



## Short communication

## Anisometric charge dependent swelling of porous carbon in an ionic liquid

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## ABSTRACT

*In situ* electrochemical dilatometry was used to study, for the first time, the expansion behavior of a porous carbon electrode in a pure ionic liquid, 1-ethyl-3-methyl-imidazolium-tetrafluoroborate. For a single electrode, an applied potential of  $-2$  V and  $+2$  V against the potential of zero charge resulted in maximum strains of 1.8% and 0.5%, respectively. During cyclic voltammetry, the characteristic expansion behavior strongly depends on the scan rate, with increased scan rates leading to a decrease of the expansion. Chronoamperometry was used to determine the equilibrium specific capacitance and expansion. The obtained strain versus accumulated charge relationship can be fitted with a simple quadratic function. Cathodic and anodic expansion data collapse on one parabola when normalizing the surface charge by the ratio of ion volume and average pore size. There is also a transient spike in the height change when polarity is switched from positive to negative that is not observed when changing the potential from negative to positive indicating the size and the shape of the ion is influencing the expansion behavior.

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## 1. Introduction

Electrical double-layer capacitors (EDLC), more commonly known as ultra- or supercapacitors, have attracted significant interest for energy storage and management because of their high power density, high charge/discharge efficiency, and long service life [1]. Recently, it has been demonstrated that the process of charge storage *via* ion electrosorption is associated with volume variations of porous carbon electrodes upon successive charge/discharge cycles [2–4]. The magnitude of height expansion varies significantly depending on the carbon material used and three different kinds of electrode expansion have been identified so far:

- (i) Expansion due to initial electrode conditioning. This process corresponds, for example, to carbon nanotubes de-bundling ( $\approx 10\%$  irreversible expansion) [5].
- (ii) Expansion in the regime of electrochemical stability yielding fully reversible expansion in the range of *circa* 1% [5,6].

- (iii) Expansion related to intercalation, such as intercalation of acetonitrile-solvated/desolvated tetrafluoroborate ions into graphitic carbon causing strain of up to 60% [3].

Until now, two *in situ* methods have been employed to study the expansion behavior of supercapacitor electrodes: electrochemical dilatometry (eDilatometry) in organic electrolytes [2–7] and electrochemical atomic force microscopy (eAFM) using an ionic liquid with added lithium salt [8]. As shown in these studies, carbon expansion is an intrinsic property that occurs with or without the presence of a polymer binder. The expansion also depends on the ion size, with enhanced swelling occurring when the average pore size is below the dimensions of the ions [6]. The observed level of swelling differs for positive and negative polarizations; the latter usually exhibiting higher electrode expansion because of the large size of the cations [7].

In this paper, for the first time, the swelling of electrodes is reported in a pure ionic liquid (IL; 1-ethyl-3-methylimidazolium tetrafluoroborate, [Emim]<sup>+</sup>[BF<sub>4</sub>]<sup>−</sup>). Our work was motivated by the increasing interest in ILs because of their low vapor pressure, non-flammable character, and wide electrochemical stability window. The study of the expansion behavior of carbon in ILs is equally important for supercapacitors and ionic electroactive polymer composite actuators [9], as both technologies rely on the formation kinetics of the electrical double-layer.

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## 2. Experimental

### 2.1. Material characterization and electrode preparation

Carbide-derived carbon (CDC)[10] obtained by chlorine treatment of boron carbide ( $B_4C$ ) was purchased from Y-Carbon Inc. (USA) and commercial grade YP50 activated carbon was obtained from Kuraray Co. Ltd (Japan). The CDC material was characterized with  $N_2$  gas sorption at  $-196.15$  °C using a Quantachrome (USA) Autosorb-6 system; the pore characteristics were calculated using the Brunauer–Emmett–Teller Equation (BET) [11] and quenched solid density functional theory (QSDFT) [12].

Electrodes were prepared by mixing the porous carbon  $B_4C$ -CDC for the working electrode (WE; thickness: 90  $\mu m$ , diameter: 8 mm, mass:  $3.0 \pm 0.1$  mg) and activated carbon for the counter electrode (CE; thickness: 110  $\mu m$ , diameter: 18 mm, mass:  $17.8 \pm 0.1$  mg); both mixtures contained 5 mass% polytetrafluoroethylene (60 mass% dispersion in water from Sigma-Aldrich) and were roll-pressed to form freestanding films.

### 2.2. eDilatometry setup and electrochemical measurements

An ECD-nano-DL eDilatometer (similar to the setup in Ref. [3]) from EL-Cell (Germany) was used with gold current collectors. The electrochemical cell was assembled in an Argon filled glovebox ( $O_2$ ,  $H_2O < 1$  ppm) and  $[Emim]^+ [BF_4]^-$  (purity  $\geq 99.0\%$ , Sigma Aldrich) was used as the electrolyte. Electrochemical and dilatometric measurements were performed at  $20 \pm 1$  °C with a Biologic VSP-300 potentiostat and displacements were recorded with an Agilent 34972 A data acquisition system. The expansion, perpendicular to the separator, measured with an accuracy of approximately 5 nm, was normalized by the electrode thickness and the point of zero strain was corrected for instrumental shifts. To facilitate data comparison, the net zero expansion at 0 V was normalized to its initial value after each cycle.

## 3. Results and discussion

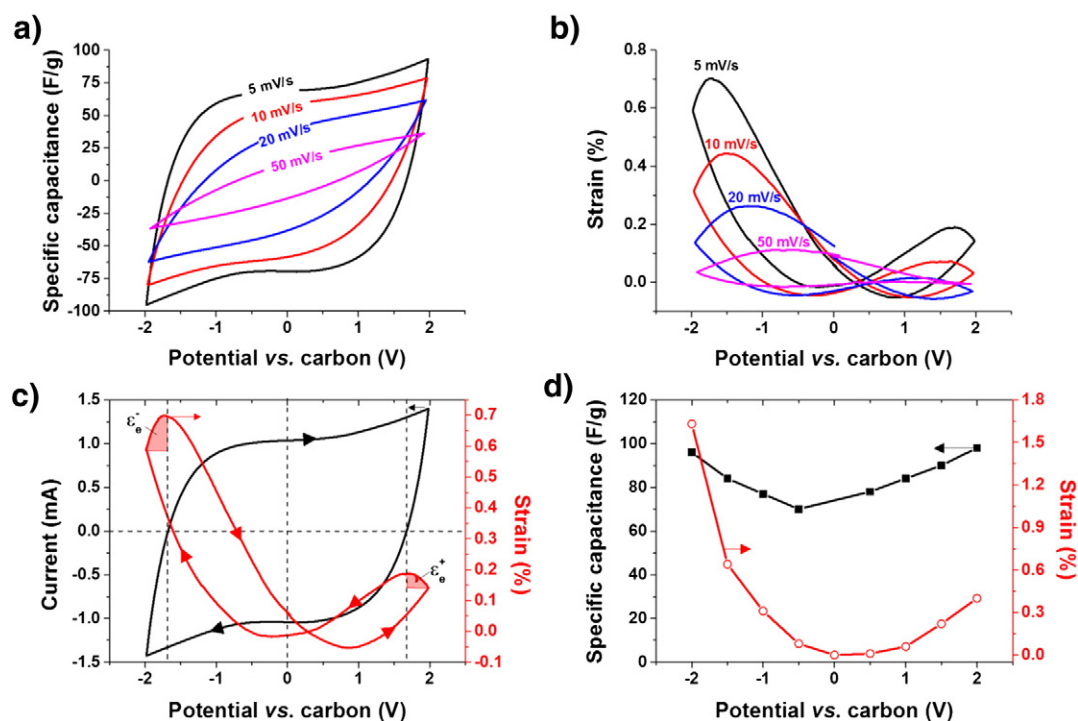
### 3.1. Porosity analysis of the electrode material

$B_4C$ -CDC shows a specific surface area  $S_{BET}$  of 1405  $m^2/g$  ( $S_{QSDFT} = 1375$   $m^2/g$ ) in agreement with literature [13,14]. This material exhibits a bimodal pore size distribution with maxima at  $\approx 8$  and  $\approx 17$  Å and a volume-weighted average pore size ( $d_{50}$ ) of 16 Å. The porosity is 0.92  $cm^3/g$  with  $\approx 60$  vol.% of the pore volume associated with micropores ( $< 20$  Å) and  $\approx 20$  vol.% associated with ultramicropores ( $< 8$  Å).  $B_4C$ -CDC with these pore characteristics was chosen considering the ionic radii (values from DFT calculations) [15] of  $[Emim]^+$  (approx.  $9.5$  Å  $\times$   $6.3$  Å  $\times$   $5.3$  Å;  $V_{ion} = 118.8$  Å<sup>3</sup>) and  $[BF_4]^-$  (approx.  $4.7$  Å  $\times$   $4.9$  Å  $\times$   $4.7$  Å;  $V_{ion} = 48.6$  Å<sup>3</sup>) to enable access to the majority of pores.

### 3.2. eDilatometry and electrochemical characterization

The cyclic voltammograms (CVs) and the corresponding expansions are depicted in Fig. 1a–c in the case of potential sweeping between +2 V and –2 V. Starting from a nearly rectangular-shaped CV typical for EDLCs at 5 mV/s, the influence of resistance (IR-drop) becomes more pronounced as the scan rate is increased (Fig. 1a). All recorded strain was reversible, with larger expansions observed at negative polarization. The smaller accumulated charge at higher scan rates is accompanied by a smaller expansion and flatter hysteresis and the difference between the maximum anodic and cathodic expansion decreases with increasing scan rate (Fig. 1b). This can be explained by the limited ion migration speed of the ionic liquid inside porous carbon at room temperature. Additionally, the increasing scan rate leaves too little time to reach the adsorption equilibrium.

The data at 5 mV/s show that the expansion continues even after reversal of the potential scan direction (labeled  $\epsilon_e^-$  and  $\epsilon_e^+$  in Fig. 1c) and continued expansion can be observed until the net current is zero. In the literature, this dynamic behavior has also been observed for microporous CDC [6] and activated carbon in 1 M tetraethylammonium



**Fig. 1.** Cyclic voltammetry data (a–c) and data from chronoamperometry (d). Cyclic voltammograms, CV, (a) and strain versus potential curves (b) carried out at 5, 10, 20, and 50 mV/s in pure  $[Emim]^+ [BF_4]^-$ . Overlay of CV and expansion curve at a scan rate of 5 mV/s (c); the vertical and horizontal dashed lines represent zero current and/or zero potential. Specific capacitance and expansion derived from chronoamperometry (i.e., charging at incremental potentials and discharging to 0 V for 1 h) (d).

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