1 Aqueous-Processed, High-Capacity Electrodes 2 for Membrane Capacitive Deionization

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16 Keywords: Capacitive Deionization, Membrane, Polymer, Activated Carbon, Desalination.

Abstract: Membrane Capacitive Deionization (MCDI) is a low-cost technology for desalination. Typically, MCDI electrodes are fabricated using a slurry of nanoparticles in an organic solvent along with polyvinylidene fluoride (PVDF) polymeric binder. Recent studies of the environmental impact of CDI have pointed to the use organic solvents in the fabrication of CDI electrodes as key contributors to the overall environmental impact of the technology. Here, we report a scalable, aqueous processing approach to prepare MCDI electrodes using water-soluble polymer polyvinyl alcohol (PVA) as a binder and ion-exchange polymer. Electrodes are prepared by depositing aqueous slurry of activated carbon and PVA binder followed by coating with a thin layer of PVA based cation- or anion-exchange polymer. When coated with ion-exchange layers, the PVA-bound electrodes exhibit salt adsorption capacities up to 14.4 mg/g and charge efficiencies up to 86.3%, higher than typically achieved for activated carbon electrodes with a hydrophobic polymer binder and ion-exchange membranes (5 - 13 mg/g). Furthermore, when paired with low-resistance commercial ion-exchange membranes, salt adsorption capacities exceed 18 mg/g. Our overall approach demonstrates a simple, environmentally friendly, cost-effective and scalable method for the fabrication of high capacity MCDI electrodes.

Introduction

Membrane capacitive deionization (MCDI) is an emerging desalination technology that requires a lower energy input compared with pressure-driven or thermal desalination methods for the desalination of low salinity waters^{1,2}. In capacitive deionization (CDI), an electrical potential applied between porous electrodes drives reversible electrosorption of ions³⁻⁹. In MCDI, ion-exchange membranes are placed in front of the electrodes, as shown schematically in Figure 1a and b. The advantages of MCDI over CDI include an increase in the overall salt removal and charge efficiency due to blocking of co-ions¹⁰⁻¹⁵ and preventing or minimizing faradic reactions at the electrode surface that can degrade performance¹⁶⁻¹⁸.

Figure 1. Schematic for MCDI operation during a) ion uptake, b) ion desorption; c) schematic for MCDI cell assembly, and d) schematic for bench scale desalination CDI test set up.

A recent analysis of the environmental impact of CDI determined that material and chemical uses, including organic solvents used in the fabrication of CDI electrodes, account for most of the environmental impacts of the technology¹⁹. CDI electrodes are typically fabricated using a slurry of activated carbon in an organic solvent along with polyvinylidene fluoride (PVDF) as the polymeric binder²¹. Additionally, ion-exchange membranes for MCDI are fabricated separately and stacked on top of the electrodes^{10,11,13,18,22,23}. Recent work has explored the use of polymeric coatings as ion-exchange layers^{11,22,24–28}. Polymeric ion-exchange coatings reduce overall module size, but work to date with polymer coatings has given limited salt adsorption capacities and relied on organic solvents in other stages of the processing. To give some examples, Kim et al.¹¹, Lee et al.²², Jeong et al.²⁴ and Kwak et al.²⁶, Kim et al.²⁷ used organic solvents to prepare ion

exchange polymers via multi-step synthesis procedures. Alternatively, Asquith et al.²⁵ and Ahualli et al.²⁸ used activated carbon electrodes prepared from the organic solvent-based slurry and coated with aqueous processed ion-exchange polymers. With the exception of the work by Ahualli et al.²⁸ (8.79 mg/g) these studies did not report the salt adsorption capacities and charge efficiencies. Other examples of CDI electrode materials along with their salt adsorption capacities are reported in review articles^{1,29}.

Clearly, an alternative process for fabricating electrodes and ion-exchange layers for MCDI that does not rely on organic solvents would be desirable to simplify the fabrication process, reduce electrode size and weight, and avoid the use of organic solvents^{18,20}. For example, Park et al.^{30,31} have previously reported an aqueous-based activated carbon electrode fabrication procedure using a water-soluble polymer binder polyvinyl alcohol (PVA). Kim and Choi^{13,32} found enhanced desalination efficiency for a PVDF binder-based electrodes coated with PVA and sulfosuccinnic acid (SSA) cation exchange polymer, and Tian et al.³³ reported enhancement in the salt removal performance for PVDF binder-based electrodes coated with quaternized PVA (QPVA) anion exchange polymer. These studies demonstrate aqueous processes for fabricating electrodes or ion-exchange coatings, but a fully aqueous-processed MCDI system has not been reported.

Here, we report a scalable aqueous-processing route to fabricate high-capacity porous electrodes with polymeric ion-exchange coating layers. Our approach uses slurry casting of aqueous suspensions to fabricate the electrodes and to subsequently deposit ion-exchange polymer coatings. The resulting MCDI electrodes exhibit high adsorption capacities, up to 14.4 mg/g, compared with 5 - 13 mg/g for most PVDF-based CDI and MCDI electrodes^{1,5,29}. Furthermore, the charge efficiency of the polymer coated MCDI electrode system (86.3 %) was found to be significantly improved as compared to bare CDI electrode system (57 %). When

paired with low-resistance commercial ion-exchange membranes, PVA-bound electrodes exhibit salt adsorption capacities higher than 18 mg/g. While some previous reports have produced adsorption capacities exceeding 15 mg/g,²⁷ they have not relied on aqueous-based electrode processing as reported here. This work successfully demonstrates a simple and environmentally friendly aqueous approach to fabricate polymer coated MCDI electrodes with enhanced salt removal performance and charge efficiency.

Materials and Methods

Activated carbon CEP21K (surface area 2040 m²/g) was purchased from Power Carbon Technology Co., Ltd, Republic of Korea. Graphite sheets of 0.005-inch thickness (Mineral Seal Corporation, USA) were used as current collectors. Cation exchange membranes (CMI-7000, 450 μm thick, electrical resistance < 30 Ω cm²) and anion exchange membranes (AMI-7001, 450 μm thick, electrical resistance < 40 Ω cm²) exchange membranes were purchased from Membranes International Inc., USA. These membranes were chosen for analysis due to their known permselectivities (0.94) and ion-exchange capacities (1.6 meq/g), provided by the supplier. CMX membranes (electrical resistance 3.0 Ω cm² and thickness 170 μm) were purchased from ASTOM-Neosepta. These membranes were chosen due to their lower thickness and electrical resistance. More information on the ion-exchange membranes is provided in Table S1. Polyvinyl alcohol (PVA, fully hydrolyzed, M_w = 89,000 – 98,000 g/mol), glutaraldehyde (GA, 25 wt % solution in water), sulfosuccinic acid (SSA, 75 wt % solution in water), glycidyltrimethylammonium chloride (GTMAC), polyvinylidene fluoride (PVDF, M_w = 534,000), dimethyl acetamide (DMAc) and potassium hydroxide were purchased from commercial suppliers and used as received. Deionized water (E-Pure, resistivity 18 Mohm) was used for the synthesis of the electrodes, polymer samples as well as salt solution preparation.

103 *Electrode preparation*

104 Electrodes with PVA binder were prepared with modifications to procedures reported in the
105 literature^{30,31}. Generally, the composition of electrodes consisted of 90 wt % of high surface area
106 powdered activated carbon (PAC) and 10 wt % of the polymeric binder (linear polymer PVA and
107 crosslinker GA) based on the total mass of dry electrodes. The electrode preparation involved
108 three main steps: slurry preparation, casting, and drying/annealing. First, 6 wt % PVA solution
109 was prepared by mixing a desired amount of PVA in DI water at 90 °C for 4 h. Next, GA solution
110 (5 mol % relative to PVA repeat units) was added and mixed for an hour. PAC was added slowly
111 along with additional DI water, giving the final solid content of the slurry of approximately 30 wt
112 %. The resulting mixture was stirred for 12 h to ensure homogeneity. Next, the homogeneous
113 carbon slurry was deposited directly onto graphite sheets through slurry casting with a gap height
114 of 300 µm. The graphite sheets served as current collectors and were rinsed with DI water first
115 and then adhered to a glass plate using polyimide tape. After slurry deposition, electrodes were
116 dried in air and annealed at 130 °C. Various steps in the procedure and photographs of
117 representative electrodes are shown in the Supporting Information Figure S1. These uncoated
118 electrodes could be used directly for capacitive deionization. For MCDI configuration, the
119 electrodes were further coated with an ion-exchange polymer, as described in the next section.

120 PVDF bound electrodes were prepared by adapting the procedure reported in the literature²¹.
121 First PVDF was dissolved in DMAc (4 wt % solution) for 1 h followed by addition of activated
122 carbon (90 wt % of the total dry mass). The resulting mixture (approx. 30 wt % solid) was
123 continuously stirred for 12 h. The homogeneous slurry was deposited on a graphite sheet using
124 the slurry casting method (Supporting Information Figure S1b) with a gap height of 250 µm and
125 dried in the oven at 60 °C for 2 h followed by overnight vacuum drying for complete solvent
126 removal. Prior work has shown that the different mass (or carbon content) and thickness of the

electrodes can lead to a different degree of electrode utilizations for similar operating conditions³⁵. In this work, the gap height was chosen to produce a similar final electrode mass and thickness comparable to that of PVA-bound electrodes.

Ion Exchange Polymer synthesis and Electrode Coating

The cation-exchange polymer coating was comprised of polyvinyl alcohol (PVA) and sulfosuccinic acid (SSA) and was synthesized by adapting procedures reported in literature^{13,32}. A 6 wt % PVA solution was prepared in DI water and SSA (20 wt % relative to PVA weight) was added followed by mixing for 1 h at room temperature to ensure homogeneity. The resulting mixture was deposited onto the electrode (with PVA binder) surface and crosslinked by annealing at 130 °C, as shown in Scheme 1. The cation-exchange polymer coated electrode was used as the cathode in the MCDI system.

Scheme 1. Synthetic scheme for crosslinked cation-exchange polymer using polyvinyl alcohol (PVA) and anionic crosslinker sulfosuccinic acid (SSA).

The anion-exchange polymer coating was comprised of quaternized polyvinyl alcohol (QPVA) crosslinked with GA and was synthesized using procedures adapted from the literature^{33,36}. KOH

(50 mol % relative to PVA repeat units) and glycidyl trimethyl ammonium chloride (GTMAC, 50 mol % relative to PVA repeat units) were added to a 6 wt % PVA solution in DI water. Next, the mixture was heated at 70 °C for 4 h while stirring continuously. After cooling down to room temperature the resulting mixture was precipitated in pure ethanol and dried overnight under vacuum to obtain QPVA as a white solid. This product was dissolved in deionized water at 90 °C, and the pH was lowered to 5 by adding 1.0 M HCl solution. To this solution, GA crosslinker (10 wt % relative to PVA) was added and stirred for 1 h. The resulting mixture was deposited onto the electrode (with PVA binder) surface and crosslinked at 130 °C for 1 h as shown in Scheme 2. The anion-exchange polymer coated electrode was used as the anode in the MCDI system.

Scheme 2. Synthetic scheme for the preparation of anion-exchange coating showing first the quaternization of PVA by coupling PVA to glycidyltrimethylammonium chloride (GTMAC) followed by crosslinking with non-ionic crosslinker glutaraldehyde (GA).

Fourier-transform infrared spectroscopy (FTIR) analysis

161 The chemical structure of free-standing ion-exchange polymer membranes and ion-exchange
162 polymer coated electrodes were analyzed using a Nicolet iS50 FT-IR, Thermo Scientific, Inc.

163

164 *Scanning Electron Microscopy (SEM)*

165 The surface and cross-section morphology of the bare and ion-exchange polymer coated
166 electrodes were analyzed using scanning electron microscopy. All the samples were sputter
167 coated with thin layer of gold. For cross-sectional analysis, electrodes were frozen in liquid
168 nitrogen, fractured, and mounted on an SEM mount.

169

170 *Contact angle measurements:* Static contact angle measurements of DI water on ion-exchange
171 polymer coated electrodes were carried out using a Drop Shape Analyzer (DSA 100, Kruss
172 Instruments) at ambient conditions. Contact angle results are provided in the Supporting
173 Information Figure S2.

174

175 *Desalination Tests*

176 A “flow-by type” CDI unit cell was fabricated and assembled into a lab scale set up as shown
177 in Figure 1**Error! Reference source not found.**d. The setup includes feed solution tank, a
178 peristaltic pump (Cole-Parmer Masterflex, feed pressure < 20 kPa), a CDI cell assembly (Figure
179 **1Error! Reference source not found.**c), an electrochemical analyzer for power supply (CH
180 Instruments, model 600E), in-line pH and conductivity meters at the exit of the CDI cell and
181 effluent collection tank. The CDI assembly consisted of two electrodes, cation/anion exchange
182 membranes, and graphite current collectors. The two sides of the assembly were separated by a 1

mm thick woven non-conductive nylon spacer (61% porosity). Additionally, a computer system interfaced with the electrochemical analyzer and the pH and conductivity meters to automatically log the electrical current, pH and conductivity data, respectively. Current and conductivity values were recorded at 1 s intervals. The pH values were recorded at 10 s intervals and linearly interpolated to estimate the pH for 1 s intervals. Changes in the effluent pH are common for both CDI and MCDI systems and reflect a combination of Faradaic reactions and migration of H^+ and OH^- ions to the electrodes³⁷. The contribution of H^+ and OH^- ions to the measured effluent conductivity were accounted for based on the standard molar conductivities for each ion, 329.82 and 198.6 $mS\ L\ mol^{-1}\ cm^{-1}$ for H^+ and OH^- , respectively. The molar concentrations of H^+ and OH^- were calculated based on the effluent pH, and the conductivity contribution of H^+ and OH^- ions was then subtracted from the measured effluent conductivity value to give corrected conductivity values. The corrected conductivity values were then converted to NaCl concentration (mg/L) using feed solution conductivity-concentration relationship (10 mM NaCl, 1.130 mS/cm).

The salt removal performance of the electrodes was evaluated using 10 mM NaCl feed solution and 10 cm x 1 cm electrode size (10 cm^2 electrode cross-sectional area). Prior to testing, electrode assembly was equilibrated by running the feed solution continuously for one hour with no voltage bias. During testing, a constant DC voltage was cycled on (1.2 V) and off (0.0 V) at intervals of 1000 s (16.67 min). The performance of the different types of systems was quantified in terms of the salt adsorption capacity (SAC), average salt adsorption rate (ASAR), salt removal efficiency (SRE), and charge efficiency (CE).

The salt adsorption capacity (*SAC*) represents the total salt removed during one adsorption cycle normalized by the total electrode weight. The electrode weight $w_{electrode}$ is the combined

weight of both electrodes including the activated carbon and binder but excluding the ion-exchange polymer layer or ion-exchange membrane:

$$SAC = \frac{Q \cdot \int (C_o - C_t) dt}{W_{electrode}} \quad (1)$$

Where Q is the volumetric flow rate of the solution, and C_o and C_t are the feed and effluent NaCl concentrations (mg/L) respectively. The feed concentration C_o is constant during desalination.

The average salt adsorption rate (ASAR) is calculated by dividing the SAC by the duration of the adsorption cycle ($t_{cycle} = 1000$ s):

$$ASAR = \frac{SAC}{t_{cycle}} \quad (2)$$

The salt removal efficiency (SRE) represents the fraction of salt removed per adsorption cycle normalized by the inlet salt concentration:

$$SRE = \frac{\int (C_o - C_t) dt}{(C_o \cdot t_{cycle})} \quad (3)$$

The charge efficiency (CE) is the ratio of moles of salt removed relative to the charge supplied during the adsorption step:

$$CE = \frac{(Q \cdot \int (C_o - C_t) dt / m)}{(\int I \cdot dt / F)} \quad (4)$$

Where, m is the molecular weight of NaCl (58.44 g/mol) and F is Faraday's constant, 96485 C/eq. The round-trip charge efficiency or coulombic efficiency accounting for both charge and discharge cycles is reported in the Supporting Information Table S4.

Results and Discussion

The electrodes were fabricated by deposition of an aqueous slurry containing activated carbon, PVA, and GA onto a graphite current collector, and the polymer binder was crosslinked by thermally annealing the deposited slurry. Ion exchange coatings were similarly deposited followed by the crosslinking of charged hydrophilic polymers. The cathode was coated with a cation-exchange polymer layer comprised of PVA crosslinked with SSA (Scheme 1), and the anode was coated with an anion-exchange polymer layer comprised of PVA quaternized with GTMAC and crosslinked with GA (Scheme 2).

Figure 2. FTIR spectra for (a) PVA (black), (b) cation-exchange polymer PVA/SSA (green), and (c) anion-exchange polymer QPVA (red), free-standing polymer films.

FTIR spectra of the three different types of the polymer membranes are shown in Figure 2, including the spectra (Figure 2a) for uncharged and uncrosslinked PVA. The FTIR spectra for the PVA/SSA cation exchange polymer (Figure 2b) reveals a stretching vibration at 1034 cm^{-1} corresponding to sulfonic (SO_3) groups and a vibration at 1712 cm^{-1} corresponding to carbonyl functional groups, in good agreement with prior studies³². Similarly, the anion-exchange QPVA membrane spectra (Figure 2c) exhibit an FTIR absorbance at 963 cm^{-1} indicating the presence of aliphatic C-N³⁶. FTIR spectra of the polymer-coated electrodes (Supporting Information Figure S3) revealed the presence of the expected functional groups.

Figure 3. Photograph (a) and SEM images (b-d) of the fabricated electrodes. a) Photograph of an activated carbon electrode fabricated via slurry casting, showing ion-exchange polymer coated region (left) and uncoated region (right), b) top view SEM image of ion-exchange polymer coated electrode, c) top view SEM image of the uncoated electrode, d) cross-section SEM image of the ion-exchange polymer coated electrode showing 10 μm thick coating on top of the activated carbon electrode.

Photographs and SEM micrographs of the fabricated electrodes are presented in Figure 3. Figure 3a is a photograph of an activated carbon electrode fabricated via slurry casting, showing ion-exchange polymer coated region (left) and uncoated region (right). Top view SEM image of the polymer coated electrode (Figure 3b) shows smooth and uniform coating, while the bare electrode (Figure 3c) is highly porous and consists of grains of different sizes. Cross-sectional SEM micrograph of the polymer coated electrode (Figure 3d) indicates approximately 10 μm thick ion-exchange polymer layer on the top of the activated carbon electrode (250-300 μm thick).

Desalination test results

Desalination tests were conducted using both PVA and PVDF bound electrodes and either using bare electrodes (CDI), electrodes coated with ion-exchange coatings (PC-MCDI), or using bare electrodes along with commercial ion-exchange membranes (MCDI). PVA and PVDF bound electrodes of identical size (10 cm x 1 cm) and similar total mass was used for comparison. The coatings and electrodes were stable when immersed in water during desalination tests. Details of the various samples are provided in the Supporting Information Table S2. Below, we first compare the performance of PVA-CDI and PVDF-CDI systems, followed by an analysis of the PVA-PC-MCDI system with the ion-exchange polymer coatings and PVA-MCDI and PVDF-MCDI systems that contain commercial ion exchange membranes. The performance parameter values reported in the main text are for the average of 5 cycles of the same sample. Detailed studies on repeatability were not carried out, but in general, there was a variation of 5% in performance for electrodes fabricated using the same processing conditions and composition. A comparison of two electrodes fabricated and tested separately is presented in the Supporting Information Table S3. We also conducted a control experiment using only graphite electrodes coated with ion-exchange polymer coatings (Figure S4). Roughly 0.04 mg salt was removed in one adsorption cycle for the graphite charge collector compared with 2.65 mg of salt adsorbed with the activated carbon electrodes. This demonstrates that the porous carbon electrodes are responsible for the vast majority of salt uptake.

280

Performance comparison of PVA-CDI and PVDF-CDI systems

Electrodes were prepared using either PVA or PVDF binder materials and are otherwise identical in composition (90 wt % powdered activated carbon and 10 wt % binder) and overall mass. These two types of electrodes are denoted PVDF-CDI and PVA-CDI systems respectively.

285 Desalination tests were conducted to understand the effect of binder on the salt removal
286 performance and charge efficiency.

287 Figure 4a shows the effluent conductivity for both systems over 5 cycles of operation. During
288 the adsorption cycle on the application of a constant voltage (1.2 V), the effluent conductivity
289 decreases sharply and then increases over time as the electrodes saturate. During the desorption
290 cycle (0.0 V), the effluent conductivity rises sharply and then again decreases as it returns to the
291 feed conductivity. Effluent conductivity for one adsorption/desorption cycle shown in Figure 4b
292 indicates the presence of the small inverted peak at the beginning of adsorption cycle for PVDF-
293 CDI system. This has been reported previously and is known as the “inversion effect”^{13,17,38,39}
294 attributed to co-ion expulsion from the electrodes. This inversion effect leads to reduced salt
295 removal and charge efficiency. It is unclear why an inversion effect is observed for PVDF-bound
296 electrodes only, but this may indicate lower co-ion adsorption for the PVA-CDI system. Further
297 work is needed to understand the lack of an inversion peak in the PVA-bound electrodes.

298 As presented in the Figure 4c, the PVA-CDI system has a 41% higher salt adsorption capacity
299 (SAC) and average salt adsorption rate (ASAR) relative to PVDF-CDI system. Similarly, the salt
300 removal efficiency (SRE) and charge efficiency (Figure 4d) is 48% and 59% higher for the PVA-
301 CDI system. We attribute this performance difference, in part, to the minimized inversion effect
302 in the PVA-CDI system as compared to PVDF-CDI system. Cyclic voltammetry measurements
303 presented in the Supporting Information Figure S2 show a much higher specific capacitance for
304 the PVA-bound electrodes compared with PVDF-bound electrodes. Furthermore, as demonstrated
305 through water contact angle analysis (Supporting Information Figure S2), PVA bound electrodes
306 are more hydrophilic, which may lead to enhanced ion uptake. Complete performance parameter
307 values for these two systems are provided in the Supporting Information Table S4.

308 Effluent conductivity data for 24 h operation indicates a significant reduction in the
309 performance over several cycles of operation for both CDI systems (see Supporting Information
310 Figure S5 and Tables S4 and S5). Additionally, both systems produce large changes in the
311 effluent pH (Supporting Information Figure S6), consistent with the occurrence of faradic
312 reactions (anode oxidation and oxygen reduction at the cathode)^{16,17,38,40}. A high co-ion adsorption
313 for PVDF-CDI is reflected in a relatively large current supplied/discharged compared with other
314 CDI and MCDI systems, as shown in the Supporting Information Figure S7.

315 These studies demonstrate that, in addition to the straightforward and scalable fabrication
316 procedures without the use of the organic solvents, the uncoated PVA-CDI system is superior to
317 PVDF electrodes in terms of salt removal performance and charge efficiency. However, the
318 charge efficiency is low and significant long-term degradation is observed in both systems
319 (Supporting Information Table S4), which we attribute primarily to faradaic reactions.

320

321

322 **Figure 4.** Performance comparison of PVDF-CDI and PVA-CDI systems. (a) effluent
 323 conductivity over 5 cycles of operation, (b) effluent conductivity over one cycle showing the
 324 inversion effect for PVDF-CDI at the beginning of the adsorption cycle, as indicated by the circle
 325 (c) comparison of SAC and ASAR for PVDF-CDI and PVA-CDI showing a 41% higher SAC
 326 and ASAR for PVA-CDI as compared to PVDF-CDI system, and (d) salt removal and charge
 327 efficiencies for both systems with a 48% and 59% increase in salt removal and charge efficiency,
 328 respectively, for PVA-CDI system compared to PVDF-CDI system.

329

330 *Performance comparison of PVA-CDI and PVA-PC-MCDI systems*

331 Here we compare the performance of PVA-CDI and PVA-PC-MCDI systems, which contain
 332 PVA bound electrodes and are either bare (PVA-CDI) or coated with an ion-exchange polymer

333 (PVA-PC-MCDI). The electrode masses were nearly identical for these studies, 190 mg and 185
334 mg for PVA-CDI and PVA-PC-MCDI systems, respectively, resulting in a comparable thickness
335 of both electrodes.

336 Analysis of the effluent conductivity (Figure 5a and b) revealed a larger salt uptake in the case
337 of PVA-PC-MCDI. Averaged over five cycles, the amount of the salt removed per adsorption
338 cycle was 1.74 mg (29.8 μmol) and 2.66 mg (45.5 μmol) for PVA-CDI and PVA-PC-MCDI
339 systems, respectively. Furthermore, the SAC and ASAR (Figure 5c) were both higher for PVA-
340 PC-MCDI system by approximately 57%, and the SRE and charge efficiency (Figure 5d) were
341 improved by 53% and 51%, respectively for the PVA-PC-MCDI system relative to PVA-CDI
342 system. We attribute this performance enhancement to the presence of the ion exchange polymer
343 coatings. The ion-exchange polymer coatings block co-ions from penetrating the electrodes and
344 give increased salt adsorption capacity and charge efficiency^{13,17,18,38}. Notably, the salt adsorption
345 capacity of the coated PVA bound electrodes is higher than typically reported (5 -13 mg/g) in the
346 literature for other activated carbon-based electrodes^{1,5,29}. This is attributed to a combination of
347 improved wettability of the electrodes due to hydrophilic polymer binder, the high surface area of
348 activated carbon, and the presence of the ion-exchange polymer coating. Detailed performance
349 parameter values for both the systems are provided in the Supporting Information Table S4.

350 Analysis of the effluent conductivity (Supporting Information Figure S5) and effluent pH
351 (Supporting Information Figure S6) over a 24 h experiment suggest that the ion-exchange
352 polymer coatings significantly reduce the occurrence of faradic reactions¹⁶⁻¹⁸ and hence improve
353 stability and long-term performance. Long-term performance is quantified in the Supporting
354 Information Table S5, indicating slight (<5%) performance reduction for PVA-PC-MCDI system
355 over 40 cycles of operation.

Figure 5. Performance comparison of PVA-CDI and PVA-PC-MCDI systems. (a) effluent conductivity over 5 cycles of operation, (b) effluent conductivity over one cycle showing greater ion uptake for the PVA-PC-MCDI system, (c) comparison of SAC and ASAR showing a 57% higher SAC and ASAR for PVA-PC-MCDI as compared to PVA-CDI system, and (d) salt removal and charge efficiencies for both systems with a 53% and 51% increase in salt removal and charge efficiency, respectively, for PVA-PC-MCDI system compared to PVA-CDI system.

Performance comparison of PVA-PC-MCDI, PVA-MCDI and PVDF-MCDI systems

A variety of ion-exchange membranes are available commercially, and a common approach to fabricate MCDI systems is to place commercial ion-exchange membranes on top of porous electrodes. As shown in the Supporting Information Figure S1d, commercial ion-exchange membranes are as thick as the electrodes (250-300 μm), resulting in significantly increased

module size and weight. The thickness of commercial ion-exchange membranes used in this work (Membranes International Inc.) is 450 μm thick, roughly 45 times the thickness (10 μm) of the ion-exchange polymer coating. To evaluate the effectiveness of the ion-exchange polymer coating, we compared the PVA-PC-MCDI system to a similar PVA-MCDI system with PVA bound electrodes and commercial ion-exchange membranes. In addition, we compared the performance of the PVA-PC-MCDI system to PVDF-MCDI, which included commercial ion exchange membranes on top of PVDF bound electrodes.

Analysis of the effluent conductivity over 5 cycles of operation, presented in Figure 6, indicates reversible electrosorption for all the three systems. Careful analysis of one adsorption/desorption cycle (Figure 6b) indicates a higher initial salt uptake rate for the PVA-PC-MCDI system as compared to the other two systems. This suggests that the thin (10 μm) ion exchange polymer coating layer has lower area resistance ($<2.0 \Omega \text{ cm}^2$, as reported previously³²) and therefore higher initial salt uptake rates compared to the thick (450 μm) commercial ion-exchange membranes (electrical resistance approximately $30 \Omega \text{ cm}^2$).

Furthermore, the quantitative comparison of salt removal performance presented in Figure 6c and d indicates that the PVA-PC-MCDI system has a reduced SAC, ASAR, SRE, and charge efficiency when compared with the PVA-MCDI system (Supporting Information Table S4). We attribute this reduced performance (salt removal and charge efficiency) to ion leakage through the thin ion-exchange coatings, resulting in co-ion adsorption in the PVA-PC-MCDI system. In order to improve the performance of the PVA-PC-MCDI electrodes, optimization of coating layer thickness, composition (charge and crosslinking density), and uniformity is needed.

For these comparisons between MCDI systems, the adsorption capacity (SAC) was measured relative to the electrode mass excluding the mass of the ion-exchange coating or membranes. If the mass of the ion-exchange coating (20 – 30 mg) or commercial ion-exchange membrane (450

393 – 500 mg) is taken into consideration, the adsorption capacity of the PVA-PC-MCDI system is
394 significantly higher (roughly double) than that of the PVA-MCDI systems due to the added mass
395 of the commercial ion-exchange membranes. This indicates a significantly reduced system mass
396 and size when using ion-exchange polymer coatings.

397 The commercial IEMs used in this work were chosen to achieve highest possible charge
398 efficiency, dependent strongly on the permselectivity (selective transport of cations or anions
399 through ion-exchange polymer layer). For comparison, we also tested PVA-bound electrodes
400 paired with lower resistance membranes (ASTOM-Neosepta CMX, thickness 170 μm , electrical
401 resistance 3.0 $\Omega\text{ cm}^2$). The results presented in the Supporting Information Figure S8 show an
402 even higher salt adsorption capacity and similar charge efficiency, 18.2 mg/g and 95 %,
403 respectively. This demonstrates the exceptional performance of PVA-bound electrodes and
404 suggests significant room for further improvement of the PVA-PC-MCDI system. We also note
405 that the initial uptake rate of the PVA-PC-MCDI system is still higher than that of the PVA-
406 MCDI system with the low resistance ion-exchange membranes.

407 Finally, the effluent conductivity (Supporting Information Figure S5) and effluent pH
408 (Supporting Information Figure S6) indicate a very stable performance for all the three systems.
409 This suggests little or no faradaic in all MCDI systems. Detailed performance results for the long-
410 term operation are provided in the Supporting Information Tables S4 and S5.

Figure 6. Performance comparison of PVA-PC-MCDI, PVA-MCDI and PVDF-MCDI systems.

(a) effluent conductivity over 5 cycles of operation, (b) effluent conductivity over one cycle

showing the higher initial ion uptake rate for the PVA-PC-MCDI system, (c) SAC and ASAR for

all systems showing a 11% lower SAC and ASAR for PVA-PC-MCDI as compared to PVA-

MCDI system, and (d) salt removal and charge efficiencies for the three systems indicating a 13

% reduction in salt removal and charge efficiency for PVA-PC-MCDI system compared to PVA-

MCDI.

In summary, we demonstrated a simple and scalable aqueous-based approach for the preparation of electrodes using activated carbon and water-soluble PVA binder without the use of organic solvents. The as-fabricated electrodes were further coated with aqueous solutions of sulfonated (cation exchange) and aminated (anion exchange) polymers to produce MCDI system. Desalination tests for the polymer coated electrodes exhibit salt adsorption capacities up to 14.4

424 mg/g and charge efficiencies up to 86.3%. Furthermore, PVA binder-based electrodes exhibited
425 an adsorption capacity and charge efficiency of 16.1 mg/g and 97.1%, respectively, when paired
426 with commercial ion exchange membranes (Supporting Information Table S4). PVA-bound
427 electrodes exhibited salt uptake capacities exceeding 18.0 mg/g when paired with low-resistance
428 commercial ion-exchange membranes. Notably, the obtained salt adsorption capacities and charge
429 efficiencies are higher than typically achieved for activated carbon electrodes with a hydrophobic
430 polymer binder. Further optimization of the coating layer composition, thickness, charge density,
431 and uniformity can produce additional increases in both the charge efficiency to be comparable to
432 commercial ion-exchange coatings (90-95%) and salt adsorption capacities increasing to 17-20
433 mg/g based on the increase in charge efficiency. This work demonstrates a straightforward
434 approach to the fabrication of high-capacity electrodes for MCDI applicable for the treatment and
435 reuse of brackish and industrial wastewater.

436

437 **Associated Content**

438 **Supporting Information.** Details on electrode fabrication, additional electrochemical
439 characterization, surface energy measurements, detailed data on effluent conductivity, pH, current
440 and CDI performance metrics are provided in the Supporting Information. This information is
441 available free of charge via the Internet at <http://pubs.acs.org>.

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447 **Funding Sources**

448 National Science Foundation (NEWT EEC-1449500, CBET-1604666) and the Welch Foundation
449 for Chemical Research (C-1888).

450 **ACKNOWLEDGEMENT**

451 This work was supported by the National Science Foundation Nanosystems Engineering
452 Research Center for Nanotechnology Enabled Water Treatment (NEWT EEC 1449500), NEWT
453 Center Research Experience for Undergraduates EEC-1449500, National Science Foundation
454 CBET-1604666, and the Welch Foundation for Chemical Research (C-1888),

455 **ABBREVIATIONS**

456 Various CDI configurations used in this work

457 PVDF-CDI: Bare activated carbon electrode with PVDF binder

458	PVDF-MCDI:	Bare activated carbon electrode with PVDF binder and commercial ion-
459		exchange membranes
460	PVA-CDI:	Bare activated carbon electrode with PVA binder
461	PVA-MCDI:	Bare activated carbon electrode with PVA binder and commercial ion-
462		exchange membranes
463	PVA-PC-CDI:	Polymer coated activated carbon electrode with PVA binder

464

465 CDI, Capacitive Deionization; MCDI, Membrane Capacitive Deionization; SAC, Salt Adsorption
 466 Capacity; ASAR, Average Salt Adsorption Rate; SRE, Salt Removal Efficiency; CE, Charge
 467 Efficiency; PVA, Polyvinyl Alcohol; SSA, Sulfosuccinic Acid; GA, Glutaraldehyde; QPVA,
 468 Quarternized Polyvinyl Alcohol; IEM, Ion-exchange Membrane; GTMAC,
 469 glycidyltrimethylammonium chloride.

470

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577 TOC Graphic

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