Atlung Method for Intercalant Diffusion — AMID

Marc M. E. Cormier

Dalhousie University

marc.cormier@dal.ca

June 21, 2021

Theory of Diffusion

$$\vec{j} = -D\vec{\nabla}(c); \; \frac{\partial c}{\partial t} = D\nabla^2(c)$$

- A continuum theory: ∇ is derivative w.r.t. to spatial coordinates.
- c is the Li concentration and depends on the spatial coordinate of the particle and time: $c(x, y, z, t)$ or $c(\theta, \phi, r, t)$
- For *spheres*, c is assumed to be spherically symmetric $\rightarrow$ only depends on r.
- Assumes D is *not* concentration dependent ... !
- These are coupled partial differential equations. Generally very difficult to solve.

General Solution

$$c(t, x) = \frac{j_0 r}{D} \left[a\frac{Dt}{r^2} + \frac{z^2}{2} - b - 2\sum_i \frac{\exp(-\alpha_i^2 Dt/r^2)}{\alpha_i^2} C(\alpha_i z) \right]$$

Where $z = x/r$ is a normalized coordinate
$\rightarrow z = 1$: surface, $z = 0$: center.

Plane sheet: $S_m = V_m/r.$ $j_0 = \dfrac{nr}{TV_m}$

Cylinders: $S_m = 2V_m/r.$ $j_0 = \dfrac{nr}{2TV_m}$

Spheres: $S_m = 3V_m/r.$ $j_0 = \dfrac{nr}{3TV_m}$

Table I. Constants and functions in Eq. [6]

Shape	a	b	$C(\alpha z)$	$g(\alpha)$	α_1	α_2	α_3
Plane sheet	1	1/6	$\cos \alpha z/\cos \alpha$	$\sin \alpha$	π	2π	3π
Cylinders	2	1/4	$J_0(\alpha z)/J_0(\alpha)$	$J_1(\alpha)$	3.8317	7.0156	10.1735
Spheres	3	3/10	$\sin \alpha z/\sin \alpha$	$\alpha \cot \alpha - 1$	4.4934	7.7253	10.9041

J_0 and J_1 are Bessel functions of first kind of order zero and 1.

j_0 is a flux density that depends on the particle shape. This assumes that on average, all areas of particle surfaces see the same amount of Li ions enter the material (all surfaces are equally active).

Normalized Solution (for spheres)

$$X(z,\tau) = \tau + \frac{1}{3Q}\left(\frac{z^2}{2} - \frac{3}{10} - 2\sum_i\left[\frac{\exp(-\alpha_i^2 Q\tau)}{\alpha_i^2}\frac{\sin(\alpha_i z)}{\sin(\alpha_i)}\right]\right)$$

- $X = \frac{cV_m}{n}$: local fractional Li concentration.
- $z = x/r$: normalized coordinate $\rightarrow z = 1$: surface, $z = 0$: center.
- $\tau = t/T$;
  T: capacity/current ((dis)charge time), t: elapsed (dis)charge time
  $\therefore \tau =$ fractional capacity
- $Q = T/(r^2/D)$;
  (r^2/D) is characteristic diffusion time (average time it takes a Li ion to travel from center to surface)
  $\therefore Q$ is fractional time: ((dis)charge time) / (diffusion time)

Solution, at the surface

At the surface, $x = r \therefore z = 1$, and denote $X(z = 1, \tau) = X^*(\tau)$:

$$X^*(\tau) = \tau + \frac{1}{AQ}\left[\frac{1}{B} - 2\sum_i \frac{\exp(-\alpha_i^2 Q\tau)}{\alpha_i^2}\right]$$

Where,

	Plane sheet	Cylinders	Spheres
A	1	2	3
B	3	4	5

What about the α_i's?

From Table 1, the generating functions are:

- Plane sheet: $g(\alpha) = \sin(\alpha)$
- Cylinders: $g(\alpha) = J_1(\alpha)$
- Spheres: $g(\alpha) = \alpha \cot(\alpha) - 1$

α_i are the roots of the generaing equations $\rightarrow g(\alpha_i) = 0$
There are infinitely many solutions for each shape! For spheres,

$$\alpha_i \cot(\alpha_i) = 1$$

Fig. 4. Cathode efficiency (cathode utilization at $X^* = 1$) as function of log Q. Average load with no peak loading. Particle shape indicated on graphs.

τ^* is the fractional capacity when $X^* = 1$ (i.e., when the surface concentration reaches its (fractional) saturation value):

$$X^* = 1 = \tau^* + \frac{1}{AQ}\left[\frac{1}{B} - 2\sum_i \frac{\exp(-\alpha_i^2 Q\tau^*)}{\alpha_i^2}\right]$$

Everyone has seen, but where does it come from? (cont'd)

$$\tau^* + \frac{1}{AQ}\left[\frac{1}{B} - 2\sum_i \frac{\exp(-\alpha_i^2 Q\tau^*)}{\alpha_i^2}\right] = 1$$

is an *implicit* equation of τ^* and Q. There is no analytical solution, must be solved numerically to get:

$$\tau^*(Q)$$

The result is sensitive to the number of α_i's inlcuded in the expansion...

Numerical solutions for spheres
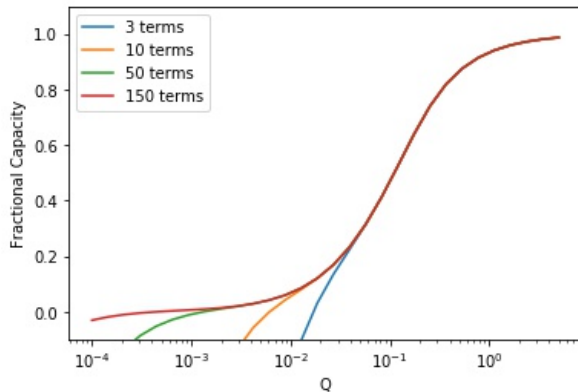
How do we get D?

Recall that $Q = T/(r^2/D)$. But since T is the (dis)charge time, $T = 3600n$, for n in C/n.

$$\therefore Q = \frac{3600nD}{r^2}$$

$$\therefore \tau^* + \frac{r^2}{3600nDA} \left[\frac{1}{B} - 2 \sum_i \frac{\exp(-3600nD\alpha_i^2\tau^*/r^2)}{\alpha_i^2} \right] = 1$$

If the particle size, r, is known, then this equation relates the fractional capacity, τ^* to the rate, n, for a given D.
$\Rightarrow$ Capacity-rate data can be fit to this expression to extract D!
(We actually write $\tau = c/c_{max}$, where c_{max} is maximum available capacity, in case the lowest rate did not achieve saturation capacity)

Capacity-rate data

$$Li_{1.12}Ni_{0.44}Mn_{0.44}O_2$$
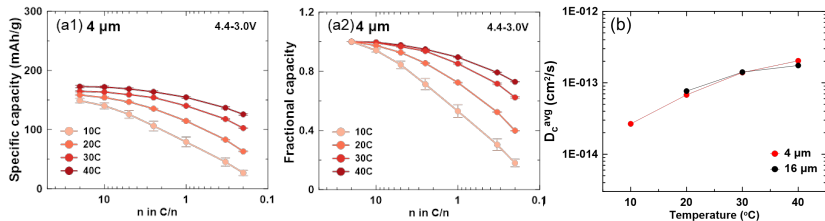
In this case, we can extract D as a function of T (temperature); each curve can be fit to the equation on the previous slide.

There is a problem here: recall that D is supposed to be constant - but it is NOT constant in the $4.4 - 3.0$ V interval!

K.K. paper, N.P.

Getting capacity-rate data: signature curves
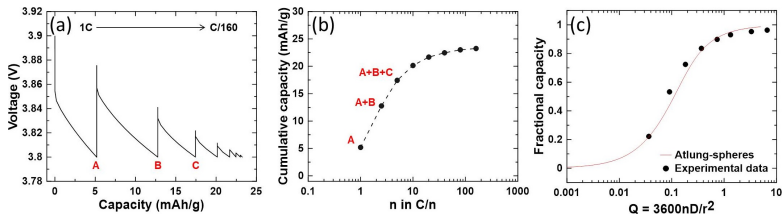
Signature curve: sequential (dis)charge at lower and lower rates with OCV in between.

- Fix voltage interval
- Fix OCV time.
- Select rates.

Should give the same cumulative capacity for each rate. Much faster than charging back to starting V each time and does not require CV holds.

KH paper, A.L., N.P.

D(V): advanced signature curve protocol

$Li_{1.12}Ni_{0.44}Mn_{0.44}O_2$
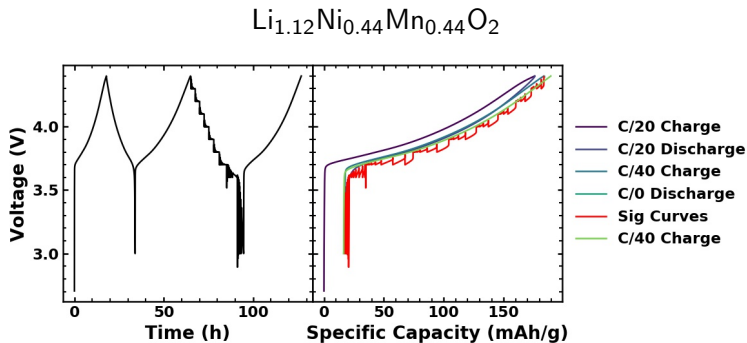
- This protocol performs sequential signature curves within 0.1 V intervals from $4.4 - 3.6$ V and one 0.6 V interval from $3.6 - 3.0$ V
- Note the C/0 discharge — this is an OCV at top of charge before signature curves begin and *should not* be there.

D(V): capacity-rate data and effective rates

$Li_{1.12}Ni_{0.44}Mn_{0.44}O_2$

Legend:
- 4.39 V - 4.30 V
- 4.30 V - 4.20 V
- 4.20 V - 4.10 V
- 4.10 V - 4.00 V
- 4.00 V - 3.90 V
- 3.90 V - 3.80 V
- 3.80 V - 3.70 V
- 3.70 V - 3.60 V
- 3.60 V - 3.00 V
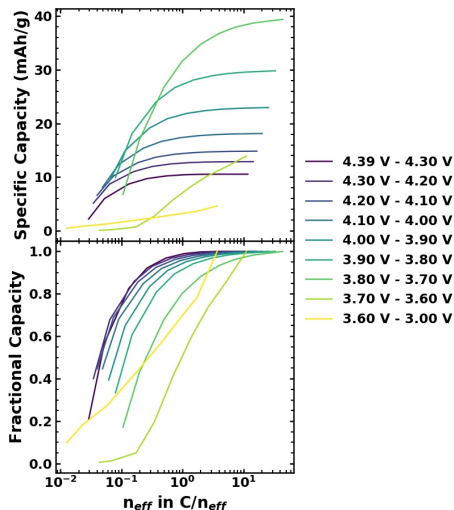
What is the (dis)charge time for an arbitrary voltage interval?

Since the capacity within each votlage interval is not known *a priori*, currents input in the protocal are determined from the full theoretical capacity.

The (dis)charge time, $3600n$, to be used in the fit must be computed for each voltage interval based on the cumulative capacity achieved within that interval.

D(V): IR contribution to V
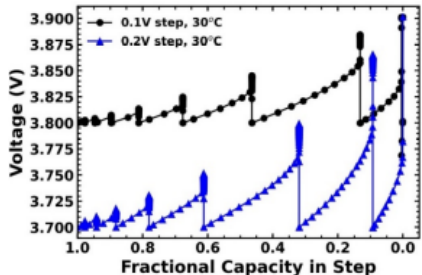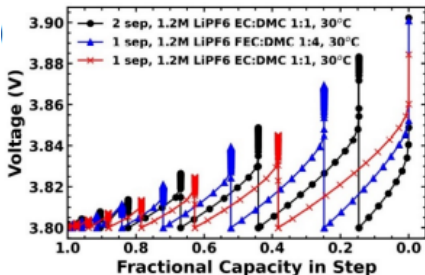
- Coin cells for diffusion measurement must be constructed to minimize IR contributions to V.
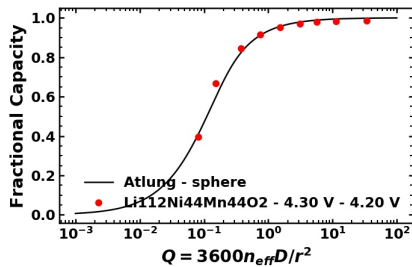- Larger V intervals can help, but remember that D is supposed to be constant.
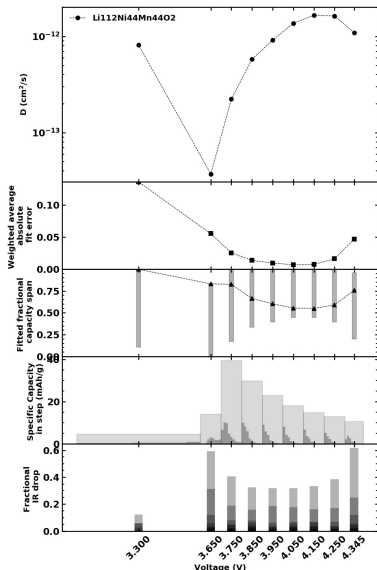
AMID: How-to, EZ

D(V): fits
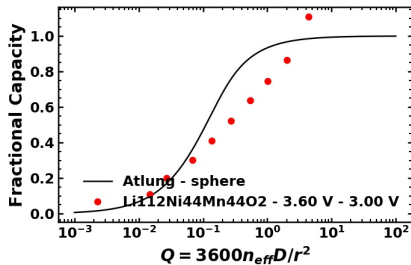
Once D and c_{max} are fit, we can plot the measured data on top of the theoretical $\tau^*(Q)$ curve to get a visual of fit quality.

The weight of each rate in the fit is scaled by the magnitude of the IR contribution to V.

D(V): fit quality

- Average fit error
  $= \sum_{i=1}^{n_{rates}} IR_i^{norm}|\tau_i - \tau_{Atlung}|$
- Capacity span: which portion of the theoritical curve is covered by the fitted data.
  Length of grey bar $\rightarrow$ black triangle
- Specific capacities: light grey bars give cumulative capacity achieved in each voltage interval; dark grey bars gives additional capacity achieved at each rate. The sum of the dark grey bars give the height of their respective light grey bar.
- IR drop: Sequentially darker shades correspond to sequentially lower rates. Lightest shade $\rightarrow$ highest rate. Computed by dividing IR for a particular rate by the size of the voltage interval.
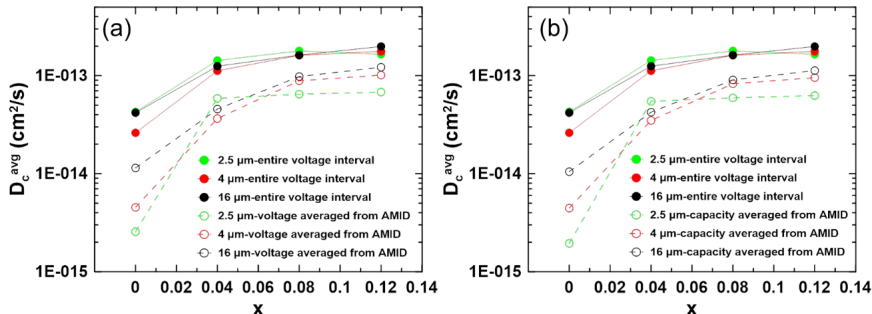
Particle size
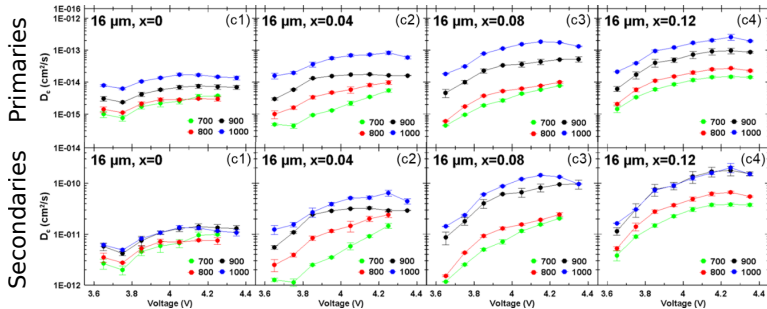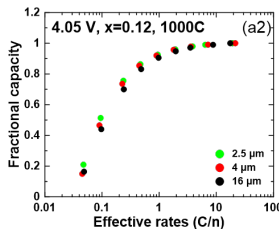
Particle shape

SC-LiNi$_{0.975}$Mg$_{0.025}$O$_2$
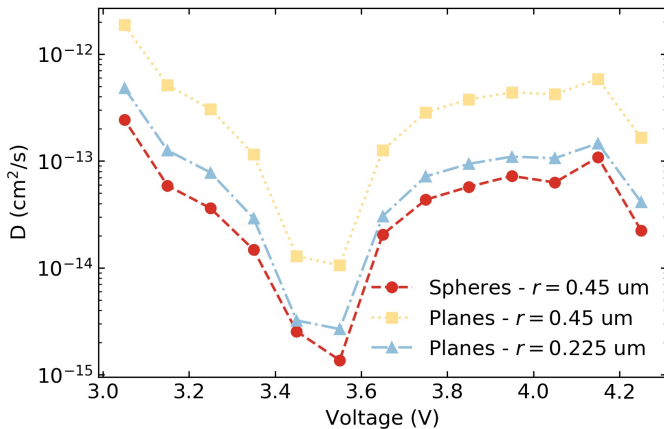
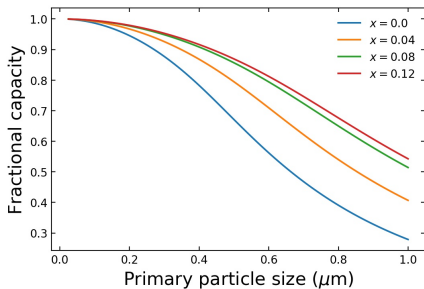# How to obtain D for full V range?

Recall: solution to couple PDEs assume D was constant.
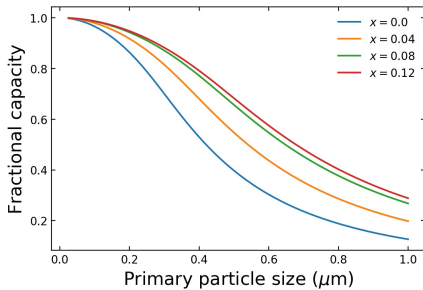Provided modest IR, I trust D(V) data more than full range D.

AMID tells us the positive electrode rate capability
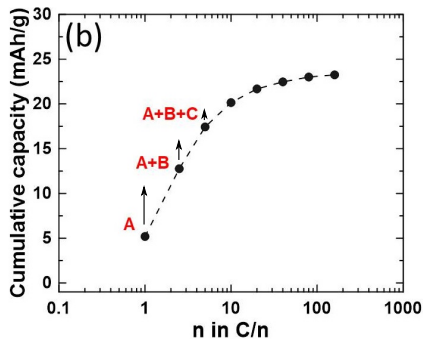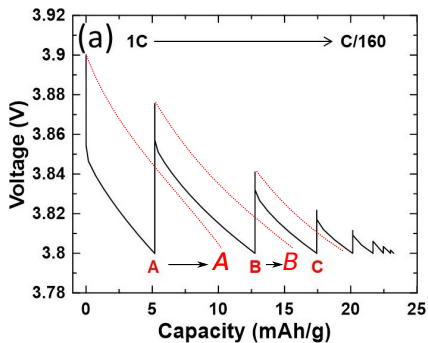

$Li_{1+x}(Ni_{0.5}Mn_{0.5})_{1-x}O_2$

Assuming no other kinetic limitations in the cell (i.e., electrolyte)

Can we correct for IR?

Install AMID API and Jupyter Notebook

- Install Python through Anaconda:
  https://www.anaconda.com/products/individual
- Install spyder-notebook. In Windows search bar type "Conda prompt". Then run "conda install spyder-notebook".
- Create folder ".matplotlib\stylelib" (if it does not exist already) in your home directory.
  On Windows: "C:\\Users\user_name\"
- Copy grapher.mplstyle from "dahn-share\marc cormier\amid-api\" into the ".matplotlib\stylelib\" folder.
- Copy "amid.py" and "amid-analysis.ipynb" into the same folder, wherever you like on your computer.
- Open Spyder. If you don't see a "Notebook" tab, select View→panes→Notebook.
- Use the small gear wheel in the top right of the Notebook panel to open amid-analysis.ipynb