



# Electrochemical Impedance of a Battery Electrode with Anisotropic Active Particles



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## ABSTRACT

Electrochemical impedance spectra for battery electrodes are usually interpreted using models that assume isotropic active particles, having uniform current density and symmetric diffusivities. While this can be reasonable for amorphous or polycrystalline materials with randomly oriented grains, modern electrode materials increasingly consist of highly anisotropic, single-crystalline, nanoparticles, with different impedance characteristics. In this paper, analytical expressions are derived for the impedance of anisotropic particles with tensorial diffusivities and orientation-dependent surface reaction rates and capacitances. The resulting impedance spectrum contains clear signatures of the anisotropic material properties and aspect ratio, as well as statistical variations in any of these parameters.

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## 1. Introduction

Electrochemical impedance spectroscopy (EIS) is used in various fields, such as energy storage and conversion [1–6], cell biology [7,8], corrosion science [9,10], and catalysis [11,12], to characterize transport, reaction, and accumulation of charge carriers in the systems. For insertion battery electrodes, it has also been widely used across many different material compositions [1–3]. Various models have been introduced to interpret the battery impedance behavior. After adopting the Randles model for combined contribution of charge accumulation, insertion reaction, and transport in active material [13,14], models were further developed to consider different particle shape [15,16], size distribution [16–19], phase transformation [20,21], and additional layers on the active particles [17,22,23]. Some also incorporate the concentration gradient along the thickness of a porous electrode [17,23,24] and its heterogeneous thickness [18,19,25]. Nevertheless, essentially all models assume isotropic properties for the active particles, regardless of their area of application.

In contrast, most battery materials currently under investigation are strongly anisotropic, which means that behavior of charge

carriers in the materials varies with the direction in respect to the crystallographic axes [26–32]. The anisotropy is attributed to different activation barriers along the hopping paths of charge carriers depending on the direction. Since many battery materials have high electron mobility compared to that of ions [15,27], it is the ion hopping that determines the anisotropy in transport of charge carriers as well as in surface insertion kinetics [15,33,34]. For example,  $\text{Li}_x\text{CoO}_2$  has a layered metal oxide structure, where lithium ions can move quickly through the plane between the metal oxide layers, but their movement across the layers is less likely and very slow [28,29]. On the other hand,  $\text{Li}_x\text{FePO}_4$  has an olivine structure, where lithium ions can move quickly through one-dimensional channels in the *b*-crystallographic direction [30–32]. Models also predict that intercalation kinetics [35], phase separation dynamics [36], and nucleation [37] are highly anisotropic due to tensorial coherency strain and different composition-dependent surface on each crystal facet [38,39]. Like  $\text{Li}_x\text{FePO}_4$ , other important battery materials tend to phase-separate when they are alloying with Li ions [40–42], and their impedance characteristics are beginning to be considered [20,21]. In this paper, however, we confine our scope to the materials forming a single phase solid solution. This also includes materials that tend to phase-separate, such as  $\text{Li}_x\text{Mn}_2\text{O}_4$  and  $\text{Li}_x\text{FePO}_4$ , while outside of their miscibility gaps for  $x \approx 0$  or  $x \approx 1$ .

Isotropic models of active particles are still widely employed in EIS studies of batteries, in part because traditional active particles were large enough to have many randomly oriented crystal

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**Nomenclature**

$A_p$	particle surface area
$c$	local ion concentration
$c_s$	surface ion concentration
$(\nabla c)_s$	ion concentration gradient at surface
$\tilde{c}$	$= (-\partial\Delta\phi_{eq}/\partial c) \tilde{c} / \Delta\hat{\phi}$ , dimensionless local ion concentration
$C_p$	particle surface capacitance
$C_{surf}$	surface capacitance
$C_{surf,x}$	$= C_{surf}(\mathbf{e}_x)$ , surface capacitance on $x$ normal surface
$C_{surf,y}$	$= C_{surf}(\mathbf{e}_y)$ , surface capacitance on $y$ normal surface
$\mathbf{D}_{ch}$	chemical diffusivity tensor
$D_{ch,x}$	chemical diffusivity in $x$ direction
$D_{ch,y}$	chemical diffusivity in $y$ direction
$D_{ch,z}$	chemical diffusivity in $z$ direction
$e$	elementary electric charge
$\mathbf{e}_x$	unit vector in $x$ direction
$\mathbf{e}_y$	unit vector in $y$ direction
$i$	$= \sqrt{-1}$ , unit imaginary number
$j_0$	exchange current density
$j_{acc}$	accumulation current density
$j_{ins}$	insertion current density
$j_{tot}$	total current density
$J_p$	total current on particle surface
$J_{ov}$	overall electrode current
$k$	Boltzmann's constant
$l_x$	one half of particle length in $x$ direction
$l_y$	one half of particle length in $y$ direction
$\tilde{l}_x$	$= l_x / \bar{L}_x$ , dimensionless particle length in $x$ direction
$\tilde{l}_y$	$= l_y / \bar{L}_y$ , dimensionless particle length in $y$ direction
$L_x$	one half of particle length in $x$ direction, a random variable
$L_y$	one half of particle length in $y$ direction, a random variable
$\bar{L}_x$	mean value of $L_x$
$\bar{L}_y$	mean value of $L_y$
$\tilde{L}_x$	$= L_x / \bar{L}_x$ , dimensionless particle length in $x$ direction, a random variable
$\tilde{L}_y$	$= L_y / \bar{L}_y$ , dimensionless particle length in $y$ direction, a random variable
$\mathbf{n}$	surface normal vector
$n_p$	index of summation for active particles
$N_p$	total number of active particles
$Pr_{\mathbf{V}_d}$	joint probability density function of $\mathbf{V}_d$
$Pr_{\tilde{L}_x, \tilde{L}_y}$	joint probability density function of $\tilde{L}_x$ and $\tilde{L}_y$
$R_p$	particle surface resistance
$t$	time variable
$T$	temperature
$\mathbf{v}_d$	vector of distributed parameters, a realization
$\mathbf{V}_d$	vector of distributed parameters, a random vector variable
$x$	spatial variable in $x$ direction
$\tilde{x}$	$= x / l_x$ , dimensionless spatial variable in $x$ direction
$X$	arbitrary variable
$X_0$	reference state response in $X$
$X_1$	$\varepsilon$ -order perturbation in $X$
$\tilde{X}$	Fourier coefficient of perturbation in $X$
$y$	spatial variable in $y$ direction
$\tilde{y}$	$= y / l_y$ , dimensionless spatial variable in $y$ direction
$z_{acc}$	local accumulation impedance
$z_D$	local diffusion impedance

$z_G$	local Gerischer impedance
$z_{ins}$	local insertion impedance
$z_{tot}$	local total impedance
$Z_p$	particle impedance
$Z_{ov}$	overall electrode impedance
$\tilde{z}_{tot}$	$= z_{tot} / \rho_{ct,x}$ , dimensionless local total impedance
$\tilde{Z}_p$	$= 8l_y Z_p / \rho_{ct,x}$ , dimensionless particle impedance
$\tilde{Z}_{p,G}$	Gerischer limit of dimensionless particle impedance
$\tilde{Z}_{ov}$	$= 8\bar{L}_y N_p Z_{ov} / \rho_{ct,x}$ , dimensionless overall electrode impedance

**Greek letters**

$\alpha$	charge transfer coefficient
$\beta_x$	$= \rho_{D,x} / \rho_{ct,x}$ , ratio of diffusion characteristic resistance in $x$ direction and charge transfer resistance on $x$ normal surface
$\beta_y$	$= \rho_{D,y} / \rho_{ct,y}$ , ratio of diffusion characteristic frequency in $y$ direction and charge transfer resistance on $y$ normal surface
$\chi_x$	$= \omega_{RC,x} / \omega_{D,x}$ , ratio of RC characteristic frequency on $x$ normal surface and diffusion characteristic frequency in $x$ direction
$\chi_y$	$= \omega_{RC,y} / \omega_{D,y}$ , ratio of RC characteristic frequency on $y$ normal surface and diffusion characteristic frequency in $y$ direction
$\varepsilon$	arbitrary small number
$\Delta\phi$	potential drop across electrolyte/active material interface
$\Delta\phi_{eq}$	equilibrium potential drop of insertion reaction
$-\partial\Delta\phi_{eq}/\partial c$	Nernst shift coefficient
$\gamma$	$= l_x / l_y$ , geometric aspect ratio of a rectangular particle
$\eta$	surface overpotential
$\nu$	$= \rho_{ct,y} / \rho_{ct,x}$ , ratio of charge transfer resistances
$\rho_{xy}$	correlation between $\tilde{L}_x$ and $\tilde{L}_y$
$\rho_{ct}$	$= kT / j_0 e$ , charge transfer resistance
$\rho_{ct,x}$	$= \rho_{ct}(\mathbf{e}_x)$ , charge transfer resistance on $x$ normal surface
$\rho_{ct,y}$	$= \rho_{ct}(\mathbf{e}_y)$ , charge transfer resistance on $y$ normal surface
$\rho_{D,x}$	$= (-\partial\Delta\phi_{eq}/\partial c) l_x / eD_{ch,x}$ , diffusion characteristic resistance in $x$ direction
$\rho_{D,y}$	$= (-\partial\Delta\phi_{eq}/\partial c) l_y / eD_{ch,y}$ , diffusion characteristic resistance in $y$ direction
$\Sigma_{xx}$	variance in $\tilde{L}_x$
$\Sigma_{yy}$	variance in $\tilde{L}_y$
$\Sigma_{xy}, \Sigma_{yx}$	covariance of $\tilde{L}_x$ and $\tilde{L}_y$
$\tau$	$= \omega_{D,y} / \omega_{D,x}$ , ratio of diffusion characteristic frequencies
$\omega$	applied frequency
$\omega_{D,x}$	$= D_{ch,x} / l_x^2$ , diffusion characteristic frequency in $x$ direction
$\omega_{D,y}$	$= D_{ch,y} / l_y^2$ , diffusion characteristic frequency in $y$ direction
$\omega_{RC,p}$	RC characteristic frequency of particle impedance
$\omega_{RC,x}$	$= (\rho_{ct,x} C_{surf,x})^{-1}$ , RC characteristic frequency on $x$ normal surface
$\omega_{RC,y}$	$= (\rho_{ct,y} C_{surf,y})^{-1}$ , RC characteristic frequency on $y$ normal surface
$\tilde{\omega}$	$= \omega / \omega_{D,x}$ , dimensionless applied frequency
$\Omega$	domain of $\mathbf{V}_d$

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