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# Impedance-based study of capacitive porous carbon electrodes with hierarchical and bimodal porosity

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## HIGHLIGHTS

- Novel framework for characterizing hierarchical and bimodal supercapacitor electrodes.
- First detailed characterization of hierarchical carbon aerogel monolith electrode set.
- Novel measurements and analysis of an HCAM electrode with sub-nanometer sized pores.

## ARTICLE INFO

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## ABSTRACT

Porous electrode capacitors are used extensively in systems which store energy, harvest mixing energy, or desalinate water. These electrodes can possess a hierarchical pore structure with larger macroscale pores allowing for facile ion and fluid transport, and smaller, nanometer-scale pores enabling significant ion storage. We here present a combined theoretical (linear circuit model) and experimental (electrochemical impedance spectroscopy) study of porous carbon electrode capacitors which integrate nanoscale pores into a micron-scale porous network. Our experiments are performed on a set of custom-fabricated hierarchical carbon aerogel electrodes with varying pore structure, including electrodes with sub-nanometer (sub-nm) pores. Our combined theory and experimental approach allows us to demonstrate the utility of our model, perform detailed characterizations of our electrodes, study the effects of pore structure variations on impedance, and propose hierarchical electrode design and characterization guidelines. Further, we demonstrate that our approach is promising toward the detailed study of ion storage mechanisms in sub-nm pores.



## 1. Introduction

Porous carbon electrodes are extensively used as capacitors in many applications, including energy storage, energy harvesting, and water desalination [1–3]. In these systems, a pair of porous electrodes are filled with electrolyte and electrically charged. The resulting electric field causes ions in the liquid phase to transport into electric double layers (EDLs) on electrode surfaces. In electric double layer capacitors used for energy storage, ions are first stored in the EDLs, and subsequently the electrode pair is discharged through a load to deliver power on demand [3,4]. In energy harvesting applications, charged electrode pairs harvest the mixing energy of sea and river water through mechanisms such as EDL expansion/contraction or by leveraging the Donnan potential [2,5,6]. In desalination applications, charging the electrode pair removes significant amounts of salt ions from a liquid electrolyte (such as brackish water), and energy can be recovered when the ions are released into a brine stream [1,7–11].

In many porous electrode capacitor systems, the electrode pore structure consists largely of nanoscale pores in order to maximize ion storage capacity [1,11–13]. However, such a pore structure can limit charge and discharge kinetics by impeding ion transport [14]. High impedance to ion transport within the pore structure slows the temporal response, and so reduces device power density or increases time required for desalination. To prevent such transport limitations, several studies have proposed and analyzed electrode materials with

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a hierarchical pore structure [7,15–19]. These electrodes typically contain a continuous, larger diameter pore network for low-resistance ion transport (typically macro- or mesoscale pores). These larger pores connect to smaller diameter pores that provide high specific surface areas used for ion storage (typically micro- or mesoscale pores). In addition to potentially improving ion transport, hierarchical electrodes lower the resistance to fluid flow through the electrode. Low impedance to fluid flow is essential for desalination devices with "flow-through" architecture wherein feed stream is transported primarily through the electrode itself [7].

Electrochemical impedance spectroscopy (EIS) measurements of porous electrode impedance have proven to be a powerful tool in electrode design and characterization, and have been used extensively [4]. However, circuit models commonly used to interpret porous electrode impedance are not appropriate for porous electrodes with a hierarchical pore structure, as they are either overly-simple (e.g., an RC circuit) [20], consist of transmission line or ladder network representations of porous electrodes with unimodal, non-hierarchical pore structure [3,21,22], or capture the effects of a continuous pore size distribution of parallel pores [23]. Surprisingly, despite the widespread development of hierarchical porous electrode capacitors and their frequent characterization by EIS [24–27], few previous studies interpreted their EIS results using circuit models specifically for hierarchical electrodes. Exceptions include the work by Eikerling et al. and Yoon et al. [19,28]. Eikerling et al. presented a circuit model capturing the impedance of a hierarchical electrode consisting of an amalgamation of porous carbon agglomerates [19]. Yoon et al. described a model capturing the impedance of templated hexagonal mesoporous carbon electrodes [28]. However, each of these ad hoc circuit models was material specific and complex. For example, the model of Eikerling et al. captures the impedance of a multi-scale pore structure within the carbon agglomerates by using a complex self-affine Cantor-block model [19]. Further, in these works, limited experimental results were presented. The work of Eikerling et al. and Yoon et al. each presented EIS results from a single electrode material with varying electrode thickness [19,28].

We here present a combined theory (linear circuit model) and experimental (EIS) study using a set of newly-developed hierarchical carbon aerogel monolith (HCAM) electrodes which have a bimodal pore size distribution. These electrodes have been applied successfully to energy storage [29,30], and water desalination systems [7]. HCAM electrode materials are fabricated initially with a continuous micron-scale pore network. Nanoscale features are then etched into the surfaces of this network by thermal activation [31]. The set of electrodes we use in this study includes both unactivated samples and activated samples with varying activation times (time the sample is exposed to a high temperature $CO_2$ environment). By tuning the activation time, we can controllably vary the pore structure of our hierarchical electrode, and study the effects of this alteration on measured impedance. Additionally, we present and analyze a simple circuit model representing a hierarchical electrode with strongly bimodal porosity (i.e. with nanoscale pores integrated into a micron-scale pore network). Our combined model and experimental results allow us to demonstrate the utility of our model, provide detailed characterizations of our HCAM electrode set, study the effect of pore structure variations on electrode impedance, and present guidelines toward hierarchical electrode design and characterization. We further show evidence suggesting our techniques can enable the detailed study of hierarchical electrodes with sub-nanometer (sub-nm) diameter pores, where sub-nm pores have generated significant interest for enabling high energy density electrochemical capacitors [32,33].

## 2. Theory

We here present a linear circuit model representing the impedance of a hierarchical porous electrode with bimodal porosity. The model represents a morphology where smaller nanometer or sub-nm scale "storage" pores are integrated into the surfaces of a network of larger "transport" pores. We build our circuit model based on the idealized structure shown in Fig. 1a: A finite length transport pore with an amount $m$ of smaller, branching storage pores equally distributed along the length of the transport pore. Consistent with traditional and widely-used assumptions for porous electrode impedance models [3,19,21], we model each of the two sets of pores as having a uniform cross-section; we assume negligible resistance of the electrode solid phase; and we assume that the pores are completely filled with a uniform electrolyte. As per Fig. 1b, we model the hierarchical pore impedance, $Z$, as a distributed network of the transport pore electrolyte resistance, $R_{t,1}$, and the transport pore wall impedance, $Z_{w,1}$ [21,34]:

$$Z = \left(R_{t,1}Z_{w,1}\right)^{1/2}\coth\left[\left(R_{t,1}/Z_{w,1}\right)^{1/2}\right]. \quad (1)$$

In our notation, the first subscript denotes a property of the transport pore, "t", the transport pore wall, "w", or of the storage pore, "s". With the second subscript, we denote either a property of a single pore, "1", or the effective property of "$m$" pores in parallel. In Eq. (1), $R_{t,1}$ and $Z_{w,1}$ are each in units of Ohms. We describe $Z_{w,1}$ as a parallel combination of the EDL capacitance of the transport pore wall, $C_{t,1}$, and the impedance of the $m$ branching storage pores, $Z_{s,m}$:

$$Z_{w,1} = \frac{Z_{s,m}j}{j - \omega C_{t,1}Z_{s,m}}. \quad (2)$$

Here, $\omega$ is the angular frequency of the input signal and $j$ is the unit imaginary number. We further model each individual storage pore as a distributed network of the storage pore electrolyte resistance,

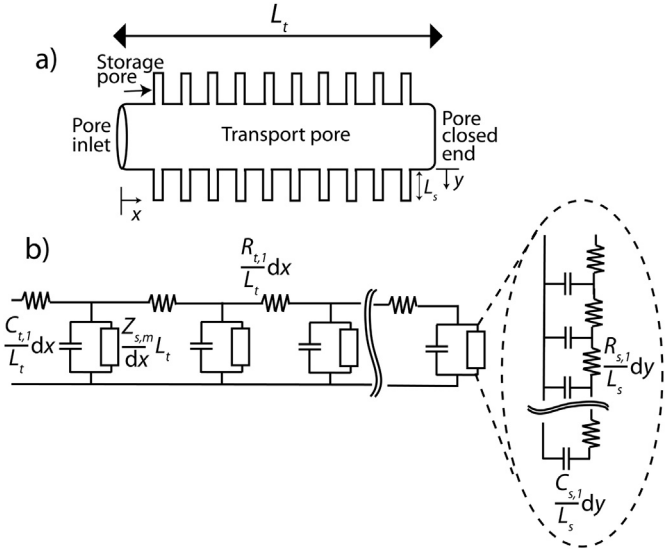


**Fig. 1.** a) Schematic of a single, finite length transport pore with a number $m$ of equally spaced, branching storage pores. b) The circuit model used to describe the impedance of the structure shown in a). This impedance consists of a distributed network of the transport pore resistance, $R_{t,1}$, and the transport pore wall impedance, $Z_{w,1}$. $Z_{w,1}$ is a parallel combination of the transport pore EDL capacitance, $C_{t,1}$, and the impedance attributed to the $m$ storage pores $Z_{s,m}$. Within the dotted lines, we show the circuit model representing the impedance of a single storage pore, which is a distributed network of that pore's resistance, $R_{s,1}$ and capacitance, $C_{s,1}$.