

# Atlung Method for Intercalant Diffusion — AMID

Marc M. E. Cormier

Dalhousie University

*marc.cormier@dal.ca*

June 21, 2021

# Theory of Diffusion

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

- A continuum theory:  $\nabla$  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

→  $z = 1$ : surface,  $z = 0$ : center.

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

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

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

Table 1. Constants and functions in Eq. [6]

Shape	$a$	$b$	$C(\alpha z)$	$g(\alpha)$	$\alpha_1$	$\alpha_2$	$\alpha_3$
Plane sheet	1	1/6	$\cos \alpha z / \cos \alpha$	$\sin \alpha$	$\pi$	$2\pi$	$3\pi$
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
<b>A</b>	<b>1</b>	<b>2</b>	<b>3</b>
<b>B</b>	<b>3</b>	<b>4</b>	<b>5</b>

## What about the $\alpha_i$ 's?

From Table 1, the generating functions are:

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

$\alpha_i$  are the roots of the generating equations  $\rightarrow g(\alpha_i) = 0$

There are infinitely many solutions for each shape! For spheres,

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

# Everyone has seen, but where does it come from?

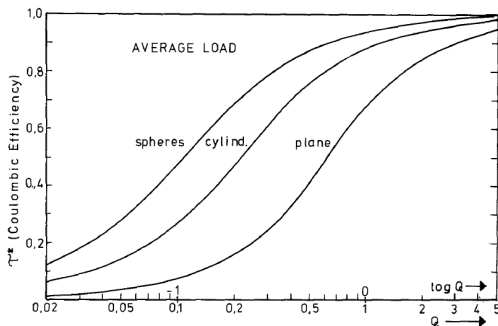


Fig. 4. Cathode efficiency (cathode utilization at  $X^* = 1$ ) as function of  $\log Q$ . Average load with no peak loading. Particle shape indicated on graphs.

$\tau^*$  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)

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

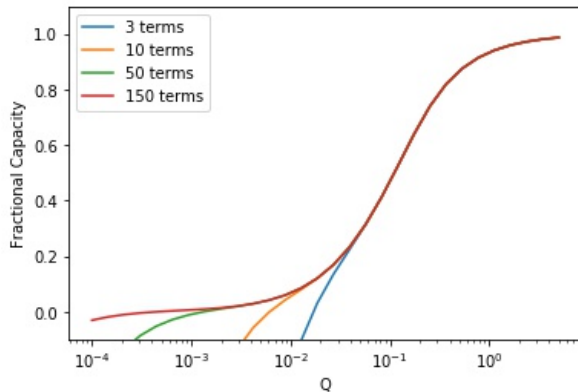
is an *implicit* equation of  $\tau^*$  and  $Q$ . There is no analytical solution, must be solved numerically to get:

$$\tau^*(Q)$$

The result is sensitive to the number of  $\alpha_i$ 's included 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  $C/n$ .

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

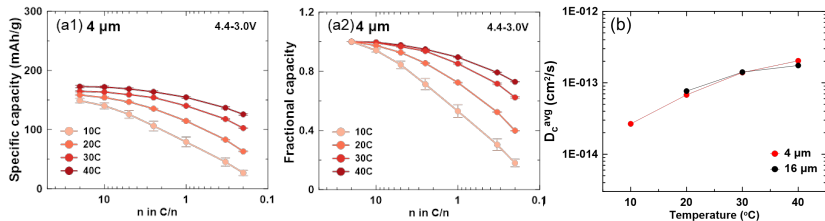
$$\therefore \tau^* + \frac{r^2}{3600nDA} \left[ \frac{1}{B} - 2 \sum_i \frac{\exp(-3600nD\alpha_i^2\tau^*/r^2)}{\alpha_i^2} \right] = 1$$

If the particle size,  $r$ , is known, then this equation relates the fractional capacity,  $\tau^*$  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

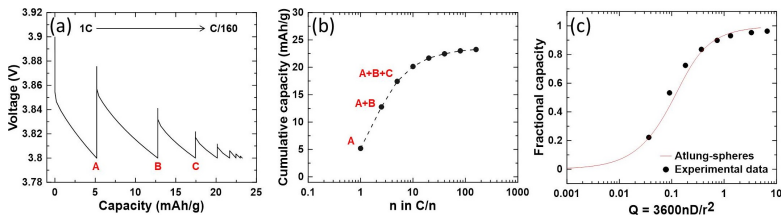


In this case, we can extract  $D$  as a function of  $T$  (temperature); each curve can be fit to the equation on the previous slide.

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



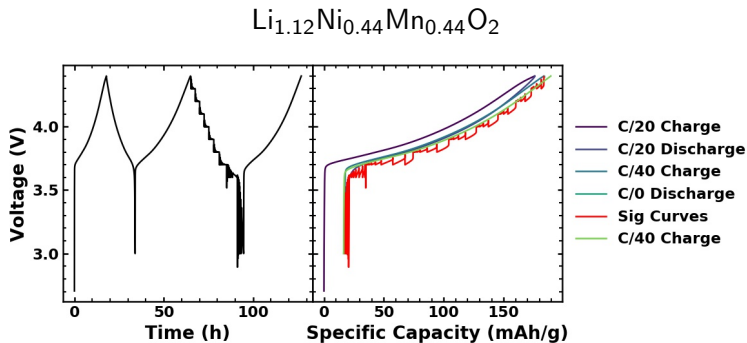
Signature curve: sequential (dis)charge at lower and lower rates with OCV in between.

- 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.

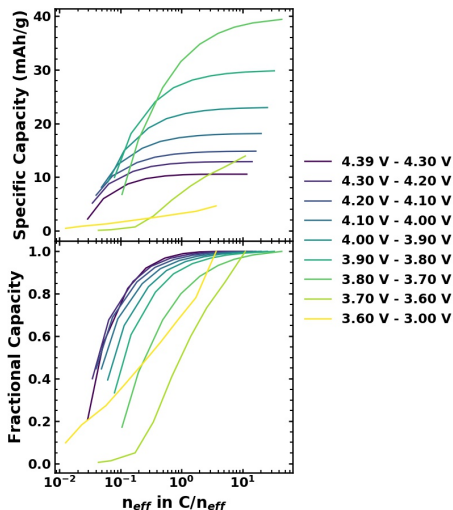
KH paper, A.L., N.P.

## D(V): advanced signature curve protocol



- 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

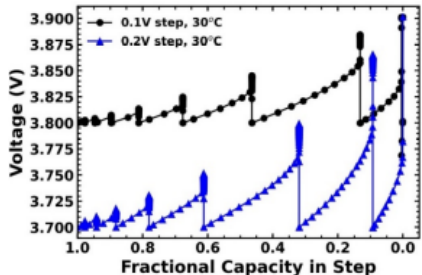
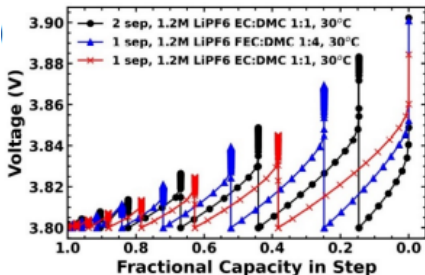


What is the (dis)charge time for an arbitrary voltage interval?

Since the capacity within each voltage interval is not known *a priori*, currents input in the protocol 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

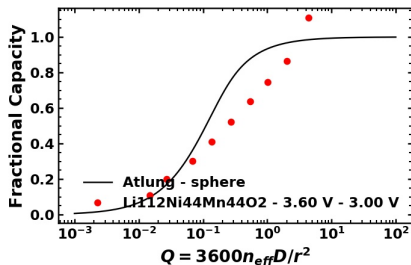


- Coin cells for diffusion measurement must be constructed to minimize IR contributions to V.
- Larger V intervals can help, but remember that  $D$  is supposed to be constant.

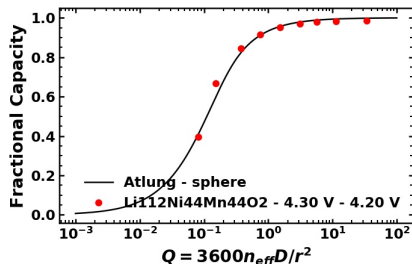
AMID: How-to, EZ

## D(V): fits

A bad fit



A good fit

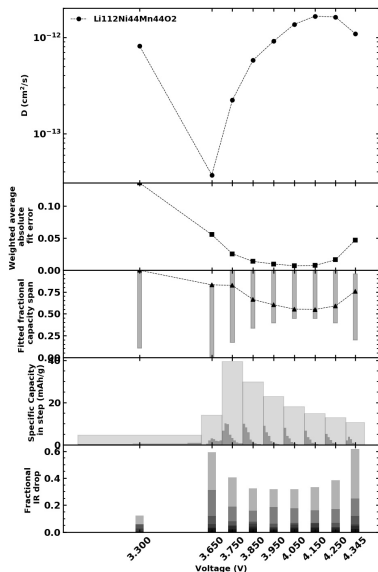


Once  $D$  and  $c_{\text{max}}$  are fit, we can plot the measured data on top of the theoretical  $\tau^*(Q)$  curve to get a visual of fit quality.

Note that here  $n$  is actually  $n_{\text{eff}}$ .



# D(V): fit quality



- Average fit error  

$$= \sum_{i=1}^{n_{\text{rates}}} IR_i^{\text{norm}} |\tau_i - \tau_{\text{Atlung}}|$$