UC Berkeley
UC Berkeley Previously Published Works

Title
Additive Manufacturing of Electrodes for Desalination

Permalink
https://escholarship.org/uc/item/2kp1k3v0

Authors
Tsai, Shao-Wei
Kumar, Arkadeep
Kalyan, Bavisha
et al.

Publication Date
2019

DOI
10.1016/j.promfg.2019.06.147

Peer reviewed

47th SME North American Manufacturing Research Conference, Penn State Behrend Erie, Pennsylvania, 2019

Additive Manufacturing of Electrodes for Desalination

Shao-Wei Tsai [a,b,#], Arkadeep Kumar [b,c#] *, Bavisha Kalyan [c], Chia-Hung Hou [a],

Pen-Chi Chiang [a], Ashok J. Gadgil [b,c]

[a] Graduate Institute of Environmental Engineering, National Taiwan University, No.1, Sec. 4. Roosevelt Rd., Taipei 10617, Taiwan
[b] Energy Technologies Area, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, United States
[c] Department of Civil and Environmental Engineering, University of California, Berkeley, California 94720, United States
* Corresponding author. Tel.: +1-404-834-5317; E-mail address: arkadeepkumar@lbl.gov
# first two authors equally contributed to the paper

Abstract

Capacitive deionization (CDI) is an energy-efficient process for desalination of brackish (low-salinity) waters, and will be able to meet the freshwater demands of agriculture, industry, and potable water. One of the key challenges in widespread adoption of CDI is mechanical reliability of the electrodes manufactured by additive manufacturing processes. Mechanical reliability of electrodes depends on the optimal chemical composition of activated carbon-based electrode material. Traditional materials used for CDI electrodes are known to have adverse environmental effects from solvents such as N-Methyl-2-pyrrolidone (NMP) and Dimethyl sulfoxide (DMSO), and fluorine containing binders such as polyvinylidene difluoride (PVDF). In this paper we present (1) electrodes based on 'green chemistry' with reduced environmental impact, (2) stable chemical composition of electrodes with required mechanical reliability. We present the alternative CDI electrode composition using activated carbon, toluene as solvent, and polyvinyl butyral (PVB) as binder. We also mixed ion-exchange resins to produce composite electrode materials with toluene and PVB, which showed similar salt removal characteristics as composite electrodes with PVDF and NMP. Thus, the new electrode composition is a viable alternative for sustainable additive manufacturing of CDI electrodes with mechanical reliability and reduced environmental impact.

1. Introduction

Climate change and population growth will lead to severe freshwater shortages globally [1, 2]. The issue disproportionately affects populations in lower-income countries, with the poorest among them being worst affected. Hence, there is a critical need to design and develop affordable solutions that generate new freshwater supplies from currently unused water sources. One such widely dispersed, potentially new source of water is low salinity brackish water. Brackish water is considerably lower in salinity than seawater and is found in vast amounts around the world [3]. Hence treatment of brackish water can provide a new source of freshwater to address the growing water demands [4]. Capacitive deionization (CDI) has emerged as the energy and cost-

efficient technology for desalination of brackish water with low or moderate salt content. CDI consists of two steps: (1) Ion electrosorption or charging, which immobilizes ions in porous electrodes and results in deionized water (2) Ion desorption, where ions are released into a saturated brine solution, and electrodes are regenerated. Figure 1 shows a schematic of the standard CDI process.

From the classical work in CDI which started years ago in the 1960s [5], CDI methods have evolved, to include ion-exchange thin membrane barriers in front of the electrodes to reduce the unwanted co-ion adsorption. Substantial research has been done on membrane-CDI, such as prior work by Andelman et al.[6] and Biesheuvel et al. [7]. Membrane CDI or m-CDI system also increased salt removal efficiencies from

32.8-55.9% (CDI) to 83.9-91.3% (m-CDI) [8] [9-18] [10] [19-21]. However, membranes increase the cost and hence the affordability of the CDI process. In this paper, we restrict ourselves to non-membrane configurations of CDI, and introduce a new composite electrode material with ion-exchange resins mixed with activated carbon.

With the increase in demand for freshwater throughout the world, the demand for energy has also increased because of energy intensive water treatment processes such reverse osmosis, thermal methods such as multi-stage flash (MSF), Multi Effect Distillation (MED), and electrodialysis (ED) [22]. In comparison, capacitive deionization (CDI) has been regarded as a potential alternative method with reduced energy demands for low-salinity brackish water desalination [3, 23, 24]. Figure 2 shows the graph of reduced energy consumption in CDI versus reverse osmosis, with significant reduced energy consumption at low salinity brackish waters (1000 to 10,000 ppm of salt in water) which is widely available [3, 23]. Thus, CDI has the potential as a future technology in the Water-Energy nexus for highly energy efficient and affordable brackish water desalination [3, 24].

One of the key challenges in realizing CDI as a technology at scale is the mechanical reliability of the carbon electrodes made for CDI using additive manufacturing processes. These electrodes are made of activated carbon, mixed with a binder and solvent and then additively manufactured on current collectors (metal plates). The electrodes are further heat-treated over certain time to allow the binder and solvent polymerize with the carbon, and then remove the excess solvent through evaporation. First, these electrodes often lack mechanical reliability, with failure modes such as fracture and delamination/peeling from the backing substrate metal and swelling of the electrode while being used. Secondly, the materials used in the manufacturing of these carbon-based CDI electrodes are known to have adverse environmental effects, and is not sustainable for the future [4]. Hence, there is an urgent need of research on new electrode material compositions which manufacture electrodes with (1) mechanical reliability (2) reduced impact on the environment. Such innovations would lead to manufacturing sustainability for both the *product sustainability* by reduced mechanical failure of electrodes, and manufacturing *process sustainability* using less harmful chemicals. Additionally recent manufacturing research has aimed to incorporate principles of "green chemistry" for sustainability in manufacturing, taking into consideration the 4 E's of green chemistry, which are Environment, Economics, Energy (consumption) and Engineering [4].

The mechanical reliability of the electrode is determined by the durability of the carbon-based material throughout the manufacturing process and lifetime (casting, drying, and usage). The ratio and type of solvent, binder, and carbon are all factors which affect the reliability of the electrode. Thus, our research is motivated by the need to manufacture CDI electrodes which are mechanically reliable and also reduce the environmental footprint, and provide affordable and energy-efficient method of desalination of low-salinity brackish waters to meet the demands for freshwater in future.
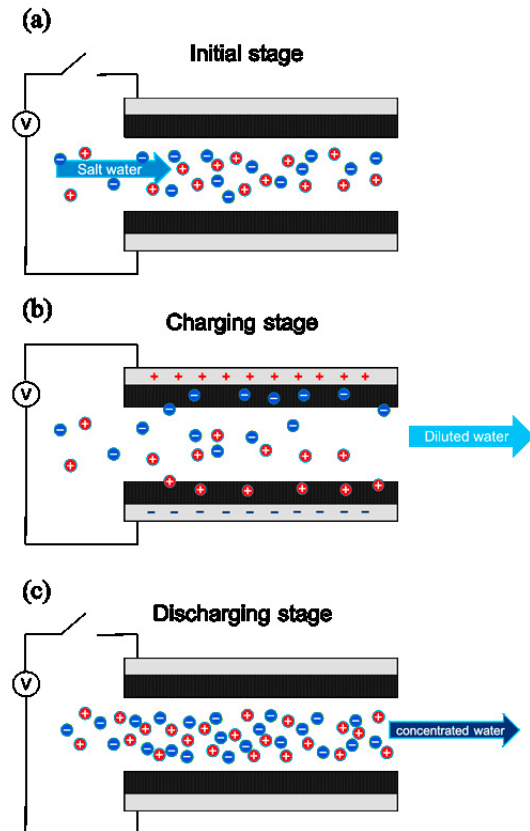

Figure 1. Schematic of the desalination and regeneration process by capacitive deionization. (a) Initial stage has salt water coming in between the electrodes which are similar to parallel plate capacitor. (b) During charging, electrosorption of the positively and negatively charged ions occur, leading to desalination and clean water as output, (c) During discharging, ions are released from the electrodes to regenerate the electrodes resulting in concentrated brine as output.

CDI electrodes are generally made with activated carbon mixed with solvents such as N-Methyl-2-pyrrolidone (NMP) and Dimethyl sulfoxide (DMSO) and binders such as polyvinylidene difluoride (PVDF) such as those given by studies by Porada et al. [25, 26] and previous work by the authors [4, 27]. The manufacturing processes using these solvents and binder compositions are not environmentally friendly. First, we aimed to find solvents which have reduced impact on the environment, such as Ethanol and Toluene [4]. Second, we wanted to avoid fluorine containing binders such as polyvinylidene difluoride (PVDF) by using alternatives such as Polyvinyl Alcohol (PVA) and Polyvinyl Butyral (PVB). Based on some initial trial experiments, we finalized PVB as the possible alternative binder to PVDF. Prior research on heterogeneous ion-exchange membranes in electrodialysis has shown that polarity match of solvent and binder combination is critical for additive blending of the components [28-30]. We build on the knowledge of ion-exchange membranes in prior literature, and translated to activated carbon electrodes in CDI, and investigate ethanol and toluene as possible solvents which can combine with PVB as the binder for reliable electrodes. We hypothesized that using a compatible binder-solvent with matching polarity will produce adequate polymerization and strong bonds within the solvent-binder matrix along with the

activated carbon, resulting in CDI electrodes with mechanical reliability. Moreover, the chemicals in the new formulation are expected to have reduced environmental impact than the conventional formulation of CDI electrodes using NMP and PVDF as found in prior literature [4].
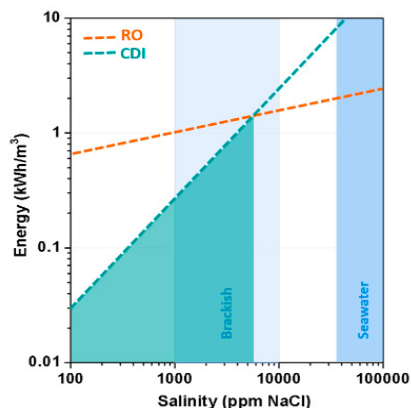

Figure 2. Energy consumption increases with salinity for both CDI and RO processes, however with low salinity brackish water (less than 1000 to 10,000 ppm of salt), CDI has potential to be more energy efficient than RO [23].

After finding the optimal combination of solvent and binders with activated carbon for pure carbon electrodes, we incorporated commercially available ion-exchange resins (IERs) into the matrix to produce composite electrodes, to improve salt-capture. Mixing of ion-exchange resins promises of passive desalination without application of energy, and active regeneration by applying a small voltage, called Electrically Regenerated Ion-Exchange or ERI (patent filed in 2017, Gadgil et. al) and is expected to produce more energy efficient desalination process. Finally, we compare the desalination performance of the carbon-resin composite electrodes with the new and conventional solvent-binder combination. We run the capacitive deionization cell with applied voltage 1.2 V and regeneration at 0 V. Researchers have used a range of voltages which affect salt absorption capacity, but high voltages may also cause water splitting or faradaic reactions [13, 25, 26, 31]. To quantify the desalination performance, we compare the metrics of salt absorption capacity (SAC) of these electrodes for different electrode formulations. Salt absorption capacity (SAC) of the electrodes is defined as amount of salt in milligrams captured per unit grams of the electrode material.

In this paper, we present the results of additive manufacturing of an optimized activated carbon-binder-solvent composition of the electrode (carbon-toluene-PVB) which produces similar salt absorption capacity as traditional electrodes (carbon-NMP-PVDF), but alternative chemicals reduce environmental impact following green chemistry. In the following sections, we describe the experimental methods, present the results of electrode material characterization and desalination tests, and discuss the implications of our findings for additive manufacturing of CDI electrodes.

2. Experimental Methods

CDI electrodes are made with activated carbon, a binder,

and a solvent mixture applied to substrate (current collector) metal plate by additive manufacturing. As the first step, the binder-solvent solution was made by using binder (PVB or PVDF) with the solvent (Ethanol, Toluene, NMP) in 1:10 weight by volume ratio. As an example, we used 0.4 gm PVB with 4 ml of the solvent Toluene. Next, the glass beaker containing the binder-solvent mixture was put on a stir plate with a magnetic stirrer for a minimum of 2 hours to ensure a homogenous mixture. We took care to have uniform non-turbulent mixing by adjusting the magnetic stirrer intensity. Next, activated carbon is slowly mixed with the solvent-binder solution. This mixture is allowed to mix uniformly by stirring for 1 more hour on the stir plate. The mixing time for the carbon slurry was set as 1 hour to ensure the polymerization of the binder-solvent among the activated carbon particles. To note, this mixing procedure was followed for the pure-carbon electrodes.

For the composite carbon electrodes with ion-exchange resins, the results were best-achieved by mixing the solid binder and milled ion-exchange resins *in dry conditions*, before wetting in the solvent. The ion-exchange resins were milled in a ball-milling machine for 15 minutes total with three steps of 5 minutes milling time in each step. This method of intermittent milling was done to avoid the polymer ion-exchange resins from melting, which we observed in case of continuously milling for longer time such as 15 minutes. Figure 3 shows the progression of the size of the milled resins along with milling time, larger sized particles were along the wall of the container. To note, there are two types of ion-exchange resins, Cation Ion-Exchange Exchange (CER) and Anion Ion-Exchange Resin (AER) for the cathode and anode respectively. After mixing the powders uniformly in solid state, they are dissolved and stirred in the solvent for a minimum of 2 hours as mentioned for the pure-carbon case. After uniformly mixing, carbon was added to the solvent-binder-resin mixture, and stirred for 1 more hour on the stir plate. The next step of casting the electrodes is done only after all the components are mixed uniformly.
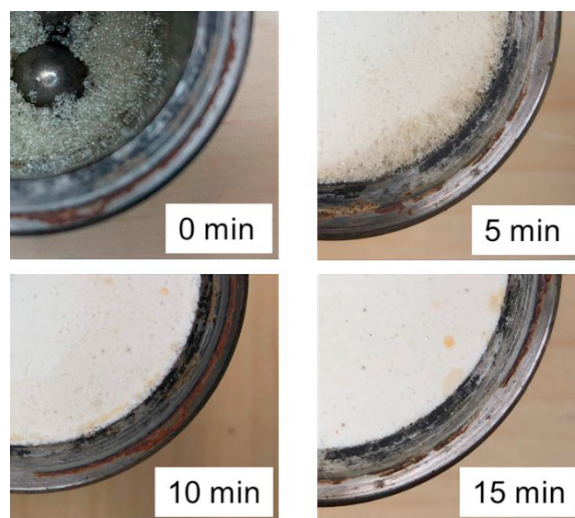

Figure 3. Progression of the ion-exchange resins size along with milling time from 0 minute to 15 minutes, in 5 minute intervals of ball milling.

The general mixture of the activated carbon weight to binder

weight is 9:1 (gm:gm) by weight ratio, and total weight of activated carbon and binder to volume of solvent is 1:3 (gm:mL). This mixture is coated on titanium current collector plates at a height of 150 micrometers. We use a manual doctor blade (Tester Sangyo CO., LTD, Japan) to ensure precise control over the height of the electrode. The doctor blade allows precise control of the height using a micrometer screw gauge as shown in figure 4a. The mixture of activated carbon is supplied to the top of the substrate metal (Titanium current collector) at regular intervals while the doctor blade moves over the plate to spread the mixture. The doctor blade is moved perpendicular to the sharp edge. In Figure 4a, the blade is moved from bottom of the image towards the top, as shown by the blue arrow, completing the casting of the carbon slurry on the metal. After the electrodes are additively manufactured by the doctor blade, they are dried in the heating oven at 80 °C for 2 hours to evaporate the solvent. After the solvent is completely dried, the electrode is cut to size of the active area (Figure 4b). By this method of additive manufacturing, a layered electrode structure can be made for membrane-based CDI electrodes.

The activated carbon used in this study is YP-50F, and the polyvinyl butyral (PVB) is Mowital-60HH, both obtained from Kuraray Chemicals. Ethanol was obtained from Sigma Aldrich and Toluene from Honeywell company. The other reagents such as PVDF and NMP used to make CDI electrodes with conventional composition, and sodium chloride (NaCl) used for the desalination experiments were obtained from Sigma Aldrich. We used commercially available ion exchange resins - AER (Amberlite® IR-402, Cl-form, strong base, gel-type) was obtained from Fluka, and the CER (Amberlite® IR 120(Na), strong acid, gel-type) was obtained from Alfa Aesar.

We first found out the effect of the solvent mixture with binder in manufacturing electrodes with higher mechanical reliability. Hence, we used the PVB binder with 3 solvent combinations: (1) ethanol, (2) ethanol and toluene (50% each) (3) toluene. The results of the electrode manufacturing are discussed in the next section. Based on these experiments, we found that the electrodes with toluene provided more mechanical reliability after the drying and evaporation of the solvent, compared to ethanol for the same PVB binder. Hence, we used toluene with PVB and activated carbon for the next experiments. We wanted to measure the performance of CDI electrodes made with the new formulation versus electrodes made using conventional formulation (NMP solvent with PVDF binder). Thus, we made a design of experiments to compare 4 electrode materials: (1) Activated carbon with PVB-Toluene, (2) Activated carbon with PVDF- NMP, (3) 25% resin mixed with activated carbon with PVB-Toluene, (4) 25% resin mixed with activated carbon with PVDF-NMP.

We performed desalination experiments with capacitive deionization for each electrode with desalination cycle of 20 minutes at 1.2 V voltage, and regeneration cycle of 20 minutes at 0 V voltage, with 3 repeated cycles. The flow rate was set as 9 mL/min for all experiments. We used a Gamry potentiostat (Interface 1000) for running the experiments. We used inlet water with a salt concentration of 250 ppm of the sodium chloride (NaCl). The NaCl solution was made by mixing 1 gm of NaCl in 4 liters of distilled water (DI). The DI water was obtained in the lab with Milli-Q system.
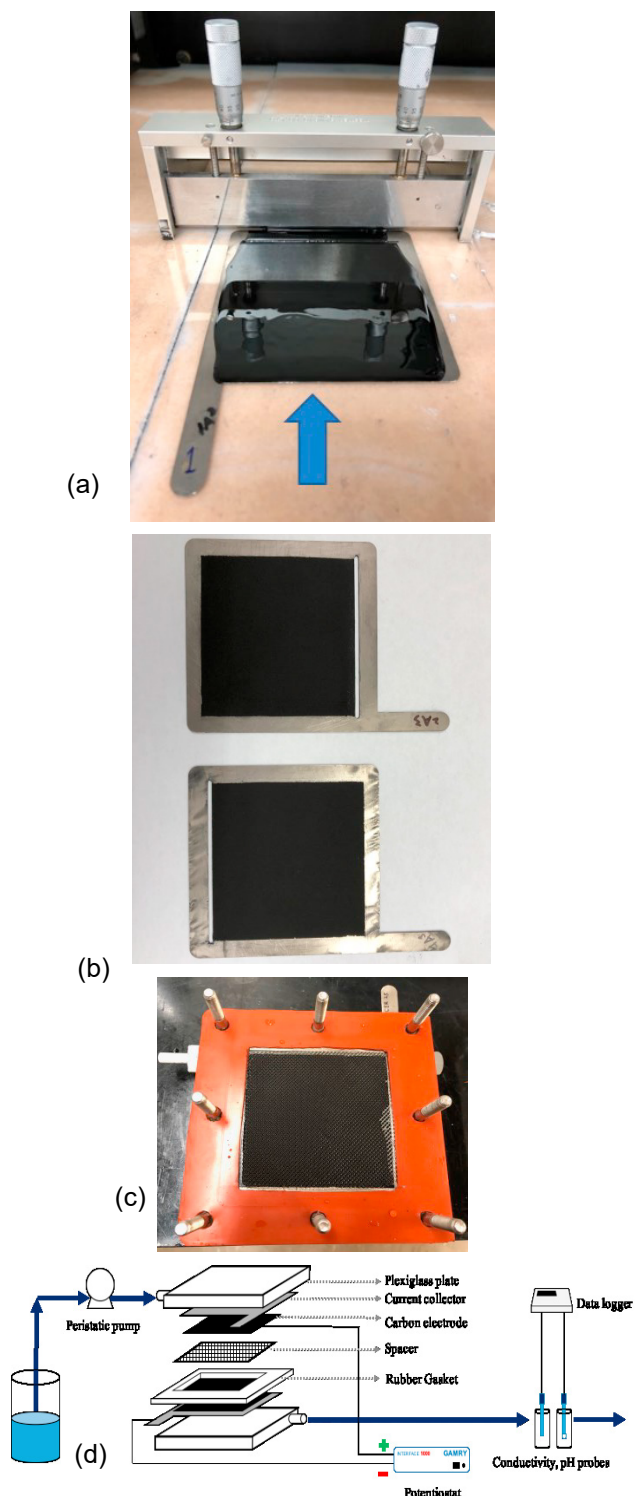

(a)

(b)

(c)

(d)

Figure 4. (a) Doctor blade used to make the electrodes with micrometer screw gauge on the top to control precisely the gap between the substrate metal and top of the blade, for the 150 micrometers thickness of the electrode; (b) Finished electrodes after doctor blading. (c) The capacitive deionization (CDI) cell (d) The schematic of the CDI setup

We used the salt adsorption capacity (SAC) to compare the performance of the electrodes in capacitive deionization process. SAC (mg/g) is defined as:

$$SAC = \frac{M}{m} \int_0^t Q(C_{feed} - C_{out}) dt$$

where M is the molecular weight of the salt (g/mol), m is the total mass of electrodes, t is the charging time, Q is the volumetric flow rate through the CDI cell, C_{feed} and C_{out} are the feed salt concentration and effluent salt concentration, respectively.

3. Results and Discussion

3. 1 Toluene as effective solvent for PVB binder and pure activated carbon

We found that the electrodes made with toluene as the solvent and PVB as the binder showed higher mechanical reliability compared to ethanol as the solvent and PVB as the binder. The electrodes using only ethanol as solvent cracked within few minutes of the manufacturing process during drying (solvent evaporation). The electrodes using 50:50 mix of ethanol and toluene also cracked on the edges, though the fracturing was less intense. However, the electrode with only toluene as solvent did not fracture at all. Hence, we found toluene as the compatible solvent with PVB binder and activated carbon, for manufacturing of CDI electrodes with mechanical reliability and avoiding NMP solvent and PVDF binder composition. Table 1 summarizes our findings about the solvent-binder compatibility.

We explain our observations from prior literature which found that solvent-binder compatibility is critical for stability of mixtures [30]. The solvent binder compatibility is important for developing the polymerization framework of the binder. From our experimental observations, we hypothesize that toluene and polyvinyl butyral (PVB) form more strong bonds and polymerization, compared to ethanol and PVB. The polymerization of PVB also depends on the polarity of the solvent, for which toluene is favorable compared to ethanol [28-30]. The rate of evaporation of toluene versus ethanol influences the stress produced on the electrodes during drying which cause fracture and peeling off. The hydrophilic and hydrophobic nature of the solvent is expected to also affect the interaction between the solvent and other components in the mixture [30]. Ethanol is hydrophilic and toluene is hydrophobic, which affects how the solvent interacts with the binder and forms the network. Based on the results of these experiments, we conducted our next experiments using the combination of toluene as the solvent and PVB as the binder.

Table 1. Comparison of mechanical reliability of electrodes using pure activated carbon with PVB binder and different solvent compositions

Solvent	100 % Ethanol	50:50 mix of Ethanol and Toluene	100% Toluene
Result	cracks immediately after drying	cracks within 3-5 minutes after drying	stable electrode

3. 2 Surface and subsurface characterization of the electrodes

The CDI process of electrosorption and regeneration depends on the surface and bulk characteristics of the carbon-based electrodes. We used high resolution scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX) to characterize the top surface and subsurface (cross-section) of electrodes. First, we investigate the microstructure of the electrodes manufactured using the new composition with activated carbon mixed with toluene and PVB, and compare to the traditional CDI electrode composition of activated carbon with NMP and PVDF.

The micro-structure of the electrodes made with the new composition of activated carbon with toluene and PVB was similar to the traditional composition of activated carbon with NMP and PVDF. Figure 5 below compares the surface morphology of the electrodes with representative SEM images at a range of magnifications (10,000X, 5000X, 2000X). We found no significant differences in surface morphology between the two electrode compositions. Multiple locations were examined to confirm our results. To note, we could not analyze the results of ethanol-PVB electrodes since that composition did not produce a stable electrode without fracture.
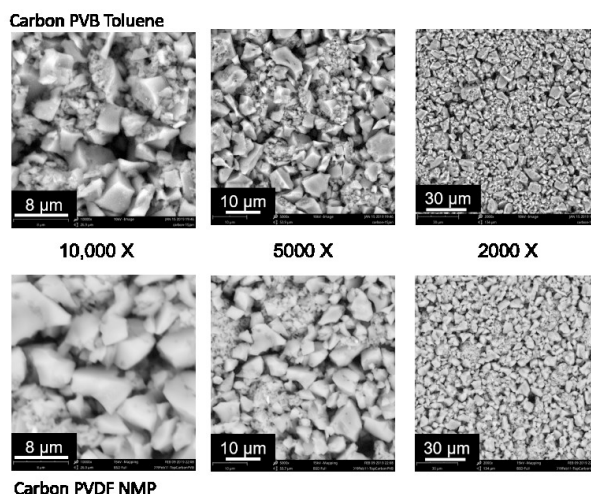

Figure 5. SEM of the pure carbon-PVB-Toluene electrode (top row) and pure carbon-PVDF-NMP electrode (bottom row) showing similar surface morphology at a range of magnifications from high (10,000X), middle (5000X) and low (2000X).

For the carbon-resin composite electrodes, we took the EDX of the surface to find the spatial distribution of the milled resin particles. Figure 6 shows the SEM and corresponding EDX of the cation exchange resin (CER) composite electrode with PVB and Toluene. The CER has the sulfonic group which attracts the sodium (Na^+) ions. Hence, the EDX elemental map scan shows sulfur (S) from sulfonic functional group marked by yellow, co-located with sodium (Na^+) marked by red (see Figure 6). Figure 7 shows the anion-exchange resin electrode (AER) with PVB-Toluene composition. AER has the ammonium group which attracts the chloride (Cl^-) ion. Hence, the EDX elemental map scan shows that nitrogen marked by

purple from the ammonium functional group co-located with chloride (Cl⁻) ion marked by blue (See Figure 7).

For the cross-section characterization, we show representative images for the distribution of the ion-exchange resins in the carbon-resin composite electrodes, which are expected to influence the ion-absorption characteristics. Figure 8 shows the cross-section SEM and EDX results of the CER with PVB-toluene and with PVDF-NMP combinations for the electrode material. We found that the ion exchange resins were more uniformly distributed in case of the PVB-toluene electrode compared to PVDF-NMP (comparing composite electrode with CER as representative results). More research is needed to understand if such differences in distribution of the resins in composite electrodes can have significant effect on the ion absorption differences.

Figure 8. Figure 7. Cross section EDX of the carbon-resin composite containing the cation exchange resin (CER) compares the electrode composition of PVB-Toluene and PVDF-NMP. The functional group is sulfonic and marked by yellow on the micrographs and EDX maps, carbon is marked by green. The distribution of the sulfonic groups shows some differences between the two electrode formulations.
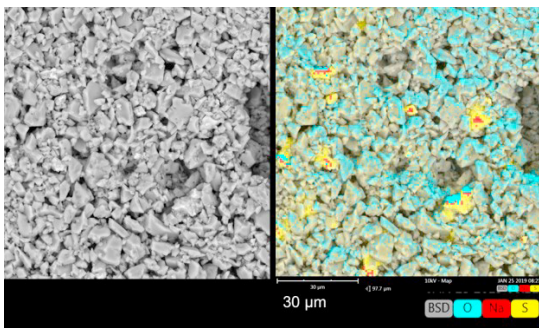

Figure 6. SEM EDX of the carbon-resin composite with PVB-toluene containing the cation exchange resin (CER) shows sulfur (S) ions co-located with the sodium (Na) ions, since the sulfonic groups are the responsible for cation exchange. The magnification was chosen to have a representative area which shows the resin particles distinctly with the carbon composite.

3.3 Desalination characteristics of the electrodes

In this section, we present the results of desalination using the electrodes we made with carbon-resin composite material, mixed with anion exchange resin (AER) or cation exchange resin (CER). Desalination characteristics were measured by concentration of salts in the effluent of the CDI process. Since concentration is difficult to measure and monitor during the desalination process dynamically, conductivity is used as a proxy of the concentration of salts in the water. Conductivity is measured using sensors in the output stream of the capacitive deionization (CDI) cell, which is shown in Figure 4c and Figure 4d. Conductivity decreases when salt is adsorbed on the electrodes during charging step, and increases when salt is discharged from the electrodes during regeneration or discharging step. The results of change in effluent concentration during the desalination step by resin-mixed carbon composite electrodes is shown in Figure 9.

The normalized effluent concentration is plotted in Figure 9 to compare the desalination performance of the two cases using ion-exchange resins (25% by weight) mixed with PVB as the binder and toluene as the solvent, and ion-exchange resins (25% by weight) mixed with PVDF as binder and NMP as solvent.
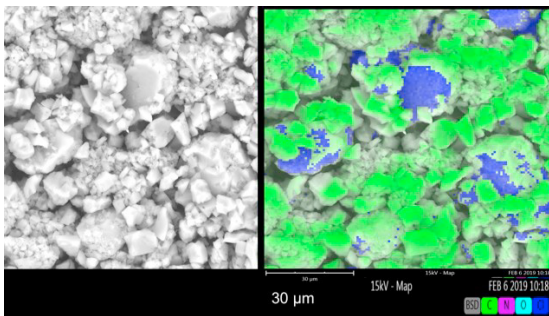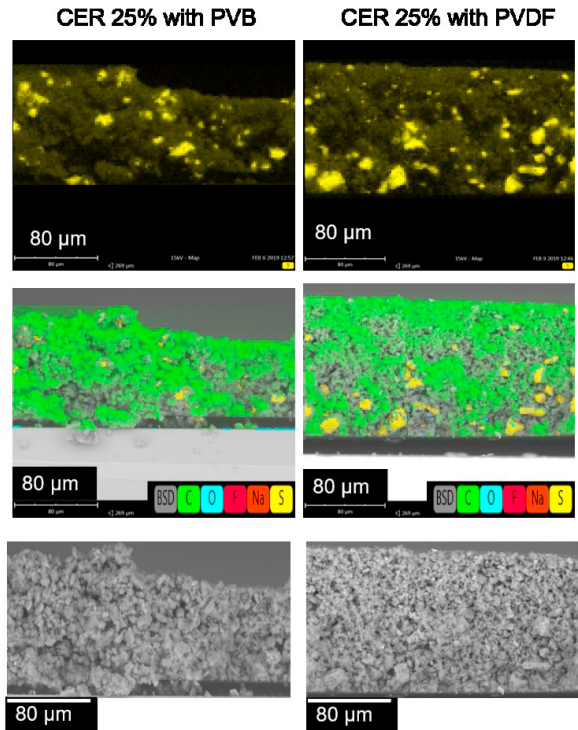

Figure 7. SEM EDX of the carbon-resin composite with PVB Toluene containing the anion exchange resin (AER) shows the ammonium group with Nitrogen (N) co-located with Chloride (Cl), which are shown by the EDX map scan. The magnification was chosen to have a representative area which shows the resin particles distinctly with the carbon composite material.
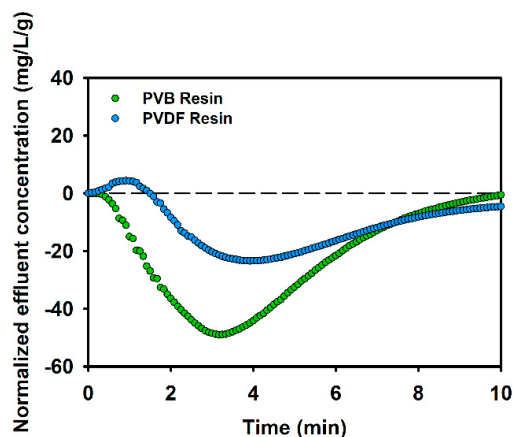
Figure 9. Effluent concentration normalized by the weight of the electrode, to compare the desalination characteristics of the electrodes –25% resin mixed carbon with PVB and toluene, and 25% resin mixed carbon with PVDF and NMP.

We showed that the electrodes manufactured using the new composition of PVB as binder and toluene as solvent had the required mechanical reliability. Moreover, the new electrode formulation resulted in salt absorption capacity (SAC) similar to the electrodes produced by conventional composition of PVDF binder and NMP solvent. The SAC was calculated by numerically computing the area under the conductivity versus time curve (similar to the graph of concentration versus time curve in Figure 9) in the charging or desalination step. The results of salt capture came comparable to the 1-3 mg/g range of values found in CDI by other researchers and reported in literature [25, 26]. The SAC values for the resin mixed with PVB-toluene and resin mixed with PVDF-NMP is summarized in Figure 10. We hypothesize that the variation in the salt absorption capacity between these two cases are caused by the differences in distribution of the resins in composite electrodes.
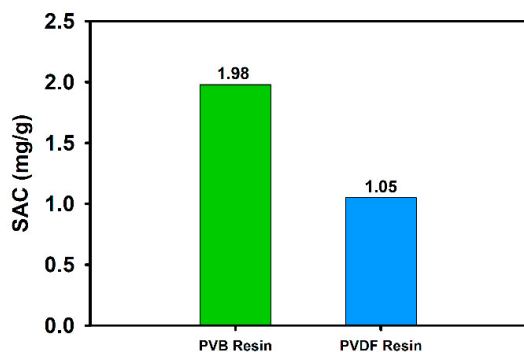

Figure 10. Salt absorption capacity calculated for the two electrodes- 25% resin mixed carbon with PVB and toluene, and 25% resin mixed carbon with PVDF and NMP.

The results from this study will be applicable for future development of stable and reliable electrodes for CDI, using chemicals which have reduced adverse effects on the environment.

4. Conclusions

To address the challenges in additive manufacturing of electrodes for capacitive deionization (CDI), we had two aims for manufactured electrodes: (1) using materials with reduced adverse effects on the environment (2) having the mechanical strength and reliability to prevent failure (fracture). We found that a new electrode composition with toluene as the solvent and polyvinyl butyral (PVB) as the binder mixed with activated carbon addressed these challenges. The electrodes manufactured using toluene and PVB with activated carbon was mechanically reliable, and uses chemicals with reduced adverse effects on the environment, based on the principles of green chemistry, compared to NMP and PVDF. We also used ion-exchange resins mixed with activated carbon, to produce composite electrode materials. The ion-exchange resins composite electrode with toluene as solvent and PVB as binder showed salt absorption capacity similar to the ion-exchange resins composite electrode with NMP as the solvent and PVDF as the binder. Hence, toluene-PVB resin composite electrodes could be a viable option for sustainable additive manufacturing of CDI electrodes with required mechanical reliability.

5. Acknowledgements

References

[1]   A. Baker, "Cape Town Is 90 Days Away From Running Out of Water," *http://time.com/5103259/cape-town-water-crisis/,* vol. Accessed Feburary 2019, 2018.

[2]   C. J. Vörösmarty, P. Green, J. Salisbury, and R. B. Lammers, "Global water resources: vulnerability from climate change and population growth," *Science,* vol. 289, no. 5477, pp. 284-288, 2000.

[3]   J. J. Urban, "Emerging scientific and engineering opportunities within the water-energy nexus," *Joule,* vol. 1, no. 4, pp. 665-688, 2017.

[4]   T.-H. Yu, H.-Y. Shiu, M. Lee, P.-T. Chiueh, and C.-H. Hou, "Life cycle assessment of environmental impacts and energy demand for capacitive

deionization technology," *Desalination,* vol. 399, pp. 53-60, 2016.

[5]   D. D. Caudle, *Electrochemical demineralization of water with carbon electrodes*. US Dept. of the Interior;[for sale by the Superintendent of Documents, US Govt. Print. Off.], 1966.

[6]   M. D. Andelman, "Flow-through capacitor," ed: Google Patents, 1993.

[7]   P. Biesheuvel and A. Van der Wal, "Membrane capacitive deionization," *Journal of Membrane Science,* vol. 346, no. 2, pp. 256-262, 2010.

[8]   L. Wang *et al.*, "Capacitive deionization of NaCl solutions using carbon nanotube sponge electrodes," *Journal of Materials Chemistry,* vol. 21, no. 45, pp. 18295-18299, 2011.

[9]   N. Pugazhenthiran *et al.*, "Cellulose derived graphenic fibers for capacitive desalination of brackish water," *ACS applied materials & interfaces,* vol. 7, no. 36, pp. 20156-20163, 2015.

[10] W. Zhang and B. Jia, "Toward anti-fouling capacitive deionization by using visible-light reduced TiO2/graphene nanocomposites," *MRS Communications,* vol. 5, no. 4, pp. 613-617, 2015.

[11] B. Jia and W. Zhang, "Preparation and Application of Electrodes in Capacitive Deionization (CDI): a State-of-Art Review," *Nanoscale research letters,* vol. 11, no. 1, p. 64, 2016.

[12] J. Zhang, K. B. Hatzell, and M. Hatzell, "A combined heat and power driven membrane capacitive deionization system," *Environmental Science & Technology Letters,* 2017.

[13] D. He, C. E. Wong, W. Tang, P. Kovalsky, and T. D. Waite, "Faradaic reactions in water desalination by batch-mode capacitive deionization," *Environmental Science & Technology Letters,* vol. 3, no. 5, pp. 222-226, 2016.

[14] Y.-J. Kim and J.-H. Choi, "Enhanced desalination efficiency in capacitive deionization with an ion-selective membrane," *Separation and Purification Technology,* vol. 71, no. 1, pp. 70-75, 2010.

[15] Y.-J. Kim, J. Hur, W. Bae, and J.-H. Choi, "Desalination of brackish water containing oil compound by capacitive deionization process," *Desalination,* vol. 253, no. 1, pp. 119-123, 2010.

[16] Y.-J. Kim and J.-H. Choi, "Selective removal of nitrate ion using a novel composite carbon electrode in capacitive deionization," *Water research,* vol. 46, no. 18, pp. 6033-6039, 2012.

[17] C. J. Gabelich, T. D. Tran, and I. M. Suffet, "Electrosorption of inorganic salts from aqueous solution using carbon aerogels," *Environmental science & technology,* vol. 36, no. 13, pp. 3010-3019, 2002.

[18] P. Xu, J. E. Drewes, D. Heil, and G. Wang, "Treatment of brackish produced water using carbon aerogel-based capacitive deionization technology," *Water research,* vol. 42, no. 10, pp. 2605-2617, 2008.

[19] W. Zhang, M. Mossad, and L. Zou, "A study of the long-term operation of capacitive deionisation in inland brackish water desalination," *Desalination,* vol. 320, pp. 80-85, 2013.

[20] M. Mossad and L. Zou, "Study of fouling and scaling in capacitive deionisation by using dissolved organic and inorganic salts," *Journal of hazardous materials,* vol. 244, pp. 387-393, 2013.

[21] C.-H. Hou, N.-L. Liu, and H.-C. Hsi, "Highly porous activated carbons from resource-recovered Leucaena leucocephala wood as capacitive deionization electrodes," *Chemosphere,* vol. 141, pp. 71-79, 2015.

[22] T. Humplik *et al.*, "Nanostructured materials for water desalination," *Nanotechnology,* vol. 22, no. 29, p. 292001, 2011.

[23] Y. Oren, "Capacitive deionization (CDI) for desalination and water treatment—past, present and future (a review)," *Desalination,* vol. 228, no. 1-3, pp. 10-29, 2008.

[24] M. Qin *et al.*, "Comparison of energy consumption in desalination by capacitive deionization and reverse osmosis," *Desalination,* vol. 455, pp. 100-114, 2019.

[25] S. Porada, R. Zhao, A. Van Der Wal, V. Presser, and P. Biesheuvel, "Review on the science and technology of water desalination by capacitive deionization," *Progress in Materials Science,* vol. 58, no. 8, pp. 1388-1442, 2013.

[26] M. Suss, S. Porada, X. Sun, P. Biesheuvel, J. Yoon, and V. Presser, "Water desalination via capacitive deionization: what is it and what can we expect from it?," *Energy & Environmental Science,* vol. 8, no. 8, pp. 2296-2319, 2015.

[27] Y.-H. Liu, T.-C. Yu, Y.-W. Chen, and C.-H. Hou, "Incorporating Manganese Dioxide in Carbon Nanotube–Chitosan as a Pseudocapacitive Composite Electrode for High-Performance Desalination," *ACS Sustainable Chemistry & Engineering,* vol. 6, no. 3, pp. 3196-3205, 2017.

[28] D. Ariono and I. Wenten, "Heterogeneous structure and its effect on properties and electrochemical behavior of ion-exchange membrane," *Materials Research Express,* vol. 4, no. 2, p. 024006, 2017.

[29] I. G. Wenten and Khoiruddin, "Recent developments in heterogeneous ion-exchange membrane: Preparation, modification, characterization and performance evaluation," *Journal of Engineering Science and Technology,* vol. Vol. 11, no. No. 7, pp. 916-934, 2016.

[30] A. C. Young, L. Jane-Chyi, Y. Tsung-Shou, and C. Chian-Lii, "Characteristics of tape casting slurries containing forsterite, PVB and organic solvent," *Materials chemistry and physics,* vol. 34, no. 2, pp. 147-153, 1993.

[31] C. Zhang, D. He, J. Ma, W. Tang, and T. D. Waite, "Faradaic reactions in capacitive deionization (CDI)-problems and possibilities: A review," *Water research,* vol. 128, pp. 314-330, 2018.