Effects of structural disorder and surface chemistry on electric conductivity and capacitance of porous carbon electrodes†

Boris Dyatkin and Yury Gogotsi*

Received 21st March 2014, Accepted 6th May 2014
DOI: 10.1039/c4fd00048j

This article reports on changes in electric double layer charge storage capacity as a function of surface chemistry and graphitic structure of porous carbon electrodes. By subjecting 20 nm to 2.0 μm sized carbide-derived carbons (CDCs) synthesized at 800 °C to high-temperature vacuum annealing at 700–1800 °C, we produce three-dimensional internal surface architectures with similar pore sizes and volumes but divergent surface chemistry and wall graphitization. Annealing increases carbon ordering and selectively removes functional groups, and both transformations affect conductivity and wettability. Contrary to an expected increase in gravimetric capacitance, we demonstrate no increases in charge storage despite increased conductivity and pore accessibility. At the same time, annealing improves the charge/discharge rates in EMIm-TFSI ionic liquid electrolyte. The annealing process eliminates faradaic reactions that limit the voltage window, but potentially accelerates catalytic breakdown of the ions themselves. We therefore corroborate the theory that surface groups and defects in the graphitic structure act as dopants that allow facile movement of ions into pores, improve screening in the superionic state, and affect the quantum capacitance contribution from the carbon structure.

1 Introduction

Electric double layer capacitors (EDLCs), also known as supercapacitors and electrochemical capacitors (ECs), are attracting substantial interest as electrical energy storage solutions for hybrid electric vehicles and other systems.1 The primary charge storage harvesting mechanism, which relies on the electrosorption of ions from an electrolyte onto a porous electrode,2 offers essential advantages such as extended cyclability, stable operation in a wide temperature range,3 versatile geometric configuration, and scalability.4 Porous carbon
electrodes can provide a tuneable, electrically conductive structure with over 3000 m² g⁻¹ in accessible surface area,⁵ extending their gravimetric power densities above 10 kW kg⁻¹.⁶ However, the small operating potential of traditional supercapacitors (<2.7 V) has so far capped their energy densities under 10 W h kg⁻¹,¹ hindering their implementation in automotive and grid storage applications. Most fundamental materials research in the field has therefore focused on tuning the carbon structure and electrolyte composition to maximize capacitance and minimize electrolyte breakdown at high potentials.

Recent research efforts have detailed significant progress optimizing porous carbon structures to accommodate ions. Previous work has repeatedly shown that a tailored pore structure that matches its diameter with the ion that it confines maximizes capacitance due to ion desolvation.⁷ Diameter deviations of ±0.05 nm have been shown to drastically (40%+) affect capacitance.⁸ Moreover, molecular simulations predict a superionic state⁹ of conductive pore walls that, under an applied critical potential, effectively screen similar charges and eject counterions; this process further maximizes capacitance.¹⁰ While single-layer graphene exhibits a theoretical 2630 m² g⁻¹ specific surface area (SSA),¹¹ it cannot offer a sufficient aerial energy density that would make it practical as a standalone material in most power applications.¹² Conversely, activated and carbide-derived carbons (CDCs)¹³ provide 1000–3000 m² g⁻¹ SSA and can be easily scaled up and integrated into various device-specific applications using configurations such as polymer-bonded flexible films.¹⁴

CDC materials, which are synthesized by halogen etching of various carbides (SiC, TiC, B₄C, Ti₃AlC₂, etc.),¹⁵ produce highly tuneable porous structures that can be tailored by varying Cl₂ treatment temperatures (300–1200 °C) and precursor materials.¹⁶ The resulting structures exhibit robust surface chemistry, including C–Cl, C–H, and C–NH₂ groups present as a result of halogen treatment and subsequent H₂/NH₃ annealing.¹⁷ Various hydroxyl and carbonyl groups originate from exposure of the material to air.¹⁸ Additionally, structural defects and lattice strain points are present¹⁹ in the carbon architecture. The structure is composed of a mostly amorphous carbon, with predominant short-range sp² bonding.²⁰ The material’s graphitization increases with synthesis temperature, since thermally-induced mobility facilitates growth of crystallites in the [100] direction and enhances stacking along the [002] direction.²¹ The CDC’s electric conductivity improves as a result: as delocalized π-bonding becomes more prevalent, the graphitic segments’ size and concentration increase and push the material’s electron transport mode from semiconducting to metallic behaviour.²²

While CDC materials have previously demonstrated gravimetric capacitances exceeding 100 F g⁻¹,⁵ and novel organic electrolytes and room-temperature ionic liquids (RTILs) have expanded operating voltage limits,²³ the fundamental relations between carbon structure and corresponding ion behaviour are not fully understood. Standard CDC synthesis convolutes pore diameter, graphitization, and surface chemistry, making it difficult to decouple the standalone effects of each. The thermodynamically limited 4.0–5.6 V windows²⁴ of organic electrolytes and RTILs are reduced to 2.3–2.7 V due to potential-induced breakdown reactions of molecules with functional groups on pore surfaces.²⁵ The reactions also convolute pure double layer charge accumulation with pseudocapacitive contributions from surface redox processes.²⁶ While defunctionalization increases hydrophobicity,²⁴ it is unclear how this affects the ion dynamics, the carbon-
electrolyte interface, and subsequent charge transfer resistance. This critical knowledge can optimize the dynamics of ions with divergent size, hydrophobicity, and charge distributions (EMIm+, TFSI−, NET4+, BF4−, etc.) entering and exiting narrow pores.

Recent mathematical modelling efforts predict that the pores’ fundamental structural properties significantly impact interactions with electrolytes and subsequently affect double layer charge storage. The traditional approach has simulated their behaviour according to the Stern model; however, coupled with an energetically-favourable confinement in pores, ion configuration in internal surface carbons is impacted by surface chemistry and roughness of the latter. The presence of defects (functional groups and lattice deformations) disrupts sp²-inherent π bonding symmetry, magnifying the p₂-controlled density of states and subsequently enhancing the carbon material’s quantum capacitance (CQ) by over 300%. Impurity-driven enhanced CQ reduces the screening length of similarly charged ions from 30 nm to ion-sized dimensions, while pristine graphene requires 0.66 nm to isolate ions in the superionic state. At the same time, excessive n- and p-type dopant impurities interfere with ballistic conductivity along the graphitic plane and may maximize resistance losses in the system. While maximization of CQ is important for electrodes composed of few-layer graphene, its impact on total capacitance is diminished when compared to double-layer induced capacitance (CDL), with an increase in the number of stacked graphite layers. Furthermore, it is unclear how these simulations, which model carbon as an infinite graphene surface, translate to a polycrystalline material that best describes the CDC structure. In particular, narrow graphene ribbons, which can be assumed to make up the majority of pore surfaces, have lower intrinsic carrier concentrations and impeded electron transport behaviour. The correlation of these simulations with 3-dimensional porous architectures is complicated by divergent pore wall thicknesses, pore tortuosity, and the heterogeneous nature of surface morphology. The latter has an additional (but difficult to empirically quantify) factor of enhancing the electric field at points of surface edges and extreme curvature, potentially boosting capacitance by over 250%. In addition to changing the quantum capacitance contribution, functional groups with different surface charges also affect the ions’ geometrical orientation and interface with the pore surface, impacting charge storage density.

Similar fundamental problems impede the integration of novel carbons as high-performance electrodes in electroanalytical chemistry. Glassy carbon (GC) electrodes have been traditionally used to determine redox potentials, reaction kinetics, and concentrations of various aqueous systems (As/As3+, NO2−, tryptophan, ferrocene, etc.). Peak currents have been shown to correlate with the active species’ concentrations, with theoretical limits typically precluding measurements below 10⁻⁷ M. Increasing accessible surface areas significantly magnifies these currents (10³ fold increase from µA to mA range). Various electrodes composed of carbon functionalized graphene, highly ordered pyrolytic graphite (HOPG), and single walled carbon nanotubes (SWCNTs) have been developed to transition from a low-SSA semi-infinite planar diffusion behaviour to a thin layer cell with convergent diffusion. These materials are commonly functionalized with Au nanoparticles to maximize electrical conductivity, limit over-potential reactions, and reduce mass transport limitations. GC electrodes
typically face problems with fouling and irreversibility, as 2nd cycle performance decreases current intensity by 35%. Graphitic electrodes have shown enhanced electron transport rates, improved cyclabilities, and higher sensitivities to reactions. This further underscores the need for optimized porous materials that are electrochemically stable and contribute no additional redox peaks to highly sensitive systems. Depending on the electrochemical process in question (Nernstian, quasi-reversible, or irreversible), different surface areas may be required from the electrode material to ensure that redox peaks can be properly identified.

The objective of our work is to partially deconvolute the key properties of double layer charge storage and provide more fundamental information regarding ion dynamics, charge storage density, and electrochemical stability in confined porous environments. We rely on high-temperature (700–1800 °C) vacuum annealing (10−3 Pa) to transform the surface chemistry and carbon ordering of pore surfaces. This technique has been previously effectively used to modify structural ordering of the material and its surface area without compromising narrow pore size distributions. The procedure allows us to develop passivated, stable 3-dimensional porous architectures with different degrees of functionalization and graphitization to understand the effects of those parameters on key charge storage characteristics. By correlating key structural parameters and corresponding electrochemical behaviour, we can compare materials with different defect concentrations and derive the effects of hydrophobicity, unstable oxygen species, and graphitization-induced conductivity on the dynamics and the double layer configuration of the electrolyte. We rely on different CDC particle sizes to demonstrate effects of vacuum annealing at different scales and pore lengths. Our goal is to provide key information regarding the “ground state” configuration that maximally resembles the structures implemented in simulated models in order to correlate experimental evidence with predicted behaviour.

2 Experimental approach

Synthesis and annealing

Carbide precursors. TiC (Alfa Aesar, 99.5% purity, 2 μm diameter flakes) was selected for the microparticle system. SiC (MTI crystal, 99% purity, <30 nm diameter) was selected for the nanoparticle system.

Halogen etching. Carbide powders were loaded into quartz boats and placed in a tube furnace. Using a previously described procedure, the samples were purged with Ar, heated under Ar to 800 °C, and subjected to flowing Cl2 gas for 6 h. They were subsequently cooled to 600 °C under Ar and treated with H2 for 3 h. After removal from the furnace, samples were dried at 80 °C under a low vacuum (0.5 Pa) for 24 h to remove any trapped adsorbed species.

Vacuum annealing. CDC materials were loaded into graphite crucibles and placed in a graphite vacuum furnace (Solar Atmospheres). The furnace was outgassed for 24 h at room temperature, during which time the pressure decreased to approximately 10−3 Pa. The samples were subsequently heated at a rate of 10 °C min−1 to the following temperatures: 700 °C, 1200 °C, 1400 °C, and 1800 °C. They were held at those conditions for 8 h each and subsequently cooled to room temperatures under the same low pressure.
Materials characterization

Gas sorption and porosimetry. Adsorption/desorption isotherms were collected using N2 gas at ~196 °C using a Quadrasorb (Quantachrome Instruments). The Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface area in the P/P0 0.05–0.10 adsorption range.49 Quenched Solid Density Functional Theory (QSDFT) model for slit-shaped carbon pores was used to calculate SSA, pore volume, and the pore size distribution.50 DFT analyses were performed using only the adsorption branches. QuadraWin software was used for all calculations.

Structural characterization. Raman spectra of the materials were collected using a Renishaw inVia Spectrometer and a 514 nm Ar laser excitation (5% power, ~5 μm beam diameter). Spectra were deconvoluted using an 1800 grooves cm⁻¹ grating. WIRE 3.2 (Renishaw Instruments) software was used for peak fitting. Transmission Electron Microscopy (TEM) was done using a JEM 2100 (JEOL Instruments) with a 200 kV accelerating voltage. Thermogravimetric analysis (TGA) was carried out using a Q50 TGA Analyzer (TA Instruments); samples were dried at 150 °C for 1 h (in an Al₂O₃ crucible on a Pt pan) and heated at a 2 °C min⁻¹ rate in a flowing air atmosphere to 750 °C. WIRE 3.2 software was used for dM/dT peak deconvolution.

Surface chemistry. X-Ray Photoelectron Spectroscopy (XPS) analysis was performed using a Kratos AXIS surface analysis system (Ultra DLD). CasaXPS Version 2.3.16 RP 1.6 software was used to calculate elemental analysis and deconvolute functional group bands. Dynamic Water Vapour Sorption (DVS) was performed using a Q5000 SA Analyzer (TA Instruments); samples were placed in Pt-coated pans and the relative humidity of the chamber was increased while the temperature was held at a constant 25 °C. Inert TGA analysis was carried out using similar parameters as the air TGA tests, except that an Ar atmosphere was used to heat the samples to 800 °C and a 2 h preliminary purge time was used.

Intrinsic material conductivity. CDC particles were rolled into films typical of those used for supercapacitor electrodes. Powders were mixed with PTFE (60 wt% solution in water, Sigma Aldrich) polymer in a 95 : 5 ratio, and the slurry was blended using ethanol at 25 °C. The subsequent films were rolled to maintain a 6.7 mg cm⁻² mass loading for each material, producing 95 μm thick microparticle films and 150 μm thick nanoparticle films. For 4-point probe measurements, 4 cm × 4 cm pieces of each film were cut and a 4-point probe (2.09 mm separation) was used in conjunction with a DC power source (Keithley Instruments). Intrinsic conductivity derived from applied voltage (V), measured current (I), and film thickness (t) was calculated using the following equation:

$$\sigma = \frac{I \ln(2)}{V \pi t}$$

Electrochemical testing

Electrode setup. 1.5 cm × 1.5 cm squares (2.25 cm²) were cut from main electrode films, resulting in identical masses for working (WE) and counter (CE) electrodes. After 48 h drying at 80 °C under 0.5 Pa, the samples were placed in an Ar glovebox (Vacuum Atmospheres, <1 ppm content of H₂O and O₂). The cells were assembled into a standard “sandwich” configuration,31 using 2 layers of separator (Celgard) and a carbon-coated aluminium current collector (Exopack). Ag/AgCl wire was implemented as a quasi-reference electrode.52 C-Clamps were used to maximize compression between electrodes and current collectors.
Electrochemical testing. All experiments were conducted at room temperature (~25 °C). 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIm-TFSI, IoLiTec Ionic Liquids Technologies Inc.) room temperature ionic liquid was used in a solvent-free state. A VMP3 Potentiostat (Bio-Logic Instruments) was used for cyclic voltammetry (CV), galvanostatic cycling (GCPL), electrochemical impedance spectroscopy (EIS), and square wave chronoamperometry (CA). CV sweep rates varied between 2 mV s$^{-1}$ and 1000 mV s$^{-1}$, while galvanostatic cycling was conducted to test various current densities between 0.1 A g$^{-1}$ and 6.0 A g$^{-1}$. Values were normalized by mass and accessible SSA (derived from gas sorption). Samples were held at open circuit potential (OCP) for 1 h prior to the beginning of each experiment series, and an OCP 10 minute segment was used between different experiments. The same sequence of tests was used for each material. From cyclic voltammetry, capacitance was derived from the voltage window ($V_w$), measured current, ($I$), sweep rate ($dV$), working electrode mass ($m_{WE}$) and vertex potentials ($V_0$ and $V_f$), and calculated using the following equation:

$$C_{sp} = \frac{1}{m_{WE}} \int_{V_0}^{V_f} \frac{2I}{V_w} dV \quad (2)$$

Capacitance derived from galvanostatic cycling was derived from the slope of the voltage line ($dV/dt$) using the following equation:

$$C_{sp} = \frac{2I}{m_{WE} dV/dt} \quad (3)$$

Discharge segments of each cycle were used for calculations for both techniques. Impedance spectroscopy was collected using a 10 mV dampening oscillation in the 200 kHz to 0.01 Hz range. Series resistance ($R_s$) was derived for the value of $Z'$(ω) at which $Z''$(ω) = 0. Time constant was derived from the −45° impedance angle frequency. Ionic resistance was derived from the $Z'$(ω) range between the 1 Hz range and the −45° Z angle (mid-frequency regime). The Randles–Sevcik coefficient ($x$) was calculated from both CV and GCPL techniques using the following equation relating peak current ($I$), charge transfer coefficient ($n$), Faraday constant ($F$), SSA ($A$), molar IL concentration ($c$), diffusion constant ($D$), temperature ($T$), gas constant ($R$), and the scan rate ($v$):

$$I = 0.4463(nF)^{1.5}Ac \left( \frac{D}{RT} \right)^{0.5}v^{1/2} \quad (4)$$

Chronoamperometry was conducted by holding a cell at a given potential for 30 min, measuring current, and subtracting the current measured at 0.0 V using the same conditions.

3 Results and discussion

Structural transformations

The main processes that occurred during vacuum annealing were, in order of prevalence, removal of functional groups from pore surfaces, graphitic reorganization and increase in size of ordered sp$^2$ domains, and limited pore
restructuring. The procedure removed 10–15% of the mass of annealed CDC, with the amount of lost material proportional to the annealing temperature. It is expected that this loss accounts for chemical groups, attached carbons, and any species chemisorbed or trapped in tight pores.

**Pore structure changes.** The TiC–CDC microparticles and SiC–CDC nanoparticles underwent very similar pore structure transformations under the influence of vacuum annealing. The initial materials had SSA values of 1682 m² g⁻¹ and 2001 m² g⁻¹, respectively, and pore distributions showcase a predominant 0.61 nm pore diameter for TiC–CDC and 0.85 nm for SiC–CDC. When annealed at 700 °C, the SSA of the microparticles increased by 15%, while the pore diameter increased marginally to 0.67 nm. Higher annealing temperatures decreased SSA by 19% (1371 m² g⁻¹ after a 1400 °C anneal), with the micropore distribution remaining relatively unchanged and an increase in mesoporosity. Fig. 1 shows the pore size distributions and changes in accessible SSA and pore volume. The SiC–CDC nanoparticles reported similar responses to annealing temperatures: the SSA increased by 55% to 3100 m² g⁻¹ (1.01 nm pores) after 700 °C treatment and decreased by 30% to 1401 m² g⁻¹ (0.79 nm pores) after a 1400 °C anneal. While the systems (synthesized at 800 °C) in their initial, non-annealed states exhibited similar structural and chemical properties, the effects of high temperature vacuum treatment differed for materials with divergent initial structures. Low-temperature annealing removed functional groups and attached carbon atoms from outer pore walls, opening closed channels and increasing SSA, while the high-temperature restructuring merges some pores, collapsing small branches and decreasing the cumulative surface area. The ESI† includes a comprehensive summary of annealing effects on porosity (Table S1†) and demonstrates effects of 1400 °C annealing on TiC–CDC synthesized at 1000 °C, for comparison (Fig. S1(a) in ESI†). For all annealed materials, the micropore structure remained generally intact. The increase in mesoporosity for materials annealed at high temperatures was expected to enhance the mobility of ions during charging and discharging, improving rate handling abilities.

**Changes in graphitic structure.** The high-temperature annealing resulted in increased graphitization, as sp² domains became larger and more ordered. However, this was only observed for materials annealed at 1100 °C and above. Treatment at 700 °C removed surface functional groups, yet did not provide sufficient energy-dependent mobility for the carbon atoms to induce significant graphitization. Raman spectroscopy (Fig. 2) shows a temperature-dependent narrowing of both D and G bands, as well as the emergence of the resonant 2D and D + G bands. These observations confirm the expected increase in graphitic ordering. The material retains a generally amorphous carbon structure before and after annealing, and its three-dimensional architecture (featuring small interlocked sp² domains) impedes the formation of long-range, defect-free graphene sheets on pore wall surfaces. As a result, the full widths at half maxima (FWHM) of the D band are more appropriate than \( I_D/I_G \) ratios (compared in Fig. S2 in ESI†) to describe graphitization. The appearance of the D' band at the ~1610 cm⁻¹ for both materials after an 1800 °C anneal suggests the eventual collapse of the CDC particles to non-porous, polycrystalline structures; this is described well by the porosimetry data from Fig. 1.

Air TGA analysis (Fig. S3 in ESI†) shows an increase in oxidation temperature for samples annealed at higher temperatures, corroborating the increased
Fig. 1  (a) Pore size distributions for TiC–CDC microparticles in their initial state and annealed at 700 °C, 1200 °C, 1400 °C, and 1800 °C. (b) Pore size distributions for SiC–CDC nanoparticles annealed using the same conditions. Similar trends are observed. (c) Changes in surface area and cumulative pore volume from all pores <1 nm in diameter for the two systems.
prevalence of ordered carbon. Analysis of the FWHM of the oxidation profiles showed the broadest oxidation profile for the 700 °C samples, further confirming a large dispersity and a generally disordered structure of both microparticles and nanoparticles annealed at that temperature. Previous experiments correlated narrower dM/dT peaks with a larger structural defect concentration in MWCNTs (inter-wall faults, broken walls, etc.). However, the narrowing of the peaks shown for CDCs, which have a more heterogeneous structure, more likely corresponds with an increase in uniformity in the annealed materials. The G-band shifted to the left by 7 cm⁻¹ (for microparticles) and 5 cm⁻¹ (for nanoparticles) after an 1800 °C anneal (Fig. S2 in ESI†). This effect has been correlated with an increase in p doping (or minimization of n doping) of carbon’s electron density of states in graphene before, but it is unclear whether these minor shifts can be assigned to such transformations.

![Figure 2](attachment:figure2.png)

**Fig. 2** Raman spectroscopy offset spectra for the (a) microparticle and (b) nanoparticle systems. As annealing temperature increases, the resonant modes become more prominent and (c) the full width half maxima of the main bands become narrower, indicating increases in ordering. Low-temperature annealing (700 °C) appears to slightly decrease ordering, as chemical species removal occurs without giving carbon thermal energy to rearrange itself into sp² domains. (d) Effects of annealing on electric conductivity of PTFE-bound electrode films. Resistance values measured using the four-point probe were very small for nanoparticles, so deviations translated to more significant distributions than the calculated conductivity values for microparticles.
The effects of annealing and increased graphitization on intrinsic electric conductivity are shown in Fig. 2(d). Conductivity generally increases with annealing temperature for both CDC materials, with nanoparticles generally exhibiting greater electron transport due to improved interparticle connectivity.$^{57}$ Both materials exhibited a 33–38% conductivity drop after a 700 °C anneal, caused in part by a lack of increase in ordering and a significant increase in pore volume, which impedes electron transfer.$^{58}$ Annealing at 1400 °C increased conductivity of TiC–CDC by 14 S cm$^{-1}$ and SiC–CDC by 21 S cm$^{-1}$. The 16–50 S m$^{-1}$ microparticle conductivities and 98–168 S m$^{-1}$ nanoparticle conductivities were smaller than the values reported for monolithic, chemically reduced graphene oxide with high sp$^2$ ordering.$^{59}$

**Surface chemistry changes.** Increasing the annealing temperature defunctionalized the surfaces of the CDC materials. The elemental analysis of the materials, which is shown in Table 1, shows that elements such as oxygen, nitrogen, and chlorine steadily decreased in atomic % after the 700 °C anneal and were almost completely eliminated after the 1400 °C treatment. The SiC–CDC material, which had a lower relative amount of starting surface chemistry, did not experience such drastic defunctionalization, which could be related to both its higher SSA (increasing the prevalence of contaminants adsorbed from air) and its particle aspect ratio, which could facilitate re-functionalization. TGA analysis in an Ar environment (Fig. S3 in ESI$^+$) shows that the functional group content, which constituted 7–9% of the total CDC mass in its initial state, decreased to <3% after the high-temperature treatment.

It should be noted that neither analysis can accurately quantify the hydrogen content, which is assumed to be present on the surfaces of as-produced samples. Functional group analysis revealed predominantly C–OH, C=O, and C–Cl bonds, with trace amounts of acid, ether, and C–O–Cl groups. Chlorine was found only on the insides of particles (after Ar sputtering), so its presence could be limited to the XPS-induced opening of previously closed channels. For both systems, the materials did not become noticeably functionalized during exposure to air after annealing, indicating that the treatment produced passivated and stable structures.

The defunctionalization process influenced the hydrophobicity of the materials, as shown in Fig. S4 in ESI.$^+$ As the number of surface species decreased,

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Atomic percentages of key chemical species identified for the two systems using X-ray Photoelectron Spectroscopy (XPS). Entries indicating a range of values signify amounts found outside of particles (before Ar sputtering) and inside (after sputtering away several nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TiC–CDC microparticles</td>
</tr>
<tr>
<td></td>
<td>SiC–CDC nanoparticles</td>
</tr>
<tr>
<td>Carbon</td>
<td>Initial CDC</td>
</tr>
<tr>
<td>Oxygen</td>
<td>92.3</td>
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<tr>
<td>Nitrogen</td>
<td>4.1</td>
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<tr>
<td>Chlorine</td>
<td>2.3</td>
</tr>
<tr>
<td>Titanium/silicon</td>
<td>1.3</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.0</td>
</tr>
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water vapour uptake commenced at higher relative humidity states; this suggests adsorbance dominated by capillary action and not attraction from chemical groups. This effect was more pronounced for microparticles than for nanoparticles. While the trend was still observed for the latter system, the low pore lengths diminished the energy limitation of water adsorption on CDC surfaces. Given that pore wetting significantly affects the mobility of ion dynamics, and ions are likely to be more mobile in hydrophobic pores, it is expected that these transformations will facilitate electrolyte mobility.

Summary. Vacuum annealing modified several material properties of microparticle and nanoparticle CDCs. The following transformations have the most significant impact on the systems’ electrochemical behaviour:

1. Pores retain their overall diameter distribution. At 700 °C annealing temperatures, SSA and pore volume increase, but the accessible surface area starts to decrease (and pores merge or collapse) for materials annealed at or above 1100 °C.

2. Materials become more ordered and contain fewer surface functional groups after annealing at higher temperatures. Conductivity and hydrophobicity increase as a result, although these properties are partially convoluted with porosity.

Electrochemical behaviour: effects of annealing on capacitance

Gravimetric capacitance. Effects of vacuum annealing on gravimetric capacitances of both materials are shown in Fig. 3. The microparticle sample (Fig. 3(a)) shows a 19% increase in capacitance after the 700 °C anneal. This is explained in part by the 16% increase in SSA and a slightly larger pore diameter, which minimizes the ion-sieving effect that is somewhat present in the initial CDC material (based on the resistive nature of the discharge curve) and hinders its capacitance. The capacitance of the 1400 °C annealed microparticle material decreased by over 30%, despite retaining 81% of its SSA and sufficiently large pores. The decreasing capacitance trend was even clearer for the SiC–CDC nanoparticle system (Fig. 3(b)): with no ion sieving limitations, capacitance decreased slightly for the 700 °C annealed material (despite gaining 1000 m² g⁻¹) and by over 20 F g⁻¹ for the 1400 °C annealed material. While certain inflection points in the cyclic voltammograms suggest possible side reactions (and, consequently, faradaic contributions to capacitance) present in both initial CDC systems, they noticeably diminish after a 700 °C anneal and completely disappear in materials annealed at 1400 °C. The “butterfly”-shape of cyclic voltammograms observed for TiC–CDC after the 1400 °C anneal was also found for the nanoparticle sample. This corresponds to improved electric conductivity of both materials and suggests voltage-dependent capacitance.

Capacitance retention (Fig. 3(c)) indicates that the microparticle CDC system best handled high sweep rates after undergoing 700 °C annealing; however, above a 250 mV s⁻¹ scan rate, the 1400 °C material performs the best. The nanoparticle system clearly improved rate handling abilities at low and high sweep rates after 1400 °C annealing. Analysis of capacitance derived from galvanostatic cycling (Fig. 3(d)) shows the best performance for materials annealed at 700 °C, underscoring the importance of high SSA and accessible pore diameter to handle high current loads.
Capacitance normalized by surface area of carbon. Considering that the amount of accessible surface area is different for each sample, effects of annealing on aerial capacitance are shown in Fig. 4. For the TiC–CDC microparticles, both sweep rate and current density comparisons show that the 700 °C annealed material performs best, although cyclic voltammograms indicate a convergence in stored charge at 500 mV s⁻¹ sweep rates. The SiC–CDC nanoparticle system indicates that the 1400 °C material stores the largest amount of charge per unit of area (Fig. 4(b)). However, this is partially convoluted with rate handling, as current density comparisons (Fig. 4(d)) show that the initial material exceeds the annealed counterpart’s capacitance per surface area at very low scan rates.

Given the convergent appearance of the rate handling response to increased sweep rates, it is likely that the initial material stores more charge per m² than the 1400 °C annealed CDC below the minimum 2 mV s⁻¹ tested rate. Although the BET-derived SSA values were used for normalization of aerial capacitances, DFT-
derived SSA values would produce very similar trends: the SSA differences between the two are insignificant. The BET equation consistently calculated slightly higher m$^2$ g$^{-1}$ values than the DFT simulation (16–75 m$^2$ g$^{-1}$ greater SSA for microparticles and 44–240 m$^2$ g$^{-1}$ for nanoparticles). The corresponding 3–12% changes would slightly affect the absolute F m$^{-2}$ numbers, but the trends will remain consistent.

**Discussion.** Since the capacitance per area is different for each material, and the pore diameters exhibit insignificant changes, the removal of functional groups and the increase in graphitization change the relative contributions from quantum capacitance, the charge confinement in the superionic state, and the ion mobility. It is also likely that the annealing process produces different types of pore morphologies for microparticles with longer pores and nanoparticles with shallow pores. For instance, 700 °C annealing may create more mono- or divacancies in the microparticle system (disorder indicated by Raman spectroscopy

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**Fig. 4** Capacitance changes with increasing sweep rates derived from cyclic voltammetry normalized by SSA (BET value) for (a) microparticles and (b) nanoparticles. Galvanostatic cycling shows a similar trend for (c) microparticles, with the large pore diameters of the 700 °C annealed system providing greatest ion mobility. The higher cyclic voltammetry aerial capacitances of the 1400 °C annealed systems are shown to depend on its improved rate handling, as the initial and annealed materials show similar performance when galvanostatic cycling (d) is executed at 0.1 A g$^{-1}$.
and TGA), while graphitization-induced strain in the sp² carbon network may produce more hillocks and Stone–Wales type transformations for the 1400 °C annealed nanoparticles. Given that the types and amounts of those defects and curvature changes may influence the quantum capacitance of the materials, additional theoretical analysis and structural characterization of pore morphology is needed to identify and quantify these contributions. The defects affect charge storage density by changing both the screen lengths (controlling ion spacing) and ion-pore distance (via steric forces). The impact of quantum capacitance on overall capacitance is dependent on interlayer carbon thickness.

While nanoparticles are expected to have thinner pore walls, the number of graphitic layers separating each channel has not, to date, been accurately determined. The concentration of these defects has proven to be significant in these CDC systems, however, as the expected benefit of increased charge screening facilitated by conductive pore walls did not translate into enhanced gravimetric capacitance.

It is unlikely that the decrease in gravimetric capacitance for the annealed materials (or, conversely, a higher $C_{sp}$ for the initial CDCs) is due to significant changes in contributions from faradaic reactions of the ionic electrolyte with functional groups. A more direct observation is the positive correlation between increased surface defunctionalization and improved rate handling capabilities. Defect-free pores facilitate rapid EMIm⁺ and TFSI⁻ movement, as previously reported for similar systems. This approach should therefore be considered for development of high-power systems to minimize resistance and facilitate charge and discharge. It should be noted that improved graphitic ordering and electrode conductivity are somewhat convoluted with this relationship: nanoparticles, although exhibiting relatively less defunctionalization, showed the greatest increases in capacitance retention.

The effects of pore defunctionalization depend on properties of the electrolyte. Previous experiments evaluated TiC–CDC microparticles synthesized at 1000 °C and annealed at 1400 °C. The treatment increased SSA and hydrophobicity, which translated to capacitance-impeding resistance in Na₂SO₄ (in H₂O) that was less evident for NEt₄BF₄ (in AN). This data is shown in Fig. S1 in ESI.

Summary. The following key effects of annealing-induced defunctionalization and graphitization were observed for CDC materials:

1. Microparticles exhibit a slightly higher gravimetric capacitance after 700 °C annealing (with a higher SSA) but lower after 1400 °C annealing. Annealed nanoparticles show decreases in gravimetric capacitance regardless of surface area changes.
2. Although aerial capacitance of nanoparticles increases after 1400 °C annealing, low charge/discharge rates show similar or slightly higher values for the initial material.
3. Defect removal and increased conductivity achieved after high-temperature annealing improve rate handling and capacitance retention.
4. Surface defects, which are removed or transformed during annealing, significantly contribute to total charge storage. Annealing modifies these defects differently for microscale and nanoscale systems, uniquely affecting quantum capacitance.
Electrochemical behaviour: ionic resistance

**Impedance spectroscopy results.** Nyquist impedance plots for the TiC–CDC microparticles and SiC–CDC nanoparticles are shown in Fig. 5. Microparticles (Fig. 5(a)) show different impedance behaviour when comparing the initial material and its 700 °C annealed counterpart. This divergence stemmed primarily from sieving effects: the larger pore diameter of the annealed material decreases ionic resistance and produces a more capacitive behaviour at low frequencies. The 1400 °C annealed material features a larger $R_s$ and a higher ionic resistance. While electrode assembly could affect the interfacial resistance between the electrode and current collector, the absence of a significant semi-circular region at high frequencies suggests that the intrinsic material structure is mostly responsible for impedance of ions. A combination of the smaller ion diameter (0.05 nm larger than the initial material) and the presence of annealing-induced defects most likely increases ionic resistance.

As the annealing temperature increases, the time constant decreases and impedance becomes more capacitance-dominated. The Bode impedance and phase angle response to frequency are shown in Fig. S4 in ESI†. Nanoparticles (Fig. 5(b)) indicate a decrease in ionic resistance, which corroborates the previously discussed improved rate handling abilities of these materials. The time constant monotonically decreases with higher annealing temperatures, as it does with the microscale system. The real capacitance ($C'$) normalized by SSA showcases the same trends that CV and GCPL showed for aerial charge storage densities. Table 2 includes the key parameters regarding the system’s ionic resistance and capacitance derived from EIS.

**Charge/discharge dynamics.** The diffusion limitations of the systems that calculated the Randles–Sevcik equation showed a correlation between annealing temperature and prevalence of capacitance-dominated behaviour (Table 3). The maximum coefficient value for the microparticles was obtained on the 700 °C annealed CDC, mostly because of the larger pore diameter that facilitates ion...
mobility. This was not the case for the nanoparticles: the 1400 °C material exhibited minimal diffusion-limited behaviour despite having a smaller pore diameter. This further suggests the possible differences in the structure and defects that are present on the surfaces of the two materials.

While the ionic resistance decreases for the nanoscale particles from 1.02 Ω (initial CDC) to 0.48 Ω (1400 °C annealed), the same process increases this resistance from 3.39 Ω to 4.27 Ω for microparticles. It is possible that the annealing-induced morphology developed on the surface of large TiC–CDC particles increases Warburg impedance and hinders ion diffusion at semi-infinite length scales.68,69 These impediments could include out-of-plane graphite sheets that increase the mean free path, increased interparticle separation in films due to repulsion between similarly-functionalized particles, and formation of bottlenecks at pore openings. Extensive finite element analysis modelling and small-angle X-ray scattering (SAXS)45 may shed more light on the prevalence of these features.

**Summary.** Annealing-induced graphitization and defunctionalization produce the following key changes in the behaviour of EMIm-TFSI ions:

1. Annealed materials exhibit lower time constants and a general decrease in diffusion limitations and ionic resistance. Pore diameter and any ion sieving effects have an equally significant impact and are coupled with these observations.
2. Types and quantities of defects on pore surfaces, which depend on both particle size and annealing temperature, affect ion dynamics. Mathematical modelling and further investigation of the structure are required for system optimization.

**Electrochemical behaviour: charge distribution and symmetry**

The quasi-reference 3-electrode configuration allowed CV measurements of both working and counter electrodes. Performances for the two systems (collected using a 5 mV s\(^{-1}\) sweep rate) showing the contribution of each electrode to total capacitance are shown in Fig. 6. Identical trends are observed for nanoparticles and microparticles: in its initial state, CDC materials store charge predominantly in the working electrode, while the counter electrode extends to a significantly lower potential (vs. Ag/AgCl). It should be re-iterated that the masses and thicknesses of the electrodes for each sample are almost identical. This suggests that the materials’ structure (both pore diameter and surface chemistry) facilitates TFSI\(^{-}\) anion’s entry over the EMIm\(^{+}\) cation.

After the 700 °C vacuum annealing treatment, both the microscale and nanoscale materials experience a negative shift in potential, with the samples’ charge distribution becoming even more asymmetric. Nanoscale and microscale materials annealed at 1400 °C show near-perfect charge distribution symmetry, with the equilibrium potential shifting closer towards 0.00 V vs. Ag/AgCl. The “butterfly” shape is evident for the working electrodes for both microscale and nanoscale powders annealed at this condition. Evaluating the capacitance contributions for each system, however, shows the almost-symmetrical behaviour that was expected. Table S3 in ESI† provides a quantitative summary of effects of annealing on symmetry.

**Discussion.** The changes in symmetry cannot be attributed to porosity changes alone: while materials annealed at 700 °C have the largest pore diameters...
(expected optimal access to both ions), they respond most asymmetrically to EMIm-TFSI electrosorption. Therefore, surface chemistry and morphologically-induced structural defect transformations govern charge distribution. These changes also control ion sieving: the TiC–CDC initial and 700 °C annealed microparticles showcase noticeable resistance-induced deviation from the ideal rectangular shape of the discharge voltammograms of the working electrodes. Annealing transformations also influence contributions from faradaic reactions, which are completely absent for both WE and CE after a 1400 °C anneal. The 700 °C annealed micro- and nanoparticles exhibit inflection points during the charge cycle of the CE at –1.00 V; it is unclear whether this is evidence of voltage-dependent capacitance or electrochemical breakdown. This behaviour is not observed for the 1400 °C systems.

**Summary.** Surface chemistry has a significant effect on electrolyte ion and, subsequently, charge distribution in symmetrical cells. A defunctionalized surface makes it equally favourable for EMIm⁺ and TFSI⁻ to enter and exit pores.

**Electrochemical behaviour: voltage window analysis**

While the majority of CV and GCPL experiments were conducted in the 0.00–2.50 V potential range, final experiments assessed the systems’ operations with vertex potentials of 2.75 V, 3.00 V, and 3.25 V. Voltammograms of these measurements performed at 2 mV s⁻¹ are shown in Fig. 7. The behaviour at vertex potentials suggests that electrochemical breakdown occurs above 2.50 V for all microscale and nanoscale samples, regardless of defunctionalization or ordering. The materials annealed at 700 °C showcase the highest breakdown and the lowest overall coulombic efficiencies. However, this is partially convoluted with the large accessible surface areas of these materials, providing more ion reaction and decomposition sites. Analysis of parasitic currents and voltammograms shows that the 1400 °C annealed systems (with fewest functional groups) are the most stable ones under high potentials, but still show signs of electrolyte breakdown above 2.50 V.

Separate analysis of the working and counter electrodes (Fig. S5 in ESI†) suggests that breakdown occurs for both EMIm⁺ and TFSI⁻ ions. Excessive vertex potentials show different charge distribution asymmetry than those shown in Fig. 6 and likely indicate changes in pore structure and chemistry (such as gas evolution and grafting of new chemical species). Analysis of respective coulombic efficiencies of the microparticle electrodes (Table S3 in ESI†) consistently shows greater resistance and breakdown associated with the positive electrode and, subsequently, the predominance of anion decomposition.

Significant contributions from impurities in the IL (trapped water, synthesis byproducts, etc.) are possible but unlikely: no decomposition is observed below the 2.50 V initial threshold. Furthermore, the differences between materials annealed at different temperatures account for over 30% of breakdown-induced contributions to capacitance, suggesting the overwhelming significance of surface chemistry effects compared to any present impurities. These differences are less significant for the annealed SiC–CDC systems, further corroborating the difference in the amounts and types of defects produced in nanoscale carbons as a result of annealing.
Discussion. Although high-temperature annealing slightly decreases electrolyte decomposition, pure defunctionalization is still insufficient for ILs to operate in their theoretical 4.0 V window. The differences in magnitude of the breakdowns between materials annealed at different temperatures can be attributed to different mechanisms affecting the reactions. These processes probably depend on ion confinement, pore wall conductivity (derived from graphitization), and chemical species present at the ion–carbon interface. Reactions with –OH and –COOH groups may yield to dimerization-induced breakdown of EMIm+ (releasing H2 that blocks pores and degrades charge storage). Alternative simulations predict a potential-induced breakdown of the S–C bonds and subsequently the C–H bonds (both of which are present in the TFSI– anion) under applied potentials.

While both processes require overcoming substantial activation energy barriers, a conductive, accessible surface (i.e., the structure of annealed pores) may catalyse these processes and increase the dominance of their contribution to
electrolyte decomposition. Furthermore, the three-dimensional confinement of ions in pores changes the interaction and distortion of the ions’ electron cloud, creating a very different environment than the conditions that have been used for simulation and tests with GC electrodes. Defunctionalizing the surface will not completely solve the problem of low voltage windows, and a combination of materials (introducing specific stable groups) and device design (asymmetrical electrodes) is required.

**Summary.** Extending the voltage window of materials with different surface chemistries and graphitic ordering showed the following key properties:

1. Defunctionalization slightly reduces breakdown. This is also convoluted with pore size and carbon surface defects.
2. Cations and anions likely decompose *via* different processes and at different rates, as observed by increased asymmetry between the positive and negative electrodes.
3. As surface-chemistry related breakdown behaviour diminishes, ion dimerization catalysed by conductive pore walls may dominate decomposition in identical voltage windows.

**Conclusions**

We presented experimental analysis to assess the existing predictions that anticipate an increase in double layer charge storage densities and facilitated ion screening for materials with defunctionalized, conductive pore walls. We found that vacuum annealing, which created these properties for carbon electrodes with internal surfaces, did not yield expected higher gravimetric capacitances. Our primary explanation of this phenomenon is that surface defunctionalization and passivation removes chemical defects and subsequently decreases the carbon walls’ quantum capacitance contributions and ion screening, reducing double layer capacitance as a result. The magnitude of these changes depends on the carbon structure, including degree of sp² ordering, accessible surface area, and pore length and tortuosity. As expected, we observe fewer faradic reactions in defunctionalized materials under applied potentials. However, they remain difficult to classify and quantify, so their pseudocapacitive impact on total charge storage remains an open question.

Charge and discharge behaviour at high loads suggests that surface defunctionalization, increased mesoporosity, and graphitization facilitate ion mobility in and out of pores, improving rate handling ability. Diffusion limitations decreased with increased annealing temperatures independently of pore diameter or the presence of mesopores. This effect is likely a combination of the presence of an EMIm-TFSI favourable defect-free surface and conductive pore walls. Although surface defects have been shown to enhance quantum capacitance in static modes, there is little knowledge of dynamic effects of quantum capacitance and charge screening on ion mobility.

We found that charge distribution between the positive and negative electrodes is strongly affected by surface chemistry, with the robust surface species that are present in typical non-annealed CDCs favouring TFSI⁻ ion electrosorption. A defunctionalized, defect-free surface with increased sp² ordering creates a more mutually favourable ion–carbon interface and improves the system’s symmetry. Effects of hydrophobicity are different for every electrolyte (see
Fig. S1(c) and S1(d) in ESI† to compare performance of aqueous and organic systems).

When we extended the operating voltage window beyond the conventional 2.50 V limit, we found that defunctionalization of pore walls slightly decreased electrochemical breakdown. However, we also noticed that the severity of decomposition is correlated with accessible surface area, which should be considered for future electrode design. Some of the potential-induced breakdown reactions were likely accelerated by the conductive pore walls that acted as catalysts. It remains unclear whether the theoretical 4.00+ V operating limit of ILs can ever be reached in confined pore environments, but pure defunctionalization will not accomplish this goal.

Although a wide array of characterization techniques was used for this study, it remains difficult to identify every aspect of the pore structure that subsequently affects electrochemical performance. The treatment produces heterogeneous morphological effects that cannot be calculated using conventional means. This may partially explain the divergent effects of annealing on aerial capacitance for microscale and nanoscale systems. TEM imaging (Fig. S6 in ESI†) showed the formation of various graphitic barrels,73 ribbons, and protruding features. These defects have as significant of an effect on quantum capacitance as surface functionalities.32 The trade-off between quantum and double layer contributions to total charge storage depends on the pore wall thickness,35 which needs to be properly calculated. ESI† contains a discussion of relative quantum capacitance contributions from the six tested materials. For subsequent optimization of porous carbons for electrochemical energy storage, extensive mathematical modelling is required to properly assess effects of defects. This knowledge can be subsequently used to select a combination of thermal treatments and chemical grafting with appropriate functional groups to increase capacitance end electrochemical stability.

Acknowledgements

Research was funded by the NSF grant CNS-0960061. TEM imaging was conducted at Drexel’s Centralized Research Facility (CRF). TGA was conducted in the Polymers and Composites Laboratory (Department of Chemical and Biological Engineering, Drexel University). The authors gratefully acknowledge the assistance of Dr K. M. Cook with XPS analyses, F. W. Richey with DVS measurements, and O. Mashotalir (Drexel University) with TEM imaging. The authors thank M. R. Lukatskaya, K. B. Hatzell, and M. Sipics (Drexel Unviversity) for valuable comments on the manuscript. The authors wish to additionally acknowledge Prof. P. Simon (Université Paul Sabatier) and Prof. V. Presser (Leibniz-INM, Saarbrücken) for helpful discussions, as well as Dr. J. Chmiola and Prof. S. Osswald (NPS) for producing initial experimental results that inspired this study.

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