Prediction of Charge-Discharge and Impedance Characteristics of Electric Double-Layer Capacitors Using Porous Electrode Theory

Muhammad R. Hasvim,a,b Danhao Mac, Ramakrishnan Rajagopaland,e,f and Clive Randalle,,f

aDepartment of Engineering Science and Mechanics, the Pennsylvania State University, University Park, Pennsylvania 16802, USA
bDepartment of Chemical Engineering, the Pennsylvania State University, University Park, Pennsylvania 16802, USA
cDepartment of Energy Engineering, the Pennsylvania State University, University Park, Pennsylvania 16802, USA
dDepartment of Engineering, Penn State, DuBois, Pennsylvania 15801, USA
eMaterials Research Institute, the Pennsylvania State University, University Park, Pennsylvania 16802, USA
fDepartment of Materials Science and Engineering, the Pennsylvania State University, University Park, Pennsylvania 16802, USA

Two first-principles modeling methods were used to analyze and quantitatively predict performance characteristics of Electric Double-Layer Capacitors (EDLCs), namely Time-Domain Current Method (TDCM) and Frequency-Domain Admittance Method (FDAM). TDCM was used to model galvanostatic discharge characteristics of capacitor while FDAM was used to model the impedance spectra. Both the methods showed excellent agreement with experimental impedance and galvanostatic discharge performance of various electrochemical capacitors made using two different commercial carbons. Details at the macroscopic (porous electrode theory) and microscopic (double layer theory) level were incorporated into the models. The methods were also able to follow changes in capacitance and resistance of the capacitor during cycling. Furthermore, FDAM was used to validate the performance of a large-scale commercial EDLC capacitor.

© The Author(s) 2017. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.005171jes] All rights reserved.

Manuscript submitted June 21, 2017; revised manuscript received August 22, 2017. Published September 22, 2017.

Electrochemical capacitors are receiving considerable attention as energy storage devices that can meet the energy and power demands for electric vehicles, renewable energy storage, smart grid, and energy harvesting technologies.1,4 Energy in these capacitors is stored either in the form of electrostatic ionic charge at electrode/electrolyte interface or through fast faradaic interactions that contribute to pseudo-capacitance at the interface.1,2,12,13 Transient electroanalytical techniques such as galvanostatic charge/discharge and impedance spectroscopy are the key tools that are used to assess both the EDLC’s characteristics and device performance. Development of mathematical models that accurately describe the interfacial phenomenon and validation through experimental observation is critical to further our understanding of the complexity of electrostatic/electrochemical interaction that occurs at the electrode/electrolyte interface.

The development of models for EDLCs ties very deeply with the mathematical modeling of non-faradaic phenomena at the microscopic level. In these length scales, the double layer structure is described in terms of a diffuse/Gouy-Chapman layer and compact/Helmholtz layer. The compact layer will then be further divided into inner Helmholtz plane (IHP), that contain specifically adsorbed ions, and outer Helmholtz plane, which contains solvated ions that are attracted to the electrode due to charge interactions. To apply this conceptual picture to transient electroanalytical techniques, many different variations exist based upon the mathematical details and the choice of non-faradaic effects to be included/excluded in the models, e.g. specific adsorption, diffuse layer, and compact layer.

Among all non-faradaic phenomena related to the double layer structure, the diffuse layer is one of the most intensively studied. The earliest treatment came by direct incorporation of the Gouy-Chapman-Stern theory for different electroanalytical techniques, with some analytical solutions in the form of hypergeometric functions given in cases where they are possible.10–15 Only in the more recent times that the studies of diffuse charge dynamics were revived, with several key developments tying into applications in electrochemical capacitors.16 The diffuse charge dynamics formalism was later extended to carbon porous electrodes and ionic liquids.17–20 The Poisson-Nernst-Planck (PNP) models and their variations, which include anomalous diffusion effects, can also be thought as another type of diffuse charge dynamical models, although their usage is primarily used for analyzing the impedance spectra of both solid and liquid electrolytes.21–26 Another interesting development came by using the Debye-Falkenhagen equation to study impedance spectra of partially blocking microscopically heterogeneous electrodes,27 macroscopically rough (anomalous diffusion) electrodes,28 and ionic liquids.29

An equally important component of modeling EDLCs is the macroscopic level description of the EDLCs. At the macroscopic level, the complex geometry of the porous electrodes is handled by the porous electrode theory. The theory assumes that the current passing through the electrode is distributed between two co-continuous phases that are described as solution phase (electrolyte inside porous electrode) and solid matrix phase (corresponding to active electrode material). Application of this theory can be found in intercalating Li-ion batteries30–33 as well as EDLCs and desalination.34,35 Another variant of the theory assumes bulk migration of ions across the entire porous electrode, creating a coupled non-linear PDE system. Such variant was extensively applied to model ruthenium oxide pseudocapacitors37–39 and Li-ion batteries.40 While these studies have largely focused on charge-discharge simulation, a study has also been made to find an analytical solution for the impedance of a porous electrode assuming bulk migration across the electrode and linearized faradaic kinetics.41 When the assumption of bulk migration is relaxed, an analytical solution for the transient behavior of a porous electrode was obtained.42 Mathematical models are very helpful in providing a quantitative understanding of the complex electrode/electrolyte interfaces of EDLCs as well as the macroscopic effects of the electrode morphology. However, rigorous validation toward experimental data can be lacking, especially in the form of accurate prediction of device’s performances. To alleviate this problem, this paper proposes two first-principles experiment-driven modeling methods applied to EDLCs that serve two goals:

1. To interpret the experimental data and provide a deeper understanding of the nature of electrochemical interactions at the electrode/electrolyte interface.
2. To predict experimental data for the devices that utilize the same electrode materials.
Figure 1. An illustration of two modeling approaches described in this work. In Time-Domain Current Method (TDCM), a model is used to parametrize a discharge curve to predict impedance characteristics. In Frequency-Domain Admittance Method (FDAM), a model is used to parametrize an impedance spectra to predict discharge curves. In both methods, the model is based on physical relevant theories combined at different levels of complexity.

Figure 1 provides an illustration of the two methods that will be described in this paper. The first method is the Time-Domain Current Method (TDCM), which utilize galvanostatic charge/discharge data to predict impedance characteristics of an EDLC. The second method is the Frequency-Domain Admittance Method (FDAM), which utilize electrochemical impedance spectroscopy data to predict charge-discharge characteristics of a device, including capacitance, energy, and power density. Each method will utilize models that consider both the macroscopic (porous electrode) and microscopic (double layer interface) aspects of an EDLC, in a general and unified manner. Thus, the methods described will serve both as a tool to understand electrochemical phenomena and make quantitative predictions.

Experimental

For both TDCM and FDAM, we chose two commercially available EDLC carbon materials, YP50F from Kuraray Chemical Co. and ACS carbon from ACS Materials Inc. and assembled a two-electrode capacitor using a 2032 stainless steel coin cell prototype. The mean pore size of YP50 was ~0.8 nm and that of ACS carbon was 2 nm, respectively. The pore volume and surface area of these materials differ significantly and provided a good starting case study for both the methods. Additionally, the model associated with FDAM was tested using two more as-synthesized carbons that include PFA-PEG, a high surface area carbon derived from a mixture of polyfurfuryl alcohol (PFA) and polyethylene glycol (PEG), and carbon nanotube (CNT).43,44 All the capacitors except carbon nanotube based electrodes were assembled in 1 M tetraethylammonium hexafluorophosphate dissolved in propylene carbonate. The CNT capacitor was tested in 1 M aqueous sulfuric acid using a polyvinyl alcohol (PVA) hydrogel membrane.44

Cycling study was done on YP50-based EDLC which was cycled up to 10000 cycles at 1 A/g and corresponding impedance data were collected intermittently during various stages of cycling (1000 cycle, 6000 cycle, and 10000 cycle). We used the collected data to track the degradation in EDLC performance using both the methods during cycling. For the studies, constant current charge/discharge measurements at various current densities and the electrochemical impedance data ranging from $10^{-3}$ Hz to $10^3$ Hz were measured using Reference 600 Gamry potentiostat/galvanostat.

FDAM was further used to study commercial 2600 F/2.5 V large EDLC.45 The capacitor module was sized in order to predict the electrode properties at the cell level and FDAM was used to analyze the EDLC performance.

Model Development

The modeling section will first discuss the development of suitable porous electrode model both in time and frequency domain. Afterwards, each model specific to each method will be developed with heavy consideration on the type of experimental data used. This includes varying the microscopic and device level description for both methods.

Porous electrode model.—In both TDCM and FDAM, it is assumed that there is no bulk concentration polarization in the electrode and no change in bulk physical properties such as the electrode and electrolyte conductivities during the charge/discharge process. The current densities in the matrix phase and solution phase can be expressed using Ohm’s law in equations 1 and 2.

$$i_1 = -\sigma \frac{\partial \phi_1}{\partial x}$$  \[1\]

$$i_2 = -k \frac{\partial \phi_2}{\partial x}$$  \[2\]

$$I_{cell} = i_1 + i_2$$  \[3\]

Eq. 3 is a charge-conservation statement, indicating that the cell current can be sourced solely from both the matrix and solution phases. It does not assume any parallel arrangement of impedance contribution.
coming from both the matrix and solution phases. With Eq. 3, a relation can be obtained which describe the connection between the change in spatial current density in solution and matrix to the interfacial current density:

\[
\frac{\partial i_2}{\partial x} = - \frac{\partial i_1}{\partial x} = -at_i \quad [4]
\]

The potential drop across the solution/electrode interface will be defined as \( \eta = \phi_1 - \phi_2 \), where \( \phi_1 \) is the potential at the solid matrix phase and \( \phi_2 \) is potential at the electrolyte/solution phase. This quantity is sometimes referred to as the ‘overpotential’. By combining Eqs. 1–4, a generalized equation can be obtained with the following boundary and initial conditions:

\[
\frac{\partial^2 \eta (x, t)}{\partial x^2} = \left( \frac{1}{\kappa} + \frac{1}{\sigma} \right) a t_i (\eta, t) \quad [5]
\]

\[
BC : \frac{\partial^2 \eta (L, t)}{\partial x^2} = \frac{I_{cell}}{\kappa}; \quad \frac{\partial \eta (0, t)}{\partial x} = - \frac{I_{cell}}{\sigma}; \quad [5a]
\]

\[
IC : \eta (x, 0) = 0 \quad [5b]
\]

In general, the interfacial current term \( i_2 (\eta, t) \) is non-linear and coupled with other equations, such as the diffusion equation and the Butler-Volmer equation, creating a highly non-linear and coupled system of partial differential equations (PDEs). However, suppose that the solution for \( \eta \) is found, either analytically or numerically, the potential drop across the porous electrode \( V_p \) can still be obtained through several algebraic steps. The equation thus obtained takes the form:

\[
V_p (t) = \phi_1 (0, t) - \phi_2 (L, t)
\]

\[
= \frac{L}{\kappa + \sigma} \left[ I_{cell} (t) + \frac{\sigma}{L} \int_0^t \frac{\partial \eta (x, t)}{\partial x} \, dx \right] + \eta (0, t) \quad [6]
\]

Assuming a symmetric sandwich configuration for the whole cell, the total potential drop across the cell \( V_0 \) can be obtained:

\[
V_0 (t) = 2V_p (t) + Z_{ESR} (t) I_{cell} (t)
\]

\[
= 2 V_0 \left[ \frac{2L}{\kappa + \sigma} \left[ I_{cell} (t) + \frac{\sigma}{L} \int_0^t \frac{\partial \eta (x, t)}{\partial x} \, dx \right]
\right. \\
+ \left. 2 \eta (0, t) + Z_{ESR} I_{cell} (t) \right] \quad [7]
\]

where \( V_0 \) is the initial voltage of a single electrode and \( Z_{ESR} \) is collective device impedance, in which the mathematical details vary depending upon the specific device.

A simplification can be obtained in the linearized regime of impedance spectroscopy. If Eq. 5 is transformed into Laplace domain, the interfacial current can be represented by a product of an interfacial admittance \( Y_n (\eta, t) \) and the Laplace-domain potential \( \eta (x, s) \):

\[
i_2 (\eta, s) = Y_n (s) \cdot \tilde{\eta} (x, s) \quad [8]
\]

where \( s \) denotes the Laplace variable. Substituting \( s = j \omega \), this transformation will help turning the generalized non-linear PDE into a linear second-order ODE:

\[
\frac{d^2 \tilde{\eta} (x)}{dx^2} = \left( \frac{1}{\kappa} + \frac{1}{\sigma} \right) a t_i \tilde{\eta} (x) \quad [9]
\]

\[
BC : \frac{d \tilde{\eta} (L)}{dx} = \frac{I_{cell}}{\kappa}; \quad \frac{d \tilde{\eta} (0)}{dx} = - \frac{I_{cell}}{\sigma}; \quad [9a]
\]

where \( \omega = \sqrt{\left( \frac{1}{\kappa} + \frac{1}{\sigma} \right) a t_i L} \). Solving for \( \tilde{\eta} \), the solution can be obtained in terms of hyperbolic functions:

\[
\tilde{\eta} = \frac{I_{cell} L}{\sqrt{v} \sinh \sqrt{v}} \left[ \frac{1}{\kappa} \cosh \left( \sqrt{v} x \right) \right. \\
+ \left. \frac{1}{\sigma} \cosh \left( \sqrt{v} (1 - x) \right) \right] \quad [10]
\]

Furthermore, by setting \( V_0 = 0 \) and turning Eq. 7 into the Laplace/frequency domain, an equation for the voltage drop across the whole device can be obtained:

\[
\tilde{V}_0 (j \omega) = 2 \tilde{V}_p (j \omega) + Z_{ESR} (j \omega) I_{cell}
\]

\[
= \frac{2L}{\kappa + \sigma} \left[ I_{cell} + \left( \frac{\sigma}{L} \right) \int_0^\infty \frac{d \eta (j \omega, p)}{dx} \, dp \right]
\]

\[
+ \eta (0, j \omega) + Z_{ESR} (j \omega) I_{cell} \quad [11]
\]

which can be further used to derive the impedance formula for the whole device or the cell impedance \( Z_0 \), by simply plugging in Eq. 10 into Eq. 11 and divide both sides by \( I_{cell} \):

\[
Z_0 (j \omega) = \tilde{V}_0 \quad \frac{2L}{\kappa + \sigma} \left[ 1 + \frac{\eta (0, j \omega)}{v \sinh \sqrt{v}} + Z_{ESR} (j \omega) \right] \]

\[
[12]
\]

where \( v = \sqrt{\left( \frac{1}{\kappa} + \frac{1}{\sigma} \right) a t_i L} \).

The above equation can be interpreted as a generalized impedance formula for any electrochemical device with symmetric porous electrodes. Furthermore, Eq. 5 coupled with Eq. 7 serve as the time-domain porous electrode equation while Eq. 12 serves as the frequency-domain porous electrode equation. For both TDCM and FDAM, these equations will be used identically.

There are two components in both TDCM and FDAM that need to be further specified:

1. The interfacial current \( i_2 (\eta, t) \) or equivalently the interfacial admittance \( Y_n (j \omega) \) representing microscopic level description.

2. The collective device impedance \( Z_{ESR} \) representing device level description.

The depth of derivations in these two components will be heavily influenced by the information that is obtainable from a given experimental data. In TDCM, chronopotentiometry data (time-domain) will be used to predict impedance spectroscopy data (frequency-domain). Since chronopotentiometry is not geared toward elucidating different microscopic phenomena, it is more practical to model the interfacial current as concise as possible, capturing only the most essential behavior. On the other hand, FDAM uses the impedance spectroscopy data (frequency-domain) to predict the chronopotentiometry data (time-domain). As a spectroscopic tool, EIS will elucidate many microscopic behaviors such as reaction-diffusion and double layer phenomena. Therefore, a successful fitting will require a more in-depth microscopic and device level description.

In the next sections, detailed derivation for the interfacial current/admittance current \( i_n \) or \( Y_n \) as well as the collective device impedance \( Z_{ESR} \) is given for both TDCM and FDAM.

**Time-domain current method (TDCM).**—Chronopotentiometry data is limited in how much microscopic phenomena it can elucidate, and usually, only equivalent series resistance and device capacitance can be obtained. Thus, it is more practical to model the collective device impedance as a pure external resistor, e.g. \( Z_{ESR} = R_{ESR} \); and the interfacial current as a compact double layer capacitance current:

\[
i_n (\eta, t) \approx i_{dl} = C_{dl} \frac{\partial \eta (x, t)}{\partial t} \quad [13]
\]

Inserting Eq. 13 into Eq. 5, the following parabolic PDE can be obtained:

\[
\frac{\partial^2 \tilde{\eta} (x, t)}{\partial x^2} = \left( \frac{1}{\kappa} + \frac{1}{\sigma} \right) a t_i \frac{\partial \eta (x, t)}{\partial t} \quad [14]
\]

\[
BC : \frac{\partial \tilde{\eta} (L, t)}{\partial x} = \frac{I_{cell}}{\kappa}; \quad \frac{\partial \tilde{\eta} (0, t)}{\partial x} = - \frac{I_{cell}}{\sigma}; \quad [14a]
\]

\[
IC : \eta (x, 0) = 0 \quad [14b]
\]
At this point, a numerical method can be used to solve it. However, TDCM will be easier to implement in a dimensionless form. Thus, the following dimensionless variables can be defined:\(^\text{27}\)

\[
I^* = \frac{I_{cell}}{V_0} \left( \frac{1}{\kappa} + \frac{1}{\sigma} \right); \quad \gamma = \frac{\kappa}{\sigma};
\]

\[
\eta^* = \frac{\eta}{V_0}; \quad \xi = \frac{\tau}{L};
\]

\[
\tau = \frac{L}{a_d C_{dl}} (\frac{1}{\kappa} + \frac{1}{\sigma})^{-1}; \quad \beta = \frac{R_{ESR}}{L} (\frac{1}{\kappa} + \frac{1}{\sigma})^{-1}; \quad V^* = \frac{V_0}{2V_0}
\]

This will turn the previous PDE into the following:

\[
\frac{\partial^2 \eta^* (\xi, \tau)}{\partial \xi^2} = -\frac{\partial \eta^* (\xi, \tau)}{\partial \tau} \quad \text{[15]}
\]

\[
BC : \frac{\partial \eta^* (1, \tau)}{\partial \xi} = \frac{I^*}{1 + \gamma}; \quad \frac{\partial \eta^* (0, \tau)}{\partial \xi} = - \frac{I^* \gamma}{1 + \gamma}; \quad \text{[15a]}
\]

\[
IC : \eta (\xi, 0) = 0 \quad \text{[15b]}
\]

The dimensionless cell potential \(V^*\) that accounts for potential drop due to capacitive contribution and the ohmic drop from the separator can then be further obtained as follow:

\[
V^* (\tau) = 1 + \frac{1}{1 + \gamma} \left[ I^* \gamma + \int_0^\tau \frac{\partial \eta^* (\xi, \tau)}{\partial \xi} d\xi \right] + \eta^* (0, \tau) + \frac{\beta I^*}{2} \quad \text{[16]}
\]

Eq. 15 is solved using the finite element analysis PDE toolbox in MATLAB to obtain the numerical solution for the dimensionless overpotential function \(\eta^*(\xi, \tau)\). The resulting solution was numerically differentiated to obtain the derivative of the dimensionless overpotential \(\frac{\partial \eta^*}{\partial \xi}\). Both overpotential and its derivative can be plugged into Eq. 16 to obtain the dimensionless cell potential, which contain two dimensionless model parameters, \(\gamma\) and \(\beta\), respectively.

The impedance formula can also be turned into its dimensionless form by defining the dimensionless angular frequency:

\[
\omega^* = \left( \frac{1}{\sigma} + \frac{1}{\kappa} \right) a_d C_{dl} L^2 \omega
\]

This will provide the following expression for the dimensionless impedance:

\[
Z^* (j \omega^*) = \frac{V^*}{T^*} = \left( \frac{1}{1 + \gamma} \right) \left[ \gamma + \frac{2 \gamma + (1 + \gamma^2) \cosh \sqrt{j \omega^*}}{\sqrt{j \omega^*} \sinh \sqrt{j \omega^*}} \right] + \frac{\beta}{2} \quad \text{[17]}
\]

This equation will be useful in evaluating the impedance spectra based on the information obtained by the chronopotentiometry data.

**Frequency-domain admittance approach (FDAM).**—An impedance data of an EDLC will typically feature diffusional effects from the diffusion charge layer, faradaic leakage, e.g., decomposing reaction, as well as interfacial contact resistance and capacitance. These effects can be systematically treated in a simple manner, under the linearized conditions of impedance spectroscopy.

Diffuse charge layer can be treated systematically by the Poisson-Nernst-Planck equations. These equations simply constitute a diffusion equation with a migration term for each ionic species as well as Gauss’ law. When the diffusion coefficient is assumed to be the same for the cation/anion, and the charge density is expressed as \(\rho = e (z_+ c_++ z_- c_-)\), the Poisson-Nernst-Planck equations can be collapsed into a single equation known as the Debye-Falkenhagen equation:\(^\text{27}\)

\[
\frac{\partial \rho^* (z, t)}{\partial t} = D \left( \frac{\partial^2 \rho^* (z, t)}{\partial z^2} - \frac{\rho^* (z, t)}{\lambda_D^2} \right) \quad \text{[18]}
\]

where \(\lambda_D\) is the Debye length. Furthermore, if the charge and concentration of ions and cations are symmetric (\(z_+ = z_- = Z\) and \(c_+ = c_- = c_0\)), the charge density \(\rho\) can be modelled through a Boltzmann-type of distribution:

\[
\rho = 2eZ c_0 \sinh \frac{Ze \phi}{k_B T} \quad \text{[19]}
\]

Eq. 26 can be linearized to obtain:

\[
\rho \approx \frac{2zeZc_0}{k_B T} \phi \quad \text{[20]}\]

which can then be further inserted into Eq. 25 to obtain a modified and linearized Debye-Falkenhagen equation with its boundary conditions as follows:\(^\text{27, 28}\)

\[
\frac{\partial \phi (z, t)}{\partial t} = D \left( \frac{\partial^2 \phi (z, t)}{\partial z^2} - \frac{\phi (z, t)}{\lambda_D^2} \right) \quad \text{[20a]}
\]

\[
BC : -k_{int} \frac{\partial \phi (0, t)}{\partial z} = \frac{\phi (0, t)}{Z_S^* (t)} \quad \phi (\infty, t) = 0 \quad \text{[20b]}
\]

where the first boundary condition is a simple statement that the interfacial current density at the compact/Stern layer is the same as the diffuse layer. By further transforming the PDE system into the Laplace domain and solving for \(\phi\), the solution can be transferred to an equation relating it to the interfacial admittance:

\[
Y_s (j \omega) = -k_{int} \frac{\partial \phi (0, j \omega)}{\partial z} = \frac{1}{Z_S (j \omega) + \frac{\eta_{0}}{\sqrt{\lambda_D j \omega}}} \quad \text{[21]}
\]

where \(\eta_{0} = \lambda_D^2 / D\) is the Debye time constant and \(Z_0 = \lambda_D / k_{int}\) is a coefficient associated with the diffuse layer impedance (the units are in \(\Omega \cdot cm^2\)).

To obtain an expression for the compact/Stern layer impedance \(Z_S\), it may be assumed that both faradaic and non-faradaic phenomena are present: double layer polarization, which is responsible for the primary charge storing mechanism, and a decomposing side reaction. This results in the following non-linear equation to handle for the interfacial current:

\[
i_n = C_{dl} \frac{\partial \Delta \Phi_S}{\partial t} + j_0 \left[ \frac{C_O}{C_R} \exp \left( \frac{\alpha n F \Delta \Phi_S}{k_B T} \right) \right] - \frac{C_R}{C_R} \exp \left( \frac{(1 - \alpha) n F \Delta \Phi_S}{k_B T} \right) \quad \text{[22]}
\]

Upon linearization, transformation into the Laplace domain, and substitution of variable \(s = j \omega\), one may obtain the following expression for the interfacial current density:

\[
i_n = j \omega C_{dl} + j_0 \left[ \frac{C_O}{C_R} - \frac{C_R}{C_R} \right] \frac{n F \Delta \Phi_S}{k_B T} \quad \text{[23]}
\]

If kinetic control is assumed, effectively neglecting concentration gradient between the interface and the bulk solution due to diffusion (\(\Delta C_O \rightarrow 0\) and \(\Delta C_R \rightarrow 0\)) and define the leakage charge transfer resistance as \(R_L = \frac{\eta_{0}}{2k_B T}\) then the compact layer admittance will be defined by the following:

\[
Y_s (j \omega) = \frac{1}{Z_S (j \omega)} = \frac{\bar{i}_n}{\Delta \Phi_S} = j \omega C_{dl} + \frac{1}{R_L} \quad \text{[24]}
\]

Plugging Eq. 24 into Eq. 21, the full expression for the interfacial admittance can be obtained as:

\[
Y_s (j \omega) = \frac{1}{j \omega C_{dl} + \frac{\eta_{0}}{2k_B T}} + \frac{\eta_{0}}{\sqrt{\lambda_D j \omega}} \quad \text{[25]}
\]

This leaves only the contact resistance and capacitance to be modeled. It is well known that resistivity will increase when EDLCs are...
The LMFIT package available in Python.46 The LMFIT package supports non-linear regression fitting. The regression procedure is handled by L where the resistance of two different contributions: the previously mentioned contact resistance and capacitance, as well as an external resistance, which include both separator, wire, and solution/electrolyte resistances combined.

\[
Z_{ESR}(j\omega) = \frac{1}{j\omega C_c + \frac{1}{\sigma}} + R_{ext}
\]  

Therefore, the macroscopic impedance formula can be obtained as

\[
Z_\mu(j\omega) = \frac{2L}{\kappa + \sigma} \left[ 1 + \frac{2 + \left(\frac{2}{\kappa} + \frac{1}{\sigma}\right) \cosh \nu}{\nu \sinh \nu} \right] + \frac{j\omega L_\mu + R_{ext}}{N}
\]

where \(L_\mu\) is the inductance of a single EDLC in the module, and \(N\) is the number of EDLCs stacked in parallel. The basic assumption being taken here is that the inductance effect of a module is contributed equally from a single EDLC. This assumption can be relaxed, where the inductance effect may be assumed to have come collectively from a single module. However, since the inductance effect is not an important component of the device, spreading identical inductors to each EDLC in parallel is a justifiable assumption.

Eqs. 25, 27, and Eq. 28 are used together to perform the complex non-linear regression fitting. The regression procedure is handled by the LMFIT package available in Python.46 The LMFIT package supports not only multi-dimensional parametric non-linear regression but also statistical and error analysis, making it an invaluable tool in the fitting process of the impedance equations obtained previously.

The model is then validated by using the parameters obtained from impedance spectroscopy to predict the galvanostatic discharge curve. To perform this simulation, the voltage relation of the EDLC in galvanostatic conditions needs to be obtained in the Laplace domain:

\[
V_\mu(s) = \frac{2V_0}{s} + \frac{I_{cell}}{s} Z_\mu(s)
\]
Table II. TDCM model parameters (γ and β) and experimental parameter (I*) used to fit charge/discharge data and impedance plots of EDLCs.

| Sample  | Surface area (m²/g) | Specific capacitance (F/g) | I (mA/cm²) | I* | γ | τc | β |
|---------|---------------------|---------------------------|------------|----|---|----|---|
| YP50    | 1600                | 19.56                     | 2.27       | 0.086 | 0.0006 | 12 | 0.2 |
| ACS     | 3000                | 24.12                     | 2.32       | 0.067 | 0.0008 | 14.75 | 0.1 |
| C1000   | 1600                | 15.3                      | 41.8       | 0.16  | 0.0028 | 5.9 | 0.33 |
| C6000   | 1600                | 15.2                      | 41.8       | 0.16  | 0.0028 | 5.8 | 0.47 |
| C10000  | 1600                | 14.5                      | 41.8       | 0.16  | 0.0028 | 5.7 | 0.72 |

Eq. 29 can be inverted into the time domain using the Bromwich integral.

\[ V_\psi(t) = 2V_0 + \frac{1}{2\pi i} \int_{\gamma - i\infty}^{\gamma + i\infty} e^{st} I_{\text{cell}}(s) Z_\psi(s) ds \quad [30] \]

where \( \sigma \) is a vertical contour in the complex plane such that all singularities/poles in the function \( V_\psi(s) \) can be found in the left side of the plane. Unfortunately, closed-form analytical expression will be difficult to be found for Eq. 30 and numerical methods must be employed. Many specialized methods for numerical inverse Laplace transform exist such as the Talbot method, Gaver-Stehfest method, Papoulis Legendre polynomial method, Durbin-Crump method, and Piessens Gaussian quadrature method. Different methods will specialize in different types of functions exhibiting a wide variety of behaviors and singularities. For this work, the Gaver-Stehfest method is employed, which is very useful for precision in small-time resolution. The Gaver-Stehfest method will provide an approximate series solution of the following form:

\[ V_\psi(t) \approx 2V_0 + \ln 2 \sum_{n=1}^{N} \frac{I_{\text{cell}} t_n}{n \ln 2} Z_\psi \left( \frac{n \ln 2}{t} \right) \quad [31] \]

In principle, the series should diminish the error as \( N \) gets larger. However, due to the nature of asymptotic expansion series solutions, practical applications will only use roughly with \( 6 \leq N \leq 20 \). In this work, \( N = 6 \) was used and will be sufficient for all discharge simulations.

**Results and Discussion**

Table I provides values for the set parameters used in the analysis of impedance data, as well as the discharge simulation for capacitors made using two commercial carbons, YP50 and ACS. The fixed parameters include the following: the length of electrode based on experimental observation, electrode and electrolyte conductivity based on literature values, and specific interfacial area, based on the pore volume and N\(_2\) BET surface area of each carbon material.

---

**Figure 3.** (a) Fitted charge/discharge data of YP50 based EDLC cycled from 0 to 2.5 V at 2 A/g over 10000 cycles. TDCM predicting change in (b) Nyquist, (c) Real capacitance Bode plot and (d) Imaginary capacitance Bode plot as a function of cycling.
Time domain current method (TDCM).—Three dimensionless parameters, $I^*$, $\gamma$ and $\beta$ are used to describe the voltage-time curve as shown in Eq. 16. The parameter $I^*$ is determined by the experimental conditions during constant current discharge. Figure 2a shows the fitted experimental discharge data of EDLC made using two different carbon electrodes charged to 2.5 V. The specific cell capacitance of two commercial carbons, YP50 and ACS was 19.56 F/g and 24.12 F/g, respectively, when measured at a current density of 0.1 A/g. Table II summarizes the key parameters used to fit the discharge curve. The model is then validated by fitting the impedance plot of the capacitors. Figures 2b and 2c shows the simulated dimensionless real and imaginary capacitance plot as a function of frequency. The model accurately predicts the time constant of the capacitor (Figure 2b). Some discrepancy was observed in the prediction of the real capacitance at the intermediate and high-frequency region. This discrepancy can be attributed to the lack of electrode morphological/microstructural details in the model that contributes to interfacial capacitance related to pore geometry, particle packing, and compaction.

The capacitance fading and change in impedance with cycling are often used to determine cycling stability. Electrode impurities and solvent play a vital role in inducing parasitic faradaic reactions that result in the formation of deleterious compounds leading to pore clogging in electrodes. The pore clogging often manifests itself in increasing the resistance of the capacitor which can be seen clearly in the impedance spectra. This can be represented by a change in the model parameter $\beta$. Figure 3a shows the discharge of EDLC made using YP50 carbon cycled over 10,000 cycles when cycled at 2 A/g. The discharge curve shows linear behavior and shows very small change up to 6000 cycles. After 10,000 cycles, we see an increase in ohmic drop due to increased resistance as well as over 6% fading in capacitance. The Bode plot of the capacitor (Figures 3b–3d) starts to show more distinct changes with cycling. The impedance at higher frequency shows increasing trend while the time constant also increases with cycling. These changes can be mainly attributed to increased resistance due to electrolyte loss. The model can accurately represent the increased impedance contribution due to aging as seen from the changing in the value of $\beta$ from 0.33 to 0.72 as shown in Table II.

To further assess the impact of the model parameters on the capacitor, voltage –time discharge curves and impedance plots were simulated for various values of $I^*$, $\gamma$ and $\beta$. Figure 4a shows the effect of $I^*$ on a simulated voltage-time curve. For small values of $I^*$, the voltage profile is linear and resembles an ideal capacitor behavior. As the value of $I^*$ is increased, the voltage varies non-linearly at short discharge time as seen by the curvature in voltage profile. The effective utilization of charge ($\tau l^*$) is also reduced to 68% of the total charge stored. The curvature in the voltage profile at high current density may be attributed to non-uniform current distribution across the electrode at shorter discharge times. At these higher current densities, change in $\beta$ leads to considerable ohmic drop during discharge and the effective utilization of charge further drops to 20%.

The effect of varying $\gamma$ from 0.08 to 0.8 on the cell potential and energy efficiency is shown in Figure 4b and Figure 4c. At higher load, current densities (large values of $I^*$), the curvature in the voltage profile was reduced with an increase in $\gamma$ and the effective charge utilization significantly decreased (Figure 5a). Increasing $\gamma$ also has an adverse effect on energy efficiency $E_*$, which asymptotically decreases (Figure 5b). The energy efficiency $E_*$ was computed as:

$$E^* = I^* \gamma \int_0^t \frac{V^* \gamma}{t}$$

where $\tau_c$ is the cutoff dimensionless time at which the capacitor is fully discharged.

Figure 5 shows the impact of $\gamma$ and $\beta$ on dimensionless Nyquist, real and imaginary capacitance Bode plot. The dimensionless Nyquist plot shows three distinct regions: a real intercept at a high-frequency region corresponding to the series resistance of the capacitor, a Warburg region at an intermediate frequency that considers the diffusion effects in the porous electrode and a vertical slope at low frequency indicating the capacitive behavior (Figure 5a). We saw a gradual increase in the real intercept with $\gamma$ which starts to significantly increase when $\gamma$ becomes greater than 0.01. While the overall real impedance increases with $\gamma$, the Warburg contribution to the impedance becomes smaller. Figure 5b shows that increasing $\gamma$ decreases the time constant which is consistent with decreased discharge time in the time domain as shown in Figure 4b. The increased overall impedance along with decreased time constant shows that the overall energy efficiency of the
Figure 5. Plot of (a) Dimensionless Nyquist plot and (b) Imaginary capacitance Bode plot as a function of $\gamma$. (c) Dimensionless Nyquist plot and (d) Imaginary capacitance Bode plot as a function of $\beta$.

capacitor decreases with increase in $\gamma$. The increase in $\beta$ significantly impacts both the Warburg resistance as well as the real intercept indicating decreased bulk electrolyte conductivity as shown in Figure 5c. This increased resistance with $\beta$ was also reflected in increased time constant (Figure 5d).

It is to be noted that TDCM is based on a simplistic two parameter model necessary to fit the chronopotentiometry and hence it captures only the overall contribution of porosity effect on the conductivity of the electrode ($\gamma$) and resistance ($\beta$) of the capacitor. To get more details on the electrode at the microscopic level, we propose a second method, FDAM, which is based on fitting impedance data.

**Frequency-Domain Admittance Approach (FDAM).—** Figure 6a shows impedance data for EDLCs made from YP50 and ACS carbon with their respective fitted curves using Eq. 25 and 27. The model uses 7 parameters as derived from the previous section ($G_0$, $\tau_D$, $R_L$, $C_{dl}$, $C_c$, $R_c$, and $R_{ext}$) to describe the behavior of capacitor ranging from $10^5$ Hz to $10^{-3}$ Hz as shown in Table III. Overall, the impedance model shows very precise fitting with uncertainty below 10% for most parameters. A good fit with minimal error was also obtained for EDLCs made from PFA-PEG and CNT carbons, as shown in the Supplementary Material (Figure S1-S2 and Table S1 –S2). Figure 6b represents the discharge simulation using Gaver-Stehfest method compared to the experimental discharge data. The simulation validates the model and predicts the discharge curves, resulting in an accurate prediction of device capacitance, energy, and power density, as shown in Table IV. As an example, the capacitance of YP50 was calculated to be 20.0 F/g and the simulation predicts 19.8 F/g corresponding to a 1.4% deviation from the actual value.

The double layer capacitance of ACS was shown to be higher ($12.40 \pm 0.01 \mu F/cm^2$) than that of YP50 ($4.23 \pm 0.01 \mu F/cm^2$). This is consistent with the larger surface area as well as the slightly larger pore size of ACS as shown in Table III. Both devices show Debye time constant at an order of seconds ($6.1 \pm 0.6 s$ for ACS and $5.8 \pm 0.6 s$ for YP50), which correspond to a Debye screening length of 30 $\sim$ 100 nm when micropore diffusion coefficient is assumed (at an order of $10^{-14}$ to $10^{-15}$ m$^2$/s). This result is expected for applying a simple model such as the Gouy-Chapman-Stern model to a hierarchically complex microporous carbon used in both devices. In addition, the model was also able to parametrize the contact resistances of each device. The YP50 carbon has a higher contact resistance of $20.3 \pm 0.2 \Omega/cm^2$ while the ACS carbon has $4.4 \pm 0.2 \Omega/cm^2$, indicating that the former suffers
Figure 6. (a) Nyquist plot, imaginary and real capacitance Bode plot of YP50 and ACS based EDLCs with the fitted model. (b) Comparison of discharge experimental data (dashed) and FDAM model simulation (bold) for YP50 and ACS based EDLCs.

from interfacial contact issue and poorer packing in comparison to the latter. It is to be noted that the experimental data was collected using pressed carbon disc and stainless steel spacer was used as the current collector.

Figure 7 provides the impedance fitting for YP50 based capacitor as a function of cycling and Table III shows the fitted parameters for all cycling. As with the previous data, precise fitting was obtained through the model with most parameters obtaining an error of less than 10%. Since each data correspond to different cycling, the fitting results show the model’s ability to quantitatively capture the cycling effects through its resistive parameters. Furthermore, the interfacial contact resistance ($R_c$) stays within a similar value indicating that the
Table III. Fitted parameters for YP50 and ACS carbon based EDLC obtained through complex non-linear regression of impedance data. YP50 did not require any faradaic leakage. Note the increase in external resistance $R_{\text{ext}}$ for carbon cycling data.

| Parameters | YP50         | ACS         | Cycle 1000 | Cycle 6000 | Cycle 10000 |
|------------|--------------|-------------|------------|------------|-------------|
| $G_0$ ($\Omega \cdot \text{cm}^2$) | $(8.2 \pm 0.2) \cdot 10^5$ | $(3.6 \pm 0.1) \cdot 10^5$ | $(5.1 \pm 0.1) \cdot 10^4$ | $(5.1 \pm 0.1) \cdot 10^4$ | $(5.0 \pm 0.2) \cdot 10^4$ |
| $\tau_D$ (s) | $5.8 \pm 0.6$ | $6.1 \pm 0.6$ | $0.26 \pm 0.01$ | $0.26 \pm 0.01$ | $0.24 \pm 0.01$ |
| $R_L$ ($\Omega \cdot \text{cm}^2$) | $-\cdot 10^8$ | $(3.5 \pm 0.2) \cdot 10^7$ | $(2.7 \pm 0.2) \cdot 10^7$ | $(2.8 \pm 0.6) \cdot 10^7$ | $(2.6 \pm 0.6) \cdot 10^7$ |
| $C_D$ ($\mu \text{F/cm}^2$) | $4.23 \pm 0.01$ | $12.40 \pm 0.01$ | $3.65 \pm 0.01$ | $3.81 \pm 0.02$ | $3.83 \pm 0.01$ |
| $C_c$ ($\mu \text{F/cm}^2$) | $3.4 \pm 0.1$ | $6.3 \pm 0.6$ | $18 \pm 1$ | $38 \pm 4$ | $48 \pm 5$ |
| $R_e$ ($\Omega \cdot \text{cm}^2$) | $20.3 \pm 0.2$ | $4.4 \pm 0.2$ | $0.50 \pm 0.01$ | $0.40 \pm 0.01$ | $0.42 \pm 0.01$ |
| $R_{\text{ext}}$ ($\Omega \cdot \text{cm}^2$) | $3.2 \pm 0.2$ | $3.2 \pm 0.1$ | $1.39 \pm 0.01$ | $2.20 \pm 0.01$ | $3.43 \pm 0.01$ |

Table IV. Calculated device capacitance, specific energy and power from experiment and simulation for YP50 and ACS carbon as well as the carbon cycling data.

|          | YP50 (Experimental) | YP50 (Simulation) | ACS (Experimental) | ACS (Simulation) |
|----------|----------------------|-------------------|--------------------|------------------|
| $C_{\text{EDLC}}$ ($\text{F/g}$) | $19.6$ | $19.4$ | $24.6$ | $24.5$ |
| $E_{\text{EDLC}}$ ($\text{Wh/kg}$) | $17.0$ | $16.8$ | $21.3$ | $21.3$ |
| $P_{\text{EDLC}}$ ($\text{kW/kg}$) | $0.125$ | $0.125$ | $0.125$ | $0.125$ |
| Cycle 1000 | Cycle 1000 (Simulation) | Cycle 6000 (Exp.) | Cycle 6000 (Simulation) | Cycle 10000 (Exp.) | Cycle 10000 (Simulation) |
| $C_{\text{EDLC}}$ ($\text{F/g}$) | $15.4$ | $14.0$ | $15.3$ | $14.4$ | $14.6$ | $14.2$ |
| $E_{\text{EDLC}}$ ($\text{Wh/kg}$) | $13.3$ | $12.2$ | $13.2$ | $12.5$ | $12.6$ | $12.4$ |
| $P_{\text{EDLC}}$ ($\text{kW/kg}$) | $2.5$ | $2.5$ | $2.5$ | $2.5$ | $2.5$ | $2.5$ |

packing of the carbon particles was not affected by long term cycling. However, the external resistance of the device changes with an appreciable increase from $1.39 \ \Omega \cdot \text{cm}^2$ to $3.42 \ \Omega \cdot \text{cm}^2$. The contribution to external resistance include contact resistance due to current collectors and primarily the electrolyte resistance that is outside of the porous electrode, such as the separator. The increase in external resistance can thus be attributed to loss of electrolyte conductivity in separator due to solvent decomposition, which is a well-known ageing phenomenon in EDLCs.57 Table IV also compiles the calculated device capacitance, specific energy, and specific power.

Figure 7. Nyquist plot as well as imaginary and real capacitance Bode plots for YP50 based EDLC collected as a function of cycling and their corresponding fitted model.
In order to further demonstrate the validity of FDAM model, we fitted the model for a commercial 2600F/2.5 V capacitor. It was assumed that the module comprises of various cells connected in series and parallel. For the modeling, the electrode capacitance was assumed to be 100 F/g with a bulk density of 0.6 g/cc and using these values, the electrode area and thickness for each cell was computed. We then fitted experimental impedance data measured at a bias voltage of 2.0 V (Figure 8a) to compute the fitted parameters as shown in Table V. The discharge data was then simulated and compared with experimental discharge data measured at a constant cell current of $I = 200$ A at a voltage window of 1.3 V to 2.5 V as shown in Figure 8b. The simulation of the discharge curve agrees well with the discharge data for the cell module. Furthermore, the calculated capacitance, energy and power shows remarkable agreement, with an error as little as 0.2%
Table V. Fitted parameters for the 2600 F/2.5 V cell obtained through complex non-linear regression of impedance data. Notice that only four parameters were needed to describe the impedance. Calculated device capacitance, energy, and power from experiment and simulation of a 2600 F/2.5 V cell.

| Parameters | Values |
|------------|--------|
| $C_{dl}$ ($\mu$F/cm$^2$) | 5.49 ± 0.02 |
| $L_{eq}$ (mH cm$^2$) | 0.47 ± 0.02 |
| $R_{ext}$ ($\Omega$ cm$^2$) | 1.52 ± 0.03 |
| $\kappa$ (mS/cm) | 10.2 ± 0.4 |
| $\omega$ (rad/s) | 1000 |
| $\eta$ (deg) | 45 |
| $\phi$ (deg) | 0 |
| $\theta$ (deg) | 45 |
| $\alpha$ (deg) | 45 |

on the calculated device capacitance as shown also in Table V. It was found that the impedance characteristics can be adequately described using only the double layer capacitance. Furthermore, we predicted conductivity of the electrolyte to be 10.2 ± 0.4 mS/cm which is in close agreement with electrolyte conductivity of a typical EDLC.

For parametric studies, the base parameters were taken from the fitting results for the YP50 carbon. Figure 9 shows parametric study done on double layer capacitance. When the double layer capacitance is increased, impedance spectroscopy shows a clearer separation between the diffuse region and the capacitive region at intermediate and lower frequency, illustrating the effect of the larger difference in characteristic relaxation frequency. As expected, in the imaginary and real capacitance Bode plots, we see increase in low-frequency real capacitance response and the peak of the imaginary capacitance as $C_{dl}$ is increased. In the time domain, the double layer capacitance changes the slope of the curve or the differential capacitance of the device. This will lead to increase in device capacitance and energy density.

A parametric study was also done on electrode thickness $L$, shown in Figure 10. To accentuate the effect, the base parameters were changed such that the dimensionless current $I^*$ ≥ 1. Varying the electrode length from 150 μm to 250 μm, the model predicts an increase in ohmic drop in the discharge simulation, which can be attributed to the simple consequence of adding more resistivity in the electrode as the thickness is increased. In the impedance spectra, this is also observed with the overall increase in real impedance at all frequencies as shown with the Bode plots. The relaxation peak at the imaginary capacitance is also incomplete, signifying a very low value for the characteristic frequency of the whole device. It must be noted that to make the effect much more noticeable, significant reduction of electrolyte conductivity was needed. Such reduction may not be necessary if bulk/macroscopic concentration polarization is assumed, where thicker electrode can have a large impact on how concentration of ions are distributed across the porous electrode.

The electrolyte conductivity also provides an interesting parameter to analyze as many research have been dedicated to obtain electrolytes with higher conductivity. Figure 11 shows parametric study done on the electrolyte conductivity, starting at a much lower value to elucidate the effect further. At a very low conductivity value, a broadening in the diffuse region is observed, varying the phase angle from below 45° to above. While it is usually true that the distributive effects of the porous electrode show at this particular region of the electrode, all models indicate a phase angle of 45° ± 5°. The variance in phase angle is attributed to the coupling between the distributive effects from the porous electrode with the diffuse layer contribution. The span of the

Figure 9. Parametric study demonstrating the effect of increasing compact double layer capacitance $C_{dl}$ on (a) Imaginary capacitance Bode plot, (b) Real capacitance Bode plot, (c) Nyquist plot and (d) Galvanostatic discharge data.
Figure 10. Parametric study demonstrating the effect of electrode thickness $L$ on (a) Imaginary capacitance Bode plot, (b) Real Bode plot, (c) Nyquist plot and (d) Galvanostatic discharge data.

Figure 11. Parametric study demonstrating the effect of electrolyte conductivity $\kappa$ on (a) Imaginary capacitance Bode plot, (b) Real Bode plot, (c) Nyquist plot and (d) Galvanostatic discharge data.
diffuse region, i.e. its real impedance, affect the discharge behavior where larger diffuse region lowers the time that the device takes to discharge, which further lowers device capacitance, energy and power density. This result is also consistent with TDCM.

Conclusions

Time-Domain Current Method (TDCM) and Frequency-Domain Admittance Method (FDAM) were described as tools to interpret and predict electrochemical data of EDLCs in both time-domain and frequency domain. The equations used for both methods are summarized in Table VI. Both methods were tested on YPSO and ACS carbon devices as benchmarks and an EDLC measured at different cycles to test both methods’ capability to explain the impact of cycling on EDLC performance. In TDCM, normalized impedance characteristics were accurately described through dimensionless parameters $\gamma$ and $\beta$ obtained from discharge curves. In FDAM, discharge curves, specific energy, and power were predicted through parameters relevant to the double layer interface and the porous electrode, obtained from impedance spectra. The influence of various key model parameters in TDCM ($\gamma^\ast$, $\beta^\ast$) and in FDAM ($C_{dl}$, $L$, and $\kappa$) on the discharge performance of the capacitors as well as their impedance spectra have been elucidated. The range of validity in both methods and summary of influence in key parameters have also been summarized.

Acknowledgments

This work was supported by the National Science Foundation ASSIST Nanosystems ERC under Award Number EEC-1160483. The authors would also like to acknowledge the financial support from NSF I/UCRC Center for Dielectrics and Piezoelectrics and ETCE Research Development grant from The Pennsylvania State University.

| List of Symbols |
|-----------------|
| $a$ | specific interfacial area, cm$^2$/cm$^3$ |
| $c_0$ | concentration of electrolyte solution, M |
| $c_c$ | concentration of cations in solution, M |
| $C_{dl}$ | Stern/compact double-layer capacitance, $\mu$F/cm$^2$ |
| $C_e$ | interfacial contact capacitance, $\mu$F/cm$^2$ |
| $C_p$ | concentration of oxidants in solution, M |
| $C_r$ | concentration of reductants in solution, M |
| $C'$ | real capacitance, $\left[\text{Ret}(1/\text{JoZ})\right]$ |
| $C^{\prime\prime}$ | imaginary capacitance, $\left[\text{Im}(1/\text{JoZ})\right]$ |
| $C^{\prime\prime\prime}$ | dimensionless real capacitance, $\left[C/C_{\text{max}}\right]$ |
| $C^{\prime\prime\prime\prime}$ | dimensionless imaginary capacitance, $\left[C^{\prime\prime}/C_{\text{max}}\right]$ |
| $D$ | diffusion coefficient, cm$^2$/s |

Greek

$\alpha$ | charge transfer coefficient |
$\beta$ | dimensionless collective device impedance |
$\gamma$ | dimensionless conductivity, $[\text{cm}^2/\text{s}]$ |
$\Delta \phi_S$ | potential difference at the Stern layer, V |
$\eta$ | potential difference of solid electrode and electrolyte, V |
$\eta^\ast$ | dimensionless overpotential, $[\eta/V_0]$ |
$\kappa$ | electrolyte conductivity, S/cm |
$\kappa_{\text{ext}}$ | electrolyte conductivity near the interface, S/cm |
$\lambda$ | Debye length, cm |
$\xi$ | dimensionless length, $[\text{cm}/L]$ |

Table VI. Summary of equations used to perform fitting and simulation for TDCM and FDAM.

| TDCM Time-Domain Current Method | FDAM Frequency-Domain Admittance Method |
|-------------------------------|----------------------------------------|
| Goal                          | Fit frequency-domain data, simulate time-domain data |
| Equation(s) for fitting       | $Z_{E_{\text{SR}}} (j\omega) = \frac{j\lambda^2}{\kappa + \frac{1}{\kappa}} + \left[(\frac{\lambda}{\kappa}) + \frac{1}{\kappa}\right] + \left[(\frac{\lambda}{\kappa})^2 + \frac{1}{\kappa}\right] + \frac{1}{\kappa}$ |
| Equation(s) for simulation    | $Y_{\text{DF}} (j\omega) = \frac{j\lambda^2}{\kappa + \frac{1}{\kappa}} + \left[(\frac{\lambda}{\kappa}) + \frac{1}{\kappa}\right] + \left[(\frac{\lambda}{\kappa})^2 + \frac{1}{\kappa}\right] + \frac{1}{\kappa}$ |

where $\lambda$ is obtained by numerical simulation of the following PDE:

$$\frac{\partial^2 \eta}{\partial \xi^2} + \frac{\partial \eta}{\partial \xi} = 0$$

with $\xi$ being the distance across porous electrode, m.

Other quantities are:

- $\lambda$ = electrochemical cell, cm$^2$ |
- $\kappa$ = current density in the solid matrix/electrode phase, A/cm$^2$ |
- $\mu$ = current density in the electrolyte phase, A/cm$^2$ |
- $\nu$ = current of electrochemical cell, A/cm$^2$ |
- $\delta$ = current density of electrochemical cell, A/cm$^2$ |
- $\eta^*$ = dimensionless collective device impedance, $\Omega$ cm$^2$ |
- $\xi$ = dimensionless overpotential, $[\eta/V_0]$ |
- $\kappa_{\text{ext}}$ = electrolyte conductivity near the interface, S/cm |
- $\lambda$ = Debye length, cm |
- $\xi$ = dimensionless length, $[\text{cm}/L]$ |
- $\eta$ = potential difference at the Stern layer, V |
- $\Delta \phi_S$ = potential difference at the Stern layer, V |
- $\kappa$ = electrolyte conductivity, S/cm |
\( \rho \) charge density, C/cm\(^3\)
\( \sigma \) solid matrix/electrode conductivity, S/cm
\( \tau \) dimensionless time, \([t/\alpha C_d L^2(1/k + 1/\sigma)^{-1}]\)
\( \tau_{el} \) cutoff dimensionless time
\( \tau_{dl} \) diffuse layer time constant, s
\( \phi_1 \) potential in the solid matrix/electrode phase, V
\( \phi_2 \) potential in the electrolyte phase, V
\( \omega \) angular frequency, rad/s
\( \omega^* \) dimensionless angular frequency, \([\alpha C_d L^2 \omega (1/\sigma + 1/k)]\)

References

1. H. Budde-Meieres et al., *Proc. Inst. Mech. Eng. Part D J. Automob. Eng.*, 227, 761 (2013).
2. N. S. Choi et al., *Angew. Chemie - Int. Ed.*, 51, 9994 (2012).
3. M. S. Whittingham, *Proc. IEEE*, 100, 1518 (2012).
4. H. D. Yoo, E. Markevich, G. Salitra, D. Sharon, and D. Aurbach, *J. Power Sources*, 172, 2930 (2007).
5. P. Sharma and T. S. Bhatti, *Energy Convers. Manag.*, 40, 332 (2000).
6. W. Gu and G. Yushin, *Wiley Interdiscip. Rev. Energy Environ.*, 3, 424 (2014).
7. P. Sharma and T. S. Bhatti, *Energy Convers. Manag.*, 51, 2901 (2010).
8. G. Yu, X. Xie, L. Pan, Z. Bao, and Y. Cui, *Nano Energy*, 2, 213 (2013).
9. L. L. Zhang, Y. Gu, and X. S. Zhao, *J. Mater. Chem. A*, 1, 9395 (2013).
10. H. Matsuda and P. Delahay, *J. Phys. Chem.*, 64, 332 (1960).
11. H. Matsuda, *J. Phys. Chem.*, 64, 336 (1960).
12. H. Matsuda, *J. Phys. Chem.*, 64, 339 (1960).
13. S. K. Rangarajan, *Can. J. Chem.*, 41, 983 (1963).
14. S. K. Rangarajan, *Can. J. Chem.*, 41, 1007 (1963).
15. S. K. Rangarajan, *Can. J. Chem.*, 41, 1469 (1963).
16. M. Z. Bazant, K. Thornton, and A. Ajdari, *Phys. Rev. E*, 70, 1 (2004).
17. P. M. Biesheuvel and M. Z. Bazant, *Phys. Rev. E*, 81, 1 (2010).
18. P. M. Biesheuvel, Y. Fu, and M. Z. Bazant, *Phys. Rev. E*, 83 (2011).
19. P. M. Biesheuvel, S. Forada, M. Levi, and M. Z. Bazant, *J. Solid State Electrochem.*, 18, 1365 (2014).
20. M. Z. Bazant, B. D. Storey, and A. A. Kornyshev, *Phys. Rev. Lett.*, 106, 046102 (2011).
21. J. R. Macdonald, *J. Phys. Condens. Matter*, 22, 1 (2010).
22. J. R. Macdonald, L. R. Evangelista, E. K. Lenzn, and G. Barbero, *J. Phys. Chem. C*, 115, 7648 (2011).
23. J. R. Macdonald, *J. Phys. Chem. A*, 115, 13370 (2011).
24. L. R. Evangelista, E. K. Lenzn, G. Barbero, and J. R. Macdonald, *J. Phys. Condens. Matter*, 23, 485005 (2011).
25. J. R. Macdonald, *J. Phys. Chem. C*, 117, 23433 (2013).
26. J. Lelis, J. R. Macdonald, and G. Barbero, *J. Phys. D. Appl. Phys.*, 49, 25503 (2016).
27. M. B. Singh and R. Kant, *J. Electroanal. Chem.*, 704, 197 (2013).
28. M. B. Singh and R. Kant, *J. Phys. Chem. C*, 118, 5122 (2014).
29. M. B. Singh and R. Kant, *J. Phys. Chem. C*, 118, 8766 (2014).
30. J. Fuller, Thomas F. Doyle, and Marc. Newman, *J. Electrochem. Soc.*, 141, 1 (1994).
31. D. Dunn and J. Newman, *J. Electrochem. Soc.*, 146, 4560 (1999).
32. D. Dunn and J. Newman, *J. Electrochem. Soc.*, 147, 99 (2000).
33. D. Dunn and J. Newman, *J. Electrochem. Soc.*, 147, 2930 (2000).
34. A. M. Johnson and J. Newman, *J. Electrochem. Soc.*, 118, 510 (1971).
35. V. Srinivasan and J. W. Weidner, *J. Electrochem. Soc.*, 146, 1650 (1999).
36. D. Dunn and J. Newman, *J. Electrochem. Soc.*, 147, 820 (2000).
37. C. Lin, J. A. Ritter, B. N. Popov, and R. E. White, *J. Electrochem. Soc.*, 146, 3168 (1999).
38. C. Lin, B. N. Popov, and H. J. Ploehn, *J. Electrochem. Soc.*, 149, A167 (2002).
39. H. Kim and B. N. Popov, *J. Electrochem. Soc.*, 150, A1153 (2003).
40. G. Sikha, R. E. White, and B. N. Popov, *J. Electrochem. Soc.*, 152, A1682 (2005).
41. S. Devan, V. R. Subramanian, and R. E. White, *J. Electrochem. Soc.*, 151, A905 (2004).
42. S. Devan, V. R. Subramanian, and R. E. White, *J. Electrochem. Soc.*, 152, A947 (2005).
43. W. Q. E. Dorjpalam, R. Rajagopalan, and C. A. Randall, *ChemSusChem*, 7, 1162 (2014).
44. J. Kalupson, D. Ma, C. A. Randall, R. Rajagopalan, and K. Adu, *J. Phys. Chem. C*, 118, 2943 (2014).
45. W. Lajnef, J. M. Vinassa, O. Briat, S. Azzopardi, and E. Woirgard, *J. Power Sources*, 168, 553 (2007).
46. M. Newville, T. Stensitzki, D. B. Allen, and A. Ingargiola, (2014).
47. A. Talbot, *I MA J. Appl. Math.*, 23, 97 (1979).
48. H. Stehfest, *IMA J. Appl. Math.*, 23, 97 (1979).
49. A. Papoulis, *Q. Appl. Math.*, 14, 405 (1957).
50. K. S. Crump, *J. ACM*, 23, 89 (1976).
51. W. T. Weeks, *J. ACM*, 13, 419 (1966).
52. R. Piessens, *J. Eng. Math.*, 5, 1 (1971).
53. A. H. D. Cheng, P. Sidaauruk, and Y. Aboueleiname, *Math. J.*, 4, 76 (1994).
54. T. G. Palanisamy, S. E. LaCroix, A. A. Sigdel, and M. Fooken, (2005).
55. J. Sánchez-González, A. Macías-García, M. F. Alexandre-Franco, and V. Gómez-Serrano, *Carbon N. Y.*, 43, 741 (2005).
56. D. Pantea, H. Darmstadt, S. Kaliaguine, and C. Roy, *Appl. Surf. Sci.*, 217, 181 (2003).
57. O. Bohlen, J. Kowal, and D. U. Sauer, *J. Power Sources*, 172, 468 (2007).
58. B. V. Tkil, C. P. Chen, and S. K. Rangarajan, *J. Electroanal. Chem.*, 324, 405 (1992).