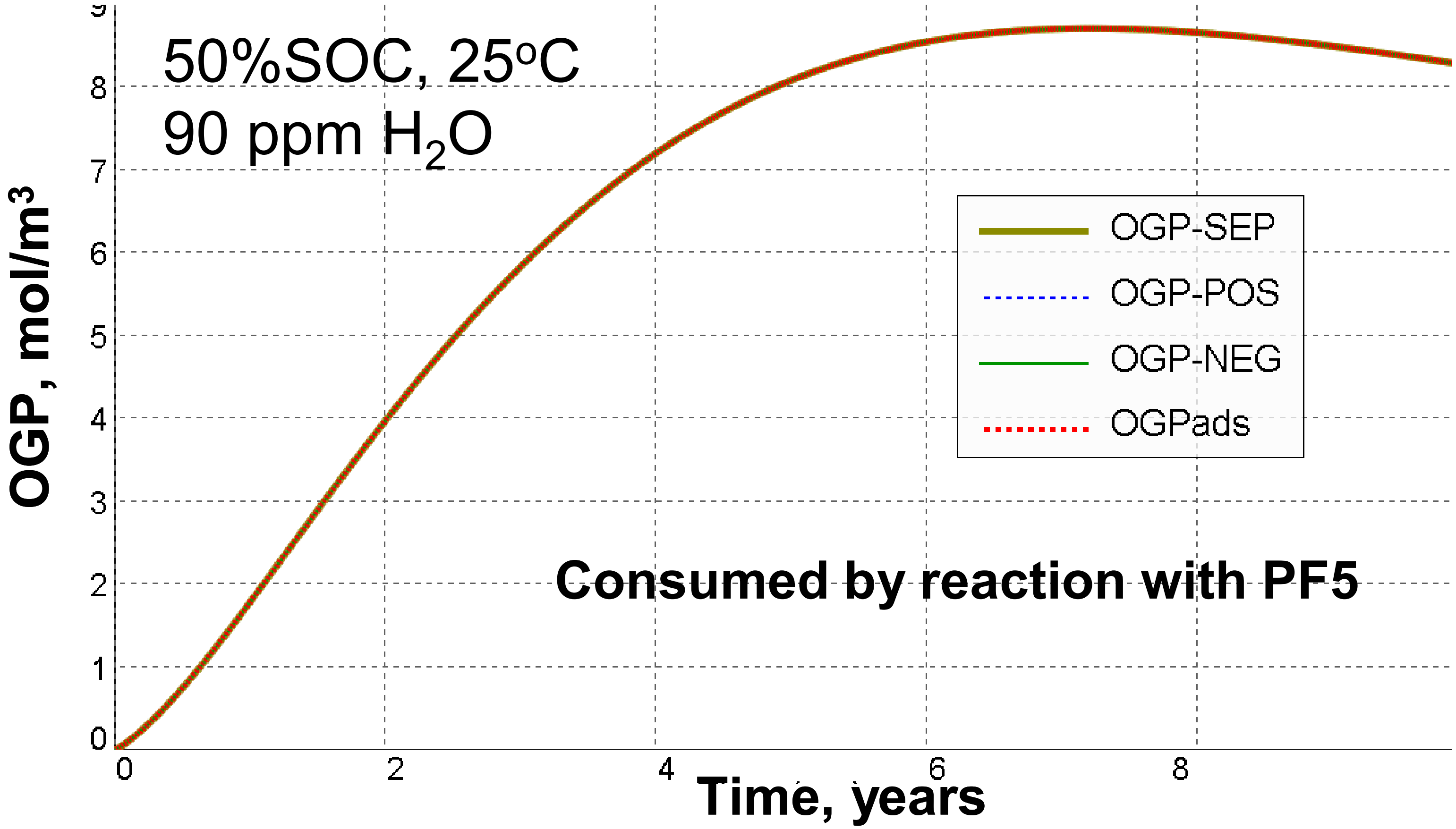
Positive Chemistry



Concerns

- B phase formation creates diffusion resistance
- OGP buildup increases resistance
- Acid generation

OGP Concentration History in Simulated Aging Test



OGP Concentration History in Simulated Aging Test

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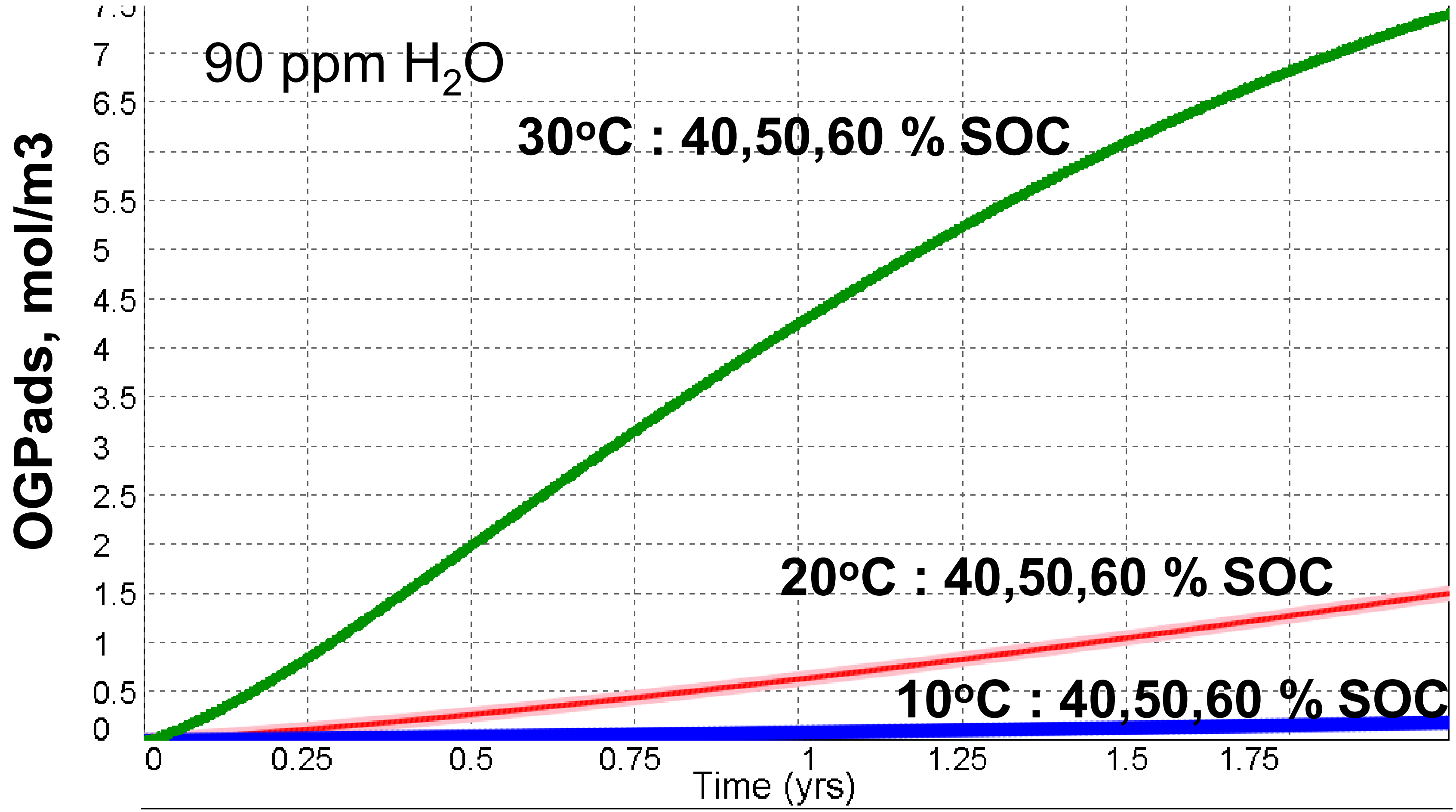
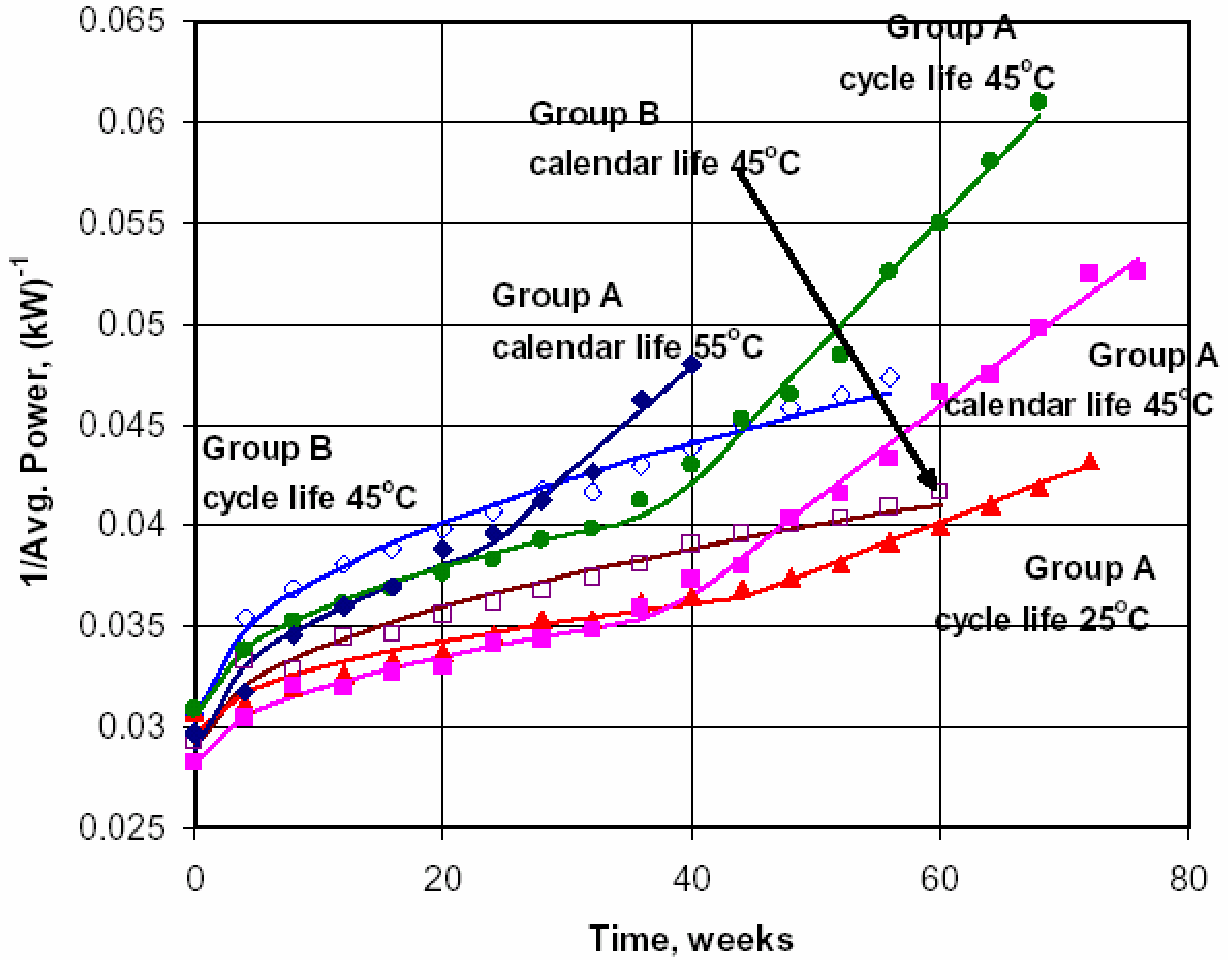


Fade in High-Power Li-Ion Cells

I. Bloom et al., *J. Power Src*. 124(2003) 538.



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Summary

- Modeling SEI growth as a resistive layer or as electron tunnel gives comparable behavior.
- Reversible and irreversible capacity loss should be considered in evaluating SEI growth at negative.
- Model presented that accounts for side reactions (at positive and negative, and in electrolyte) and interactions.
- Positing that Li_2CO_3 complexes OPF_3
  - rationalizes the stability of $LiPF_6$ electrolytes in lithium-ion cells,
  - predicts a linear increase in OGP for some time, and
  - indicates that increasing temperature increases OGP (impedance).