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A Review: Flow Electrode Capacitive Deionization for Improved Electrochemical Water Desalination

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A review: flow electrode capacitive deionization for improved electrochemical water desalination

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ABSTRACT: In many places of the world people have continued to suffer from major droughts and water shortages. With climate change climbing in intensity, these dry conditions will only worsen. With much of the world's water in the ocean, both saltwater and brackish water have been identified as key water sources. Currently, there are several technologies available for water desalination and treatment such as reverse osmosis, capacitive deionization, electrodialysis, and flow electrode capacitive deionization. This paper will briefly review each of these technologies and propose a new design to improve the current flow electrode capacitive deionization architecture. The new design uses a current collector flow-electrode architecture that has the potential to achieve record thermodynamic energy efficiencies. This formulation is proprietary to Lawrence Livermore National Laboratory. IM release number: LLNL-TR-839527.

INTRODUCTION

One out of seven people worldwide still do not have access to clean water, a basic human right acknowledged by the United Nations.[1] With climate change becoming more severe and droughts extending indefinitely, water has become a sacred resource. Climate change is reducing the predictability of water availability and affecting the water quality around the world.[2] Many countries and people suffer from inadequate access to clean potable water and poor sanitation. Not only will we see the scarcity of water directly affect humans and human health, water scarcity will also affect the agricultural sector (i.e., soil properties, crop yields, and crop nutrients), natural ecosystems (i.e., wetlands) and their biodiversity.[3] Yet, global water usage has increased by a factor of six over the past century and is not slowing down any time soon.[2]

Several global organizations have identified two sources that could help remediate the global water crisis: saltwater and wastewater.[4,5] Most of the water (96.5%) on Earth is located in the oceans and seas and has salinity levels around 30,000-45,000 mg/L of total dissolved solids (TDS).[6] However, saltwater desalination plants will mostly affect and benefit coastal societies. The other source of potential water is brackish water which contains more salts than freshwater but less salts than seawater and can be sourced from waste water, estuaries, or groundwater.[6] Brackish water has flexible saline water concentrations ranging from 3000 to 30000 mg/L and lacks the suspended sediment content that is present in seawater which is less costly to treat. Brackish groundwater is characterized by high alkalinity and high hardness due to dissolved polyvalent cations, and can also contain hazardous minerals such as arsenic, radium, uranium, and chromium which require additional treatment schemes. [7]

Water desalination technologies are important to treat brackish groundwater. While the main goal for desalination plants is to achieve water with <500 mg/L of TDS, desalination facilities can also be used to produce water for other purposes which do not need to meet drinking water standards (<1000mg/L of TDS) to help relieve the strain on the world's main freshwater sources (i.e., rivers, lakes, and reservoirs). These other purposes include irrigation water in agriculture or industrial applications such as thermoelectric power generation. Irrigation for agriculture uses around 32% of the freshwater while thermoelectric power generation uses around 45% of the freshwater available in the United States.[8]

Desalination can be broken up into two different categories, thermal processes and membrane processes. Thermal desalination includes processes such as multi-effect distillation and multi-stage flash distillation which account for 26% of the total seawater desalination capabilities.[7] For these processes, the feed solution is heated, and the vapor is condensed to produce fresh water. Today, thermal desalination development is largely focused on pairing the technology to a renewable energy source such as solar energy.[9] Now, because membrane technology has improved greatly, thermal desalination has decreased in popularity due to its high energy needs. Membrane technology includes processes such as nanofiltration and reverse osmosis which account for 60% of the total number of worldwide plants.[10] Although these processes operate at much lower energy costs compared to thermal desalination, they still consume electrical energy for the high pressure systems required for membrane desalination especially since seawater has a higher osmotic pressure. Additionally, membranes suffer from the trade-off between membrane selectivity (salt rejection) and membrane permeability (permeate flux).[6]

Other desalination techniques include electrochemical processes such as capacitive deionization (CDI) and electrodialysis (ED) which use potential differences to remove ions from the water feed solution. CDI is an emerging and promising technique for water desalination, particularly brackish water desalination, where the ions are adsorbed on the surface of charged electrode material.[11] CDI can be combined with additional membrane technology to improve water recovery and efficiency. The electrodes are also regenerative when the electrical potential is removed allowing the ions to desorb from the electrodes. Unfortunately, this process is discontinuous and can waste valuable time at an industrial scale. Electrodialysis (ED) also uses an electrical potential along with ion exchange membranes (IEMs) to generate brine and freshwater channels. However, ED is not ideal at an industrial scale yet due to high electrical energy consumption, high resistance, and membrane fouling.[12] Both technologies, CDI and ED, are less sensitive to clogging and therefore require less extensive pre-treatment.[13] Additionally they are usually run at low-pressures and room temperatures.

LLNL seeks to combine ED and CDI in flow electrode capacitive deionization (FCDI) to improve on the current thermodynamic energy efficiencies (TEEs). FCDI uses an electrical potential to separate ions through IEMs and absorb into a carbon slurry which can be regenerated like the electrodes in CDI by removing the electrical potential. FCDI is advantageous over CDI and ED because the energy use is low while also being a continuous operation with high water recovery. LLNL seeks to modify the architecture of the flow electrode to decrease resistance by increasing the contact time between the conductive carbon slurry and current collector. The purpose of this paper is to give a brief overview of current and relevant technologies and describe the new architecture we plan to use to achieve record TEEs for FCDI.

CURRENT TECHNOLOGY

Reverse Osmosis (RO)

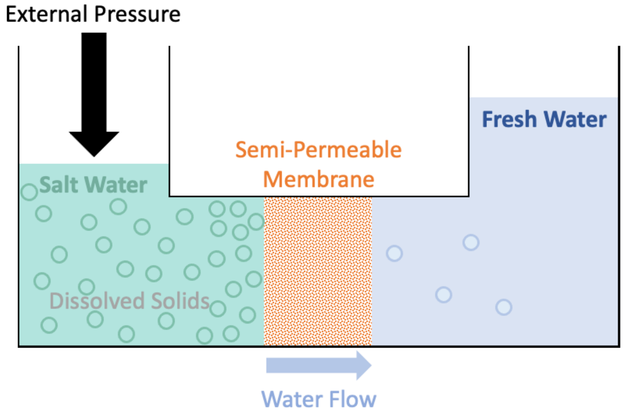

Figure 1. Mechanism behind reverse osmosis. An external pressure larger than the osmotic pressure is applied to allow water to flow from water of high concentrations to low concentrations.

Reverse osmosis is a diffusion-controlled process in which the mass transfer of permeant through the membranes diffuses via solution-diffusion mechanism where the permeants dissolve in membrane material and then diffuse through the membrane.[10] Solution-diffusion occurs in three separate steps: absorption onto the membrane surface, diffusion through the thickness of the membrane, and desorption from the permeate surface of the membrane.[6] RO membrane diffusion is controlled by achieving a hydrostatic pressure greater than the osmotic pressure of the solution. The positive pressure creates a chemical concentration gradient across the membrane driving the liquid through the membrane against the natural direction of osmosis (movement of water from high to low concentrations) (**Figure 1**).[6] So, to analyze the performance and efficiency of the membrane, water recovery is measured (**Equation 1**),

$$R_W = \frac{Q_P}{Q_F} \quad \textbf{(1)}$$

where Q_P is the permeate volumetric flow rate and Q_F is the feed volumetric flow rate. Typical membranes afford water recovery anywhere from 35-85% depending on the feed water composition, feed water salinity, pretreatment, concentrate disposal options, and optimum energy design configuration.[6]

A suitable membrane for reverse osmosis should have metrics such as high water permeability, good mechanical strength, thermal stability, and high chemical resistance.[4] Most of the membranes for RO used today are designed as spiral wound modulus, where the membranes are wound around an inner tube that collects the permeate (**Figure 2**).[10] The most significant disadvantage to using membranes is they slowly deteriorate within 1-3 years due to membrane compaction, fouling, and degradation from hydrolysis, chlorine attack, or cleaning which can decrease the membrane flux by 20% and salt rejection around 0.2-0.3%.[14]

The most common membrane materials today are often polymeric materials such as cellulose acetate and polyamide thin films. Cellulose acetate has low protein adsorption, good water affinity, high mechanical strength, a low cost, low fouling resistance, and poor thermal stability.[4] Typically these membranes are easy to make, mechanically tough, resistant to degradation by chlorine and other oxidants (up to 1 ppm of chlorine), and can be used for sterilizing feed water. The exact composition for cellulose acetate varies but usually contains 40 wt% acetate with 2.7 degree of acylation which produces 98-99% sodium chloride rejection with reasonable fluxes. Annealing can have great effects on the salt rejection to water flux ratio because the properties of the membrane change with heat. Higher annealing temperature leads to less micropores, higher salt rejection, but less water flux. On the other hand, cellulose acetate membranes will hydrolyze over time and are most stable at pH 4-6.[14]

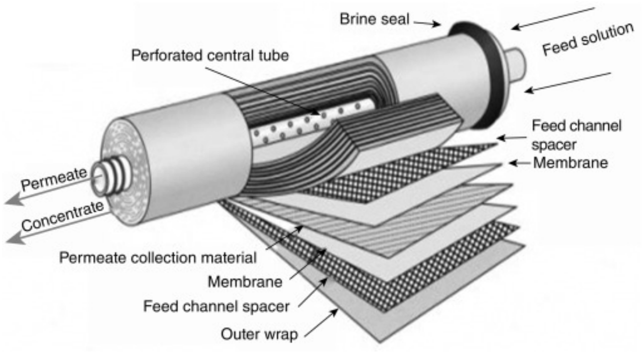

Figure 2. Reverse osmosis spiral wound modules with thin composite membranes containing an active polyamide layer with a porous polysulphone layer wound round a central collection tube.[15]

Another common material that makes up RO membranes are polyamide thin film composites. These membranes have a dense top layer and highly porous support layer which affords high water permeability, low operating pressure, and separation of organic foulant.[4] These thin film composites are synthesized by interfacial polymerization which is a common technique used to make these membranes and produces extremely high salt rejections with good water fluxes.[14] Typical membranes, tested with 3.5% sodium chloride solutions, have a salt rejection of 99.5% and water flux of 30 gal/ft^2 • day at 800 psi. These metrics show that polyamide thin film composites have more than half the salt passage of cellulose acetate membranes and twice the water flux with far better rejection of low-molecular-weight dissolved organic solutes. On the other hand, these membranes are very sensitive to even ppb levels of chlorine or hypochlorite disinfectants. The rate of degradation of the membrane is significantly slowed if tertiary amines or aromatic polyamides are used with high crosslink density.[14]

Capacitive Deionization (CDI)

Capacitive deionization (CDI) relies on porous carbonous materials as solid electrodes to temporary store ions when a potential difference is applied. The water feed solution is flowed between two electrodes and the ions are attracted to their respective charge through electrostatic forces and are adsorbed onto the electrode. Once the electrodes are saturated, the electrodes can be regenerated by removing the external electric field which causes the ions to desorb from the electrode material and creates concentrate (**Figure 3**). CDI is advantageous because CDI operates at low-pressures and does not require a membrane which can deteriorate over time.[13]

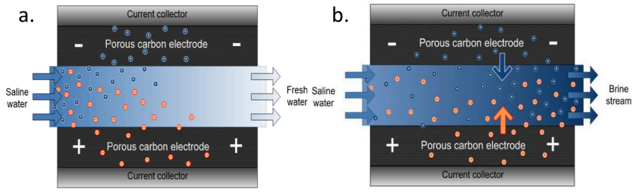

Figure 3. Pictorial representation of CDI during a) adsorption and b) desorption of ions.[13]

On the other hand, CDI can suffer from co-ion adsorption since there no way to screen off oppositely charged ions which leads to low charge efficiency of the system if operated around the wrong point of zero charge and/or voltage window. The use of ion exchange membranes (membrane capacitive deionization, MCDI); however, can solve the problem of low charge efficiency in CDI.[13]

The mechanism of ion transport and adsorption in CDI can be described by the electrical double layer (EDL) when an accumulation of ions is formed at the electrode-electrolyte interface due to the electrical potential.[1,13] The EDL model further dates back to Helmholtz where he assumed that all surface charge is charge-compensated by a countercharge adsorbed to the surface. So, in an ideal environment, for every anion adsorbed onto the anode, one cation would be adsorbed onto the cathode resulting in 100% charge efficiency. Realistically, ions do not condense in the plane adjacent to the electrode, but remain in a diffusively distributed layer close to the surface described by the Gouy-Chapman model.[1] The thickness of the diffuse layer is defined by the 2 or 3 times the Debye length, the characteristic distance for the counterion concentration and potential to decrease by a factor of *e* (~2.7). The Gouy-Chapman theory predicts two different pathways that the diffuse layer takes to compensate surface charge: 1) counterion adsorption in the diffuse layer, and 2) co-ion desorption.[1] These pathways imply that the ions close to the surface, in the absence of charge, are now being expelled because they have the same charge as the surface charge that builds up. This effect lowers the charge efficiency of CDI to around 60-80%.[1] Furthermore, when the EDL voltage drops below the thermal voltage, the system can reach the Debye-Hückel limit and zero salt adsorption can occur. When the Debye-Hückel limit is reached, co-ions within the electrode, prior to applying the electrical potential, desorb into the flow channel. Thus, no salt is removed from the water feed solution (**Figure 4**).

With these theories in affect, one would except with increasing cell voltages, both the charge and the charge efficiency would increase along with salt adsorption. At typical voltages for CDI (1.0 V), far above the Debye-Hückel limit, one would expect charge efficiencies close to 1, however, this is not observed. This discrepancy is contributed to the Stern layer, the thin dielectric layer between the charged surface and the beginning of the diffuse layer. The thickness of this Stern layer corresponds to the hydrated radius of the ion and is considered the closest-approach-plane for the center of the ions to the charged surface.[1] The dielectric layer creates a space that does not contain ions and acts like a capacitor causing relatively high voltage drops up to 80%.[1]

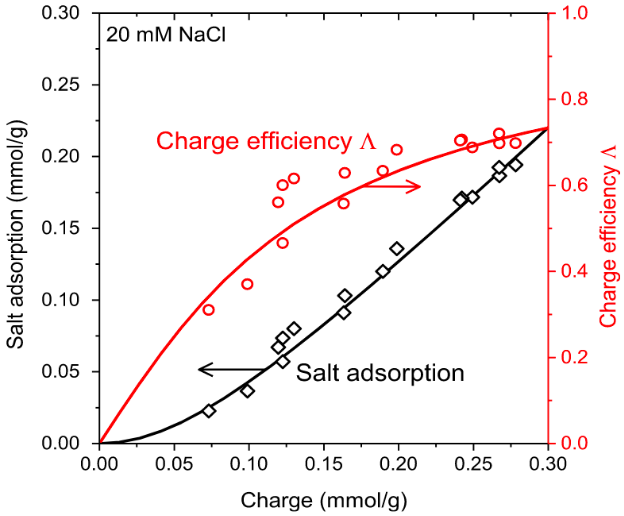

Figure 4. The effect of co-ion desorption from electrical double layers on salt adsorption in a symmetric two-electrode cell pair containing activated carbon electrodes, quantified by the charge efficiency.[1]

The material of the electrode is the key contributor to the overall efficiency of CDI technology. A good electrode has properties such as high porosity, good electronic conductivity, high surface area, high capacitance, good stability, hydrophilicity, and economic feasibility.[13] The most common material used for CDI are carbon-based materials which possess many of the properties listed above. Carbon-based electrodes often contain activated carbon, carbon nanotubes, graphene, or carbon sheets and are made by depositing a dispersion solution onto a support (the current collector). While carbon-based materials are known for high specific surface area and comparatively low cost, they also have major limiting factors such as low porosity, conductivity, and wettability.[11,13] These shortcomings can be improved upon by chemically and physically treating the electrodes with various gases to increase pore size, etching to increase surface area, and functionalizing to increase hydrophilicity.[13]

Electrodialysis (ED)

Electrodialysis membranes operate under electric current causing ions to move through parallel membrane and are typically only used for brackish water desalination.[6] Like capacitive deionization, electrodialysis employs an electrical potential as the driving force to extract charged compounds from a saline solution. Ions travel through cation- and anion-exchange membranes (CEM and AEM) to generate fresh water and a brine solution.[13] Using the CEMs and AEMs allows for high salt removal rate with water salinity less than 5,000 mg/L and energy consumption of 0.8-1.5 kWh/m^3 of 45 L/m^{2}h. Compared to CDI this technology is cyclic, so there is no time wasted trying to regenerate the membranes and does not require extensive pre- or post-treatment. ED affords high removal rate of salt, generation of high brine concentrate, high segregation of metals, and is less susceptible to scaling.[12] Additionally, using monovalent perm-selective IEMs allow for selective separation of monovalent ions against multivalent ions (i.e., for the production of irrigation water). On the other hand, electrodialysis has higher energy consumption, is more susceptible to clogging, and relies on membrane technology which naturally deteriorate over time.

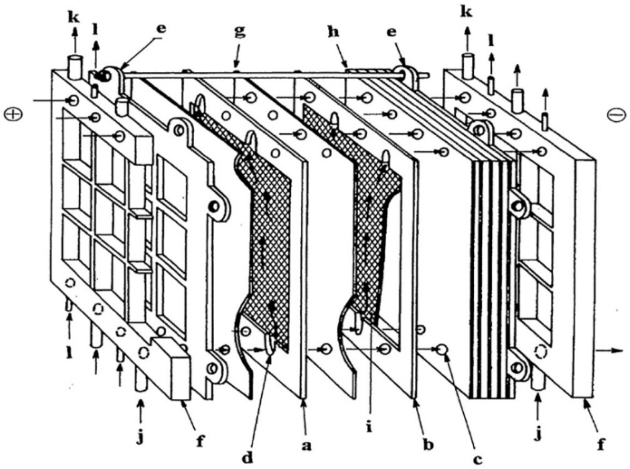

Figure 5. Diagram of a constructed electrodialysis setup: a) desalting cell; b) concentrating cell; c) duct; d) slot; e) fastening frame; f) feeding frame; g) cation exchange membrane; h) anion exchange membrane; i) spacer; j) feeding solution; k) desalted solution; l) concentrated solution.[12]

The electrodialysis setup includes a stack of IEM membranes, electrodes, spacers, gasket seals, and compartments for the feed and concentrate (**Figure 5**). Within the electrodialysis stack, anion and cation exchange membranes are placed alternating between the anode and cathode and situated between the feed and brine compartments. Spacers act as manifolds for collecting and distributing the solutions to and from the different channels. These spacers are often made of polypropylene so that the equal area is the effective area of the installed IEMs with a thickness of 0.42-10 mm.[12] The IEMs are commonly thin polymeric films with charged groups such as polysulphone, polystyrene, and polyethylene. CEMs have negatively charged functional groups (i.e., carboxylic acid, phosphoryl, sulfonic acid, phosphonic acid) attached to the polymeric backbone which prevent negatively charged groups from passing through while allowing positive ions to pass. Alternatively, AEMs have positive charged functional groups (i.e., quaternary, tertiary, secondary amines, and ammonium) bonded to the polymeric backbone which prevent positively charged groups from passing through but allows negative ions to pass (**Figure 6**).[12] Different supports can be made to tune the mechanical strength of the membranes but can reduce conductivity or perm-selectivity. To minimize potential ohmic loss, one can reduce the thickness of the IEM except thin IEMs have been found to have poor permeability to gases, produce low selectivity, and have crucial mechanical properties.[12]

The electrodes themselves are conventional capacitive electrodes and made of a mixture of poly(vinylidene fluoride) and activated carbon. Activated carbon is common due to its high surface area and pore size distribution. These electrodes do not require any toxic materials but can suffer from carbon layer saturation.[12]

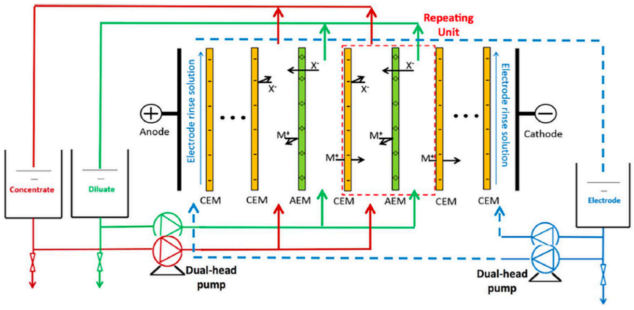

Figure 6. Schematic of the ED system where charged ions (M^+ and X^-) pass through CEM and AEM to generate concentrate and dilute streams.[12]

The main reason why ED has not been scaled up is because of membrane fouling. Membrane fouling is typically caused by the molecular size of organic particles which range from 200-700 Da and cause internal clogging.[12] Others have done studies to limit membrane fouling such as adding pre-treatment through ultrafiltration or nanofiltration, using activated carbon and cleanings actions to prevent clogging, or using porous membranes instead of IEMs.[12]

Flow Electrode Capacitive Deionization (FCDI)

Flow electrode capacitive deionization combines elements of both electrodialysis and capacitive deionization to deliver a new water desalination technology. FCDI incorporates the capacitive adsorption of salt ions while also using flowable electrodes to continuously replenish the electrode chamber with new or regenerated particle electrodes.[16] This new configuration improves upon aspects where electrodialysis and capacitive adsorption are disadvantaged. Future works are even trying to integrate FCDI technology with renewable energy sources to use in remote off-grid power areas.[16]

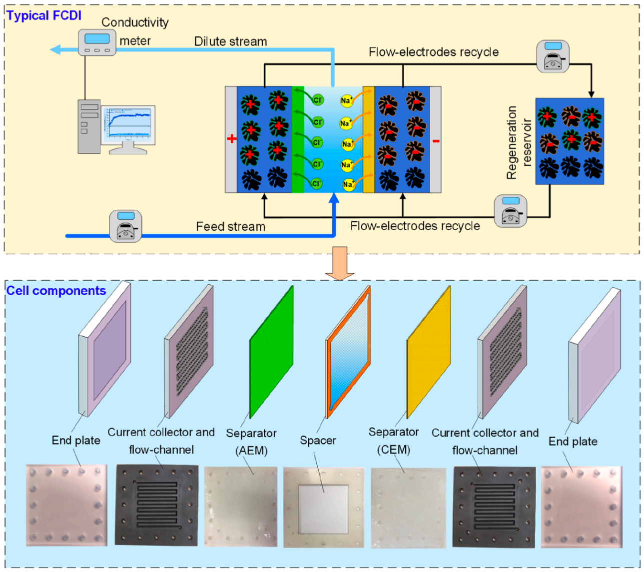

Figure 7. Typical laboratory scale FCDI device and its major components incorporating both IEMs and flowable electrodes to maximize salt removal and minimize energy usage.[16]

Several different factors go into creating a FCDI such as cell architecture, electrode/current collector/membrane material, and operation of the cell. Like a CDI setup, a FCDI includes separators, current collectors, and spacers which are held together by end plates. **Figure 7** shows a standard configuration of a FCDI cell where the feedwater flows through the spacer channel.[16]

The ion transfer in flow electrodes can be tricky. When the electrical potential is applied, ions move through IEMs and are adsorbed into the carbon slurry where electrons are transferred to the current collector to complete the circuit. Flow-electrodes contain a mixture of active materials, electrolyte, and conductive additives to a desired ratio (**Equation 2**),[1]

$$\text{solid content (wt\%)} = \frac{\text{active materials} + \text{solid conductive additives}}{\text{active materials} + \text{conductive additives} + \text{electrolyte}} \quad \textbf{(2)}$$

Typical active materials and conductive additives found in FCDI devices include carbon-based materials (i.e., activated carbon, carbon black, graphene, and carbon nanotubes), highly conductive solid substances (i.e., molybdenum carbide and graphene/reduced graphene oxide), and aqueous electron-mediators (i.e., hydroquinone, indigo carmine, and *m*-phenylenediamine).[16,17] Each bring their own set of advantages and disadvantages but, generally, bring large specific surface area, good conductivity, and are relatively low cost. However, current mass loading is limited by 5-20 wt% to balance viscosity and conductivity.[1] Furthermore, the electrolyte also plays a key role in the flow-electrode since the electrolyte is usually >80 wt% of the slurry. Finding the correct balance of salts is crucial since additional ions will be added during desalination. While increasing the salinity of the electrolyte increases electronic conductivity, slurry stability can decrease and lead to severe particle aggregation and higher viscosities.[16,17] The flow-electrode is crucial to the electrodialytic and capacitive processes and strongly influence the efficacy of ion removal in the FCDI device.

Another crucial component of the FCDI is the current collector and flow channels. The current collectors not only transfer current and charge distribution to the electrode particles but also direct the flow of the electrode suspension and provide structural support to the chamber separators.[16] Current collectors with ideal properties would possess high electrical conductivity, robust mechanical strength, be lightweight, self-supporting, and low cost. Materials like stainless steel or graphite-based plates can be used but each come with their own disadvantages. Stainless steel is strong and has good conductivity but is easily susceptible to corrosion and can be difficult to modify. On the other hand, graphite has a resistance to corrosion and can be designed for various configurations except these carbon plates can quickly become costly. Designing FCDI cells are not a trivial task since one has to consider these three main principles: i) high effect contact surface area between the current collectors and flow-electrodes for rapid distribution of charge to the carbon slurry, ii) minimized hydraulic resistance to flow of the slurry, and iii) minimized weight and cost.[16]

PROJECT SCOPE

With electrochemical devices and systems making advances, this project aims to mark the turning point where electricity-driven desalination becomes more efficient than osmotic-driven desalination. Using flow electrode capacitive deionization technology, LLNL seeks to create a desalination device that can achieve >90% water recovery for brackish water desalination at a record thermodynamic energy efficiency (TEE) of significantly greater than 30%. This reduction of energy use by >4x can be achieved by combining engineering advantages of electrodialysis reactor design with energy-barrier-free sorption. Along with the desalination device, the group will also use an engineering process model to predict and verify optimal performance.

As with any electrochemical devices and systems which require a large amount of current to perform anything measurable, managing the resistances within the device will determine both the energy efficiency and rate capability. The key limiting factor identified for the desalination device is the low interfacial contact area, at any given moment in time, between the flowing carbon particles and the current collector within the flow electrode. This electron transfer from the current collector to the carbon slurry particles dictates the current conduction within the entire system and has been identified as the rate limiting step. Much of this low electronic conductivity within the flow electrode is contributed to voltage drops due to ohmic losses. Currently, the flowable capacitive electrodes are limited to 10-30 wt% carbon, and thus have percolation electronic conductivities of only 0.1-1 mS/cm.[16,18,19] On the other hand, the brine concentrate will have conductivities 40-100x higher depending on the chosen water recovery and feed concentration. This causes the conduction pathways to be limited by electronic conduction. So, to maximize the time-average contact area between the carbon slurry and current collector and achieve low resistance and record thermodynamic efficiency, the group proposes to construct a templated membrane electrode assembly (MEA) using a structed carbon current collect inspired by heat-exchanger flow plates (**Figure 8**). LLNL proposes to use a pillared heat-exchanger flow plate design to maximize charge transfer while minimizing pressure drop. This design was chosen because heat-exchangers are highly optimized to maximize heat transfer while minimizing pressure drop. LLNL hopes the design will provide an excellent and novel solution to the problem.

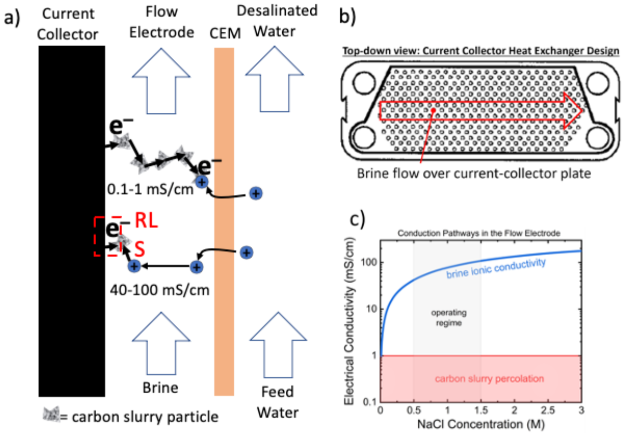

Figure 8. (a) Current conduction pathways in the flow electrode chamber, (b) proposed membrane electrode assembly for the structure current collector for increased time-averaged contact with the carbon slurry, (c) conductivity comparison for electronic percolation vs. ionic conduction within the flow electrode.[20]

To start the project, we will begin by fabricating a FCDI device from stainless steel, aluminum, or even copper, to optimize the geometry before more electrochemical testing. Based on previous estimates, this plate structure could reduce the resistance by ~7x due to increased charge transfer between the carbon slurry and current collector. Once the geometry is optimized, more electrochemically stable plates can be made from graphite or titanium. For example, a prototype could be 3D printed from a polymeric material and then carbonized to increase conductivity.

This project incorporates several milestones and stop points to monitor progress and successes. Once the plates are fabricated, we aim to recreate efficiency values from literature to show and compare the promising results of FCDI by replicating their plates. In tandem, we will also be designing and fabricating the heat-exchanger flow plates and evaluating their performance. They will be individually characterized using half-cells to quantify their hydraulic permeability for the carbon slurry and conductivity measured by impedance. The half-cell design allows us to quickly measure the merits of each current collector structure to assess the tradeoff between conductivity and pressure drop.

CONCLUSIONS

With this new FCDI plate design, the project has three main goals: 1) can we reproduce a FCDI TEE of >10% from literature for a water recovery of >90% for a flow of 2 g/L → 0.5 g/L?[21] 2) Can we reduce the overall resistance by 2x or great with the new flow-through architected current collector design? And 3) can we achieve a record TEE >25% for brackish water desalination at a water recovery of >90% for 2 g/L → 0.5 g/L? With this new FCDI current collector design, we hope to unlock a whole new fresh water source by targeting brackish water and greatly improve water resilience across the United States.

ACKNOWLEDGMENT

This formulation is proprietary to Lawrence Livermore National Laboratory. IM release number: LLNL-TR-839527.

REFERENCES

(1) Porada, S.; Zhao, R.; van der Wal, A.; Presser, V.; Biesheuvel, P. M. Review on the Science and Technology of Water Desalination by Capacitive Deionization. *Prog. Mater. Sci.* **2013**, *58* (8), 1388–1442. https://doi.org/10.1016/j.pmatsci.2013.03.005.

(2) UNESCO World Water Assessment Programme. *The United Nations World Water Development Report 2020: Water and Climate Change*; UNESCO, 2020.

(3) Boretti, A.; Rosa, L. Reassessing the Projections of the World Water Development Report. *Npj Clean Water* **2019**, *2* (1), 1–6. https://doi.org/10.1038/s41545-019-0039-9.

(4) Woo, Y. C.; Kim, S.-H.; Shon, H. K.; Tijing, L. D. Introduction: Membrane Desalination Today, Past, and Future. In *Current Trends and Future Developments on (Bio-) Membranes*; Basile, A., Curcio, E., Inamuddin, Eds.; Elsevier, 2019; pp xxv–xlvi. https://doi.org/10.1016/B978-0-12-813551-8.00028-0.

(5) Fragkou, M. C.; McEvoy, J. Trust Matters: Why Augmenting Water Supplies via Desalination May Not Overcome Perceptual Water Scarcity. *Desalination* **2016**, *397*, 1–8. https://doi.org/10.1016/j.desal.2016.06.007.

(6) Greenlee, L. F.; Lawler, D. F.; Freeman, B. D.; Marrot, B.; Moulin, P. Reverse Osmosis Desalination: Water Sources, Technology, and Today's Challenges. *Water Res.* **2009**, *43* (9), 2317–2348. https://doi.org/10.1016/j.watres.2009.03.010.

(7) Gude, V. G.; Maganti, A. Desalination of Deep Groundwater for Freshwater Supplies. In *Global Groundwater*; Elsevier, 2021; pp 577–583. https://doi.org/10.1016/B978-0-12-818172-0.00042-6.

(8) US EPA, O. *How We Use Water*. https://www.epa.gov/watersense/how-we-use-water (accessed 2022-08-22).

(9) Wang, Z.; Horseman, T.; Straub, A. P.; Yip, N. Y.; Li, D.; Elimelech, M.; Lin, S. Pathways and Challenges for Efficient Solar-Thermal Desalination. *Sci. Adv.* **2019**, *5* (7), eaax0763. https://doi.org/10.1126/sciadv.aax0763.

(10) Wenten, I. G.; Khoiruddin. Reverse Osmosis Applications: Prospect and Challenges. *Desalination* **2016**, *391*, 112–125. https://doi.org/10.1016/j.desal.2015.12.011.

(11) Datar, S. D.; Mane, R.; Jha, N. Recent Progress in Materials and Architectures for Capacitive Deionization: A Comprehensive Review. *Water Environ. Res.* **2022**, *94* (3), e10696. https://doi.org/10.1002/wer.10696.

(12) Al-Amshawee, S.; Yunus, M. Y. B. M.; Azoddein, A. A. M.; Hassell, D. G.; Dakhil, I. H.; Hasan, H. A. Electrodialysis Desalination for Water and Wastewater: A Review. *Chem. Eng. J.* **2020**, *380*, 122231. https://doi.org/10.1016/j.cej.2019.122231.

(13) Folaranmi, G.; Bechelany, M.; Sistat, P.; Cretin, M.; Zaviska, F. Towards Electrochemical Water Desalination Techniques: A Review on Capacitive Deionization, Membrane Capacitive Deionization and Flow Capacitive Deionization. *Membranes* **2020**, *10* (5), 96. https://doi.org/10.3390/membranes10050096.

(14) Baker, R. W. *Membrane Technology and Applications*; Professional engineering; McGraw-Hill: New York, 2000.

(15) Maynard, E.; Whapham, C. 3 - Quality and Supply of Water Used in Hospitals☆. In *Decontamination in Hospitals and Healthcare (Second Edition)*; Walker, J., Ed.; Woodhead Publishing Series in Biomaterials; Woodhead Publishing, 2020; pp 45–69. https://doi.org/10.1016/B978-0-08-102565-9.00003-0.

(16) Zhang, C.; Ma, J.; Wu, L.; Sun, J.; Wang, L.; Li, T.; Waite, T. D. Flow Electrode Capacitive Deionization (FCDI): Recent Developments, Environmental Applications, and Future Perspectives. *Environ. Sci. Technol.* **2021**, *55* (8), 4243–4267. https://doi.org/10.1021/acs.est.0c06552.

(17) Yu, F.; Yang, Z.; Cheng, Y.; Xing, S.; Wang, Y.; Ma, J. A Comprehensive Review on Flow-Electrode Capacitive Deionization: Design, Active Material and Environmental Application. *Sep. Purif. Technol.* **2022**, *281*, 119870. https://doi.org/10.1016/j.seppur.2021.119870.

(18) Doornbusch, G. J.; Dykstra, J. E.; Biesheuvel, P. M.; Suss, M. E. Fluidized Bed Electrodes with High Carbon Loading for Water Desalination by Capacitive Deionization. *J. Mater. Chem. A* **2016**, *4* (10), 3642–3647. https://doi.org/10.1039/C5TA10316A.

(19) Porada, S.; Weingarth, D.; Hamelers, H. V. M.; Bryjak, M.; Presser, V.; Biesheuvel, P. M. Carbon Flow Electrodes for Continuous Operation of Capacitive Deionization and Capacitive Mixing Energy Generation. *J. Mater. Chem. A* **2014**, *2* (24), 9313–9321. https://doi.org/10.1039/C4TA01783H.

(20) Hawks, S. A.; Oyarun, D.; Cerón, M. R.; Chandrasekaran, S.; Campbell, P.; Stadermann, M. *LDRD-DR The Ultra-High Water Recovery Desalination with Record Thermodynamic Efficiencies*; 2022.

(21) Zhang, C.; Wu, L.; Ma, J.; Pham, A. N.; Wang, M.; Waite, T. D. Integrated Flow-Electrode Capacitive Deionization and Microfiltration System for Continuous and Energy-Efficient Brackish Water Desalination. *Environ. Sci. Technol.* **2019**, *53* (22), 13364–13373. https://doi.org/10.1021/acs.est.9b04436.