On transport and kinetics in Li-Ion cell cathodes

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Why bother storing energy?

- Great existing demand to power all sorts of devices
- **Decouple availability** of electrical power from natural phenomena (e.g. wind, sun, ...)
- **Mobile** application in medicine and everyday life:



Global Li-Ion Battery Sales Volume and Growth Rate Split by Application 2013 – 2023E



[Source: Interact Analysis]

Li-Ion cell: Active materials

Negative electrode (anode): Graphite or metallic Lithium



Situation at positive electrode Free Energy $Me^+ + e^- \overset{Red}{\longrightarrow} Me$ — Redu



Reaction Coordinate

Positive electrode (cathode): Metal oxides

LiCoO₂ : layered structure

LiMn₂0₄ : spinel structure



LiFePO4: olivine structure





Li-Ion cell: Structure

Schematic drawing



Cathode (+)



Anode materials

- Graphite $Li_xC_6 \{0 < x < 1\}$
- Metallic Lithium Li
- Lithium titanate (LTO) $Li_xTi_5O_{12}$ {2 < x < 4}
- Amorph Aluminum $\text{Li}_x \text{Al} \{0.5 < x < 1\}$



Working combinations have distinct benefits

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Electrolytes

Combination: Solvent & conducting salt Solvents: PC, EC, DMC, and many more Conducting salts: $LiPF_6$, $LiClO_4$, LiBOB, a.m.m. Concentration typ. 0.3 to 3 – molar (mol/l)



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Cathode materials

- Lithium-Cobalt oxide Li_xCoO₂
- partly substition of Co by Ni, Mn, Al, ..
- NCM333, NCM523, NCM811, NCA
- Lithium-Iron phosphate LFP
- a.m.m.



Working combinations have distinct benefits

Cell voltage depends on <u>combination</u> of active materials (chosen chemistry)





What to calculate?

Idealy understand charge and discharge behavior under several conditions

→ Individual processes?

Simulation of Li – diffusion into TiO₂-Nanotubes, D unknown



Mahmoud Madian, PhD, TU Dresden 2017, Fig. 2.12





Mahmoud Madian, PhD, TU Dresden 2017, Fig. 4.7



Simulation of Lithium - diffusion into TiO₂-Nanotubes

Isotrope diffusion

Lithium – conzentration distribution $t = 200 \,\mathrm{s}$







[A. Nickol, C. Heubner, Fraunhofer IKTS]

 $\eta_{\rm total}$ for 0.1C and 3.8V (x_{Li} ~ 0.75)

Modeling: Full cell / Pseudo - 2D (1d+1D)



4

Heating at different discharge rates and initial Temperatures

Adiabatic condition = perfect thermal insulation from environment



Charge consumption for battery (cell) heating

Part of the available capacity required for self-heating from -10 to +20°C

- adiabatic $h = 0 \rightarrow$ perfect insulation from environment
- non-adiabatic $h > 0 \rightarrow$ heat dissipation proportional with h and ΔT



→ Efficient self heating requires $h < 10 \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$

- Better knowledge of diffusion and inner losses

→ Diffusion can be accessed by Galvanostatic Intermittent Titration Technology (GITT)

 \rightarrow Inner losses correspond to overvoltages associated with several processes

Galvano static intermittend titration technique (GITT) is a widely used electrochmical characterization method

- Electrons are drawn from oxide and "pushed" to the graphite
- Electron excess in graphite causes Li⁺ to enter graphite to keep charge neutrality
- For the same reason: $\mathrm{Li}^{\scriptscriptstyle +}$ leaves the oxide material
- On graphite-side Li⁺ are removed from... and on oxide-side Li⁺ are added to... the electrolyte
- One cause: Anion-concentration (counterparts Li⁺) shifts to the oxide-side



Galvano static intermittend titration technique (GITT) is a widely used electrochmical characterization method



Determining material properties: GITT

- State of lithiation or (State of "charge" .. SOC) x changes during pulse
- Potential values *E*₄ after relaxation are regarded as "equilibrium"



Typical method: Weppner-Huggins

- assumes palanar geometry
- assumes perfect square-root-like behaviour
- Modified for spherical particles one gets:

$$D = \frac{4}{9\pi} \left(\frac{r_{\rm p}}{t_{\rm p}} \frac{E_4 - E_0}{dE(t) / d\sqrt{t}} \right)^2$$



[J. Electrochem. Soc. 167,090546 (2020)]

Modeling: Pseudo - 2D (1d+1D) for charging case



Modeling: Single Particle Model (SPM)



SPM: Diffusion (GITT applys small currents)+ one more equation for double layercapacitance including charge transfer resistance





- EIS measured after each GITT pulse → covering accessible range of lithiation states
- Replacement circuit fitting yields resistances and capacitances



Determining material properties: single simulated GITT pulse(s)

- T = 25°C,
$$k_r = 10^{-5} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$$
, $i_{GS} = 0.01 \text{ A} \cdot \text{m}^{-2}$

- atempting to find D by Weppner method: formula $D = \frac{4}{9\pi} \left(\frac{r_{\rm p}}{t_{\rm p}} \frac{E_4 - E_0}{dE(t)/d\sqrt{t}} \right)$



- Only left points seem to get moderate accuracy
- Increasing deviation when using larger part of the pulse
- Weppner method not ideal



3.75

3.70

potential *E* [V]

- 3.60

3.55

45

- Calculated for T = -40°C, k = $1 \cdot 10^{-8}$ mol·m⁻²·s⁻¹ and **0.01 A·m⁻²**

- Large charging time of double layer capacity due to low temperature (high R_{CT})
- No accuracy for $D = 10^{-14}$, although fit region looks "good"
- Overlap of "good" region and double layer charging region
 - → what is the "good" region to fit?

- Calculated for T = -40°C, k = $1 \cdot 10^{-8}$ mol·m⁻²·s⁻¹ and **0.1 A·m⁻²**



- Non-linear behaviour of BV-formula causes decrease of resistance
- → Charging time can be reduced by increased GITT current
- here: 100s to about 10s

There is more: Aging



- Recent pulse simulation yields more realistic pulse shapes

Use curve simulation model as basis for parameter optimization

That is 200 − 1000 simulation for one optimization
 → need to increase speed of pulse calculation

Employ full model to calculate GITT
 Complete GITT simulation as basis for optimization
 To find rate of aging behaviour

Summary

- Simulation of a lithium cell's inner workings require large amount of input data
- Some require modeling for proper determination, such as $D(T, c_{Solid})$
- Standard methods often inaccurate due to simplifications, particularly at low T
- Need to employ more complex models **plus** fast enough sim. software
 offers possibility to do optimization calculations

Other topics:

- Find more accurate dependency of rate coefficient: $k_r(T, c_{Solid}, c_{Elyte})$

Thanks