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Electrochemical Redox Cells Capable of Desalination and Energy Storage: Addressing Challenges of the Water−Energy Nexus

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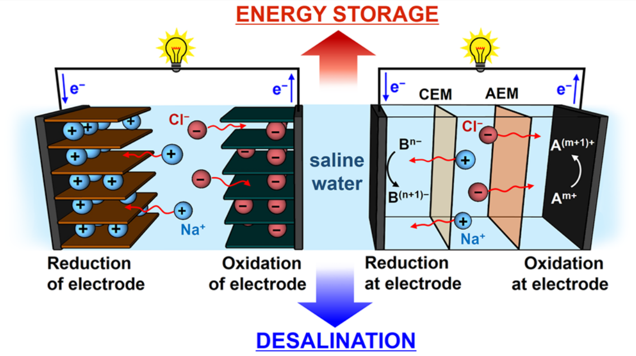
ABSTRACT: Lack of access to freshwater has become an urgent global challenge, and desalination offers a viable strategy to address the growing gap between global freshwater supply and demand. The development of desalination technologies that can store/release energy concurrently with desalination is particularly attractive, as these technologies have the potential to address challenges at the intersection of the water−energy nexus. In this Perspective, we will discuss three such types of electrochemical desalination cells that use redox reactions: desalination batteries, rocking chair desalination batteries, and desalination cells based on the use of redox couples in solution. The operating principles of each cell type are discussed, and their advantages and challenges are compared. By providing an overview of the exciting recent advancements in coupling electrochemical desalination and energy storage, this Perspective aims to motivate researchers to formulate effective approaches that can help to achieve more practical and efficient desalination in the near future.



Water is an essential resource for human consumption, agriculture, energy generation, and the natural environment. However, population growth and climate change have contributed to heightened water stress throughout the world. Currently, ∼4 billion people (66% of the world's population) suffer from freshwater scarcity for at least one month of the year, and ∼500 million people face severe water scarcity all year round.[1] As global water demand is expected to increase by 70% from 2016 to 2050, securing access to freshwater has become an urgent global challenge.[2−5] Considering the abundance of seawater on Earth, desalination, which is used to separate dissolved salt ions from a saline feedwater source, is considered one of the most viable options to meet the increasing global demand for freshwater.[3−5] Thermal distillation and reverse osmosis (RO) are the primary methods currently used for the desalination of seawater, but both methods require a considerable electrical energy input to achieve desalination.[5−7]

Electrochemical desalination technologies have been investigated as alternatives to thermal distillation and RO.[8−17] Unlike thermal distillation and RO, where water molecules are separated from saline water, in electrochemical desalination, salt ions are separated from saline water. As the amount of salt is less than the amount of water in saline water, electrochemical desalination has the potential to achieve desalination with a higher water recovery and lower cost than thermal distillation and RO. The two most well-established electrochemical desalination methods are capacitive deionization (CDI) and electrodialysis (ED). In CDI, desalination is achieved through the adsorption of salt ions in the electrical double layer of high surface area electrodes when a voltage is applied between the two electrodes (Figure 1a).[14,15] Although CDI has long been considered a promising approach for energy-efficient desalination, its limited capacity for ion storage and excessive co-ion expulsion hinder the practical application of CDI for the desalination of highly concentrated saline water, like seawater.[8−14] Thus, CDI is limited only to the desalination of brackish water.

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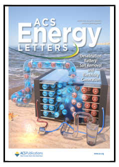

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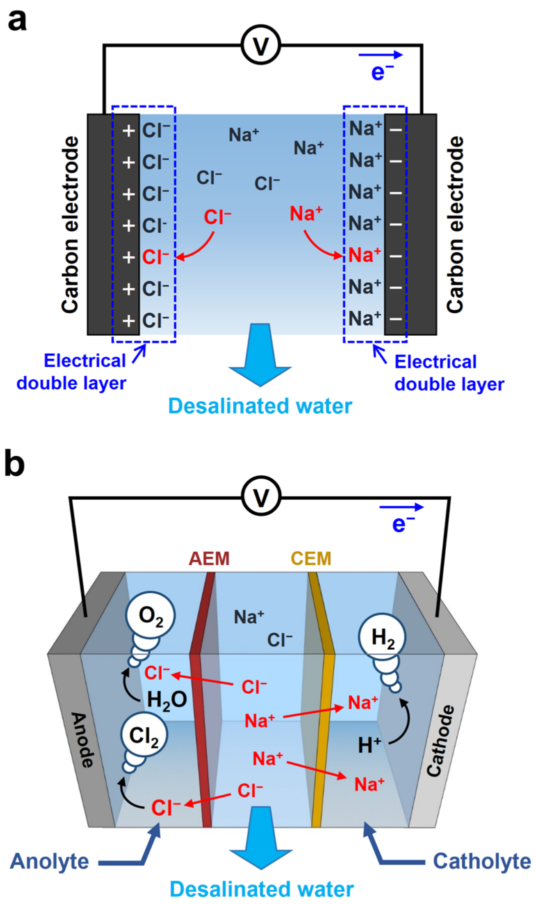

Figure 1. Scheme for desalination performed by (a) a CDI cell and (b) a three-compartment ED cell.

In ED, desalination is achieved through the transport of salt ions through ion-exchange membranes when a voltage is applied between the anode and cathode to induce oxidation and reduction reactions, respectively.[18,19] The anode reaction either consumes anions or generates cations, while the cathode reaction either consumes cations or generate anions. Thus, when a voltage is applied and electrochemical reactions occur, the anions move toward the anode and the cations move toward the cathode to maintain charge neutrality. Therefore, when an anion exchange membrane (AEM) is placed in front of the anode and a cation exchange membrane (CEM) is placed in front of the cathode, the compartment between these two membranes can be desalinated (Figure 1b). The most commonly used cathode and anode reactions in ED are water reduction and water oxidation or chloride oxidation, respectively.[18−20] The electrical energy required for desalination by ED is the product of the operating voltage and the charge required for desalination. The charge required for desalination is proportional to the amount of salt to be removed from the feedwater. With the current operating voltage of conventional ED cells, seawater desalination is considered cost-prohibitive, and ED, like CDI, is primarily used for brackish water desalination.[18]

Recently, various electrochemical desalination methods have been explored to address the major limitations of CDI and ED. For example, in order to increase the capacity for salt removal, desalination cells that use electrodes that can store Na^+ and Cl^- in the bulk of the electrodes (i.e., Na-storage and Cl-storage electrodes) have been developed.[21−30] These electrodes undergo redox reactions to store and release salt ions, which is different from CDI where the electrodes are electrochemically inert during the storage and release of salt ions. Because Na-storage and Cl-storage electrodes have a much higher capacity for salt removal, cells that use Na-storage and Cl-storage electrodes can potentially be used for seawater desalination. Various new ED strategies have also been reported, where alternative redox reactions are used as the electrode reactions to induce ion movement.[31−47] These new ED cells can achieve desalination with a lower operating voltage than conventional ED cells, offering possibilities to reduce the electrical energy consumption of desalination.

Another notable feature of many recently reported electrochemical desalination methods is that they can store/release energy concurrently with the storage/release of salt ions. In other words, these cells perform desalination through charging and discharging processes, and so the energy consumed for desalination is not really consumed but stored through charging. The energy stored during charging can be at least partially recovered during discharging. This feature can not only considerably decrease the net energy required for desalination but also create new opportunities to use desalination cells as energy storage systems to more efficiently utilize electricity generated from intermittent renewable sources (e.g., solar, wind). Undoubtedly, a device that can simultaneously achieve desalination and energy storage is ideally positioned to have a remarkable impact on the water−energy nexus.

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The purpose of the current Perspective is to present and discuss recent electrochemical desalination cells that (i) use redox reactions for the storage and release of salt ions and (ii) have the ability to couple desalination and energy storage/release functions. Thus, neither CDI that does not use redox reactions nor conventional ED that cannot store energy during desalination is included. Interested readers can reference reviews already available for CDI and conventional ED.[14−17,19,20] The current Perspective is not intended to provide an extensive review of the desalination cells covered here in terms of performance and efficiency analyses. (Such analyses can be found in other recent reviews.[8,10,12,13]) Rather, the particular focus of this Perspective is to explain and compare the configurations and operating principles of representative desalination cells that meet the aforementioned criteria. The similarities and differences between these cells in terms of how they achieve desalination and how they achieve energy storage/release are discussed in detail. The configurations of these cells will also be compared with those of batteries that achieve only energy storage/release or those of ED cells that achieve only desalination. By providing an overview of the exciting recent advancements in coupling electrochemical desalination and energy storage, this Perspective aims to enable researchers to easily identify areas to which they can contribute with effective strategies for further development.

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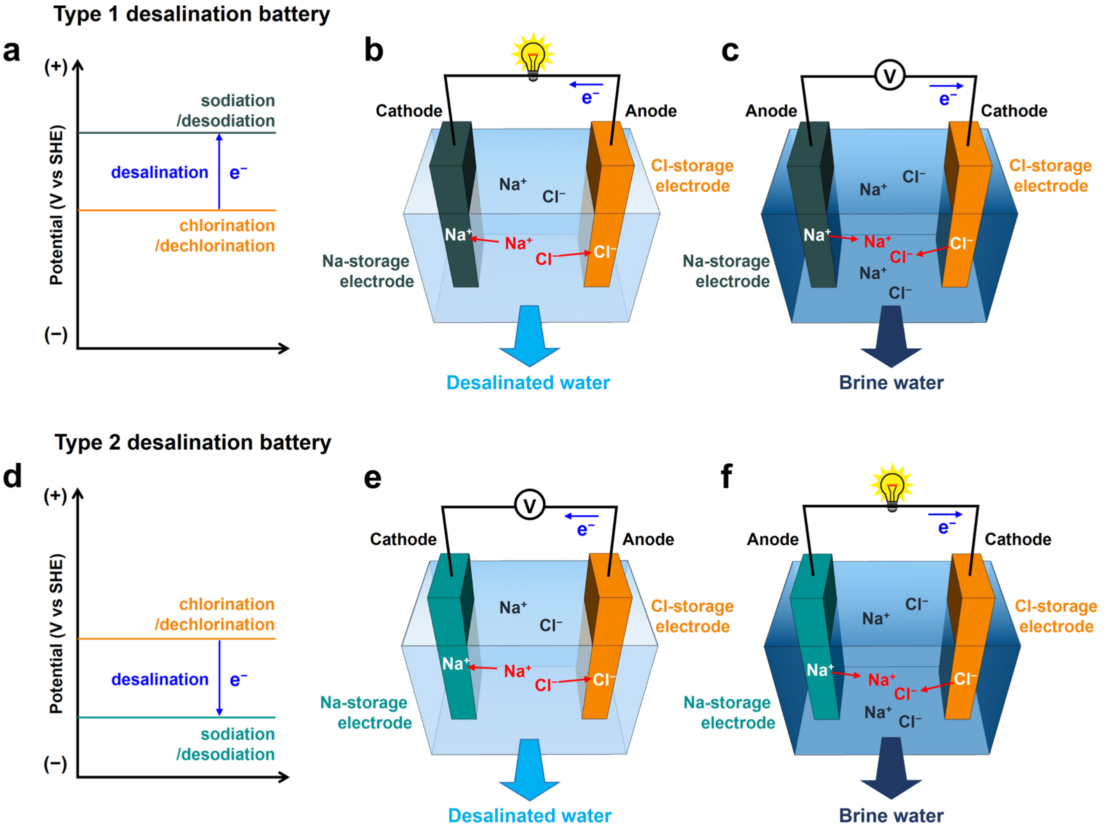

Figure 2. Schematic illustration of Type 1 (top) and Type 2 (bottom) desalination batteries: (a, d) relative redox potentials of the Na-storage and Cl-storage electrodes, (b, e) the desalination process, and (c, f) the salination process.

DESALINATION BATTERIES

Desalination batteries are rechargeable batteries that specifically couple the storage and release of energy with the storage and release of Na^+ and Cl^-.[21,24] Desalination batteries consist of a Na-storage electrode and a Cl-storage electrode. These electrodes undergo redox reactions to store Na^+ and Cl^- in the bulk of the electrode: the Na-storage electrode is reduced to store Na^+, and the Cl-storage electrode is oxidized to store Cl^-, to maintain the charge neutrality of each electrode (eqs 1−3).

Desalination Process.

- Cathode Reaction (Na^+ storage reaction or sodiation of the Na-storage electrode):

$$\text{Na-storage electrode} + Na^+ + e^- \rightarrow [\text{Na-storage electrode}]^-{:}Na^+ \quad (1)$$

- Anode Reaction (Cl^- storage reaction or chlorination of the Cl-storage electrode):

$$\text{Cl-storage electrode} + Cl^- \rightarrow [\text{Cl-storage electrode}]^+{:}Cl^- + e^- \quad (2)$$

- Overall Reaction (desalination of the electrolyte):

$$\text{Na-storage electrode} + \text{Cl-storage electrode} + Na^+ + Cl^- \rightarrow [\text{Na-storage electrode}]^-{:}Na^+ + [\text{Cl-storage electrode}]^+{:}Cl^- \quad (3)$$

Once the Na-storage and Cl-storage electrodes are saturated with Na^+ and Cl^-, respectively, the electrodes can be moved to another cell to release Na^+ and Cl^- through the reverse of the aforementioned desalination reactions. This reverse process is referred to as salination (eqs 4−6) and is used to regenerate the Na-storage and Cl-storage electrodes so that they can be used for subsequent desalination processes.

Salination Process.

- Anode Reaction (Na^+ release reaction or desodiation of the Na-storage electrode):

$$[\text{Na-storage electrode}]^-{:}Na^+ \rightarrow \text{Na-storage electrode} + Na^+ + e^- \quad (4)$$

- Cathode Reaction (Cl^- release reaction or dechlorination of the Cl-storage electrode):

$$[\text{Cl-storage electrode}]^+{:}Cl^- + e^- \rightarrow \text{Cl-storage electrode} + Cl^- \quad (5)$$

- Overall Reaction (salination of the electrolyte):

$$[\text{Na-storage electrode}]^-{:}Na^+ + [\text{Cl-storage electrode}]^+{:}Cl^- \rightarrow \text{Na-storage electrode} + \text{Cl-storage electrode} + Na^+ + Cl^- \quad (6)$$

Salination (eq 6) is the reverse process of desalination (eq 3), and the Gibbs free energy changes (ΔG) for these processes are not zero. Thus, one of these processes must be thermodynamically uphill (charging process, $\Delta G > 0$, $E^e_{cell} < 0$), while the other must be thermodynamically downhill (discharging process, $\Delta G < 0$, $E^e_{cell} > 0$). (E^e_{cell} is the thermodynamic equilibrium cell voltage, which is the equilibrium cathode potential ($E^e_{cathode}$) minus the equilibrium anode potential (E^e_{anode}).) The choice of Na-storage and Cl-storage electrodes determines which process corresponds to charging and which process corresponds to discharging. As shown in eqs 1 and 2, during desalination, the Na-storage

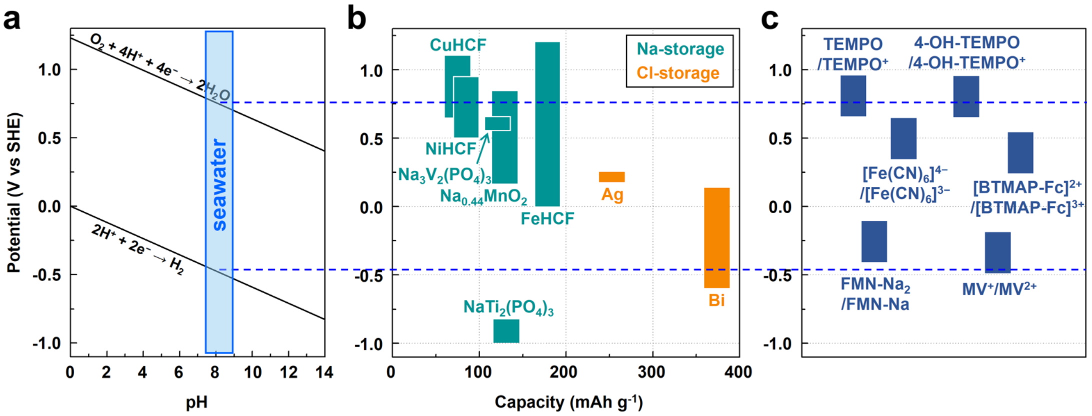

Figure 3. (a) Thermodynamic water oxidation and reduction potentials as a function of pH, (b) redox potential ranges and specific capacities of Na-storage and Cl-storage electrodes, and (c) redox potential ranges of redox mediators that have been used in desalination cells. The blue dashed lines show the water oxidation/reduction potentials in typical seawater (pH 7.5−9.0).[48]

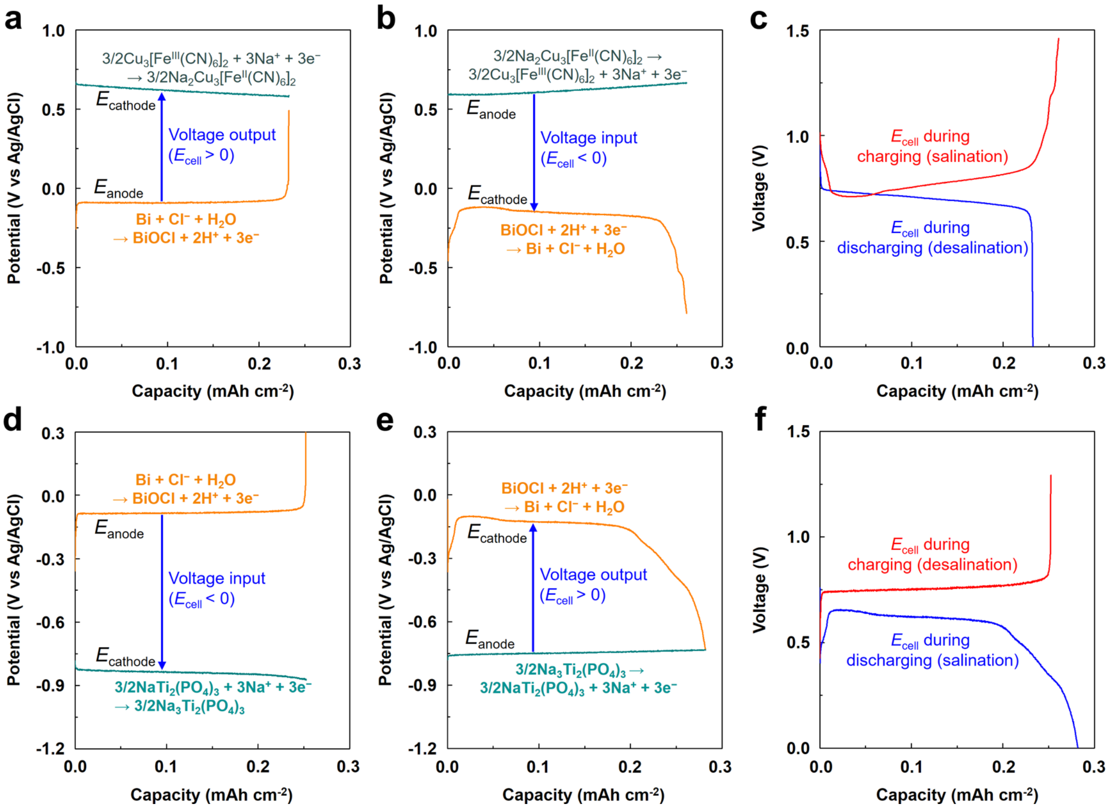

Figure 4. Potential−capacity plots for the CuHCF/Bi cell (Type 1 desalination battery) measured vs an Ag/AgCl reference electrode during (a) the desalination (discharging) process and (b) the salination (charging) process, and (c) the corresponding cell voltage−capacity plots. Adapted with permission from ref 29. Copyright 2019 American Chemical Society. Potential−capacity plots for the Bi/$NaTi_2(PO_4)_3$ cell (Type 2 desalination battery) measured vs an Ag/AgCl reference electrode during (d) the desalination (charging) process and (e) the salination (discharging) process, and (f) the corresponding cell voltage−capacity plots. Adapted with permission from ref 24. Copyright 2017 American Chemical Society. In (c, f) the sign of the voltage for charging, which is negative, is shown as positive for ease of comparison.

electrode is the cathode, and the Cl-storage electrode is the anode. Thus, if the Na-storage and Cl-storage electrodes are chosen such that the sodiation/desodiation potential of the Na-storage electrode is more positive than the chlorination/dechlorination potential of the Cl-storage electrode (Figure 2a), E^e_{cell} is positive, and the desalination process corresponds to discharging. This also means that E^e_{cell} is negative during the salination process, which corresponds to charging. We define this type of cell as a Type 1 desalination battery. A Type 1 desalination battery generates an electrical energy output during desalination (Figure 2b) and requires an electrical energy input during salination (Figure 2c). In contrast, if the sodiation/desodiation potential of the Na-storage electrode is more negative than the chlorination/dechlorination potential of the Cl-storage electrode (Figure 2d), a Type 2 desalination battery is constructed. In a Type 2 desalination battery, the desalination process corresponds to charging (Figure 2e), while the salination process corresponds to discharging (Figure 2f).

The Na-storage electrodes that have been investigated for use in desalination batteries include Na_xMnO_2,[21−23] $NaTi_2(PO_4)_3$,[24−27] $Na_3V_2(PO_4)_3$,[28] copper hexacyanoferrate (CuHCF),[29] nickel hexacyanoferrate (NiHCF),[35,49] and iron hexacyanoferrate (FeHCF).[35] The Cl-storage electrodes that have been investigated for use in desalination batteries include Ag[21−23,25−28] and Bi.[24,29,30] Figure 3a,b shows the sodiation/desodiation potential ranges and chlorination/dechlorination potential ranges of these Na-storage and Cl-storage electrodes in comparison with the electrochemical stability window of water.

The information shown in Figure 3b can be used to predict the type of desalination battery that will result when specific Na-storage and Cl-storage electrodes are combined. For example, a Type 1 desalination battery will be constructed when CuHCF is chosen as the Na-storage electrode and Bi is chosen as the Cl-storage electrode. Figure 4a,b shows the actual potential profiles of CuHCF and Bi obtained when a CuHCF/Bi desalination battery was used to perform the desalination and salination processes in constant current mode.[29] Indeed, $E_{\text{cathode}} - E_{\text{anode}}$ is positive during desalination (discharging), and $E_{\text{cathode}} - E_{\text{anode}}$ is negative during salination (charging). The cell voltage−capacity plots obtained during the charging and discharging steps are shown in Figure 4c, where voltage on the y-axis represents E_{cell}. The E_{cell} obtained during charging, which is negative, is shown as positive so that the magnitudes of the charging and discharging voltages can be easily compared. In these plots, the integrated area below the charging curve represents the energy input required for charging (salination), and the integrated area below the discharging curve represents the energy output generated during discharging (desalination). The difference between the energy input required for charging and the energy output generated during discharging is the net energy required for one desalination/salination cycle. The more the voltage profile of discharging resembles that of charging, the higher the energy recovery and the lower the net energy required for desalination.

Similarly, it can be predicted that, when Bi is coupled with $NaTi_2(PO_4)_3$ as the Na-storage electrode, a Type 2 desalination battery will be constructed. Figure 4d,e shows the actual potential profiles of $NaTi_2(PO_4)_3$ and Bi obtained when a Bi/$NaTi_2(PO_4)_3$ desalination battery was used to perform the desalination and salination processes in constant current mode.[24] In this case, $E_{\text{cathode}} - E_{\text{anode}}$ is negative during desalination (charging), and $E_{\text{cathode}} - E_{\text{anode}}$ is positive during salination (discharging). Figure 4f shows a comparison of the cell voltage−capacity plots during desalination and salination. (Again, the E_{cell} during charging is shown as positive for ease of comparison.)

Among various desalination batteries that have been reported to date, MnO_2/Ag,[21] $Na_{0.44}MnO_2$/Ag,[22,23] $Na_3V_2(PO_4)_3$/Ag,[28] CuHCF/Bi,[29] and $Na_{0.44}MnO_2$/BiOCl[30] cells are Type 1, and Bi/$NaTi_2(PO_4)_3$[24] and Ag/$NaTi_2(PO_4)_3$[25−27] cells are Type 2.

When constructing Type 1 and Type 2 desalination batteries, the Na-storage and Cl-storage electrodes can be chosen to either maximize or minimize the difference between the sodiation/desodiation potential and the chlorination/dechlorination potential, which creates different advantages. When the electrodes are chosen so that the potential difference is maximized, both the energy input required for charging and the energy output generated during discharging will also be maximized. Although this cell will require a greater energy input for the charging process, this energy should be thought of not as being consumed but as being stored. Therefore, such a cell can maximize its energy storage capabilities as long as the cell can operate with a high energy recovery efficiency (energy recovery efficiency (%) = [energy output generated during discharging/energy input required for charging] × 100%). When the electrodes are chosen so that the potential difference is minimized, both the energy input required for charging and the energy output generated during discharging will also be minimized. In this case, the desalination battery may not serve as an efficient energy storage device, but this type of cell has the advantage of operating with a minimal energy input during the charging process.

For all the different types of desalination batteries discussed above, the net energy consumption for the complete desalination/salination cycle is always equal to the difference between the energy input required for charging and the energy output generated during discharging. Therefore, regardless of the cell type selected, the electrodes need to be optimized to minimize the potential difference between the forward and reverse reactions. Also, for practical use of desalination batteries, it is critical to significantly improve the cyclability of the Na-storage and Cl-storage electrodes beyond what has been reported to date. Furthermore, as the goal of desalination batteries is not to provide portable power but to produce desalinated water, it is vital to fabricate large-scale electrodes that can achieve performances comparable to those of electrodes used in proof-of-concept cells.

The Na-storage electrodes that have been reported for desalination batteries are those that have already been used for Na-ion and Li-ion batteries.[50] In general, these materials store/release Na^+ through intercalation into a host structure that does not involve considerable structural changes. As a result, many Na-storage electrodes show good cyclability after an appropriate electrolyte has been chosen to optimize their performance. However, the electrolyte used in desalination batteries cannot be tuned in the same way as it can for Na-ion batteries; the purpose of desalination batteries is to perform desalination, and so the electrolyte used in the desalination cell must be a neutral saline solution. Therefore, it is necessary to identify Na-storage electrodes that exhibit good cyclability in neutral saline solutions and further optimize their performances.

Compared with Na-storage electrodes, the candidates for Cl-storage electrodes are extremely limited. The only two metals that are known to store and release Cl^- through reversible electrochemical reactions, whose chlorinated forms are also stable in neutral saline solutions, are Ag[21−23,25−28] and Bi.[24,29,30,51] Unlike Na-storage electrodes, Ag and Bi undergo phase transformations when they store Cl^- to produce AgCl and BiOCl, respectively. Ag requires only one electron to store/release one Cl^- ($Ag + Cl^- \rightleftharpoons AgCl + e^-$),[23] while Bi requires three electrons to store/release one Cl^- ($Bi + Cl^- + H_2O \rightleftharpoons BiOCl + 2H^+ + 3e^-$).[24] Thus, Bi requires 3 times as much charge as Ag or has 3 times the capacity of Ag when removing Cl^-. The low cost of Bi (1.3 USD/mol in 2019) compared with Ag (56.1 USD/mol in 2019) is a clear advantage of Bi for the construction of large-scale desalination cells.[52] Recently, polypyrrole has also been demonstrated as a Cl-storage electrode.[53,54]

While the development of desalination batteries is still in its infancy, there are two critical compelling advantages that motivate further investigation of desalination batteries. The first is that desalination batteries show promise for the electrochemical desalination of seawater, which has been inaccessible with CDI and ED. This is because of the combined use of Na-storage and Cl-storage electrodes, which significantly enhances the salt removal capacity of the cell, and the considerable decrease in the net electrical energy required for desalination, which is achieved by coupling energy storage/release with salt removal/release. The second is that desalination batteries enable membrane-free desalination. As Na^+ is stored in the Na-storage electrode and Cl^- is stored in the Cl-storage electrode, a membrane is not necessary to remove NaCl from the feedwater. We note that all other electrochemical desalination methods in addition to RO require the use of a membrane. Eliminating the need for a membrane can significantly reduce the costs associated with the prevention of membrane fouling and can simplify the overall cell design and cell maintenance.[3,6,18] Because desalination batteries are ion-specific, not all ions present in seawater can be removed by desalination batteries, and the remaining salt ions need to be removed by another method, such as RO, CDI, or ED. However, as brackish water desalination can be achieved economically by these existing methods, and the conversion of seawater to brackish water is the step that consumes the majority of the energy required for seawater desalination, energy-efficient, membrane-free desalination batteries are ideally suited to make a distinctive and considerable impact on seawater desalination.

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■ ROCKING CHAIR DESALINATION BATTERIES

Rocking chair desalination batteries are composed of two Na-storage electrodes with different sodiation/desodiation potentials, just like rocking chair Na-ion batteries.[35] During cell operation, one Na-storage electrode will be oxidized to release Na^+ (desodiation, anode), and the other Na-storage electrode will be reduced to store Na^+ (sodiation, cathode). Suppose that the sodiation/desodiation potential of Na-storage electrode A is more negative than the sodiation/desodiation potential of Na-storage electrode B (Figure 5a). In this case, the movement of Na^+ from electrode A to electrode B is thermodynamically downhill and corresponds to discharging ($E^e_{cell} > 0$), while the

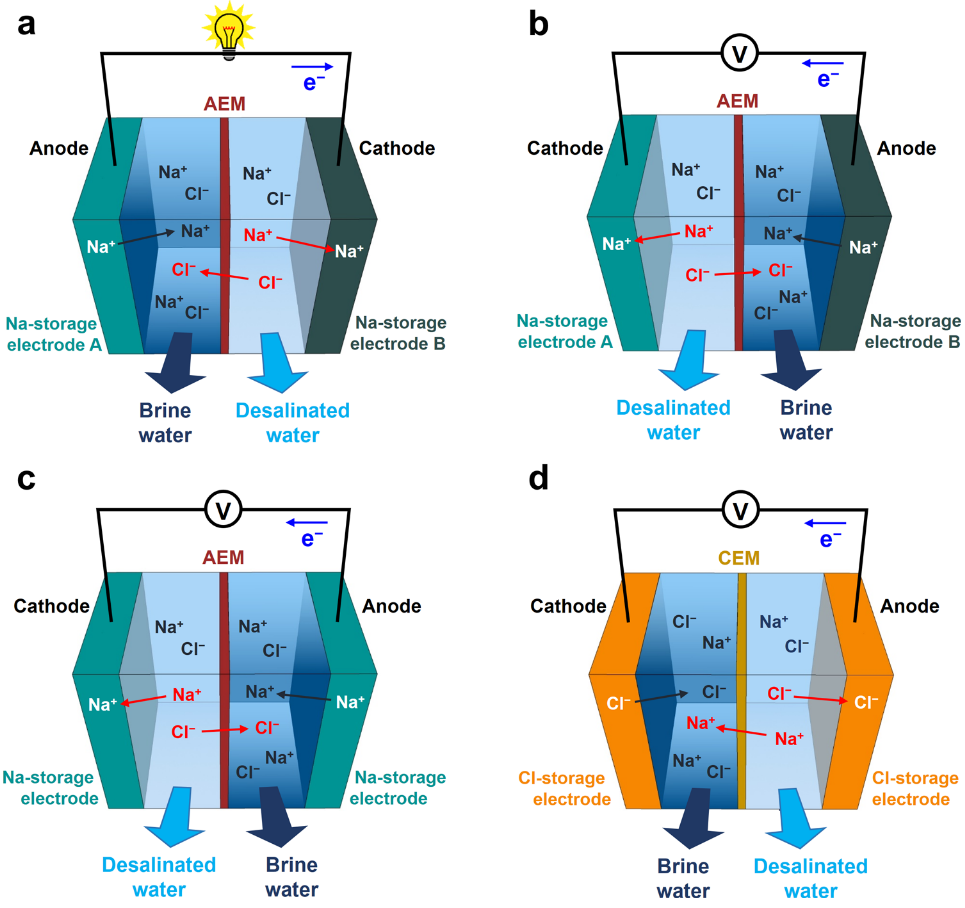

Figure 5. Top: Schemes showing (a) the discharging process and (b) the charging process of a rocking chair desalination battery that contains two different Na-storage electrodes. In this example, the sodiation/desodiation potential of Na-storage electrode A is more negative than the sodiation/desodiation potential of Na-storage electrode B. Bottom: Schemes showing (c) a symmetric Na-ion desalination cell containing two identical Na-storage electrodes and (d) a symmetric Cl-ion desalination cell containing two identical Cl-storage electrodes.

reverse process is thermodynamically uphill and corresponds to charging ($E^{\mathrm{e}}_{\mathrm{cell}} < 0$).

In this cell, the removal of Cl^- is achieved not by a Cl-storage reaction of the electrode but by Cl^- transport through an AEM placed between the two electrodes. During the discharging process, electrode A in the anode compartment releases Na^+, and electrode B in the cathode compartment stores Na^+. In order to maintain charge neutrality in both compartments, Cl^- will move from the cathode compartment to the anode compartment through the AEM, thereby achieving desalination in the cathode compartment and producing brine in the anode compartment (Figure 5a). When electrode A has been depleted of Na^+ and electrode B has been saturated with Na^+, the reverse reactions are performed through the charging process (sodiation of electrode A and desodiation of electrode B). The direction of Cl^- transport is also reversed (Figure 5b). During charging, electrode A is the cathode and electrode B is the anode. In both the discharging and charging processes, desalination is achieved in the cathode compartment, and salination is achieved in the anode compartment.

The critical difference between rocking chair desalination batteries and desalination batteries is that rocking chair desalination batteries require a membrane; without a membrane, they cannot achieve desalination and can function only as energy storage devices (i.e., aqueous sodium-ion batteries). Because Cl^- removal is achieved by ion transport through a membrane, rocking chair desalination batteries resemble ED in terms of their operating principles, although these two technologies use different electrode reactions to induce ion movement (water reduction, water oxidation, and chloride oxidation for conventional ED cells vs Na^+ storage and release for rocking chair desalination batteries). Another difference between rocking chair desalination batteries and desalination batteries is that desalination and salination occur simultaneously in different compartments of the rocking chair desalination battery during both charging and discharging. In desalination batteries, which have a single compartment, only desalination or salination occurs during charging or discharging.

As for the case of desalination batteries, the electrodes used in rocking chair desalination batteries can be chosen to maximize or minimize the potential difference between the two electrodes. When the electrodes are chosen so that the potential difference is maximized, the amount of energy stored and the amount of energy released are also maximized. However, if the goal of the cell is to minimize the energy input required during charging, the two electrodes can be chosen to minimize the difference between the sodiation/desodiation potentials of the two electrodes.

The most extreme example of minimizing the difference between the potentials of the two Na-storage electrodes is to use the same Na-storage electrode as both the anode and cathode (Figure 5c). This cell is called a symmetric Na-ion desalination cell.[31] (In contrast, rocking chair desalination batteries composed of two different Na-storage electrodes can be called asymmetric Na-ion desalination cells.) Symmetric Na-ion desalinations use the forward and reverse of the same electrode reaction as the cathode and anode reactions, which makes $E^{\mathrm{e}}_{\mathrm{cell}}$ equivalent to zero. As only the kinetic overpotentials, IR drop, and membrane potentials contribute to the operating voltage, the electrical energy required to operate the cell can be minimized. However, a symmetric Na-ion desalination cell can no longer store and release energy; there are no charging and discharging processes. Instead, the movement of Na^+ between the two electrodes in any direction will always require an energy input, and the energy input required will ideally be the same regardless of the direction of ion movement. To date, a NiHCF/FeHCF cell has been demonstrated as a rocking chair desalination battery,[35] and Na_xMnO_2/Na_xMnO_2,[31] $NaTi_2(PO_4)_3/Na_3Ti_2(PO_4)_3$,[31] NiHCF/NiHCF,[32,33] and CuHCF/CuHCF[34] cells have been demonstrated as symmetric Na-ion desalination cells.

Inspired by the cell architecture and operating principles of symmetric Na-ion desalination cells, Cl-storage electrodes have also been used to construct symmetric Cl-ion desalination cells.[36−38] In these cells, Cl^- is removed by the Cl-storage electrode, and Na^+ is removed through transport of Na^+ through a CEM; the chlorination/dechlorination reactions of the two Cl-storage electrodes drive Na^+ transport through the CEM (Figure 5d). Like symmetric Na-ion desalination cells, symmetric Cl-ion desalination cells cannot serve as energy storage devices, and they only achieve desalination. To date, a Bi/BiOCl cell[36] and an Ag/AgCl cell[37,38] have been demonstrated as symmetric Cl-ion desalination cells.

Like desalination batteries, successful scale-up and improvement of the cycle performance of the electrodes will be critical for rocking chair desalination batteries and symmetric Na-ion and Cl-ion desalination cells to be used for practical desalination.

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■ DESALINATION CELLS BASED ON THE USE OF REDOX COUPLES IN SOLUTION

The last type of electrochemical desalination cell that will be discussed in this Perspective is not based on redox reactions of the electrode materials but based on the oxidation and reduction of redox couples present in solution using electrochemically inert electrodes. These redox reactions induce salt ion transport through ion-exchange membranes to achieve desalination. Therefore, the cells discussed here are ED cells in principle. The difference between these cells and conventional ED cells is the type of redox reaction that occurs at the electrode to induce ion movement.

Most of the redox couples used in these cells involve one-electron reduction/oxidation reactions with minimal structural reorganization. As a result, these redox couples can have fast redox kinetics and require lower kinetic overpotentials than those of the reactions used in conventional ED cells. The redox couples that have been used in desalination cells include $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$,[39,41,42,44] 1,1′-bis[3-(trimethylammonio)propyl]ferrocene dichloride-based $[BTMAP\text{-}Fc]^{2+}/[BTMAP\text{-}Fc]^{3+}$,[42] 2,2,6,6-tetramethyl-1-piperidinyloxy-based $TEMPO/TEMPO^+$,[43] riboflavin-5′-phosphate sodium salt-based $FMN\text{-}Na_2/FMN\text{-}Na$,[45] methyl viologen-based MV^+/MV^{2+},[46] and 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl-

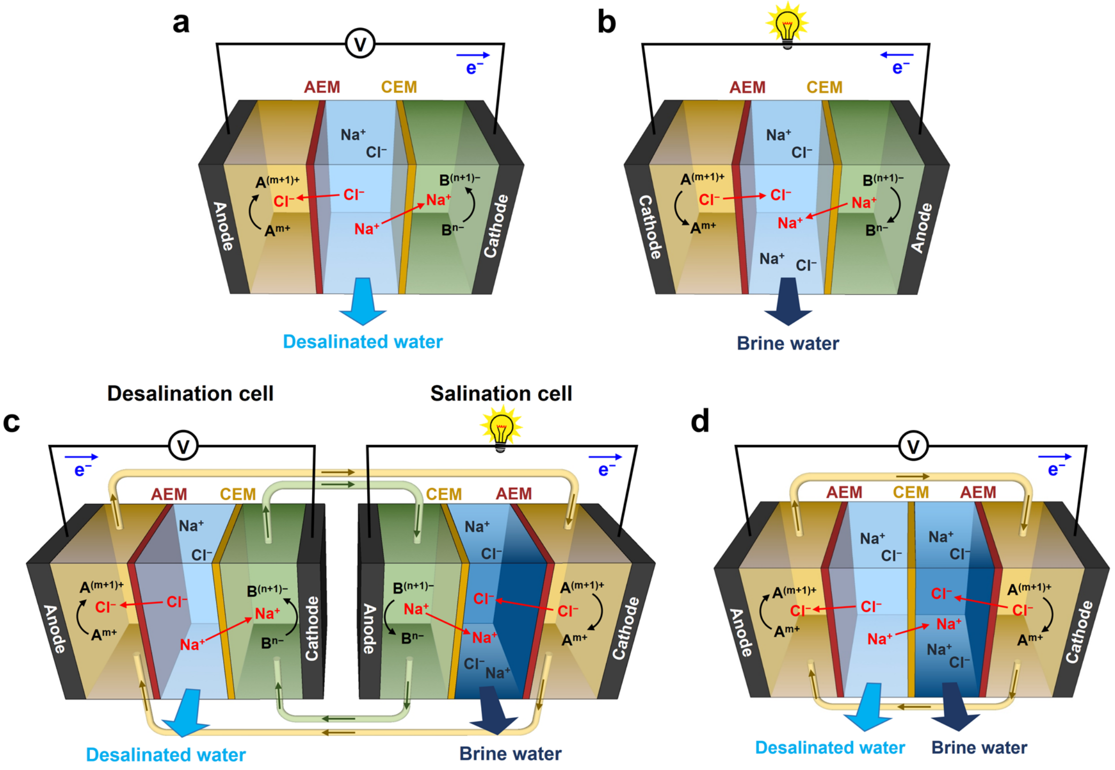

Figure 6. Schemes for a three-compartment (a) desalination and (b) salination ED cell and (c) tandem operation of the desalination and salination ED cells. In this example, the redox potential of $A^{m+}/A^{(m+1)+}$ is more positive than that of $B^{(n+1)-}/B^{n-}$. (d) A four-compartment ED cell with an $A^{m+}/A^{(m+1)+}$ redox couple in both the anolyte and catholyte.

based 4-hydroxy-TEMPO/4-hydroxy-TEMPO$^+$.[47] Their redox potentials are summarized in Figure 3c.

The redox couples used in the anolyte and catholyte can be different or the same, which results in different advantages, as for the case of symmetric and asymmetric Na-ion and Cl-ion cells. When the redox couples used in the anolyte and catholyte are different, the cell can store and release energy like a redox flow battery.[39] However, while redox flow batteries have two compartments (anolyte and catholyte), the simplest ED cell requires three compartments to perform desalination, as shown in Figure 6a. The schematic cell in Figure 6a is composed of an anolyte containing an $A^{m+}/A^{(m+1)+}$ redox couple, a catholyte containing a $B^{(n+1)-}/B^{n-}$ redox couple, and a middle compartment containing the saline feedwater to be desalinated. The anode compartment is separated from the middle compartment by an AEM, and the cathode compartment is separated from the middle compartment by a CEM. When the cell is operated, A^{m+} is oxidized to $A^{(m+1)+}$ at the anode, and B^{n-} is reduced to $B^{(n+1)-}$ at the cathode. To maintain charge neutrality in each compartment, Na^+ in the middle compartment moves through the CEM to the cathode compartment, and Cl^- in the middle compartment moves through the AEM to the anode compartment. Thus, desalination is achieved in the middle compartment, and this cell is called a desalination ED cell.

When the anode compartment is depleted of A^{m+} and the cathode compartment is depleted of B^{n-}, the electrolytes need to be regenerated by performing the reverse reactions: reduction of $A^{(m+1)+}$ at the cathode and oxidation of $B^{(n+1)-}$ at the anode (Figure 6b). In this process, Na^+ and Cl^- that accumulated in the electrode compartments during desalination can be transported to the middle compartment. Thus, salination is performed in the middle compartment, and this cell is called a salination ED cell.

If the redox potential of $A^{m+}/A^{(m+1)+}$ is more positive than the redox potential of $B^{(n+1)-}/B^{n-}$, the desalination cell is the charging cell ($E_{cell} < 0$) and the salination cell is the discharging cell ($E_{cell} > 0$), as is depicted in Figure 6a,b. If the redox potential of $A^{m+}/A^{(m+1)+}$ is more negative than the redox potential of $B^{(n+1)-}/B^{n-}$, the desalination cell is the discharging cell and the salination cell is the charging cell. As the difference between the redox potentials of $A^{m+}/A^{(m+1)+}$ and $B^{(n+1)-}/B^{n-}$ increases, the cell can store and release a greater amount of energy. We note that the redox couples employed in these desalination cells must be chemically and electrochemically stable in neutral saline solutions. This is a unique requirement compared with redox flow batteries where the pH and solvent type can be optimized for a specific redox couple.

To minimize the number of charging/discharging cycles necessary to remove a given amount of salt, the concentrations of the redox couples or volumes of the anolyte and catholyte must be increased. However, if the redox couples are expensive, using a greater amount of the redox couples may be cost-prohibitive. This concern can be addressed by operating desalination and salination ED cells in tandem, as shown in Figure 6c.[47] In this setup, the anolyte of the desalination cell and the catholyte of the salination cell are constantly circulated so that any change in the $A^{m+}/A^{(m+1)+}$ ratio and the Cl^- concentration made in the anolyte of the desalination cell can be exactly reversed in the catholyte of the salination cell. In the same manner, the catholyte of the desalination cell and the anolyte of the salination cell are circulated to maintain the same solution composition. Thus, this tandem ED cell design provides a possibility to achieve seawater desalination with the use of a minimal amount of redox species, regardless of whether the redox couples used in the anolyte and catholyte are different or the same.[47]

When the same redox couple is used in the anolyte and the catholyte, the resulting ED cell can no longer store and release energy. The advantage of the resulting cell is a decrease in the operating voltage by making E^{e}_{cell} equivalent to zero. The simplest device that demonstrates this concept is a four-compartment cell, as shown in Figure 6d.[42,43,45] In this cell, the anolyte and catholyte are circulated so that any compositional change made in the anolyte is reversed in the catholyte to prevent accumulation of A^{m+}, $A^{(m+1)+}$, and other salt ions in the anolyte and catholyte. When the redox couple is composed of cationic species like $A^{m+}/A^{(m+1)+}$, the catholyte and anolyte must be compartmentalized using an AEM to prevent the transport of $A^{m+}/A^{(m+1)+}$ through the membrane during cell operation. If the redox couple is composed of anionic species like $B^{(n+1)-}/B^{n-}$, a CEM must be used instead to prevent the transport of $B^{(n+1)-}/B^{n-}$ through the membrane during cell operation. In both cases, one of the middle compartments achieves desalination, while the other achieves salination.

A clear advantage of desalination cells based on the use of solution redox couples compared with CDI, desalination batteries, and rocking chair desalination batteries is that the salt removal capacities of the electrodes are irrelevant. Compared with conventional ED, the use of solution redox couples may reduce the electrical energy input necessary for desalination. This is achieved either by using desalination and salination ED cells, where the energy consumed by one cell can be partially recovered by the other, or by using the same redox couple for the cathode and anode reactions to minimize E^{e}_{cell}.

> A clear advantage of desalination cells based on the use of solution redox couples compared with CDI, desalination batteries, and rocking chair desalination batteries is that the salt removal capacities of the electrodes are irrelevant.

A critical challenge for desalination cells based on the use of solution redox couples is to identify inexpensive redox couples that not only possess long-term chemical and electrochemical stability in near neutral saline solutions but also do not exhibit crossover through ion-exchange membranes into the desalination and salination streams. The development of customized membranes that can prevent the crossover of promising redox couples may also be necessary.

In summary, the discovery and development of electrochemical desalination technologies that use redox reactions (either electrode redox reactions or redox reactions of redox couples in solution) have paved the way for innovative solutions for more energy-efficient desalination. Many of the technologies discussed in this Perspective have energy storage capabilities, allowing for more flexibility in managing and saving energy. Promising results demonstrated from proof-of-concept studies and the rapid evolution of cell architectures to address challenges of electrochemical desalination systems are encouraging. However, further development of electrode materials, redox couples, and ion-exchange membranes is necessary to enable these technologies to be used for practical, sustainable, large-scale desalination. If these challenges can be successfully addressed, electrochemical desalination technologies have the potential to provide innovative, energy-efficient solutions to challenges at the intersection of the water−energy nexus.

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■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on February 17, 2021. Due to production error, several negative signs were not superscripts in the section “Desalination Cells Based on the Use of Redox Couples in Solution”. The corrected version was reposted on February 18, 2021.