Increase in Capacitance by Subnanometer Pores in Carbon

Electrical double-layer capacitors (EDLCs, also known as supercapacitors or ultracapacitors) store energy by electrosorption of ions at the electrode/electrolyte interface. To achieve a high-energy storage capacity, electrodes with a high surface area and well-developed pore structure in the range from several Angstroms to several tens of nanometers are required. However, neither natural precursor-derived carbons nor templated carbon materials present an ideal, infinitesimally narrow pore size dispersion.

In EDLCs, the use of salt dissolved in an organic or aqueous solvent makes it important to consider the solvation shell around the ions. The bare ion size is usually below 1 nm, whereas the solvation shell can increase the size significantly. Several studies have provided strong evidence of ion desolvation during electrosorption, which is the only way to explain why carbon materials with pore sizes smaller than the solvated ion but larger than the bare ion have high charge storage capacities. A maximized capacitance (normalized by the surface area) was found in experimental and theoretical studies when matching the pore size with the ion size. This effect seems to be universally applicable for solvent-containing and solvent-free electrolytes (ionic liquids), while important secondary differences are to be considered for the latter. For example, the oscillatory dependency of capacitance on pore size predicted for neat ionic liquids and ideal carbons with slit pores is lost when introducing a solvent, where a single maximum is observed when the ion size and the pore size are identical.

This Viewpoint clarifies the correlation between capacitance and pore size, which is of high practical importance for the design of advanced carbon electrode materials. Two extreme cases are obvious: excessively large pores, accompanied by large pore volumes and limited specific surface area, will lead to a low energy storage capacity, whereas very small pores will limit the ion access due to steric effects (Figure 1), in addition to imposing obstacles to ion transport. Yet, for the intermediate range, down to the point when the pores are too small for the bare ion to fit, there is no consent in the literature about the correlation between the pore size and the corresponding area-normalized capacitance. For example, there has been criticism about the method of surface area determination and normalization, especially considering the inadequacy of the Brunauer–Emmett–Teller (BET) model for microporous carbons. Benchmarking various kinds of carbons, including carbon monoliths, a "regular pattern" was presented, suggesting that the area-normalized capacitance does not depend on the pore size. This lack of dependence can be explained by neither the ab initio or molecular dynamics models nor geometric considerations as when the pore diameter increases by 50–90%, there is still just one ion in each pore contributing to charge storage and the remaining surface area and pore volume remain unused, decreasing the capacitance normalized by the pore surface or volume.

Recently, we developed a model for understanding the capacitance of microporous carbons, taking into account the entire measured pore size distribution, and have established a comprehensive data set of electrochemical measurements. Density functional theory (DFT) kernels were used, which are currently the most advanced methodology to extract porosity data from gas sorption isotherms for meso- and microporous carbons and effectively avoid the fundamental limitations of the BET theory. Activated carbon showed the highest specific surface area (SSA), followed by two different titanium caride-derived carbons (CDCs), activated carbon black (CB), and carbon onions. Yet, when normalizing electrochemical performance data on porosity values, we first have to consider differences between dry powder and film electrodes. Then, we have to assess the differences in pore size distributions; these are shown in Figure 2A normalized to 100% for the aforementioned carbon materials. Many carbons display a significant dispersion width; this is why the often-used volume-weighted average pore size \( d_{45} \) does not fully capture the pore size distribution width, as we show by adding values for \( d_{25} \) and \( d_{75} \), representing the pore width encompassing 25 and 75% of the total pore volume, respectively (Table 1, Figure 2A).

More differences in the surface area of the different electrode materials become evident when we calculate the electrochemically active surface, that is, the ion-accessible surface area (Table 1, Figure 2B). Taking into account the bare ion size of BF\(_4^-\) (0.45 nm) and TEA\(^+\) (0.67 nm), pores smaller than these...
values are inaccessible to the ions. The result is a further reduction of the specific surface area, and we have to consider different cutoff values for the positively (cutoff pore size of 0.4 nm) and negatively (cutoff at 0.6 nm) polarized electrodes. In the case of CDC, only about 40–50% of the total SSA is accessible to TEA⁺ compared to about 70% for activated carbon and carbon black (Figure 2A).

The reported electrochemical measurements using a three-electrode configuration (for experimental methods see the Supporting Information) showed a nonlinear correlation of SSA and gravimetric capacitance measured in F·g⁻¹ (Table 1) for 1 M TEA-BF₄ in acetonitrile (ACN) or propylene carbonate (PC). A very high Coulombic efficiency (up to 99%) underlines the absence of significant Faradaic reactions in the chosen potential window (Table 1). When we normalize the measured electrode capacitance by the surface area accessible to cations or anions at +1 and −1 V vs carbon, respectively, we see a clear difference between positive and negative polarization (Figure 3, Table 1). Instead of just discussing the electrochemical data in the context of average pore width (d₅₀), we added error bars for the x-axis, which spread between d₂₅ and d₇₅ (Figure 3). Even when considering pore size dispersity, we still see a clear trend of increased normalized capacitance in subnanometer pores, which is significantly larger for negative polarization (i.e., electrosorption of the larger TEA⁺ cation).

The more effective use of available pores in the case of matching sizes results in a strong increase in capacitance, which was already shown by a geometric model of Huang et al. (ref 22; see also the data line in Figure 3). For larger pore sizes, in
particular, for mesopores, the capacitance converges toward an average value below 0.1 F·m⁻², which aligns well with the "regular pattern" value reported by Centeno et al. (ref 15) and with the calculated value limiting the double-layer capacitance at the planar carbon interface (or larger than the few-nm pores; ref 17).

For electrolytes with significant differences between the size of anions and cations, our data clearly show the importance of differentiating between ion electro sorption during positive or negative polarization with use of half-cell measurements (Figure 3). With a larger size of TEA⁺, and smaller corresponding surface area accessible to the cations, the values of areal capacitance during negative polarization are significantly larger than those for BF₄⁻ electro sorption (i.e., positive polarization). Accordingly, advanced EDLC cell design could achieve performance enhancement by developing nanoporous carbon with slightly different pore sizes for the positive and negative electrodes.²³,²⁴

In summary, our data analysis clearly supports the increase in surface-normalized capacitance when most of the pores are below 1 nm, in agreement with previous studies (e.g., see refs 7 and 25). This was shown for carbons with very different pore structures considering the complexity of pore size dispersity and for two different solvents (i.e., PC and ACN). This effect is seen at different amplitudes for positive and negative polarization, with a smaller increase for BF₄⁻ within the range of investigated pore sizes.

Nicolas Jäckel¹,³
Patrice Simon⁷,⁸,∥
Yury Gogotsi*¹,†,∥
Volker Presser*¹,†,∥
¹INM - Leibniz Institute for New Materials, 66123 Saarbrücken, Germany
²Department of Materials Science and Engineering, Saarland University, 66123 Saarbrücken, Germany
³Université Paul Sabatier, CIRIMAT UMR, CNRS 5085, 5085, 31062 Toulouse Cedex 4, France
∥Réseau sur le Stockage Electrochimique de l’Energie, RS2E FR CNRS 3459, 80039 Amiens Cedex, France
†Department of Materials Science and Engineering, and A. J. Drexel Nanotechnology Institute, Drexel University, Philadelphia, Pennsylvania 19104, United States

■ ASSOCIATED CONTENT

* Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.6b00516.

Experimental methods (PDF)

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: simon@chimie.ups-tlse.fr (P.S.).
*E-mail: gogotsi@drexel.edu (Y.G.).
*E-mail: volker.presser@leibniz-inm.de (V.P.).

Notes
Views expressed in this viewpoint are those of the authors and not necessarily the views of the ACS.
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Dr. Weingarth, Dr. Aslan, Anna Schreiber, Jeon Jeongwook (all at INM), and Katherine Van Aken (Drexel University) for their technical support and helpful discussion. N.J. and V.P. also thank Prof. Eduard Arzt (INM) for his continuing support. Y.G. was supported by the Fluid Interface Reactions, Structures and Transport (FIRST) Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences.

■ REFERENCES