# Energy & Environmental Science

### PAPER

**Cite this:** *Energy Environ. Sci.*, 2013, **6**, 3700

# Direct prediction of the desalination performance of porous carbon electrodes for capacitive deionization<sup>†</sup>

**RSC** Publishing

S. Porada,<sup>ab</sup> L. Borchardt,<sup>c</sup> M. Oschatz,<sup>c</sup> M. Bryjak,<sup>b</sup> J. S. Atchison,<sup>d</sup> K. J. Keesman,<sup>ae</sup> S. Kaskel,<sup>c</sup> P. M. Biesheuvel<sup>af</sup> and V. Presser<sup>\*dg</sup>

Desalination by capacitive deionization (CDI) is an emerging technology for the energy- and cost-efficient removal of ions from water by electrosorption in charged porous carbon electrodes. A variety of carbon materials, including activated carbons, templated carbons, carbon aerogels, and carbon nanotubes, have been studied as electrode materials for CDI. Using carbide-derived carbons (CDCs) with precisely tailored pore size distributions (PSD) of micro- and mesopores, we studied experimentally and theoretically the effect of pore architecture on salt electrosorption capacity and salt removal rate. Of the reported CDCmaterials, ordered mesoporous silicon carbide-derived carbon (OM SiC-CDC), with a bimodal distribution of pore sizes at 1 and 4 nm, shows the highest salt electrosorption capacity per unit mass, namely 15.0 mg of NaCl per 1 g of porous carbon in both electrodes at a cell voltage of 1.2 V (12.8 mg per 1 g of total electrode mass). We present a method to quantify the influence of each pore size increment on desalination performance in CDI by correlating the PSD with desalination performance. We obtain a high correlation when assuming the ion adsorption capacity to increase sharply for pore sizes below one nanometer, in line with previous observations for CDI and for electrical double layer capacitors, but in contrast to the commonly held view about CDI that mesopores are required to avoid electrical double layer overlap. To quantify the dynamics of CDI, we develop a two-dimensional porous electrode modified Donnan model. For two of the tested materials, both containing a fair degree of mesopores (while the total electrode porosity is ~95 vol%), the model describes data for the accumulation rate of charge (current) and salt accumulation very well, and also accurately reproduces the effect of an increase in electrode thickness. However, for TiC-CDC with hardly any mesopores, and with a lower total porosity, the current is underestimated. Calculation results show that a material with higher electrode porosity is not necessarily responding faster, as more porosity also implies longer transport pathways across the electrode. Our work highlights that a direct prediction of CDI performance both for equilibrium and dynamics can be achieved based on the PSD and knowledge of the geometrical structure of the electrodes.

Received 1st July 2013 Accepted 13th August 2013

DOI: 10.1039/c3ee42209g

www.rsc.org/ees

#### **Broader context**

Capacitive deionization (CDI) is one of the most important small-scale and low-energy alternatives to reverse osmosis for the desalination of brackish water. Key components of this electro-kinetic method of water treatment are porous carbon electrodes with well-developed porosity. However, until now, the exact correlation between CDI performance and material parameters of the electrodes has largely remained unknown. To guide the ongoing research and development, quantitative methods to predict the equilibrium and dynamic behavior of CDI cells are essential. For direct practical implementation, predictive tools have to include the salt adsorption capacity and desalination rate as functions of the pore size distribution of the carbon electrode material, and of the geometrical measures of the electrodes, such as interparticle porosity. We present such a method based on a two-dimensional porous electrode theory, in combination with a predictive salt adsorption capacity analysis based on the pore size distribution. A high correlation between salt adsorption and pore size data for more than 15 different carbon materials presents evidence that sub-nm micropores are essential to achieve a high salt storage capacity. The reported work serves as an important step in making CDI a predictable electro-kinetic method, presenting clear guidelines for electrode materials' choice, synthesis, and electrode design.

<sup>e</sup>Wetsus, Centre of Excellence for Sustainable Water Technology, Agora 1, 8934 CJ Leeuwarden, The Netherlands

<sup>b</sup>Department of Polymers and Carbon Materials, Faculty of Chemistry, Wroclaw University of Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland <sup>c</sup>Department of Inorganic Chemistry, Dresden University of Technology, Bergstraße 66, 01069 Dresden, Germany

<sup>d</sup>INM-Leibniz-Institute for New Materials, Energy Materials Group, 66123 Saarbrücken, Germany. E-mail: volker.presser@inm-gmbh.de <sup>e</sup>Biomass Refinery & Process Dynamics, Wageningen University, Bornse Weilanden 9, 6708 WG Wageningen, The Netherlands

<sup>1</sup>Department of Environmental Technology, Wageningen University, Bornse Weilanden 9, 6708 WG Wageningen, The Netherlands

Saarland University, Campus D2 2, 66123 Saarbrücken, Germany

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3ee42209g

#### **Energy & Environmental Science**

### 1 Introduction

Providing access to affordable and clean water is one of the key technological, social, and economical challenges of the 21<sup>st</sup> century.<sup>1-3</sup> For the desalination of water, commercially available methods include distillation,<sup>4</sup> reverse osmosis,<sup>5</sup> and electrodialysis.<sup>6</sup> Novel approaches include ion concentration polarization in microporous media,<sup>7</sup> systems based on batteries,<sup>8,9</sup> forward osmosis,<sup>10</sup> and capacitive deionization (CDI).<sup>11-15</sup>

CDI is based on an electrochemical cell consisting of an open-meshed channel for water flow, in contact with sheets of porous electrodes on both sides. Upon applying a cell voltage between the two electrodes, ions become immobilized by an electrosorption process, that is, cations move into the cathode (the electrode into which negative electrical charge is transferred), while anions move into the anode (Fig. 1). After some time, when the electrodes reach their adsorption capacity (which depends on cell voltage), a discharge cycle is initiated by reducing or reversing the cell voltage, thereby releasing the salt as a concentrated stream. In the discharging step of the cell, energy recovery is possible.<sup>16,17</sup>

Salt immobilization by CDI is considered an energy-efficient method for the desalination of water.<sup>15,18</sup> Though typically applied to the desalination of brackish water sources, seawater can also be desalinated by CDI.<sup>19</sup> In combination with ionselective membrane layers placed in front of the electrodes, CDI can be used to selectively remove a certain ionic species from a mixture of salts or to harvest compounds such as acetic acid, sulphuric acid, insulin, and boron.<sup>20–26</sup> Such separation processes may find use in the treatment of wastewater from agriculture (mining), industry, and hospitals.

Various configurations for the design, stacking, and water management of CDI cells are possible. Most studies consider a design where the salt water is directed parallel to two equal electrodes, while a constant cell voltage is maintained, see Fig. 1.<sup>13,27,28</sup> However, stacks of electrodes do not necessarily have to consist of symmetrical cells and, instead, varying the carbon mass between the two electrodes provides the possibility to optimize the usable voltage window.<sup>29</sup> Another approach



**Fig. 1** Schematic illustration of desalination *via* capacitive deionization (CDI). Upon applying a cell voltage between the two electrodes, anions and cations are electrosorbed within highly porous carbon electrodes to counterbalance the electrical charge. This immobilization of ions decreases the salt concentration in the flow channel, and results in the production of freshwater.

utilizes carbon rods (called wires) which are sequentially dipped and taken out of the water, instead of using film electrodes forming a stack through which the water flows.<sup>30</sup> Instead of using bare carbon electrodes, improved energy efficiency has been reported for membrane-CDI (MCDI), where ion-exchange membranes are placed in front of one or both of the electrodes.<sup>26,31-34</sup> Further modifications are the use of constant current operation,<sup>33,35</sup> directing the water flow straight through the electrodes,<sup>13,28</sup> or the use of flowable electrode suspensions.<sup>19</sup> Recently, CDI electrodes have also been used to produce energy from the controlled mixing of river and seawater, based on a reversal of the CDI process.<sup>36-42</sup>

Electrosorption of ions is an interfacial process and in order to have a maximum contact area between the electrode and the water, CDI employs high surface area porous carbon electrode materials. At the water-carbon interface, electrical double layers (EDLs) are formed in which ions are electrosorbed. It has been stated that for optimum performance, pores should be large enough to have only a weak EDL-overlap, that is, mesopores are to be preferred over micropores.43-45 However, some microporous carbons, such as activated carbons14,46 and carbide-derived carbons<sup>47</sup> actually outperform mesoporous carbons. Recently, Porada et al.47 reported that CDI desalination capacity positively correlates with the volume of pores in the range below 1 nm, while obtaining a negative correlation with the total pore volume, or with the BET specific surface area (BET SSA, ref. 48). The importance of pores <1 nm has also been demonstrated for the capacitance of EDL-capacitor electrodes,<sup>49,50</sup> for H<sub>2</sub> gas storage,<sup>51</sup> and for CO<sub>2</sub> gas removal capacity.<sup>52</sup> These results relate to equilibrium conditions, and micropores (<2 nm) and especially ultramicropores (<0.8 nm) can pose severe limitations to ion transport in CDI flow cells. Thus, porous electrodes that combine a large micropore volume (for a high deionization capacity) with a network of mesopores (between 2 and 50 nm) and macropores (>50 nm) may yield a highly efficient deionization process.43,53,54

For an optimum performance, the design of the various components of the CDI system must be tuned to achieve both high salt electrosorption capacity and fast kinetics at the same time. Desalination by porous electrodes is by nature a non-linear phenomenon. Classical transmission-line models applied to CDI are unsatisfactory as they predict zero salt electrosorption and assume a constant ionic resistivity in the electrode.15,55 Instead, when ions are being electrosorbed in the EDLs formed in intraparticle pores (within carbon particles), the interparticle pores (the pores in between the carbon particles) are subjected to ion starvation and the ionic conductivity will drop dramatically during desalination. This phenomenon results in an internal ionic electrode resistance that is much higher than expected on the basis of the performance derived for high salinity electrolytes, as common in EDLC research. EDLCs are specifically designed to operate at large salt concentrations to have a high ionic conductivity and maximum capacity. Such a free choice of electrolyte is obviously not possible for water desalination. Note that the effect of ion starvation and the temporal increase in local resistivity to ion transport in the interparticle pores is included in the porous electrode theory of our paper.

A variety of carbon materials, including activated carbons, carbon aerogels, carbon xerogels, and carbon nanotubes, have been studied for desalination by CDI.15,18 New developments of advanced CDI electrode materials include asymmetric electrodes made of activated carbon coated with alumina and silica nanoparticles,<sup>56</sup> reduced graphene oxide and activated carbon composites,57 graphene electrodes prepared by exfoliation and reduction of graphite oxide,58 carbon nanotubes with polyacrylic acid,59 carbon fiber webs obtained from electrospinning,<sup>60,61</sup> and mesoporous activated carbons.<sup>62</sup> Templated carbons, although they require a more elaborate synthesis, are of particular interest as they provide additional means to precisely tailor the pore network, in order to combine a high electrosorption capacity with fast salt removal rates. A particularly high level of pore size control has been documented for carbons synthesized by selective etching of metal carbides with chlorine gas, called carbide-derived carbons, or CDCs.63 Lately, templated CDCs have been reported<sup>60,61</sup> that combine a large micropore volume with hierarchic mesopores. Compared to conventional CDCs, templated ordered mesoporous CDCs (OM CDCs) show significantly larger specific surface areas  $(\sim 3000 \text{ m}^2 \text{ g}^{-1})$  and total pore volumes  $(\sim 2 \text{ mL g}^{-1})$ .<sup>64</sup> Furthermore, using foam-like CDCs, synthesized by the "high internal phase emulsion" (HIPE) approach, it is possible to obtain control over macropores. The resulting material has both high surface areas of up to  $2300 \text{ m}^2 \text{ g}^{-1}$  and extremely large pore volumes of up to  $\sim 9 \text{ mL g}^{-1}$ .<sup>65</sup>

Despite many studies on various kinds of porous carbons, describing both equilibrium salt adsorption and the dynamics of the process, tools are not yet available to directly predict the performance of a certain carbon material and CDI design. The present work is aimed to be a first step towards a method for direct prediction of desalination performance in CDI. Our approach consists of two main routes.

(1) To extract data of the equilibrium salt adsorption and kinetics of CDI for carbon materials with precisely tailored and designed pore architectures. With these data we demonstrate how we can directly predict the desalination performance of a carbon material based on its pore size distribution (PSD).

(2) To use a two-dimensional porous electrode CDI transport model to predict the actual salt electrosorption kinetics. This model demonstrates how desalination kinetics depend not only on the intraparticle pore morphology, but also on the electrode thickness and interparticle porosity.

In the next sections we briefly describe the porous electrode transport theory, and discuss the synthesis of carbon materials and electrode architecture. We describe the salt adsorption performance in terms of equilibrium adsorption and kinetics, present a method to correlate equilibrium adsorption with PSD, and compare the dynamics of ion adsorption with theoretical predictions.

### 2 Theoretical section

To describe salt electrosorption and electrical current in porous carbon electrodes forming a CDI cell, we extend existing onedimensional porous electrode theory to two dimensions, to consider both the flow direction of the aqueous solution through the spacer channel, and the movement of salt in and out of the electrodes. Within the electrodes, we consider simultaneously ion transport through the space between the carbon particles, that is, the large transport pathways across the electrode (interparticle pore volume), and the electrosorption of ions inside carbon particles (intraparticle pore volume). To describe the latter, a powerful and elegant approach is to assume that the EDLs inside the intraparticle pore volume are strongly overlapping and, therefore, that the potential in these pores does not vary with position in the pore. This is the common "Donnan" approach for charged porous materials. The electrical potential in the intraparticle pore volume is different from that in the interparticle pore volume (the transport pathways) by a value  $\Delta \phi_d$ . The direct Donnan approach is modified<sup>29,31,47</sup> to consider the Stern layer located in between the electronic and ionic charge, and to include a chemical



Fig. 2 Schematic view of the time-dependent two-dimensional porous electrode model, combining a sequence of sub-cells in the flow direction, with ion fluxes into the electrode. A symmetric CDI geometry is assumed, thus only half of a cell is depicted. The electrode contains an electrolyte-filled volume allowing for ion transport, and carbon material in which ions and charge are stored. Electrical current (denoted by "+") flows through the conductive carbon material.

attraction energy for the ion when it transfers into the intraparticle pores, described by a term  $\mu_{\rm att}$ .<sup>66</sup> The modified Donnan (mD) model equals the limit situation of the Gouy–Chapman– Stern (GCS) theory when approaching full EDL overlap in micropores where the Debye length is of the order or larger than the pore size. In addition to GCS theory it includes the nonelectrostatic adsorption energy  $\mu_{\rm att}$  that reflects that also uncharged carbons adsorb some salt. A difference between the mD and GCS model is that in the mD model, EDL properties are described per unit pore volume, whereas in the GCS model charge and salt adsorption are described as functions of pore area. Numbers in either definition can be converted when the pore area/volume ratio is known.

To describe the dynamics of ion transport and charge formation, we set up a two-dimensional porous electrode theory for a CDI cell consisting of two porous electrodes placed in parallel, with a flat planar slit, or transport channel, or spacer, in between. In the direction of flow, this transport channel is mathematically divided into M subsequent sub-cells, see Fig. 2.34 In the porous electrode, two coupled partial differential equations describe the salt concentration in the interparticle pores, the electrostatic potential there,  $\phi$ , the charge density, and the salt electrosorption in the intraparticle pores as a function of time and depth in the electrode. The porous electrode transport theory requires various geometrical measures as inputs (thickness, porosity) that can be calculated from electrode dimensions. Besides, it requires an estimate of the diffusion coefficient of the ions in the macropores, which may be lower than the corresponding value in free solution. There are no other fitting functions. The present model neglects a transport resistance between interparticle pores and intraparticle pores, which can be incorporated, but requires an additional transport coefficient. Further details of the mD and transport model are provided in section 5 of the ESI.†

### 3 Experimental section

Electrodes from three different CDCs were prepared and compared to establish a basis of reference materials for further analysis of the salt electrosorption capacity. Details of material synthesis, electrode manufacturing and CDI testing are given in the ESI.† The synthesis methods are summarized in Fig. 3 for titanium carbide-derived carbon (TiC-CDC, Fig. 3A), ordered mesoporous silicon carbide derived carbon (OM SiC-CDC, Fig. 3B), and HIPE SiC-CDC (Fig. 3C).

Electrodes were prepared from these powders following the procedure outlined in ref. 47. A carbon slurry was prepared by mixing 85 mass% of CDC, 5 mass% of carbon black (Vulcan XC72R, Cabot Corp., Boston, MA), and 10 mass% of polyvinylidene fluoride (Kynar HSV 900, Arkema Inc., Philadelphia, PA); the latter was previously dissolved in N-methyl-2-pyrrolidone. Thus, the final electrode contains 85 mass% of porous CDC carbon. Electrodes were prepared by painting of the carbon slurry directly on one or both sides of a graphite current collector, taking care that approximately the same mass was coated on each side. Results for thickness and total electrode mass density are provided in Table S5.† Together with openmeshed porous spacer materials (thickness  $\delta_{sp} = 350 \ \mu m$ ) the current collector/electrode layers are stacked together forming three parallel cells (*i.e.*, one stack).<sup>29,47</sup> The flow of salt solution through the stack is kept constant, flowing first into a housing around the stack, entering the spacer layers from all four sides, and leaving via a centrally placed outlet to flow along a conductivity meter placed in-line.

An array of activated carbons and other carbon materials (see ESI<sup>†</sup>) were investigated along with the CDC materials for comparison. These materials were not painted, but prepared by a wet-casting technique following the procedure explained in



Fig. 3 Schematic illustration and SEM images of the synthesis of (A) TiC-CDC, (B) OM SiC-CDC, and (C) HIPE SiC-CDC.

ref. 47. In addition, carbon onions were tested as a representative of the class of fully graphitic, dense carbon nanoparticles (Fig. S9, ESI†) with no intraparticle porosity. The synthesis of carbon onions is based on the vacuum treatment of nanodiamonds at 1750  $^{\circ}$ C as outlined in more detail in the ESI.†

Ion electrosorption occurs when applying a cell voltage  $V_{cell}$  to each of the three cells, defined as the voltage difference between the positively and negatively polarized electrodes. At the end of the salt electrosorption step, the cell voltage is reduced to zero and ion desorption begins. The electrical current running from the cathode to the anode is measured and is integrated over time to provide a measure for the total charge transferred between the electrodes. This total charge is divided by the total electrode mass in the stack,  $m_{\text{tot}}$ , to obtain the charge expressed in C g<sup>-1</sup>, see Fig. 5A, 7A and 8A. From the conductivity of the effluent solution, the salt concentration is calculated and, thus, by integrating over time, the salt electrosorbed,  $\Gamma_{salt}$ , is calculated, see ref. 15 and 47. For each new experiment, the salt electrosorption/desorption cycle was repeated several times until the differences between cycles became negligible. We like to stress that in this work, the salt removal data are not obtained from the first cycle after a new condition has been applied, but instead are obtained when the system has reached the limit cycle, also called dynamic equilibrium (DE). This is the situation that the same amount of salt is electrosorbed during the adsorption step as is being removed in the desorption step of the cycle, as will be typical during practical long-term operation of a CDI system. All experiments were done using a  $c_{\infty} = 5$  mM NaCl-solution (290 ppm, 550  $\mu$ S cm<sup>-1</sup>).

#### 4 Results and discussion

#### 4.1 Structure of the porous carbons

The CDC materials used for this study are produced from selective etching of silicon or titanium atoms out of a carbide precursor (SiC or TiC), a procedure which results in a material with a high BET SSA which, in the case of OM SiC-CDC, is as high as 2720 m<sup>2</sup> g<sup>-1</sup> (Table 1). Fig. 4 displays the cumulative pore volume of these materials, together with the salt adsorption capacity, or  $\zeta(\sigma)$ -curve, which is discussed below.

All CDCs investigated in this study are predominantly amorphous, as evidenced by the broad D- and G-bands observed

**Table 1** Pore volume, specific surface area (SSA; calculated with the BET equation<sup>48</sup> and quenched solid density functional theory, QSDFT<sup>72</sup>), average pore size and local pore size maxima of the three CDC-materials. The average pore size is the volumetric average, *i.e.*, half of the total pore volume is associated with pores larger or smaller than this value and not reflect, for example, the bimodal pore size distribution in OM SiC-CDC

Carbon material	Total pore volume (mL g <sup>-1</sup> )	$\begin{array}{c} \text{BET SSA} \\ (\text{m}^2 \text{ g}^{-1}) \end{array}$	$\begin{array}{l} QSDFT \ SSA \\ (m^2 \ g^{-1}) \end{array}$	Average pore size $d_{50}$ (nm)
TiC-CDC	0.52	1309	1376	0.67
OM SiC-CDC	1.98	2720	2260	4.00
HIPE SiC-CDC	1.14	2351	2120	1.24



**Fig. 4** Cumulative pore size distributions calculated from QSDFT models of the three tested CDC-materials, as well as the suggested correlation function for the ion adsorption capacity,  $\zeta(\sigma)$ . PSD curves shifted up by 0.4 mL g<sup>-1</sup> for HIPE SiC-CDC and 1.0 mL g<sup>-1</sup> for OM SiC-CDC.

in Raman spectroscopy (see ESI<sup>†</sup>). TiC-CDC (Fig. 3A) powders are composed of anisometric particles with a size distribution ranging from approximately 1 to 10 µm and an average size of  $\sim$ 5 µm. Compared to that, the structures of OM SiC-CDC and HIPE SiC-CDC differ in many aspects. HIPE SiC-CDC has a cellular pore structure as can be seen from Fig. 3C. Owing to the HIPE synthesis route, the material exhibits 2 to 4 µm sized cages that are interconnected by 300 to 500 nm sized windows. The walls are highly porous, but yet in the nanometer range. Thus, this material exhibits a hierarchical pore structure consisting of macro-, meso-, and micropores. For the other materials used in this study, macropores are only present in the form of large pores between carbon particles, but not within the porous particles themselves. OM SiC-CDC was synthesized as a powder of strand-like particles (Fig. 3B) having an average strand diameter of approximately 1 µm. These strands are built from nanorods which are arranged in a hexagonal ordered fashion and have very narrowly distributed mesopores located in between (Fig. 3B). The narrow distribution in the mesopore size is due to the method of nanocasting which employs ordered mesoporous silica templates as conformally corresponding exotemplates for the resulting CDC.64,67-71 Besides the ordered mesopores, micropores are also present in OM SiC-CDC. As a consequence, this material has a hierarchy of micro- and mesopores but no internal macropores.68

The data for cumulative pore volume, see Fig. 4, show a hierarchical pore size distribution (PSD) with contributions from micro- and mesopores for HIPE and OM SiC-CDC, while TiC-CDC is predominantly microporous: more than 90 vol% of the pores is smaller than 2 nm (see Table S1 in the ESI†). HIPE SiC-CDC shows a total percentage of 37 vol% of mesopores and for OM SiC-CDC the majority of the total pore volume is associated with mesopores (~75 vol%). In that regard, HIPE SiC-CDC has

#### 4.2 Equilibrium desalination performance

Equilibrium data for salt adsorption and charge are presented in Fig. 5, based on underlying data for the desalination cycle for which examples given in Fig. S5 and S6 of the ESI,† using a symmetric CDI cell. Fig. 5A and B present data for salt adsorption and charge per gram of both electrodes, as functions of cell voltage. In Fig. 5B and C, the salt adsorption is presented relative to that at zero cell voltage in a two-electrode CDI cell. Fig. 5D presents the calculated total ion concentration in the pores (relative to an uncharged electrode), per mL intraparticle pore volume (for all pores below a size of 30 nm), as a function of the charge, also expressed per mL of intraparticle pores. The data for pore volume are given in Table 1 and Fig. 4. Fig. 5A and B show that the material with the highest capacitance (22.3 F  $g^{-1}$ at 5 mM NaCl, low-voltage limit), OM SiC-CDC, also has the highest salt adsorption capacity, 12.8 mg  $g^{-1}$  at a cell voltage of  $V_{\text{cell}} = 1.2$  V. Per gram of carbon (not total electrode) the adsorption is 15.1 mg  $g^{-1}$  at 1.2 V.

Figs. 5A and B clearly show how with increasing cell voltage both charge and salt adsorption increase non-linearly. This is different from typical results for EDL capacitors where the charge increases linearly with voltage (see ref. 15). Fig. 5C plots salt adsorption vs. charge (both expressed in mol  $g^{-1}$ ; for salt by dividing the data of Fig. 5B by M<sub>w.NaCl</sub> and for charge by dividing the results of Fig. 5A by Faraday's number), which is a novel representation, which shows how all three datasets overlap. Fig. 5C also shows that the total ion adsorption is always somewhat less than the charge, *i.e.*, the charge efficiency ( $\Lambda$  = salt adsorption/charge) is below unity.73 The high suitability of the materials tested for CDI can be deduced from the fact how close the measured charge efficiency is to unity, with measured values of  $\Lambda$  generally beyond 0.85. Indeed, Fig. 5C shows how close the data points are to the "100% charge efficiency line", the ideal limit where for each electron transferred one full salt molecule is removed. Interestingly, beyond the first data points (charge density  $\sim 0.1 \text{ mmol g}^{-1}$ ) the data run parallel to the "100% charge" efficiency line" which demonstrate that in this range, for each additional electron transferred, a full salt molecule is adsorbed, *i.e.*, the differential salt efficiency is unity.<sup>15,74</sup> Fig. 5C clearly makes the point that a strong correlation exists between the capacitance of a material (how much charge can be stored for a given cell voltage, typically evaluated under conditions of use for EDL capacitors) and desalination performance in CDI.47



**Fig. 5** Equilibrium salt adsorption and charge in porous carbon electrodes prepared from OM SiC-CDC (squares), HIPE SiC-CDC (circles), and TiC-CDC (triangles). (A) Equilibrium charge  $\Sigma_{\rm F}$  and (B) equilibrium salt electrosorption  $\Gamma_{\rm salt}$  as functions of cell voltage, both per gram of both electrodes. (C) Charge and salt adsorption recalculated to mol g<sup>-1</sup>, and plotted one *versus* the other. (D) Total pore ion concentration *vs.* charge per unit intraparticle volume (<30 nm). Salt concentration  $c_{\infty}$  5 mM NaCl. Lines represent fits using the modified Donnan model with in (D),  $\mu_{\rm att,ref}$  as the single fitting parameter. (\*) Data relative to adsorption at  $V_{\rm cell} = 0$ .

Evaluating the data in Fig. 5B per unit pore volume (all pores <30 nm), one can calculate a salt adsorption of 0.39 M for TiC-CDC, 0.20 M for HIPE SiC-CDC, and 0.13 M for OM SiC-CDC, at a cell voltage of 1.2 V. This salt adsorption, SA, having dimension *M*, just as the  $\zeta$ -function that will be discussed shortly, see Fig. 4, is equal to half the total ion concentration in the intraparticle pores (<30 nm) as given in Fig. 5D (relative to salt adsorption at zero voltage), evaluated for a symmetric two-electrode cell. Clearly, per unit pore volume the performance is decreasing in this order, which is opposite to the order when the more common metric of mg g<sup>-1</sup> is used (as plotted in Fig. 5B). Careful assessment of the influence of pore size increments on desalination performance is required, and care must be taken in defining what is the "best" material, which may relate to electrode mass or volume, dependent on the final application.

Next, we define the performance ratio of a material, or PR. As we will take HIPE SiC-CDC as the reference, for HIPE this value is unity, PR = 1. For TiC-CDC, which has twice the desalination per unit pore volume compared to HIPE at the reference conditions, PR = 2. Likewise for OM SiC-CDC the value is PR = 0.66.

In a later section we will discuss how well the value of PR correlates with known data of the material's total pore volume, BET SSA, and full pore size distribution. If here a correlation can be found, this would allow one to estimate the PR of a new material when only the PSD is known, without having data of CDI experiments available. From the PR-value, desalination performance at the reference conditions of a symmetric CDI cell operating at  $V_{cell} = 1.2$  V and for a salinity level of 5 mM NaCl can then be calculated. But in addition, knowing PR it will also be possible to calculate desalination at any other condition (different salinity, voltage, cell design), with the aid of the mDmodel, which requires knowledge of the three parameters  $\mu_{att}$ ,  $C_{\rm St,vol,0}$  and  $\alpha$  that are used in the mD-model. Thus, we first address, when the value of PR is known, how we can calculate appropriate values to be used in the mD-model, which then predicts desalination, not only under the reference conditions as defined above, but also at other voltages (see Fig. 5B), other salinities, and very different CDI cell designs. The procedure that we propose is that relative to the reference material (HIPE SiC-CDC), for which the three parameters in the mD-model, being  $\mu_{\text{att}}$ ,  $C_{\text{St,vol},0}$  and  $\alpha$ , are determined as explained below, for materials with a different PR, the following rescalings are used: to  $\mu_{\rm att}$  is added a term ln(PR),  $C_{\rm St,vol,0}$  is multiplied by PR, and  $\alpha$ is divided by PR. This procedure is based on the finding that rescaling the total pore volume by PR gave a perfect match to the data. However, to avoid introducing the concept of a theoretical volume different from the actual one, for which there is no physical basis, the above procedure is proposed. In this way, once the value of PR of a new material is calculated (from the PSD data and using the  $\zeta(\sigma)$ -curve), then by correlating to the known performance of HIPE SiC-CDC, its CDI performance can be directly predicted.

The values for  $\mu_{\text{att}}$ ,  $C_{\text{St,vol,0}}$ , and  $\alpha$  for HIPE SiC-CDC are calculated as follows. The novel representation in Fig. 5D is the starting point to derive by a structured method the parameters in the mD-model. Moreover the data in Fig. 5D can be fitted only by adjusting the value of  $\mu_{\text{att}}$ , without any influence of Stern

layer properties on this fit, see eqn (S3) and (S4) in the ESI.<sup>†</sup> For HIPE an optimum value of  $\mu_{att} = 2.0$  kT is found, in line with values used in previous work.<sup>29,30</sup> Next, for HIPE the full data of Fig. 5A and B must be fitted by optimizing  $C_{St,vol,0}$  and  $\alpha$ , for which only one combination fits the curves well (namely,  $C_{St,vol,0} = 72$  MF m<sup>-3</sup> and  $\alpha = 50$  F m<sup>3</sup> mol<sup>-2</sup>). Having established all of these values, the curves for the other two materials in Fig. 5A, B, and D automatically follow, and a very satisfactory fit is obtained. Using a constant Stern layer capacity does not fit the data well, see Fig. S5 in the ESI<sup>†</sup> for a comparison with a calculation with  $\alpha = 0$ .

# 4.3 Direct prediction of the desalination performance based on porosity analysis

We aim to find a method to correlate desalination performance in CDI to the porosity analysis of the carbon material. This is a hotly debated topic and the claim is often made that for CDI pores must be mesoporous (*i.e.*, above 2 nm),<sup>43,44</sup> or even beyond 20 nm (ref. 45) to avoid overlap of electrical double layers in the pores, an effect that is claimed to be deleterious for CDI. However, electrodes made of microporous AC and CDC powders showed very high performance in CDI, higher than electrodes based on mesoporous carbon aerogels.<sup>15,47,75</sup> Also for the materials tested in this work, the predominantly microporous carbons (TiC-CDC, and HIPE SiC-CDC) show a general trend of higher salt adsorption per unit pore volume than the predominantly mesoporous OM SiC-CDC.

One question remains: what porosity metrics are most suitable to predict CDI performance? In agreement with ref. 47, we find that desalination is positively correlated, even proportional, with the volume of pores smaller than 1 nm (see Fig. S3A and Table S1 in the ESI<sup>†</sup>), but only for materials that are mainly microporous. However, when including in the correlation materials with a significant portion of mesopores, such as HIPE SiC-CDC and even more so for OM SiC-CDC, for these materials a significant deviation from this proportionality (between salt adsorption and pore volume in pores <1 nm) is observed, with a much higher salt electrosorption than predicted based on this correlation, which can be explained by the contribution of mesopores to the ion immobilization. This contribution is not as high, per unit volume, as for micropores, but mesopores nevertheless also contribute to the ion electrosorption capacity. Thus, this measure of pore volume <1 nm cannot be the input parameter for a reliable predictive method. This situation is quite different from that in ref. 47 where it was demonstrated that for microporous carbons (AC and TiC-CDC), a positive correlation between the volume of pores smaller than 1 nm and the CDI performance could be established with a negative correlation of salt adsorption with BET SSA and with the total pore volume.

An appropriate metric based on PSD is not just correlated with salt adsorption, but ideally is proportional with desalination. Proportionality implies that the metric is a true measure of desalination, with an increase in this metric by a factor 2, resulting also in a two-times increased desalination. Such a metric is more likely to have a chemical-physical basis than a metric that is merely correlated with desalination. In Fig. S3 of ESI† we show four metrics based on the PSD and their proportionality with the salt adsorption performance: micropore volume <1 nm, <2 nm, total pore volume, and BET SSA. However, a satisfying fit is not observed in either case. Thus, we cannot establish a clear and unambiguous proportionality between the salt electrosorption capacity and either of these metrics (see Fig. S3 in the ESI†).

Still, porosity measurements present a very facile method to characterize porous carbons and it remains very attractive to base a predictive CDI performance method on porosity data. We, thus, propose a new approach to predict the CDI performance, based on considering the relevance to salt adsorption of each pore size increment, which we call "salt adsorption capacity analysis" (or, ζ-analysis), which determines the relevance of each size increment to the measured desalination under one reference condition ( $V_{cell} = 1.2 \text{ V}, c_{\infty} = 5 \text{ mM}$  NaCl, symmetric cell). The function  $\zeta$  is a property with dimension *M* and describes for the reference condition the contribution to desalination by a CDI cell of a certain pore size,  $\sigma$ , per unit pore volume (within the carbon in one electrode). Deriving the  $\zeta(\sigma)$ -function is done by the simultaneous fit of the experimentally available PSD of a set of materials to their desalination performance. This analysis quantifies the fact that salt electrosorption depends not only on the total pore volume, but also on the pore size distribution: the volume associated with some pores contributes more to the total sorption capacity than other pores.

Mathematically, the aim of the analysis is to find the  $\zeta(\sigma)$ -function, see Fig. 4, by which the salt adsorptions (SAs) of a set of materials (at the reference condition) predicted by eqn (1), fit as closely as possible the measured values of SA. Note that the ratio of this SA to the SA of our reference sample (HIPE SiC-CDC) is the performance ratio, PR. In the  $\zeta(\sigma)$ -analysis, the total salt adsorption in mg g<sup>-1</sup> of a symmetric two-electrode cell is given by eqn (1)

SA (mg g<sup>-1</sup>) = 
$$M_{w,NaCl} \int_{0}^{V} \zeta(\sigma) dV$$
  
=  $M_{w,NaCl} \int_{0}^{\sigma_{max}} \{\zeta(\sigma)f\} d\sigma, f = \frac{dV}{d\sigma}$  (1)

where  $M_{w,NaCl}$  is the molar mass of NaCl (58.44 g mol<sup>-1</sup>) and *V* is the pore volume (we will consider in all cases the pore size distribution up to a size of 30 nm) in mL g<sup>-1</sup>, see Table 1. In the  $\zeta(\sigma)$ -analysis it is assumed that each material will have a different PSD, see Fig. 4, but that only one common function for  $\zeta(\sigma)$  is allowed. Note that eqn (1) describes the salt adsorption not per gram of electrode material, but per gram of carbon, which in all of our experiments is 85% of the electrode mass.

To find the optimum  $\zeta(\sigma)$ -function we have used various methods, using *e.g.* predefined functions, but in the end we decided to use a "function-free" approach in which the value of  $\zeta$  is adjusted separately for each increment in size  $\sigma$ , with the only imposed constraint that  $\zeta$  must be decreasing with size  $\sigma$ .

Assuming, instead, as a first approximation  $\zeta$  to be invariant with pore size  $\sigma$ , we obtain the parity plot of Fig. 6A, where for the three CDC-materials, and also for twelve other materials (listed in Table 2) we show the correlation between the predicted value of SA and the measured value. As can be observed in Fig. 6A, there is a large deviation between the measured and predicted salt adsorption when assuming  $\zeta$  to be constant at  $\zeta$  = 0.21 M and not varying with pore size.

Next we discuss our results of using a modified  $\zeta(\sigma)$ -function. The optimized  $\zeta(\sigma)$ -function is found by a least-square fitting procedure of the difference of predicted (see eqn (1) above) and measured desalination. Several *a priori* constraints are imposed:

(1) The full PSD curve is divided in short size ranges of 0.1 nm, for each of which the value of  $\zeta$  can be adjusted by the optimization routine, independently of the others.



**Fig. 6** Parity plots for salt adsorption ( $c_{\infty} = 5 \text{ mM}$ ,  $V_{cell} = 1.2 \text{ V}$ ) for three carbide-derived carbons (grey diamonds) and twelve other materials (red triangles) per gram of carbon in both electrodes combined. (A) Salt adsorption capacity  $\zeta$  assumed independent of pore size  $\sigma$ . (B) Optimized  $\zeta(\sigma)$ -function, see Fig. 4.

**Table 2** Salt electrosorption performance reported for different electrodematerials applied for CDI (equilibrium adsorption of NaCl as a function of totalmass of both electrodes combined).  $\Gamma_{salt}$ : equilibrium salt electrosorption; CNT-RGO: carbon nanotubes and reduced graphene composite; MWCNTs: multi-walled carbon nanotubes; RGO: reduced graphite oxide; AC: activated carbon;CDC: carbide-derived carbon. Entries sorted by ascending salt electrosorptioncapacity

	Cell voltage (V)	Salt concentration $(mg L^{-1})$	$\Gamma_{\rm salt}$ (mg g <sup>-1</sup> )	Ref.
CNT-RGO	12	$\sim$ 50	0.7	77
	1.6	$\sim 50$	0.9	,,
MWCNTs	1.2	~3000	1.7	78
RGO	2.0	$\sim 65$	1.8	79
Carbon xerogel	1.2	$\sim 260$	3.1	80
Carbon xerogel	1.2	$\sim 260$	3.3	80
Carbon onions	1.2	$\sim 290$	3.9	This work
CWZ-22 (AC)	1.2	$\sim 290$	5.3	This work
Carbon aerogel	1.3	$\sim 2000$	7.1	75
Mast carbon	1.2	$\sim 290$	7.6	This work
S-TE3 (AC)				
Norit DLC	1.2	$\sim 290$	7.7	This work
Super50 (AC)				
Mast carbon	1.2	$\sim 290$	8.5	This work
S-TE11 (AC)				
Kuraray	1.2	$\sim 290$	9.1	This work
YP50-F (AC)				
Microporous	1.25	$\sim 2900$	9.6	13
carbon aerogel				
monoliths				
TiC-CDC	1.2	$\sim 290$	10.1	This work
TiC-CDC	1.2	$\sim 290$	10.4	47
HIPE SiC-CDC	1.2	$\sim 290$	11.1	This work
		$\sim 290$	13.6	
TiC-CDC	1.2	$\sim 290$	12.4	47
OM SiC-CDC	1.2	$\sim 290$	12.8	This work
MSP-20 (AC)	1.2	$\sim 290$	14.3	This work, 81

(2) With increasing size  $\sigma$ ,  $\zeta$  is not allowed to increase, but only to stay constant or decrease. Thus, we impose the rather stringent condition that the  $\zeta(\sigma)$ -curve must monotonically decrease and the smallest pore size will have the highest  $\zeta$ .

(3) We assume that beyond a certain size, when EDL overlapping starts to become minor, and desalination must be proportional with area, that desalination per unit volume must be inversely proportional with pore size. We impose this condition from a rather arbitrarily chosen point of a size of  $\sigma =$ 6 nm.

We apply this analysis method to the three CDC-materials discussed before, and we arrive at the  $\zeta(\sigma)$ -curve as sketched in Fig. 4, where for a size  $\sigma$  from 1.1 to 6.0 nm a constant  $\zeta$  is predicted of  $\zeta = 0.11$  M, from a size  $\sigma$  0.7–1.1 nm we have  $\zeta = 0.28$  M and below  $\sigma = 0.7$  nm  $\zeta = 0.51$  M. (Note that the computer routine predicts tiny variations within each "block", and we removed these slight changes manually giving the  $\zeta(\sigma)$ -curve plotted in Fig. 4, which was used as input in Fig. 6B). Next the optimized  $\zeta(\sigma)$ -correlation function is validated by applying it to twelve different materials, see Fig. 6B. As can be observed, for the three CDC-materials the fit is now perfect, while also for the other materials, the fit between predicted desalination

(*x*-axis) and actual desalination (*y*-axis) has improved substantially.

This analysis demonstrates that pores smaller than 1.1 nm contribute more substantially to desalination than larger pores. The finding of a very high value of the electrosorption capacity associated with these micropores is in good agreement with our previous study on a comparison of CDC and AC materials<sup>47</sup> and is also in line with the data presented in Table 1 and Fig. S3A (see ESI).† It is closely related to the reported phenomenon of the anomalous increase in capacitance in EDL-capacitors in subnanometer-sized pores.<sup>49,76</sup>

In conclusion, the  $\zeta(\sigma)$ -analysis gives the possibility to predict the CDI performance for both common and specialized carbons, purely based on easy-to-access cumulative PSD data. In contrast to this accuracy, our results (Fig. 6A and S3†) also underline that a convoluted, single value of pore analysis such as average pore size, total specific surface area, or total pore volume is not suited for direct prediction of the salt electrosorption capacity. Clearly, the complexity of carbon porosity must be appreciated and PSD data must be combined with consideration of the desalination efficiency of each pore size increment.

A spreadsheet file for the  $\zeta$ -analysis based on arbitrary PSDdata is provided as ESI.†

#### 4.4 Kinetics of salt electrosorption and charge transfer

Besides equilibrium electrosorption, the dynamics of ion sorption is of great importance for the practical application of CDI devices, and for a comprehensive understanding of differences between different porous carbon materials. In this section we apply for the first time a rigorous procedure based on a twodimensional porous electrode theory that predicts the dynamical CDI behavior of a porous carbon electrode, see the ESI,† based on ion electrodiffusion through the interparticle pores in the electrodes, and ion electrosorption in the intraparticle pores. Electrosorption is described by the modified Donnan (mD) model for which appropriate parameter values for  $\mu_{att}$ ,  $C_{\text{St,vol},0}$ , and  $\alpha$  were derived in Section 4.2 (see Fig. 5). The mD model not only predicts desalination at the reference condition of  $V_{\text{cell}} = 1.2$  V and for  $c_{\infty} = 5$  mM NaCl, but also for other conditions, and in addition, also describes electrosorption in a dynamic calculation during which the salt concentration in the interparticle pores becomes significantly different from  $c_{\infty}$ , to drop for a short period during desalination, while increasing sharply, again only for a short period, during ion release.<sup>31</sup> The only dynamic fitting parameter is the ion diffusion coefficient.

As depicted in Fig. 7, the porous electrode theory describes the rate of salt electrosorption and charge accumulation in CDI electrodes very well for the materials with a fair amount of mesopores (HIPE SiC-CDC, and OM SiC-CDC). The only difference in the input values for these calculations is the electrode thickness and inter- and intraparticle porosity, all calculated from geometrical measurements (see also Tables 2 and S6 in the ESI†), and the parameters for the mD model obtained from the equilibrium analysis of Section 4.2. The dynamics are described by the ion diffusion coefficient, for which a value of D =1.34 10<sup>-9</sup> m<sup>2</sup> s<sup>-1</sup> is used for all materials (see ESI†).



Fig. 7 (A) Kinetics of charge transfer during the adsorption step and (B) salt electrosorption in CDI, as a function of time for OM SiC-CDC (squares), HIPE SiC-CDC (circles) and TiC-CDC (triangles). Lines are fits using two-dimensional porous electrode theory.

While hierarchic porous carbons, that is, OM SiC-CDC and HIPE SiC-CDC, yield an excellent agreement between the measured and calculated dynamic behavior, for TiC-CDC which has practically no mesopores, and is much denser (Table S5 in ESI†), we do obtain a good fit of the salt electrosorption rate, but at the same time the charge accumulation rate (current) is underestimated initially. This possibly relates to a transport resistance from the interparticle space to the intraparticle space, see Section 5.3 in the ESI.†

# 4.5 Effect of electrode thickness on salt electrosorption and charge transfer

As we have seen, ion transport is strongly influenced by the structure of the pore network, with a very good description of the dynamics of desalination performance for the hierarchical materials, as shown in Fig. 7. To further validate the twodimensional porous electrode theory for these hierarchical materials, electrodes characterized by the same mass density



**Fig. 8** (A) Salt electrosorption and (B) charge transfer during the electrosorption step in CDI, as a function of time and electrode thickness, *L*, for electrodes made of OM SiC-CDC. Lines are predictions using two-dimensional porous electrode theory. (C and D) Calculation results as a function of electrode packing density.

but different thicknesses were prepared from OM SiC-CDC. The choice of this material was motivated by the excellent correlation between data and model shown in Fig. 7. As shown in Fig. 8A and B, there is a very strong influence of the electrode thickness on both the salt electrosorption and the charge transfer rate. By increasing the thickness of the electrodes, the rate by which the maximum desalination is reached in the CDI process slows down, while as expected the final equilibrium values (defined per gram of material) remain exactly the same. We see that this applies for both the charge accumulation rate and the salt electrosorption rate. Fig. 8C and D analyze theoretically the effect of higher (or lower) electrode packing density (the overall electrode mass density, as presented in column 2 of Table S5<sup>†</sup>), by reducing the interparticle volume while keeping the mass and total intraparticle volume the same. Fig. 8D shows the interesting effect that a reduction of the interparticle volume is at first advantageous, with the time to reach 50% of the maximum desalination first decreasing (reaching a minimum value in the range of porosities between 30 and 60%), with this time increasing again for even lower porosities. The positive effect of a higher packing density of the electrode is that the length of the pathways for ions to traverse across the electrode goes down (the deepest regions of the electrode are more quickly reached), while the opposite effect at low porosity is because the transport pathways are being squeezed out of the electrode, with the apparent resistance for ion transport increasing (i.e., simply no transport pathways remain).

These observations have a number of important implications, because optimized kinetics are very important for actual CDI application. As Fig. 8 demonstrates, faster ion electrosorption (per unit mass of electrode) can be achieved by decreasing the electrode thickness and by optimizing the electrode porosity. Thus, our study demonstrates that it is not only important to appreciate the micro- and mesopores present inside a carbon particle, but also to understand the porous carbon electrode in its entirety. The latter also entails the pores in between the carbon particles, and the total thickness of an electrode.

### 5 Conclusions

We have studied capacitive deionization of water using three carbide-derived porous carbon materials with strongly varying contributions to the total pore volume originating from microand mesopores, and compared performance with various reference materials. We have demonstrated that there is no direct relationship between salt electrosorption capacity and typical pore metrics such as BET SSA and the total volume of pores. However, we have demonstrated that the salt electrosorption capacity can be predicted by analysis of the pore size distribution and the pore volume correlated with incremental pore size ranges, considering that differently sized pores exhibit a different electrosorption capacity for the removal of salt ions. This analysis has been validated by comparison to literature data and other carbon materials and we were able to quite reliably predict the CDI performance of a range of carbons used for CDI.

Modeling is an important part of CDI performance analysis, not only to access information on the equilibrium salt removal capacity but also to gain understanding of the ion electrosorption process. Using the diffusion coefficient as the only dynamic fit parameter, two-dimensional porous electrode theory is capable of predicting the dynamics of charge accumulation and the resulting process of salt electrosorption for the CDC-materials with sufficient amounts of mesopores. For materials without pores in this size range, the theory underestimates the initial current. Although CDI is a complex process depending on various parameters, such as pore volume, pore size distribution and process parameters, our work demonstrates that prediction of the CDI dynamic equilibrium salt adsorption capacity and the kinetics for flow-by electrodes is feasible. These results will facilitate the rational development of carbon electrode designs for CDI. An important next step will be to adapt our model to more advanced CDI techniques, such as flow-through CDI,13,82 CDI using wires,30 or CDI using flowing electrodes.19

### Acknowledgements

Part of this work was performed in the TTIW-cooperation framework of Wetsus, Centre of Excellence for Sustainable Water Technology. Wetsus is funded by the Dutch Ministry of Economic Affairs, the European Union Regional Development Fund, the Province of Friesland, the City of Leeuwarden, and the EZ/Kompas program of the "Samenwerkingsverband Noord-Nederland". We thank the participants of the themes "Capacitive Deionization" and "Advanced Waste Water Treatment" for their involvement in this research. The authors also thank Matthew Suss (Stanford University, USA) and James London (University of Kentucky, USA) for providing pore size distribution data, and Taeyoung Kim for providing activated carbon sample called MSP-20. Dr Mesut Aslan and Dr Emilie Perre (both at INM) are thanked for their help with the gas sorption analysis. Rudolf Karos (INM) is thanked for his help with XRD analysis. VP acknowledges funding received from the Bayer Early Excellence in Science Award and Prof. Eduard Arzt (INM) is thanked for his continuing support.

### Notes and references

- M. A. Shannon, P. W. Bohn, M. Elimelech, J. G. Georgiadis, B. J. Marinas and A. M. Mayes, *Nature*, 2008, 452, 301–310.
- 2 T. Humplik, J. Lee, S. C. O'Hern, B. A. Fellman, M. A. Baig, S. F. Hassan, M. A. Atieh, F. Rahman, T. Laoui, R. Karnik and E. N. Wang, *Nanotechnology*, 2011, 22, 292001.
- 3 http://www.un.org/News/Press/docs/2010/ga10967.doc.htm.
- 4 A. D. Khawaji, I. K. Kutubkhanah and J.-M. Wie, *Desalination*, 2008, **221**, 47–69.
- 5 L. F. Greenlee, D. F. Lawler, B. D. Freeman, B. Marrot and P. Moulin, *Water Res.*, 2009, **43**, 2317–2348.
- 6 H. Strathmann, *Ion-Exchange Membrane Separation Processes*, Elsevier, Amsterdam, 2004.
- 7 A. Mani and M. Z. Bazant, Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys., 2011, 84, 061504.

- 8 M. Pasta, C. D. Wessells, Y. Cui and F. La Mantia, *Nano Lett.*, 2012, **12**, 839–843.
- 9 M. Pasta, A. Battistel and F. La Mantia, *Energy Environ. Sci.*, 2012, 5, 9487–9491.
- 10 T. Y. Cath, A. E. Childress and M. Elimelech, *J. Membr. Sci.*, 2006, **281**, 70–87.
- 11 K.-L. Yang, T.-Y. Ying, S. Yiacoumi, C. Tsouris and E. S. Vittoratos, *Langmuir*, 2001, 17, 1961–1969.
- 12 C. J. Gabelich, T. D. Tran and I. H. M. Suffet, *Environ. Sci. Technol.*, 2002, **36**, 3010–3019.
- 13 M. E. Suss, T. F. Baumann, W. L. Bourcier, C. M. Spadaccini, K. A. Rose, J. G. Santiago and M. Stadermann, *Energy Environ. Sci.*, 2012, 5, 9511–9519.
- 14 H. Li, L. Zou, L. Pan and Z. Sun, *Environ. Sci. Technol.*, 2010, 44, 8692–8697.
- 15 S. Porada, R. Zhao, A. van der Wal, V. Presser and P. M. Biesheuvel, *Prog. Mater. Sci.*, 2013, **58**, 1388–1442.
- 16 O. N. Demirer, R. M. Naylor, C. A. Rios Perez, E. Wilkes and C. Hidrovo, *Desalination*, 2013, 314, 130–138.
- 17 P. Dlugolecki and A. van der Wal, *Environ. Sci. Technol.*, 2013, 47, 4904–4910.
- 18 L. Zou, in *Expanding Issues in Desalination*, ed. R. Y. Ning, INTECH, 2011.
- 19 S.-I. Jeon, H.-R. Park, J.-G. Yeo, S. Yang, C. H. Cho, M. H. Han and D.-K. Kim, *Energy Environ. Sci.*, 2013, **6**, 1471–1475.
- 20 H.-H. Jung, S.-W. Hwang, S.-H. Hyun, K.-H. Lee and G.-T. Kim, *Desalination*, 2007, **216**, 377–385.
- 21 C.-H. Hou, T.-S. Patricia, S. Yiacoumi and C. Tsouris, *J. Chem. Phys.*, 2008, **129**, 224703.
- 22 E. Avraham, M. Noked, A. Soffer and D. Aurbach, *Electrochim. Acta*, 2011, **56**, 6312–6317.
- 23 R. Zhao, M. van Soestbergen, H. H. M. Rijnaarts, A. van der Wal, M. Z. Bazant and P. M. Biesheuvel, *J. Colloid Interface Sci.*, 2012, **384**, 38–44.
- 24 Y.-J. Kim and J.-H. Choi, Water Res., 2012, 46, 6033-6039.
- 25 S.-J. Kim, J.-H. Choi and J.-H. Kim, *Process Biochem.*, 2012, 47, 2051–2057.
- 26 Y.-J. Kim, J.-H. Kim and J.-H. Choi, *J. Membr. Sci.*, 2013, **429**, 52–57.
- 27 A. M. Johnson and J. Newman, *J. Electrochem. Soc.*, 1971, **118**, 510–517.
- 28 Y. Bouhadana, E. Avraham, M. Noked, M. Ben-Tzion, A. Soffer and D. Aurbach, *J. Phys. Chem. C*, 2011, 115, 16567–16573.
- 29 S. Porada, M. Bryjak, A. van der Wal and P. M. Biesheuvel, *Electrochim. Acta*, 2012, 75, 148–156.
- 30 S. Porada, B. B. Sales, H. V. M. Hamelers and P. M. Biesheuvel, J. Phys. Chem. Lett., 2012, 3, 1613– 1618.
- 31 P. M. Biesheuvel, R. Zhao, S. Porada and A. van der Wal, *J. Colloid Interface Sci.*, 2011, **360**, 239–248.
- 32 J.-Y. Lee, S.-J. Seo, S.-H. Yun and S.-H. Moon, *Water Res.*, 2011, 45, 5375–5380.
- 33 R. Zhao, P. M. Biesheuvel and A. Van der Wal, *Energy Environ. Sci.*, 2012, 5, 9520–9527.
- 34 R. Zhao, O. Satpradit, H. H. M. Rijnaarts, P. M. Biesheuvel and A. van der Wal, *Water Res.*, 2013, **47**, 1941–1952.

- 35 E. Garcia-Quismondo, R. Gomez, F. Vaquero, A. L. Cudero, J. Palma and M. A. Anderson, *Phys. Chem. Chem. Phys.*, 2013, 15, 7648–7656.
- 36 D. Brogioli, Phys. Rev. Lett., 2009, 103, 058501.
- 37 B. B. Sales, M. Saakes, J. W. Post, C. J. N. Buisman, P. M. Biesheuvel and H. V. M. Hamelers, *Environ. Sci. Technol.*, 2010, 44, 5661–5665.
- 38 D. Brogioli, R. Zhao and P. M. Biesheuvel, *Energy Environ. Sci.*, 2011, 4, 772–777.
- 39 F. Liu, O. Schaetzle, B. B. Sales, M. Saakes, C. J. N. Buisman and H. V. M. Hamelers, *Energy Environ. Sci.*, 2012, 5, 8642– 8650.
- 40 R. A. Rica, R. Ziano, D. Salerno, F. Mantegazza and D. Brogioli, *Phys. Rev. Lett.*, 2012, **109**, 156103.
- 41 D. Brogioli, R. Ziano, R. A. Rica, D. Salerno, O. Kozynchenko,
  H. V. M. Hamelers and F. Mantegazza, *Energy Environ. Sci.*, 2012, 5, 9870–9880.
- 42 D. A. Vermaas, S. Bajracharya, B. B. Sales, M. Saakes, B. Hamelers and K. Nijmeijer, *Energy Environ. Sci.*, 2013, **6**, 643–651.
- 43 L. Zou, L. Li, H. Song and G. Morris, *Water Res.*, 2008, 42, 2340–2348.
- 44 L. Li, L. Zou, H. Song and G. Morris, *Carbon*, 2009, **47**, 775–781.
- 45 C. J. Gabelich, P. Xu and Y. Cohen, *Sustainability Science and Engineering*, 2010, 2, 295–326.
- 46 Z. Peng, D. Zhang, L. Shi and T. Yan, *J. Mater. Chem.*, 2012, 22, 6603–6612.
- 47 S. Porada, L. Weinstein, R. Dash, A. van der Wal, M. Bryjak,
  Y. Gogotsi and P. M. Biesheuvel, *ACS Appl. Mater. Interfaces*,
  2012, 4, 1194–1199.
- 48 S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, 1938, **60**, 309–319.
- 49 J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon and P. L. Taberna, *Science*, 2006, **313**, 1760–1763.
- 50 S. Kondrat, V. Presser, C. R. Perez, Y. Gogotsi and A. A. Kornyshev, *Energy Environ. Sci.*, 2012, 5, 6474–6479.
- 51 Y. Gogotsi, C. Portet, S. Osswald, J. M. Simmons, T. Yildirim,
  G. Laudisio and J. E. Fischer, *Int. J. Hydrogen Energy*, 2009,
  34, 6314–6319.
- 52 V. Presser, J. McDonough, S.-H. Yeon and Y. Gogotsi, *Energy Environ. Sci.*, 2011, 4, 3059–3066.
- 53 H. B. Li, T. Lu, L. K. Pan, Y. P. Zhang and Z. Sun, *J. Mater. Chem.*, 2009, **19**, 6773–6779.
- 54 X. Wen, D. Zhang, L. Shi, T. Yan, H. Wang and J. Zhang, *J. Mater. Chem.*, 2012, 22, 23835–23844.
- 55 P. M. Biesheuvel and M. Z. Bazant, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2010, **81**, 031502.
- 56 L. Han, K. G. Karthikeyan, M. A. Anderson, K. Gregory, J. J. Wouters and A. Abdel-Wahab, *Electrochim. Acta*, 2013, 90, 573–581.
- 57 H. Li, L. Pan, C. Nie, Y. Liu and Z. Sun, J. Mater. Chem., 2012, 22, 15556–15561.
- 58 H. Wang, D. Zhang, T. Yan, X. Wen, L. Shi and J. Zhang, *J. Mater. Chem.*, 2012, 22, 23745–23748.
- 59 C. Nie, L. Pan, Y. Liu, H. Li, T. Chen, T. Lu and Z. Sun, *Electrochim. Acta*, 2012, **66**, 106–109.

- 60 M. Wang, Z.-H. Huang, L. Wang, M.-X. Wang, F. Kang and H. Hou, New J. Chem., 2010, 34, 1843–1845.
- 61 G. Wang, Q. Dong, Z. Ling, C. Pan, C. Yu and J. Qiu, *J. Mater. Chem.*, 2012, 22, 21819–21823.
- 62 G. Wang, B. Qian, Q. Dong, J. Yang, Z. Zhao and J. Qiu, Sep. Purif. Technol., 2013, 102, 216–221.
- 63 V. Presser, L. Zhang, J. J. Niu, J. McDonough, C. Perez, H. Fong and Y. Gogotsi, *Adv. Energy Mater.*, 2011, 1, 423–430.
- 64 P. Krawiec, E. Kockrick, L. Borchardt, D. Geiger, A. Corma and S. Kaskel, *J. Phys. Chem. C*, 2009, **113**, 7755–7761.
- 65 M. Oschatz, L. Borchardt, M. Thommes, K. A. Cychosz,
  I. Senkovska, N. Klein, R. Frind, M. Leistner, V. Presser,
  Y. Gogotsi and S. Kaskel, *Angew. Chem., Int. Ed.*, 2012, 51, 7577–7580.
- 66 B. Kastening and M. Heins, *Electrochim. Acta*, 2005, **50**, 2487–2498.
- 67 P. Krawiec, D. Geiger and S. Kaskel, *Chem. Commun.*, 2006, (23), 2469–2470.
- 68 E. Kockrick, C. Schrage, L. Borchardt, N. Klein, M. Rose, I. Senkovska and S. Kaskel, *Carbon*, 2010, **48**, 1707–1717.
- 69 Y. Korenblit, M. Rose, E. Kockrick, L. Borchardt, A. Kvit, S. Kaskel and G. Yushin, *ACS Nano*, 2010, **4**, 1337–1344.
- 70 M. Oschatz, E. Kockrick, M. Rose, L. Borchardt, N. Klein, I. Senkovska, T. Freudenberg, Y. Korenblit, G. Yushin and S. Kaskel, *Carbon*, 2010, 48, 3987–3992.

- 71 M. Rose, Y. Korenblit, E. Kockrick, L. Borchardt, M. Oschatz, S. Kaskel and G. Yushin, *Small*, 2011, 7, 1108–1117.
- 72 P. I. Ravikovitch and A. V. Neimark, *Langmuir*, 2006, 22, 11171–11179.
- 73 R. Zhao, P. M. Biesheuvel, H. Miedema, H. Bruning and A. van der Wal, *J. Phys. Chem. Lett.*, 2010, **1**, 205–210.
- 74 M. D. Levi, S. Sigalov, D. Aurbach and L. Daikhin, *J. Phys. Chem. C*, 2013, **117**, 14876–14889.
- 75 P. Xu, J. E. Drewes, D. Heil and G. Wang, *Water Res.*, 2008, 42, 2605–2617.
- 76 R. K. Kalluri, M. M. Biener, M. E. Suss, M. D. Merrill, M. Stadermann, J. G. Santiago, T. F. Baumann, J. Biener and A. Striolo, *Phys. Chem. Chem. Phys.*, 2013, **15**, 2309– 2320.
- 77 H. Li, S. Liang, J. Li and L. He, *J. Mater. Chem. A*, 2013, **1**, 6335–6341.
- 78 K. Dai, L. Shi, J. Fang, D. Zhang and B. Yu, *Mater. Lett.*, 2005, 59, 1989–1992.
- 79 Z. Wang, B. Dou, L. Zheng, G. Zhang, Z. Liu and Z. Hao, *Desalination*, 2012, **299**, 96–102.
- 80 J. Landon, X. Gao, B. Kulengowski, J. K. Neathery and K. Liu, J. Electrochem. Soc., 2012, 159, A1861–A1866.
- 81 T. Kim and J. Yoon, J. Electroanal. Chem., 2013, 704, 169–174.
- 82 I. Cohen, E. Avraham, M. Noked, A. Soffer and D. Aurbach, J. Phys. Chem. C, 2011, 115, 19856–19863.

# **Direct Prediction of the Desalination Performance**

### of Porous Carbons Electrodes

# for Capacitive Deionization

S. Porada, L. Borchardt, M. Oschatz, M. Bryjak, J. S. Atchison, K. J. Keesman, S. Kaskel, P. M. Biesheuvel and V. Presser

### **Electronic Supplementary Information**

### 1. Nitrogen Gas Sorption Analysis of CDC Samples

Gas sorption analysis with Nitrogen was carried out following the experimental procedure outlined in the experimental section. As seen from **Fig. S1**, the shape of the TiC-CDC isotherm is of type I (according to IUPAC classification), indicating dominant presence of micropores (i.e., < 2nm). The shape of the HIPE SiC-CDC isotherm represents the transition from type I to type V, due to sufficiently large amount of pores around 1 nm in size (**Table S1**). In this material small mesopores are present which contribute 37 vol% of the total pore volume (not including macropores). In case of OM SiC-CDC the isotherm shape is type IV including a type H4 hysteresis that proves the presence of a secondary mesoporosity along with a slit-shaped pore geometry. Very narrowly distributed micropores of 1 nm and mesopores of 4 nm are seen in **Fig. 3**; the latter encompass a pore volume of 1.5 cm<sup>3</sup>/g, and, therefore, contribute significantly to the overall pore volume of this material (**Table S1**). Macropores, which do not account to the salt electrosorption capacity, are present in all electrodes, but only in the case of HIPE SiC-CDC, such macropores are not only present between the particles but also within the particles (see also Ref. 1).



Fig. S1 Nitrogen gas sorption isotherms of TiC-CDC, HIPE SiC-CDC, and OM SiC-CDC at -196°C. STP stands for standard temperature and pressure.

Table S1Pore volume and volume / fraction of micro- and mesopores. As defined by IUPAC, micropores are<br/>pores with a diameter smaller than 2 nm whereas mesopores are pores with a diameter between 2<br/>and 50 nm. No macropores can be determined with the nitrogen sorption method. The pore volumes<br/>were calculated using the quenched solid density functional theory (QSDFT, Ref. 2) assuming slit-<br/>shaped pores (marked with \*) or a mixed QSDFT model for slit and cylindrical pore shapes<br/>(marked with <sup>+</sup>).

	Total pore volume (mL/g)	Micropore volume (mL/g)	Fraction of micropores (%)	Mesopore volume (mL/g)	Fraction of mesopores (%)	Volume of pores smaller than 1 nm (mL/g)
TiC-CDC*	0.52	0.47	91.3	0.05	8.7	0.43
HIPE SiC-CDC <sup>+</sup>	1.14	0.72	63.3	0.42	36.7	0.40
OM SiC-CDC <sup>+</sup>	1.98	0.48	24.1	1.50	75.9	0.22

### 2. Raman Spectroscopy of CDC samples

Raman spectroscopy was carried out on an inVia Raman Spectrometer (Renishaw) using an excitation wavelength of 514 nm with  $\leq 2$  mW output power on the sample and a 50x magnification objective lens (numeric aperture: 0.75). The focus plane spot size of the laser beam was approximately 2  $\mu$ m and the spectral resolution ranged from 0.8 to 1.3 cm<sup>-1</sup> within the studied Raman shift range using a grating of 2400 lines/mm.

All Raman spectra showed a typical spectrum for amorphous carbon, with various degrees of ordering (**Fig. S2**, **Table S2**). Structurally, especially regarding the degree of carbon ordering, both types of SiC-CDC (i.e., OM and HIPE) are virtually identical. They also exhibit the lowest  $I_D/I_G$  band ratios which is indicative of a high degree of carbon ordering and a narrow G<sub>2</sub>-bandwidth of  $\approx$ 50 cm<sup>-1</sup>. The lower degree of carbon ordering found in TiC-CDC is exhibited by the elevated  $I_D/I_G$  band ratio but most noticeably by the broad D-band (**Fig. S2**).



Fig. S1 Raman spectra TiC-CDC, HIPE SiC-CDC, and OM SiC-CDC

Table S2Parameters of spectral fitting assuming a 4-peak deconvolution of the D- and G-band along with<br/> $I_D/I_G$  band ratios (Lorentzian peak shape is assumed).

		<b>Band</b> position	FWHM	Peak area
		(1/cm)	(1/cm)	(arb. units)
TiC-CDC	$D_1$	1154.7	137.1	441100
I <sub>D</sub> /I <sub>G</sub> : 1.57	$D_2$	1343.5	185.7	4359540
	$G_1$	1543.8	144.8	2092624
	$G_2$	1598.8	62.2	964116
HIPE SiC-CDC	$D_1$	1210.3	171.5	15561359
I <sub>D</sub> /I <sub>G</sub> : 1.22	$D_2$	1358.3	125.8	73394112
	$G_1$	1563.7	160.2	50542740
	G <sub>2</sub>	1610.0	46.2	22310958
OM SiC-CDC	$D_1$	1179.8	135.9	3583756
I <sub>D</sub> /I <sub>G</sub> : 1.26	$D_2$	1332.5	130.3	15820094
	$G_1$	1528.7	160.1	9457017
	G <sub>2</sub>	1597.7	53.9	5995670

### 3. Salt Electrosorption Performance

**Table S3** summarizes the performance of nine types of carbon materials and its BET specific surface area, total pore volume and average pore size applied for capacitive deionization. As can be seen from **Table S3**, the specific surface area as calculated by the BET method, BET SSA does not perfectly correlate with the desalination capacity of porous carbons, and the same conclusion applies to the total pore volume, volume of pores <1nm and <2nm, and the average pore size, see also **Fig. S3**.

Table S3Selection of salt electrosorption performance reported for different electrode materials applied for<br/>CDI. AC: activated carbon; CDC: carbide-derived carbon; MWCNTs: multi-walled carbon<br/>nanotubes. All entries are sorted by ascending salt adsorption capacity per 1 g of total electrode<br/>mass. \*Number given per total electrode volume.

	Cell voltage	Salt concentration	Salt adsorption	Salt adsorption	BET SSA	Total pore volume	Average pore size	Ref.
	(V)	(mg/L)	(mg/g)	$(mg/mL^*)$	$(m^2/g)$	(mL/g)	(nm)	
MWCNTs	1.2	~3000	1.7	-	130	0.38	-	3
Carbon xerogel	1.2	~260	3.1	-	239	0.42	6.9	4
Microporous carbon aerogel monoliths	1.25	~2900	9.6	-	500	0.584	-	5
Norit DLC Super50 (AC)	1.2	~290	7.7	3.4	1707	0.80	1.23	this
	1.4	~290	9.7	5.2				study
Kuraray YP50-F (AC)	1.2	~290	9.1		1450	0.71	1.01	this
	1.4	~290	11.0					study
TiC-CDC	1.2	~290	10.1	5.4	1309	0.52	0.67	this
	1.4	~290	13.3	7.2				study
HIPE SiC-CDC	1.2	~290	11.1	1.2	2351	1.14	1.24	this
	1.4	~290	13.6	1.5				study
OM SiC-CDC	1.2	~290	12.8	1.6	2720	1.98	4.0	this
	1.4	~290	16.0	2.0				study



**Fig. S3** Plot of electrosorption capacity versus (A) volume of pores <1nm, (B) volume of pores <2 nm, (C) total pore volume, and (D) BET SSA.



**Fig. S4** Cumulative pore size distribution of the studied sample materials. Synthesized CDC materials (A), activated carbons (B), activated carbon and carbons with only outer surface (exohedral carbon; C), and comparison between TiC-CDCs and carbon aerogel (D). The data in Fig. S4A is identical with the data shown in Fig. 4 except that the data has no *y*-offset and, for that reason, is easier to compare.

**Table S4 and S5** provide the input parameters that have been used to fit the equilibrium data with the modified Donnan model (Ref. 6).

	Performance ratio PR	Volumetric Stern layer capacitance at zero charge	Parameter to describe the non- linear part of the Stern capacity	Chemical attraction term for ions to go into an intra- particle pore	
	(-)	$\begin{array}{c} C_{\mathrm{St,vol,0,(Ref)}} \cdot \mathrm{PR} \\ (\mathrm{MF/m^3}) \end{array}$	$\begin{array}{c} \alpha_{(Ref)}/PR \\ (F {\cdot} m^3/mol^2) \end{array}$	$ \substack{ \mu_{att,(Ref)} + ln(PR) \\ (kT) } $	
TiC-CDC	2.0	144	25.0	2.7	
HIPE SiC-CDC	1.0	72	50.0	2.0	
OM SiC-CDC	0.666	48	33.3	1.6	

Macroporosity " $p_{mA}$ " (i.e., interparticle porosity) and microporosity " $p_{mi}$ " (i.e., intraparticle porosity) used to describe the dynamics of salt electrosorption and charge in porous carbon electrodes were calculated according to

$$p_{\rm mA} = \frac{d_{\rm elec} A - \left(m_{\rm elec} w_{\rm carbon} / \rho_{\rm carbon} + m_{\rm elec} w_{\rm polymer} / \rho_{\rm polymer} + V_{\rm mi}\right)}{d_{\rm elec} A}$$
(S1)

$$p_{\rm mi} = \frac{d_{\rm elec} A - \left(m_{\rm elec} w_{\rm carbon} / \rho_{\rm carbon} + m_{\rm elec} w_{\rm polymer} / \rho_{\rm polymer} + V_{\rm mA}\right)}{d_{\rm elec} A}$$
(S2)

where  $d_{\text{elec}}$  and A stand for the thickness and exchange area of the electrode,  $m_{\text{elec}}$ ,  $w_{\text{carbon}}$ , and  $w_{\text{polymer}}$  are electrode mass and weight fractions of the carbons equal to 0.9 and polymer material (*i.e.*, polymer binder added for mechanical stability) equals to 0.1. Next,  $\rho_{\text{carbon}}$  and  $\rho_{\text{polymer}}$  are densities of the carbon, assumed to be constant and equal to 1.95 g/cm<sup>3</sup> for all carbons investigated and for the carbon black used in this study, and polymer, as provided by the supplier, equals 1.78 g/cm<sup>3</sup>. Finally,  $V_{\text{mi}}$  is the volume of pores inside carbon (in transport theory called micropores), and  $V_{\text{mA}}$  is the volume of transport pathways outside the particles (called in transport theory macropores). For summary of all the geometrical measures and calculated porosities, see **Table S5**.



**Fig. S5** Equilibrium salt adsorption and charge in porous carbon electrodes prepared from OM SiC-CDC. Lines represent fits using modified Donnan model with  $\alpha$ =33.3 F·m<sup>3</sup>/mol<sup>2</sup> (red line) and  $\alpha$ =0 F·m<sup>3</sup>/mol<sup>2</sup> (blue dashed line).

**Table S5**Geometrical values, as used for modeling of the salt electrosorption and charge kinetics. Thedifference of the sum of both kinds of pores and unity represents the solid volume fraction.

	Electrode density	Thickness of one electrode	"Microporosity" = intraparticle pores,	"Macroporosity" = interparticle pores,
	(g/mL)	(µm)	<b>р</b> <sub>ті</sub> ()	<b>р</b> <sub>mА</sub> ()
TiC-CDC	0.540	112	0.239	0.478
HIPE SiC-CDC	0.107	330	0.101	0.843
OM SiC-CDC	0.127	270	0.205	0.723

In the transport model, the dead volume  $V_{dead}$  is equal to 10 mL for the entire stack of 3 cells, the spacer thickness  $\delta_{sp}$  is 250 µm, and the spacer porosity  $p_{sp}$  is 0.50. Finally, the ideal free solution diffusion coefficient of the average of Na and Cl is  $D_{i0}=1.68 \cdot 10^{-9} \text{ m}^2/\text{s}$ . However, to fit to the data we reduced this number by multiplying by a factor 0.8. Thus, in all calculations, *D* is taken as  $1.34 \cdot 10^{-9} \text{ m}^2/\text{s}$ , both in the spacer channel and in the macropores in the electrodes.

**Fig. S6 (A)** shows experimental data of the ion electrosorption step, after a step change in cell voltage to  $V_{cell} = 0.8$  and 1.2 V. As expected, the salt concentration in the effluent water decreases rapidly reaching a minimum, after which the concentration increases again because the salt adsorption capacity of the electrode pair is slowly reached. After t = 2000 s, when the electrosorption step is finished, desorption takes place by setting the cell voltage to zero, which leads to rapid ion release and increase in the effluent salt concentration. **Fig. S6 (B)** shows the corresponding data of the current density from which by integration the charge transfer in C/g is calculated. **Fig. S7** shows the corresponding data at 1.4 V.



**Fig. S6** Data of a single "dynamic equilibrium" CDI adsorption/desorption cycle for HIPE SiC-CDC.-(A) Effluent salt concentration and (B) Current density ( $V_{cell} = 0.8$  and 1.2 V,  $c_{in} = 5$  mM).



**Fig. S7** Data of a single "dynamic equilibrium" CDI adsorption/desorption cycle for OM SiC-CDC. (A) Effluent salt concentration and (B) Current ( $V_{cell} = 1.4 \text{ V}, c_{in} = 5 \text{ mM}$ ).

### 4. Further Theory-Data Comparison Using Two-Dimensional Porous Electrode Theory

In this section we present further data and comparison with theory for the dynamics of salt adsorption and charge formation for three CDC-materials and for two voltage levels, see **Fig. S8**.



**Fig. S8** Salt adsorption and charge formation in CDI cell for (A) TiC-CDC; (B) OM SiC CDC, and (C) HIPE SiC-CDC as function of time ( $c_{\infty}$ = 5 mM NaCl inflow) and cell voltage. Lines represent comparison with 2D porous electrode theory.

### 5. Theoretical Section

### 5.1 Salt Electrosorption and Charge Storage in Porous Carbon

To describe the dynamics of salt electrosorption and charge in porous carbon electrodes forming a CDI cell, we jointly consider ion transport through the space between the carbon particles, that is, the large transport pathways across the electrode (interparticle pore volume), and the electrosorption of ions inside carbon particles (intraparticle pore volume). To describe the latter, a powerful and elegant approach is to assume that the EDLs inside the intraparticle pore volume are strongly overlapping and, therefore, that the potential in these pores does not vary with position in the pore. This is the common "Donnan" approach for charged porous materials. The electrical potential in the intraparticle pore volume is different from that in the interparticle pore volume (the transport pathways) by a value  $\Delta \phi_d$ .

It has been recognized that the simple Donnan approach does not describe well various data sets for salt electrosorption and charge in most microporous carbons, and two modifications are required.<sup>6-8</sup> The first modification is to consider the presence of a charge-free Stern layer located in between the electronic charge in the carbon matrix and the ions that reside in the water-filled intraparticle pore volume. The second modification is to include a chemical attraction energy for the ion when it transfers from the space between the carbon particles into the internal carbon pore volume, described by a term  $\mu_{att}$ .<sup>9</sup> Thus, in the modified Donnan model, we consider an additional, non-electrostatic, attraction for the ion to enter the pores of carbon. This attraction term also reflects the experimental reality that uncharged carbons also adsorb some salt.

The modified Donnan model containing these two modifications is described by the following equations. First of all, the volumetric concentrations (in  $mM=mol/m^3$ ) of an arbitrary ion j in the pores inside a carbon particle is given by

$$\boldsymbol{c}_{j,mi} = \boldsymbol{c}_{mA} \cdot \exp\left(-\boldsymbol{z}_{j} \cdot \Delta \boldsymbol{\phi}_{d} + \boldsymbol{\mu}_{att}\right)$$
(S3)

where "mi" stands for the pores inside the carbon (intraparticle space, in transport theory called micropores), and mA for the transport pathways outside the particles (interparticle space, called macropores). Note that except for the equations in the theory-section, in the remainder of this paper we adhere to the IUPAC definition of pores,<sup>10</sup> where the size of the pore, not the position (i.e., inside or in between carbon) defines the differentiation between micropores, mesopores, and macropores.

Considering only a monovalent salt solution, in the interparticle pores (the space within the electrode located between carbon particles), the anion and cation concentrations are equal because of local electroneutrality. Hence,  $c_{j,mA}$  can be replaced by the corresponding salt concentration,  $c_{mA}$ , which will be a function of time, *t* (in seconds), and position *x* (in m) within the electrode, and  $c_{j,mi}$  is a function of *t* and *x*. In Eq. S3,  $z_j$  equals +1 for the cation and -1 for the anion, while  $\Delta \phi_d$  is the dimensionless Donnan electrostatic potential difference between the pores inside and in between the particles which can be multiplied by the thermal voltage,  $V_T = R \cdot T/F \approx 25.7$  mV, to obtain a voltage with unit Volt.

Summing up Eq. S3 for both ions directly gives the total ion density in the pores inside a carbon particle:

$$\boldsymbol{c}_{\text{ions,mi}} = \boldsymbol{c}_{\text{cation,mi}} + \boldsymbol{c}_{\text{anion,mi}} = 2 \cdot \boldsymbol{c}_{\text{mA}} \cdot \exp(\mu_{\text{att}}) \cdot \cosh(\Delta \phi_{\text{d}})$$
(S4)

and though it is possible to consider a different  $\mu_{att}$  for anions and cations, in the present work we will assume that they are the same.

The local ionic charge density,  $c_{charge,mi}$ , in the pores inside a porous carbon particle follows from Eq. S3 as

$$\boldsymbol{c}_{\text{charge,mi}} = \boldsymbol{c}_{\text{cation,mi}} - \boldsymbol{c}_{\text{anion,mi}} = -2 \cdot \boldsymbol{c}_{\text{mA}} \cdot \exp(\mu_{\text{att}}) \cdot \sinh(\Delta \phi_{\text{d}})$$
(S5)

and this volumetric charge density (in mM) relates to the Stern layer potential difference,  $\Delta \phi_{St}$ , according to

$$c_{\text{charge,mi}} = -C_{\text{St,vol}} \cdot \Delta \phi_{\text{St}} \cdot V_{\text{T}} / F$$
(S6)

where  $C_{\text{St,vol}}$  is a volumetric Stern layer capacity in F/m<sup>3</sup>. Note that capital *C* with subscript "St,vol" is a volumetric Stern layer capacity in F/m<sup>3</sup>, and small *c* with subscript "charge,mi", "mA", "j,mi" is a concentration in mM. For  $C_{\text{St,vol}}$  we use the expression

$$C_{\rm St,vol} = C_{\rm St,vol,0} + \alpha \cdot c_{\rm charge,mi}^2 \tag{S7}$$

where the second, empirical, term reflects the experimental observation from previous work that the Stern layer capacity goes up quadratically with micropore charge, see also section 5.3.<sup>6, 11</sup>

The modified Donnan model equals the limit situation of the Gouy-Chapman-Stern (GCS) theory when approaching full EDL overlap in micropores where the Debye length is of the order of, or larger than, the pore size. In addition to GCS theory it includes a non-electrostatic adsorption energy  $\mu_{att}$ . A difference is that in the Donnan representation EDL properties are described per unit pore volume, whereas in the GCS model charge and salt adsorption are described as function of pore area. Numbers in either definition can be converted when the pore area/volume ratio is known.

### 5.2 Two-Dimensional Theory for Transport and Ion Storage in Porous Electrodes

In this paper, we utilize a novel two-dimensional model for transport and storage of ions and electrical charge in a CDI cell consisting of two porous electrodes placed parallel, with a flat planar slit, or transport channel, or spacer, in between. In the direction of flow, this transport channel is mathematically divided into M subsequent sub-cells, see **Fig. 2**.<sup>12</sup> In the following section, we first focus on a single sub-cell, and describe ion transport in the perpendicular direction, from electrode to electrode. Next we describe how all sub-cells are combined together in a unified model for the full CDI system. We focus on a monovalent salt solution, assuming that the two ion diffusion coefficients are equal (as for KCI). Note that this is an effective diffusion coefficient for transport in the pores between the porous carbon particles that may include a contribution of pore tortuosity. Extensions to mixtures with ions of different diffusion coefficients (as must formally also be considered for NaCI) are described in Ref. 13, 14.

In the porous electrode transport model, two coupled partial differential equations must be solved along with additional algebraic equations.<sup>14-16</sup> The complete model contains, as a function of the depth in the electrode x, and time t, four coupled variables: (1) the salt concentration in the pores between carbon particles,  $c_{mA}$ , (2) the electrostatic potential,  $\phi_{mA}$ , (3) the charge density in pores inside the carbon particles,  $c_{charge,mi}$ , and (4) the net salt electrosorption in such internal pores. The latter variable will be described by the effective salt concentration,  $c_{eff}$ , which is a summation of the total ion concentration times volume fraction, in the macropores and in the micropores (at location x), which we have to divide by a factor of 2 to obtain a salt concentration defined per unit total electrode volume. The effective salt concentration is thus given by

$$\boldsymbol{c}_{\text{eff}} = \boldsymbol{p}_{\text{mA}}\boldsymbol{c}_{\text{mA}} + \frac{1}{2}\boldsymbol{p}_{\text{mi}}\boldsymbol{c}_{\text{ions,mi}}$$
(S8)

where  $p_j$  is a porosity (volume fraction) defined per total electrode volume. The summation of  $p_{mi}+p_{mA}$  is not equal to one, and the difference is made up of the solid matter in the electrode, such as the polymeric binder, the skeleton of porous carbon itself, and any other solid component of the carbon electrode such as conductive additives, see **Table S6**.

The porous electrode transport theory requires various geometrical measures as inputs (thickness, porosities) that can be calculated from known electrode dimensions. Besides, it requires an estimate of the diffusion coefficient of the ions in the macropores, which may be lower than the corresponding value in free solution. There are no other fitting functions related to transport part of the theory. The present model neglects a transport resistance between macropores and micropores, which can be incorporated, but will require an additional transport coefficient, see the section 5.3.

Note that the four variables for which the model is solved (i.e.,  $c_{mA}$ ,  $\phi_{mA}$ ,  $c_{charge,mi}$  and  $c_{eff}$ ) depend all on depth x and time t. It is only after sufficient time that all these variables level off to their equilibrium value, when all time derivatives become zero. This equilibrium situation can also be described directly by considering that after sufficient time (after application of a voltage signal), everywhere the macropore concentration  $c_{mA}$  has become the same as the inflow salt concentration  $c_0$ . Then, using the modified Donnan model, we can directly calculate the equilibrium situation without having to solve the full porous electrode transport model.

The spacer channel between the two electrodes is described in the model by a series of continuously stirred tanks (sub-cells) with a salt concentration  $c_{sp}$  that is only a function of time, described by the salt mass balance

$$\boldsymbol{\rho}_{sp} \boldsymbol{V}_{sub-cell} \frac{\partial \boldsymbol{c}_{sp}}{\partial t} = -J_{ions} \boldsymbol{A} + \phi_{v} \left( \boldsymbol{c}_{sp,in} - \boldsymbol{c}_{sp} \right)$$
(S9)

where  $V_{\text{sub-cell}}$  (in m<sup>3</sup>) is the geometrical volume of the sub-cell,  $p_{\text{sp}}$  is the open porosity of the spacer channel, A the exchange area of a sub-cell with one electrode (in m<sup>2</sup>), and  $\phi_v$  the water volumetric flow rate running through the cell, i.e., along the electrodes (in m<sup>3</sup>/s). We assume that the two electrodes behave symmetrically, and as a consequence the ion flux to one electrode,  $J_{\text{ions}}$ , is equal to the salt flux to both electrodes.<sup>8</sup>

In addition to the salt mass balance in the spacer channel, we have to specify two coupled partial differential equations that describe the transport in the porous electrode. First, within the electrode, a differential salt mass balance can be set up, given by

$$\frac{\partial \boldsymbol{c}_{\text{eff}}}{\partial t} = \boldsymbol{p}_{\text{mA}} \boldsymbol{D} \frac{\partial^2 \boldsymbol{c}_{\text{mA}}}{\partial x^2} \tag{S10}$$

with  $0 \le x \le L_{elec}$ , where  $L_{elec}$  is the electrode thickness, and *D* the salt diffusion coefficient in the pores between porous carbon particles. As Eq. S10 shows, we consider all fluxes to be in only one direction, namely the direction into the electrode, i.e., at cross-angles with the general flow direction of the solution through the channel, see **Fig. 2**. The second partial differential equation describes the charge density in the intraparticle pores of carbon particles and is given by

$$\boldsymbol{\rho}_{\rm mi} \frac{\partial \boldsymbol{c}_{\rm charge,mi}}{\partial t} = 2\boldsymbol{\rho}_{\rm mA} D \frac{\partial}{\partial x} \left( \boldsymbol{c}_{\rm mA} \frac{\partial \boldsymbol{\phi}_{\rm mA}}{\partial x} \right)$$
(S11)

Finally, we need to solve at each position in the electrodes two algebraic equations: (1) Eq. S8; and (2) the equation for the potential  $\phi_{mA}$  that is related to the potential  $\phi_1$  in the carbon matrix according to

$$\Delta \phi_{d} + \Delta \phi_{St} = \phi_{1} - \phi_{mA} \tag{S12}$$

with expressions for  $\Delta \phi_d$  and  $\Delta \phi_{St}$  given by Eqs. S5, S6, and S7.

Boundary conditions required to solve the two partial differential equations are as follows. First of all, at the backside of the electrode ( $x=L_{elec}$ ), we have  $\partial c_{mA}/\partial x=0$  and  $\partial \phi_{mA}/\partial x=0$ . At the front-side (where x=0), the spacer channel concentration,  $c_{sp}$ , is equal to that in the electrode,  $c_{mA}$ . The potential gradient at x=0 relates to the current J, a relation which will be discussed below.

Initial conditions are as follows. At time zero, we have a certain value for  $c_{mA}$  (the same everywhere, also the same as in the spacer channel). With  $c_{charge,mi}=0$  everywhere in the electrode, we can use Eq. S4 and S8 to determine  $c_{eff}$  at time zero.

To calculate voltages and currents after time zero, we must consider the overall cell voltage relationship. Namely, in the experiment we apply a voltage,  $V_{cell}$ , between the two electrodes. As explained above (see also **Fig. 2**) we assume symmetry in the CDI cell, and thus at time zero we make a step-change in applied voltage from zero to  $\frac{1}{2} \cdot V_{cell}$ , which is the voltage between the mid-plane in the spacer channel and that in the carbon matrix,  $\phi_1$ , in one of the electrodes. Note that  $V_{cell}$  has unit of Volt and must be divided by the thermal voltage,  $V_T$ , to obtain a dimensionless potential,  $\phi$ . In the carbon matrix, we assume a constant potential  $\phi_1$  and thus we neglect possible electrical resistances in the carbon; in the current collectors; or in the connecting wires. This assumption is not so common in EDLC modeling, but note that in desalination the electrolyte salt concentration is typically 5 to 50 mM, much lower than the values of the order of 1 M used in EDLCs. Consequently, in CDI the ionic resistance is much more prominent than the electrical resistances for electronic charge to distribute across the electrode.

The condition of applied voltage translates directly into a relation for the potential  $\phi_{mA}$  at the frontside of the electrode (where *x*=0), according to

$$\phi_{mA}\big|_{x=0} = \frac{V_{cell}}{2V_{T}} - \Delta\phi_{sp}$$
(S13)

with the voltage drop across half the spacer,  $\Delta \phi_{sp}$ , obtained from

$$J = -2c_{\rm sp}\rho_{\rm sp}D\frac{\Delta\phi_{\rm sp}}{L_{\rm sp}/2}$$
(S14)

where J is the current density (in mol/m<sup>2</sup>/s). Multiplying by the electrode area and by F we get a current in Ampere (note the difference between J and  $J_{ions}$ ). The ions flux,  $J_{ions}$ , directed out of the spacer channel, Eq. S9, is equal to the flux into the electrode

$$J_{\text{ions}} = -2 p_{\text{mA}} D \frac{\partial c_{\text{mA}}}{\partial x} \bigg|_{x=0}$$
(S15)

and a similar boundary condition for the current density J is given by

$$J = -2p_{mA}D\left(c_{mA}\frac{\partial\phi}{\partial x}\right)\Big|_{x=0}.$$
(S16)

In our model we consider a number of M=6 sub-cells placed sequentially in the direction of flow along the electrode, to describe the approximate plug-flow behavior of our system where salt and fluid are transported convectively downstream. By using a finite number of sub-cells, longitudinal dispersion is included. Note that in the model each sub-cell's electrode region is disconnected from neighboring ones. Transport from one spacer channel sub-cell to the next is described by Eq. S9, with  $c_{sp}$  the concentration in sub-cell i and  $c_{sp,in}$  the concentration in the up-stream sub-cell i-1. The concentration in the last sub-cell (*i=M*) is equal to the effluent concentration. The sub-cell volume is equal to the total cell volume (height x electrode area) divided by the number of sub-cells, *M*. A small mixing volume present in the CDI unit before the conductivity sensor, is modeled using Eq. S0, with  $V_{sub-cell}$  replaced by *V* "dead volume", with  $p_{sp}=1$  and with the term  $J_{ions}A$  set to zero. The current *I* (in A) in the stack is calculated from  $I= F \cdot N/M \cdot \Sigma_s J_i$ , where  $\Sigma_i$  is a summation over all sub-cells. Current *I* can be integrated over time to obtain the charge. Dividing by electrode mass gives us the charge per gram,  $\Sigma_F$ , as plotted in **Fig. 5B**, **7B**, and **8B**.

### 5.3 Assumptions made in the Modified-Donnan-Based Porous Electrode Theory

The porous transport theory as described in sections 5.1 and 5.2 and used in **Fig. 7** and **8** is based on various assumptions which are listed below:

- Ion transport is based on the Nernst-Planck equation for electrodiffusion which assumes ideal statistics (all activity coefficients equal to one) for ions as point charges moving in a mean electrical field. We assume the diffusion coefficient to be constant.
- Across the spacer channel we assume that concentration gradients are negligible, and thus the voltage drop across the spacer channel can be described by a simple voltage-current relation.
- We describe transport in the spacer channel in longitudinal direction (along the electrodes) by assuming a series of subsequent stirred-tanks ("sub-cells"). By taking a fairly high number of these subcells, we approximate plug-flow behavior with superimposed effects of longitudinal dispersion. This dispersion is mainly caused by the fact that the water flow velocity is not constant across the spacer thickness (direction perpendicular to flow).
- Within the electrode we assume there is only transport in the interparticle macropores, not through the intraparticle meso- and micropores. We assume that the electrodiffusional ion transport process needs only to be considered in one direction, namely the direction from spacer channel to current collector, thus across the thickness of the electrode which is the direction perpendicular to the water flow through the spacer channel. The electrode thickness is of the order of 200 µm and is much smaller than the longitudinal direction in the cell, which is of the order of 4 cm, and thus about 200-times the electrode thickness. This high ratio suggests that we can neglect the relevance of diffusional transport in the longitudinal direction.
- In addition, we neglect convective transport through the electrode in both the perpendicular and longitudinal direction. Our rationale for this assumption is that the macropores have sizes in the order of a few micrometers, much smaller than the transport paths of the order of 100  $\mu$ m in size in the spacer. Thus, in the spacer the resistance to viscous flow is much less and we can expect water velocities to be much higher there than within the electrode.
- We neglect a possible transport resistance for ionic diffusion for the ion adsorption from macropores into the micropores. However, as our results presented in Fig. 7 demonstrate, for materials without much mesoporosity, there may be such a local resistance, see Ref. 17. One option to include this effect in our model is by explicitly considering a local transport resistance between macro- and micropores. Such an approach can be based on describing the individual ion adsorption fluxes into the carbon micropores by

$$j_{i} = k_{\rightarrow} \cdot c_{mA} \cdot \exp(-z_{i} \cdot \alpha \cdot \Delta \phi_{d}) \cdot k_{\leftarrow} \cdot c_{mi,i} \cdot \exp(z_{i} \cdot (1 - \alpha) \cdot \Delta \phi_{d}),$$
(S17)

where  $\alpha$  is a transfer coefficient (0< $\alpha$ <1) and the kinetic adsorption and desorption constants,  $k_{\rightarrow}$  and  $k_{\leftarrow}$ , relate to the chemical attraction term  $\mu_{att}$  according to  $\mu_{att}=\ln(k_{\rightarrow}/k_{\leftarrow})$ . For high values of the kinetic constants, or low values of the flux  $j_i$ , the equilibrium Donnan model is recovered.

The modified Donnan (mD) model is used to describe the structure of the electrical double layer (EDL) in the carbon particle. Its predictions have been compared to a large range of data in Ref. 8, 13, 15, as well as in Fig. 5 of our paper to describe both charge and salt adsorption. The mD model is the mathematical limit of the Poisson-Boltzmann equation in the limit of highly overlapped diffuse layers, valid when the ratio of Debye length to pore width is sufficiently high. In this limit, the exact pore geometry is no longer of relevance, but solely the pore volume. This is why in the mD model charge and ion adsorption are defined per unit pore volume, not per unit electrode area, which is more typical in Gouy-Chapman-Stern based EDL models. The mD model includes the fact that there is a small chemical attraction of salt into carbon micropores, via the adsorption energy term,  $\mu_{att}$ , while also considering that the ionic charge and electronic charge cannot approach one another infinitely close. This effect leads to the development of a Stern layer with an associated Stern capacity in between the electronic and ionic charge. Our data in this and previous papers suggest that the capacity of this layer depends on the charge, see Fig. S5. To describe this effect we choose an empirical function where capacity increases according to  $C_{st}=a+b\cdot\sigma^2$  where  $\sigma$  is micropore charge. Such a positive dependency of Stern capacity on charge has been more often observed and reported, see Ref. 18 and 17, 19.

### 6. Experimental Section

### 6.1 CDC Materials

**Titanium carbide-derived carbon (TiC-CDC)** was synthesized according to Ref. 20 (**Fig. 3A**). In a quartz tube furnace (diameter: 25 mm, GERO GmbH, Germany), TiC powder (Sigma Aldrich, Germany, particle size  $\approx$ 5 µm) was heated to 600 °C in Argon (100 mL/min), then subjected to thermal treatment at 600 °C in dry chlorine gas (chlorine flow rate: 80 mL/min mixed with 70 mL/min argon) for 6 h. Then, after 1 h at 600 °C in flowing argon (150 mL/min), the sample was subjected to hydrogen treatment (80 mL/min) for 30 minutes to remove residual chlorine and metal chloride species.

Ordered mesoporous silicon carbide derived carbon (OM SiC-CDC) was synthesized according to the procedure outlined in Ref. 20 (Fig. 3B). A SiC polymer precursor, 6.45 g of polycarbosilane (StarPCS<sup>TM</sup> SMP-10, Starfire Systems), and 1.61 mL of para-divinylbenzene (Sigma Aldrich, 80% mixture of isomers) were drop-wise added to 6.0 g of ordered mesoporous silica (SBA-15, synthesized according to Ref. 21 and thoroughly mixed. Afterwards, the obtained mixture was evacuated over night at room temperature to obtain a homogeneous and complete pore filling. The pre-ceramic composite system was then pyrolyzed at 800 °C. Ordered mesoporous silicon carbide was obtained by removing the silica template via etching with hydrofluoric acid (33% water, 33% ethanol, and 33% of 40 mass% HF) for 3 h. The resulting OM SiC-CDC was derived after chlorine treatment of the ordered mesoporous silicon carbide materials at 800 °C. The material was heated in a quartz boat inside a quartz tube (inner tube diameter: 25 mm) in a horizontal tubular furnace (GERO GmbH) in 70 mL/min argon flow to the desired temperature (450 K/h). Subsequently, Cl<sub>2</sub> gas was introduced for 3 h (80 mL/min flow) while the argon flow was maintained at the same level. After that time, the  $Cl_2$  gas flow was stopped and the sample was cooled down to room temperature in flowing argon. Residual chlorine and metal chlorides trapped in the carbon pores were subsequently removed in flowing hydrogen. For that the material was heated in a quartz boat inside quartz tube in horizontal tubular furnace in 80 mL/min H<sub>2</sub> flow to 600 °C for 2 h (300 K/h).

HIPE SiC-CDC was synthesized according to Ref. 1 (Fig. 3C). 4.37 g of SMP-10 (Starfire Systems) was mixed with 1.71 g of divinylbenzene (Sigma Aldrich, 80% mixture of isomers) under mild stirring to form the organic phase of the high internal phase emulsion (HIPE) with a volume of 6.25 mL including 30 vol% of the crosslinker. The resulting mixture was blended with 2.13 g of the nonionic surfactant Span<sup>TM</sup> 80 (Fluka, Switzerland). After one minute, 346 mg  $K_2S_2O_8$  (Fluka) dissolved in 18.75 mL distilled water was added drop wise to the organic phase by continuously rising up the stirring rate in order to ensure a homogeneous commingling of the phases. The resulting emulsion was then treated at 80 °C for 24 h. The removal of the surfactant was achieved by soxhlet extraction with a mixture of MeOH/water (30/70) for 24 h resulting in what we refer to as Poly-HIPE. After drying at 80 °C, the monolithic pieces of the Poly-HIPE were pyrolyzed in a horizontal alumina furnace under flowing argon at 700 °C for 2 h with a heating rate of 1 K/min. The obtained SiC monoliths were converted to carbon by thermal chlorine treatment. 2 g of the starting material were placed in a quartz boat inside a quartz tube in a horizontal tubular furnace and heated up to 700 °C with a rate of 450 K/h under an argon flow of 150 mL/min. Then, the gas flow was changed to a mixture of 80 mL/min chlorine and 70 mL/min argon. After 2 h of chlorine treatment, the furnace was cooled down to 600 °C under 150 mL/min argon and kept at that temperature for 1 h. Then, the gas flow was changed from argon to 80 mL/min hydrogen in order to remove residual chlorine and metal chlorides. This procedure was carried out for 1 h and the materials were then cooled down under argon atmosphere.

### 6.2 Carbon Onions

Carbon onions were prepared following the procedure outlined in Ref. 22. In short, detonation nanodiamond powder (NaBond Technologies Co. Ldt., China) with an average particle size of 4 to 6 nm was treated at 1750°C in vacuum (~  $10^{-7}$  bar) for 3 h. The heating and cooling rate was 10 K/min and a graphite crucible was used to hold the sample material. The resulting material was sp<sup>2</sup>-hybridized carbon and X-ray diffraction (XRD) analysis showed full conversion of the nanodiamond in onion-like carbon (**Fig. S9**).



Fig. S9 XRD diffractograms of carbon onions and the precuros material, nanodiamonds. Subscript "g" denotes reflections associated with graphite and "d" denotes peaks correlating with diamond

### 6.3 Structural Characterization

Scanning electron microscopy (SEM) images were recorded using no sputter coating and employing a Quanta 400 ESEM (FEI, The Netherlands) in high vacuum mode at 15 kV for TiC-CDC and Gemini DSM 982 (Zeiss, Germany) at 4 kV for OM SiC-CDC and HIPE SiC-CDC.

X-ray diffraction was carried out using a D8 system (Bruker, Germany) using a Lynxeye detector. Within the  $2\theta$  range between 10 and 140 °2 $\theta$ , the step width was 0.02 ° and the measurement time per each step was 1 s.

Prior to all gas sorption measurements, the samples were kept under vacuum (1 mbar) at 150 °C for 16 h. The porosity was analyzed using N<sub>2</sub> gas sorption at -196 °C up to 1 bar using an Autosorb iQ MP (Quantachrome Instruments, Germany). BET SSA values were calculated using the multipoint-BET method<sup>23</sup> in the linear range from 0.01-0.20 P/P<sub>0</sub>. Total pore volumes were derived from the cumulative pore volume using the quenched solid density functional theory (QSDFT), and does not include the HIPE SiC-CDC macropores.<sup>2</sup> For HIPE SiC-CDC, and OM SiC-CDC a mixed model assuming slit and cylindrical pores was assumed, while for TiC-CDC only slit-shaped pores were considered. Slit shaped pores were also assumed for the analysis of all activated carbons. For all pore size distributions (PSDs), only the adsorption branch was used to eliminate the emergence of desorption-related artifacts.

### 6.4 Electrode Preparation

Electrodes were prepared following the procedure outlined in Ref. 6, except that now the electrodes were directly coated on the graphite foil current collector. First, a carbon slurry was prepared by mixing 85 mass% of CDC, 5 mass% of carbon black (Vulcan XC72R, Cabot Corp., Boston, MA), and 10 mass% of polyvinylidene fluoride (Kynar HSV 900, Arkema Inc., Philadelphia, PA); the latter had been dissolved in N-methyl-2-pyrrolidone. To obtain a homogeneous mixture, the slurry was deaerated and stored at 50 °C for 1 h. Finally, electrodes were prepared by painting of the carbon slurry directly on one or both sides of a graphite current collector, taking care that approximately the same mass was coated on each side. The current-collector/electrode assemblies are then left for drying at room temperature. Results for thickness and total electrode mass density provided in **Table S5**. Materials AC-CWZ-22, AC-S-TE3, AC-S-TE11, and AC-MSP20 were not painted, but prepared by the wet-casting technique following procedure explained in Ref. 6.

### 6.5 CDI Experiments

Experimental details of the CDI test system have been described in Ref. 6, 8. In brief, a stack consisting of N = 3 cells is built from electrodes, current collectors, and spacers. Each current collector is coated on both sides with a layer of 6x6 cm<sup>2</sup> of the carbon electrode and is used in two adjacent cells (one above, and one below). The two current collectors at the upper and lower end of the stack only have a single layer of electrode coating. Together with open-meshed porous spacer materials (Glass fibre prefilter; Millipore, Ireland; thickness  $\delta_{sp}=350 \ \mu m$ ) the current collector/electrode layers are stacked together forming three parallel cells (i.e., one stack). The flow of salt solution through the stack is kept constant at  $\Phi=10 \ mL/min$ . The solution flows first into a housing around the stack, enters the *N* spacer layers from all four sides, and leaves via a centrally placed outlet (1.5x1.5 cm<sup>2</sup> channel) to flow along a conductivity meter placed in-line.

Ion electrosorption occurs when applying a voltage  $V_{cell}$  to the cell, defined as the voltage difference between the positively and negatively polarized electrodes. In our experiments, no reference electrodes are included. At the end of the salt electrosorption step, the cell voltage is reduced to zero and ion desorption begins. The electrical current running from the cathode to the anode is measured online by a potentiostat (Autolab, PGSTST30, The Netherlands) and is integrated over time to provide a measure for the total charge transferred between the electrodes. This total charge is divided by the total electrode mass in the stack,  $m_{tot}$ , to obtain the charge expressed in C/g, see Figs. 5C, 7A, and 8A. Parallel to the charge transfer measurements, the electrical conductivity of the effluent is measured and this value is used to calculate the effluent salt concentration and, thus, the salt removal,  $\Gamma_{salt}$ , see Ref. 6. The latter is calculated by integrating the difference between the inflow  $(c_{in})$  and outflow salt concentration ( $c_{\text{eff}}$ ) over time, multiplying by the flow rate  $\Phi$  and dividing by  $m_{\text{tot}}$  see Figs. 5D, 7B, and 8B. For each new experiment, the salt electrosorption/desorption cycle was repeated several times until the differences between cycles became negligible. We like to stress that in this work, the salt removal data is not obtained from the first cycle after a new condition has been applied, but instead is obtained when the system has reached the limit cycle, or dynamic equilibrium (DE). This important condition defines that the same amount of salt was electrosorbed during the adsorption step as was being removed in the desorption step of the cycle, as will be typical during practical long-term operation of a CDI system. All experiments were done using a  $c_{in} = 5$  mM NaCl-solution (290 ppm, 550  $\mu$ S/cm). The pH value of the feed solution was maintained constant at pH 7.5 during testing by automatic addition of small amounts of 0.1 M hydrochloric acid or 0.1 M sodium hydroxide to the 10 L storage vessel from which the CDI-stack was fed and to which the effluent was returned. The vessel is continuously flushed with  $N_2$  gas to purge the water from dissolved oxygen. Note that we do not measure the conductivity decrease in this storage vessel, but in the exit tube right after the water leaves the stack, before being returned to the storage vessel. This is why after application of a cell voltage, the salinity first decreases and then goes up again, even though the voltage is still applied.

### References

- 1. M. Oschatz, L. Borchardt, M. Thommes, K. A. Cychosz, I. Senkovska, N. Klein, R. Frind, M. Leistner, V. Presser, Y. Gogotsi and S. Kaskel, *Angewandte Chemie International Edition*, 2012, **51**, 7577-7580.
- 2. P. I. Ravikovitch and A. V. Neimark, *Langmuir*, 2006, **22**, 11171-11179.
- 3. K. Dai, L. Shi, J. Fang, D. Zhang and B. Yu, *Materials Letters*, 2005, **59**, 1989-1992.
- 4. J. Landon, X. Gao, B. Kulengowski, J. K. Neathery and K. Liu, *Journal of the Electrochemical Society*, 2012, **159**, A1861-A1866.
- M. E. Suss, T. F. Baumann, W. L. Bourcier, C. M. Spadaccini, K. A. Rose, J. G. Santiago and M. Stadermann, Energy & Environmental Science, 2012, 5, 9511-9519.
- S. Porada, L. Weinstein, R. Dash, A. van der Wal, M. Bryjak, Y. Gogotsi and P. M. Biesheuvel, ACS Applied Materials & Interfaces, 2012, 4, 1194-1199.
- 7. P. M. Biesheuvel, R. Zhao, S. Porada and A. van der Wal, *Journal of Colloid and Interface Science* 2011, **360**, 239-248.
- 8. S. Porada, M. Bryjak, A. van der Wal and P. M. Biesheuvel, *Electrochimica Acta*, 2012, 75, 148-156.
- 9. B. Kastening and M. Heins, *Electrochimica Acta*, 2005, 50, 2487-2498.
- 10. K. S. W. Sing, D. H. Everett, R. A. V. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol and T. Siemieniewska, *Pure and Applied Chemistry*, 1985, **57**, 603-619.
- S. Porada, B. B. Sales, H. V. M. Hamelers and P. M. Biesheuvel, *The Journal of Physical Chemistry Letters*, 2012, 3, 1613-1618.
- R. Zhao, O. Satpradit, H. H. M. Rijnaarts, P. M. Biesheuvel and A. van der Wal, *Water Research*, 2013, 47, 1941-1952.
- R. Zhao, M. van Soestbergen, H. H. M. Rijnaarts, A. van der Wal, M. Z. Bazant and P. M. Biesheuvel, *Journal of Colloid and Interface Science*, 2012, 384, 38-44.
- 14. P. M. Biesheuvel, Y. Fu and M. Z. Bazant, Russian Journal of Electrochemistry, 2012, 48, 580-592.
- R. A. Rica, D. Brogioli, R. Ziano, D. Salerno and F. Mantegazza, *The Journal of Physical Chemistry C*, 2012, 116, 16934–16938.
- R. A. Rica, R. Ziano, D. Salerno, F. Mantegazza, M. Z. Bazant and D. Brogioli, *Electrochimica Acta*, 2013, 92, 304–314.
- R. K. Kalluri, M. M. Biener, M. E. Suss, M. D. Merrill, M. Stadermann, J. G. Santiago, T. F. Baumann, J. Biener and A. Striolo, *Physical Chemistry Chemical Physics*, 2013, 15, 2309-2320.
- 18. D. C. Grahame, Chemical Reviews, 1947, 41, 441-501.
- 19. M. Z. Bazant, K. T. Chu and B. J. Bayly, SIAM Journal on Applied Mathematics, 2005, 65, 1463-1484.
- E. Kockrick, C. Schrage, L. Borchardt, N. Klein, M. Rose, I. Senkovska and S. Kaskel, *Carbon*, 2010, 48, 1707-1717.
- 21. M. Choi, W. Heo, F. Kleitz and R. Ryoo, *Chemical Communications*, 2003, 1340-1341.
- J. K. McDonough, A. I. Frolov, V. Presser, J. Niu, C. H. Miller, T. Ubieto, M. V. Fedorov and Y. Gogotsi, *Carbon*, 2012, 50, 3298–3309.
- 23. British Standards, BS ISO 9277 Determination of the specific surface area of solids by gas adsorption BET method, 2010.