Multi-scale impedance model for supercapacitor porous electrodes: Theoretical prediction and experimental validation

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HIGHLIGHTS

- A multi-scale impedance model is developed for porous carbon electrodes.
- The lower-frequency line deviating from 90° is ascribed to a faradaic process.
- Both charge storage capacity and ion transfer rate are studied via AC impedance.

GRAPHICAL ABSTRACT
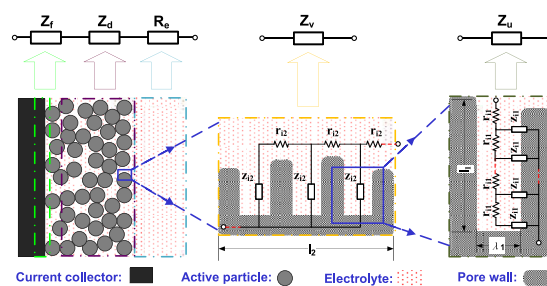
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ABSTRACT

In this paper, a multi-scale impedance model is developed for evaluating the charge storage capacity and ion-transfer rate of supercapacitor porous electrodes. This model can be used to theoretically understand the contributions of the intra-particle pore at nano-scale, the inter-particle pore at micron-scale, and the porous electrode at millimeter-scale to the performance of supercapacitor. Then, impedance spectrum characteristics of porous electrodes are screened via numerical simulation based on the developed multi-scale impedance model, especially for different electrode thicknesses and various faradaic processes with different time constants. Subsequently, seven supercapacitor samples, four of them with electrode thicknesses of 60, 100, 180, and 370 μm respectively, and three of them with different types of current collectors (nickel, carbon-coated stainless-steel, and stainless-steel), are fabricated and characterized to validate the developed model. The fitting results and residuals of the measured impedance data validate the linear relationship of the scaled equivalent resistance of electrolyte v. s. electrode thickness and the scaled characteristic time constant v. s. the square of electrode thickness. The validated multi-scale impedance model might offer an effective method to rationally balance or optimize charge storage and charge transfer via morphology design for porous electrodes.

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1. Introduction

Supercapacitors (SCs) have been recognized as promising devices for rapid energy storage and delivery [1]. Furthermore, SCs well fill the power/energy gap between traditional dielectric capacitors and batteries/fuel cells [2]. In principal, SCs can be classified into two types: one is the electrical double layer supercapacitor (EDLC), and the other is the faradaic supercapacitor [3]. Regarding the electrode materials, carbon-based ones are the most widely used mainly due to their low-cost, ease of processability, relatively inert electrochemistry, and controllable porosity [4]. The morphologies of porous carbon electrodes are of technological importance for SC charge storage capacity and ion transfer rate [5]. In general, the nano-scale pores of such materials benefit to maximizing the charge storage capacity, but such pore structure may limit charge and discharge rate by impeding ion diffusion [6]. To fundamentally understand the morphology effect of electrode materials on the SC performance, both theoretical and experimental approaches are necessary.

For an optimization of SC charge storage capacity and ion transfer capability, a complete interpreting how can the morphologies affect the charge storage capacity and charge transfer rate is required [5,7]. In this regard, electrochemical impedance spectroscopy (EIS) can be employed for both measurement and theoretical data interpretation with both accurate chemical and physical meanings in wide frequency range and quasi-steady state [8]. With respect to this, continuing efforts for more than half a century have resulted in a large body of literature on impedance modeling for porous electrodes. Impedance models for porous electrodes can be classified into two types based on the studied focuses: **1)** modeling open pores. For instance, Itagaki et al. [9] developed a multi-scale impedance model for porous electrodes with fractional structure, focusing on three-scale pores, i.e. meso pores embedded into macro-pores and micro-pores embedded in meso-pores; and **2)** modeling the active materials. For example, Huang et al. [10,11] developed an impedance model for porous electrodes based on an agglomerate impedance model, focusing on active materials with three-scale, i.e. primary particles, agglomerates, and porous electrodes.

Those two types of model above could resolve or answer some questions and be roughly reviewed as follows: **1)** Levie firstly used a transmission line model (TLM, called Levie Equation) to analyze impedance response with a purpose to profile charge transport and charge storage in porous electrodes [12,13]. The Levie equation is regarded as the simplest but the most attractive impedance model for porous electrodes due to its ease of implementation. This model is widely used, for instance, Kandy et al. [14] and Barcia et al. [15,16] separately employed it to characterize porous electrodes; **2)** Ho and Raistrick et al. [17,18] also developed the impedance model for porous thin film electrodes with the purpose to investigate the competition effects between charge transfer and mass transport, in which lithium diffusion, double layer charging and gas diffusion were studied; **3)** Lasia [19,20] presented a numerical solution and also developed impedance model for the distributions of pore potential and current in the presence of concentration gradient of electroactive species in porous electrodes; **4)** To address the intercalation reaction and uneven pore sizes of the porous electrodes, Meyers et al. [21] developed the impedance model and investigated charge-transfer, double-layer, and solid-phase diffusion. Song et al. [22,23] considered pore size distribution (PSD) in porous electrodes and developed an impedance model to analyze the impedance data; **5)** Bisquert et al. [24,25] incorporated the anomalous transport into the standard double-channel transmission line model for porous electrodes, in which the influence of boundaries on impedance response was also studied; **6)** Yoon et al. [26,27] developed two-scale hyperbolic cotangent equations to represent the impedance response for both intra-particle and inter-particle pores in the porous electrode, the rate capabilities of porous carbon electrodes were also quantitatively evaluatedin terms of the ionic accessibility profile; and **7)** Based on the assumption that nano-scale pores are connected to the micron-scale

pores, Suss et al. [28] developed bi-modal porosity impedance model for the purpose to optimize charge storage capacity and ion transport rate. Oz et al. [29] used the bi-modal porosity network to characterize the degradation of SCs, and Kant and Singh [30] developed a model of EDLC dynamics for porous electrodes with surface heterogeneity.

In order to quantitatively evaluate the charge storage capacity and ion-transfer rate for supercapacitor porous electrodes, a multi-scale impedance model is definitely required. The multi-scale model is expected to pass through three scales: the nano-scale intra-particle pore, the micron-scale inter-particle pore connected to a series of intra-particle pores, and the millimeter-scale porous electrode of supercapacitor. The developed multi-scale impedance models serve to optimize the electrode design, which benefits to a faster charge transfer rate and larger charge storage capacity.

In our previous work [31], the performance of BP2000-based supercapacitor was systematically evaluated via DC test methods under conditions of different electrode thicknesses, electrolyte concentrations, binder concentrations and conducting carbon concentrations. In this paper, our intention is to further reveal how morphologies affect charge storage capacity and ion transfer rate for the porous electrodes, based on the constructed multi-scale impedance model and the measured data of the supercapacitors.

2. Multi-scale impedance modeling for porous carbon electrodes

As demonstrated, EIS can be used to investigate redox reaction mechanism [32,33], to evaluate interlayer of electrolyte/anode [34], to study species diffusion coefficient [35], as well to study properties of porous electrodes [12–30]. However, the EIS data explanation is not easy; it requires extensive knowledge involving material science, electrochemistry, and mathematic skills. This strict requirement sometimes impedes exploring the full potential of EIS function [36].

2.1. Levie's equations for porous electrodes

2.1.1. General interface

A transmission line model for cylindrical pores with aqueous electrolyte filled was proposed by Levie [12,13]. The whole impedance for a general cylindrical pore with electrolyte filled can be expressed as Z_p:

$$Z_p = \sqrt{r_i z_i} \coth\left(l\sqrt{\frac{r_i}{z_i}}\right) \tag{1-1}$$

$$r_i = \frac{4\rho_i}{\pi\lambda^2} \tag{1-2}$$

$$z_i = \frac{z'_i}{\pi\lambda} \tag{1-3}$$

The definitions for paramters in Eq. (1) refer to nomenclatures.

For a general pore considered, the overall resistance of electrolyte and the impedance of electrolyte/electrode interface can be defined as r_p and z_p, respectively:

$$r_p = r_i l \tag{2-1}$$

$$z_p = \frac{z_i}{l} \tag{2-2}$$

Combining Eqs. (1) and Eq. (2) yields:

$$Z_p = \sqrt{r_p z_p} \coth\left(\sqrt{\frac{r_p}{z_p}}\right) \tag{3}$$

2.1.2. Ideal interface

More often, the interface of electrolyte/active layer in pores is assumed to exhibit an ideal capacitance behavior. In this case, the total impedance can be named as Z_{p0} and expressed as follows: