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Prediction of Discharge Performances of Pseudocapacitors Using Their Impedance Characteristics

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A first principle model was used to fit the impedance data of intrinsic pseudocapacitors based on polypyrrole and manganese dioxide electrodes and was validated by successfully predicting charge/discharge characteristics. The model performs non-linear regression to an electrochemical impedance spectroscopy (EIS) data using a rigorous prototypical model of pseudocapacitance, which emphasizes an integrated description of the various components of the capacitor at the microscopic and macroscopic level. Parametric studies showcase further how important microscopic variables in pseudocapacitors influence both impedance spectra and galvanostatic discharge.

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List of Symbols

Alphabetical

a	specific interfacial area, cm^2/cm^3
A_{aW}	concentration of electrolyte solution, M
A_{ea}	electrochemically accessible area, cm^2
C_{dl}	stern/compact double-layer capacitance, $\mu\text{F cm}^{-2}$
C_o	concentration of oxidants in solution, M
C_R	concentration of reductants in solution, M
C_{Z^*}	concentration of soluble species for Faradaic leakage, M
C_ϕ	pseudocapacitance, $\mu\text{F cm}^{-2}$
D_o	diffusion coefficient, $\text{cm}^2 \text{s}^{-1}$
D_o^*	fractal diffusion coefficient, $\text{cm}^{4-D_f}/\text{s}^{3-D_f}$
D_f	fractal dimension
F	Faraday's constant, 96500 C mol^{-1}
i_{dl}	double layer current, A cm^{-2}
i_f^1	Faradaic current for pseudocapacitive reaction, A cm^{-2}
i_f^2	Faradaic current for side reaction/leakage, A cm^{-2}
i_n	interfacial current, A cm^{-2}
I_{cell}	current of electrochemical cell, A cm^{-2}
j	imaginary number, $\sqrt{-1}$
j_0^1	exchange current density for pseudocapacitive reaction, A cm^{-2}
j_0^2	exchange current density for side reaction, A cm^{-2}
K	fractal proportionality constant, $\Omega \text{ cm}^2$
L	electrode thickness, μm
q_Γ^*	surface charge density of electrochemically adsorbed species, C mol^{-1}
R	ideal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}$
R_{ct}	charge transfer resistance, $\Omega \text{ cm}^2$
R_{ext}	external resistance, $\Omega \text{ cm}^2$
R_L	faradaic leakage resistance, $\Omega \text{ cm}^2$
s	Laplace-domain variable
t	time, s
T	temperature, K
V_0	initial voltage during experiment, V
V_ϕ	potential across full cell, V

x	distance across porous electrode, m
Y_n	interfacial admittance, S cm^{-2}
z	microscopic distance from electrode/electrolyte interface, m
Z_{ESR}	collective device impedance, $\Omega \text{ cm}^2$
Z_ψ	impedance of full cell, $\Omega \text{ cm}^2$

Greek

α	charge transfer coefficient
Γ_l	surface excess of adsorbed species, mol cm^{-2}
η	potential difference of solid electrode and electrolyte, V
κ	electrolyte conductivity, S cm^{-1}
σ	solid matrix/electrode conductivity, S cm^{-1}
ϕ_1	Potential in the solid matrix/electrode phase, V
ϕ_2	Potential in the electrolyte phase, V
ω	angular frequency, rad s^{-1}

There is considerable interest in increasing energy density of electrochemical capacitors by introducing Faradaic reactions, which include surface-bound fast redox reactions that induce pseudocapacitance.¹⁻⁵ Examples of pseudocapacitive materials include ruthenium oxide (RuO_2), manganese oxide (MnO_2), and polypyrrole.^{6,7} Pseudocapacitance can be described as an electrochemical phenomena where the presence of fast sequences of adsorption and intercalation charge transfer, without any change or consumption in the bulk material, induce charge storage.^{6,8,9} Instead of electrostatically attracted ions, the Faradaic charge transfer drives the adsorption and/or small intercalation onto an electrode's surface, producing a Faradaic capacitive-type current that behaves similarly to a double layer capacitive current.

Well-engineered electrodes have porous morphology and possess hierarchical structures that tune to a specific pore size distribution. In addition, pseudocapacitors commonly use composite electrodes that mix the active material with conductive materials due to the low conductivity found in many pseudocapacitive metal oxides. The most common conductive component in pseudocapacitors is carbon in the form of activated carbon, graphene, nanorods, and nanoparticles.¹⁰⁻¹² Carbon may also act as a support or substrate in the form of carbon papers and textile, which form the basis of

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flexible supercapacitors.^{12,13} Textile and filament structures create electrode morphology that differs greatly from the usual space-filling spherical aggregates. In summary, the complexity of electrode morphology provides a challenge in modeling the electrochemical kinetics, e.g. reaction mechanism, and transport phenomena, e.g. interfacial diffusion, of pseudocapacitors.

Previous theoretical studies from both the kinetics and transport point of view provide a starting ground in modeling pseudocapacitors. From the kinetics point of view, pseudocapacitance is intimately related to adsorption phenomena and early investigation had indeed focused on adsorption and insertion steps in hydrogen evolution reactions as well as underpotential deposition.^{14–18} More general studies on pseudocapacitance can also be found in investigation of non-equilibrium adsorption/desorption,^{19,20} and their extension to include Faradaic processes.²¹ However, the general basis for pseudocapacitance studies arise during the investigation of coupling phenomena between Faradaic (charge-transfer reactions) and non-Faradaic (double-layer interface) currents.^{22–27} With the introduction of a “systems-theoretic” approach on linear electrochemical systems, the coupling behavior between Faradaic and non-Faradaic processes was understood in a more general sense and pseudocapacitive reactions became one class of such coupled phenomena.^{28–31} Therefore, pseudocapacitance behavior can be introduced properly in modeling actual pseudocapacitors by appreciating the elementary steps in the mechanism and the mode of coupling involved.^{6,32,33}

From the transport point of view, standard porous electrode theory can connect the local interfacial electrochemistry to the observed total potential drop and impedance. Furthermore, it is also possible to model macroscopic concentration gradients across the electrode.^{34–37} Meanwhile, the microscopic diffusion towards the local interface inside the pores can be modelled in a standard manner using the diffusion equation with proper boundary conditions. However, some anomalous effects can be observed in the presence of rough surfaces, where the transport is governed by its fractional differential counterpart of the normal diffusion equation.^{38–40} Such equations arise naturally when analyzing the flux of a surface that has fractal properties.^{41–43} Another approach to model diffusion on rough surfaces is to describe the surface as a stochastic process, e.g. fractional Brownian motion, which would only modify the boundary condition albeit in a very sophisticated manner.^{44–46} Regardless of the mathematical approach, a parameter which characterizes the fractal properties of the surface, often a fractal dimension, can be commonly found.

The diversity of modeling approaches and the complexity of real-life electrodes should make it clear that no single model can encapsulate all applications and therefore, it must be tailored to specific goals. If the goal is to perform realistic first-principles simulations, then it is desirable to perform detailed calculations at all length scales. For instance, kinetic and transport parameters can be obtained from atomic or molecular many-body simulations and they may be inputted to the proper continuum (coupled and non-linear) equations. However, it is also possible to use *prototypical models* that have less “realism” but contain the correct phenomenology if the goal is to gain deeper insight from existing electrochemical data.

This work takes the latter perspective and elevate it to a higher level of rigor and validity by bringing a new modeling method called *Frequency Domain Admittance Method* (FDAM), which serve two specific goals:

1. To fit electrochemical impedance spectroscopy (EIS) data and obtain key physical parameters that elucidate the interfacial electrochemistry.
2. To predict discharge curves and calculate specific capacitance, energy, and power of a pseudocapacitor.

The motivation of FDAM is not to obtain “realistic” microscopic parameters and description but to accurately replicate transient electrochemical data with estimated parameters that are within the order of magnitude that makes sense given the assumptions made in

the model. With FDAM, a bridge can be formed between heuristics circuit modeling in impedance spectroscopy and sophisticated coupled transport and non-linear electrochemical equations.

In an earlier work, FDAM has been proven to be successful to predict the performances of electric double-layer capacitors (EDLCs), both for lab-fabricated and commercial capacitors.⁴⁷ The method works by having a suitably constructed model to describe the pseudocapacitor at the *macroscopic* level using porous electrode theory and the *microscopic* level using suitable electrochemical and transport equations. This model can then be fitted to EIS data to estimate all of its parameters. Using the parametrized model, galvanostatic discharge data can be simulated device capacitance, specific energy, and power can be calculated with ease. Therefore, FDAM can show that with a prototypical model and a single impedance data, one can simulate transient electrochemical experiments, maintain validity with experimental data, and obtain useful insights on device dynamics from the estimated model parameters.

Experimental

The procedure for synthesizing manganese oxide powder are detailed in several works.^{48,49} First, 0.1 N potassium permanganate (Fisher Scientific, Certified Grade) was mixed with ethanol (Sigma-Aldrich, ≥99.5%) in a 1:1 volume ratio. Afterwards, the dark purple solution was ultra-sonicated for 30 min and centrifuged to yield a dark brown precipitate. The dark brown precipitate was repetitively washed to bring down the pH to neutral, before being dried at room temperature. The resulting MnO₂ powder was mixed for a day with activated carbon and PVA binder in a 3 ml THF solution with a mass ratio of 80:15:5 of MnO₂, activated carbon, and the PVA binder respectively to form the electrode slurry. The slurry was casted on top of a porous carbon substrate (Optiveil™, 17 m² g⁻¹), washed with DI water, and dried at room temperature.

An aqueous solution containing 1 M pyrrole (purchased from Sigma Aldrich) and 0.5 M HCl (purchased from VWR) was used as electrolyte for electropolymerization of pyrrole. A 3-electrode cyclic voltammetry experiment was devised to deposit polypyrrole onto a porous carbon substrate with Ag/AgCl as the reference electrode and platinum foil as the counter electrode. Cyclic voltammetry was performed at a rate of 10 mV s⁻¹ from 0.0 V to 0.8 V for 40 cycles. This resulted in the formation of thick black coating on the porous substrate. The coated porous carbon substrates were then dried at room temperature.

Symmetric pseudocapacitors were assembled using both MnO₂ and polypyrrole coated electrodes sandwiched together using a cellulose filtration paper acting as the separator. The MnO₂ and polypyrrole pseudocapacitors were assembled with a geometric area of 0.5 cm² and 1 cm² respectively. Tantalum foils were used as current collectors. The assembled MnO₂ pseudocapacitor was soaked and tested in a 1 M KCl aqueous electrolyte while the polypyrrole pseudocapacitor utilized a 1 M H₂SO₄ aqueous solution as the electrolyte. Both constant current charge/discharge data measured at various current densities as well as electrochemical impedance data ranging from 10⁻³ Hz to 10⁵ Hz were measured using Reference 600 Gamry Potentiostat/Galvanostat. Scanning electron microscopy (SEM) was utilized (FEI Nova NanoSEM 630 FESEM) to obtain the cross-section of the pseudocapacitors and estimate the thickness of the electrodes.

Model Development

Microscopic formulation.—Model development starts from the microscopic length scale, where the electrochemical reaction takes place at the interface. As mentioned previously, the derived model must be minimal in construction but still keep all the correct phenomenology. The concept of simplicity is incredibly important in the context of fitting impedance spectra, which is the first step of FDAM. A model with a large number of parameters, in the attempt to describe realistic reaction mechanism and transport, is simply

unfeasible to be parametrized with a single impedance data. Hence, many approximations and assumptions must be made along the way.

The first part of the microscopic problem is the electrochemical kinetics. As mentioned previously, most literature agree that a pseudocapacitive reaction must involve at least some form of a surface redox reaction mechanism on the active material. The real-life process involves complicated sequences of adsorptions, insertions, and redox steps. Therefore, any choice of reaction mechanism must involve several elementary steps that include at least the adsorption/desorption of reactants and products as well as charge transfer in adsorbed intermediates. However, it is almost impossible for elementary steps to be deconvoluted in impedance spectra, where only one rate-determining step can be observed. Hence, either the original mechanism must be reduced to a single rate-determining step through proper rate sensitivity analysis or a *prototypical single reaction step* is proposed that captures the correct phenomenology.

The latter approach is used and the electrochemical adsorption reaction (EAR) scheme^{50–52} was chosen to model the prototypical pseudocapacitive reaction. In EAR, a soluble active species adsorbs/desorbs onto a surface and simultaneously performs redox reaction.



where O is the soluble species and I_{ads} is the adsorbed intermediate. This scheme is a first-pass approximation to the real-life example, such as MnO_2 electrode in a KCl solution. The active soluble species (K^+ and H^+ , depending on the pH) will effectively “adsorb” onto the MnO_2 surface and simultaneously change the oxidation state of the Mn atoms from III to IV.^{9,53} It is also important to note that the EAR should be intuitively non-elementary in nature but treating it as elementary gives an enormous simplification while still keeping the important phenomenology.

A “side” reaction independent of the pseudocapacitive reaction can also be added:



where Z^* is some unknown species that diverts some of the electrons needed to perform pseudocapacitive reaction to a side reaction that acts as a source of Faradaic leakage. While the side reaction can be modelled as irreversible, such assumption is not needed a priori.

In the next step, the total current at the interface or the interfacial current i_n is defined by breaking it into three components: the double layer (charging) current i_{dl} , Faradaic current for the EAR i_f^1 , and Faradaic current for the side reaction/Faradaic leakage i_f^2 :

$$i_n = i_{dl} + i_f^1 + i_f^2 \quad [3]$$

The double layer is a subject of enormous complexity of its own. However, the double layer or charging current may come from two contributions based on how the total accumulated charge on the surface changes. It may change from either (1) changing the potential or (2) changing the number of accumulated adsorbed species. This leads to the following equation

$$i_{dl} = C_{dl} \frac{\partial \eta}{\partial t} + q_{\Gamma}^* \frac{\partial \Gamma_{\Gamma}}{\partial t} \quad [4]$$

where η is the potential difference between the electrode and electrolyte, sometimes defined as the “overpotential,” Γ_{Γ} is the surface excess of adsorbed species, C_{dl} is the overall double layer capacitance, and q_{Γ}^* represents the molar electric charge of adsorbed species with units in C/mol . The notations used conform with Refs. 32, 33. Notice that it is possible to set $q_{\Gamma}^* = n_1 F$ since n_1 represents the stoichiometric number of electrons used in the pseudocapacitive reaction and therefore determines the valency of the adsorbed species. However, it is expected that there could be a slight valency change due to some additional process that is not taken to account in the current model. In addition, keeping q_{Γ}^* to be arbitrary will affect the derivation very trivially and hence it shall be kept as arbitrary.

It is also good to keep in mind that the potential difference η is a function of both time and position across the porous electrode. This potential can be connected to the overall potential difference of the porous electrode using porous electrode theory. The theory will model the heterogeneous porous electrode into a pseudo-homogeneous continuum media with effective transport and electrical coefficients that can take account how the potential difference as well as the interfacial electrochemistry are distributed across the electrode in a rigorous manner.

To describe the Faradaic kinetics, the standard procedure on electrode kinetics can be done (see Ref. 54) by relating the net rate of reaction to the observed Faradaic current and collecting some constants to express the currents in terms of the exchange current density. The obtained equations are similar to the Butler–Volmer equations:

$$i_f^1 = j_0^1 \left[\frac{C_o(0, t)}{C_o^0} \exp\left(\frac{\alpha n_1 F \eta}{RT}\right) - \frac{\Gamma_{\Gamma}}{\Gamma_{\Gamma}^0} \exp\left(-\frac{(1 - \alpha) n_1 F \eta}{RT}\right) \right] \quad [5]$$

$$i_f^2 = j_0^2 \left[\frac{C_{Z^*}(0, t)}{C_{Z^*}^0} \exp\left(\frac{\alpha n_2 F \eta}{RT}\right) - \frac{C_R(0, t)}{C_R^0} \exp\left(-\frac{(1 - \alpha) n_2 F \eta}{RT}\right) \right] \quad [6]$$

where j_0^1 and j_0^2 represents the exchange current densities of both the EAR and side reaction respectively. Other constants will follow their standard definition or can be found in the List of Symbols. Typically, the kinetics should include the dependence of the open circuit potential with the state of charge^{55,56} but Eqs. 5 and 6 imply that this dependency is assumed to be constant and is absorbed into the exchange current density. Real-life electrodes will have complicated dependence upon the state of charge and these details will be ignored for now to formulate the prototypical model that can be feasibly and easily applied to impedance spectroscopy data. Also note that the position “0” in the concentration term is evaluated at the electrode/electrolyte microscopic interface.

The redox and adsorption phenomena are related through a simple relation:

$$\frac{\partial \Gamma_{\Gamma}}{\partial t} = \frac{i_f^1}{n_1 F} \quad [7]$$

which tells us that the rate of adsorbed species accumulation is proportional or driven by the EAR’s Faradaic current. Furthermore, Eq. 7 can be combined with Eq. 4 to manifest the coupling behavior between Faradaic and non-Faradaic currents:

$$i_{dl} = C_{dl} \frac{\partial \eta}{\partial t} + \frac{q_{\Gamma}^*}{n_1 F} i_f^1 \quad [8]$$

Since the charge transfer process is intrinsically linked to the formation of adsorbate intermediates, it is not surprising that non-Faradaic and Faradaic currents are coupled. Furthermore, the molar surface charge associated with adsorbed species is now part of the coefficient which couples both the Faradaic and non-Faradaic phenomena.

After performing linearization and Laplace transform to Eqs. 5–8, the following system of equations may be obtained:

$$\tilde{i}_{dl} = j\omega C_{dl} \tilde{\eta} + \frac{q_{\Gamma}^*}{n_1 F} \tilde{i}_f^1 \quad [9]$$

$$\tilde{i}_f^1 = j_0^1 \left[\frac{\delta \tilde{C}_o(0, \omega)}{C_o^0} - \frac{\delta \tilde{\Gamma}_{\Gamma}(\omega)}{\Gamma_{\Gamma}^0} + \frac{n_1 F \tilde{\eta}}{RT} \right] \quad [10]$$

$$\tilde{i}_f^2 = j_0^2 \left[\frac{\delta \tilde{C}_{Z^*}(0, \omega)}{C_{Z^*}^0} - \frac{\delta \tilde{C}_R(0, \omega)}{C_R^0} + \frac{n_2 F \tilde{\eta}}{RT} \right] \quad [11]$$

$$\delta \tilde{\Gamma}_I(\omega) = \frac{\tilde{i}_f^1}{n_1 F(j\omega)} \quad [12]$$

At this point, we have adequately addressed the electrochemical kinetics. The second part of the microscopic problem is to formulate the interfacial transport mechanism, keeping in mind the complexity of the electrode morphology. We may walk through and briefly discuss some possible analytical attempts. For instance, it is tempting to formulate the microscopic problem on a spherical particle using diffusion equation in spherical coordinates. But when electrode morphology is closer to filaments and celluloses, which is the case for this work, a cylindrical description might be more appropriate. However, neither of these geometric descriptions would be sufficient to describe the hierarchical mesoscale structures that would be encountered in real-life electrodes. Furthermore, the choice of boundary conditions will be highly depended upon pore sizes and mean free path of the ions. While typical analytical approaches utilize either a set of semi-infinite or finite boundary conditions, either set will be insufficient if broad or bimodal pore size distributions are present.

To decide the inclusion of curvature and geometrical effects, it is important to consider how they manifest in the impedance spectra. Generally, transport effects are observed at intermediate-to-low frequencies. Intermediate frequencies are dominated by the 45° phase angle and this characteristic is shared by almost all types of diffusional impedances. Curvature and geometrical effects occur subtly at the low frequencies. In fact, finite-length Warburg impedances how different onsets to the low-frequency “capacitive” behavior for flat, cylindrical, and spherical surfaces.⁵⁷ Pore size distribution effects also occur subtly in the low frequencies, as exemplified in the impedance spectroscopy simulation of a realistic Li-ion battery.⁵⁸ The fact that important mass transfer effects happen at low-frequencies is consistent with other electrochemical data, most notably chronopotentiometry where the prominent “cliff” region at long times, as determined by the Sand equation, is clearly identified as a mass transport effect.

However, low-frequency behavior of electrochemical capacitors is not dominated by mass transport but by their *energy storage mechanism*. For EDLCs and pseudocapacitors, this mechanism will be the double layer capacitance and pseudocapacitance respectively. This implies that any subtle curvature or pore size distribution effects on mass transport will be over-dominated by the device’s capacitance. The word “domination” is an understatement since the onset of capacitive behavior can be observed at frequencies as high as 1–5 kHz, overlapping with the region of charge transfer. This should also make sense since chronopotentiometry or constant-current discharge curves of electrochemical capacitors are typically linear even at long times, which is unique to the capacitive response of the device. Furthermore, slight deviations from this non-linearity if more often attributed to some resistive leakage as indicated from the Faradaic efficiency of the device, and not necessarily mass transport alone. Therefore, the effects of pore size distribution or curvature can be essentially neglected for the prototypical model and the surface can be treated locally as a 1D flat surface.

However, 1D flat surfaces themselves will not be enough to model the interfacial diffusion since deviation of 45° phase angle at intermediate frequencies can still occur due to presence of rough surfaces. Excluding roughness effects will certainly impact the quality of the fitting in the intermediate frequencies. Therefore, it is important to use the anomalous diffusion formalism to correct the behavior at intermediate frequencies. By using the fractional derivative approach, the diffusion equation can be transformed

into a fractional PDE.^{40,43} Different than the stochastic process approached mentioned in the introduction, the fractional derivative formalism will allow seamless incorporation of roughness effects into the prototypical model.

With the geometry problem settled, the derivation can be continued by assuming the pseudocapacitive reaction to be diffusion-controlled. Since Faradaic leakage resistance is expected to be high, the side reaction can be assumed to be slow and kinetically controlled, i.e. $\delta \tilde{C}_{Z^*}(0, \omega) \rightarrow 0$ and $\delta \tilde{C}_R(0, \omega) \rightarrow 0$. The diffusion equation that governs the transport of soluble species is replaced with a fractional PDE with the following boundary conditions^{38,40,43}:

$$\frac{\partial^{3-D_f} \delta C_o(z, t)}{\partial t^{3-D_f}} = D_o^* \frac{\partial^2 \delta C_o(z, t)}{\partial z^2} \quad [13]$$

$$\text{BC: } -D_o^* \frac{\partial^{D_f-2}}{\partial t^{D_f-2}} \frac{\partial \delta C_o(0, t)}{\partial z} = -\frac{i_f^1}{n_1 F};$$

$$\delta C_o(z \rightarrow \infty, t) = 0 \quad [13a]$$

$$\text{IC: } \delta C_o(z, 0) = 0 \quad [13b]$$

where $D_o^* = K^{4-2D_f} D_o^{3-D_f} A^{3D_f/2-2}$.

Within this formalism, the fractal dimension D_f is the parameter that controls roughness. A smooth surface will have a fractal dimension of $D_f = 2$ while the highest roughness corresponds to $D_f = 3$. Fractal dimension also modifies the diffusion coefficient D_o and turns it into the fractal diffusion coefficient D_o^* . The fractal diffusion coefficient is controlled by the normal diffusion coefficient D_o , electrochemically accessible surface area A_{ea} and a proportionality constant K that depends on the specific geometry of the rough surface. The new diffusion equation also includes semi-infinite boundary conditions, which are chosen to avoid adding a new parameter associated with assigning some boundary layer length. As discussed previously, any effects related to specific geometry will be difficult to be deconvoluted from the low-frequency pseudocapacitive response of the system. The semi-infinite boundary conditions will still adjustments in the intermediate frequencies, i.e. deviations of 45° phase angle.

In frequency domain, the Laplace transform of the solution of Eq. 13 takes a similar form to the solution for a normal semi-infinite diffusion:

$$\delta \tilde{C}_o(z, \omega) = -\frac{\tilde{i}_f^1}{n_1 F \sqrt{D_o^*} (j\omega)^{\frac{D_f-1}{2}}} \exp\left(-\frac{(j\omega)^{\frac{D_f-1}{2}}}{\sqrt{D_o^*}} z\right) \quad [14]$$

Evaluating $z = 0$, Eqs. 14 and 12 can be substituted into Eq. 10 to obtain an implicit but solvable relation for i_f^1 :

$$\tilde{i}_f^1 = j_0^1 \left[-\frac{\tilde{i}_f^1}{n_1 F C_o^0 \sqrt{D_o^*} (j\omega)^{\frac{D_f-1}{2}}} - \frac{\tilde{i}_f^1}{n_1 F (j\omega) \Gamma_I^0} + \frac{n_1 F \tilde{\eta}}{RT} \right] \quad [15]$$

At this stage, the key *model parameters* can be defined which almost follows the traditional definition:

$$A_{aw} = \frac{RT}{(n_1 F)^2 C_o^0 \sqrt{D_o^*}}; \quad R_{ct} = \frac{RT}{n F j_0^1}$$

$$C_\phi = \frac{(n_1 F)^2 \Gamma_I^0}{RT}; \quad R_L = \frac{RT}{n F j_0^2}$$

where A_{aw} is the anomalous Warburg coefficient, R_{ct} is the charge transfer resistance, C_ϕ is the pseudocapacitance, and R_L is the Faradaic leakage resistance. The role of these constants in the model after re-arrangements of Eq. 15 to obtain a compact expression for the Faradaic currents:

$$\tilde{i}_f^1 = \frac{\tilde{\eta}}{R_{ct} + \frac{1}{j\omega C_\phi} + \frac{A_{aW}}{(j\omega)^{\frac{D_f-1}{2}}}} \quad [16]$$

$$\tilde{i}_f^2 = \frac{\tilde{\eta}}{R_L} \quad [17]$$

And thus, knowing that the interfacial current is just a summation of non-Faradaic and Faradaic currents, the interfacial admittance $Y_n(j\omega)$ can be obtained using Eqs. 9, 16, and 17:

$$Y_n(j\omega) = \frac{\tilde{i}_n}{\tilde{\eta}} = j\omega C_{dl} + \frac{1 + \frac{q_\Gamma^*}{n_1 F}}{R_{ct} + \frac{1}{j\omega C_\phi} + \frac{A_{aW}}{(j\omega)^{\frac{D_f-1}{2}}}} + \frac{1}{R_L} \quad [18]$$

Notice that the coupling coefficient $\left(1 + \frac{q_\Gamma^*}{n_1 F}\right)$ is contained within the term that governs the pseudocapacitive reaction. Because this coupling coefficient cannot be separated from the rest of the parameters, this forces some new “effective” constants to be defined:

$$A'_{aW} = A_{aW} \left(1 + \frac{q_\Gamma^*}{n_1 F}\right)^{-1}; \quad R'_{ct} = R_{ct} \left(1 + \frac{q_\Gamma^*}{n_1 F}\right)^{-1}$$

$$C'_\phi = C_\phi \left(1 + \frac{q_\Gamma^*}{n_1 F}\right)$$

where the prime indicates effective parameters. These parameters will be referred to by their usual names with the understanding that there are intrinsic coupling coefficients contained within them. Subsequently, a more compact form can be obtained:

$$Y_n(j\omega) = j\omega C_{dl} + \frac{1}{R'_{ct} + \frac{1}{j\omega C'_\phi} + \frac{A'_{aW}}{(j\omega)^{\frac{D_f-1}{2}}}} + \frac{1}{R_L} \quad [19]$$

The derived interfacial admittance is very similar to the Frumkin-Melik-Gaykazyan model, which is a purely non-Faradaic model of physisorption in double layer interfaces.⁵⁹ The principal difference is that the currently derived model has Faradaic component, with additional coupling to the double layer current.

Macroscopic formulation and numerical methods.—The interfacial admittance from Eq. 19 characterize the microscopic or interfacial response of the system completely. Standard porous electrode theory can now be used to describe overall electrode response by connecting Eq. 19 into some potential distribution across the porous electrode. The derivation of porous electrode theory applied to simple reaction systems can be found in several literature.^{34,47,58,60,61} Only the sketch of the derivation for porous electrode impedance will be provided for a general interfacial admittance. Assuming no concentration polarization across the electrode and no changes in bulk physical properties such as electrode/electrolyte conductivity, the relevant equation is a generalized PDE of the following form:

$$\frac{\partial^2 \eta(x, t)}{\partial x^2} = \left(\frac{1}{\kappa} + \frac{1}{\sigma}\right) a i_n(\eta, t) \quad [20]$$

$$BC: \frac{\partial \eta(L, t)}{\partial x} = \frac{I_{cell}}{\kappa}; \quad \frac{\partial \eta(0, t)}{\partial x} = -\frac{I_{cell}}{\sigma}; \quad [20a]$$

$$IC: \eta(x, 0) = 0 \quad [20b]$$

where η is the same potential drop across the solution/electrode interface, $i_n(\eta, t)$ is the interfacial current I_{cell} is the applied current on the device, κ and σ are the electrolyte and electrode conductivities respectively, and x denotes the lateral position at the porous electrode with zero defined at the current collector and L is defined at the interface between the porous electrode and the separator. The interfacial current is connected to the interfacial admittance when Eq. 20 is analyzed in the linearized regime of impedance spectroscopy. Therefore, the interfacial current can be expressed as the pduct of interfacial admittance $Y_n(s)$ and the potential drop in the Laplace domain $\tilde{\eta}(x, s)$ since it is linearized:

$$\tilde{i}_n(\eta, s) = Y_n(s) \cdot \tilde{\eta}(x, s) \quad [21]$$

where s denotes the Laplace-domain variable. Turning Eq. 20 into frequency domain by Laplace transform and inserting Eq. 21, the generalized PDE can then be transformed into a linear ODE:

$$\frac{d^2 \tilde{\eta}(x)}{dx^2} = \frac{\nu^2}{L^2} \tilde{\eta} \quad [22]$$

$$BC: \frac{d\tilde{\eta}(L)}{dx} = \frac{\tilde{I}_{cell}}{\kappa}; \quad \frac{d\tilde{\eta}(0)}{dx} = -\frac{\tilde{I}_{cell}}{\sigma}; \quad [22a]$$

$$\text{where } \nu = \sqrt{\left(\frac{1}{\sigma} + \frac{1}{\kappa}\right) a Y_n(j\omega) L^2}$$

And the solution can be expressed in terms of hyperbolic functions:

$$\tilde{\eta} = \frac{\tilde{I}_{cell} L}{\nu \sinh \nu} \left\{ \frac{1}{\kappa} \cosh \left[\frac{\nu x}{L} \right] + \frac{1}{\sigma} \cosh \left[\nu \left(1 - \frac{x}{L} \right) \right] \right\} \quad [23]$$

where it can finally be used to derive the expression for the *porous electrode impedance* $Z_p(j\omega)$:

$$\begin{aligned} Z_p(j\omega) &= \frac{L}{\kappa + \sigma} \left[1 + \frac{\sigma}{\tilde{I}_{cell} L} \int_0^L \frac{d\tilde{\eta}(j\omega, p)}{dx} dx \right] + \frac{\tilde{\eta}(0, j\omega)}{\tilde{I}_{cell}} \\ &= \frac{L}{\kappa + \sigma} \left[1 + \frac{2 + \left(\frac{\kappa}{\sigma} + \frac{\sigma}{\kappa}\right) \cosh \nu}{\nu \sinh \nu} \right] \end{aligned} \quad [24]$$

The porous electrode impedance represents how the conductivity of the electrolyte and electrode and the interfacial admittance manifest in the overall impedance of the electrode. The first term of Eq. 24 is a purely resistive term $\frac{L}{\kappa + \sigma}$ that represents how both electrolyte and electrode resistances are observed at high frequencies. The second term, containing hyperbolic functions, introduce a Warburg-like response at intermediate frequencies providing nature of distribution of interfacial admittance across the porous electrode.

With the porous electrode impedance obtained, it is only a matter of adding external resistances and/or inductances to complete the description of the entire device. These contributions are highly dependent upon the device fabrication method. These contributions can be lumped together as a collective impedance term Z_{ESR} . While this term is generally frequency-dependent, it is safe to assume that only separator/electrolyte resistance would be observed in the device level. Therefore, $Z_{ESR} = R_{ext}$ where R_{ext} is the external resistance and the final *cell impedance* $Z_\psi(j\omega)$ can be expressed as the porous electrode impedance in series with the external resistance:

$$Z_\psi(j\omega) = 2Z_p(j\omega) + R_{ext} \quad [25]$$

Note that if the porous electrode conductivity is low enough, it is also possible to neglect contribution from external resistance entirely and leave the electrode conductivity as a model parameter. This is a

reasonable decision given the composite nature of pseudocapacitive electrodes.

With the *interfacial admittance* $Y_n(j\omega)$ (Eq. 19), *porous electrode impedance* $Z_p(j\omega)$ (Eq. 24), and the *cell impedance* $Z_\psi(j\omega)$ (Eq. 25), the prototypical model that contains both macroscopic and microscopic descriptions is complete. Figure 1 provides an illustration of what phenomena that the model can take account for in relation to where they are observed in a typical impedance spectra. The illustration shows that all model parameters can take account the impedance spectra at all frequencies despite the simplifications and assumptions that have been made.

The complex non-linear regression procedure was performed using the LMFIT package available in Python, which also provided a convenient way to perform statistical and error analysis.⁶² To perform the second part of FDAM, which is the discharge simulation, the cell potential needs to be expressed in terms of the original Laplace variable:

$$V_\psi(s) = \frac{2V_0}{s} - \frac{I_{\text{cell}}Z_\psi(s)}{s}$$

Afterwards, the Gaver-Stehfest method can be used to perform the numerical inverse Laplace transform.^{63,64} The Gaver-Stehfest method provides an explicit solution for the cell potential, approximated by a series shown below:

$$V_\psi(t) \approx 2V_0 - \frac{\ln 2}{t} \sum_{n=1}^N c_n \frac{I_{\text{cell}} t}{n \ln 2} \cdot Z_\psi\left(\frac{n \ln 2}{t}\right) \quad [26]$$

$$c_n = (-1)^{n+\frac{N}{2}} \sum_{k=\frac{n+1}{2}}^{\min(n, N/2)} \frac{k^{N/2} (2k)!}{(N/2 - k)! k! (k-1)! (n-k)! (2k-n)!} \quad [27]$$

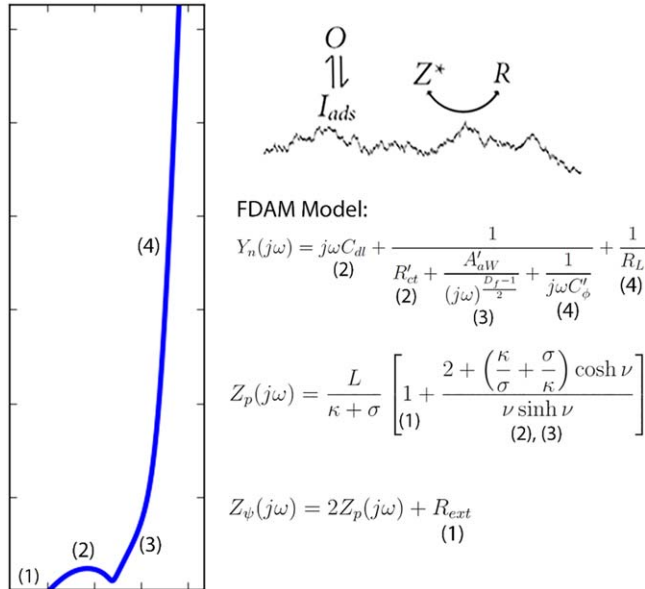


Figure 1. Impedance spectra created from the final model, as defined by Eqs. 19, 24, and 25, along with an illustration of the interfacial electrochemistry that the model describes. Numerical labels indicate correspondence between model parameters and regions in impedance spectra. Region (1) is dominated by high-frequency resistance created from electrode/electrolyte conductivity and R_{ext} . Region (2) is a $R_{et}C_{dl}$ semicircle modified by the porous electrode, Region (3) is the diffusion region that deviates from 45° due to roughness and modified slightly by the porous electrode. Region (4) is the low-frequency pseudocapacitance response that deviates from ideality due to Faradaic leakage. Note that the low-frequency line will extend even further since the material mostly act as a capacitor.

Table I. Set parameters for MnO₂ and polypyrrole pseudocapacitors. Electrode conductivity is taken as free parameter.

Parameters	MnO ₂	Polypyrrole
$L(\mu\text{m})$	200	200
$a(\text{cm}^2 \text{cm}^{-3})$	$1.02 \cdot 10^5$	$1.02 \cdot 10^5$
$\kappa(\text{S cm}^{-1})$	0.112	0.370
$I_{\text{cell}}(\text{mA cm}^{-2})$	0.62	1.0
Mass (mg)	3.1	7.0
$2V_0(\text{V})$	0.8	0.8

In this work, six terms or $N = 6$ was used for all discharge simulations.⁶⁴

Results and Discussion

Table I summarizes the set parameters for both MnO₂ and polypyrrole pseudocapacitors. Since both materials utilize the same macroporous carbon paper as substrate, the specific interfacial area and electrode thickness are the same for both devices. The specific interfacial area was estimated by the external surface area of carbon substrate ($17 \text{ m}^2 \text{g}^{-1}$) and the bulk density of the activated carbon mixed in. The electrode thickness was calculated directly from the cross-sectional SEM. Bulk electrolyte conductivity for both solutions were obtained from literature.^{65,66} Due to the complex composition of each electrode material, electrode conductivity is taken as a free parameter.

Impedance spectra and discharge simulation results for MnO₂ pseudocapacitor are shown in Fig. 2. The impedance model captured the overall capacitive response of the device, as indicated from the capacitance Bode plots. The high-frequency semicircle arc was also fitted well, although the simple $R_{et}C_{dl}$ semicircle did not provide a perfect fit due to various contributions such as contact resistance/capacitance that cannot be deconvoluted effectively from the data. External resistance is not needed as the electrode conductivity was adequate to take account the small high-frequency resistance. Furthermore, anomalous diffusion was necessary to obtain a better fit, where the obtained fractal dimension indicated a slightly rougher interface ($D_f = 2.04 \pm 0.03$). The resulting discharge simulation can be found in Fig. 2b and the calculated device capacitance, specific energy, and power can be found in Table II. Consistent with the impedance fitting, FDAM was able to predict discharge data accurately and a sensitivity analysis using the error in fitted parameters showed very small error (0.27%) in calculated specific capacitance, showcasing the precision of the simulation also.

Figure 3 shows the result of impedance fitting of symmetric polypyrrole pseudocapacitor. Similar situation arises where high-frequency semicircle arc was not fitted as well, although this did not change the impedance model's capability to capture the overall capacitive response of the device. Since the high-frequency external resistance is small, external resistance was also neglected. Furthermore, anomalous diffusion was not needed unlike the MnO₂ pseudocapacitor. Comparing the pseudocapacitance value for both the pseudocapacitors,

Table II. Fitted parameters for MnO₂ and polypyrrole pseudocapacitors through complex non-linear regression of impedance data. Note that external resistance R_{ext} was not needed for both pseudocapacitors.

Parameters	MnO ₂	Polypyrrole
$A_{dW}'(\text{M}\Omega \text{cm}^2 \text{s}^{-(D_f-1)/2})$	0.23 ± 0.03	0.040 ± 0.002
D_f	2.05 ± 0.03	2
$R_L(\text{M}\Omega \text{cm}^{-2})$	40 ± 2	9.9 ± 3
$C_{dl}(\mu\text{F cm}^{-2})$	0.03 ± 0.01	0.16 ± 0.02
$C'_\phi(\mu\text{F cm}^{-2})$	100 ± 1	259 ± 0.9
$R_{et}'(\text{k}\Omega \text{cm}^2)$	1.8 ± 0.6	3.6 ± 0.3
$\sigma(\text{S cm}^{-1})$	$(1.6 \pm 0.3) \cdot 10^{-3}$	$(1.12 \pm 0.08) \cdot 10^{-3}$

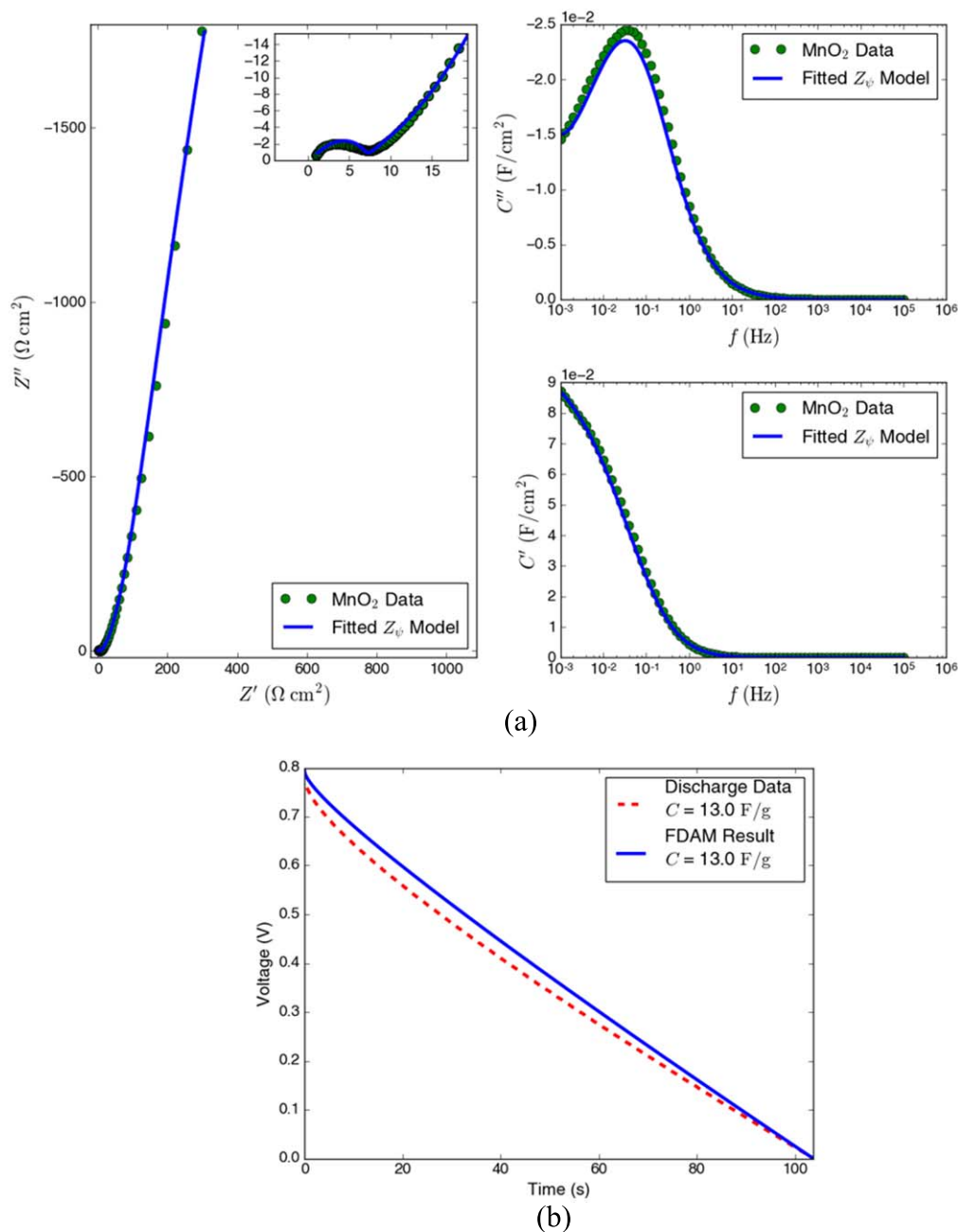


Figure 2. (a) Nyquist plot, imaginary and real capacitance bode plot of MnO_2 pseudocapacitor. (b) Comparison of discharge experimental data (dashed) and FDAM model simulation (bold) for MnO_2 pseudocapacitor.

MnO_2 has lower capacitance ($C_\phi' = 100 \pm 1 \mu\text{F cm}^{-2}$) than polypyrrole ($C_\phi' = 259.0 \pm 0.9 \mu\text{F cm}^{-2}$). This is confirmed with calculated device capacitance, specific energy, and power compiled in Table III. Similar to the MnO_2 pseudocapacitor, FDAM was able to accurately and precisely predict the specific capacitance, energy, and power and sensitivity analysis using the error in fitted parameters shows

also shows very small error (0.11%) for the calculated specific capacitance.

We studied the influence of three important model parameters that affects the performance of MnO_2 pseudocapacitor. We first looked at the impact of varying relative contribution of pseudocapacitance and double layer at the electrode/electrolyte interface by

Table III. Calculated device capacitance, specific energy and power from experiment and simulation.

	MnO_2 (Experimental)	MnO_2 (Simulation)	Polypyrrole (Experimental)	Polypyrrole (Simulation)
C (F g^{-1})	13.0	13.0	35.6	35.7
E (Wh kg^{-1})	1.15	1.15	3.17	3.17
P (W kg^{-1})	40.0	40.0	57.1	57.1

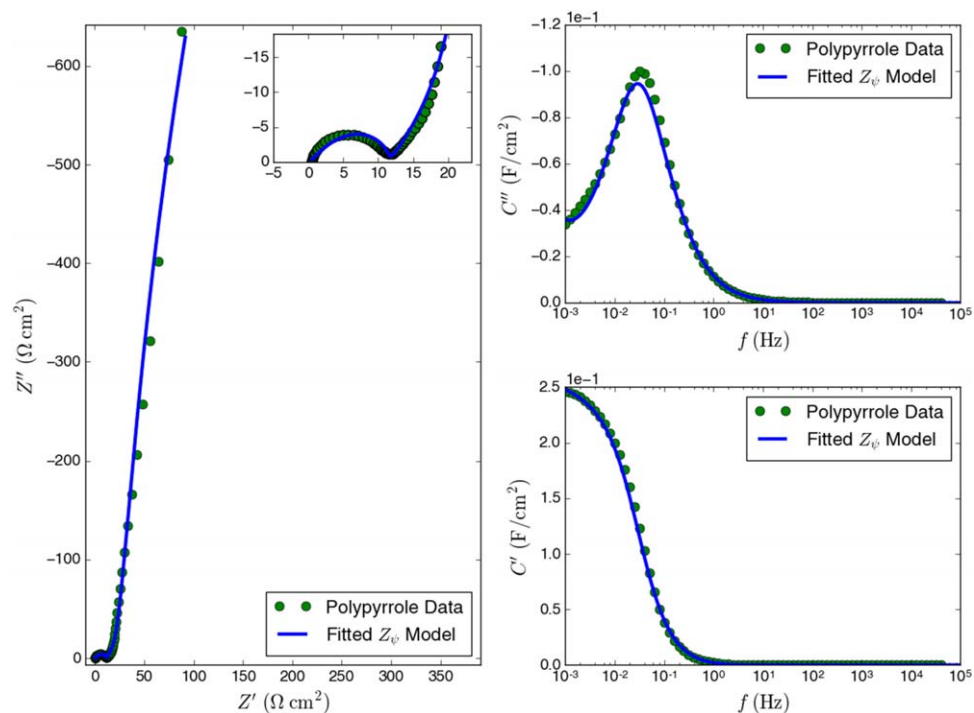


Figure 3. Nyquist plot as well as imaginary and real capacitance bode plots for polypyrrole pseudocapacitor.

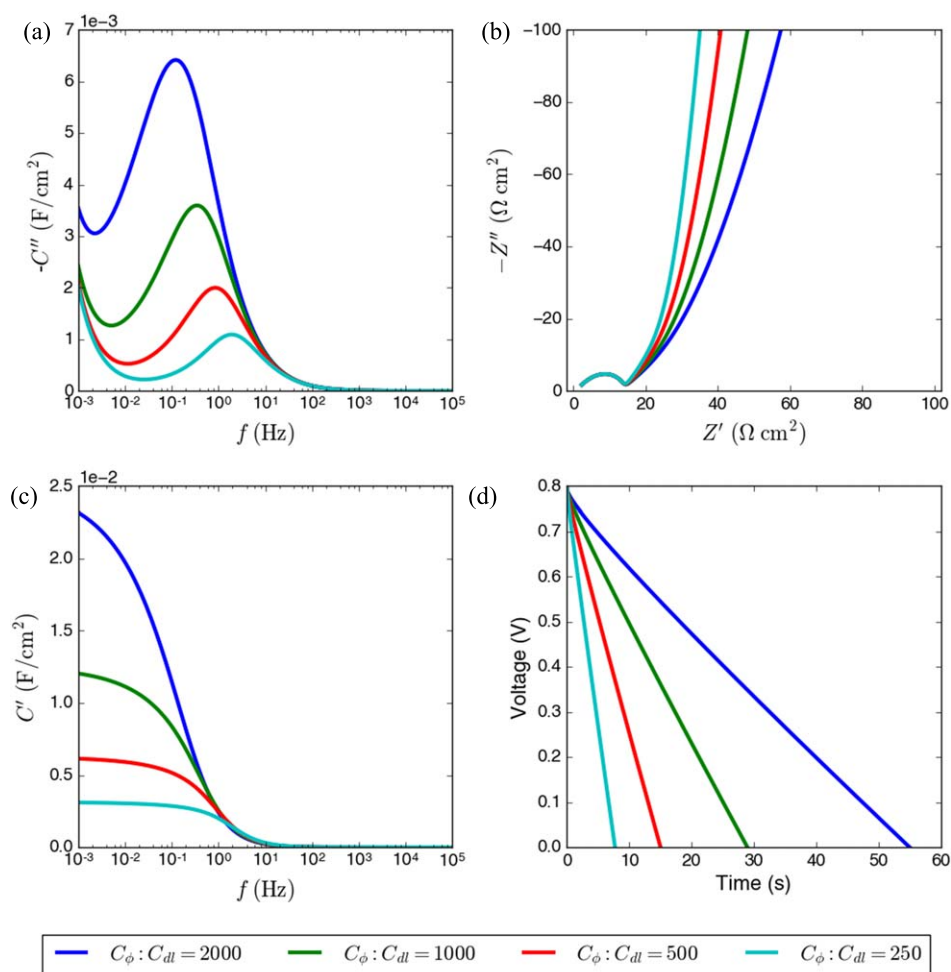


Figure 4. Parametric study demonstrating the effect of different ratios of pseudocapacitance and double layer capacitance (a) Imaginary capacitance bode plot, (b) Real capacitance bode plot, (c) Nyquist plot and (d) Galvanostatic discharge data.

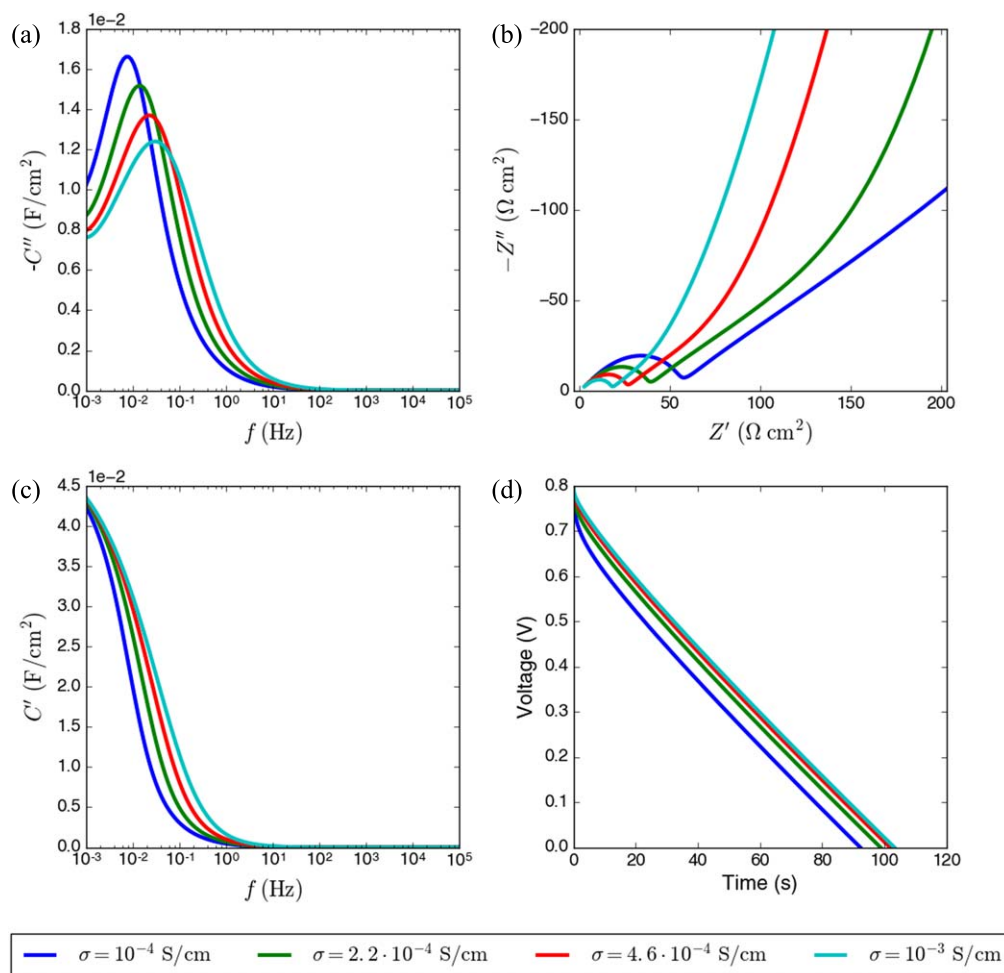


Figure 5. Parametric study demonstrating the effect of electrode conductivity on (a) Imaginary capacitance bode plot, (b) Real bode plot, (c) Nyquist plot and (d) Galvanostatic discharge data.

changing the ratio of pseudocapacitance and double layer capacitance $C_p : C_{dl}$. In the design of pseudocapacitive electrodes, more often, a thin layer of pseudocapacitive material is coated onto a high surface area substrate with the goal of maximizing pseudocapacitive interfacial area while minimizing contribution from charge transfer resistance or an attempt is made to make high surface area porous pseudocapacitive electrode material. In both cases, it is important to understand the confluence of pseudocapacitive interaction at the interface along with the available surface area for the double layer formation. Our model can study the coupled influence of pseudocapacitance and double layer on the overall performance of the device. Figure 4 shows the simulated impedance spectra, capacitance Bode plots by varying the ratio of $C_p : C_{dl}$ from 2000:1 to 250:1 while keeping the C_{dl} constant. Changes in pseudocapacitance are reflected at low frequencies, such as the shift of characteristic frequency in imaginary capacitance Bode plots. A decrease in ratio changes the slope and allowed the device to discharge faster, which is indicative of smaller overall capacitance and lower energy storage capability.

Next, we looked at the effect of varying electrode conductivity. The electrode conductivity can be affected when the pseudocapacitive layer produces a thicker coating on the underlying substrate or clogs the interconnected porous network of the substrate. Figure 5 shows the effect of varying electrode conductivity σ within the expected range of 10^{-4} – 10^{-3} S cm $^{-1}$. The effect on discharge simulation was very clear, where an increase in electrode conductivity decreases the initial voltage drop. In the impedance spectra, we saw there was changes in the high-frequency semicircle along with shift in the “Warburg” region at intermediate frequencies. The

parametric study confirms the significance of electrode conductivity in designing oxide-based pseudocapacitive materials, where it is desirable to obtain the highest conductivity possible.^{11,67}

Finally, we look at the impact of smooth vs rough surface. Most deposition process of pseudocapacitive materials are going to create a rough electrode/electrolyte interface. Figure 6 shows the parametric study on the fractal dimension D_f , from an ideally smooth surface to a relatively rough surface. Because the anomalous Warburg coefficient is also a function of D_f , some additional parameters needed to be assumed. It is convenient to choose $K = 1$ and diffusion coefficient $D_o = 2 \cdot 10^{-5}$ cm 2 s $^{-1}$ and A_{ea} was adjusted to produce the current value for A_{aW} . The increase of fractal dimension was understood as an increase in roughness led to increase in capacitance as indicated by longer discharge times and an increase in low-frequency capacitance from its real Bode plot. Another important note is that the phase angle in the diffusion region increases with increasing fractal dimension towards a more capacitive behavior, which is consistent with results from literature.^{38,40}

To illustrate the impact of MnO $_2$ pseudocapacitive coatings on carbon substrate on the energy and power performance of the pseudocapacitor, we incorporate the effect of the parameters to investigate both the positive and detrimental effects.

For our study, we assumed a symmetric capacitor which utilizes an activated carbon (600 m 2 g $^{-1}$ of surface area and 0.6 g/cc of pore volume) as electrode substrate. The carbon electrodes are assumed to be subsequently coated with MnO $_2$, which led to reduction in surface area. We assumed various percentage reduction in surface area and

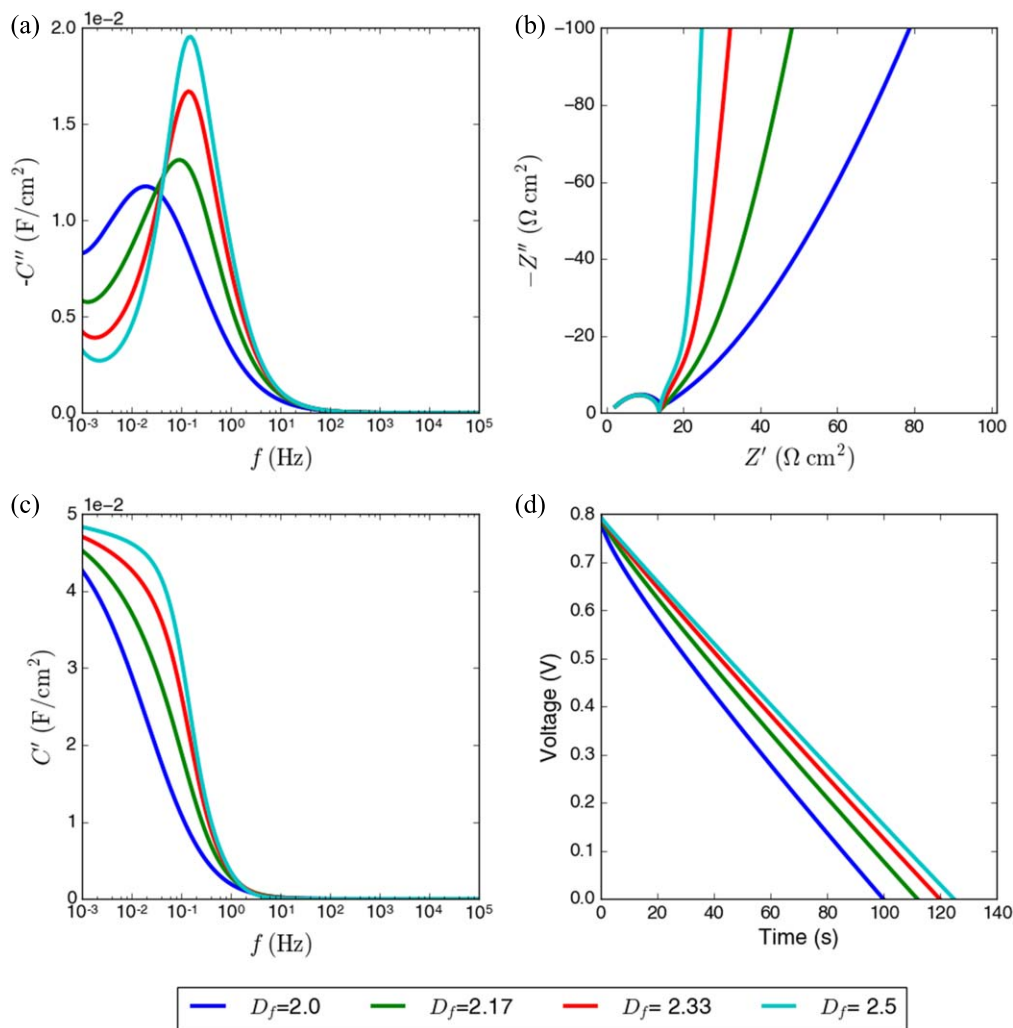


Figure 6. Parametric study demonstrating the effect of fractal dimension on (a) Imaginary capacitance bode plot, (b) Real bode plot, (c) Nyquist plot and (d) Galvanostatic discharge data.

increase in resistivity through the external resistance R_{ext} and electrode conductivity σ to mimic the effect of deposition of pseudocapacitive layer. To conduct parametric studies of such devices, previously defined parameters such as those in Table II are used. Additionally, we constrain the maximum specific capacitance of MnO₂ to 1370 F g⁻¹ based on the theoretical capacitance. The parameters used to simulate both the original uncoated capacitor and the new MnO₂-coated pseudocapacitor at various surface area reductions are summarized in Table IV. The value for the electrode conductivity, σ was based on literature values.⁶⁸ Using these constraints, the impedance spectra and the discharge profile was simulated for varying degrees of pseudocapacitive layer deposition as denoted by change in the percentage of surface area.

Figure 7 shows the effect of surface area reductions in the performance of MnO₂-coated pseudocapacitor. Because energy density is proportional to surface area utilization, lower surface area results in a faster discharge, indicating a decrease in energy density. The effect of surface area on discharge time can also be found in the Bode plot where the characteristic frequency shifts to higher frequencies with decreasing surface area. Figure 8a shows a more explicit illustration of how surface area affects specific capacitance at 1 A g⁻¹. An almost linear relationship can be found where surface area reduction leads directly to significant reduction in capacitance. However, the capacitance of these coated devices was still higher than the uncoated carbon-based capacitor. In Fig. 8b, the detrimental effect of surface area reduction was much clearer. While

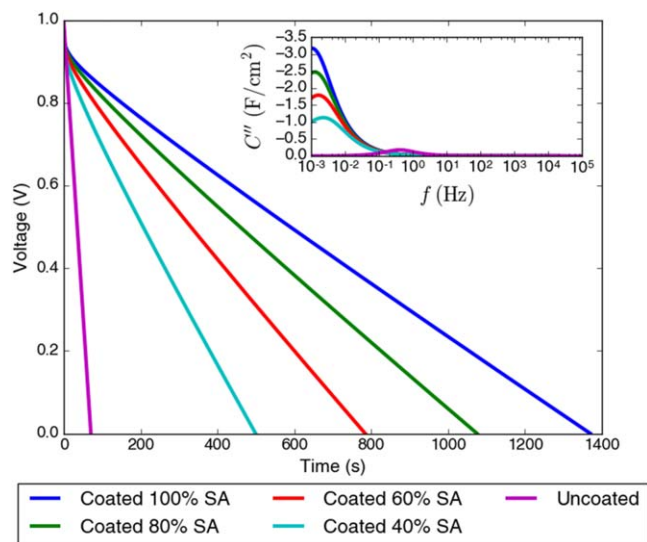


Figure 7. Discharge curves and imaginary capacitance Bode plot of hypothetical MnO₂-coated carbon-based pseudocapacitors at various surface area reductions compared to the original uncoated carbon-based capacitor. Percentage denotes the surface area (SA) retained, e.g. 80% SA means 80% of the original surface area is retained.

Table IV. New values for previously defined parameters to simulate an uncoated carbon-based capacitor and the MnO₂-coated pseudocapacitors.

Parameters	Uncoated	MnO ₂ -coated	Sources
C_{dl} ($\mu\text{F cm}^{-2}$)	10	10	Estimate
C_{ϕ}' ($\mu\text{F cm}^{-2}$)	—	239.7	Match 1370 F g ⁻¹ limit for operation at 1 A g ⁻¹
a ($\text{cm}^2 \text{cm}^{-3}$)	$3.6 \cdot 10^6$	$3.6 \cdot 10^{6a)}$	Assuming 600 m ² g ⁻¹ surface area and 0.6 g/cc carbon
σ (S cm^{-1})	8	$(1.6 \pm 0.3) \cdot 10^{-3}$	For uncoated, ⁶⁸
C_{dl} ($\mu\text{F cm}^{-2}$)	10	10	Estimate
R_{ext} (Ωcm^2)	1	5	Estimate
Mass	5.00	5.15	Estimate, based on MnO ₂ density of 5 g/cc

a) Reductions will be made in percentages, e.g. 80% surface area (SA) means only 80% of surface area is retained.

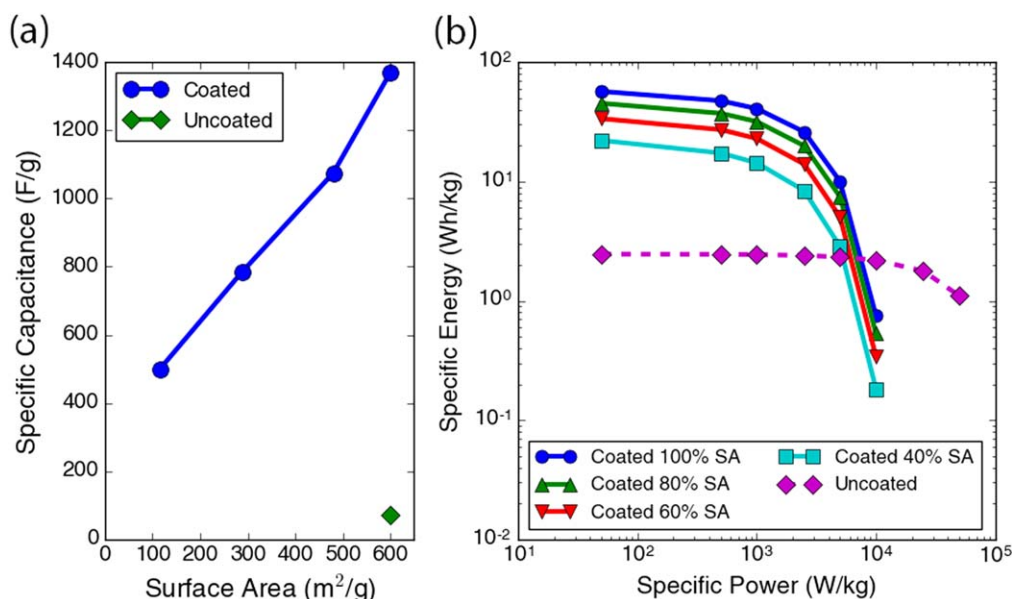


Figure 8. (a) Specific capacitance of coated carbon-based capacitors in comparison to the uncoated capacitor. (b) Ragone plot of coated carbon-based capacitors in comparison to uncoated capacitor. Percentage denotes the surface area (SA) retained, e.g. 80% SA means 80% of the original surface area is retained.

the uncoated device can stably maintain its energy density at high power operations, the MnO₂-coated capacitors cannot perform as well due to the increase in resistivity. Coupled with surface area reduction, the pseudocapacitor may even have lower much lower energy density than their uncoated counterpart at very higher power operations. The potential enhancement of energy density at lower power density could be as high as 23 times that of the uncoated capacitor.

Conclusions

Frequency-Domain Admittance Method (FDAM) was applied as a tool to interpret and predict electrochemical data of pseudocapacitors in both time-domain and frequency domain. The method was tested and validated using symmetric MnO₂ and polypyrrole pseudocapacitors. The microscopic description of pseudocapacitance was developed using electrochemical adsorption reaction mechanism and anomalous diffusion process at electrode/electrolyte interface. The results show successful impedance fit and discharge simulation. Parametric studies on various key model parameters (C_{ϕ} , R_{ct} , and D_f) and their influence on the discharge performance and impedance spectra have been also been shown. Simulations have also shown the positive and detrimental effects of coating pseudocapacitive materials onto high surface-area carbon electrodes. Overall, FDAM was able to provide both qualitative and quantitative information regarding the influence of pseudocapacitor's microscopic parameters on the device performance.

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