Capacitive Deionization Using Alternating Polarization: Effect of Surface Charge on Salt Removal

X. Gao,^a A. Omosebi,^a N. Holubowitch,^a J. Landon,^{a,*} and K. Liu,^{a,b,*}

a: Center for Applied Energy Research, University of Kentucky, Lexington, Kentucky 40511, USA

b: Department of Mechanical Engineering, University of Kentucky, Lexington, Kentucky 40506, USA

*: James.Landon@uky.edu and Kunlei.Liu@uky.edu

Abstract

Alternating polarization (AP) at $\pm 1.2/0$ V is performed on a capacitive deionization stack assembled with carbon xerogel (CX) electrodes. Long-term testing shows enhanced cycling stability without the formation of inversion peaks. AP also leads to an arch-shaped plot of salt adsorption capacity (SAC) versus cycling time, with the highest SAC of approximately 3 mg (NaCl) g⁻¹ (CX) during this long-term test. Characterization of both the freshly prepared and cycled electrodes depict that AP results in surface charge of all the electrodes being modified from positive to negative character. By leveraging balances of electronic, surface, and ionic charges in carbon micropores, it is found that a portion of the electronic charge contributes to the ionic charge for salt adsorption, and another portion is parasitically consumed to balance the surface charge during the charge reconciliation process. When the consumption of electronic charge for charge reconciliation becomes minimal, both the positive and negative surface charges are nearly equivalent on the CX electrode. Under such a condition, the highest SAC values can be achieved for AP testing.

Keywords

Capacitive deionization, alternating polarization, carbon xerogel, charge balance, Donnan model

1 Introduction

Capacitive deionization (CDI) employs porous carbon electrodes to desalinate various salt solutions, and desalination is achieved in a flow cell by regulating the applied voltage or current from an external power source.^{1,2} CDI has certain advantages over conventional methods such as reverse osmosis and distillation. For example, at low salinity, CDI theoretically offers a lower energy consumption in comparison to reverse osmosis,^{3,4} which is mainly accounted for by the fact that CDI removes ionized salts from water while membrane technology extracts water from the salt solution.⁵ Additionally, CDI has no pressure/heat requirement, no secondary contamination, and minimal operating and maintenance costs,⁶⁻⁸ thus reducing the environmental and economic impact of desalination.

Recent literature shows that besides carbon pore structure,⁹ knowledge of the carbon electrode's surface charge has become fundamentally important for interpreting salt removal behavior for CDI.¹⁰⁻¹³ For instance, by leveraging balancing of Na^+ or Cl^- in carbon micropores in the modified Donnan (mD) model for the electrical double layer,¹⁴ mobile ionic charges ($\sigma_{\text{ionic,Na}}$ or $\sigma_{\text{ionic,Cl}}$) in the electrode's micropores are balanced by both electronic charges (σ_e) in the electrode matrix and fixed chemical surface charges ($\sigma_{\text{chem,+}}$ or $\sigma_{\text{chem,-}}$) on the electrode surface, which is given by

$$\sigma_{\text{chem,+}} - \sigma_{\text{chem,-}} + \sigma_{\text{ionic,Na}} = \sigma_{\text{elec}} \quad (1a)$$

$$\sigma_{\text{chem,-}} - \sigma_{\text{chem,+}} + \sigma_{\text{ionic,Cl}} = -\sigma_{\text{elec}} \quad (1b)$$

where Eq. (1a) and (1b) are associated with the cathode (negative electrode) and anode (positive electrode), respectively. Since the cathode and anode in a CDI cell are serially connected, the σ_{elec} at the cathode and anode are assumed equal. As a result, in order to maximize NaCl

adsorption, an enhanced CDI (e-CDI) effect can be achieved by sufficiently increasing the ratios of $(\sigma_{\text{chem},-}/\sigma_{\text{chem},+})$ and $(\sigma_{\text{chem},+}/\sigma_{\text{chem},-})$ at the cathode and anode, respectively.^{10,14} In contrast, an inverted CDI (i-CDI) process will be established if the ratios $(\sigma_{\text{chem},-}/\sigma_{\text{chem},+})$ and $(\sigma_{\text{chem},+}/\sigma_{\text{chem},-})$ are decreased sufficiently at the cathode and anode, respectively.^{15,16}

In the contemporary CDI literature, long-term CDI testing using conventional polarization, e.g., 1.2 V charging and 0 V discharging, often results in diminished salt removal with the formation of inversion peaks at the beginning of each charging step.^{12,17-21} To improve the long-term stability, modifying/treating carbon electrodes, adding ion-exchange membranes, and reducing applied voltages have been recently investigated.^{18,21-23} In addition to those studies, it was also discovered that using alternating polarization (AP), i.e., reversing electrode polarity every charging step, can effectively minimize inversion peaks and enhance cycling stability.²⁴ Cohen et al. interpreted this stabilization pathway based upon a potential distribution diagram combined with the positively shifted potential of zero charge (E_{PZC}) due to carbon oxidation,²⁵ consequently detailing the impact of the E_{PZC} on salt removal behavior.²⁴ In addition, recent results suggest that oxygen reduction at the cathode may significantly contribute to carbon oxidation,^{26,27} where further work should be performed.

In this study, AP is repeated for a CDI stack configured with carbon xerogel (CX) electrodes, and additional interpretations are provided. Characterizations of both the freshly prepared and cycled CX electrodes are compared. We present the CDI behavior resulting from AP, demonstrate the effect of surface charge on salt removal based upon charge balancing such as in Eq. (1), and estimate the changes in the surface charge combined with the mD model. Finally, we believe that besides the E_{PZC} shift with respect to its potential distribution, knowledge of carbon surface charge provides the capability of interpreting CDI behavior.

2 Experimental

2.1 Electrode Preparation and Characterization

We have prepared and characterized carbon xerogel (CX) electrodes for CDI applications.²⁸ To produce CX electrodes, we first prepared a solution by adding 20.0 g resorcinol ($\text{C}_6\text{H}_6\text{O}_2$, Sigma-Aldrich), 29.5 g formaldehyde (CH_2O , 37 wt% in methanol, Sigma-Aldrich), 6.3 g of 0.02 M Na_2CO_3 solution (Sigma-Aldrich), and 6.0 g of deionized H_2O in a sealed glass bottle. After stirring for 0.5 hours, the solution was used to infiltrate a conductive carbon cloth (untreated, Fuel Cell Earth). The wetted cloth was fixed between two glass slides, sealed using aluminum foil overnight, and heated at 85°C for 24 hours in air. A solvent-exchange process for the dried cloth was performed as follows: soaking in deionized water for 2 hours, soaking in acetone for 2 hours, and air-drying for 2 hours. Finally, the dried sheet was carbonized in a quartz tube in a computer-controlled furnace (Lindberg M, Thermo Scientific), where the temperature was held at 1050°C for 2 hours using a ramp rate of 5°C min⁻¹ for both heating and cooling from room temperature under N_2 atmosphere. The resulting electrode had a density of ~0.48 g cm⁻³, a conductivity of ~55 S cm⁻¹, and a thickness of ~0.046 cm. To reproduce our cycling results, a similar route without using Na_2CO_3 solution was used to prepare another CX electrode with a smaller total pore volume.

To estimate the E_{PZC} of the CX electrode, cyclic voltammetry was carried out using a potentiostat (Reference 600, Gamry) attached to a three-electrode cell containing 0.36 cm² of sample working electrode, a saturated calomel reference electrode (SCE), and a titanium mesh (Dexmet Corporation) counter electrode with a geometric surface area of approximately 18 cm². To examine surface species, Fourier-transform infrared (FTIR) spectra were recorded by co-adding 256 scans at 4 cm⁻¹ resolution using approximately 0.07 g of sample at a ratio of 0.3 wt%

(sample vs KBr) in a FTIR spectrometer (6700, Nicolet). Surface morphology and elemental analysis were carried out with a scanning electron microscope (SEM) (S-4800, Hitachi) attached with energy-dispersive X-ray spectroscopy (Oxford Instruments). To study pore structure, approximately 0.15 g of sample was degassed at 160°C for at least 4 hours, and N₂ adsorption/desorption isotherms were constructed with a surface area and porosity analyzer (ASAP2020, Micromeritics). Since the non-localized density functional theory (NLDFT) and its fitting mechanism comprehensively accommodate various pore geometries,²⁹ the NLDFT was selected to calculate cumulative pore volume and pore size distribution of the CX electrodes before and after AP cycling. Conventional characterization results such as SEM micrographs, FTIR spectra, and N₂ adsorption/desorption isotherms are provided in Fig. S1.

Figure 1 (a) Diagram of flow system for CDI testing. This flow system was also used to identify the initial surface charge of the dry electrodes by opening and closing valves 1 and 2. (b) Demonstration of voltage sequence for alternating polarization.

2.2 CDI Testing Using Alternating Polarization

A flow-through CDI stack, an in-line conductivity sensor (Alpha Cond 500, Thermo Scientific), an in-line pH sensor (Alpha pH 500, Thermo Scientific), a polyethylene tank, and a peristaltic pump (Masterflex L/S, Cole-Parmer) were assembled, and a diagram of this setup is shown in Fig. 1(a). The CDI stack was composed of 16 pairs of CX electrodes separated by 0.15 cm thick silicon rubber spacers. The geometric area of each CX electrode directly exposed to NaCl solution was $3.2 \times 6.5 \text{ cm}^2$. Both the conductivity and pH sensors were calibrated and

maintained using procedures recommended by the manufacturer. Two valves were added in the solution loop to track changes in the effluent pH and concentration before AP testing, thus identifying the initial surface charge of the freshly prepared CX electrodes once the solution was introduced to the dry electrodes.

CDI testing (valve 1 closed, valve 2 open) was carried out using AP at $\pm 1.2/0$ V, meaning all of the electrodes served alternatively as anodes and cathodes during charging for salt adsorption, followed by directly shorting the electrical circuit during discharging for salt desorption (Fig. 1(b)). About 31 L of 4.3 mM deaerated NaCl solution was continuously circulated through the flow system at about 80 mL min^{-1} . The total salt adsorption capacity (SAC) at equilibrium for each cycle was calculated by multiplying the volumetric flow rate (Φ) by the integration of the concentration (c) with time (t) using

$$\text{SAC} = (M\Phi/m) \int (c(t) - c_{\text{in}}) dt \quad (2)$$

where M is the molecular weight of NaCl, m is the total mass of the dry electrodes used in the CDI stack (approximately 16 g), and c_{in} is the influent salt concentration. The charge passed (Q) for the charging (or salt adsorption) step was calculated by integration of the current curves with time. Finally, the charge efficiency, Λ , is calculated using

$$\Lambda = (\text{SAC } F)/(MQ) \quad (3)$$

where F is the Faraday's constant ($96,485 \text{ C mol}^{-1}$).

2.3 Characterization of Cycled Electrodes

After AP testing, the first pair (at feed inlet) of the cycled CX electrodes in the stack was resized for post-characterization. To study the pore structure, the cycled electrode sample was first dried in air at room temperature and then degassed to obtain the N₂ adsorption/desorption isotherms. To find the E_{PZC} , a cycled electrode was configured into a three-electrode setup, and deaerated 4.3 mM NaCl solution was used. Details of these characterization methods have been reviewed in section 2.1.

Figure 2 Selected profiles of (a) salt concentration, (b) current density, and (c) effluent pH resulting from alternating polarization at $\pm 1.2/0$ V. This experiment was carried out using a CDI stack with 16 pairs of freshly prepared carbon xerogel electrodes in 31 L of 4.3 mM deaerated NaCl solution at 80 mL min⁻¹. Each charging and discharging step lasted for duration of 4000 s.

Figure 3 Plots of (a) salt adsorption capacity, (b) charge passed during charging, and (c) charge efficiency using Eq. (2) and (3) according to Fig. 2.

3 Results and Discussion

3.1 Effect of Alternating Polarization on Salt Removal, Charge Passed, and pH

AP at $\pm 1.2/0$ V was used to study salt removal with a CDI stack. Fig. 2(a) shows selected profiles of effluent salt concentration. During the first 10 hours, typical profiles for salt concentration are achieved in which salt adsorption is reflected by a decrease in the salt concentration during the charging step while salt desorption is observed by an increase in the salt concentration during the discharging step. As the cycles are continuously repeated (100-110

hours), the profiles become more pronounced with both expanded adsorption valleys and desorption peaks. At the end of testing (210-220 hours), the span between the peaks and valleys decreases, showing that using $\pm 1.2/0$ V cannot maintain the improved salt removal, however inversion peaks (desorption peaks at the onset of charging) never emerge.

Performance evaluations were performed using Eq. (2) and (3) according to Fig. 2(a) and (b). In Fig. 3(a), an arch-shaped plot of the SAC versus cycling time is established with the highest SAC of $\sim 3 \text{ mg g}^{-1}$ at ~ 100 hours, which differs substantially from the continuously diminished SAC when the same CX electrodes were tested at $1.2/0$ V under similar experimental conditions in ref. (15,19). Thus, we support the conclusion drawn in ref. (24) that using AP can effectively mitigate inversion peaks and enhance cycling stability. Moreover, the SAC reported in the present study is relatively low; however, it can be improved by increasing the microporosity of the carbon electrode.^{4,9} Since a nearly stable charge of $\sim 12.5 \text{ C g}^{-1}$ was observed in Fig. 3(b) during each charging step, another arch-shaped plot of charge efficiency versus cycling time resulted in Fig. 3(c). Such low charge efficiency may be attributed to the CDI stack design, parasitic reactions, operational methods, reduction in net charge passed, and/or location of the E_{PZCS} with respect to the potential distribution.^{26,30-35} In the supplementary information section 2.3, a possible mechanism regarding carbon oxidation is proposed to discuss the resulting charge efficiency for our case.

In addition to salt concentration and charge passed, Fig. 2(c) depicts the effluent pH during AP testing. It is found that, due to carbon oxidation at the anode,^{18,19} the overall trend of the effluent pH drops over the course of testing, which results in increased surface acidity of the CX electrodes and thus yields substantial negative surface charge on the CX electrodes. Furthermore, by looking at the segmented pH at different operational stages in Fig. 2(c), during

the first 10 hours, the effluent pH increases during the charging step. In contrast, between 210 and 220 hours, the effluent pH decreases during the charging step. Besides the side reactions often discussed in the contemporary CDI literature,^{26,31} these pH responses may also be related to fixed surface charges, naturally attracting not only $\text{Na}^+ / \text{Cl}^-$ but also some H^+ / OH^- to balance charge at the electrode surface.³⁶ For example, during the first 10 hours, we propose that if electronic charge is used to repel naturally adsorbed OH^- at the positively charged sites, the effluent pH will increase. Similarly, due to the formation of the negatively charged sites with electrode oxidation, electronic charge will be used to repulse naturally adsorbed H^+ , consequently causing a decreased effluent pH. We believe that this discussion is consistent with the following characterization regarding both the E_{PZC} shifting for the cycled electrodes (Fig. 4) and increased pH response before AP testing (Fig. 5).

A similar CX electrode with a smaller total pore volume was also tested under similar experimental conditions. As shown in Fig. S2, using AP shows similar profiles of salt removal in comparison to those observed in Fig. 2, in which the magnitude between the adsorption valley and desorption peak initially increases and then decreases during long-term operation, developing arch-shaped plots for the SAC and charge efficiency as a function of cycling time. To the best of our knowledge, arch-shaped performance trends resulting from AP have not been reported and detailed in the contemporary CDI literature. In the following section, we use additional characterizations to interpret the formation of this peak in SAC based upon the concept of balancing electronic, mobile ionic, and fixed chemical surface charges.

Figure 4 Changes in physical and chemical properties of carbon xerogel electrodes before and after alternating polarization. Cumulative pore volume and pore size distribution as a function

of pore size for (a) freshly prepared and (b) cycled electrodes. Cyclic voltammograms at 0.25 mV s^{-1} in 4.3 mM deaerated NaCl solution for (c) freshly prepared and (d) cycled electrodes. Blue bars denote the E_{PZC} location as a range of potentials covering capacitance minima in the anodic and cathodic scan directions. The starting cathode and anode in (b) and (d) indicate the polarization condition for the first charging cycle. Adsorption isotherms for freshly prepared and cycled electrodes can be found in Fig. S1 and S4, respectively.

3.2 Electrode Characterization before and after Alternating Polarization

In Fig. 4(a), the cumulative pore volume first exhibits an increase at $0.4 - 1.5 \text{ nm}$ and second an increase at $4 - 40 \text{ nm}$, resulting in a micropore volume of 0.08 mL g^{-1} and a total pore volume of 0.55 mL g^{-1} . In contrast, for both of the cycled CX samples, Fig. 4(b) depicts reduced values for both the micropore and total pore volumes, although the featured two-step increase in the cumulative pore volume is retained. We consider that using the reduced porosities to solely interpret the arch-shaped plots in Fig. 2 cannot be argued. This is because the cycled samples offer more open voltammograms (Fig. 4(c) and (d)), suggesting that more pore volume is accessible for ion adsorption, and CDI performance should not be diminished.

Previous work suggests that knowledge of the E_{PZC} has been fundamentally important to investigating various CDI behavior.^{17,25,37,38} To estimate the location of the E_{PZC} in these studies, cyclic voltammetry was performed at 0.25 mV s^{-1} in 4.3 mM deaerated NaCl solution. In Fig. 4(c), the voltammogram measured before AP illustrates that the freshly prepared CX electrode has a distinct V-shaped ion-swapping region containing the estimated E_{PZC} at -0.1 to 0.0 V vs. SCE. By comparison, the voltammograms in Fig. 4(d) display positively shifted ion-swapping regions at 0.2 to 0.5 V vs. SCE for both of the cycled CX electrodes. This E_{PZC} shift is

accounted for by the formation of negative surface charges via deprotonation of oxidized surface species, resulting in the cycled electrode surface and bulk solution being acidic,^{18,31,33,39,40} which is consistent with the overall descending pH response in Fig. 2. Compared to cycled electrodes, we deduce that the surface of the freshly prepared CX electrode should be naturally less acidic, thus possessing less negative surface charge. This point can be verified by examining changes in the effluent pH before AP commenced.

Figure 5 Changes in the effluent pH and NaCl concentration before CDI testing by switching on and off valves (V1 and V2) in the flow system depicted in Fig. 1(a). This test was performed using the same CDI stack in 31 L of 4.3 mM deaerated NaCl solution at 80 mL min⁻¹.

3.3 Effluent pH before Alternating Polarization

By leveraging knowledge of the point of zero charge (pH_{PZC}) for carbon surface charge,^{16,41,42} the effluent pH was characterized by opening and closing valves (V1 and V2) in the flow system (Fig. 1) to investigate the surface charge character of the freshly prepared CX electrodes. The plot in Fig. 5 is divided into regions A, B, and C to facilitate our description and discussion. In region A, by opening V1 only, the effluent pH of deionized water is ~6, and the slight acidity is typically attributed to dissolved ambient carbon dioxide leading to the formation of carbonic acid.⁴³ In region B, addition of 1 M NaCl into the solution container results in negligible changes to the effluent pH bypassing the CDI stack. When flow is switched through the cell in region C, the effluent pH sharply increases and levels off temporarily at ~9.0 in the present test. (In Fig. S5, the effluent pH slowly decreases when the circulation time was extended before

polarizing the CX electrodes.) It should be noted that during bypass there was no solution in the CDI stack, and all of the electrodes were dry.

According to the carbon literature, a surface with aromatic character (C_π) in carbon's basal planes may behave as a Lewis base capable of complexing protons to its π structure and thus increasing the pH of an interfacial solution.⁴⁴ A reaction with water at equilibrium can be established via $C_\pi + 2H_2O = C_\pi H_3O^+ + OH^-$.^{44,45} As a consequence, the surface of freshly prepared or unpolarized CX electrodes in deionized water is predominantly composed of positively charged surface sites with nearby, charge-balancing OH^- . Since an increase in the effluent pH is clearly depicted in region C in Fig. 5, the produced OH^- must leave from the electrode surface to the bulk solution, likely displacing Cl^- in solution. (This point has been discussed and verified in the supplementary information section 2.1.) This type of anion exchange property is found when a carbon surface is treated at $>950^\circ C$ under vacuum or an inert gas atmosphere,⁴⁶ and this reported temperature is comparable to the carbonization temperature of $1050^\circ C$ used for our CX preparation. In addition, constant effluent concentration in region C indicates that no residual salt remained in the CX electrode after carbonization, which is consistent with the speciation characterization in both the FTIR and EDX spectra (Fig. S1). In summary, compared to the cycled CX electrode, the surface of freshly prepared CX electrodes has more positively charged sites.

3.4 Discussion of Charge Balances

Based upon the results discussed above, changes in surface charge during AP testing can be summarized in the following order. (1) At the beginning of AP testing, all of the CX electrodes primarily possess positive surface charge. (2) Due to carbon oxidation during anodic

polarization, surface charge of the electrodes is modified from positive to negative character. (3) As cycling continues, all of the electrodes continue to oxidize, which eventually results in negative surface charge dominating the electrode surface.

Following from the summary above, Fig. 6-8 depicts three featured scenarios to envision the effect of chemically charged sites on NaCl adsorption, including pristine electrodes with positive surface charge (Fig. 6), partially oxidized electrodes with equal positive and negative surface charge (Fig. 7), and oxidized electrodes with negative surface charge (Fig. 8). In all of the figures, NaCl adsorption is also deconvoluted into three phases based upon charge balances, including (a) equilibrium at short-circuit, i.e., surface charge is only balanced by ionic charge, (b) charge reconciliation, i.e., electronic charge is balanced by surface and ionic charges, and (c) effective salt adsorption, i.e., additional electronic charge is only balanced by ionic charge.

To simplify our illustration for readers, we assume that a total of 8 electronic charges (σ_{elec}) are balanced by fixed positive/negative surface charges ($\sigma_{\text{chem},+}/\sigma_{\text{chem},-}$) and/or ionic charges of $\text{Na}^+/\text{Cl}^-/\text{H}^+/\text{OH}^-$ ($\sigma_{\text{ionic,Na}}/\sigma_{\text{ionic,Cl}}/\sigma_{\text{ionic,H}}/\sigma_{\text{ionic,OH}}$) without considering Faradaic reactions. Due to the low contribution of pH to conductivity on charge balancing in this study, we assume that the ionic charges are only $\sigma_{\text{ionic,Na}}$ and $\sigma_{\text{ionic,Cl}}$. However, as discussed earlier, we highlight our concerns regarding pH responses according to fixed positive and negative surface charges (See discussion of the effluent pH response in Fig. 2).

Figure 6 Effect of positively charged surface sites on salt adsorption at the beginning of alternating polarization. (a)-(c) Three phases of charge balance resulting in NaCl adsorption. For simplicity, we envision that 8 electronic charges are balanced by ionic and/or fixed

chemical surface charges without considering Faradaic reactions. Signs of + and – in the circular holes denote fixed positive and negative surface charges, respectively. The large black and small red dots represent Cl^- and Na^+ , respectively, from the NaCl solution. The squares represent uncharged spaces (or pores). This pictorial representation is leveraged from the amphoteric Donnan model in ref. (⁴⁷).

After placing a pair of CX electrodes in NaCl solution, Fig. 6(a) assumes that a total of $4 \sigma_{\text{chem},+}$ are produced on each electrode, thus requiring $4 \sigma_{\text{ionic,Cl}}$ to maintain electroneutrality at short-circuit. At the beginning of the charging step, Fig. 6(b) depicts that $4 \sigma_{\text{elec}}$ are injected into the cathode to balance the fixed positive surface charges by repelling $4 \sigma_{\text{ionic,Cl}}$ into solution. Consequently, $4 \sigma_{\text{ionic,Cl}}$ from solution are stored in the available pores at the anode. We consider that this Cl^- transfer alone cannot contribute to the bulk conductivity measured by a conductivity probe. After charge reconciliation, Fig. 6(c) displays salt adsorption by using the remaining $4 \sigma_{\text{elec}}$ to attract $4 \sigma_{\text{ionic,Na}}$ in the available pores at the cathode, which is compensated by adsorbing 4 additional $\sigma_{\text{ionic,Cl}}$ at the anode. During the actual CDI experiment, this net salt adsorption process is seen as one step, due to the constant voltage charging employed here. Time-dependent adsorption effects may be more easily seen if constant current charging (or stepped charging potentials) were used in a future study. Overall, in this scenario, we see that 50% electronic charge is lost due to reconciling the surface charge at the cathode, and another 50% contributes to the net adsorption of NaCl salt.

Figure 7 Effect of equal positively and negatively charged surface sites on salt adsorption during alternating polarization. Additional description can be found in Fig. 6.

During AP testing, Fig. 7(a) exhibits that each electrode possesses $2 \sigma_{\text{chem},+}$ and $2 \sigma_{\text{chem},-}$, imbuing it with amphoteric character,⁴⁷ and these surface charges attract $2 \sigma_{\text{ionic,Cl}}$ and $2 \sigma_{\text{ionic,Na}}$, respectively, to maintain electroneutrality at short-circuit. Unlike in Fig. 6(a) where solely Cl^- is transferred during charge reconciliation, Fig. 7(b) demonstrates a charge-balanced configuration by using $2 \sigma_{\text{elec}}$ to repulse both $2 \sigma_{\text{ionic,Cl}}$ from the cathode and $2 \sigma_{\text{ionic,Na}}$ from the anode into the solution, resulting in net salt desorption similar to the inverted CDI process. While this inverted response is depicted here, this characteristic is not seen by the conductivity probe in this experiment due to the use of constant voltage charging (as opposed to constant current). Therefore, as shown in Fig. 7(c), $6 \sigma_{\text{elec}}$ remains for adsorption related events, 2 more than that in Fig. 6(c) and 8(c). In summary, this scenario demonstrates that 75% electronic charge can be used to adsorb NaCl salt, leading to the highest SAC during AP testing.

Figure 8 Effect of negatively charged surface sites on salt adsorption at the end of alternating polarization. Additional description can be found in Fig. 6.

As AP is repetitively carried out, as shown in Fig. 8(a), each electrode eventually possesses fixed negative surface charge, and its surface configuration is opposite to Fig. 6(a). Under such a scenario, charge balance can be discussed oppositely to that regarding Fig. 6, and similarly only 50% electronic charge is used to adsorb NaCl salt, which has a lower SAC

compared to the surface charge character in Fig. 7. In addition, it should be mentioned that all of the percentages of electronic charge utilization are much higher compared to the measured experimental values in Fig. 3(c). This discrepancy may suggest that utilization of electronic charge contributes to not only ion movement but also other factors, e.g., the CDI stack design, parasitic reactions, operational methods, reduction in net charge passed, and/or location of the E_{PZCS} with respect to the potential distribution.^{26,30-35}

Figure 9 Estimated changes in net surface charge during alternating polarization according to both the salt adsorption capacity in Fig. 3(a) and modified Donnan model.¹⁴ In this estimation, we assumed an influent NaCl concentration $c_{inf} = 4.3$ mM, Stern capacitance $C_S = 270$ F mL⁻¹, thermal voltage $V_T = 25.6$ mV, and micropore volume $v_{mic} = 0.08$ mL g⁻¹.

By counting the number of charges for each scenario featured in Fig. 6-8, we clearly demonstrate that when positively and negatively charged surface sites are equally formed on the CX electrode during AP cycling, electronic charge can more efficiently contribute to salt adsorption, leading to the highest SAC value during AP testing. Otherwise, charge reconciliation consumes electronic charge, which results in not only diminished SACs but also unequal potential distributions (In Fig. S3, we also provide the measured potential distributions together with the estimated E_{PZCS}). Following from this understanding, combined with the mD model, a further analysis is presented to calculate the concentration of net surface charge according to the salt adsorption capacities presented in Fig. 3(a).

The calculation procedure is as follows: (1) we first averaged every 5 points of the SAC in Fig. 3(a); (2) since the highest SAC corresponds to a surface charge condition of ($\sigma_{\text{chem},+} = \sigma_{\text{chem},-}$), σ_{elec} was determined by adjusting the Stern capacitance combined with the measured physical parameters such as $v_{\text{mic}} = 0.08 \text{ mL g}^{-1}$, and the resulting σ_{elec} is assumed to be a fixed value for the following calculation; (3) by fitting the calculated SAC (from the mD model) and the averaged SAC (from Fig. 3(a)), each corresponding ionic charge is yielded; and (4) the net surface charge can be calculated via Eq. (1). The calculated net surface charge (red circles) are presented in Fig. 9. It can be seen that, for the entire AP test, the net surface charge continuously decreases from 0.45 to -0.27 M. The equivalent surface charge region ($\sigma_{\text{chem},+} = \sigma_{\text{chem},-}$) corresponds to the highest SAC region at 80-125 hours. In the other regions (<80 and >125 hours), we consider that the net surface charge must be overcome by parasitic energy input before salt adsorption and net desalination can occur. Finally, we estimate that the initial surface charge of the CX electrode is approximately 0.45 M, as we have verified that the surface of the freshly prepared CX electrode is predominantly composed of positively charged sites (Fig. 5).

4. Conclusions

In this study, AP of $\pm 1.2/0 \text{ V}$ was used to operate a CDI stack configured with CX electrodes. This operational method can effectively suppress the inversion peaks that are often observed in conventional prolonged operation at $1.2/0 \text{ V}$, thereby extending the stability of salt removal. Most interestingly, this operational method shows for the first time arch-shaped plots of the SAC and charge efficiency versus cycling time, depicting the highest SAC values in the middle of a 200+ hour test. Through both the effluent pH and E_{PZC} electrode characterizations for the

electrodes, we found that surface charge of the CX electrodes was gradually modified from positive to negative value, which was attributed to inevitable carbon oxidation when each electrode alternately became the anode. By analyzing the charge balance for a pair of electrodes containing electronic, mobile ionic, and fixed chemical surface charges, it is found that when positively and negatively charged surface sites are equally formed on the CX electrode during AP cycling, electronic charge contributes more efficiently to salt adsorption, resulting in the highest SAC value. Otherwise, a portion of the electronic charge is parasitically spent on reconciling the surface charge condition. Combined with the modified Donnan model, a further study provides estimated net surface charges during AP operation. Finally, we note that to achieve higher performance of salt removal in a CDI cell, surface charge on carbon electrodes needs to be managed to minimize the loss of electronic charge due to reconciling surface conditions.

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e^- Electronic charge

● Anion, e.g., Cl^-

● Cation, e.g., Na^+

+ Positive surface charge

- Negative surface charge

Graphic Abstract

Using alternating polarization
with carbon xerogel electrodes

Resulting SACs due to
changes in surface charge