

Exceptional Water Desalination Performance with Anion-Selective Electrodes

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Capacitive deionization (CDI) typically uses one porous carbon electrode that is cation adsorbing and one that is anion adsorbing. In 2016, Smith and Dmello proposed an innovative CDI cell design based on two cation-selective electrodes and a single anion-selective membrane, and thereafter this design was experimentally validated by various authors. In this design, anions pass through the membrane once, and desalinated water is continuously produced. In the present work, this idea is extended, and it is experimentally shown that also a choice for anion-selective electrodes, in combination with a cation-selective membrane, leads to a functional cell design that continuously desalinates water. Anion-selective electrodes are obtained by chemical modification of the carbon electrode with (3-aminopropyl)-triethoxysilane. After chemical modification, the activated carbon electrode shows a substantial reduction of the total pore volume and Brunauer–Emmett–Teller (BET) surface area, but nevertheless maintains excellent CDI performance, which is for the first time that a low-porosity carbon electrode is demonstrated as a promising material for CDI.

Capacitive deionization (CDI) is a method of water desalination based on electrodes that adsorb ions and later release them.^[1,2] Traditionally, CDI uses a cell design with one electrode that

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adsorbs and releases the cations (cathode), and another electrode that adsorbs and releases the anions (anode). Unmodified carbons do not have a significant natural preference for the adsorption of either anions or cations, but instead can adsorb both, depending on electrode potential.^[3,4] A design with two such unmodified carbons can be used to desalinate water. However, because of the large co-ion expulsion effect, the charge efficiency of such a cell is low, and thus much charge is needed to achieve a certain desalination performance.^[5]

To enhance charge efficiency, and thus to reduce the energy input corresponding to a certain desalination performance, it is advantageous to make the electrodes ion selective, either for anions or cations. This can be done by chemically modifying the electrodes,^[6–13] or by placing ion-

exchange membranes (also called ion-selective membranes) in front of the electrodes: an anion-exchange membrane in front of the anode, and a cation-exchange membrane in front of the cathode. In this way, one electrode becomes cation selective, the other anion selective. Another option is to use intercalation materials based on sodium manganese oxide (NMO) or Prussian Blue analogues (PBA; e.g., nickelhexacyanoferrate).^[14] These materials are cation selective, thus can be used as the cathode. In typical cell designs with such selective electrodes, a cell is built with one anion selective, and one cation-selective electrode. Typically, we have a spacer channel between two electrodes, and during half of the cycle time, salt ions are adsorbed, and during the other half, salt ions are released. If membranes are used, an ion passes through a certain membrane twice, once during adsorption, and once during desorption.

In 2016, Smith and Dmello published their theoretical report that showed that a novel, and very different, CDI cell design is possible.^[15] In this design, both electrodes are purely cation selective, and one anion-exchange membrane is used, which is placed between two flow channels. In 2017, this cell design was experimentally validated by various authors using electrodes based on intercalation materials,^[14,16,17] or using porous carbon electrodes coated with a cation-selective resin.^[18] In this design, only anions pass through the membrane, and do so only once in a cycle, while at the same time cations are adsorbed in one electrode and simultaneously released in the other. Therefore, at a certain moment, channel 1 is desalinating and channel 2 is producing a concentrated stream; when the current direction

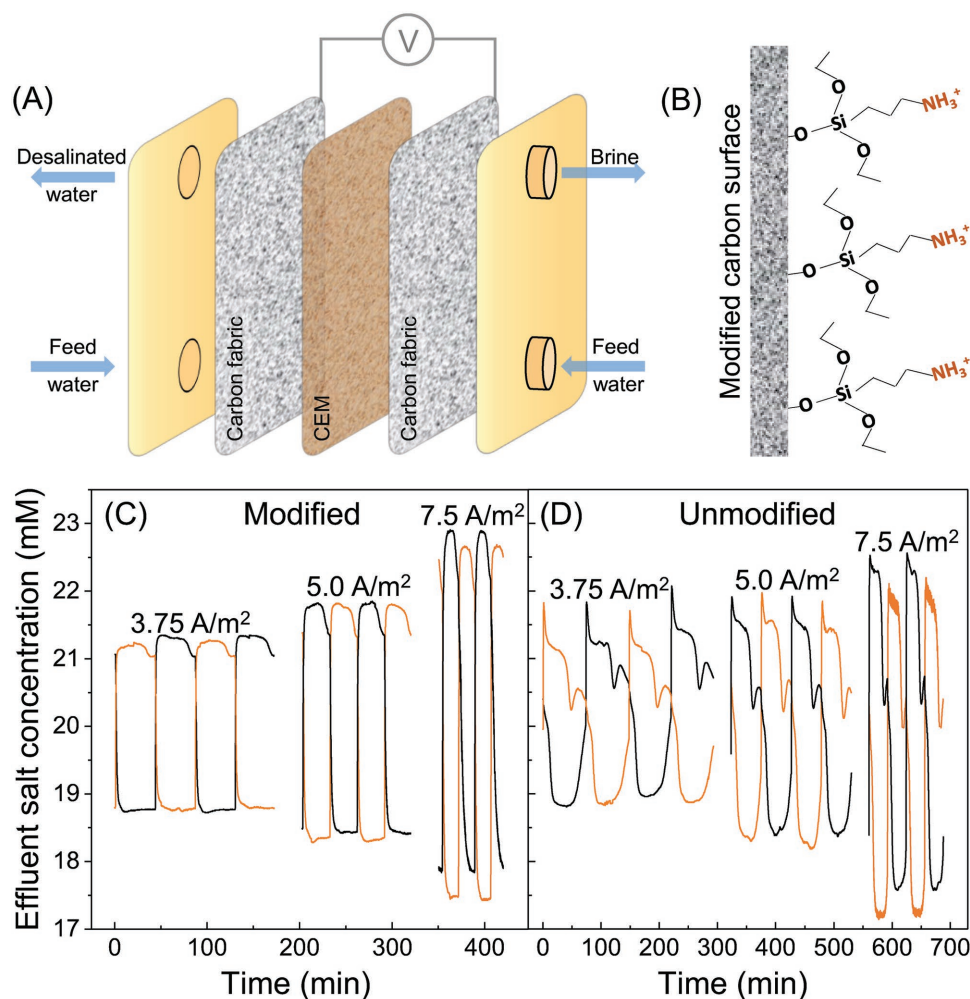


Figure 1. A) Schematic overview of desalination with anion-selective electrodes with a single cation-exchange membrane (CEM) and two identical activated carbon fabric electrodes, either both modified or both unmodified. In this cell, water flows through the porous electrodes.^[33] When current runs in one direction, one channel produces desalinated water (freshwater), while the other produces concentrated (brine). When a certain voltage is reached, the direction of the current is reversed until a lower endpoint for voltage is reached, and now freshwater is produced in the channel that previously was producing concentrate, and vice versa. B) Schematic view of modified carbon surface with silanes bearing terminal amines. C) Effluent salt concentration of both channels for desalination cycles with modified and D) unmodified activated carbon electrodes at a constant current of 3.75 A m⁻², 5.0 A m⁻², and 7.5 A m⁻² in 20 × 10⁻³ M NaCl. In Figure S1 in the Supporting Information, we show results for the cell voltage as function of time for the same desalination cycles.

is reversed, channel 1 now produces brine and channel 2 produces water of a lower salinity. Thus, at all moments in time, desalinated water is produced. In this design, intercalation electrodes based on NMO and PBA are used that are cation selective, but as we argue below, this concept is more general and can be extended to other electrode types.

In the present work we extend the approach of Dmello and Smith, which is based on cation-selective electrodes, and we show that also a reverse design is possible, using anion-selective electrodes and a cation-exchange membrane (Figure 1). We will show that desalination is possible with unmodified carbon electrodes (which have no significant natural preference for either anion- or cation-adsorption) and with carbon electrodes modified by silylation with an amino silane, which results in a positive chemical charge on the surface of the electrode material (neutral and acidic pH conditions) that makes the electrode anion selective. We use a silylation process

based on toluene condensation for the covalent attachment of (3-aminopropyl)triethoxysilane (APTES) groups onto activated carbon fabric, and we show that the synthesized electrodes are not microporous, but can be used to achieve excellent water desalination performance. In earlier work, anion-selective electrodes were synthesized by the attachment of ethylenediamine groups to activated carbon fabric (resulting in a BET-area, S_{BET} of $\approx 530 \text{ m}^2 \text{ g}^{-1}$) and to carbon xerogel ($S_{\text{BET}} \approx 100 \text{ m}^2 \text{ g}^{-1}$),^[6] and by the attachment of APTES to 3D graphene ($S_{\text{BET}} \approx 130 \text{ m}^2 \text{ g}^{-1}$).^[13]

Thus, we synthesize novel anion-selective electrodes, which we show are not microporous, and we highlight that, whereas literature focuses on the development of porous electrodes with high surface area to achieve a highly effective desalination process,^[5,19] the observations in the present work show that chemically charged electrodes with low microporosity can yield better results than unmodified electrodes with a high BET-area.

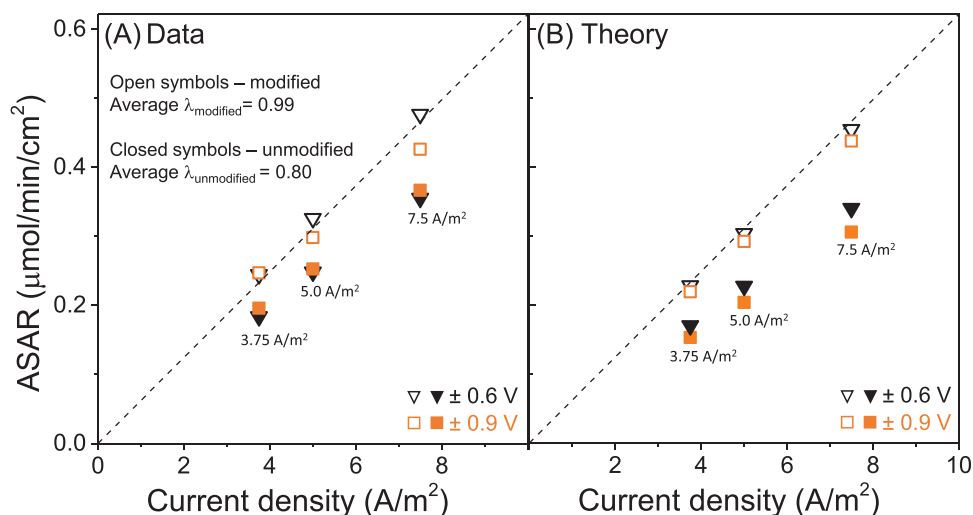


Figure 2. Average salt removal rate, ASAR, as function of current density for chemically unmodified and modified activated carbon electrodes and for different values of V_{\max} : A) experimental and B) theoretical results. Current efficiency, λ , of unity is represented by the dashed line. Theoretical results are calculated using the amphoteric Donnan model.

Desalination performance of the new cell design can be analyzed on the basis of the average salt adsorption rate (ASAR) and energy consumption (EC), which both depend on current density. The definition and measurement of these two metrics is explained in the Supporting Information. We report results of ASAR and EC in **Figures 2** and **3**, and we also plot the maximum theoretical current efficiency, $\lambda = 1$, which is calculated by dividing ASAR by current density (after converting current to the unit $\mu\text{mol min}^{-1} \text{cm}^{-2}$). For $\lambda = 1$, each electron transferred between the electrodes results in the adsorption of one cation and one anion when we have a monovalent salt. If λ has a value lower than unity, this must imply that undesired processes, such as co-ion desorption, also take place. We find, for unmodified electrodes, an average value (averaged over all experiments conducted with unmodified electrodes) of $\lambda \approx 0.80$

which is significantly below the theoretical maximum of $\lambda = 1$. For the modified electrodes we find a much higher value, close to the theoretical maximum, of $\lambda \approx 0.99$.

A theoretical model, which includes ion transport across the single ion-exchange membrane, and ion adsorption in the pair of porous electrodes, is used to describe the data, see Supporting Information for details. To describe ion adsorption, the amphoteric Donnan model is used, which describes ion adsorption in electrical double layers located inside carbon micropores combined with the effect of chemical surface charge.^[11,20,21] As shown in Figure 2, theory describes experimental data well, both for the modified and unmodified electrodes. In order to fit the theory to the data, we assume that the electrodes, also without modification, have a moderate concentration of positive chemical surface charge (see Table S1 in the Supporting

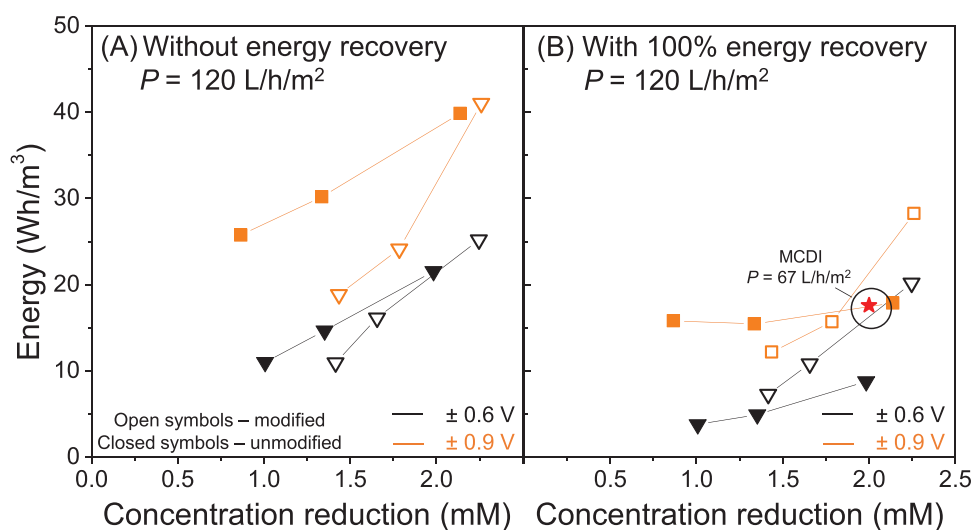


Figure 3. Energy consumption (EC) per m^3 of desalinated water produced of CDI with modified (open symbols) and unmodified electrodes (closed symbols): A) without energy recovery (ER) and B) with 100% ER. Values of EC for 100% ER are benchmarked against a standard MCDI system,^[22] operated with a salt concentration reduction of $\Delta c = 2 \times 10^{-3} \text{ M}$ and a lower water productivity of $P_{\text{MCDI}} = 67 \text{ L h}^{-1} \text{ m}^{-2}$.

Information). For the modified electrodes, this positive charge is significantly increased, in line with results of Boehm titration, which reveal that the concentration of basic groups on the surface of the modified electrodes, $\approx 0.91 \text{ mmol g}^{-1}$, is about two times larger than on the unmodified electrodes, $\approx 0.43 \text{ mmol g}^{-1}$ (experimental details are provided in the Supporting Information). As Figure S1 in the Supporting Information shows, the theory also describes full desalination cycles for both types of electrodes, which suggests our theory captures the main features of the new CDI design.

Figure 3 shows data for EC, both for modified and unmodified electrodes, with and without energy recovery (ER) during discharge. In Figure 3, we show that EC for desalination with modified electrodes is lower, and we show that for $V_{\text{max}} = 0.6 \text{ V}$, EC is lower than for $V_{\text{max}} = 0.9 \text{ V}$. Furthermore, we compare EC of our novel cell design with EC of a standard membrane capacitive deionization (MCDI) system.^[22] We find that EC of our design is significantly lower, especially with modified electrodes and for $V_{\text{max}} = 0.6 \text{ V}$. Compared to the standard MCDI system, we not only find lower EC, but also obtain a much higher water productivity, which is the flow rate of desalinated water per membrane area (see Supporting Information for details), $P = 120 \text{ L h}^{-1} \text{ m}^{-2}$, instead of $P = 67 \text{ L h}^{-1} \text{ m}^{-2}$.

Figure S2 in the Supporting Information shows the dynamics of charging and discharge, experimentally and theoretically. We find that the time dependence of the effluent concentration of both channels are well reproduced by the dynamic model (which includes the amphoteric Donnan approach for ion adsorption in carbon pores), both for the modified and unmodified electrodes. The theory reproduces that after switching from the charging to the discharge mode, the effluent salt concentration rapidly increases in the channel that starts to produce a concentrated stream, and slowly decreases in the channel that is desalinating.

The scanning electron microscopy (SEM) image (Figure S3A, Supporting Information) shows that the structure of the surface of the electrode did not change much after modification, and thus that the modification is uniform and thin. The SEM-energy-dispersive X-ray spectroscopy (EDS) elemental mapping (Figure S4, Supporting Information) of Si and C gives evidence for the uniformity of chemical modification with silane. The N_2 adsorption and desorption isotherms as function of relative pressure P/P_0 at 77 K are presented in Figure S3B in the Supporting Information and the pore volume distributions are presented in Figures S3B and S3C in the Supporting Information. The unmodified electrode shows the characteristics of microporous materials, exhibiting a Type I Langmuir monolayer isotherm (International Union of Pure and Applied Chemistry (IUPAC) classification). The unmodified electrode has a BET surface area of $1100 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of 0.55 mL g^{-1} . The surface area ($\approx 18 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($7.0 \text{ }\mu\text{L g}^{-1}$) of the modified electrode are significantly reduced as a consequence of surface functionalization, probably due to the blocking of micropores by the (3-aminopropyl)triethoxysilane, APTES, modification. This is the first time that a low-porosity carbon electrode has shown such excellent performance for desalination in CDI.

The attenuated spectra (Figure S3D, Supporting Information) of the modified electrode have peaks that were not observed for the unmodified electrodes. The peak at 665 cm^{-1}

is related to Si–O–C bending vibration, and at 1012 cm^{-1} to Si–O–C stretching vibration.^[23] The peak at 1070 cm^{-1} is due to the Si–O–Si stretching vibration.^[24,25] Thus, these peaks confirm the presence of silane on the carbon surface. Furthermore, possible polymerization of APTES on the carbon surface is confirmed, as the presence of Si–O–Si bonds can be inferred from the spectra. In addition, there is a broad peak at 1350 cm^{-1} that is convoluted with the peak at 1550 cm^{-1} , which is due to the C–N stretching vibration.^[24]

The X-ray powder diffraction (XRD) patterns (Figure S3E, Supporting Information) obtained for the modified and unmodified electrodes have the signature peaks of amorphous carbon (002) at 22.5° and graphitized carbon (101) at 44° , and thus we can conclude that both electrodes contain a significant amount of graphitized carbon.^[26] In addition, there is a broad peak around 10° in the spectrum of the modified electrode that could be due to the silane modification of the carbon.

The elemental composition of the modified electrode is given in Table S2 in the Supporting Information. The amount of N was determined by CHNS analysis, and the amounts of C, Si, and O were determined by EDS analysis. Furthermore, Figure S5 in the Supporting Information shows the results of cyclic voltammetry scans for the modified and unmodified electrodes.

In conclusion, we have demonstrated that a choice for anion-selective electrodes, in combination with a cation-selective membrane, leads to a functional cell design that continuously desalinates water. We have shown that theory describes the experimental data well, and we find that with 100% energy recovery, energy consumption of the new cell design is much lower than a standard MCDI system. Furthermore, we have shown that, after chemical modification, the porosity is reduced from 0.55 mL g^{-1} to $7.0 \text{ }\mu\text{L g}^{-1}$, and the BET-area of our electrodes is reduced from ≈ 1100 to $\approx 18 \text{ m}^2 \text{ g}^{-1}$, while the desalination performance of the electrodes is increased. Thus, we show for the first time that a low-porosity carbon electrode with additional surface charge can be a promising material for CDI.

Experimental Section

A cell design similar to that used in previous work was used,^[14,27] which is described in the Supporting Information. Two types of carbon electrodes were tested: i) unmodified activated carbon fabric electrodes (ACC 5092-15, Kynol, Germany); and ii) the same activated carbon fabric electrodes, but after chemical modification with silanes bearing a terminal amine group. In all experiments, a Neosepta CMX cation-exchange membrane (ASTOM Corp., Japan) was placed between the two electrodes.

Electrode Modification: The electrodes were chemically modified by a silanization reaction between silylating agent and hydroxyl groups on the carbon surface.^[28] In the present work, a non aqueous solvent was used to attach silane groups onto the carbon surface, similar to previously reported procedures for surface modification of carbon material and inorganic nanoparticles with silanes.^[28–31] To prepare the modified electrode, the electrode material (12 g) reacted with 150 mL of amino-silylating agent, APTES, (3-aminopropyl)triethoxysilane (99%, Sigma Aldrich, USA) in toluene (99.8%, anhydrous, Sigma Aldrich, USA) solution (30% v/v in toluene solution) in an airtight container, which was stirred at 120 rpm for 24 h to ensure maximum chemical modification of the carbon surface. The modified electrode was washed multiple times with ultrapure water and thereafter dried at room temperature.

Cell Assembly and Desalination Experiments: For the desalination experiments, either the unmodified or modified electrodes were used in a symmetric cell where the same type of electrode was used both as an anode and a cathode. A cation-exchange membrane (CEM) was placed between these two identical electrodes. Graphite sheets were used as current collectors to connect the electrodes with the external electrical circuit and a potentiostat (Ivium Technologies, The Netherlands). A salt solution was pumped through both electrodes; see Figure 1, by Stepdos 08 RC dosing pumps (KNF Neuberger) with a flow rate of 4 mL min⁻¹ per channel. The feed solution contained 20 × 10⁻³ M of NaCl. The conductivity of the effluent of both channels was measured with an interval time of 1 s. Constant current (CC) experiments^[20,32] were conducted by alternatingly applying a constant positive current until a pre-set upper cell voltage, $V_{\text{cell}} = V_{\text{max}}$, was reached, and thereafter applying the reversed current until the cell voltage reached the same pre-set value but with opposite sign, $V_{\text{cell}} = -V_{\text{max}}$. To analyze the desalination performance, the following metrics were used: average salt adsorption rate, ASAR; productivity, P ; average current efficiency, λ ; and energy consumption, EC, with and without considering the potential for energy recovery. These metrics are elaborated in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

anion-selective electrodes, capacitive deionization, water desalination

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