Anomalous or regular capacitance? The influence of pore size dispersity on double-layer formation

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HIGHLIGHTS

- Pore size incremental analysis shows non-constant capacitive contribution.
- Differential capacitance depends on type of ion and solvent.
- Ion desolvation may become more important at higher electrode potentials.
- Ionic liquids exhibit cation-anion coordination.

ARTICLE INFO

ABSTRACT

The energy storage mechanism of electric double-layer capacitors is governed by ion electrosorption at the electrode surface. This process requires high surface area electrodes, typically highly porous carbons. In common organic electrolytes, bare ion sizes are below one nanometer but they are larger when we consider their solvation shell. In contrast, ionic liquid electrolytes are free of solvent molecules, but cation–anion coordination requires special consideration. By matching pore size and ion size, two seemingly conflicting views have emerged: either an increase in specific capacitance with smaller pore size or a constant capacitance contribution of all micro- and mesopores. In our work, we revisit this issue by using a comprehensive set of electrochemical data and a pore size incremental analysis to identify the influence of certain ranges in the pore size distribution to the ion electrosorption capacity. We see a difference in solvation of ions in organic electrolytes depending on the applied voltage and a cation-anion interaction of ionic liquids in nanometer sized pores.

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1. Introduction

Electrical double-layer capacitors (EDLCs, members of the family of supercapacitors or ultracapacitors) are energy storage devices with high efficiency and long cycling stability [1–3]. Today, EDLCs are used, for example, in (hybrid) electric vehicles, systems for uninterrupted power supply, or trams [4,5]. In EDLCs, energy storage is accomplished via ion electrosorption in the electrical double-layer (EDL) at the electrically charged interface of high surface area carbon electrodes in contact with an electrolyte [6]. The electrolyte can be aqueous, organic, or an ionic liquid and the

electrochemical stability window determines the ratings for the maximum operational cell voltage [7]. While EDLCs show a moderate energy density compared to lithium-ion batteries, they enable high power performance [8]. It is commonly known that the electrochemical performance of EDLCs varies as a function of the electrode material and the pore structure has been identified as an important parameter governing power and energy ratings [9–11]. Optimized electrochemical performance requires careful matching of the electrode properties to the specifics of a certain electrolyte [7,12].

The most common parameter to describe a supercapacitor's energy storage capacity used in the community is capacitance (Farad = Coulomb/Volt). Currently, this parameter is more extensively used than the energy storage capacity (with the unit Watthour, Wh). The capacitance is usually normalized by mass of active

material ($F \cdot g^{-1}$) and in a symmetrical cell assembly recalculated for one electrode ($C_{single\text{-}electrode} = 4 \cdot C_{device}$). Per definition, capacitance reflects on the prime requisite of supercapacitors, namely, to exhibit a capacitive charge/discharge profile [9]. This means that there should be a monotonic, linear relation between applied potential or cell voltage and accumulated charge. Yet, we note (at least) three general complications to this simplification.

(1) Capacitance may even intrinsically not be a constant material property [13]. Fundamentally shown for graphite by Gerischer et al., the capacitance of carbon may increase when increasing the cell voltage [14]. This effect is not related with nanoconfinement of ions, but is a result of the non-metallic nature of carbon: as higher potentials are applied, increasingly more charges (more than predicted from a linear capacitive correlation) can be accumulated as the density of states of charge carriers changes during charging [15]. In the literature, this effect has been denoted as electrochemical doping and the resulting symmetric distortion measured during cyclic voltammetry (CV) has been coined as butterfly-shape. By this virtue, we may have to consider for carbons a non-constant capacitance as a function of applied potential, called differential capacitance. This effect depends on the structure of carbon and was found to be very pronounced for graphite [14], highly graphitic carbon onions [16], zeolite-templated carbon [17], nitrogen-doped carbon nanotubes [18], and metallic carbon nanotubes [19], but much smaller for more amorphous activated carbon [16].

(2) Another complication to non-constant differential capacitance arises from the structure of the double-layer [20–22]. At very dilute concentrations in the mM range, a constant increase in differential capacitance needs to be considered for very low potentials (e.g., below 200 mV). This effect can be explained in terms of the Gouy-Chapman-Stern model and relates to the dependency of the total potential drop at the fluid-solid-interface on the bulk concentration [22–24]. Using high potentials, we can also see a drastic reduction of the measured capacitance as an effect of ion starvation, causing a characteristic narrowing in the shape of a corresponding CV [25].

(3) A further issue relates to nomenclature and the conceptual basis of capacitance. Be it either by non-faradaic (double-layer capacitor) or faradaic (pseudocapacitor) charge transfer: the prerequisite of a system to qualify as a supercapacitor is the electric behavior of a capacitor (including the small deviations thereof caused, for example, by (1) and (2)). If clear redox-peaks are encountered, then the behavior contains battery-like components up to the point where only insignificant capacitor-like contributions to the charge storage capacity are found and the concept of capacitance becomes unsuitable [26,27]. This issue has led to the report of very large capacitance values recalculated from battery-like systems and incorrect calculation of corresponding energy ratings (esp. specific energy, $Wh \cdot kg^{-1}$). A critical discussion of this issue can be found, for example, in Ref. [28].

The large capacitance of EDLCs, compared to electrolytic capacitors, is accomplished by using nanoporous carbons with high specific surface area. Typical ACs show a large volume of micropores (i.e., pore size <2 nm) and surface area values of 1500 $m^2 \cdot g^{-1}$ or higher [3,29]. Their use brings along a further complication to capacitive considerations for pores smaller than the Debye length with typically a few nanometers. Starting with overlapping potential profiles of the double-layers and ending with pores so small that ions can only enter when (partially) shedding a solvation shell,

there is a large complexity in ion electrosorption processes in nanometer sized pores [30,31]. The seminal work of 2006 published by the Béguin Group [32] (in organic and aqueous media) and by the Gogotsi/Simon Groups [33] (in organic media) demonstrated an increase of the (surface area normalized) capacitance for microporous carbons with decreasing pore size. Similar conclusions were drawn from enhanced salt removal capacity from aqueous saline electrolytes via capacitive deionization by Porada et al. when comparing ACs and carbide-derived carbons (CDCs) [34]. However, (partial) desolvation of ions entering sub-nanometer-sized pores was discussed even earlier, for example by Salitra et al. in the year 2000 [35]. Remarkable are also the conclusions in the 1986 paper of Kastening and Spinzig [36] investigating ion electrosorption in sub-nanometer pores: "*In these narrow pores, however, the usual Gouy-Chapman layer (thickness about 1.3 nm under the conditions applied) cannot be developed because it would require a diameter of at least 2.6 nm. The ions will apparently be partially desolvated when entering these narrow pores.*" [36].

The conclusiveness of the reported experimental data is challenged by several complications.

(1) A first issue concerns the measurement of the pore structure and specific surface area of the dry powder, and relating such data to the electrochemical performance of binder-containing film electrodes induces inconsistencies. The use of polymer binder (esp. when being used in excess of 5 mass %) may lead to a significant reduction of the pore volume/surface area, while the pore size distribution remains less affected [37,38]. Thus, normalizing the measured electrochemical performance to the electrode pore structure should be favored over the porosity of the dry carbon powder only.

(2) Another issue arises from pore size dispersity. No actual carbon material has an ideal monodisperse pore size distribution (PSD). While some optimized AC [39] or CDC [40] materials may come close to being unimodal, we commonly have to consider a spread of the pore volume across a certain pore size range from sub-nanometer to several nanometers. A microporous carbon's pore structure with multimodal PSDs or very broad distributions cannot adequately be expressed by stating one average pore size value [41]. As such, the concept of average pore size may not be suitable when comparing very diverse carbons. Nevertheless, the term average pore size, defined as the pore size up to which 50% of the pore volume is encompassed, itself remains useful for structural comparison.

(3) A third complication is caused by the way values for the surface area or pore volume are determined. Most commonly, gas sorption techniques are used to derive pore characteristics [42]. For example, it has been widely accepted that the BET method [43] fails to accurately represent the pore structure of microporous carbons [44]. Relating electrochemical data to the BET surface area, for microporous carbons, is not recommended and more adequate models have been devised. In particular, deconvolution of nitrogen, carbon-dioxide, or argon sorption data with density functional theory (DFT) approaches have been proven to be powerful tools to investigate microporous carbons [44–46]. The mathematical approach of such complex carbon surface structures with DFT methods leads to certain artefacts. Regarding nitrogen sorption analysis, the most known artifact in non-local DFT (1D-NLDFT) is the gap at about 1 nm pore width which is related to the inadequate assumption of infinite flat, homogenous pore walls and corresponds to the pressure where the first layer of nitrogen fluid is formed [47]. This was improved by the implementation of molecularly