OSMOTIC BALLASTS FOR MEMBRANE-BASED ENERGY PROCESSES

Electrodialysis

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Solutions

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CONCENTRATED

DILUTE

SOLUTION

SOLUTION

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Published:
— with international search report (Art. 21(3))
OSMOTIC BALLASTS FOR MEMBRANE-BASED ENERGY PROCESSES

PRIORITY CLAIM

This application claims the benefit of U.S. Provisional Patent Application Serial No. 62/357,206 filed June 30, 2016, the disclosure of which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

This specification relates generally to closed-loop membrane processes and more particularly to electrodialysis and reverse electrodialysis systems.

BACKGROUND

There is a widely-acknowledged need for scalable and economical means of storing electric energy to support the increased deployment of intermittent energy sources [1]. Reversible desalination is a novel approach to this challenge that can be used to store energy using electrolyte concentration gradients. In previous work [2], we demonstrated a novel concentration battery that uses electrodialysis (ED) to convert electric energy into a concentration difference between two salt solutions, while the reverse process—reverse electrodialysis (RED)—converts this chemical potential energy back into electricity.

In addition to the concentration difference, an osmotic pressure difference is created across the ion-conducting membranes inside the system, resulting in the unwanted transport of water between the two solutions. Water transport by osmosis has been acknowledged as a source of energy loss in the context of RED for energy generation [3-5], but the impact of osmosis on RED efficiency is often neglected because RED-based energy generation is a flow-through, steady-state process in which the limited osmosis that occurs as the solutions flow through the membrane stack is counteracted to some extent by electro-osmosis [3-5]. In contrast, RED based energy storage is a closed-loop, non-steady state process, in
which the unwanted movement of water between solutions accumulates over time and results in a significant loss of efficiency [2].

In principle, water transport could be controlled by applying differential pressure between the two solutions (as in reverse osmosis); however the plate-and-frame geometry of RED stacks and the need for thin, low-resistance membranes makes this approach difficult in practice, particularly if large concentration gradients are employed.

SUMMARY

This specification describes the use of an "osmotic ballast"—a non-charged solute added to one of the electrolyte solutions—that balances the osmotic pressure and eliminates the driving force for water transport without requiring the development of new materials or the use of differential pressure. We present experimental results using two different ballasts that demonstrate significant improvements in the energy efficiency of an RED-based concentration battery, while illustrating some of the tradeoffs inherent in the selection of a ballast molecule. In some examples, a system includes a first channel containing a concentrated electrolyte solution, a second channel containing a dilute electrolyte solution that has a lower electrolyte concentration than the concentrated electrolyte solution, and at least one ion-conducting membrane between the first and second channels. The dilute electrolyte solution includes an osmotic ballast to balance an osmotic pressure across the membrane caused by the dilute electrolyte solution having a lower electrolyte concentration than the concentrated electrolyte solution. The system can also include a control system for charging or discharging electrical energy from the first and second channels.

The control systems described in this specification may be implemented in hardware, software, firmware, or combinations of hardware, software and/or firmware. In some examples, the control systems described in this specification may be implemented using a non-transitory computer readable medium storing computer executable instructions that when executed by one or more processors of a computer cause the computer to perform operations. Computer readable media suitable for implementing the
subject matter described in this specification include non-transitory computer-readable media, such as disk memory devices, chip memory devices, programmable logic devices, random access memory (RAM), read only memory (ROM), optical read/write memory, cache memory, magnetic read/write memory, flash memory, and application-specific integrated circuits. In addition, a computer readable medium that implements the subject matter described in this specification may be located on a single device or computing platform or may be distributed across multiple devices or computing platforms.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1A is a diagram of an example system for electrodialysis;
Figure 1B is a diagram of an example system for reverse electrodialysis;
Figure 1C is a diagram illustrating operation of a reversible electrodialysis system;
Figure 2 illustrates an example of transport of water across ion-conducting membranes by osmosis during operation of a reversible electrodialysis system;
Figure 3 is a schematic diagram of an example system of osmotically-balanced electrolyte solutions;
Figures 4A-F illustrate example results for the impact of the osmotic ballast on the performance achieved during the energy storage cycles;
Figure 5 illustrates example results for the impact of the type of osmotic ballast on net ballast crossover and conductivity of the dilute electrolyte solution; and
Figure 6 is a flow diagram of an example method for reversible electrodialysis.

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DESCRIPTION

A system for storing energy using a closed loop reversible electrodialysis process includes a first channel containing a concentrated electrolyte solution, a second channel containing a dilute electrolyte solution
that has a lower electrolyte concentration than the concentrated electrolyte solution, and an ion-conducting membrane separating the first and second channels. The dilute electrolyte solution includes an osmotic ballast to balance the osmotic pressure across the membrane caused by the dilute electrolyte solution having a lower electrolyte concentration than the concentrated electrolyte solution. The system can also include a control system for charging or discharging electrical energy from the first and second channels. This specification describes the system, experiments that were performed to verify aspects of the system, and a discussion related to determining an appropriate amount of osmotic ballast for the system.

Introduction

Figure 1A is a diagram of an example system 100 for electrodialysis. System 100 includes a first flow channel 102 and a second flow channel 104. System 100 also includes ion-conducting membranes 106, 108, and 110. Membranes 106 and 110 are cation exchange membranes, and membrane 108 is an anion exchange membrane. Membrane 108 is between flow channel 102 and flow channel 104. For purposes of illustration, system 100 is shown having two flow channels, but in general system 100 can have various combinations of numbers of channels, numbers of membranes, and types of membranes. For example, system 100 can include a stack of many membranes arranged side-by-side, with two electrodes at the end of the whole stack of membranes.

System 100 also includes first and second electrodes 112 and 114 and a source 116 of electrical power. In operation, feed solution is pumped into flow channels 102 and 104 and electrical source 116 applies a voltage across electrodes 112 and 114, resulting in concentrated solution in flow channel 102 and dilute solution in flow channel 104. Membranes 106, 108, and 110 allow counter-ions (i.e., cations for cation exchange membranes and anions for anion exchange membranes) to pass while ideally blocking other parts of solution such as water from passing. The transport of ions results in energy from electrical source 116 being stored in system 100 as chemical energy in the form of a chemical potential gradient between the
concentrated and dilute solutions. In practice, some water also passes between the solutions, as will be discussed further below.

Figure 1B is a diagram of an example system 120 for reverse electrodialysis. System 120 includes flow channels 102 and 104; ion-conducting membranes 106, 108, and 110; and electrodes 112 and 114. Instead of an electrical source, system 120 includes an electrical load 122. In operation, concentrated solution and dilute solution are pumped into flow channels 102 and 104, resulting in mixed solution exiting flow channels 102 and 104. The difference in concentration between the solutions in flow channels 102 and 104 creates a voltage across electrodes 112 and 114. This results in energy from system 120 being provided to electrical load 122.

Figure 1C is a diagram illustrating operation of a reversible electrodialysis system 150. System 150 operates like a battery that can be charged and discharged, going from a battery discharged state 152 to a battery charged state 154 and states between states 152 and 154. From the battery discharged state 152, system 150 charges using electrodialysis. From the battery charged state 154, system 150 discharges using reverse electrodialysis.

Figure 2 illustrates an example of transport of water across ion-conducting membranes in a closed-loop reversible electrodialysis system by showing the system in a first state 202 before the transport of water and in a second state 204 after the transport of water by osmosis. The reversible electrodialysis system includes an electrical system 206 configured to act as a power source or a load, an electrodialysis stack 208 of one or more ion-conducting membranes, a first pump 210 for pumping a first electrolyte solution from a first tank 212, and a second pump 214 for pumping a second electrolyte solution from a second tank 216. The reversible electrodialysis system can also include a control system 218 for controlling pumps 210 and 214 and/or electrical system 206. In the first state 202, the amount of water in each of tanks 212 and 216 is approximately the same. In the second state 204, water has been transported from tank 216 to tank 212 across electrodialysis stack 208. In general, between the first state 202 and the second state 204, some of the water from tank 216 crosses over to tank 212.
as a result of the difference in osmotic pressure between the solutions in tank 212 and 216. The amount of water in tanks 212 and 216 in the first state 202 need not be approximately the same.

Figure 3 is a schematic diagram of an example system 300 of osmotically-balanced electrolyte solutions. System 300 includes a compartment 302 for a concentrated electrolyte solution and a compartment 304 for a dilute electrolyte solution. System 300 includes an ion-conducting membrane 306 between compartments 302 and 304. System 300 also includes an osmotic ballast 308 that has been added to compartment 304 to balance the osmotic pressure across the membrane that is caused by the dilute solution being diluted with respect to the concentrated electrolyte solution. Compartments 302 and 304 include positive ions 310 and negative ions 312.

Osmotic ballast 308 can comprise a particle or molecule that by virtue of its properties (e.g., size, shape, charge, magnetism, or other chemical characteristics) does not permeate through ion-conducting membrane 306 or permeates it much more slowly than the dissolved electrolyte. For example, osmotic ballast 308 can comprise a non-charged solute that does not permeate through ion-conducting membrane 306, e.g., by virtue of osmotic ballast 308 comprising particles or molecules having a particle or molecule size large enough for ion-conducting membrane 306 to block those particles or molecules, or a solute that permeates through the membrane relatively slowly compared to the dissolved electrolyte (e.g., 100x to 100,000x more slowly). For example, where the concentrated electrolyte solution and the dilute electrolyte solution comprise water and sodium chloride as electrolyte, osmotic ballast 308 can comprise an ethylene glycol monomer or oligomer, e.g., mono-ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, etc. Osmotic ballast 308 is described further below.

As used in this document, a particle or molecule that permeates an ion-conducting membrane more slowly than the dissolved electrolyte is considered "non-permeable." A non-permeable solute is blocked from crossing the ion-conducting membrane to a greater degree than the ions are blocked.
In addition to being non-permeable, it is desirable that osmotic ballasts increase the viscosity of the dilute electrolyte solution as little as possible. High viscosity is generally associated with low conductivity (e.g., Walden's rule [6]), and low conductivity solutions are detrimental to the performance of the concentration battery and similar energy processes.

Preliminary results described below indicate that ballasts with a higher molecular weight have a more detrimental impact on conductivity. However, large size is necessary in order to provide more complete rejection of the ballast by the ion-conducting membranes. Both ballasts tested below were linear polymers, but polymers with other topologies or shapes (e.g., cyclic or star-shaped) may be rejected at lower molecular weights than linear polymers, making them suitable for use as osmotic ballasts. For example, it has been shown that cyclic polymers have lower viscosities and smaller volumes than their linear counterparts [7] while cyclic and star-shaped polymers can have lower diffusion coefficients [8,9].

**Preparation of Osmotically-Balanced Solutions**

The osmotic pressure is given by the Gibbs equation

\[
\pi = -\frac{RT}{V_w} \ln \gamma_w x_w
\]

where \( \pi \) is the osmotic pressure of the solution, \( V_w, x_w \) and \( \gamma_w \) are the molar volume, mole fraction, and activity coefficient of water, respectively, \( R \) is the universal gas constant, and \( T \) is the temperature.

The concentration battery derives its potential from two salt solutions of different concentration. By introducing a non-ionic solute into the more dilute solution, it is possible to create an ionic concentration difference while keeping the same total solute concentration (and by extension, mole fraction of water) in both solutions (See Figure 3). In essence, the ballast molecules take the place of water molecules that would otherwise be present. As long as the ballast does not pass through the ion-conducting membrane (or does so very slowly compared to the charged ionic solutes), the concentration of water in both solutions remains essentially the same, and there is no driving force for osmosis.
An ideal ballast is a substance that is highly soluble in aqueous solution, has a low viscosity (so as not to adversely impact the electrical conductivity in the solution), does not permeate through the ion-conducting membranes, and has relatively low cost and toxicity. Ethylene glycols are highly miscible with water, compatible with polymeric ion-conducting membranes [10,11] and are widely used in applications such as antifreezes and de-icing solutions where manipulation of the osmotic pressure is desired [12]. Moreover, aqueous solutions of ethylene glycol monomer up to 45% by weight increase the conductivity of pure water [13]. Accordingly, in this work we selected two ethylene glycol oligomers (n=1 and n=4; hereinafter mono-EG and tetra-EG, respectively) as illustrative ballasts. Relevant properties of these osmotic ballasts are provided in Table 1.

Table 1. Properties of ethylene glycol oligomers used as osmotic ballasts in this study

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>Molecular Weight (g/mol)</th>
<th>Self-Diffusion Coefficient (10^-5 cm^2/s)</th>
<th>Viscosity at Room Temperature (cP)(^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>tetra-EG (n=4)</td>
<td>194.23 [14]</td>
<td>0.18 [14]</td>
<td>2.0 [14]</td>
</tr>
</tbody>
</table>

\(^1\) Viscosity of a 10% by weight mixture of ethylene glycol oligomer in water

Example ballasted dilute solutions were prepared with reference to a concentrated solution containing only 0.513M sodium chloride and water. Dilute solutions were prepared from water, sodium chloride, and either mono-EG or tetra-EG ballast in such a way that the volume-averaged concentration of salt (0.257M) remained constant, regardless of the amount of ballast added. For each of the two ballasts, solutions were prepared containing 100%, 150%, and 200% of the theoretical amount of ballast required to achieve the same osmotic pressure as the concentrated solution. The theoretical amount of ballast required was determined based on the
mole fraction of water in the final mixture, and was 2.7 %v/v and 7.6 %v/v for mono-EG and tetra-EG, respectively. Solutions with more than the theoretical amount were prepared in order to compensate for the tendency of the ballast to diffuse through the ion-conducting membranes, lowering its effective concentration.

**Concentration Battery Testing Procedure**

A concentration gradient battery based on RED was constructed using a commercially-available electrodialysis stack (PCCell GmbH) containing 10 pairs of cation and anion exchange membranes and mixed-metal oxide coated titanium electrodes. Concentrated and dilute salt solutions were circulated through the stack in a closed-loop, while Ag/AgCl reference electrodes (BaSi, Inc. RE-5B) placed near the exterior face of the outermost membranes were used to measure the potential across the membranes. The concentration battery was taken through a single, potential-limited, galvanostatic cycle by means of a potentiostat (Bio-Logic VMP3). Each cycle began by performing electrodialysis, increasing the concentration difference until a target potential was reached. Then, current was reversed and the battery was discharged by RED until it returned to the potential at the beginning of the test. As described in previous work [2], there is an optimum current density that maximizes the round-trip energy efficiency of this type of energy storage cycle. Preliminary experiments without ballast were used to locate the optimal current density for this stack (0.7 W/m²). All subsequent tests were conducted at this current density.

The initial potential was determined by the starting salt concentrations, while the ending potential of 425 mV was chosen based on the potential that could be achieved within approximately 2 hours of charging time. The starting salt concentrations for all cycles were 0.513 M and 0.257 M for the concentrate and dilute, respectively, approximating the conditions used in previous work [2]. Duplicate cycles were performed for each ballast type and concentration.

Three independent measurements of water transport during each energy storage cycle were obtained. The volume of both the concentrated and dilute solutions was measured periodically by means of graduated
cylinders, which also served as the reservoirs from which the solutions were recirculated. The mass of the dilute solution was also recorded by placing its graduated cylinder on an electronic balance (Ohaus N1H110).

**Osmosis and Current Efficiency**

Figures 4A-C summarize the impact of the osmotic ballast on the performance achieved during the energy storage cycles. As shown in Figure 4A, the presence of either mono- or tetra-EG ballast at 100% of the theoretical concentration reduced the net transport of water by 25% and 86%, respectively, compared to the water transport that occurred when no ballast was used. Increasing the ballast concentrations above the theoretical amount continued to decrease the net water transport, with tetra-EG causing negative osmosis (i.e. movement of water from the concentrate to the dilute solution) at 150% and 200% concentration. The larger size and lower diffusivity of tetra-EG, compared to mono-EG, likely allowed tetra-EG to be rejected more effectively by the ion exchange membranes, and therefore to maintain a more stable ballast concentration in the dilute salt solution.

Figure 4B shows that the faradaic efficiency was always higher when ballast was added to the dilute solution. Faradaic efficiency is defined as the ratio between the quantity of charge extracted from the concentration battery during the discharge stage (RED) and the quantity of charge needed to complete the charging stage (ED).

Given that osmosis from the dilute to the concentrated solution reduces the salinity gradient between the two solutions (i.e., discharges the battery), but does not produce electric current, osmosis effectively reduces faradaic efficiency [2]. Accordingly, given that ballast addition reduced osmosis from the dilute to the concentrated solution, ballast addition also increased faradaic efficiency. Specifically, mono-EG increased faradaic efficiency from 18% with no ballast to a maximum of 30%, while tetra-EG roughly quadrupled the faradaic efficiency to a maximum of 73%. It is noteworthy, however, that the current efficiency corresponding to zero water transport (which would occur at approximately 125% of the theoretically-required tetra-EG concentration), was only 50%. This implies that the remaining 50% of faradaic energy losses can be attributed to salt diffusion.
through the membranes, since the salt concentration difference was the same in all cycles. These results show that osmosis and salt diffusion play a roughly equal role in loss of faradaic efficiency for this system. Our previously reported findings using a similar energy storage system (but with a different type of ion-conducting membrane) suggested that osmosis plays a dominant role in faradaic energy loss compared to salt diffusion [2]. Taken together, these findings show that the relative impact of osmosis and salt diffusion on faradaic efficiency depends on the type of membrane used.

**Stack Resistance and Voltage Efficiency**

Next, we consider the impact of the ballast on the overall resistance of the concentration battery, illustrated in Figure 4C. In this work, the stack resistance with both mono-EG and tetra-EG at 100% theoretical concentration was within experimental error of the resistance when no ballast was added (3.2Ω). At higher concentrations, resistance with tetra-EG showed a generally upward trend, with a maximum stack resistance of 3.8Ω at 150% concentration. The trend for mono-EG was less pronounced, with a maximum resistance of 3.6 Ω. However, the stack resistance with both ballasts unexpectedly decreased between 150% and 200% theoretical concentration. The reasons for this sudden decrease are not clear. In general, we attribute the increases in stack resistance to changes in the solution conductivity caused by the addition of ballast. As shown in Figure 5 (right axis), while the conductivity of the dilute salt solution containing no ballast was 24.7 mS.cm⁻¹, the conductivity of the dilute salt solution ballasted with tetra-EG was 21.2, 19.8 and 18.6 mS.cm⁻¹ when it was added at 100%, 150% and 200% of the theoretical concentration, respectively. Similarly, the corresponding conductivities when mono-EG was added were 23.6, 23.1 and 22.7 mS.cm⁻¹. Therefore, ballast addition to the dilute salt solution decreased solution conductivity. As a result, the overall stack resistance is expected to increase as more ballast is added.

The voltage efficiency results are presented in Figure 4D, which shows that in general, the voltage efficiency decreased when ballast was added to the dilute solution. The voltage efficiency is defined as the ratio between average battery voltage during the discharge stage and the
average battery voltage during the charging stage. The stack resistance introduces energy losses that cause the battery voltage to increase (during the charging stage) or decrease (during the discharging stage) relative to the open circuit. Therefore, an increase in stack resistance decreases voltage efficiency. Given that ballast addition generally increased stack resistance, then ballast addition also correspondingly decreased voltage efficiency. Specifically, ballast addition reduced the voltage efficiency from 39.4% in the case of no ballast to 36.0% and 24.0% when mono-EG and tetra-EG, respectively, were added at their highest concentrations. The much greater reduction in voltage efficiency associated with tetra-EG compared to mono-EG is consistent with the larger decrease in solution conductivity associated with tetra-EG.

Open Circuit Voltage and Round-trip Energy Efficiency

Figure 4E illustrates the impact of the ballast on the initial open circuit voltage (OCV) of the stack and the round-trip energy efficiency. The presence of the ballasts decreased the OCV, particularly in the case of tetra-EG.

The round-trip energy efficiency of each charge-discharge cycle is the product of both faradaic efficiency (related to osmosis) and voltage efficiency (related to stack resistance). As discussed above, the presence of ballast has a negative impact on voltage efficiency, but a significant positive impact on the faradaic energy efficiency. In general, the dramatic improvements in faradaic efficiency more than compensated for the slight reductions in voltage efficiency, such that the round-trip energy efficiency increased monotonically with ballast concentration, from 7% with no ballast to 11% or 18% for mono-EG or tetra-EG, respectively, at the maximum concentration (Figure 4F). However, in the case of tetra-EG, this concentration level resulted in over-balancing the solutions, such that osmosis was actually reversed (see Figure 4A). Sustainable, multi-cycle operation is only possible when water transfer is reduced to nearly zero, which is expected to occur at a concentration of approximately 125% of theoretical tetra-EG. This concentration would correspond to a round-trip energy efficiency of approximately 15%, or more than twice that achieved with no ballast.
It should be noted that the low round-trip energy efficiencies reported in this work (7%-15%) are a reflection of our selection of stack components and geometry, and are not optimized. In previous work [2], a round-trip efficiency of 34% was achieved using similar conditions (but no ballast) and more optimized components (e.g. very low-resistance membranes and thin fluid compartments) to achieve a lower stack resistance. Since the osmotic ballasts primarily improve the faradaic efficiency without significantly altering the stack resistance or voltage efficiency, one would expect a similar doubling of round-trip efficiency to occur in a more optimized system, implying that a round-trip efficiency greater than 60% may be possible.

**Ballast Crossover**

As noted above, the most effective control of osmosis was achieved using considerably higher ballast concentrations than would be expected based on theory (>200% for mono-EG and 125% for tetra-EG). This can be explained by the fact that these small ballast molecules diffuse through the ion-conducting membranes into the concentrated solution, reducing their effective concentration. Figure 5 (left axis) presents the net ballast crossover during the cycle (as measured by total organic carbon), expressed as mmol of ballast.

The results in Figure 5 show that the maximum amounts of crossover of mono-EG and tetra-EG were 79.1 mmol and 8.7 mmol, respectively. These amounts represent approximately 45% (mono-EG) and 11% (tetra-EG) of the total amount of ballast initially present in the dilute salt solution. The observed difference in crossover of mono-EG compared to that of tetra-EG is consistent with the higher molecular weight and lower diffusivity of tetra-EG compared to those of mono-EG (see Table 1), since higher molecular weight and lower diffusivity would result in higher rejection by the ion exchange membranes.

Figure 5 also shows that the crossover of mono-EG increased linearly with the amount of ballast added. This indicates that for mono-EG, the ballast concentration was the main factor determining ballast crossover. By contrast, in the case of tetra-EG, ballast crossover did not have a linear relationship to initial ballast concentration in the dilute salt solution, but rather
maximum crossover occurred at 100% theoretical concentration and approached 0 at 200% theoretical concentration. Therefore, in addition to the initial ballast concentration in the dilute salt solution, additional factors affected ballast crossover for the tetra-EG case. One potential such factor is the direction of osmosis during experiments. As observed in Figure 4A, while for all concentrations of mono-EG, osmosis occurred in the same direction as net ballast crossover (i.e., from the dilute to the concentrated salt solution), for tetra-EG, osmosis occurred in the opposite direction to net ballast crossover at 150% and 200% of theoretical concentration. Therefore, we conclude that for tetra-EG inverted osmosis slowed down the net rate of ballast crossover through the membrane.

In summary, we have shown that the use of a non-charged solute molecule in the dilute compartment of a closed-loop RED-based energy storage system can more than double the round trip energy efficiency by eliminating the transport of water by osmosis. We also demonstrated the tradeoffs inherent in this approach (i.e. that a larger ballast molecule permeates the membranes more slowly but has a greater impact on solution conductivity). Other closed-loop, aqueous energy processes such as RED systems proposed for waste heat recovery [15,16] and aqueous-based redox flow batteries may be able to derive similar benefits from this approach.

**Determination of Theoretical Amount of Ballast Required**

The osmotic pressure of a solution is determined by the mole fraction of water (neglecting activity corrections), as shown in the main text. Therefore, in order to be osmotically balanced, two solutions must have the same mole fraction of water. In this work, the concentrated solution was always 0.513 M NaCl, and this was the solution whose mole fraction must be matched by the ballasted solutions.

To estimate the theoretical amount of ballast required in the dilute salt solution to balance the osmotic pressure of the concentrated salt solution, we began by calculating the mole fraction of water \( x_{H_2O} \) (dimensionless) in the concentrated salt solution. First we calculate the volume occupied by sodium chloride, \( V_{NaCl} \) (ml). Given that the partial molar volume of NaCl in 0.5 M NaCl is 18.5 cm\(^3\)/mol [17]:

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$V_{NaCl} = \frac{0.513 \text{ mol NaCl}}{1000 \text{ mL solution}} \left( \frac{16.6 \text{ mL}}{\text{mol}} \right) = \frac{8.5 \text{ mL NaCl}}{1000 \text{ mL solution}} \cdot$

Any remaining volume corresponds to the volume of water ($V_{H_2O}$, mL) as given by

$$V_{H_2O} = 1,000 \text{ mL solution} - 9.5 \text{ mL NaCl} = 990.5 \text{ mL} \cdot$$

The volume of water can then be used to estimate the moles of water ($n_{H_2O}$, mol) present in 1L of solution by means of the density (0.998 g.mL⁻¹) as

$$n_{H_2O} = \frac{990.5 \text{ mL} \left( \frac{0.998 \text{ g}}{\text{mL}} \right)}{18 \text{ g/mol}} = 54.91 \text{ mol} \cdot$$

Finally, the mole fraction of water, $X_{H_2O}$, is estimated by noting that 1 mol of NaCl creates 2 mol of ions in solution according to

$$X_{H_2O} = \frac{54.91}{(54.91 + 2 \times 0.513)} = 0.982 \cdot$$

Ballasted solutions were prepared by reversing this procedure as follows. The target final volume of solution (500 mL) and salt concentration (0.257 M) were known, therefore the volume occupied by the salt, $V_{NaCl}$, in the final solution could be estimated as

$$V_{NaCl} = \frac{0.257 \text{ mol NaCl}}{1000 \text{ mL solution}} \left( \frac{18.5 \text{ mL}}{\text{mol}} \right) (500 \text{ mL solution}) = 2.4 \text{ mL} \cdot$$

In this work we assumed that the volumes of water and ballast were additive, so the remaining volume occupied by water was estimated as
\[ V_{H_2O} = 500 \text{ ml solution} - 2.4 \text{ ml NaCl} - V_{\text{ballast}} = 497.6 \text{ ml} - V_{\text{ballast}} \]

where \( V_{\text{bus}} \text{(ml)} \) is the volume occupied by the ballast added.

By converting \( V_{H_2O} \) and \( V_{\text{ballast}} \) to moles, we can express the mole fraction of water, which was known from the previous calculations for unballasted salt solution, as

\[ x_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{\text{ballast}} + n_{\text{NaCl}}} = 0.982 \]

where

\[ n_{H_2O} = \frac{(497.6 - K_{\text{ballast}})(0.998 \text{ g mL}^{-1})}{18 \text{ g mol}^{-1}} \]

and

\[ n_{\text{NaCl}} = 2 \times 0.257 \text{ mol L}^{-1} \times 0.5 \text{ L} = 0.257 \text{ mol} \text{ by definition.} \]

Given that the partial molar volume in salt solution of the ballasts used are unknown, \( V_{\text{ballast}} \text{ in solution} \) was assumed to be directly proportional to the moles of ballast \( (n_{\text{ballast}}, \text{mol}) \) added to the solution, its molecular weight \( (MW_{\text{ballast}}, \text{g mol}^{-1}) \) and its density \( (\rho_{\text{ballast}}, \text{g mL}^{-1}) \) as

\[ n_{\text{ballast}} = V_{\text{ballast}} \frac{MW_{\text{ballast}}}{\rho_{\text{ballast}}} \]

We used molecular weight and density values of \( MW_{\text{ballast}} = 62.07 \text{ g mol}^{-1} \) and \( \rho_{\text{ballast}} = 1.13 \text{ g mL}^{-1} \) for mono-EG [13], and \( MW_{\text{ballast}} = 194.23 \text{ g mol}^{-1} \) and \( \rho_{\text{ballast}} = 1.12 \text{ g mL}^{-1} \) for tetra-EG [14].
By solving the above four equations for \( V_{bus} \), the only unknown, it was possible to estimate the quantity of ballast that would result in a mole fraction of water approximately equal to that in the concentrated salt solution \( (x_{H2O}=0.982) \) for a salt concentration of 0.257 M. The results of these calculations are summarized in Table S1.

### Table S1. Preparation of ballasted salt solutions, and their properties.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Total Volume (mL)</th>
<th>Ballast Added (mL)</th>
<th>NaCl Added (g)</th>
<th>NaCl Concentration (mol.L(^{-1}))</th>
<th>Conductivity (mS.cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Ballast (0.257 M NaCl)</td>
<td>500</td>
<td>0</td>
<td>7.50</td>
<td>0.257</td>
<td>25.3 ± 0.1</td>
</tr>
<tr>
<td>Ethylene Glycol – 100%</td>
<td>500</td>
<td>13.7</td>
<td>7.50</td>
<td>0.257</td>
<td>23.5 ± 0.3</td>
</tr>
<tr>
<td>Ethylene Glycol – 150%</td>
<td>500</td>
<td>20.5</td>
<td>7.50</td>
<td>0.257</td>
<td>23.0 ± 0.1</td>
</tr>
<tr>
<td>Ethylene Glycol – 200%</td>
<td>500</td>
<td>27.3</td>
<td>7.50</td>
<td>0.257</td>
<td>22.0 ± 0.1</td>
</tr>
<tr>
<td>Tetraethylene Glycol – 100%</td>
<td>500</td>
<td>38.0</td>
<td>7.50</td>
<td>0.257</td>
<td>21.2 ± 0.1</td>
</tr>
<tr>
<td>Tetraethylene Glycol – 150%</td>
<td>500</td>
<td>57.0</td>
<td>7.50</td>
<td>0.257</td>
<td>19.2 ± 0.2</td>
</tr>
<tr>
<td>Tetraethylene Glycol – 200%</td>
<td>500</td>
<td>76.0</td>
<td>7.50</td>
<td>0.257</td>
<td>17.2 ± 0.1</td>
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<td>Concentrated Solution (0.513 M NaCl)</td>
<td>500</td>
<td>0</td>
<td>15.0</td>
<td>0.513</td>
<td>46.3 ± 0.2</td>
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Example Method

Figure 6 is a flow diagram of an example method 600 for reversible electrodialysis. Method 600 includes adding, to a first channel, a concentrated electrolyte solution (602). Method 600 includes adding, to a second channel a dilute electrolyte solution that has a lower electrolyte concentration than the concentrated electrolyte solution (604). Adding the concentrated electrolyte solution and the dilute electrolyte solution can include adding the same initial solution to both channels and then charging the system with energy to create the concentrated and dilute solutions. At least one ion-conducting membrane is between the first and second channels.

Method 600 includes adding, to the dilute electrolyte solution, an osmotic ballast to balance an osmotic pressure across the ion-conducting membrane that arises when the dilute electrolyte solution becomes diluted with respect to the concentrated electrolyte solution (606). Method 600 includes charging and/or discharging electrical energy from the first and second channels (608).

It is understood that various details of the presently disclosed subject matter may be changed without departing from the scope of the presently disclosed subject matter. Furthermore, the foregoing description is for the purpose of illustration only, and not for the purpose of limitation. Numerous other families of chemical compounds, including alcohols, high molecular weight ethylene glycols (e.g. PEG400), propylene glycols, soluble polymers, organic solvents, zwitterions (i.e., neutral molecules containing both positively and negatively charged sites), "responsive solutes" such as sodium poly(acrylate) whose solubility or other properties can be modulated in response to an external signal (e.g. light, heat, pH, etc.), cyclic and star-shaped polymers, and nanoparticles may be suitable for use as osmotic ballasts. Furthermore, the presently disclosed invention may be applied to other energy processes that involve the use of one or more membranes to separate two aqueous electrolyte solutions or that use electrodialysis and/or reverse electrodialysis for purposes other than energy storage. Examples of
such processes include energy storage devices based on reversible desalination processes, redox flow batteries, aqueous primary and secondary batteries, heat recovery systems based on reverse electrodialysis or pressure-retarded osmosis, microbial fuel cells, and combinations thereof.

Such applications are within the scope of the present disclosure.

References

The disclosure of each of the following references is hereby incorporated herein by reference in its entirety.


CLAIMS

What is claimed is:

1. A system comprising:
   a first channel containing a concentrated electrolyte solution;
   a second channel containing a dilute electrolyte solution that has a lower electrolyte concentration than the concentrated electrolyte solution; and
   at least one ion-conducting membrane between the first and second channels, wherein the dilute electrolyte solution includes an osmotic ballast to balance an osmotic pressure across the ion-conducting membrane caused by the dilute electrolyte solution having a lower electrolyte concentration than the concentrated electrolyte solution.

2. The system of claim 1, comprising a control system for charging or discharging electrical energy from the first and second channels.

3. The system of claim 1, wherein the osmotic ballast comprises a non-charged solute that is non-permeable through the ion-conducting membrane.

4. The system of claim 3, wherein both the concentrated electrolyte solution and the dilute electrolyte solution comprise water and sodium chloride.

5. The system of claim 4, wherein the osmotic ballast comprises an ethylene glycol monomer or oligomer.

6. The system of claim 1, wherein the first and second channels and the ion-conducting membrane are part of an electrodialysis or reverse electrodialysis stack, and wherein the electrodialysis or reverse electrodialysis stack comprises a plurality of ion-conducting membranes and a pair of electrodes.

7. The system of claim 6, wherein the electrodialysis or reverse electrodialysis stack comprises a plurality of cation and anion exchange membranes.

8. The system of claim 1, comprising a first inlet for the concentrated electrolyte solution and a second inlet for the dilute electrolyte solution and first and second pumps for pumping concentrated electrolyte solution from a
first tank into the first inlet and for pumping dilute electrolyte solution from a second tank into the second inlet.

9. The system of claim 8, comprising a pair of electrodes coupled to the first and second channels, and wherein the control system is configured to generate electrical energy for delivery to an electrical load coupled to the pair of electrodes.

10. The system of claim 9, wherein the control system is configured to control an electrical source to apply electrical potential to the electrodes to cause movement of ions across the ion-conducting membrane.

11. A method comprising:
   - adding, to a first channel, a concentrated electrolyte solution;
   - adding, to a second channel a dilute electrolyte solution that has a lower electrolyte concentration than concentrated electrolyte solution, wherein at least one ion-conducting membrane is between the first and second channels;
   - adding, to the dilute electrolyte solution, an osmotic ballast to balance an osmotic pressure across the ion-conducting membrane that occurs when the electrolyte concentration in the dilute electrolyte solution becomes lower than the electrolyte concentration in the concentrated electrolyte solution;
   - charging or discharging electrical energy from the first and second channels.

12. The method of claim 11, wherein the osmotic ballast comprises a non-charged solute that is non-permeable through the ion-conducting membrane.

13. The method of claim 12, wherein both the concentrated electrolyte solution and the dilute electrolyte solution comprise water and sodium chloride.

14. The method of claim 13, wherein the osmotic ballast comprises an ethylene glycol monomer or oligomer.

15. The method of claim 11, wherein the first and second channels and the ion-conducting membrane are part of an electrodialysis or reverse electrodialysis stack.
16. The method of claim 15, wherein the electrodialysis or reverse electrodialysis stack comprises a plurality of ion-conducting membranes and a pair of electrodes.

17. The method of claim 11, wherein the ion-conducting membrane comprises one of:
   - an anion exchange membrane;
   - a cation exchange membrane;
   - a battery separator; and
   - a proton exchange membrane.

18. The method of claim 11, comprising:
   - pumping concentrated electrolyte solution from a first tank into a first inlet for the concentrated electrolyte solution; and
   - pumping dilute electrolyte solution from a second tank into a second inlet for the dilute electrolyte solution.

19. The method of claim 18, comprising generating electrical energy for delivery to an electrical load coupled to a pair of electrodes coupled to the first and second channels.

20. The method of claim 19, comprising controlling an electrical source to apply electrical potential to the electrodes to cause movement of ions across the ion-conducting membrane.
FIGS. 4A-C
FIGS. 4D-F
602

ADDING, TO A FIRST CHANNEL, A CONCENTRATED ELECTROLYTE SOLUTION

604

ADDING, TO A SECOND CHANNEL, A DILUTE ELECTROLYTE SOLUTION

606

ADDING, TO THE DILUTE ELECTROLYTE SOLUTION, AN OSMOTIC BALLAST TO BALANCE AN OSMOTIC PRESSURE ACROSS THE ION CONDUCTING MEMBRANE

608

CHARGING OR DISCHARGING ELECTRICAL ENERGY FROM THE FIRST AND SECOND CHANNELS

FIG. 6
INTERNATIONAL SEARCH REPORT

PCT/US 2017/040047

A. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both national classification and IPC

BOW 61/42 (2006.01)
H01M 8/04082 (2016.01)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01D61/00 - 61/42, 67/00, H01M8/00, C08J5/22, 71/44, H01M8/04 - 8/04082

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatSearch (RUPTO internal), USPTO, PAJ, Esp@cenet, DWPI, EAPATIS, PATENTSCOPE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>A</td>
<td>WO 2012/061215 A1 (SIEMENS PTE LTD ET ) 10.05.2012</td>
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<td>WO 2005/124893 A3 (ITM FUEL CELLS LTD et al) 11.02.2006</td>
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* Special categories of cited documents:

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'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

'&' document member of the same patent family

Further documents are listed in the continuation of Box C. See patent family annex.

Date of the actual completion of the international search: 10 August 2017 (10.08.2017)

Date of mailing of the international search report: 14 September 2017 (14.09.2017)

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Form PCT/ISA/210 (second sheet) (January 2015)