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2 **AMIDR: A Complete Pulse Method for Measuring Cathode Solid-State Diffusivity**

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Abstract

The Atlung Method for Intercalant Diffusion and Resistance (AMIDR) is a novel, high accuracy method for measuring solid state diffusivity and interface resistance related to the Atlung Method for Intercalant Diffusion (AMID) with several key differences. Most notably, AMIDR is designed to analyze the voltage response over time of “complete” pulses, pulses that last until an impedance steady state is reached. These differences allow for AMIDR to return diffusivity results with a higher degree of confidence than Galvanostatic Intermittent Titration Technique (GITT) and at a faster rate with higher state of charge (SOC) resolution than Electrochemical Impedance Spectroscopy (EIS). In this study, three different lithium transition metal oxides were studied. These active materials showed very similar kinetic behaviour that varied with dependence on the fraction of Ni atoms filling sites in the Li layer. AMIDR comes with a user-friendly python program complete with a user interface that is intended to assist other researchers in measuring active material diffusivity in a controlled, repeatable manner. This program, along with instruction on its use, the results of this study from raw data to the final key kinetic metrics, and a video summary of AMIDR design are available for download at <https://github.com/MitchBall/AMIDR>.

Introduction

When a current is applied to a Li-ion cell, lithium ions are transported from the electrolyte to the surface of an active material or vice versa at a certain flux. Transport within the active material from the surface to the interior and vice versa relies on solid-state diffusion. This diffusion is driven by lithium concentration gradients transporting lithium from high concentration locations to low concentration locations in the active material. Diffusion shrinks these concentration gradients over time encouraging uniform concentration throughout an active material particle. However, when a current is applied, transport between the active material and the electrolyte also occurs and concentration changes at the particle surface encourage non-uniformity. As solid-state diffusion is not often infinitely fast compared to the surface flux, this can lead to significantly low or high concentrations at the active material particle surface compared to the interior. The potential of an electrode particle is dependent upon the concentration of lithium at its surface, and therefore poor diffusion can lead to undesirably high or low potentials during charge or discharge, respectively. This change in potential from an ideal case where solid-state transport is infinitely fast is often regarded as an overpotential. This overpotential, as well as overpotential from resistance, can be the source of lost energy. Diffusion overpotential stores energy in the concentration gradient of the active material which is later expelled as heat when diffusion occurs whereas resistance overpotential is just simply expelled as heat immediately. Additionally, these overpotentials may cause the cell voltage limit to be reached prematurely, effectively limiting the capacity of an active material. It is essential that cell voltage limits are not surpassed as potentials that are too high or low can cause degradation at the surface of the active material even though the interior is at a safer potential.

Solid-state diffusion occurs at both electrodes in most Li-ion or similar cells with the exception being lithium metal cells where lithium is deposited on the surface of a lithium metal electrode and does need to be transported further. This study focuses on accurately measuring the lithium diffusivity in lithium nickel manganese cobalt (NMC) layered oxide cathode active materials which are commonly spherically shaped and have kinetically hindered capacities. However, the methods used here may be applied to other active materials, both cathode and anode, and even other transport ions such as Na^+ or K^+ , with appropriate modification.

Theory

Impact of Geometry on Diffusion Transport

Particle shape is important to consider when measuring impedance from diffusion. A change in concentration is first created at the surface and this encourages changes in concentration further and further within the active material as time goes on. Figure 1 shows common geometries for modeling diffusion.

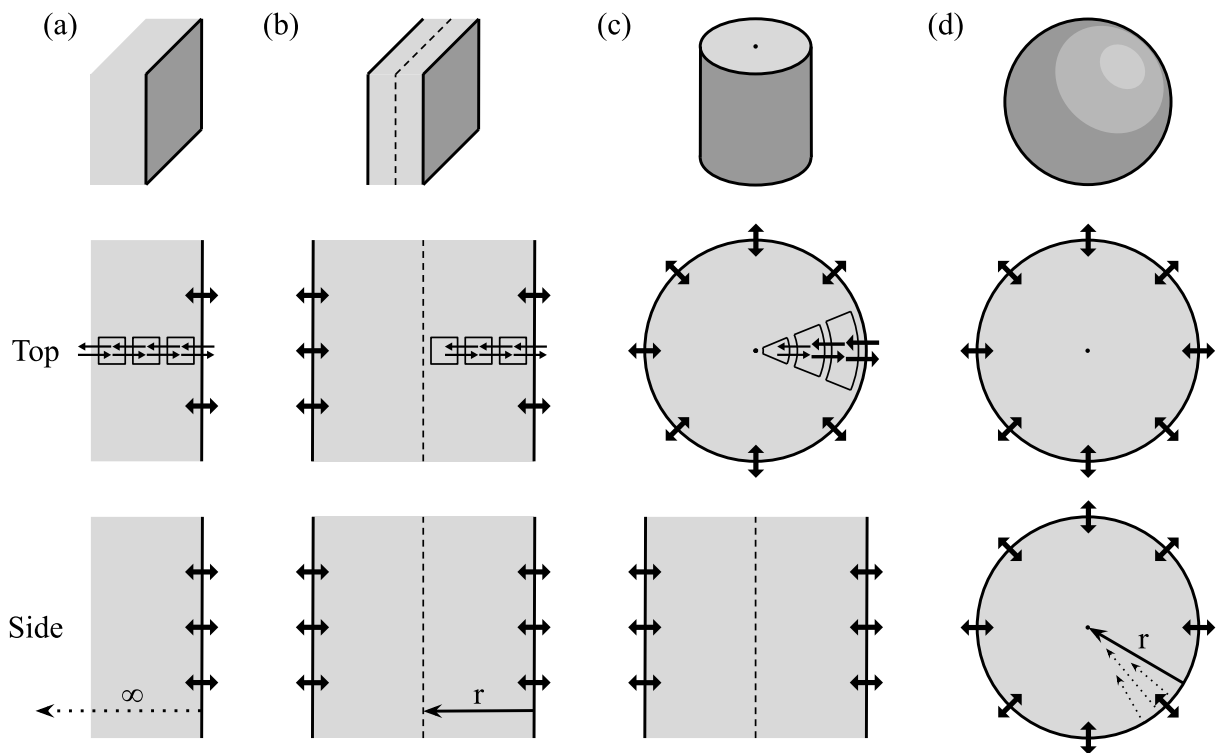


Figure 1: Simplified geometries for modeling diffusion. The given geometries are (a) semi-infinite plane, (b) planar sheet, (c) cylinder, and (d) sphere.

The simplest model is the semi-infinite plane (Figure 1a), a volume that is infinite in all directions except the surface in contact with electrolyte. This is the easiest geometry to model, but in practice, diffusion cannot continue infinitely. Ions transported from the electrolyte will eventually arrive at a position furthest into the interior of the active material and transport cannot occur further beyond this position. The distance from the electrolyte contacting surface to the furthest interior position is the diffusion length or radius (cm), r , for circular geometries. The planar sheet (Figure 1b) is similar to the semi-infinite plane but instead has two electrolyte contacting surfaces and a central plane forming the furthest interior position. The planar sheet can also be used to model a volume with one electrolyte contacting surface and one non-contacting surface by splitting the geometry in half along the central plane. When ions eventually

stop at the end of r , this slows diffusion transport along the diffusion path which causes a greater change in concentration at the electrolyte contacting surface compared to a semi-infinite plane.

The shape of the active material may cause ions to transport inwards from a larger volume to a smaller volume or vice versa. This is the case for the cylindrical and spherical models (Figure 1c-d) which have some radial rather than linear geometry. This will also similarly slow diffusion transport and cause a greater change in concentration at the surface than in a planar sheet or an ideal semi-infinite plane.¹

In practice, all active materials have finite volumes. While only the sphere is truly finite, all geometries can be used to approximate more complex finite geometries. The planar sheet and sphere mark the maximum and minimum bounds for the volume to surface area ratio (cm), \tilde{V}/S , of all geometries with a fixed r . As a result, the planar sheet and sphere also mark the maximum and minimum bounds of diffusion hindrance for geometries with a fixed r .

Surface Concentration due to Diffusion Transport

The interplay between transport at the active material surface induced by an applied current and transport within the active material determines the surface concentration. Conveniently, it has been shown that all real morphologies will approximate a semi-infinite plane at the start of a constant flux or constant current (CC) pulse applied to a “relaxed” active material, active material starting with a uniform concentration. This is because the start of a pulse only meaningfully changes concentrations within a very thin layer near the surface which can easily be approximated as a semi-infinite plane. The solution to the change in surface concentration (mol cm^{-3}), Δc_s , of semi-infinite plane experiencing a CC pulse starting from a uniform concentration has been proven to be

$$\Delta c_s(t) = \frac{2J\sqrt{\Delta t}}{\sqrt{\pi D_c}}, \quad (1)$$

where $J = Iz^{-1}F^{-1}S^{-1}$ is the ionic flux ($\text{mol s}^{-1} \text{cm}^{-2}$), Δt is the period (s) of pulse time, and D_c is chemical diffusivity ($\text{cm}^2 \text{s}^{-1}$), the material property of interest when determining the speed of ion diffusion.² I is the current (A) being applied, z is the ion charge number (+1 for lithium), F is Faraday's Constant (C mol^{-1}), and S is the surface area (cm^2) exposed to electrolyte. This equation is likely familiar to anyone with experience using the Galvanostatic Intermittent Titration Technique (GITT). It can be helpful to normalize this equation into dimensionless variables which produces

$$X_s(\tau) = \frac{2\sqrt{\tau}}{A\sqrt{\pi Q}}, \quad (2)$$

where $X_s = \Delta c_s / \Delta c_{tot}$ is the relative change in surface concentration, $\tau = \Delta q / \Delta q_{tot}$ is the relative change in capacity, $Q = \Delta q_{tot} I^{-1} D_c r^{-2}$ is the relative diffusivity, a normalized measure of how fast diffusion transport is compared to the surface flux, and A is a geometric constant sourced from the inverse \tilde{V}/S for certain geometries (1 for a planar sheet, 2 for a cylinder, 3 for a sphere). $\Delta c_{tot} = n_{tot} / \tilde{V}$ is the change in concentration if an arbitrary, desired n_{tot} number of moles (mol) of ions are transported and uniformly dispersed in a volume (cm^3), \tilde{V} , of an active material. $\Delta q_{tot} = zFn_{tot}$ is the arbitrary capacity (C) associated with n_{tot} , and $\Delta q = zFn = I\Delta t$ is the actual capacity acquired after a certain Δt where n moles are transported. τ can also be treated as relative moles transported or relative pulse time given that Δq is proportional to n and Δt when I is constant. One of the advantages of using dimensionless convention is that it

119 normalizes the variables and describes pulses of all I and active materials of all D_c and r
 120 simultaneously as long as the active material geometry is the same.

121 After the start of a pulse, modelling X_s gets more complicated. The numerical solution for
 122 X_s of active material during a pulse starting from a relaxed state has been shown to be

$$123 \quad X_s(\tau) = \tau + \frac{1}{AQ} \left(\frac{1}{B} - 2 \sum_{i=1}^{\infty} \frac{e^{-\alpha_i^2 Q \tau}}{\alpha_i^2} \right), \quad (3)$$

124 where the series α_i is defined for each geometry as

$$125 \quad \text{Planar Sheet:} \quad \sin(\alpha) = 0,$$

$$126 \quad \text{Cylinder:} \quad J_1(\alpha) = 0,$$

$$127 \quad \text{Sphere:} \quad \alpha \cot(\alpha) - 1 = 0,$$

128 B is another geometric constant (3 for a planar sheet, 4 for a cylinder, 5 for a sphere), and J_1 is
 129 the Bessel function of the first kind of order 1. This dimensionless convention and the complete
 130 equation for describing X_s resulting from diffusion transport was developed by Atlung, the
 131 namesake of AMID and AMIDR.¹ It's unfortunate that the solution to equation 3 must be
 132 numerical rather than analytical, but it is at least far simpler than more opaque numerical
 133 solutions from techniques such as the Finite Element Method (FEM).

134 Despite being numerical, equation 3 will often approximate analytical solutions.

135 $\lim_{Q \rightarrow \infty^+} X_s(\tau) = \tau$, showing that if D_c is infinitely fast, the concentration, c , in the active material
 136 is uniform and c_s has a linear relationship with Δq . This scenario is ideal as this means that no
 137 energy will be lost, and the active material can be considered impedance-free. While not

obvious, it has been shown that $\lim_{\tau \rightarrow 0^+} X_s(\tau)$ is equation 2, proving that all geometries approximate a semi-infinite plane at pulse start.² In addition,

$$\lim_{\tau \rightarrow \infty^+} X_s(\tau) = \tau + \frac{1}{ABQ}. \quad (4)$$

This shows that as Δq approaches Δq_{tot} , the active material eventually reaches a steady state where X_s approaches a linear relationship with τ , and c_s approaches a linear relationship with Δq . Once this steady state is reached, the pulse can be described as a “complete” pulse that has reached its “end”. Using this terminology, a pulse that has been stopped before a steady state has been reached is said to have been stopped before it has reached its end.

Figure 2 shows that the simple analytical equations 2 and 4 form the lower and upper bounds for the otherwise more complex numerical equation 3. While the sphere has the most diffusion limitation from shrinking volumes along the diffusion path and most quickly deviates from equation 2, it is the ideal geometry for minimizing X_s deviation from the impedance-free scenario due to its decreased \tilde{V}/S . The difference between $Q = 0.5$ (Figure 2a) and $Q = 2$ (Figure 2b) shows that larger Q is more desirable to limit X_s deviation from the impedance-free scenario. Lastly, Figures 2a and b have the same shape, but different size. These two graphs could be describing the same pulses, just with a different n_{tot} desired moles of ions to be transported.

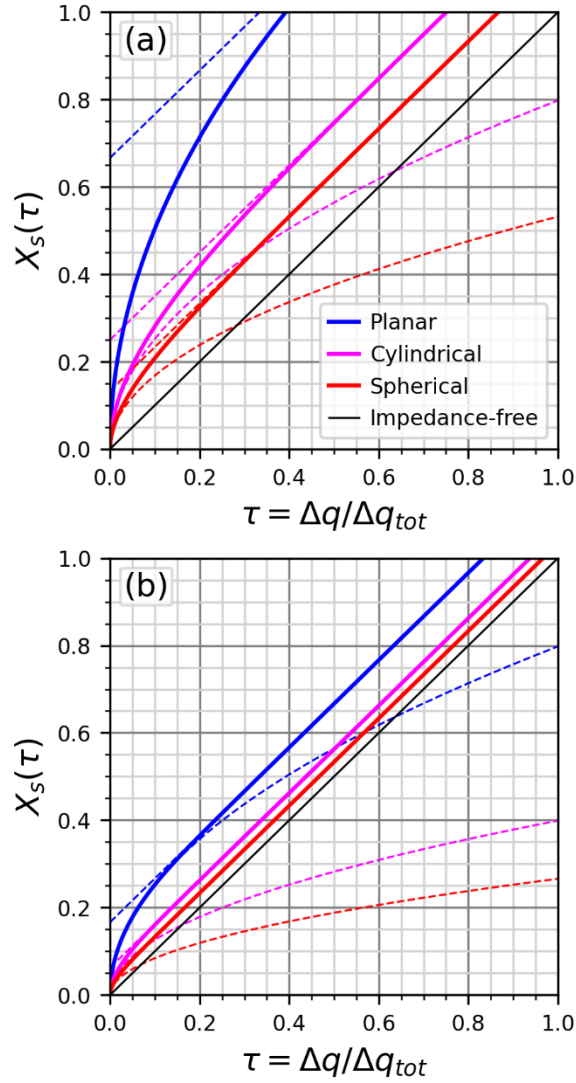


Figure 2: The relationships between relative change in capacity, τ , and relative change in surface concentration, X_s , of planar, cylindrical, and spherical active material during a short pulse when relative diffusivity, (a) $Q = 0.5$ and (b) $Q = 2$. These relationships are compared to the ideal, impedance-free relationship when $Q \rightarrow \infty^+$. The linear and inverse quadratic dashed lines, where visible, represent the lower and upper limits for X_s as τ approaches 0 and 1.

Capacity Limitation due to Diffusion Transport

Poor diffusion can cause the Δc_s to reach a certain limit defined by a voltage limit stopping a pulse before significant utilization of the interior of the active material. This is because the potential of the active material is determined by c_s . This limit can be defined as

165 when $\Delta c_s = \Delta c_{tot}$ and in dimensionless convention, defined as when $X_s(\tau) = 1$. Inserting this
 166 into equation 3 gives

$$167 \quad 1 = \tau + \frac{1}{AQ} \left(\frac{1}{B} - 2 \sum_{i=1}^{\infty} \frac{e^{-\alpha_i^2 Q \tau}}{\alpha_i^2} \right), \quad (5)$$

168 which gives a relationship between Q and τ for when this limit is reached. In the same manner as
 169 equations 2 and 4, this relationship can be given the bounds

$$170 \quad 1 = \frac{2\sqrt{\tau}}{A\sqrt{\pi Q}}, \text{ and} \quad (6)$$

$$171 \quad 1 = \tau + \frac{1}{ABQ}. \quad (7)$$

172 Figure 3 shows this relationship and its bounds. When Q is significantly small, the
 173 relationship approaches equation 6 for when τ is small and the limit is reached near the start of
 174 the pulse before a steady state is approached. This is undesirable as a small τ means far less than
 175 the desired n_{tot} moles of ions were transported. Alternatively, when Q is significantly large, the
 176 relationship approaches equation 7 for when τ is large and the limit is reached near the end of the
 177 pulse when the active material has reached a steady state. In this case, nearly all the desired n_{tot}
 178 moles of ions are transported.

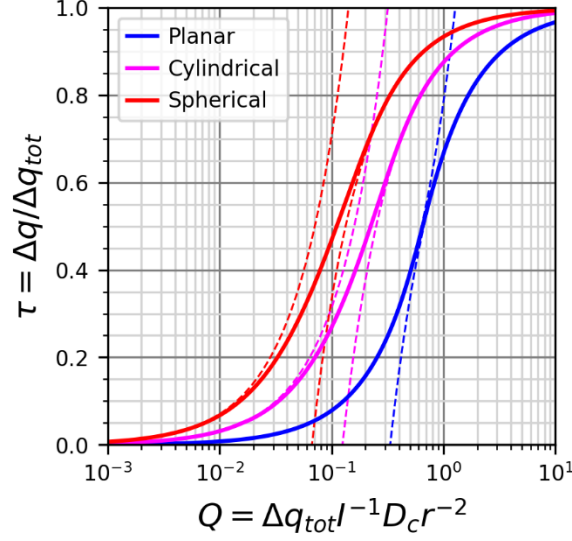


Figure 3: The relationship between relative diffusivity, Q , and relative change in capacity, τ , of planar sheet, cylindrical, and spherical active materials when a relative surface concentration limit is reached, $X_s = 1$, and a pulse is stopped. The exponential dashed lines represent the upper and lower limits for τ as τ approaches 0 and 1.

Impedance due to Diffusion Transport

In an ideal, impedance-free scenario, the concentration throughout the active material is uniform and the ideal X_s , $X_{s,ideal}$, increases from 0 to 1 equivalently with τ as shown in Figure 2 ($X_{s,ideal} = \tau$). The difference between X_s and $X_{s,ideal}$ can be defined as $X_{s,loss} = X_s - X_{s,ideal}$. $X_{s,loss}$ can also be calculated by simply subtracting τ from equation 3 to get

$$X_{s,loss}(\tau) = \frac{1}{AQ} \left(\frac{1}{B} - 2 \sum_{i=1}^{\infty} \frac{e^{-\alpha_i^2 Q \tau}}{\alpha_i^2} \right). \quad (8)$$

Next, this can be converted out of dimension-less convention to get

$$\Delta c_{s,loss}(\Delta t) = \frac{I r^2}{A z F \tilde{V} D_c} \left(\frac{1}{B} - 2 \sum_{i=1}^{\infty} \frac{e^{-\alpha_i^2 \frac{\Delta t D_c}{r^2}}}{\alpha_i^2} \right). \quad (9)$$

where $\Delta c_{s,loss}$ is the non-relative difference in surface concentration from an ideal impedance-free scenario. The surface concentration, c_s , of an active material determines its potential (V), E , so $\Delta c_{s,loss}$ implies a difference in E from an ideal, impedance free scenario. The relationship between c_s and E for any active material is complex but can be simplified to a simple linear relationship ($V \text{ cm}^3 \text{ mol}^{-1}$), dE/dc , if the E range is small enough. Accordingly, $c_{s,loss}$ can be converted into a diffusion overpotential (V), η_D , for a working electrode as

$$\eta_D(\Delta t) = -\frac{dE}{dc} \frac{Ir^2}{AzF\tilde{V}D_c} \left(\frac{1}{B} - 2 \sum_{i=1}^{\infty} \frac{e^{-\alpha_i^2 \frac{\Delta t D_c}{r^2}}}{\alpha_i^2} \right). \quad (10)$$

where positive I is now treated as current driving positive ions to leave the active material, the typical convention for working electrodes. dE/dc is not a commonly used metric in cell analysis but differential capacity (C/V), dq/dV is. $q = zF\tilde{V}(c_{sat} - c)$ is the capacity of charge stored in the active material of the working electrode where c_{sat} is the fully saturated concentration corresponding to no charge being stored. $V = E_w - E_c$ is the total voltage (V) of a cell where E_w is the potential of the working electrode and E_c is the potential of the counter electrode. This study uses a half cell arrangement where the counter electrode is lithium metal and will treat $E_c = 0 \text{ V vs. } Li^+/Li^0$. Therefore $dq/dV = -zF\tilde{V}dc/dE$. With this, equation 10 can be further simplified to

$$\eta_D(\Delta t) = \frac{Ir^2}{AD_c \frac{dq}{dV}} \left(\frac{1}{B} - 2 \sum_{i=1}^{\infty} \frac{e^{-\alpha_i^2 \frac{\Delta t D_c}{r^2}}}{\alpha_i^2} \right). \quad (11)$$

The relationship between Δt and η_D retains the same shape as the relationship between τ and X_s shown in Figure 2. Conveniently, related to equation 4, after a long period of time, equation 11 can be simplified to

$$\lim_{\Delta t \rightarrow \infty^+} \eta_D(\Delta t) = \frac{Ir^2}{ABD_c \frac{dq}{dV}}. \quad (12)$$

Even more conveniently, this can be further simplified as

$$R_{D,term} = \frac{r^2}{ABD_c \frac{dq}{dV}}, \quad (13)$$

where $R_{D,term}$ is the terminal diffusive resistance (Ω) given that $V = IR$. This is particularly powerful as this means that the impedance related to diffusion can be approximated as a simple resistance given a long enough period of time. This has a very practical application as it can be used to predict voltage polarization for long, CC charges/discharges or the maximum voltage polarization for intermittent pulses.

Combining Diffusion Impedance and Resistance

Diffusion is not the only source of impedance in a cell. Impedance can come from a variety of sources from electrical resistance in the current collectors and the conductive additive to ionic impedance in the electrolyte, both in and outside of the electrode pores, and reaction impedance at the electrode-electrolyte interfaces. In addition, many of these impedance sources are paired with capacitances such as double layer capacitance at the electrode-electrolyte interfaces, and parallel plate capacitance across the two electrodes within coin cells. The impedance of the opposing electrode can be ignored if using a reference electrode and the

electrolyte impedance inside electrode pores can be mitigated by coating thin electrodes. Thin electrodes amplify active material impedances by reducing the total amount of active material, similar to how thin wires produce more resistance. These impedances are diffusion impedance, which is dynamic on long timescales (> 1 s), and interface resistance, R_i , which is effectively instantaneous on long timescales. Remaining sources of impedance are mostly negligible resistances, R_{ohm} , electrical contact resistance and ionic electrolyte resistance, which are also effectively instantaneous on long timescales. Also included is ionic electrolyte diffusion impedance which can be dynamic over long timescales with significantly thick separators, but is effectively instantaneous with standard, commercial thin separators.³ Therefore, these can simply be treated as a single resistance, $R = R_i + R_{ohm}$, producing a resistive overpotential, $\eta_R = IR$.

In practice, η_R can limit Δq further than η_D alone by allowing a voltage limit to be reached earlier than when $X_s(\tau) = 1$. In this case, the limit can be said to be reached when relative change in voltage, $Y(\tau) = 1$. $Y(\tau) = (\Delta V_i(\Delta t) + \eta_D(\Delta t) + \eta_R)/\Delta V_{tot}$, where $\Delta V_i(\Delta t) = \Delta q(dq/dV)^{-1}$ is the ideal, impedance-free change in voltage after a certain period of pulse time, and $\Delta V_{tot} = \Delta q_{tot}(dq/dV)^{-1}$ is the total change in voltage from the initial voltage to the voltage limit. Evaluating this equation returns

$$Y(\tau) = \tau + \frac{1}{AQ} \left(\frac{1}{B} - 2 \sum_{i=1}^{\infty} \frac{e^{-\alpha_i^2 Q \tau}}{\alpha_i^2} \right) + \frac{IR(dq/dV)}{\Delta q_{tot}}. \quad (14)$$

This equation is very similar to equation 3 except for the inclusion of a new term at the end. This new term can be converted into dimensionless units as

$$Y(\tau) = \tau + \frac{1}{AQ} \left(\frac{1}{B} - 2 \sum_{i=1}^{\infty} \frac{e^{-\alpha_i^2 Q \tau}}{\alpha_i^2} \right) + \frac{P}{Q}, \quad (15)$$

248 where $P = RD_c r^{-2}(dq/dV)$ is the relative resistance, a variable comparing η_R to η_D , similar to a
 249 Biot number. When $P \ll 1/AB$, Δq is primarily limited by η_D , and the last term can be neglected
 250 to simplify the entire equation back to equation 3. However, when $P \gg 1/AB$, the last term is
 251 large, and Δq is primarily limited by η_R rather than η_D . Setting $Y(\tau) = 1$ gives the relationship
 252 between Q and τ for when a voltage limit is reached,

$$253 \quad 1 = \tau + \frac{1}{AQ} \left(\frac{1}{B} - 2 \sum_{i=1}^{\infty} \frac{e^{-\alpha_i^2 Q \tau}}{\alpha_i^2} \right) + \frac{P}{Q}, \quad (16)$$

254 similar to equation 5 except with the addition of the last term.

255 Figure 4a shows the relationship posed by equation 15 and Figure 4b shows the
 256 relationship posed by equation 16. Increasing P increases η_R and reduces the proportion of τ
 257 capable of being transported before a voltage limit is reached. Additionally, Figure 4b shows that
 258 increasing P changes the relationship between Q and τ from a pseudo-logistic shape to a pseudo-
 259 exponential shape. While the shape of the curve changes significantly with small τ , the shape of
 260 the curve remains the same at large τ . This is because η_D approximates η_R when τ is large and
 261 the difference between η_D and η_R become indistinguishable without information from earlier in
 262 the pulse.

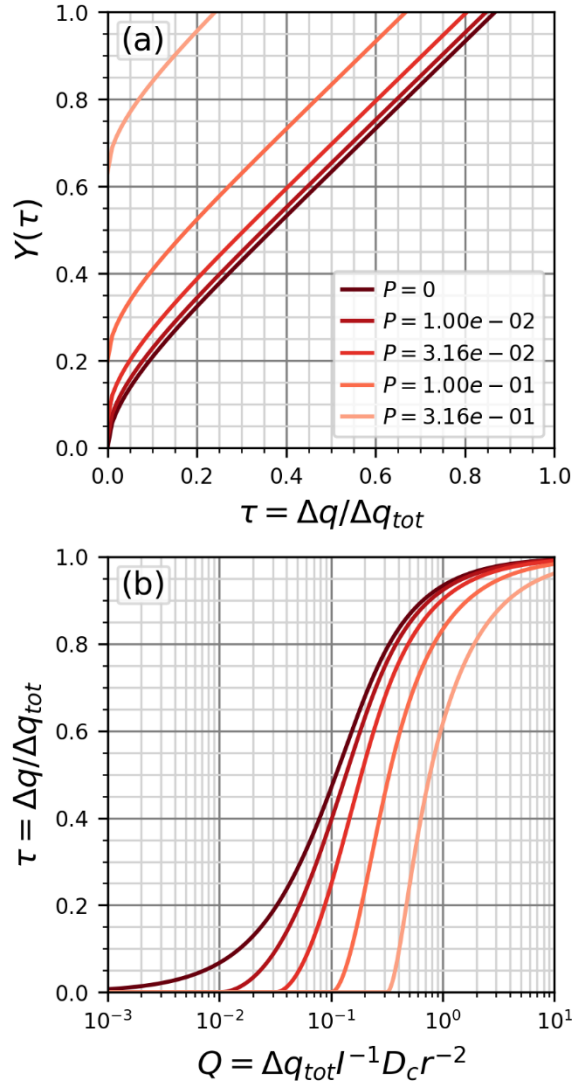


Figure 4: The relationship (a) between relative change in capacity, τ , and relative change in voltage, Y , of a cell during a short pulse when relative diffusivity, $Q = 1$ and the relationship (b) between τ and Q , when a voltage limit is reached, $Y = 1$. The active material is given a spherical geometry and relative resistance, P , is varied to show the impact of resistance.

Impact of Diffusion Length Variation due to a Particle Size Distribution

The mathematical model for impedance resulting from diffusion is designed for a single geometry but can easily be scaled up for an ensemble of geometries of identical r keeping in mind that I , q , n , and \tilde{V} should represent the total values for the entire ensemble. However, in practice, geometries such as active material particles often have a measurable variation in r . This

presents a problem because ensembles of geometries with varying r do not experience constant flux throughout a pulse which is essential for this model. While flux is equal for all geometries at the start of a pulse, flux at the end of the pulse is proportional to the \tilde{V}/S of a geometry because the I of each geometry is proportional to its q and therefore \tilde{V} . This means larger particles increase in flux and smaller geometries decrease in flux throughout the pulse. Despite not being able to develop a complete, simple mathematical model for the impedance of a pulse upon active material with a distribution in r , the bounds for pulses that stop near their start and end with active material of varying r can be calculated. These bounds are simply the original equations 6 and 7 with different average r values, \bar{r} , as inputs. These \bar{r} are calculated as $\bar{r}_s = \sum r_j^3 / \sum r_j^2$ and $\bar{r}_e = (\sum r_j^5 / \sum r_j^3)^{1/2}$ for the start and end of a pulse respectively, where r_j is r for an individual geometry (see Proofs S1 and S2). Figure 5 shows the impact of a theoretical bimodal active material on the relationship between Q and τ . The theoretical bimodal active material used in this model is composed of spheres of r equal to 1 arb. units and 3 arb. units in a 1:1 q ratio. The r used to calculate Q for this bimodal active material is calculated as the capacity-weighted geometric mean as $\bar{r} = 10^{\frac{\sum \log r_j * r_j^3}{\sum r_j^3}}$. The multiplicative change in Q between the uniform and bimodal model can be regarded as a Q -shift calculated as $(\bar{r}_s/\bar{r})^2$ or $(\bar{r}_e/\bar{r})^2$. While the complete model for bimodal active material cannot be plotted, it is clear that it would not differ from a uniform r active material by a dramatic amount. All active materials analyzed in this study have less particle size variation than this theoretical model, so while particle size variation may add some error to the model, the model is still reasonably accurate (see Table S1).

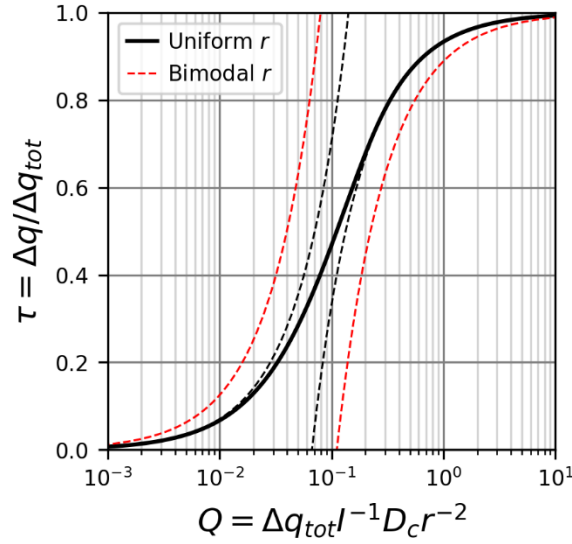


Figure 5: The relationship between relative diffusivity, Q , and relative change in capacity, τ , for uniform and bimodal spherical active materials when a surface concentration limit is reached, $X_s = 1$, and a pulse is stopped. The bimodal active material is composed of spheres of radius 1 arb. units and 3 arb. units in a 1:1 capacity ratio. The diffusion length, r , for the bimodal active material is calculated as the capacity-weighted geometric mean. The dashed lines represent the upper and lower limits for τ as τ approaches 0 and 1.

Interface Contact Resistivity

While not all resistance in a cell is sourced from the electrode-electrolyte interface, an overwhelming portion can be, especially in cells designed with little active material mass loading. If it is believed that the overwhelming majority of measured R is R_i , then that R_i can be normalized as contact resistivity ($\Omega \text{ cm}^2$), $\rho_c = R_i S$. This describes the resistivity of current traveling through a film of unknown or infinitesimally thin thickness and is separate from bulk resistivity ($\Omega \text{ cm}$), which describes the resistivity of current traveling through a bulk material, and sheet resistance (Ω), which describes the resistivity of current traveling along a film of unknown thickness.⁴ In the context of active material, ρ_c is calculated as

$$\rho_c = SR = \frac{ARm}{r\rho_d}, \quad (17)$$

where m is the mass (g) of the active material and ρ_d is the density (g cm³) of the active material.

Chemical Diffusivity vs. Tracer Diffusivity

While it is common in literature to report lithium diffusion in Li-ion cells as simply “Li diffusivity” there is more than one kind of D measurement and differentiating between them can be valuable for understanding the mechanisms of diffusion. If an isotope of a solute is used as a tracer to track random particle movement in a uniform concentration, tracer diffusivity, D_t is measured. This is different from chemical diffusivity, D_c , which is measured by observing the transport of a solute from a high concentration to a low concentration. These two are the same in dilute concentrations where all solutes have the same atomic environment and diffusion from a high to a low concentration is driven solely by solute particles independently moving at random. However, in concentrated solutions, D_t stays the same, but D_c changes due to solute-solute interactions not present in dilute concentrations. These solute-solute interactions cause solutes to have the different enthalpies at different concentrations and this difference in enthalpy can drive or hinder diffusion from high to low concentrations.

The relation between chemical potential (J mol⁻¹), μ , and c is known to be

$$\mu(c) = \mu_0 + N_A k_B T \ln(\gamma(c)c), \quad (18)$$

where μ_0 is the intrinsic chemical potential (J mol⁻¹), N_A is the Avogadro constant (mol⁻¹), k_B is the Boltzmann constant (J K⁻¹), T is temperature (K), and γ is the activity coefficient. In dilute solutions, γ is constant. In concentrated solutions, solute-solute interactions occur, γ is not constant and the relationship between μ and c is complex. Active materials often have a complex

relationship between μ and c because ions are typically stored in solids as concentrated solutions. This is easily observed in q - V plots of active materials which typically do not show a logarithmic relationship. The solute-solute interactions in active materials often present themselves as changes in occupation site enthalpies due to structural distortions at different c .⁵ The relationship between D_t and D_c is described by Darken's second equation for a single phase medium,

$$D_c(c) = D_t(c) \left(1 + \frac{d \ln(\gamma(c))}{d \ln(c)} \right), \quad (19)$$

where $D_t = D_c$ when γ is constant at dilute concentrations.⁶ This can be converted into an equation with more practical variables. Taking the derivative of equation 18 in terms of c gives

$$\frac{d\mu}{dc} = \frac{N_A k_B T}{c} \left(1 + \frac{d \ln(\gamma(c))}{d \ln(c)} \right), \quad (20)$$

which share the conversion term given in Darken's second equation. Given this, equation 19 can be simplified to

$$D_c(c) = D_t(c) \frac{c}{k_B T} \frac{d\mu}{dc}, \quad (21)$$

and given that $d\mu = -zF dV$, $zF V_m c = (q_{sat} - q)$, and $F = q_e N_A$, where q_{sat} is the theoretical capacity capable of being stored given complete saturation and desaturation and q_e is the elementary charge (C), it can be made to use dq/dV as

$$D_c(q) = D_t(q) \frac{z q_e (q_{sat} - q)}{k_B T \frac{dq}{dV}}. \quad (22)$$

While D_c is the relevant diffusivity measurement for describing ion transport in the active material of a cell under operation, D_t has a relatively simple derivation modeled by a random walk,

$$D_t = \frac{a^2 \left(1 - \frac{c}{c_{sat}}\right) \nu}{2C} e^{-\frac{\Delta G_A}{k_B T}}, \quad (23)$$

where a is the distance between two occupation sites (cm), c_{sat} is the concentration of a completely saturated active material (mol cm⁻³), ν is the vibrational frequency (s⁻¹), C is the dimensionality constant (2 for a layered oxide where ions are able to transport in 2 dimensions), and ΔG_A is the activation energy (J) of an occupation site hop.⁶ The $1 - c/c_{sat}$ term is included to account for the chance that an occupation site hop is blocked by the destination occupation site being already occupied. This term is equivalent to q/q_{sat} . It can be valuable to remove this term to form a new measurement of diffusivity, D_t^* , free-path tracer diffusivity,

$$D_t^* = \frac{a^2 \nu}{2C} e^{-\frac{\Delta G_A}{k_B T}}, \quad (24)$$

which describes diffusion transport for a solute in a uniform c with no occupation sites blocked along its path of travel. This measurement is rather abstract but can be calculated and has powerful implications. The only value in its derivation that is expected to change significantly for an active material at different states of charge is ΔG_A . In this manner, D_t^* can be used as a proxy to measure changes in ΔG_A at different states of charge. If D_t^* stays relatively the same at varying states of charge this suggest that ΔG_A is unchanged, but if D_t^* shrinks significantly, this suggests that ΔG_A has increased significantly. The relationship between D_c and D_t^* is

$$D_c(q) = D_t^*(q) \frac{zq_e q \left(1 - \frac{q}{q_{sat}}\right)}{k_B T \frac{dq}{dV}}. \quad (25)$$

Lastly $R_{D,term}$ can be calculated in terms of site hopping using equations 13, 22, and 23 returning

$$R_{D,term} = \frac{2Ck_B T e^{\frac{\Delta G_A}{k_B T}} r^2}{ABzq_e q \left(1 - \frac{q}{q_{sat}}\right) a^2 \nu}. \quad (26)$$

Prior Methods

Galvanostatic Intermittent Titration Technique (GITT)

GITT is a common single-rate pulse method for measuring D_c . This method is relatively easy to use because the active material is modeled as a semi-infinite plane allowing for the voltage response analysis to be based on equation 1 which is a relatively simple analytical solution. However, active materials of various morphologies only approximate a semi-infinite plane at the very start of a pulse when transport only occurs at the very surface of the particle, so GITT requires the inequality $\Delta t \ll r^2/D_c$ to be true for the approximation to be accurate. Because this inequality relies on D_c , the value whose accuracy is being tested, this inequality must be passed by a very large margin to not suffer from the inequality circularly proving itself. For instance, it has been shown for spherical particles that if $\Delta t D_c / r^2 \approx 0.3$, the measured D_c value will be underestimated by a factor of 10.² Because a user would use the D_c value calculated by GITT to check the inequality, the inequality would be calculated as $\Delta t D_c / r^2 = 0.03$ which an inexperienced user might consider as acceptable.

While this may make it tempting to perform GITT with the shortest pulses possible, this can also be problematic as the other sources of impedance and the capacitive effects are dynamic and relevant on short timescales.² Therefore, accurate GITT measurements must be performed within a certain window of Δt that is not always easy for the user to predict and is very unlikely to be the same at all states of charge of the cell. Additionally, it is possible that under certain conditions, such as when D_c is particularly high or r is particularly small, this window is shrunk out of existence and there is no available Δt that will produce an accurate result.

Electrochemical Impedance Spectroscopy (EIS)

EIS is a common alternating current (AC) method for measuring D_c . A sinusoidal change in voltage (potentiostatic EIS) or current (galvanostatic EIS) at various frequencies is applied to a cell and the alternating current or voltage response is analyzed respectively. The response at various frequencies is calculated into real and imaginary impedance values and can be made to fit various circuit models that include some or all of the various sources of impedance and capacitance. The sources of impedance and capacitance that are dynamic on short timescales impact the response at high frequencies and diffusion, which is typically relevant on long timescales, impacts the response at low frequencies. Because all elements are being fit simultaneously, EIS does not have the same trouble measuring D_c as GITT does when D_c and other impedance sources are relevant at similar timescales.

Diffusion is very often modeled with a semi-infinite plane as the typical frequencies used are not low enough for the concentration beyond the particle surface to be altered meaningfully. While it has been shown that with significantly low enough frequencies, the impact of active material geometry on impedance can be measured and accurately modeled, this isn't common as

low frequencies take longer periods of time to be measured.⁷ In addition, very low frequencies suffer from amplified error that must be carefully managed. This error may be introduced by trying to measure very low currents for potentiostatic EIS, applying currents for very long periods of time adjusting the SOC for galvanostatic EIS, or cell aging for either.

Acquiring D_c measurements at a high resolution versus SOC can also be challenging. Between each measurement, a pulse and a significantly long rest must first be applied to adjust the SOC and allow the cell to relax. Each EIS measurement may also take a significant amount of time if lower frequency measurements are desired. This means that measuring a single cell may take an infeasible amount of time considering the availability and affordability of EIS capable instruments. Significant time and money could be saved by using a method that utilizes the pulses for transitioning SOC as the source of the measurement data using simpler, cheaper, non-EIS capable instruments.

Atlung Method for Intercalant Diffusion (AMID)

AMID is a multi-rate pulse method for measuring D_c developed in this lab. AMID is done by performing a series of pulses at progressively slower currents all with the same voltage limit. The starting voltage of the first pulse and the voltage limit define the voltage interval of a single D_c measurement. As the last pulse in an interval has a very small current that produces very little overpotential, the starting voltage of the first pulse is very similar to the voltage limit of the previous interval. The voltage interval is used to define the Δc_{tot} for X_s and total change in capacity of the interval is used to estimate Δq_{tot} for τ . The change in capacity from the end of each pulse compared to the start of the interval is used to define the cumulative change in capacity, Δq_c , of each pulse. Δq_c is approximated as Δq for τ when $X_s = 1$. Given the selection

of spherical geometry, a r value measured with SEM images, and the I value corresponding to each pulse, the data is fit to equation 5 using D_c and Δq_{tot} as fitting parameters with the error in τ being minimized (Δq_{tot} is a fitting parameter because the total change in capacity for the interval will be somewhat less than Δq_{tot}). The D_c value acquired is recorded as representative for that interval.

The approximation of Δq_c as Δq has been shown to be a reasonable approximation for low current pulses that don't result in a small τ .⁸ This is because η_D becomes constant and approximates an η_R at the end of a pulse when τ is large. Once η_D has reached a steady state, it does not matter when the pulse started. η_D will be the same and, therefore, the Δq_c acquired at the voltage limit will be the same as Δq . AMID limits the influence of high I pulses with dynamic η_D by weighting each pulse by the sum of the η_R of all other pulses in an interval. Unfortunately, pulses with dynamic η_D are important for differentiating η_D from η_R . AMID cells are designed to mitigate other sources of impedance through cell build by selecting low impedance electrolyte and low mass loading electrodes to remove electrolyte impedance within the electrode pores and amplify η_D . Unfortunately, reducing electrode mass loading also amplifies R_i by the same proportional amount. This means that AMID will have a systemic error for all active materials with a high R_i . Additionally, the voltage intervals for AMID are typically rather large (0.1 V or greater) limiting the SOC resolution.

Atlung Method for Intercalant Diffusion and Resistance (AMIDR)

AMIDR is a new method for measuring D_c similar to AMID but with a series of modifications based on inspiration from GITT and a novel approach for accounting for

resistance. Exact details necessary for replication of this study are available in the Experimental section of the Supplementary Information.

Cell Design

AMIDR cells are quite similar to AMID cells in that they have very low mass loading and electrolyte selected to reduce impedance. Mass loading is reduced to the point that the current collector is somewhat visible beneath the electrode coating. This ensures that there are no particles layered on top of each other limiting the electrolyte impedance within the pores to be negligible. In addition, it also reduces the active material mass amplifying the active material impedance sources, diffusion impedance and interface resistance. These very low mass loading coatings can be achieved by reducing the active material:solvent ratio and selecting a very low-profile coating blade. In addition, thin separators (20 μm) are selected so that the ionic electrolyte diffusion impedance can be regarded as a resistance on long timescales.

Different from AMID, AMIDR cells typically use a reference electrode. The reference electrode allows the counter electrode impedance to be neglected which is valuable as the counter electrode typically has impedance that develops on a similar timescale as the working electrode impedance and, therefore, cannot be neglected as simply R . The reference electrode selected is a 50 μm Au wire insulated with a 7 μm polyimide coating often referred to a micro-reference electrode ($\mu\text{-RE}$). After cutting and stripping the polyimide coating on either ends of the wire to allow for electrical contact, the wire is threaded into a coin cell during the cell build process (see Figure S2). Once the cell is built, the reference electrode must be lightly lithiated to produce a AuLi alloy. This alloy has been shown to produce a stable ~ 0.31 V vs. Li^+/Li^0 which allows it be used as a reference electrode.^{9,10}

Testing Apparatus

The reference electrode has very little contact area with the electrolyte which gives it a significant amount of resistance and very little double layer capacitance at its interface. This means that even a small amount of induced current from ambient electromagnetic radiation will contribute to a very large change in the measured potential. In this manner, the reference electrode can act like an antenna unless properly shielded. The only way to ensure that the reference electrode does not produce any induced current is to shield the entire cell and all its wires up to the cell tester. This can be done with shielded cables and aluminum foil attached to a ground in combination with an insulating wrapping material such as nitrile gloves to prevent shorts and ground loops (see Figure S3).

AMIDR cannot be performed accurately on just any cell tester. The cell tester must be able to apply and measure a current with reasonable accuracy ($\pm 1 \mu\text{A}$), but great stability ($\pm 1 \text{ nA}$) within a period $< 0.1 \text{ s}$ from the start of the pulse. This is because while AMIDR will work with any current small enough, that current needs to be kept stable and measurable for the assumption of constant flux at the active material surface to be held true. Similarly, the cell tester must be able to measure and record voltage at high frequency ($< 0.1 \text{ s}$) and great accuracy ($\pm 0.1 \text{ mV}$). This voltage measurement accuracy requirement can be compensated for with even higher frequency measurements by averaging voltage measurements together to produce voltage measurements with less noise. These requirements have been determined for coin cells with Li layered oxide material and the requirements might need to be adjusted for different cell formats and active materials. For instance, a very low mass loading pouch cell will likely not require such low current accuracy and an active material with rapidly changing impedance over a small change in voltage will likely require more accurate voltage measurement.

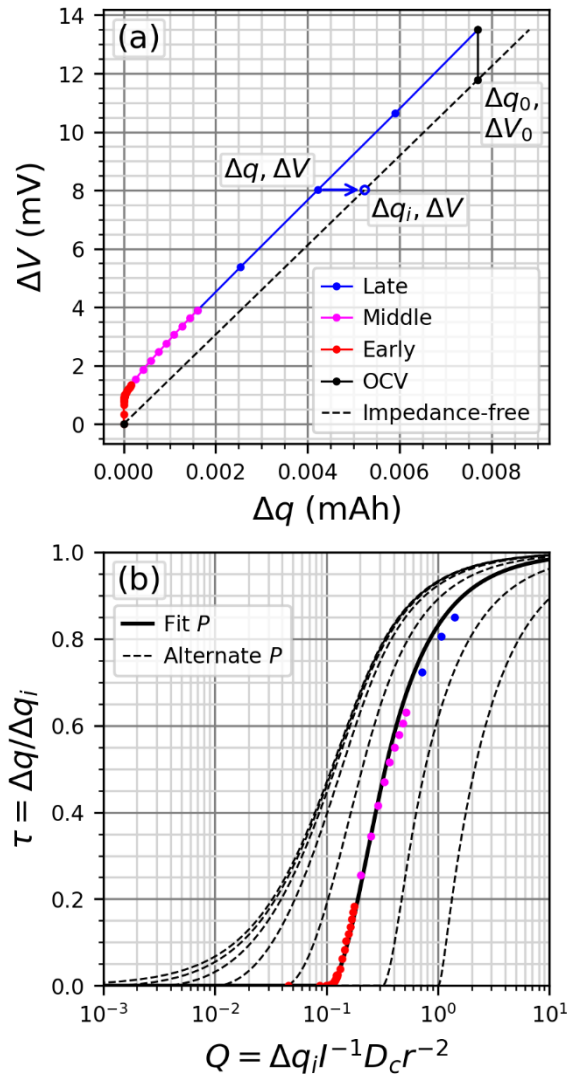
Data Analysis

Rather than using a multi-rate pulse protocol like AMID, AMIDR uses a single-rate pulse protocol similar to GITT. This allows for a greater resolution of D_c over SOC. Additionally, while AMIDR is still based upon the mathematics described by Atlung, modification is made to account for R .

While it may be tempting to define ΔV_{tot} as the total change in voltage of the pulse and simply fit Y over τ of a single pulse to equation 15 as shown in Figure 4a, this equation is not well suited for fitting. Firstly, the initial slope of Y over τ is infinite meaning that any slight error in τ due to error in current measurement or cell capacitive effects will result in a massive error in Y which is an issue if the fit is produced by minimizing error in Y . Secondly, τ and Y are much larger towards the end of the pulse which means that minimizing error in τ or Y will give significantly more weighting to the end of the pulse.

Instead, ΔV_{tot} is defined as the change in voltage from the pulse start for each individual data point and the total dataset is then fit to equation 16 as shown in Figures 6a and 6b. In this manner, $Y(\tau) = 1$ is set for each individual data point as if each data point reached its own voltage limit. For clarity's sake, it is helpful to change a few variable names. $\Delta q_{tot} = (dq/dV)\Delta V_{tot}$ can be rewritten as $\Delta q_i = (dq/dV)\Delta V$ where Δq_i is the ideal, impedance-free change in capacity corresponding to ΔV , the actual change in voltage, of every point. Q and τ are now redefined as $Q = \Delta q_i I^{-1} D_c r^{-2}$ and $\tau = \Delta q / \Delta q_i$. dq/dV is calculated as $dq/dV = \Delta q_0 / \Delta V_0$ where Δq_0 and ΔV_0 are the changes in capacity and voltage from the start of the pulse to the termination of the relaxation period after the pulse. In this manner, the calculated dq/dV is free from impedance and purely thermodynamically determined. Given the selection of spherical

516 geometry and Δq as the change in capacity for each point, the pulse is fit to equation 16 using Q
 517 and P as fitting parameters with the error in τ being minimized. Then, given a r value measured
 518 with SEM images (see Figure S1) and I for the pulse's current, R and D_c are calculated. Lastly,
 519 ion saturation and D_t^* can optionally be calculated with the assistance of regular mass loading
 520 cell data to account for poor active mass accuracy when using low mass loading cells (see Table
 521 S3).



522
 523 Figure 6: The transformation of pulse data to optimize fitting accuracy from (a) a pulse plotted with
 524 widely recognizable axes of change in capacity, Δq , and change in voltage, ΔV , to (b) the same pulse

plotted with axes of relative diffusivity, Q , and relative capacity, τ , which is much better suited for fitting because all periods of the pulse are equally weighted.

This method using equation 16 is much better suited for fitting as the greatest change in τ over change in Q is not vertical mitigating any error in τ produced by error in Q . Additionally, because error in τ is being minimized and τ is a normalized measurement of capacity, equal weighting is given throughout the pulse. Lastly, spherical geometry is selected as most active materials have a form that is more spherical than it is cylindrical or planar. Technically, layered oxides might be better represented as a series of cylinders of varying r as diffusion primarily occurs within the layers of the lattices. However, due to the inconsistent flux that these cylinders experience due to varying r , this representation cannot be explained by the simple mathematical model presented in this study. Regardless, there is relatively little difference (less than a factor of 3) between the values of D_c measured by fitting to a cylindrical or spherical model because there is relatively little difference between the values of Q for a cylindrical and spherical model as seen in Figure 3.

All of these steps of analysis as well as data visualization tools are combined into a user friendly, python program designed to allow users with minimal programming experience to run their own AMIDR experiments and rapidly analyse AMIDR test files. This program is built off the AMID framework and therefore can analyze AMID test files as well. In addition, it also includes a series of optional features to help with cell tester file format conversion, fitting of erroneous data, and even the ability to analyse AMID datasets with AMIDR mathematics (even though this is typically not recommended). Also included within the package containing this program are the datasets analyzed within this study, so that a new user can practice the analysis process, and an experienced impedance expert can verify the results presented here.

Protocol Design

AMIDR analyzes a series of single-rate discharge pulses followed by a series of single-rate charge pulses after 1.5 cycles of formation (see Figure S5). This protocol is split between multiple protocol instruction files due to cell tester limitations but also to allow for some flexibility during the entire test. Each of these instruction protocol files produces one results file each that get combined within the AMIDR program. AMIDR is designed to perform comparison between charge and discharge results to confirm accuracy. This does not necessarily have to be unique for AMIDR. While many papers simply report discharge results for GITT, a comparison of charge and discharge results could also be an easy way a lot more confidence to GITT results. Single-rate pulses require three parameters to be selected: voltage limit spacing, the pulse current, and the relaxation time between pulses.

Decreasing the voltage limit spacing increases the total number of pulses providing more resolution but also increases test time. There are also hard limits to the voltage limit spacing. The voltage limit spacing must be substantially larger than the instrument's voltage resolution for $Y(\tau) = 1$ to be accurate. Alternatively, the voltage limit spacing must be small enough for the dq/dV of the active material to be consistent throughout the pulse. If two adjacent pulses have a significant difference in dq/dV , then there is likely a large change of dq/dV within each pulse as well. A good rule of thumb is that the dq/dV of a pulse should not differ from a proceeding or succeeding pulse's dq/dV by a factor of 2 or greater. This means that AMIDR struggles with measuring D_c when dq/dV changes rapidly over a small change in V . On a q - V plot these troublesome areas appear as plateaus which are associated with phase changes. One strategy for dealing with these q - V plateaus may be to set a capacity limit in addition to a voltage limit, but this was not attempted for this study.

Increasing current decreases the total test time, but current must be set low enough that a complete pulse is achieved by the time the pulse's voltage limit is reached. This is roughly defined as when $\tau > 0.5$, but larger τ values are even more accurate. Considering equation 7 which describes the lower limit for τ as a result of Q , the maximum current limit can be estimated as $I < 0.5ABdq/dV\Delta V_{tot}D_c r^{-2}$ where ΔV_{tot} can be estimated as the voltage limit spacing. This means that reducing the voltage limit spacing also reduces the maximum current that can be applied increasing test time further. Additionally, current may need to be reduced further for cells with high resistance as this can also cause the voltage limit to be reached prematurely. While this does mean that some parameters need a broad estimate of D_c before testing begins like GITT, it is unlike GITT in that there is a process independent of D_c to detect if the parameters are inadequate after testing.

Decreasing relaxation time decreases the test time, but relaxation time must be long enough to achieve "complete" relaxation. Complete relaxation, like complete pulses, is not 100% achievable, but can be approached to a satisfactory level. The amount of time it takes for active material to relax to a uniform concentration is comparable to the amount of time it takes for active material to reach a steady state during a pulse. This is useful because this means that relaxation times that are at least as long as the complete pulses proceeding and succeeding them allow for adequate relaxation. For example, the recommended relaxation time for active material measured with 80 C/80 pulses is > 1 hour as each pulse is expected to last for about 1 hour with some variance due to changing dq/dV . It is recommended to set the relaxation time somewhat longer for active materials with significant change in dq/dV as pulses completed when dq/dV is high will be longer.

It is recommended to first determine the desired voltage limit spacing and then select appropriate current and relaxation times. These parameters can also be adjusted for different ranges of SOC. For instance, it is recommended to use smaller voltage limit spacing for ranges of SOC where D_c changes rapidly and smaller current and longer relaxation times for ranges of SOC where D_c is small. In this study, a different set of parameters were selected for active materials at low SOC to compensate for the rapid decrease in D_c typical for layered oxides (see Table S2). Especially small voltage limit spacing and current are recommended specifically for charging pulses at low SOC. This is because the initial poor D_c at low SOC can cause the first few charging pulses to hit their voltage limits rapidly producing incomplete pulses without enough pulse time for the SOC to change substantially. Eventually a pulse with a voltage limit outside the low SOC range occurs producing a rather long pulse that charges the cell until it is well outside of the low SOC range. Reducing the voltage limit spacing allows for more low SOC pulses to be performed allowing for more capacity to be drawn inside the low SOC range without the voltage limit reaching too far outside. Despite tailored parameter selection for low SOC, the lowest SOC pulses during charge or discharge are generally not complete pulses due to their very poor D_c . If a user can detect that incomplete pulses are being measured during discharge ($\tau > 0.5$), it is recommended to finish that section of the test and start the next charging protocol with a full relaxation step in between. Lastly, changing protocol parameters within the test allows for an additional method of confirmation of results. If results remain continuous when protocol parameters change this informs the user that the protocol parameters are adequate and do not contribute error to the results.

It is desired to evenly weigh the datapoints from the pulse from the start to the end. Regarding Figure 3, this suggests that a logarithmic distribution of Q values would be optimal

for sampling with even weighting throughout. Considering $Q = \Delta q_i I^{-1} D_c r^{-2}$ and $\Delta q_i = (dq/dV)\Delta V$, this suggests that a logarithmic distribution of Δq_i and therefore ΔV would be ideal, but this is not entirely feasible with most cell testers. Most cell testers do not have an option for designing protocols with logarithmic sampling rates and the voltage resolution of the cell tester might not be accurate enough to properly trigger recording of a datapoint, especially when voltage resolution is being compensated for by averaging of high frequency datapoints. Because Δq_i and Δq only vary by a factor of τ and $\Delta q = I\Delta t$, time sampling is an adequate replacement for voltage sampling. Δq_i and Δq can vary significantly on a logarithmic scale when τ is very small, but the error in τ is also very small when τ is small, so the impact of any “oversampled” datapoints will be negligible and not be consequential to the entire fit. Most cell testers do not have an option for logarithmic time sampling either, but this can be approximated by using a series of steps to approximate a logarithmic distribution. More specifically, a protocol can be designed with a series of seamless CC steps sampling every 0.1 s for 1 s, every 1 s for 9 s, every 10 s for 90 s, and so on. This gives a datapoint distribution similar to the tick distribution on a logarithmic plot and an acceptably equal weighting of datapoints across the entire pulse.

Error Management

Not all cells will return accurate results and cells can fail before testing even begins. Because coin cells are not designed with Au wire reference electrodes in mind, the reference electrode can often be the source of cell failure. It is recommended to build three times as many cells as intended to analyse due to the relatively high but manageable rate of cell failure. Firstly, the reference wire may be snapped during the cell crimping step due to the pressure required to seal the cell. Secondly, the insulation surrounding the reference wire may be pierced as well leading to shorts between electrodes. These can either be hard shorts coupling the potentials of

two electrodes together, or soft shorts which may not be immediately apparent. Occasionally, delithiation of the reference electrode can be observed when the reference electrode potential strays far away from ~ 0.31 V vs. Li^+/Li^0 , and self-discharge of the cell can be observed when the terminations of rest periods for charge and discharge do not align on a q - V plot (see Figure S6). It is likely that these are due to soft shorts within the coin cell and should be checked before further analysis. Checking for sources of error and outliers is formal part of the analysis process in the AMIDR program.

Analysis of quality cells will almost always return some erroneous pulses. There are three ways that erroneous pulses can be detected. Firstly, the pulse data may not be able to fit to the model within the fit parameter bounds. This may be due to a multitude of reasons but most commonly occurs in extreme examples of the other two ways pulses may be detected as erroneous. Secondly, significant changes in dq/dV during a pulse can lead to inaccurate fits as the model expects dq/dV to remain consistent (see Figure S7). This is detected by comparing the dq/dV of pulses with the dq/dV of their adjacent pulses. If there is a difference in dq/dV of a factor of 2 or greater between two adjacent pulses, it is recommended to ignore both pulses. Additionally, it is also recommended to ignore the first and last pulse as their dq/dV cannot be ensured to be steady. Lastly, if a pulse is stopped before diffusive impedance reaches a steady state then that pulse is considered incomplete and should be ignored (see Figure S8). This is recommended to be when the pulse ends with $\tau < 0.5$. This pulse removal process can be done within the AMIDR program and the maximum factor of dq/dV change and the minimum τ can also be adjusted within the AMIDR program. The remaining pulses typically have good fits with

low fit error calculated as $\sqrt{\sum(\tau_{exp} - \tau_{mod})^2} / (m * \max(\tau_{exp}))$ where τ_{exp} are the relative

capacities of the experimental dataset, τ_{mod} are the relative capacities of the model sharing the same Q values as τ_{exp} , and m is the total number of τ_{exp} datapoints (see Figure S9 and S10).

Results and Discussion

Single Cell Example

Figure 6 shows some of the key results returned by AMIDR of a single $\text{LiNi}_{0.95}\text{Mn}_{0.05}\text{O}_2$ (NM9505) cell. Most values are plotted with the average voltage of their pulse, but R is plotted with the initial voltage of their pulse as this is primarily where R is realized. It can be immediately observed both in D and R that kinetics get continuously worse at low SOC which aligns with other studies of layered oxides.^{11–15} This makes intuitive sense as it is expected that D_c would get worse with additional crowding of ions in the lattice. Kinetics get so sluggish for $\text{SOC} < 3.6$ V that pulses become incomplete suggesting that relaxation times are also incomplete, and the results are erroneous. This results in a lack of agreement between charge and discharge results in D_c , D_t^* , and dq/dV . R appears to still be in good agreement for $\text{SOC} < 3.6$ V because R does not require significant periods of time to develop or relax. There is a mild disagreement between charge and discharge R measurements at $\text{SOC} 3.65 - 3.85$ V which may be due to measurement error but is more likely due to cell R growing during cycling. Results for $\text{SOC} > 4.15$ V are erroneous for a different reason. At this SOC, dq/dV increases dramatically which is associated with the H2-H3 phase transition commonly found in high-Ni layered oxides.¹⁶ This dramatic change in dq/dV means that pulses within this region cannot be expected to have a consistent dq/dV and therefore calculation of τ will be inaccurate. The current and relaxation times for $\text{SOC} 3.6 - 4.15$ V can be easily validated as these protocol parameters change at 3.7 V and there are two extra long relaxation times at 3.7 V and 3.95 V between protocol sections, but all results appear continuous at these SOC.

D_c and dq/dV are shown to be inversely related to each other for SOC > 3.7 V. This is not coincidental as the greater difference in occupation site potential associated with low dq/dV encourages greater transport from high to low concentration regions. This inverse relationship has interesting implications regarding the calculation of D_t^* using equation 25. D_c and dq/dV cancel each other out leaving behind a relatively consistent D_t^* for SOC > 3.7 V. The derivation of D_t^* given by equation 23 suggests that the average ΔG_A is also mostly consistent within these SOC as ΔG_A is the only term that could conceivably change because of a change of SOC. This derivation could also be used to calculate the average ΔG_A if multiple tests were done at varying T , but this was not accomplished within this study. The cancelling out of this inverse relationship is also present when calculating $R_{D,term}$ using equation 13 leaving a $R_{D,term}$ that is relatively consistent for SOC > 3.7 V despite changing D_c and dq/dV . This makes sense as equation 26 shows that ΔG_A is the primary factor determining $R_{D,term}$ and, therefore, the overall long timescale kinetic performance.

It is known that a vacancy of the target occupation site is necessary for site hopping transportation to occur and this is accounted for in deriving D_t^* . However, it has also been shown that an additional, adjacent vacancy allows for a transport pathway through an intermediate tetrahedral site reducing ΔG_A . This is known as divacancy hopping and is the dominant mode of transport when available.¹⁵ Divacancies become uncommon when the layered oxide is more saturated at low SOC and therefore the average ΔG_A increases with further saturation in agreement with the downward trend of D_t^* for SOC < 3.7 V.

The benefits of using AMIDR to determine R are shown as well. R calculated by fitting the pulse data to the AMIDR model is shown to be higher than R calculated using a common

706 traditional method, $R = \Delta V_d / I$, where ΔV_d is the voltage drop, the initial change in voltage
707 between the first two datapoints. Using ΔV_d may not result in complete realization of R as it may
708 not be fully developed due to capacitive effects. The danger of using ΔV_d to calculate R may be
709 somewhat exaggerated here as ΔV_d was measured over a time period of 0.05 s which is shorter
710 than what might be acquired from a typical cell tester. However, this issue is still relevant with
711 ΔV_d measured over longer time periods, particularly at low SOC where higher R results in a
712 longer delay due to capacitive effects.

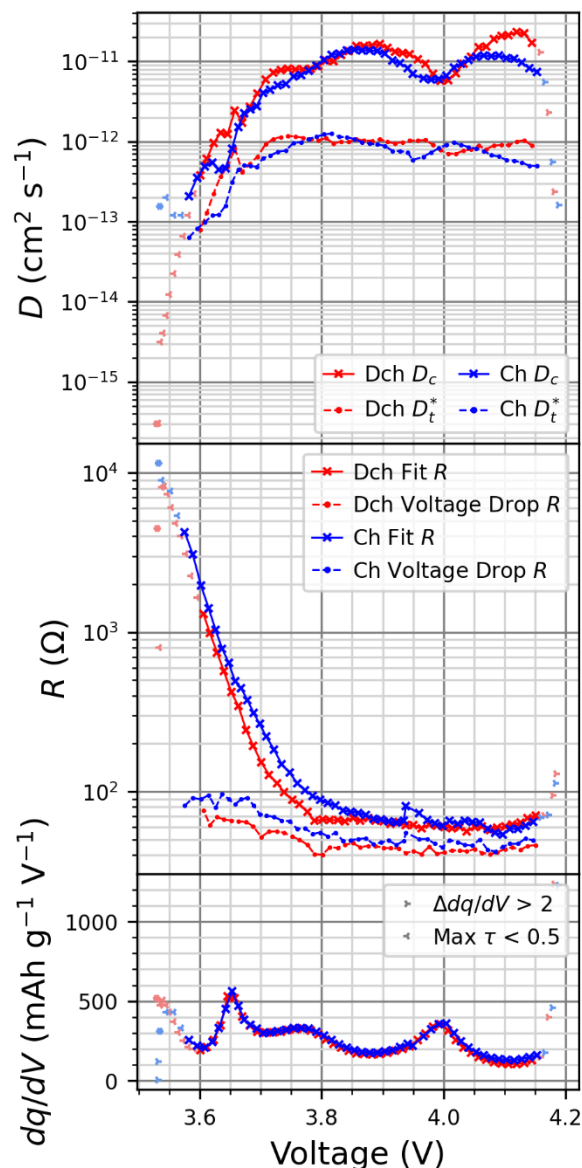


Figure 7: AMIDR results of a single NM9505 cell at 30 °C. Incomplete pulses and poor kinetics are common at low SOC and large dq/dV changes are common at the H2-H3 phase transition > 4.15 V. Chemical diffusivity, D_c , varies inversely with dq/dV leaving a relatively flat free-path tracer diffusivity, D_t^* . D_t^* and voltage drop resistance, R , results from erroneous pulses are not shown for clarity.

Charge/Discharge Disagreement

While charge and discharge results generally align, there is a measurable difference between the two that curiously revolves around dq/dV peaks and valleys. Figure 7a shows binned and averaged data from multiple cells using a beta protocol from early in AMIDR

development. It's apparent that the calculated D_c and D_t^* values are higher when dq/dV is decreasing during a pulse and vice versa. This suggests that change in dq/dV produced error in the calculated D values. One explanation is that decreasing dq/dV gives the impression that the η_D in the middle of a pulse is smaller than it's expected to be, overestimating D_c in the fitting. The opposite would occur for increasing dq/dV and the error would be minimized for pulses upon dq/dV peaks and valleys as the dq/dV change is also minimized. Figure 7b shows data from a newer, high resolution protocol developed in response to this charge/discharge disagreement with voltage limit spacing half the size of the beta protocol. Charge/discharge disagreement is still apparent with the high resolution protocol but appears to be marginally improved.

An issue making comparison of these two datasets difficult is that the beta protocol cells were coated on a rougher than ideal surface which encouraged active material agglomeration. Unfortunately, these cells were built early in development of AMIDR before the issue of a rough coating surface was realized. This agglomeration caused groups of particles to act as larger particles giving the impression of smaller D_c with higher variance. The agglomeration produced consistently higher fit errors, even for pulses upon dq/dV peaks and valleys.

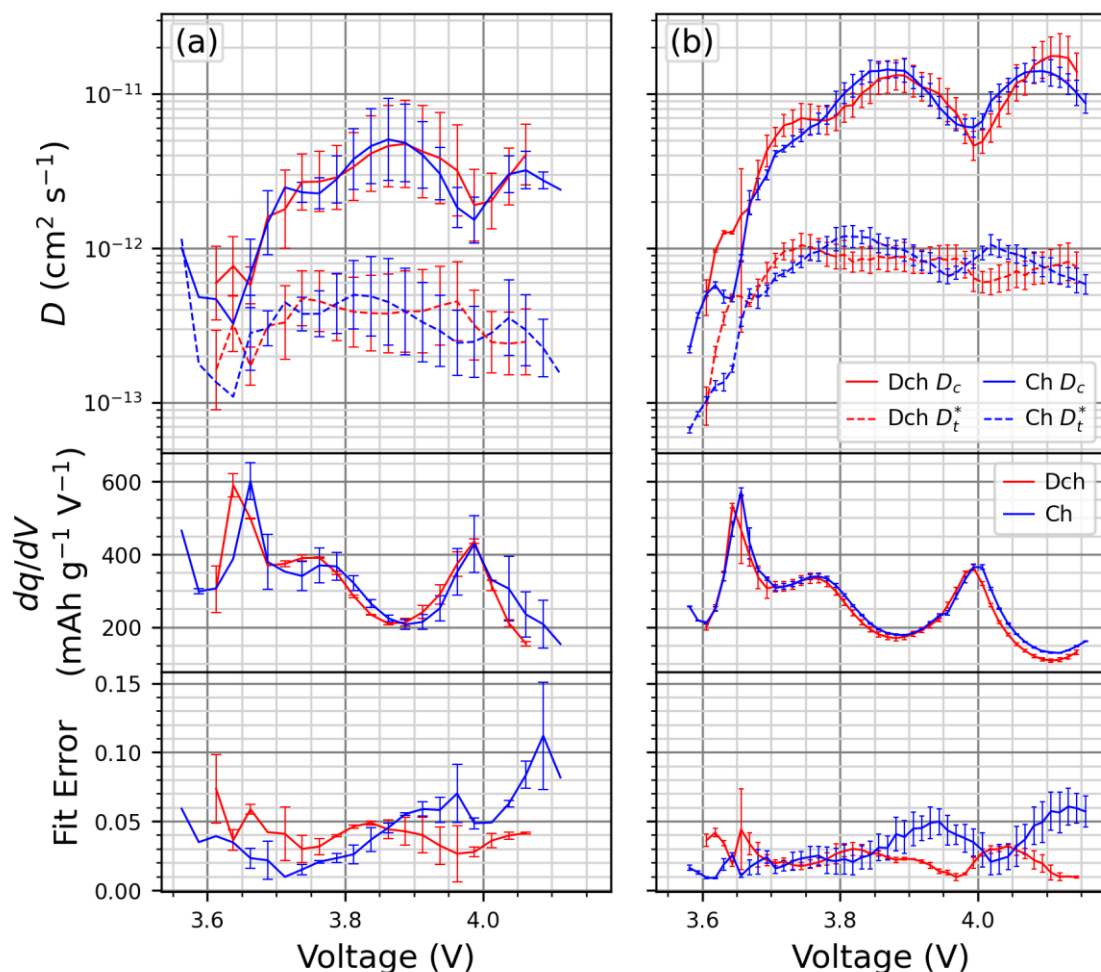


Figure 8: Comparison of NM9505 cells at 30 °C tested with (a) an early beta protocol and (b) a high resolution protocol. Additionally, the cells made for the beta protocol were coated on a rough surface and had issues with particle agglomeration. Cell data was binned into voltage ranges and averaged. Both protocols generated charge/discharge disagreement in diffusivity, D , revolving around dq/dV peaks and valleys. The high resolution protocol shows larger D values with less charge/discharge disagreement, variance, and fit error.

Counter Electrode Impact

Because charge and discharge data have opposite errors, they can be binned and averaged together to return results agnostic of current direction. Figure 8 shows averaged data from NM9505 cells with both the impedance against the reference electrode and impedance against the lithium metal anode analyzed by AMIDR. These cells had minimal cathode mass loading to amplify the cathode impedance and to eliminate electrolyte pore impedance. However, even with

751 amplified cathode impedance, the lithium metal anode still produced enough impedance to skew
752 results measurably for SOC > 3.7 V where cathode impedance is small. If high accuracy is not
753 desired, it may be acceptable to simply test 2-electrode coin cells as they are far easier to make.
754 However, if 2-electrode coin cells are tested, it is strongly recommended to compare their results
755 to the impedance of lithium metal symmetrical cells to ensure that it is not simply lithium metal
756 impedance that is being measured.

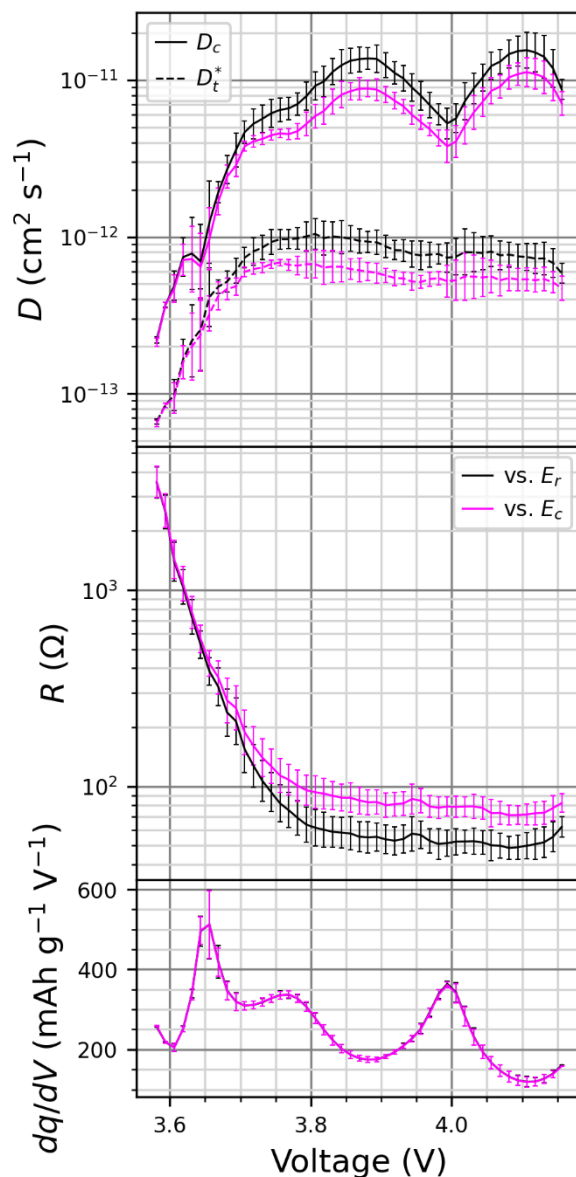


Figure 9: Comparison of NM9505 cells at 30 °C analyzed with impedance against the reference electrode potential, E_r , and impedance against the counter electrode potential, E_c . Even with minimal cathode mass loading to amplify cathode impedance, impedance from a lithium metal anode can obscure diffusivity, D , measurements.

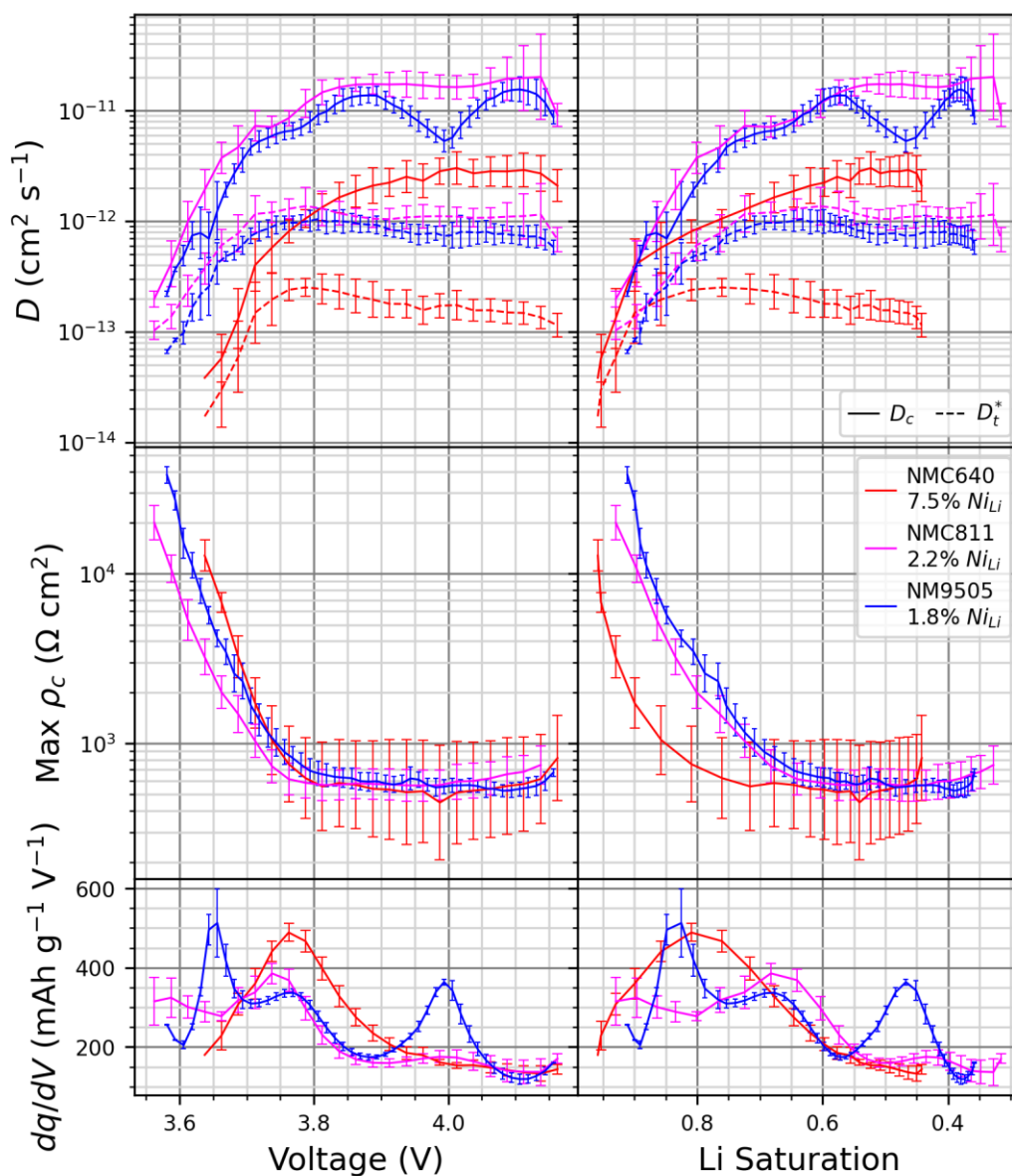
Material Comparisons

Figure 9 shows the difference in kinetics of three different types of commercial layered oxide active materials. It can be immediately seen that $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811) and NM9505 have very similar kinetic performance as high-Ni layered oxides with a similar

proportion of Ni in the Li layer, Ni_{Li} , determined with XRD (see Figure S4 and Table S4). D_c at the 4.0 V q - V plateau unique to NM9505 is somewhat worse than NMC811, but this q - V plateau has similar overall kinetic performance due to having a similar D_t^* and therefore similar $R_{D,term}$. LiNi_{0.6}Mn_{0.4}O₂ (NMC640), however, shows much worse kinetic performance at most SOC. This is because the NMC640 has higher Ni_{Li} which prevents divacancy hops at adjacent sites. However, at low SOC where the active material has high Li saturation, NMC640 shows similar kinetic performance to the other materials as divacancies are uncommon for all materials at this SOC.

The three commercial materials also have very similar maximum ρ_c as a function of voltage. It's important to recognize this measurement as a maximum value because a certain amount of R in the cell is not sourced from the active material surface. However, R_i is the only source of R that could conceivably change with SOC, so it's fair to regard the larger values of ρ_c as effectively entirely due to R_i as other sources of R would be negligible. It's hard to determine whether R_i is primarily due to a single charge transfer reaction or a thin, low D_c surface layer as they both generate R_i independent of the currents applied. If it is a single charge transfer reaction between the electrolyte and the active material, then it would be expected to follow the Butler-Volmer equation. However, the relationship between current density, $j = I/S$, and η in the Butler-Volmer equation is linear for $\eta < 25$ mV and no pulse had $\eta > 25$ mV as the voltage limit spacing was set at 25 mV or less. The expected charge transfer resistance, R_{ct} , would therefore follow Ohm's law and be consistent across varying I . R_i may also be due to a negligible charge transfer reaction and a thin, low D_c surface layer. Commercial active material is often engineered with surface treatments to extend cycle life and a reconstructed rock salt surface layer is often observed for layered oxides.¹⁷ A thin surface layer can be modeled as a thin, low D_c phase

789 effectively producing an R_i that also follows Ohm's law on a reasonably short timescale (see
 790 Proof 3). It is possible that the observed increase in R_i during the charge pulses after the
 791 discharge pulses is due to a thickening of this surface layer. However, it's also possible that the
 792 observed increase in R_i may also be due to a decrease in active material surface area accessible
 793 to charge transfer due to the growth of an impenetrable surface layer. Regardless, it's clear that
 794 R_i is heavily dependent on SOC in a manner similar to D_c .



795

Figure 10: Comparison of commercial layered oxide materials at 30 °C. NMC811 and NM9505 show similar kinetics with similar Ni in Li layer, Ni_{Li} , measured with XRD. NMC640 has additional Ni_{Li} and worse kinetics.

Conclusion

AMIDR is an improved method for measuring D_c due to a series of important design decisions that all must be considered to achieve accuracy. Notably, test cells are designed to amplify active material impedance and ignore impedance from the opposing electrode, the cell testing protocol and analysis are designed to measure complete pulses which reach a steady state, the analysis program is designed to calculate both cell R and D_c simultaneously by fitting to a complete pulse model, and extra care is taken to detect and remove erroneous outliers and achieve effective charge/discharge agreement. With careful application of this method, insight into the mechanistic construction of D_c and R_i is revealed. In addition, three different layered oxide materials were analyzed, and their results compared giving further evidence that layered oxide D_c is heavily dependent on Ni_{Li} , but not necessarily at low SOC.

List of Symbols

a	distance between two occupation sites (cm)
A	geometric constant (1 for a planar sheet, 2 for a cylinder, 3 for a sphere)
α_i	series of geometric constants defined by equations
B	geometric constant (3 for a planar sheet, 4 for a cylinder, 5 for a sphere)
c	ion concentration (mol cm ⁻³)
c_s	surface c (mol cm ⁻³)
c_{sat}	c of a completely saturated active material (mol cm ⁻³)
Δc_s	change in c_s after a certain Δt (mol cm ⁻³)
$\Delta c_{s,loss}$	deviation in c_s from impedance-free scenario (mol cm ⁻³)
Δc_{tot}	change in c if n_{tot} moles are evenly transported (mol cm ⁻³)
C	dimensionality constant
dE/dc	relationship between c and E at any given SOC

823	dq/dV	relationship between V and q at any given SOC
824	D_c	chemical diffusivity ($\text{cm}^2 \text{s}^{-1}$)
825	D_t	tracer diffusivity ($\text{cm}^2 \text{s}^{-1}$)
826	D_t^*	free-path tracer diffusivity ($\text{cm}^2 \text{s}^{-1}$)
827	E	electrode potential (V)
828	E_c	counter E (V)
829	E_w	working E (V)
830	F	Faraday's constant (C mol^{-1})
831	ΔG_A	occupation site hop activation energy (J)
832	I	applied current (A)
833	J	ionic flux ($\text{mol s}^{-1} \text{cm}^{-2}$)
834	J_1	Bessel function of the first kind of order 1
835	k_B	Boltzmann constant (J K^{-1})
836	m	active material mass (g)
837	n	moles of ions transported after a certain Δt (mol)
838	n_{tot}	moles of ions desired to be transported (mol)
839	N_A	Avogadro constant (mol^{-1})
840	P	relative resistance
841	q	capacity (C)
842	q_e	elementary charge (C)
843	q_{sat}	theoretical q of a fully saturated active material (C)
844	Δq	change in q after a certain Δt (C)
845	Δq_c	cumulative change in q of a series of pulses (C)
846	Δq_i	ideal, impedance-free change in q corresponding to ΔV (C)
847	Δq_{tot}	change in q if n_{tot} moles are transported (C)
848	Δq_0	change in q after a pulse and relaxation (C)
849	Q	relative D_c
850	r	diffusion length or radius (cm)
851	\bar{r}	capacity-weighted geometric mean of r (cm)
852	\bar{r}_e	average r for modeling end of pulse (cm)

853	\bar{r}_s	average r for modeling start of pulse (cm)
854	R	resistance (Ω)
855	$R_{D,term}$	terminal diffusive R (Ω)
856	R_i	interface R (Ω)
857	R_{ohm}	combined electrical contact R and ionic electrolyte R (Ω)
858	S	electrode surface area (cm ²)
859	t	time (s)
860	Δt	pulse time (s)
861	T	temperature (K)
862	V	cell voltage (V)
863	ΔV	change in V after a certain Δt (V)
864	ΔV_d	initial ΔV at start of pulse (V)
865	ΔV_i	ideal ΔV in an impedance-free scenario (V)
866	ΔV_{tot}	ΔV if n_{tot} moles are transported and active material allowed to relax (V)
867	ΔV_0	change in V after a pulse and relaxation (V)
868	\tilde{V}	electrode volume (cm ³)
869	X_s	relative Δc_s
870	$X_{s,loss}$	deviation in X_s from impedance-free scenario
871	$X_{s,ideal}$	ideal X_s under an impedance-free scenario
872	Y	relative ΔV
873	z	ion charge number
874	γ	activity coefficient
875	η	overpotential (V)
876	η_D	diffusion η (V)
877	η_R	resistance η (V)
878	μ	chemical potential (J mol ⁻¹)
879	μ_0	intrinsic chemical potential (J mol ⁻¹)
880	ν	vibrational frequency (s ⁻¹)
881	ρ_c	interface contact resistivity (Ω cm ²)
882	ρ_d	active material density (g cm ⁻³)

883 τ relative Δq

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889 **References**

- 890 1. S. Atlung, K. West, and T. Jacobsen, *J. Electrochem. Soc.*, **126**, 1311–1321 (1979).
- 891 2. C. Deng and W. Lu, *Journal of Power Sources*, **473**, 228613 (2020).
- 892 3. B. Choudhury, A. Jangale, and B. Suthar, *J. Electrochem. Soc.*, **170**, 070519 (2023).
- 893 4. H. H. Berger, *J. Electrochem. Soc.*, **119**, 507 (1972).
- 894 5. C. Liu, Z. G. Neale, and G. Cao, *Materials Today*, **19**, 109–123 (2016).
- 895 6. O. J. Kleppa, *Annu. Rev. Phys. Chem.*, **6**, 119–140 (1955).
- 896 7. Y. Fujihara and T. Kobayashi, *J. Electrochem. Soc.*, **169**, 080509 (2022).
- 897 8. M. Doyle, J. Newman, and J. Reimers, *Journal of Power Sources*, **52**, 211–216 (1994).
- 898 9. S. Solchenbach, D. Pritzl, E. J. Y. Kong, J. Landesfeind, and H. A. Gasteiger, *J. Electrochem.*
899 *Soc.*, **163**, A2265–A2272 (2016).
- 900 10. Y.-C. Chien, D. Brandell, and M. J. Lacey, *Chem. Commun.*, **58**, 705–708 (2022).
- 901 11. A. Liu, N. Phattharasupakun, M. M. E. Cormier, E. Zsoldos, N. Zhang, E. Lyle, P. Arab, M.
902 Sawangphruk, and J. R. Dahn, *J. Electrochem. Soc.*, **168**, 070503 (2021).
- 903 12. E. S. Zsoldos, M. M. E. Cormier, M. Ball, D. Rathore, and J. R. Dahn, *J. Electrochem. Soc.*,
904 **170**, 070502 (2023).
- 905 13. E. Zsoldos, M. M. E. Cormier, N. Phattharasupakun, A. Liu, and J. R. Dahn, *J. Electrochem.*
906 *Soc.*, **170**, 040511 (2023).
- 907 14. Y.-C. Chien, H. Liu, A. S. Menon, W. R. Brant, D. Brandell, and M. J. Lacey, *Nat Commun*,
908 **14**, 2289 (2023).
- 909 15. A. Van Der Ven and G. Ceder, *Journal of Power Sources*, **97–98**, 529–531 (2001).
- 910 16. J. Chen, H. Yang, T. Li, C. Liu, H. Tong, J. Chen, Z. Liu, L. Xia, Z. Chen, J. Duan, and L.
911 Li, *Front. Chem.*, **7**, 500 (2019).
- 912 17. F. Lin, I. M. Markus, D. Nordlund, T.-C. Weng, M. D. Asta, H. L. Xin, and M. M. Doeff,
913 *Nat Commun*, **5**, 3529 (2014).
- 914