



Isolating the effect of pore size distribution on electrochemical double-layer capacitance using activated fluid coke



Jocelyn E. Zuliani^a, Shitang Tong^b, Donald W. Kirk^a, Charles Q. Jia^{a,*}

^a Department of Chemical Engineering & Applied Chemistry, University of Toronto, 200 College St., Toronto, Ontario M5S 3E5, Canada

^b Department of Chemical Engineering, Wuhan University of Science and Technology, 947 Heping Avenue, Wuhan, Hubei 430081, China

HIGHLIGHTS

- Porous carbons with distinct pore sizes were tested for electrochemical capacitors.
- First comparison of carbons with similar surface areas, but different pore sizes.
- Micropores boost normalized capacitance even in broad pore size distribution carbon.
- A minimum voltage is needed to boost the capacitance in highly microporous carbons.
- Results strength theory that the electrical double layer is thinner in micropores.

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ABSTRACT

Electrochemical double-layer capacitors (EDLCs) use physical ion adsorption in the capacitive electrical double layer of high specific surface area (SSA) materials to store electrical energy. Previous work shows that the SSA-normalized capacitance increases when pore diameters are less than 1 nm. However, there still remains uncertainty about the charge storage mechanism since the enhanced SSA-normalized capacitance is not observed in all microporous materials. In previous studies, the total specific surface area and the chemical composition of the electrode materials were not controlled. The current work is the first reported study that systematically compares the performance of activated carbon prepared from the same raw material, with similar chemical composition and specific surface area, but different pore size distributions. Preparing samples with similar SSAs, but different pores sizes is not straightforward since increasing pore diameters results in decreasing the SSA. This study observes that the microporous activated carbon has a higher SSA-normalized capacitance, $14.1 \mu\text{F cm}^{-2}$, compared to the mesoporous material, $12.4 \mu\text{F cm}^{-2}$. However, this enhanced SSA-normalized capacitance is only observed above a threshold operating voltage. Therefore, it can be concluded that a minimum applied voltage is required to induce ion adsorption in these sub-nanometer micropores, which increases the capacitance.

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1. Introduction

Electrochemical double-layer capacitors (EDLCs) are promising energy storage devices that exhibit a high power density and moderate energy density. There is a need for a broad array of efficient electrical energy storage devices due to the rapid charging, long cycle life, and high power density demands needed for electric vehicles and for sustainable energy generation and supply. One of the main challenges facing EDLC devices is a low to moderate

energy density. Energy density is directly proportional to device capacitance; therefore, increasing a device's capacitance is critical to improving its performance [1–14].

Electrochemical double-layer capacitors store energy by physical ion adsorption onto the surface of an electrode. Highly porous, high surface area materials are used as the electrode material to improve performance. Because of its relative abundance, chemical inertness, high conductivity, and low cost, porous carbon is a common electrode material either as activated carbon or as more structured nanoporous carbon materials, such as carbon nanotubes, graphene, and carbon nanoribbons [1–14].

The energy storage mechanism in EDLCs is based on electrolyte ion separation and adsorption on the surface of the porous

* Corresponding author.

E-mail address: cq.jia@utoronto.ca (C.Q. Jia).

electrodes, which forms the capacitive electrical double layer (EDL) [1–3]. The capacitance of the EDL on a flat surface is described by Equation (1), where capacitance is proportional to the vacuum permittivity, ϵ_0 , the relative dielectric constant of the electrolyte in the EDL, ϵ , the accessible surface area for ion adsorption, A , and inversely proportional to the thickness of the EDL, d [15].

$$C = \frac{\epsilon_0 \epsilon A}{d} \quad (1)$$

The capacitance of an EDLC is influenced by both the electrode and electrolyte. The electrolyte selection defines the relative dielectric constant, and the size and shape of the ions that are adsorbed onto the electrode surface. The chemical composition of the electrode material and the electrolyte determine the ability of the electrolyte to wet the porous carbon and absorb into the pores. The properties of the electrode material determine the accessible surface area available for ion adsorption, and the pore size distribution, which has been shown to affect the thickness of the EDL [1–3,16–18]. Equation (1) represents the simplest model for the capacitance of a flat plate. There have also been equations developed to describe the capacitance of more complex pore structures, such as cylinders or narrow nanopores [12,19]. All of these models include an inverse dependence on the thickness of the EDL, represented by d in Equation (1), indicating that this is a critical parameter that affects the capacitance.

A common metric used to evaluate the performance of electrode materials in EDLCs is the specific surface area (SSA) normalized capacitance, which is defined as the capacitance divided by accessible surface area [1–14,17]. By dividing Equation (1) by the total accessible surface area for ion adsorption, A , the SSA-normalized capacitance becomes associated with fundamental system parameters, as described above. The total accessible surface area of an electrode is typically calculated by multiplying the mass of the active material in the electrode by that material's SSA [1–3]. For porous electrode materials, the SSA is calculated using isothermal adsorption data and recently developed density functional theory (DFT) models. These DFT models are also used to calculate the material's pore size distribution [20–22].

The theoretical maximum SSA-normalized capacitance for carbon is $21 \mu\text{F cm}^{-2}$, estimated using Equation (1) for a flat graphene sheet [23]. Compared to this ideal case, activated carbon materials typically have SSA-normalized capacitance values between 8 and $11 \mu\text{F cm}^{-2}$, presumably due to limited ion penetration of the total measured surface area, which is a result of the amorphous and complex internal pore network [1,3,10,11,24–26]. The ideal material would store the maximum energy per unit surface area. Since energy density is proportional to capacitance, maximizing SSA-normalized capacitance is important to improve electrode material performance.

In porous materials, the pores are broken into three categories, micropores (pore size < 2 nm), mesopores (pore size 2–50 nm), and macropores (pore size > 50 nm). It is generally accepted that the pore size distribution of the porous carbon electrode affects the capacitive energy storage [1–14].

Previous work has reported that as the pore size and the diameter of the solvated electrolyte ion become similar, an increase in SSA-normalized capacitance is observed. This was initially reported by Chmiola et al., where the SSA-normalized capacitance increased from $6 \mu\text{F cm}^{-2}$ at pore sizes of 1.1 nm, to $14 \mu\text{F cm}^{-2}$ at pore sizes of 0.7 nm [27]. Further investigation and mathematical modeling suggested that ions may undergo partial desolvation or solvation shell distortion in sub-nanometer pores. Ion solvation shell distortion will cause the EDL to become thinner (i.e. reducing the magnitude of d in Equation (1)), which results in a greater SSA-

normalized capacitance for these sub-nanometer pores [16–18,27–37].

While this theory presents an opportunity to increase the energy density of EDLC, there remains significant debate within the scientific community. As identified by Gu and Yushin [7], the enhanced capacitance in sub-nanometer pores is not observed in all EDLC systems and depends on the electrode material and the electrolyte combination. Some of the challenges cited by Gu and Yushin were variations in carbon chemistry and microstructure, and the accuracy and validity of the sorbents and models used to calculate the SSA of the porous carbon electrodes [7].

As well, there have been literature papers that show contrasting results. Centeno et al. presented a counter theory that showed while the volumetric capacitance increases as pore size decreases, the SSA-normalized capacitance does not always show the same trend. Depending on the model selected to predict the SSA and pore size distribution, the relationship between pore size and capacitance changes. Some models show a strong correlation between SSA-normalized capacitance and pore size, while others show almost no correlation. Centeno et al. concluded that if the SSA and pore size distribution were taken as the average of many models, there was no correlation between pore size and SSA-normalized capacitance [38]. There have been other papers that suggest that mesopores may be more effective for EDLCs. It is hypothesized that mesopores improve ion transport at faster charging rates, allowing for greater capacitance. Mesopores also result in a larger volume of electrolyte within the carbon electrode structure, which allows the applied surface charge to be matched by adsorbed ions without causing ion depletion in the electrolyte [24,39,40]. However, a limitation of these all studies was variation in specific surface area of the carbon electrode materials, which is known to affect the value of the materials' gravimetric and volumetric capacitances. As well, the chemical composition of the materials varied between studies.

The chemical composition of the electrode material affects the ability of the electrolyte to wet the surface, thus affecting pore accessibility. As well, specialized functional groups in the carbon structure may result in enhanced energy storage due to rapid charge transfer reactions. Both of these chemistry related phenomena can have an effect on SSA-normalized capacitance [1–14].

One of the main challenges is isolating the relative effects of pore size and surface area on the total capacitance. Preparing activated carbon samples that have significantly different pore size distributions, but with similar SSAs, chemical composition, and macroscopic structure is not straightforward. To the authors' knowledge, there has not been a direct comparison of two materials with similar specific surface areas and chemical composition, but differing pore size distributions because as the pore size increases into the mesoporous range, the specific surface area tends to decrease due to the lower surface to volume ratio of mesopores compared to that of micropores. By maintaining materials with similar specific surface area values, the relationship between capacitance and total accessible surface area is kept relatively constant. Therefore, variations in capacitance may be associated with changing pore structure, thus isolating the effects of pore diameter.

The first part of this study focuses on identifying the relative effects of surface area and pore size on capacitance. Two activated carbon materials were prepared from oil sands fluid coke using potassium hydroxide chemical activation. By varying the amount of activating agent, the pore size distribution was effectively changed, resulting in a mesoporous activated fluid coke and a microporous activated fluid coke. Unlike previously published work, one of the unique features of the current research is that while the pore size distributions are different, these two activated coke materials have

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