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# Analysis of capacitive and electrodialytic contributions to water desalination by flow-electrode CDI

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#### A R T I C L E I N F O

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## ABSTRACT

While flow-electrode capacitive deionization (FCDI) is a potential alternative to brackish and/or sea water desalination, there is limited understanding of both the fate of ions following migration across the ion exchange membranes and the mechanisms responsible for ion separation. In this study, we investigate the desalting performance of an FCDI system operated over a range of conditions. Results show that although ion transport as a result of electrodialysis is inevitable in FCDI (and is principally responsible for pH excursion in the flow electrode), the use of high carbon content ensures that a high proportion of the charge and counterions are retained in the electrical double layers of the flowing carbon particles, even at high charging voltages (*e.g.*, 2.0 V) during the deionization process. Estimation of the portions of so-dium and chloride ions adsorbed in the flow electrode after migration through the membranes suggests that the ongoing capacitive adsorption exhibits asymmetric behavior with the anodic particles demonstrating better affinity for Cl<sup>-</sup> (than the cathodic particles for Na<sup>+</sup>) during electrosorption. These findings provide an explanation for the change in electrode properties that are observed under imperfect adsorption scenarios and provide insight into aspects of the design and operation of flow electrode pairs that is critical to achieving effective desalination by FCDI.

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### 1. Introduction

Global agricultural production is undergoing huge challenges as a result of both rapid population growth and regional water shortages (Qureshi et al., 2013; Tilman et al., 2002); for example, significant declines in the irrigated area in the Murray-Darling Basin in Australia have occurred over the last decade (ABS, 2008, 2013) with this change associated with climate change-related diversion of winds that usually bring rain to Southern Australia closer to Antarctica (Abram et al., 2014). As a consequence, dryland communities are finding it necessary to draw on alternative sources of water with particular interest in utilizing brackish (*i.e.*, moderate salt content) waters provided cost effective methods of salt removal can be found (Anderson et al., 2010). Of the salt removal methods

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available, there is particular interest in the use of flow-electrode capacitive deionization (FCDI), one of the variants of the increasingly popular method of capacitive deionization (Jeon et al. 2013, 2014: Ma et al., 2016: Suss et al., 2015: Zhang et al., 2018a). Compared to conventional technologies such as reverse osmosis (RO) that extracts the majority phase (*i.e.*, the water) from the very dilute brackish water during deionization, FCDI is based on the formation of electrical double layers (EDLs) in charged suspensions of electrodes enabling capacitive energy storage with the minority constituents (i.e., ions) immobilized and selectively extracted from the saline water (Nativ et al., 2017; Porada et al., 2013a; Tang et al., 2015). FCDI technology has distinctive benefits for brackish water desalination including excellent salt removal capacity, continuous desalting operation with simultaneous regeneration of the electrodes and, if designed appropriately, harvesting of valuable products from the waste stream (Jeon et al., 2013; Linnartz et al., 2017; Rommerskirchen et al., 2015; Suss et al., 2015; Yang et al., 2016; Zhang et al., 2018b).







A variety of studies have been conducted recently aimed at improving the charge/ion transfer rates in FCDI. For example, it has been reported that higher mass densities in flow electrodes can be achieved with the use of either oxidized carbon materials or fluidized beds, leading to more effective electronic charge percolation (Doornbusch et al., 2016; Hatzell et al., 2015). Alternatively, the relatively poor electrical conductivity of the flow electrodes compared to the solid electrodes can be improved through the use of redox-active mediators and/or high salt concentration aqueous electrolytes (Ma et al., 2016; Yang et al., 2016). While it may be deduced that an increase in the rate of charge transfer in FCDI will facilitate the desalting performance, the mechanisms underlying the correlation of ion migration (and removal) with charge transfer in flow electrodes are still unclear.

According to the modified Donnan (mD-) theory, non-Faradaic interaction of ions with the charged flow electrodes is expected in FCDI-mediated brackish water desalination (Jeon et al., 2013) with ion transport from macropores to micropores sufficiently fast for this process to be close to equilibrium (Porada et al., 2013b). However, there is no avoiding the fact that the majority constituent of flow electrodes are the electrolytes with recent evidence indicating that a significant proportion of the ions removed in FCDI end up in the solution phase of the electrode chambers (i.e. as a component of the electrolytes) with this process of ion removal essentially identical to that of electrodialysis (Hand and Cusick, 2017; Nativ et al., 2017). Provided that these contributions dominate ion migration in FCDI, the electrode attraction (and adsorption) of cations and anions would be less likely to occur with the surplus charge on the electrode surface likely inducing interfacial redox reactions and the dissociation of water molecules (and production of OH<sup>-</sup> and H<sup>+</sup>) to achieve charge neutralization in the solution phase (Zhang et al., 2018a). Substantial change in pH of the electrode slurries would be expected to occur as a result of these Faradaic processes with change in pH recognized to potentially influence the adsorption capacity of the active materials (Nativ et al., 2017; Wang et al., 2016). Given the potential role of electrodialytic contributions to water desalination, the voltages applied for FCDI should be typically constrained within the non-Faradaic window (i.e., <1.23 V). However, consistent with the results from a very recent publication in which carbon black was used to facilitate charge transfer in the carbon suspensions (Liang et al., 2017), our findings in this study show that an FCDI system with a carbon loading of 10 wt% could be operated at relatively high charging voltages (i.e., 1.6-2.0 V) with the charge efficiency sustained at > 90%. As a result, a comprehensive understanding of the fundamentals underlying these contradictory observations is considered vital both to optimising the operating conditions of FCDI systems and to development of innovative flow electrode configurations and materials well suited to high-concentration brine desalination.

In this study, an FCDI system was constructed with the use of composite current collectors that were made of graphite paper and acrylic sheets. Influence of different carbon mass loadings and charging voltages on the desalting performance was investigated with consideration given to the fate of ions after passing through the ion exchange membranes. The key questions addressed in the present work include: (i) how does the desalting performance of the FCDI system change as a function of both the carbon content in the flow electrodes and the charging voltages? (ii) What are the likely mechanisms accounting for ion separation in FCDI? and (iii) what is the association between the desalting performance under different operating conditions and the ion separation mechanisms that are in play?

#### 2. Materials and methods

#### 2.1. Reagents

All chemicals were analytical reagent grade and were used as received unless otherwise stated. All solutions were prepared using 18.2 M $\Omega$  cm Milli-Q water (Millipore). 100-mesh DARCO<sup>®</sup> activated charcoal was purchased from Sigma Aldrich with average pore size and BET surface area of 1.44 nm and 917.5 m<sup>2</sup> g<sup>-1</sup> respectively.

#### 2.2. Experimental setup

Fig. 1a and b depict the structure and composition of our FCDI cell that consists of a spacer chamber (thickness of ~500  $\mu$ m) made of a silicone gasket and a nylon sheet (100-mesh, 160 mm × 70 mm) between the cation- and anion-exchange membranes (CEM-Type I/ AEM-Type I, FUJIFILM Europe) (Fig. 1a). Two composite current collectors placed against the ion-exchange membranes were made of graphite paper and acrylic sheets. The carved serpentine flow channels on the acrylic sheets were 3 mm wide and 1.5 mm deep (Fig. 1a). Each channel was 125 mm long with, in total, 9 channels connected in one line from the inlet to the outlet resulting in an effective contact area ( $A_{eff}$ ) between the ion-exchange membrane and the flow-electrode of 34.9 cm<sup>2</sup>. All parts were held together with the use of acrylic end plates (Fig. 1a).

#### 2.3. Operating conditions

The flow electrode was prepared from a dispersion of activated charcoal and commercial carbon black in a 2000 mg NaCl L<sup>-1</sup> aqueous solution. The weight ratio of charcoal to carbon black was 9:1 with total solid concentrations of 1, 2, 5 and 10 wt%. The mixtures were then stirred on a magnetic stirrer for 24 h to achieve homogeneous carbon suspensions. Our preliminary results showed that the desalting performance of the current design was comparable with the conventional design (*i.e.*, graphite carved in the same manner) at high carbon contents (10 wt%) with the similarity in performance likely a result of the frequent direct contact between particles effectively resulting in a conductive 3D network (SI Section S1 and Figs. S1 and S2). Indeed, good interparticle connectivity has previously been shown to facilitate electron transfer in similar carbon materials (Presser et al., 2012). The studies described here were carried out at carbon contents of 0, 2 (for comparison) and 10 wt% unless otherwise stated.

All FCDI experiments were conducted in batch mode with the brackish stream (25 mL of a 2000 mg L<sup>-1</sup> NaCl solution) continuously cycled using a peristaltic pump through the spacer from a storage flask at a flow rate of 25 mL min<sup>-1</sup> (Fig. 1b). The electrical conductivity of this stream was continuously monitored with the use of a conductivity meter (CON-BTA, Vernier) connected to a data acquisition system (SensorDAQ, Vernier). The flow-electrode slurries (50 g each) were recirculated between the FCDI cell and two stirred conical flasks respectively using a dual-head peristaltic pump (Longer pump, Baoding, China) at a constant flow rate of  $50 \text{ mLmin}^{-1}$  (Fig. 1a). This mode is termed isolated closed-cycle (ICC) operation. In one operating cycle, electrosorption was carried out at a constant charging voltage (0.8–2.0 V) using a DC power supply (MP3094, Powertech) followed immediately by reversed-voltage desorption (RVD) for electrode regeneration unless elsewhere stated. Note that, in this study, the "anode" is termed the electrode and/or current collector that is positively charged during the charging process while the "cathode" is the electrode and/or current collector that is negatively charged during the



Fig. 1. Schematic representations of (a) the structure and (b) the cross-section of the flow-electrode capacitive deionization (FCDI) cell.

charging process. After regeneration of the electrodes, the polarity of the electrodes was reversed in order to initiate the next cycle (in which anions were again adsorbed to the carbon particles adjacent to the "anode" with cations adsorbed to the carbon particles adjacent to the "cathode"). Preliminary results indicated that the FCDI system has a reliable cycling stability (SI Figs. S3 and S4). Control experiments were carried out with the use of 2000 mg NaCl/L aqueous solutions (no carbon) as the "flow-electrode" with other operating conditions set the same as described above.

#### 2.4. Analytical methods and calculations

The current (*I*) through the electrical circuit was recorded every second using a Vernier current probe connected to the SensorDAQ. The change of pH in the brackish stream and flow electrode was measured using an F-51 pH meter (Horiba, Japan). To quantify the concentrations of sodium and chloride species (including chloride ( $Cl^-$ ), hypochlorite ( $OCl^-$ ) and chlorate ( $ClO_3^-$ )), samples from the brackish stream and flow electrode were collected at appropriate intervals with measurements conducted on an ICP-OES spectrometer (Agilent Varian vista pro 710) and an ICS-3000 ion chromatograph (Dionex, U.S.) respectively according to the protocols

described elsewhere (Tang et al., 2015; Tsarev et al., 2016).

The average salt removal rate (ASRR,  $\mu g \text{ cm}^{-2} \text{ s}^{-1}$ ) of the FCDI cell was calculated as follows (Eq. (1)) (Ma et al., 2016):

$$ASRR = \frac{(C_0 - C_t)V_s}{At}$$
(1)

where  $C_0$  and  $C_t$  are the initial NaCl concentration and NaCl concentration at time t (g L<sup>-1</sup>) in the brackish stream, respectively.  $V_s$ , A and t represent the total volume of the salt solution (25 mL), the effective contact area between the ion-exchange membrane and the flow electrode (34.9 cm<sup>2</sup>) and operation time (s), respectively. The dynamic charge efficiency ( $\Lambda_{dyn}$ ) and specific energy consumption (P) as a function of effluent salt concentrations were evaluated using the approach described by Zhao et al. (2012) (Eqs. (2) and (3)).

$$\Lambda_{\rm dyn} = \frac{N_A e \frac{(C_0 - C_t) V_s}{M}}{\int I dt} \times 100\%$$
<sup>(2)</sup>

$$P_{(C_0 \to C_t)} = \frac{E \int I dt}{V_s}$$
(3)

where *e* is the electron charge,  $N_A$  is Avogadro's number, *M* is the molar mass of the solute (58.5 g mol<sup>-1</sup>) and *E* is the cell charging voltage.

Following correction for the non-capacitive contributions in the flow electrode, the average ion adsorption rate (AIAR,  $\mu g \text{ cm}^{-2} \text{ s}^{-1}$ ) and dynamic ion adsorption capacity (IAC<sub>dyn</sub>, mg g<sup>-1</sup>) for Na<sup>+</sup> and Cl<sup>-</sup> were determined as follows (Eqs. (4) and (5)) (Suss et al., 2015):

$$AIAR = \frac{\left(c_{0,i} - c_{t,i}V_s - \left(c_{t,i}^{ele} - c_{0,i}^{ele}\right)V_{ele}\right)}{At}$$
(4)

$$IAC_{dyn} = \frac{\left(c_{0,i} - c_{t,i}V_s - \left(c_{t,i}^{ele} - c_{o,i}^{ele}\right)V_{ele}\right)}{m}$$
(5)

where  $c_{0,i}$  and  $c_{t,i}$  are the initial i ( $i = Na^+$  or Cl<sup>-</sup>) concentrations and i concentration at time t (mg L<sup>-1</sup>) in the brackish stream, respectively.  $c_{0,i}^{ele}$  and  $c_{t,i}^{ele}$  are the initial i (Na<sup>+</sup> or Cl<sup>-</sup>) concentration and i concentration at time t (mg L<sup>-1</sup>) in the flow electrode, respectively.  $V_{ele}$  represents the aqueous volume of the flow electrode (mL). When calculating AIAR and IAC<sub>dyn</sub> for Na<sup>+</sup>, correction for the dissolved Na<sup>+</sup> concentration in the cathodic flow electrode was taken into account. Likewise, consideration was given to the presence of dissolved Cl<sup>-</sup> and its oxidation products in the anodic flow electrode the mass of the active material (*i.e.*, the activated charcoal, g). Detailed procedures for determination of the charge recovery (r) following electrosorption are documented in SI Section S2 and Fig. S5.

One-tailed and two-tailed t-tests (SigmaPlot 12.5, Systat Software, Inc.) were performed in order to assess the statistical differences at a confidence level of 95%.

#### 3. Results and discussion

#### 3.1. Desalting performance at different carbon loadings

Results of desalination using the FCDI unit with 2 and 10 *wt%* carbon contents at different charging voltages are summarized in Fig. 2. Control experiments (*i.e.*, no carbon particles present – resulting in a process that is effectively electrodialysis) were carried out with the use of 2000 mg NaCl/L aqueous solutions as the "flow-electrode". As can be seen from Fig. 2a, ASRR exhibits a positive

relationship with the charging voltage; for instance, at a carbon content of 2 *wt%*, the ASRR was 0.0514  $\mu$ g cm<sup>-2</sup> s<sup>-1</sup> at 1.2 V but increased to 0.1437  $\mu$ g cm<sup>-2</sup> s<sup>-1</sup> at 2.0 V. In accordance with the results from SI Fig. S1b, much higher ASRR values were obtained at higher carbon contents (up to 10 *wt%*).

It has been reported that electrochemical desalination technologies should be operated under a certain voltage threshold to avoid undesirable side reactions such as water splitting (He et al., 2016; Porada et al., 2013b). Fig. 2b shows that the dynamic charge efficiency  $(\Lambda_{dyn})$  of the control experiments decreases significantly when the charging voltage exceeds 1.2 V (one-tailed, p < 0.05). Indeed,  $\Lambda_{dyn}$  of the electrodialysis process dropped to 57.3% at 2.0 V. Meanwhile, results of the present work indicate that an increase in the carbon content in the flow electrode is conducive to inhibiting the charge loss during deionization at high voltages; for instance, when the FCDI cell was operated at 2.0 V,  $\Lambda_{dyn}$  was sustained at around 84.9% and 94.5% at carbon mass loadings of 2 and 10 wt% respectively (Fig. 2b). The carbon content in the flow electrodes also has significant impacts on the energy consumption for desalination. It can be seen from Fig. 2c that the use of 10 wt% results in a decrease in the gradient of the energy consumption plot with the charging voltage ranging from 0.8 to 2.0 V. This finding is presumably associated with the higher charge transfer efficiency at higher carbon mass loadings (SI Figs. S1 and S2).

#### 3.2. pH excursion and its implications to desalting mechanisms

The pH variation in the anode and cathode chambers in one operating cycle are summarized in Fig. 3. In the control tests (Fig. 3a), rapid pH increase was observed in the cathode chamber at a charging voltage over 1.2 V whilst acidification of the anolyte became severe when the charging voltage exceeded 1.6 V. It has been reported that pH increase during electrochemical desalination can be associated with the reduction of oxygen and/or hydrogen evolution (Dykstra et al., 2017; He et al., 2016). In comparison, acidification in the anode chamber may be ascribed to the oxidation of the graphite and chloride and/or splitting of water at high charging voltage (Biesheuvel et al., 2015; Dykstra et al., 2017; He et al., 2016; Tang et al., 2017; Tedesco et al., 2016). Though pH excursion was also noted in the flow electrodes with 2 and 10 wt% carbon contents (Fig. 3b and c), the change became less significant with the incorporation of carbon materials in the flow electrode. Moreover, the pH of the desalted water was maintained at around 7.0 over successive operating cycles (n = 3-5) at voltages of 1.6 and 2.0 V (SI Table S1) indicating that symmetric removal of anion and cation (and H<sup>+</sup> and OH<sup>-</sup>) from the brackish stream was occurring.



**Fig. 2.** Desalting performance of the FCDI system at different operating conditions. (a) Average salt removal rate (ASRR) and (b) dynamic charge efficiency ( $A_{dyn}$ ) as a function of charging voltages, and (c) energy consumption (Wh per mg salt removed) as a function of the effluent salt concentration following 1800-s electrosorption. Experimental conditions: carbon content = 0, 2 and 10 *wt*%. Experiments were conducted at least in triplicate.



**Fig. 3.** Temporal change of pH in the anode and cathode chambers during electrosorption with the flow electrode containing (a) 0 wt%, (b) 2 wt% or (c) 10 wt% carbon. The flow electrode with its current collector connected to the anode of the power supplier during electrosorption is termed the "anode" with the counter is termed the "cathode". Four different charging voltages (*i.e.*, 0.8, 1.2, 1.6 and 2.0 V) were evaluated in this study. Experiments were conducted (at least) in duplicate with the average results provided. Lines in the shade indicate the pH change in the cathode chamber while the lines in the non-shaded areas represent the pH change in the anode chamber.

Given that the flow anode (and anodic current collector) was positively charged during electrosorption while the flow cathode (and cathodic current collector) was negatively charged, the H<sup>+</sup> and OH<sup>-</sup> generated should be released for the most part into the solution phase. As such, the parameters  $\Delta[H^+]/ASRR$  and  $\Delta[OH^-]/$ ASRR are introduced here to indicate the concomitant production of H<sup>+</sup> and OH<sup>-</sup> during the deionization step. Consideration has been given to the consumable H<sup>+</sup> and OH<sup>-</sup> incorporated into other entities (such as carbonate) (for details see SI Section S3 and Fig. S6). It can be observed from SI Fig. S7 that, following 1800 s of reaction in the control experiments,  $\Delta[H^+]/ASRR$  and  $\Delta[OH^-]/$ ASRR values of 0.003–0.017 and 0.40–3.08 mM (µg cm<sup>-2</sup> s<sup>-1</sup>) -1respectively are obtained at low voltages while the values of these parameters increase to 2.26 and 18.44 mM ( $\mu g \text{ cm}^{-2} \text{ s}^{-1}$ )  $^{-1}$  on increasing the charging voltage to 2.0 V. In contrast, the use of porous carbon in the flow electrode largely inhibits the Faradaic reactions in the flow electrode with  $\Delta[H^+]/ASRR$  and  $\Delta[OH^-]/ASRR$ values at 2.0 V of 0.013–0.026 and 0.25–0.48 mM ( $\mu g \; cm^{-2} \; s^{-1}) \; ^{-1}$ respectively (SI Fig. S7).

A plausible explanation for these findings relates to competition for charges between the electrodialytic (i.e., ions end up in the electrolyte) and capacitive (*i.e.*, ions end up in the EDLs and pores) processes that are occurring during deionization (Fig. 4). With regard to the electrodialytic contribution, counterions migrate across the membranes in the presence of an electrical field. Redox reactions occur at high voltages resulting in the neutralization of the charge with H<sup>+</sup>/OH<sup>-</sup> (Nativ et al., 2017; Strathmann, 2010). These processes would be expected to lead to an increase in the concentrations of  $H^+/OH^-$  in the electrolyte of the flow electrodes (Fig. 3 and SI Fig. S7). Although it has been reported that an aqueous electrolyte with a high salt concentration can result in a decrease in the ionic resistance (Yang et al., 2016), critical concerns remain regarding the accumulation of ions at the electrolyte/membrane interface (*i.e.*, increase in  $c_{Na}(x, t)$  and  $c_{Cl}(x, t)$  due to the elevated concentrations in the electrolyte) which would increase the polarization resistance with the ongoing deionization likely causing back diffusion of counterions. Galama et al. (2013) also reported that the accumulation of counterions may be expected to lead to the adsorption of co-ions from the solution phase with the subsequent leakage of co-ions driven by concentration difference across the membrane resulting in a decrease in the efficiency of ion migration (Tedesco et al., 2016). Meanwhile, Faradaic reactions such as oxygen reduction and hydrogen evolution also lead to charge injection and/or exchange at the electrode/electrolyte interface with these processes competing with electron-ion transport thereby resulting in deterioration in energy efficiency (Fig. 4). In comparison, the high conductivity of the carbon clusters is conducive to a decrease in internal resistance of the flow electrode with the capacitive mechanism of deionization sustaining the coupling of charge and ion transfer due to the formation of EDLs (Porada et al., 2013b; Suss et al., 2015). In support of these hypotheses, high current density (*i.e.*, high voltage across the spacer channel), high  $\Lambda_{dyn}$  but low energy consumption was observed at 2.0 V at high carbon contents (Fig. 2).

# 3.3. Comparison of the electrodialytic and capacitive processes in FCDI

Estimates of the portions of Na<sup>+</sup> ( $p_{Na}$ ) and Cl<sup>-</sup> ( $p_{Cl}$ ) adsorbed in the EDLs of the carbon particles in the flow electrode chambers after migration through the membranes are provided in Fig. 5. Our preliminary results indicated that the removal of sodium and chloride ions due to physical adsorption was negligible (SI Figs. S8-S10). It can be observed that the flow electrode used in this study has high affinity for  $Cl^-$  during electrosorption, with  $p_{Cl}$  generally over ~90% for carbon contents of 2 and 10 wt% with this result consistent with the finding that the anodic reactions associated with H<sup>+</sup> production were significantly inhibited in the FCDI system compared to the control system (i.e. in the absence of carbon particles) (Fig. 3 and SI Fig. S7). Of particular importance is the result that typical products of Cl<sup>-</sup> oxidation including OCl<sup>-</sup> and ClO<sub>3</sub><sup>-</sup> were not detectable in this study with this finding indicating that (i) chloride oxidation at the anode is not occurring, even at relatively high voltages (e.g., 2.0 V) and/or (ii) the small amounts of oxidized chloride species that are produced are readily adsorbed by the carbon electrode. In comparison, the DARCO® activated charcoal used in the flow electrode chambers has a low affinity for Na<sup>+</sup>, with  $p_{\text{Na}}$  values between 20% and 50% (Fig. 5). A plausible explanation for the low efficiency of Na<sup>+</sup> adsorption to the EDLs might be related to the abundance of electron acceptors (e.g., oxygen) in the cathode

Capacitive mechanism Desalted water (t,t) $c_{cl}(x,$ Сľ Cathode k. Ion adsorption Back diffusion capacity (IAC)  $c_{CI}(x,t)$ Coion leakage H.O. Cathode Anode OH Brackish wate Electrodialytic mechanism Cation exchange Anion exchange membrane membrane

**Fig. 4.** Schematic representation of the capacitive and electrodialytic contributions to brackish water deionization in an FCDI system.  $c_{Na}(x, t)$  and  $c_{CI}(x, t)$  represent the concentrations of Na<sup>+</sup> and Cl<sup>-</sup> in the electrolyte (and in membranes).  $c_{Na,mA}(x, t)$  and  $c_{CI, mA}(x, t)$  relate to the concentrations of Na<sup>+</sup> and Cl<sup>-</sup> in the macropores of the carbon particles.



**Fig. 5.** Estimation of the portions of Na<sup>+</sup> ( $p_{Na}$ ) and Cl<sup>-</sup> ( $p_{Cl}$ ) adsorbed in the electrical double layers (EDLs) of the electrode after migration through the membranes. Mass balance analysis was conducted following 1800 s of charging at different voltages (*i.e.*, 0.8, 1.2, 1.6 and 2.0 V) with the flow electrode containing 0, 2 or 10 *wt*% carbon content. Experiments were conducted at least in duplicate.

chamber that undergo redox reactions near the electrodes (Figs. 3 and 4), likely resulting in (i) electron exchange at the electrode/ electrolyte interface and (ii) loss of adsorption capacity by the cathodic EDLs. The portion of Na<sup>+</sup> retained by the carbon particles is significantly higher at 2.0 V (*e.g.*, one-tailed, p < 0.05), which might account for the high  $\Lambda_{dyn}$  observed in the FCDI even when the charging voltage exceeds the typical threshold (Fig. 2) as the coupling of ion and charge in the EDLs is capable of retarding electron loss due to cathodic reactions such as hydrogen evolution and oxygen reduction (Fig. 4) (Dykstra et al., 2017; He et al., 2016; Tang et al., 2017).

In a typical CDI system, the oxidation of the carbon anode could result in a change in the point of zero charge of the carbon surface and a relocation in the potential of zero charge of the carbon electrode (Avraham et al., 2011; Gao et al., 2015). These changes in the physicochemical properties of the anode are likely to result in ongoing reduction in salt separation capacity during CDI operation (Porada et al., 2013b). Fig. 6a shows that the surface zeta potential of the anode becomes more positive following successive operation cycles. This is, however, not surprising in view of the asymmetric capacitive behavior of the system during electrosorption (Fig. 5); i.e., the decoupling of Na<sup>+</sup> and electrons from the EDLs at the cathode might be envisaged to lead to a surplus of positive charge at the anode, with the unbalanced charge pairs likely causing a positive shift in the short-circuit potential  $(E_0)$ . The change of the surface site groups (resulting in a shift in  $pK_H$  to a higher value, Fig. 6b and SI Section S4 and Fig. S11) also supports our hypothesis. It has been reported that for adsorption of similar amounts of counter-ions at both the anode and cathode,  $E_0$  should be closer to the potential of the electrode of higher adsorption rate because of the potential shift needed for thermodynamic and/or kinetic equilibrium between the electrode pairs to be achieved (Gao et al., 2014). Similar consideration should be given to the non-ideal scenario in which the occurrence of an  $E_0$  value closer to the potential of the more efficient electrode is attributed to relocation of the redundant charge on the electrode during short circuit. It should be noted that the competitive electrodialytic and capacitive processes and the resultant impacts on (F)CDI performance are also dependent on the properties of the carbon materials (e.g., surface functional groups). For example, Nativ et al. (2017) used a flow electrode comprised of 5 wt% of Norit SX Ultra activated charcoal in DI water with their results showing that this kind of carbon material had a relatively higher affinity for Na<sup>+</sup> compared to Cl<sup>-</sup>.

Following correction for the electrodialytic bias, the average ion adsorption rates (AIAR) and dynamic ion adsorption capacities (IAC<sub>dyn</sub>) under different conditions are provided in SI Figs. S12 and S13. With a charging voltage of 2.0 V, AIAR values for Na<sup>+</sup> and Cl<sup>-</sup> in the FCDI system described here are 0.133 and 0.359  $\mu$ g cm<sup>-2</sup> s<sup>-1</sup>



**Fig. 6.** Change of (a) zeta potential and (b) surface groups of the carbon material in the anode following three successive charging (1.2 V)/discharging (0 V) cycles. In titration experiments (Fig. 6b), the flow electrode was firstly diluted by 40 times with pH adjusted to 2. Aliquots of 2 M NaOH solution were added with the steady-state pH values recorded. Detailed procedure to calculate the surface site concentrations and acidity constant is provided in SI Section S4 and Fig. S11.

respectively at a carbon content of 10 *wt%*. SI Fig. S13 indicates that  $IAC_{dyn}$  of the DARCO<sup>®</sup> charcoal are more likely dependent on the charging voltages rather than the carbon concentrations with  $IAC_{dyn}$  of Na<sup>+</sup> and Cl<sup>-</sup> reaching 2.07–2.42 and 5.58–6.77 mg g<sup>-1</sup> respectively following 1800 s of electrosorption at 2.0 V.

FCDI can be used not only as a highly efficient alternative to deionization but also an innovative method to study the fundamental mechanisms that are occurring beneath the superficial observations in CDI. Results of this study clearly show that brackish water desalination in (F)CDI should be a combined process of electrodialysis and capacitive deionization. Ion transport through the membranes is followed by (i) charge neutralization in the electrolyte and/or (ii) ion immobilization with the counter charge in the EDLs. To date, ion adsorption  $(k_1 \text{ in Fig. 4})$  has been recognized as a rate-limiting step in (F)CDI, with more and more studies focusing on the development of novel materials with high capacities (Nam and Choi, 2017; Xu et al., 2016). In comparison, little consideration has been given to the concomitant electrodialysis process, which could lead to the accumulation of ions in the aqueous solution and increase in back diffusion and co-ion leakage. As such, models involving the electrodialytic contributions should be introduced to optimise the desalination process and, in particular, to prevent ion transport across the membranes ( $k_2$  in Fig. 4) becoming rate limiting prior to the electrodes reaching adsorption saturation.

It has been emphasized that CDI should be operated under a certain potential threshold to avoid unfavorable side reactions. However, our findings suggest that high  $\Lambda_{dyn}$  could be achieved at high voltages on condition that the coupling of charge and counterion is sustained in the EDLs, despite concerns remaining with regard to long-term operation. While the immobilization of counterions in the EDLs was not enhanced with the increase of carbon content from 2 to 10 wt%, FCDI with high carbon loading mass demonstrated higher charge efficiency. This fact might be related to good interparticle connectivity of the flow electrode at high carbon concentrations (i.e., low electronic resistance) with this interconnectivity facilitating electron percolation within the carbon materials (Liang et al., 2017; Yang et al., 2016). Nevertheless, it is still not clear which parameters and/or operating conditions are most important in the coupling and decoupling of charge and counter-ion in the EDLs, and considerably more insight into factors controlling desalination rate and charge (or current) efficiency is required before high-voltage (or high-current) mode could be recommended as a viable choice for (F)CDI.

This study is also of particular significance to the understanding of the asymmetric adsorption behaviors in (F)CDI with this understanding critical to the development and comparison of novel materials. While there is great progress in the preparation of electrodes of high capacitance and ion selectivity with the use of pseudocapacitive materials capable of intercalating ions into the inorganic/organic matrices via fast and reversible redox reactions at the electrode surface (Boota et al., 2015; Nam and Choi, 2017), more attention should be paid to the less efficient counter electrodes as they will be rate limiting in relation to ion adsorption with these inefficiencies leading to a change of electrode properties which can affect energy recovery during electrode regeneration (SI Fig. S14).

#### 4. Conclusions

Results of this study indicate that operating conditions (e.g., carbon content and charging voltage) have significant impacts on the contributions of electrodialytic and capacitive processes to deionization in FCDI. While a portion of the ions transported to the electrode chambers in FCDI will remain in solution and contribute to the electrolyte present in the electrode chambers (and contribute to pH excursion in the flow electrode), the use of high carbon content ensures that a high proportion of the charge and counter ions are retained in the electrical double layers of the flowing carbon particles, even at high charging voltages (e.g., 2.0 V) during the deionization process. Estimation of the distribution of Na<sup>+</sup> and Cl<sup>-</sup> in the flow electrode after migration through the membranes suggests that the ongoing capacitive adsorption exhibits asymmetric behavior, with the anodic particles demonstrating a better affinity for Cl<sup>-</sup> (than the cathodic particles for Na<sup>+</sup>) during electrosorption. These results provide an explanation for the change in electrode properties that are observed under imperfect adsorption scenarios and provide insight into aspects of the design and operation of flow electrode pairs that are critical to achieving effective desalination by FCDI.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.watres.2018.07.049.

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