Blue Refrigeration: Capacitive De-ionization for Brackish Water Treatment

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There is a growing interest in minimizing the energy and cost associated with desalination. To do this, various new desalination systems and approaches are being explored. One growing area of interest revolves around electrochemical separations for deionization. Electrochemical separations primarily consist of technologies which either intercalate or electroadorb species of interest from a bulk mixture. This can be conducted through polarizing a battery electrode, or more commonly a capacitive electrode. One example is the technology capacitive deionization (CDI). CDI is being investigated as a means to augment the current state of the art, and as a stand-alone brackish water treatment technology. Despite the potential of this technology, there is still much that is not known regarding the energetics and efficiency of both the desalination and brine formation process. Here, blue refrigeration is a term used to broadly describe desalination cycles and processes. The analogy aims to compare the energetics associated with a desalination cycle to the energetics well studied in thermal refrigeration cycles. This perspective aims to evaluate some of the emerging energetic issues associated with CDI, and to describe how new system architectures may play a role in achieving more ideal energy and desalination performance. [DOI: 10.1115/1.4037907]

1 Introduction

Within mechanical engineering, it is well known that spontaneous processes can result in usable work, and work must be consumed to drive nonspontaneous processes. The most notable application of this phenomenon discussed in undergraduate thermodynamics courses are heat engines and refrigerators [1]. In heat engines and refrigerators, work is generated or consumed as heat is transferred between high and low temperature thermal reservoirs (Fig. 1(*a*)). In a similar way, "blue engines and refrigerators" rely on generating or consuming work to transport ions between high and low chemical potential reservoirs (Fig. 1(*b*)). The term "blue" was coined between 2003 and 2007 by the research and development program in the Netherlands to describe salinity gradient energy (blue energy) [2,3]. Yet, the concept for harvesting energy from salinity gradients was envisioned over 60 years ago by Pattle [4], and explored more in depth by Mehta and Loeb [5].

Blue energy refers to energy harvested from natural mixing processes. An estuary is an example of a natural mixing process that occurs when seawater (high chemical potential) and river water (low chemical potential) converge. Investigations have suggested that both mechanical (pressure retarded osmosis) and electrochemical-based technologies (reverse electrodialysis [6] and capacitive mixing [7,8]) could be utilized to convert mixing energy into useful energy (electricity and hydrogen) [5,6,9,10]. Statkraft, a renewable energy company in Norway, attempted to commercialize pressure retarded osmosis, and conducted a pilot scale 10 KW power plant in Norway [11]. This demonstration revealed that the cost of the current state-of-the-art membranes was the limiting aspect of this technology. Reverse electrodialysis is also currently being investigated as a part of a large-scale pilot demonstration by REDstack on the Afsluitdijk in the Netherlands [12].

Blue refrigeration, or desalination, has primarily been achieved through thermal- (distillation) and pressure-driven processes (reverse osmosis) [13]. Recently, there has been growing interest in developing technologies that can perform these separation processes at low pressures and ambient working environments to minimize the energy consumption required for desalination. Several performance and efficiency challenges emerge when thermal- and pressure-driven separations are operated under these conditions [14]. Thus, this has motivated increased research efforts in electrochemical separation processes and technologies. Capacitive deionization (CDI) and electrodialysis are two examples of electrochemical technologies used for brackish water desalination.

Capacitive deionization is an example of a blue refrigeration technology. It operates by flowing an ionized solution in parallel with two high surface area porous electrodes (Fig. 2(*a*)). When a voltage is applied, ions are electroadsorbed into the porous electrode in the formation of an electric double layer (EDL). When the electrode surface area is fully utilized, energy can be recovered by applying an open circuit voltage to the cell or reversing the voltage (Fig. 2(*b*)). The resulting process leads to the formation of a brine solution. One challenge with CDI is that a negative voltage cannot be applied as ions can "ping-pong" between electrodes, which decreases the efficiency of removal. Traditionally, ion exchange membranes are placed in front of the electrodes to eliminate this ping-pong or co-ion repulsion effect (membrane CDI).

Capacitive deionization has the ability to act as a stand-alone technology to treat decentralized brackish water with intrinsic energy recovery. Furthermore, CDI may be an efficient post-treatment technology for reverse osmosis desalination plants. By combining CDI with RO, the number of passes required for desalination can be decreased. Despite this promise, there are several unknowns associated with CDI both from scientific and applied perspective. From a scientific perspective, a better understanding is needed regarding electric double layer formation and ion insertion and intercalation phenomenon in complex water sources (brine, seawater, brackish water). The complex "electrolytes" can alter separation mechanism, through the introduction of competing interactions (i.e., heavy metals, minerals, and biofoulants). From an applied perspective, improvement in the systems energy efficiency, desalination performance, and durability still hinder its implementation.

Here, the challenge of minimizing energy demand (work) and maximizing efficiency are discussed through drawing analogies between blue refrigeration thermodynamic cycles and thermal

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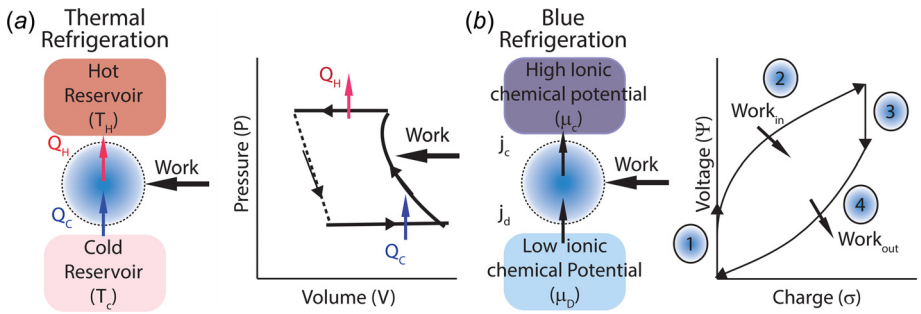

Fig. 1 In traditional refrigerators, work is consumed to move heat from a cold reservoir to a hot reservoir (*a*), whereas in a blue refrigerator, ions are transferred from a low ionic chemical potential solution to a high chemical potential solution (*b*)

refrigeration cycles. By exploring these analogies, valuable insight needed to optimize blue refrigeration cycles may be realized. In addition, we aim to provide insight into how new architectures may also allow for energy-efficient separation processes.

2 Thermodynamic Considerations

A chief challenge with desalination is the energy cost associated with the current state of the art. To address energy consumption, technologies must operate near the thermodynamic limits (Sec. 2.1), and new hybrid technologies (Sec. 2.2) must be explored. In addition, there is a growing interest in exploring desalination processes for low-saline (brackish) water sources ($C_0 \leq 0.2$ M) instead of high saline seawater ($C_0 = 0.6$ M). This is because low saline water theoretically requires less energy. Brackish waters are also found in nearly all regions of the United States, either in groundwaters or at estuaries [15].

2.1 Minimum Energy for Desalination. There are three streams of interest in blue refrigeration devices. The feed (0) or input stream is separated by the desalination device into two streams. One is termed the de-ionized (d) stream, and the other is termed the concentrate (c) (Fig. 2). The de-ionized or desalted stream represents the treated water, and the concentrate or brine refers to the waste. The minimum work required to separate a feed solution into a de-ionized and concentrated stream is independent of the technology and can be estimated from the Gibbs free energy of mixing [16].

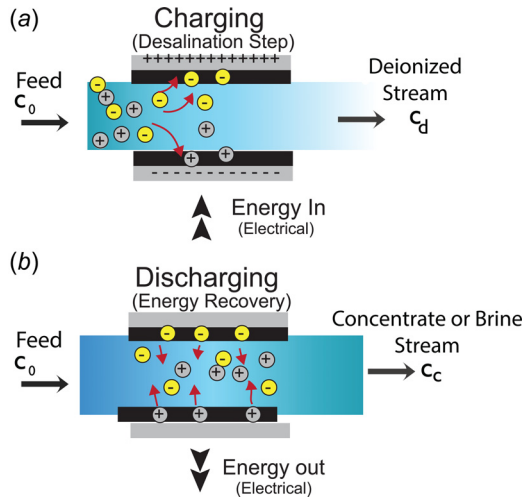

Fig. 2 CDI creates a de-ionized body of water during a charging step (*a*) and then recovers energy during a discharge process forming a brine solution (*b*)

$$\Delta G_{\text{mix}} = G_c + G_d - G_0 \tag{1}$$

ΔG_{mix} is the free energy of mixing (J/mol), G_c is the Gibbs energy of the concentrate, G_d is the Gibbs energy of the de-ionized stream, and G_0 is the Gibbs energy of the feed. The Gibbs energy of an ideal solution can be estimated as:

$$\Delta G = \sum \mu_i n_i \tag{2}$$

where μ_i is the chemical potential of component i in the solution, and n_i is the number of moles of component i in the solution. Generally, the chemical potential of an ideal solution, with no change in pressure and negligible electric potential difference, reduces to

$$\mu_i = \mu_i^0 + RT \ln (x_i) \tag{3}$$

where μ_i^0 is the standard chemical potential, R is the ideal gas constant, T is the temperature, and x_i is the mol fraction of component i. Substituting Eqs. (2) and (3), into Eq. (1), and converting moles to volume and concentration ($n_i = V_i c_i$) yields

$$W_{\text{min}} = vRT(V_c c_c \ln (c_c) + v_d c_d \ln (C_d) - V_0 c_o \ln (c_o)) \tag{4}$$

where v is the van't Hoff factor. Often, this is rewritten in terms of the water recovery ratio: $\alpha = V_d/V_0$, and the work is normalized by the product stream (volume of de-ionized water), which reduces Eqs. (4) and (5)

$$\frac{W_{\text{min}}}{V_d} = vRT\left[\frac{c_0}{\alpha}\ln\left(\frac{c_0 - \alpha c_d}{c_0(1-\alpha)}\right) - c_d \ln\left(\frac{c_0 - \alpha * c_d}{c_d(1-\alpha)}\right)\right] \tag{5}$$

The minimum energy required for desalination or separation increases as the water recovery ratio increases ($\alpha \rightarrow 1$) and as the feed concentration (c_0) increases (Fig. 3—brackish < seawater < brine). The theoretical limit for desalting seawater (0.6 M) is approximately 1 kWh per m^3 of water as you approach 0% water recovery (Fig. 3). More practically, desalination devices must be operated with higher water recoveries ($\alpha > 50\%$). At these operating conditions, reverse osmosis, the state of the art for seawater desalination, is approaching the thermodynamic limit (2–3 kWh per m^3) [13]. As the initial concentration of the feed solution decreases, however, alternative technologies such as CDI become a viable low-energy alternative to reverse osmosis. Specifically, when feed water decreases below 0.1 M, as is the case with brackish waters, there are significant energetic gains, which have been observed through the use of CDI [17].

2.2 Process Energetics of Capacitive Deionization. Traditional CDI cells operate in a four stroke cyclic process, which is similar to a four stroke heat engine. A standard CDI process can be summarized by the following:

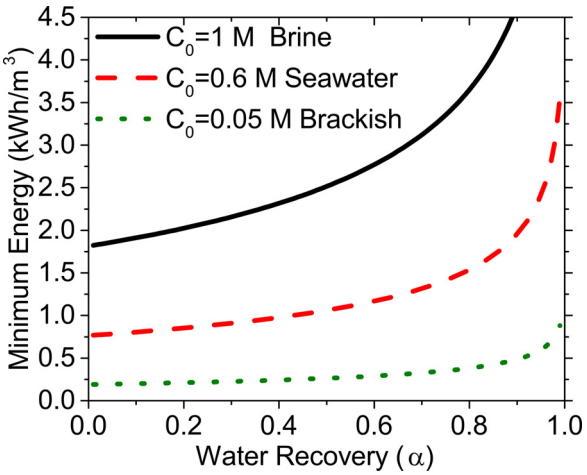

Fig. 3 Minimum energy required for desalting brine solutions (~1 M), seawater (0.6 M), and brackish water (0.05 M). In all cases, C_d was 1 mM.

Stroke 1. Feed water is introduced into cell under open circuit conditions.

Stroke 2. Capacitive electrodes are charged with an applied constant voltage or constant current to produce a *desalted stream*.

Stroke 3. Waste stream is introduced into cell under open circuit operating conditions (*concentrate stream*).

Stroke 4. Capacitive electrodes are discharged with a negative constant voltage or negative constant current to produce a third stream (*brine stream*).

Strokes 1 and 3 are constant chemical potential processes, and resemble *constant volume* processes in a thermal refrigerator. Strokes 2 and 4 are constant voltage or constant current processes, which are analogous to *constant pressure* processes (Fig. 1(*b*)). In heat engines and refrigerators, we would equate the work done on the system as $W = -\int pdV = \int TdS$ (Fig. 1(*a*)). However, for blue engines and refrigerators, work is defined as

$$W_{\text{actual}} = -\int \Psi(\sigma) d\sigma \tag{6}$$

here Ψ is the voltage of the cell and $d\sigma$ is the change in charge stored in the electrodes. The voltage of the electrode can be assumed or can be calculated through modeling the electric double layer ($\Psi_{\text{EDL}} = 2 * (\phi_d + \phi_s)$) where ϕ_d and ϕ_s are the diffuse and stern region voltage within the EDL. Various theoretical frameworks have been evaluated to describe the coupled mass and charge transfer processes, which contribute to the formation of the EDL [18,19]. The Gouy–Chapman–Stern theory provides the most comprehensive evaluation of charge and voltage processes at these relevant solid–liquid interfaces within CDI electrodes [20–22]. The modified Donnan (mD) model has also been adopted as an effective means for describing the salt adsorption and charge transfer processes, as the Debye length is much larger than the typical pore size, creating strongly overlapping EDLs. These assumptions are only valid for CDI cells operating in low saline solutions [23].

2.3 Designing CDI Cycles. Thermodynamic cycles rely on the ability to perturb a system from equilibrium and through a series of processes return that system to its initial state. An ideal thermodynamic cycle represents a specific series of processes, which results optimal performance in heat engines and refrigerators. For thermal energy systems, this ideal cycle is often termed the "Carnot" cycle. In Carnot cycles, each process undergoes perfectly reversible processes, thereby minimizing losses within the system. In reality, reversible processes are impossible, yet the Carnot limit provides a performance boundary which cannot be exceeded.

For a CDI desalination cycle, it is advantageous to minimize the energy consumed to perform a desired desalination process. This is one reason why there is a large push to move toward treating low concentration streams such as brackish water rather than seawater (Fig. 3). While there are energetic advantages, which can be achieved through simply desalting low concentration streams, ideally desalting in an efficient manner is also preferred. To efficiently separate solutions, the actual energy consumed should approach the Gibbs free energy of mixing. The ratio of the minimum required work (Gibbs free energy) to the actual work is commonly referred to as the exergy efficiency or Second law efficiency.

$$\eta_{II} = \frac{W_{\text{min}}}{W_{\text{act}}} \tag{7}$$

Most desalination plants operate below 10% efficiency, and this is primarily due to entropy production during the desalination processes (ion removal). Currently, CDI processes operate below 1% while membrane CDI systems have efficiencies which approach a 1–5% [24].

Graphically, the work required to desalinate a feed stream in a CDI cell can be represented by the area of the voltage (Ψ) versus charge (σ) diagram (Fig. 1(*b*)). Strategies (new processes or cycles), which reduce this area at fixed conditions, represent a reduction in the minimum work required for desalination. This is similar to reducing the area of a pressure versus volume diagram (Fig. 1(*a*)), or temperature versus entropy diagram common to refrigeration systems. For thermal systems, various parameters and system strategies have been designed over the years to improve the overall system performance (heat engines and refrigerators). For instance, in a reciprocating internal combustion engine, the compression ratio ($r = V_{\text{bottom dead center}}/V_{\text{top dead center}}$) is the parameter critical in order to extract greater work from an expansion process. In order to increase efficiency, this parameter must be maximized. In addition, system strategies such as cascade cycles are used in refrigerators to optimize the coefficient of performance. Cascade cycles thermally isolate the high and low temperature side of the refrigerator through the use of two cycles with different refrigerants, which meet at a common shared condenser/evaporator. Using different refrigerants, which are optimized at the various operating conditions (high or low temperatures), improves efficiency. These are just a few examples of how new thermal systems and processes have aided in reducing energy or maximizing work from heat engines and refrigerators.

The obvious advantages observed in heat engines and refrigerators provide evidence that new desalination cycles and processes, if envisioned, could reduce the energy demands associated with desalination. To date, however, most CDI cycles have operated with the same four stroke process described above. Furthermore, there is no Carnot cycle that has been described for CDI systems, so efficiency limits are unknown.

Theorists have recently begun to envision alternative blue engine and blue refrigeration cycles. This has been done through directly comparing refrigeration and heat engine cycles to desalination and mixing cycles. For example, the Helmholtz free energy of a chemical system ($dF = \mu dN + \Psi\ dQ$) has been directly related to the first law for a thermal system ($dU = TdS - pdV$), with the electric work within the capacitors related to mechanical work observed in a thermal system. Through equating predominant intensive and extensive parameters, a Carnot-like analog was modeled [25]. A typical Carnot engine is comprised of two isothermal processes and two adiabatic compression/expansion processes. The blue engine analog suggested that a capacitive mixing cycle should include constant chemical potential (μ) charging and discharging processes, with constant N charging processes during solution switching. The initial theory showed that these changes could increase the efficiency of the blue engine. It should be noted

that these new cycles have not been tested experimentally. These results can also be extended to CDI, through reversing the Carnot blue engine. Specifically, evaluating various charging and discharging processes (iso-i, iso- Ψ, iso-n) with various switching processes (iso-i, iso- Ψ, iso-n, iso-μ) should be investigated from both a theoretical and experimental perspective to improve CDI desalination efficiency.

Challenges exist when translating theory into practice; and, this is evident with both thermal and desalination cycles. For instance, in a Carnot power cycle, the "ideal" cooling process results in a two-phase mixture (vapor and liquid), which is then pumped back to the boiler (heat addition phase). Current state-of-the-art pumps, however, are not capable of efficiently pumping this mixture, and must instead completely cool the working fluid to a liquid phase (nonideal Rankine cycle). Likewise, iso-n processes are highly unlikely due to the complex nature of the pore structure in the solid electrodes.

Experimentalists are also beginning to explore new cycles based around nonisothermal or nonadiabatic operation. This is because both the electric double layer and the membranes exhibit thermoresponsive behavior. Leveraging this thermoresponsive behavior can aid in minimizing the actual electrical work (W_{act}) required to desalinate brackish water. This is the subject of the current ongoing work (Fig. 4) [26]. In addition, system architectures are being investigated, which enable better control over system operation. In Sec. 3, we will aim to broadly overview some emerging trends in system architecture, which may enable better thermodynamic processes.

3 New System Architectures

A significant amount of work has been devoted toward improving the CDI architecture in order to increase operation flexibility [27–29]. New architectures, which minimize irreversibilities, streamline energy recovery, and enable scalability of this system, have all been explored [7,30,31]. Here, the advantages and disadvantages associated with these system architectures are briefly discussed.

Four parameters that are important for a desalination system include desalination rate, desalination capacity, energy consumption, and energy recovery. Traditionally, CDI systems are characterized by two planar electrodes separated by a feed channel. To limit ohmic losses, the feed channel thickness should be optimized for ion transport kinetics and energy consumption. Fundamentally, trade-offs exist between reducing the channel thickness and minimizing electrical energy demands (reducing ohmic resistances) and increasing the energy demand for pumping (pressure drop). In addition, the desalination rate (m^3/min) will be decreased with smaller channels.

The channel thickness and transport challenges can be minimized if flow takes place perpendicular to the electrodes [32]. This approach is in terms a flow-through capacitive deionization. Flow through capacitive deionization, however, requires higher pressure pumps, to pump water through the porous electrodes. To reduce pumping, highly porous materials such as aerogels or xerogels are used. This configuration also reduces ohmic losses, but this is at the expense of pumping energy. In addition, electrically insulating separators must be placed in between the electrodes in order to reduce the propensity for electrical shorts.

One of the main limiting aspects of traditional CDI systems is the energy consumption, which is fundamentally related to a co-ion repulsion mechanism that occurs when the voltage is reversed between a charge and discharge state [33]. To mitigate co-ion repulsion dynamics, ion exchange membranes are often utilized in a technology termed membrane capacitive deionization. Ion exchange membranes add to the capitol cost CDI systems.

To improve the ion removal capacity, there has been a large body of literature focusing on the design of highly porous carbon materials. The salt removal capacity is related to the overall pore volume and thus tailored materials can potentially lead to higher removal capacities and rates. In addition to high surface area materials, thick electrodes [34] and pseudocapacitive materials have also been investigated [35] as a way to improve the ion removal capacity in CDI systems based on planar electrode systems. While all of these strategies have their merits, CDI based on film electrodes suffers from three primary challenges. First, desalination is achieved intermittently because of the discharge process. Second, the system footprint is directly linked to the area of the CDI film electrode in a single cell and third, the effluent or produced water concentration is transient. To achieve the flow rates and capacities necessary in applications such as pretreatment at thermoelectric power plants, continuous and scalable production of de-ionized water is necessary.

Capacitive deionization based on flowable electrodes was introduced to address scalability and salt-removal capacity issues in traditional CDI systems. Figure 5 demonstrates the characteristic flow architecture adopted from the flow battery community. This architecture has several benefits: (1) it decreases the materials costs, (2) decouples salt removal capacity and treated water volume, (3) enables continuous deionization and energy recovery, and (4) extends the desalination time [8].

Flow electrode capacitive de-ionization (FCDI) systems have three flow channels, two of which serve to flow the active material (activated carbon), which removes or electroadsorbs ions, and a center channel where the feed water is directed. The center channel is separated from the flowable electrodes by an anion exchange membrane and a cation exchange membrane. These membranes serve to improve the efficiency of salt removal, by avoiding a ping-pong or co-ion repulsion effect during the

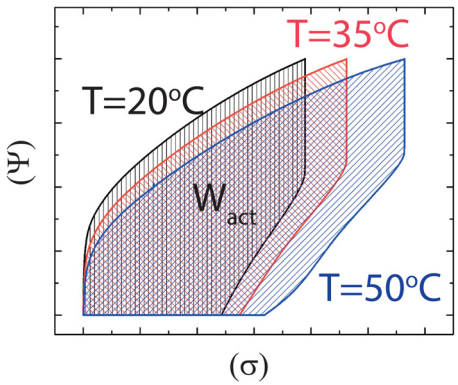

Fig. 4 New thermodynamic cycles may be based around nonadiabatic cycles. Here, experimental data detail changes in W_{act} with temperature.

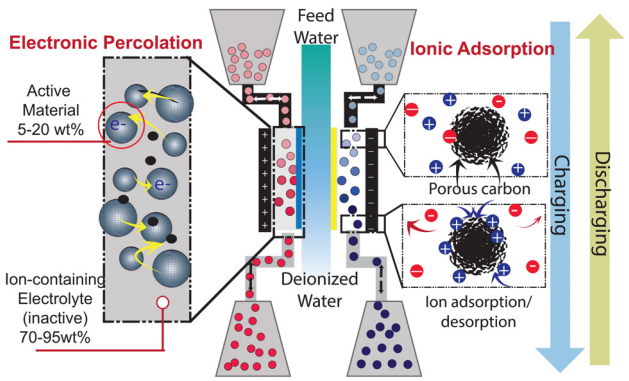

Fig. 5 Flow-electrode CDI replaces the static film electrode with flowable suspensions of carbon materials to improve scalability and elecroadsorption capacity

discharge process [33]. Tanks contain the active material in a "suspension" form and the size of the tank dictates the desalination period. During operation, the flow electrode flows down the current collector and becomes charged when it enters the charging cell. To maintain electroneutrality, ions of opposite charge are attracted from the feed water channel and adsorb on the surface of the active material. The capacity to remove ions in FCDI is not limited by the planar area of an electrode, but rather by the volume of active material. This allows for a wider range of waters, which can be treated (e.g., $C_0 = 0.01–0.6$ M). Continuous operation can be obtained through coupling the flow CDI with another secondary flow cell [36]. Once the slurry is charged, it is transported to this secondary chamber for discharge before returning to the FCDI cell. Additionally, some researchers have investigated storing the positive and negative electrode together outside the FCDI cell [37]. By doing this, the charge is constantly released from the particles to maintain electroneutrality. The only challenge with this operation is energy recovery is not possible (Fig. 6).

The flow electrode configuration also allows for new system cycles to be designed because the electrodes and feed are all stored in separate containers. This allows for unique control of i, V, σ, n, T, and P, which are not possible in planar configurations. In addition, flow electrode cells can be investigated in system architectures, which include cascading designs, where various charging and discharging stages for energy recovery could be investigated [36,38,39].

Flowable electrodes are composed of active materials (activated carbon) at loadings between 5–20 wt % and an ionic electrolyte (80–95 wt %). There are fundamental trade-offs between active material loading and flowability [28]. High loading leads to a potential for high salt removal, but at the expense of pumping power. Within the flowable electrode, there are two fundamental processes: (1) electron transfer and (2) ionic adsorption (Fig. 5). These two processes are fundamentally coupled. Ionic adsorption (salt removal) is limited to material or particles that can maintain charge. A fundamental limitation in "thick" biphasic electrode systems is the ability to create effective percolation networks for efficient electron conduction, salt removal, and energy recovery.

The flow electrode architecture is currently in its infancy and several material challenges need to be addressed. In addition, ohmic resistance in the cell increases due to nonperfect particle–particle interactions. Ideally, to promote efficient electron transport, the particles need to reach a percolated state, which is not met at low concentrations. Active means to minimize these resistances are being explored through introducing mediators [40]. Yet the ability to innately control various system parameters such as temperature, ion concentration, and charge density in the electrode and feed channel simultaneously creates an ideal architecture for validating new desalination cycles.

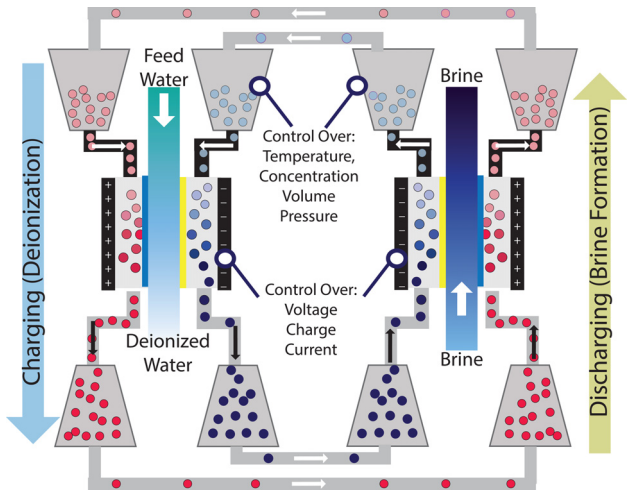

Fig. 6 Continuous operation can occur through the use of two flow cells. The first cell performs deionization, and the second forms brine. Continuous cycling through the flow cells allows for unique control of ion concentration, temperature, pressure, voltage, charge, and current.

4 Conclusions

With the growing need to increase the available water to maintain energy and food demands, a greater emphasis will be placed on introducing new water technologies and systems, which are energy efficient. This has promoted the development of alternative treatment technologies, which operate through the use of electrochemical forces rather than thermal- or pressure-driven processes. These electrochemical desalination systems have many thermodynamic similarities to thermal engines and refrigerators, yet have not been optimized to operate in an ideal fashion. As these technologies continue to grow in importance, greater emphasis will need to be placed on theoretically and experimentally verifying ideal system cycles, which minimize irreversibilities. This most likely will occur through rethinking the standard system architecture.

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Nomenclature

c_c = concentration of concentrate (waste) stream
c_d = concentration of de-ionized stream
c_0 = concentration of feed (input) stream
CDI = capacitive de-ionization
EDL = electric double layer
V_d = volume of de-ionized stream
V_0 = volume of feed (input) stream
α = water recovery ratio
ΔG_{mix} = Gibbs free energy of mixing (J/mol)
μ_C = chemical potential of concentrate (waste) stream
μ_D = chemical potential of de-ionized stream
μ_0 = chemical potential of feed (input) stream
σ = electrode charge
ϕ_D = potential of diffuse region of the EDL
ϕ_S = potential of stern region of the EDL
Ψ = potential of electrode

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