Large scale energy storage using multistage osmotic processes: Approaching high efficiency and energy density

Devesh Bharadwaj*, Henning Struchtrup†

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Abstract

With the increase in ocean levels due to global warming, there is a desperate need for clean and renewable energy at this time, more than ever before. Although the economic front of technologies, such as wind and solar power, has shown improvement, the fact remains that these energy sources are intermittently available in nature. This calls for a reliable energy storage technology that can bridge the gap between the supply and demand of electricity, leading us to a world driven by clean and renewable energy. Here, we propose a process for storing electrical energy using engineered osmosis. To store electrical energy, a salty solution is separated into brine and fresh water streams using modified reverse osmosis. When there is a demand for electricity, the chemical potential is converted back into electrical work by mixing the solutions using a modified version of pressure retarded osmosis. With modelling and simulations, we demonstrate that the proposed process can achieve roundtrip efficiencies of 50-60% and energy densities equivalent to that of a 500m high pumped-hydro plant. The results demonstrate a promising process to store electrical energy, which unlike pumped-hydro, is unconstrained by geography.

1 Introduction

Anthropogenic carbon emissions are creating irreversible changes to our climate. Ocean levels are expected to increase at a rate of 0.2-0.6 meters per degree of global warming [1]. This increase is expected to affect many coastal areas worldwide [2]. Along with changes to ocean levels, warming is linked to rainfall, as it can adversely affect water supply for humans and other ecosystems [3]. Longterm rainfall shortages have already been observed in some American and African regions [3][4][5][6][7][8]. The root cause of climate change is undoubtedly linked with the increase in carbon emissions. In order to mitigate carbon emissions, we have to replace our fossil fuel based energy infrastrucutre with renewable and clean energy sources.

There has been an increase in R&D towards clean energy technologies which has induced a growth in the renewable energy industry and improved the economics of such technologies. However, the fact remains that majority of renewable energy sources are only available intermittently in nature. This intermittent behaviour does not allow a grid to be fully dependant on a renewable energy source. For instance, the majority of solar power plants provide clean energy in the day but rely on natural gas power plants at night.

Electrical energy storage alone cannot possibly solve the climate problem, but it presents a solution to the intermittent nature of renewable energies. Moreover, energy storage has other high-value applications, including improving the power quality and reliability of the grid [9][10]. The concept of electrical energy storage is to store energy when available in abundance and recover it when availability is scarce. The concept of storage is simple; however, the technology behind such a process has numerous complications. Furthermore, such a technology has to be efficient, dense and environmentally benign.

There are a battery of choices among energy storage technologies. The leading energy storage technology is pumped hydro, which currently accounts for 99% of the world's grid energy storage [10]. A pumped hydro system needs a gravitational potential to move water up and down. Therefore, it requires a hilly region that has two reservoirs at different heights. Pumped hydro is a mature technology and it has the capability to store electricity at high roundtrip efficiencies of approximately 70-85%. On the down side, it is geographically constrained, has a long lead time (10 years) and due to restricted construction sites, possesses several environmental issues [11][12].

***Corresponding author:** Dept. of Mechanical Engineering, University of Victoria, Victoria, BC, Canada, e-mail: devesh@uvic.ca
†Dept. of Mechanical Engineering, University of Victoria, Victoria, BC, Canada, e-mail: struchtr@uvic.ca

This paper presents a technology that stores electrical energy in the form of chemical potential (difference in concentration), instead of gravitational potential (difference in height). Osmotic energy storage (OES) is a process that utilizes a modified version of reverse osmosis (RO) and pressure retarded osmosis(PRO) to create and recover this chemical potential.

RO is a mature technology and has been commercialized for use in desalination in most parts of the world. The RO process is a state of the art technology when it comes to separating salt from water. It has advanced in operation and can desalinate sea water at only 25% higher energy consumption rate than the possible practical minimum threshold constrained by the laws of thermodynamics for a single stage RO process (for comparison, in 1970, RO processes consumed energy at more than 90% of the theoretical minimum for a single stage RO process) [13]. On the contrary, although PRO was recognized half a century ago [14], the limitations and the innovations required to make PRO viable did not unfold until recently [15][16][17][18][19]. Consequently, multiple technologies have evolved from this early concept, which ultimately utilize a concentration difference to generate or recover useful work, such as the low grade osmotic heat engine [20][21] that can be used to generate electrical work from geothermal energy or waste heat and several other technologies that use PRO to reduce the energy consumption in desalination [22][23][24]. Osmotic energy storage (OES) is similar to these technologies in that prospect, where it relies on creating and utilizing a salinity gradient.

McGinnis and Mandell have previously done a detailed investigation on energy storage systems that create and exploit salinity gradients [25]. In their patent they discuss majority of the possible technologies that can be used for separation, such as conventional RO, electrodialysis, nanofiltration and distillation. Consequently, they discuss using conventional PRO and reverse-electrodialysis for energy recovery. Their patent presents some theoretical case studies where they claim efficiencies of 75%-85%, when their system can utilize abudant waste heat. If proven economical, such a design enabling use of waste heat can be attractive in multiple scenarios, however using conventional RO and PRO for scenarios where only electrical energy is available (and required to store) will constrain the energy storage system system to low roundtrip efficiencies and low energy densities. As recently (2016) shown by He and Wang, an energy storage system using single stage RO and PRO exibits inverse relationship between energy density and roundtrip efficiency. The scenario where irreversibilites in the turbomachinery were ignored, maximum cycle efficiency of 54.98% were reported with an energy density of 0.389 $\frac{kWh}{m^3}$ (i.e., m^3 of total solution used), alternatively when the system was optimized for high energy densities of 0.678 $\frac{kWh}{m^3}$, the roundtrip efficiencies faced penalties and dropped down to 41.13%. When the losses due to inefficiencies in turbomachinery were added, the system efficiency dropped from 54.98% to 42.55% [26]. He and Wang mention that system performance can be improved by multistage RO and PRO, which we discuss in detail in this paper.

Combination of electrodialysis and reverse-electridialysis for separation and mixing has also been investigated by Kingsbury et. al. as a means of storing and recovering useful work from chemical potential. The so-called 'concentration battery' was experimentally tested and it was capable of storing and recovering energy at roundtrip efficiencies in the range of 21%-34% [27]. Egmond et. al. recently (2017) investigated efficiencies of concentration gradient flow batteries at elevated temperatures that also implement electrodialysis and reverse electrodialysis. The study reported charging (electrodialysis-separation stage) efficiencies of 58% and discharging (reverse electrodialysis-mixing stage) efficiencies of 72%, yielding a possible 42% roundtrip efficiency [28].

In this paper we discuss the design of an osmotic energy storage (OES) technology and show the importance of modified multistage process for a practical energy storage system. We mathematically model the OES system and then simulate its performance with off-the-shelf components. We optimize the system for a particular number of stages and also study the effect of its performance with different component efficiencies. Overall, the proposed system enables energy storage at a large scale with unconstrained geographical requirements, supplementing the possibility of smooth integration of renewable energy sources into the grid.

2 Working principle of Osmotic Energy Storage

The OES process stores and recovers energy by creating and then utilizing a concentration gradient. At the time of storage, electrical work is consumed to separate a salty water (sw) stream into brine (br) and fresh water (fw). Doing so converts the electrical work from renewable energy sources that needs to be stored as a chemical potential. This potential is stored in the form of br and fw filled reservoirs/tanks. Unlike storing heat, which has losses associated over time, OES can store energy indefinitely without any major losses associated with time. When there is a demand for electricity, the chemical potential can be converted back into electrical work by mixing the br and fw streams, with apropriate technology, discussed later.

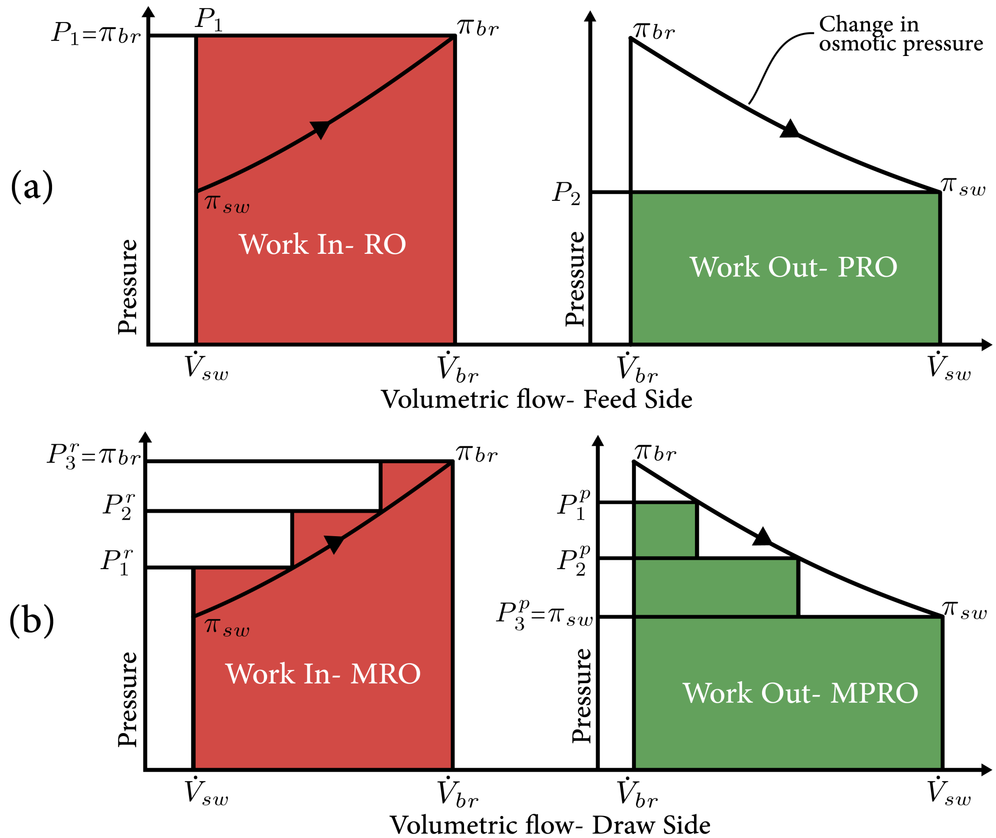


Figure 1: Visualized schematic showing the work required in RO and PRO, using P-V diagram. The x- axis represents the volumetric flow on the draw side in PRO/MPRO and feed side for RO/MRO. The y-axis represents pressure, where the applied pressure on the membrane module is marked in each graph. The red colored area in the graph shows work required for seperation in RO(a-left) and MRO (b-left). The green colored area represents work recovered in PRO(a-right) and MPRO (b-right).

The appropriate process of separation and mixing depends on the type of salt solution used and the type of energy needed to be stored. The OES process described in this paper is focused towards storing energy available in the form of electrical work. For the purpose of understanding the OES system, we consider a $NaCl$ salt solution, which is analogous to sea water's composition. Furthermore, when it comes to sea water desalination, reverse osmosis (RO) is broadly used to separate fresh water and salt. RO requires electrical work for separation, wherease the other common process of desalination, i.e. distillation, requires thermal energy. RO is inherently more efficient than distillation. Hence, for this and other reasons explained later, we choose RO as our separation technology. The obvious drawback is that RO only allows direct storage of electrical energy; therefore, for a scenario where thermal energy is needed to be stored, a distillation process can be use instead of RO. There has been some work focussing on a thermal-membrane based osmotic energy storage system [25][29]. A system that solely relies on distillation as means of separation is a clever design for places with abundant waste heat, but might not be economical or efficient when electrical energy is the only source. In this paper we focus on a system that solely uses electrical energy via a mulitstage version of RO for separation, which is crucial to achieve practical roundtrip efficiencies (discussed in detail later in this section). Using RO, salty water (sw) stream is separated into brine (br) and fresh water (fw) streams, which can be stored in reservoirs/tanks indefinetly. The two solutions stored have a large concentration difference, thermodynamically speaking, a chemical potential is created.

When there is a demand for electricity, the chemical potential can be utilized to produce electrical work. The common processes that can utlize such a chemical potential are reverse electrodialysis (RED) and pressure retarded osmosis (PRO). PRO process has proven to be more efficient in energy recovery and shows better performance when used to mix concentrated brines, compared to RED [30]. Hence, PRO is chosen to utilize the chemical potential by mixing br and fw streams.

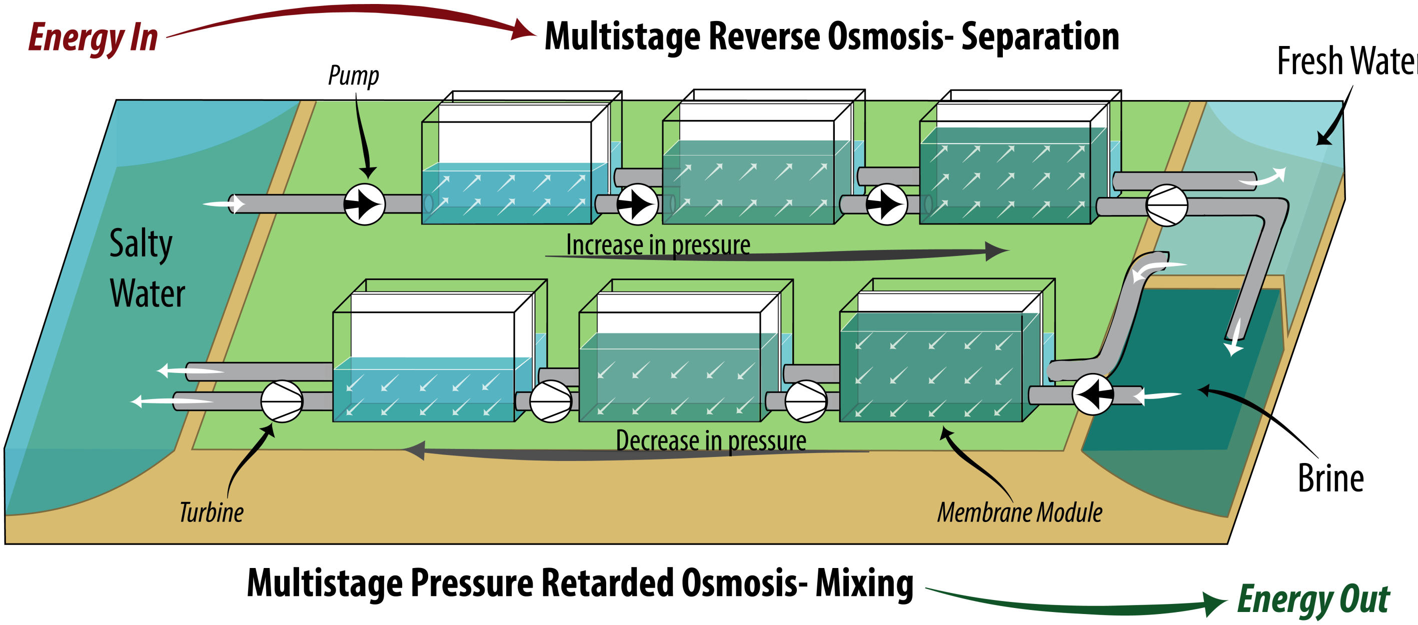


Figure 2: Simplified process diagram of a three stage OES system, with 3 stage RO- separation (top) and 3 stage PRO- mixing (bottom). The change of heights for the liquids represents the change of hydraulic pressures, whereas the change in color represents the change in concentration (darker color - more salt). For detailed OES process diagram see Fig. 3.

To achieve high roundtrip efficiency, the OES system needs to consume as little energy as possible for separation (RO) and recover as much as possible while mixing (PRO). For this reason, we study the working of RO and PRO, to better understand and decipher the losses in the design of the processes. We assume an ideal membrane for this particular explanation and we focus on the irreversibilities in the process design. Fig. 1(a) shows schematics of P-V diagrams for both RO and PRO processes. The horizontal axis shows the volumetric flow of the pressurized stream in the membrane module, while the vertical axis shows the pressure of this stream.

In RO (Fig.1(a)-left), the salty water (sw) stream enters the membrane module at an osmotic pressure, π_{sw}, with a volumetric flow rate, $\dot{V}_{sw}$. The fresh water (fw) flux across the RO membrane is proportional to the driving force, which is the difference of the hydraulic and osmotic pressure across the membrane [31],

$$J_w = A_w(\Delta P - \Delta\pi), \tag{1}$$

where A_w is the membrane water permiability coefficient, $\Delta\pi$ is the osmotic pressure difference of the streams across the membrane, and ΔP is the difference of hydraulic pressures of the streams across the membrane. If we wish to recover some of the fresh water (fw) from the salty water (sw) stream entering the membrane module, we have to apply a hydraulic pressure higher than the osmotic pressure of the sw stream, to ensure the fw flux is positive all through the membrane, which gives the equation for the power required for separation,

$$\dot{W}_{sep} = P^r \Delta\dot{V} \tag{2}$$

where $\Delta\dot{V}$ is the difference of volumetric flows between the entering sw stream and the exiting br stream, and P^r is its hydraulic pressure.

The fw crossing the membrane makes the sw stream more salty, increasing its osmotic pressure as it travels down the membrane module. The osmotic pressure curve in Fig. 1 shows the osmotic pressure of the sw stream increasing from π_{sw} to π_{br}. Ideally, we want to follow the osmotic pressure curve and apply a hydraulic pressure slightly above it, so fw can pass. However, the mechanical constraints do not allow a gradient pressure across the membrane module; hence the hydraulic pressure equal to the osmotic pressure of the exiting br is applied. Hence, the minimum possible power for separation in this case is, $\dot{W}_{sep} = \pi_{br}\Delta\dot{V}$.

The process principle is similar, but in reverse for PRO, where the theoretical maximum work that can be recovered is the area under the osmotic pressure curve. Ideally, we would follow this curve and apply hydraulic pressure slightly less than that of the curve and allow fw to enter, but, just like RO, we cannot have a gradient of pressure across the membrane module. Instead a hydraulic pressure equal to that of the exiting sw stream is applied. The maximum mixing power achievable in this scenario is, $\dot{W}_{mix} = \pi_{sw}\Delta\dot{V}$. It is important to note that the PRO schematic shown in Fig.1(a),(b)-right, assume an ideal membrane with perfect salt rejection, the schematic assumes the feed water is deionized water and has no salt. In the case of real membranes and presence of salt on the feed water side, the curves would have to account for the chemical potential loss, as discussed by Lin, Straub, and Elimelech in [32].

The round trip efficiency of the system, η_s, is the ratio of the work (power consumed to separate all the sw stream) required in separation to the work recovered in mixing, defined as

$$\eta_s = \frac{W_{sep}}{W_{mix}} = \frac{\pi_{sw}}{\pi_{br}} \tag{3}$$

If 50% of the fw is recovered from the sw stream, then the maximum attainable efficiency of such an OES system is 0.5. As in an ideal case the ratio of the osmotic pressure is equal to the inverse ratio of the volumetric flows [33]. Even in an ideal scenario with perfect membranes, one cannot achieve higher efficiency from a single stage membrane process. To reduce this process irreversibility, we need to have a multi-stage system. For instance, in RO when the process is separated into 3 consecutive stages, as shown in Fig. 2. The pressure in each stage is increased step by step, according to the increasing osmotic pressure of the entering sw stream. In a similar fashion, for multistage PRO system the pressure of the entering br stream is decreased step by step, according to the decreasing osmotic pressure of the br stream. Fig. 1(b) shows the P-V schematics for a multistage RO and PRO process. The schematic shows that even with 3 stages the work required in RO decreases and the work recovered in PRO increases significantly. Theoretically, infinitely many stages would mean that all work required for separation can be recovered in mixing. The example of 50% fw recovery would indeed result in 100% roundtrip efficiency. Obviously, infitely many stages is not practical or possible. In the next few sections, we model and simulate a multistage OES system, which shows drastic improvement in the efficiency and energy density, even with 2 to 4 stages. The sections below explain the mathematical model of the OES system, divided into the two processes of storing and recovering energy.

Looking back at Eq. 3, one might say that higher round trip efficiencies can be reached by recovering less fresh water, which in an ideal scenario is true (as $\frac{\pi_{sw}}{\pi_{br}} \rightarrow 1$). But in a realistic scenario, low recovery ratios do not give high roundtrip efficiencies and also operating at such low recovery ratios means operating at extreemely low energy densities (see Section 6).

3 Storing Energy: Multistage Reverse Osmosis (MRO)

OES taps unused electrical work and stores it as chemical potential in the form of a concentration difference. The concentration difference is created by separating sea water (sw) stream into brine (br) and fresh water (fw) streams, using Reverse Osmosis (RO). As discussed in the previous section, conventional RO process has inherent operational irreversibilities, hence a modified multistage RO process is used in OES to split the sw stream.

In this section, we show how the multistaged RO process is designed to reduce entropy generation. The OES process introduced in this paper is modelled mathematically and then simulated with data for real off-the-shelf component properties. The model uses some variables to account for membrane performance, which we explain here, as they are key to understanding OES's working. The model accounts for losses in the membrane module and the mechanical components. The pressure loss in the pipes and membrane modules is ignored, due to its insignificance.

Fig. 3-top shows a n-stage RO process. The process has n membrane modules (mm), where the pressure of the salty water (sw) stream entering the first membrane module (mm_1) is P_1^r. The hydraulic pressure of the sw stream is increased incrementally from the first to the last membrane module (mm_1 to mm_n), using pumps. The exiting brine (br) stream from the n^{th} membrane module is at a pressure of P_n^r bar.

A pressure exchanger is used to exchange the pressure of the brine (br) stream (exiting the last membrane module) with the salty water (sw) stream entering the first membrane module at P_1^r. In a single stage RO process, the pressure of the exiting brine stream is equal to the entering salty water stream, hence PEX placement is trivial. In a multistage RO process the pressures are different in each membrane module, hence the pressure of the brine stream has to be dropped from P_n^r to $(P_1^r + \delta P)$ bar, using a turbine. δP is the pressure loss in the PEX, hence this must be added to the stream by booster pump before it enters the PEX, to accomodate the loss. The benefits provided by the PEX in comparison to a pump-turbine pair and the reason behind the specific positioning of the PEX will be explained in detail in Section 5.1.

The salty water (sw) stream enters the RO part of the OES system, at a volumetric flow of $\dot{V}_{sw}$ and at environmental pressure P_0. As the PEX requires equal volumetric flow on both sides, the sw stream is split into $\dot{V}''_{sw}$ and $\dot{V}'_{sw}$, where $\dot{V}''_{sw}$ is equal to the volumetric flow of the brine (br) solution and $\dot{V}'_{sw}$ is equal to the volumetric flow of the fresh water (fw) stream. $\dot{V}''_{sw}$ stream is pressurized in a booster pump to overcome the pressure loss δP, before it is sent to the PEX, to exchange pressure between the br stream. The other $\dot{V}'_{sw}$ stream is pressurized using a high pressure pump to P_1^r and is then mixed back with the $\dot{V}''_{sw}$ stream to make $\dot{V}_{sw_1}$.

After being pressurized, the salty water (sw) stream $\dot{V}_{sw_1}$ enters the first membrane module (mm_1) where some of the fresh water (fw) crosses the membrane as $\dot{V}^r_{fw_1}$.The volumetric flow of the fw crossing the membrane is controlled by the hydraulic pressure ΔP_1^r across the membrane module, which we explain for the i^{th} membrane module (mm_i) using the membrane effectiveness factor (see Supplementary Information Section 1).

We define a fw recovery ratio for a membrane module mm_i which describes how much fw is recovered from the sw stream entering the membrane module. All of the membrane modules have their own separate fw recovery ratio X. We describe this ratio and other properties for the i^{th} membrane module (mm_i). The fw recovery ratio for mm_i is defined as

$$X_i = \frac{\dot{V}^r_{fw_i}}{\dot{V}_{sw_i}} = \frac{\dot{V}_{sw_i} - \dot{V}_{sw_{i+1}}}{\dot{V}_{sw_i}} = 1 - \frac{\dot{V}_{sw_{i+1}}}{\dot{V}_{sw_i}} \tag{4}$$

where the sw stream entering the i^{th} membrane module (mm_i) is labelled as $\dot{V}_{sw_i}$; $\dot{V}^r_{fw_i}$ is the fw stream permeating mm_i, and $\dot{V}_{sw_{i+1}}$ is the resulting saltier sw stream leaving mm_i on the retentate side. The fw recovery ratio for RO is defined such that the X value for any RO membrane module is always less than or equal to 1. A X value close to 0 indicates no fw crosses the membrane layer, on the other hand, an X value close to 1 indicates 100% of the fw is recovered from the sw stream.

The multistage RO process as shown in Fig. 3(top) has n membrane modules operating at increasing pressures, where each membrane module gradually increases the salinity of the retentate stream. For the sake of understanding, these saltier retentate streams are referred with a subscript 'sw' and with an incremental numbering. The retentate stream exiting the last membrane module is the resulting br stream. In the same fashion, the fw streams subscripts are numbered with respect to the membrane module they are permeating from.

OES is designed as a closed loop system, the streams separated in RO i.e. the resulting fw and br streams in the left of Fig. 3, are used again in PRO, no external salt or water is required. While optimizing such a system, it is important to constrict the water flow accordingly (optimization parameters are discussed later in Section 5 and 6). The authors found that using the fw recovery ratio X for modelling and optimization was more straightforward, compared to using hydraulic pressures, which leads to implicit equations and makes flow management complicated. The hydraulic pressure is the actual parameter used in a RO plant for operations, it is directly related to the fw recovery ratio X (Supplementary Information Section 1) and can be easily found after the optimized X values are known. We take this reverse approach as it is easier to work with different X values. For the PRO model, we use the same approach, see Section 4.

We also define a net fw recovery ratio A which gives the relative amount of the fw that has been recovered in total from the sw stream,

$$A = \frac{\dot{V}_{fw}}{\dot{V}_{sw}} = 1 - \frac{\dot{V}_{br}}{\dot{V}_{sw}}. \tag{5}$$

Here, $\dot{V}_{sw}$ is the net volumetric flow of sw entering the RO stage of the OES system; $\dot{V}_{fw}$ is the net volumetric flow of fw exiting the RO system and $\dot{V}_{br}$ is the net volumetric flow of br separated in RO.

It is key to note that the fw recovery ratio X is different form the net fw recovery ratio A. A tells us how much of the sw is split into br and fw, in total. On the other hand X_i tells us how much fw is recoverd for that particular membrane module mm_i (shown in Fig. 3).

In the later sections we study how choosing different A values can affect OES's performance, where for each case, X_i for a membrane module mm_i is optimized in a way that whatever the number of stages we choose to have in RO, each membrane module will recover fw, in a combination that consumes the least power possible. For instance, if 50% ($A = 0.5$) of the fw is required to be recovered from the sw stream, then the n membrane modules will individually recover a percentage of that 50%. It is not necessary that each of the n membrane modules will recover $1/n^{th}$ of the fw; the individual X ratios depend on optimization, which outputs a combination of X ratios that would require the lowest work possible. Alternatively, if we understand this with the P-V schematics (Fig. 1), we can imagine reducing the red area in the 3-stage RO graph. There is an optimum pressure combination for P_1^r, P_2^r and P_3^r (recovery ratios explicitly dictate the hydraulic pressures, Supplementary Information Section 1) where the

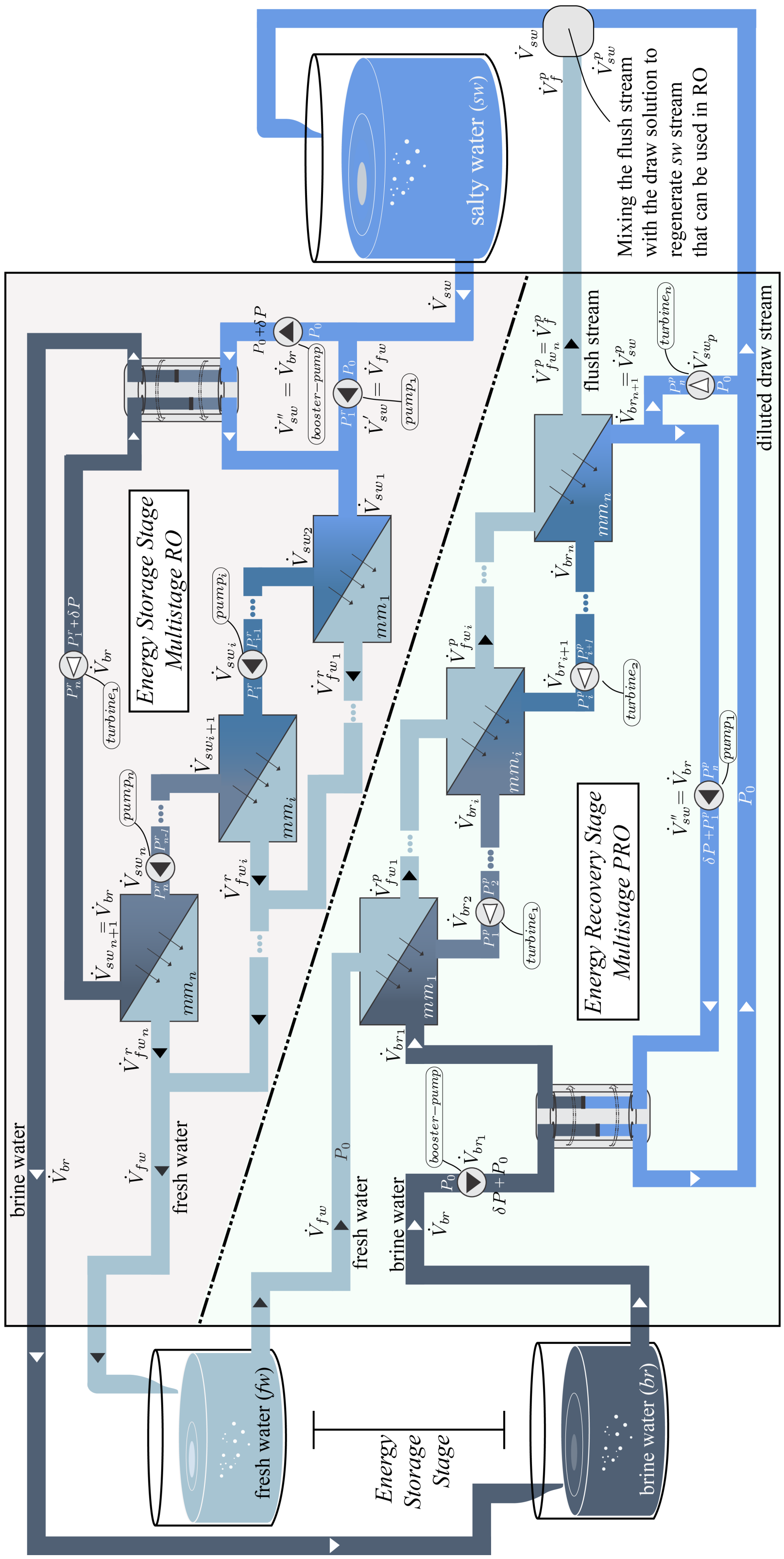


Figure 3: Process schematic of a n-stage OES system. The OES process is inside the box, where the top (light red) section is the energy storage stage when the sw is separated to fw and br, using multistage RO. The bottom (light green) section is the energy recovery stage, where the streams are mixed via multistage PRO.

red area would be minimum, that is when the required work for achieving 50% fw recovery (i.e. $A = 0.5$) would be the least.

Ideally in RO separation, the fw stream, as the name suggests, is desired to have no salt. However, with current membranes this is not possible, as some of the salt from the sw side diffuses into the fw side. It is important to minimize any salt crossover in RO, as the resulting streams are used in the energy recovery stage (PRO). The losses associated with this crossflow are discussed in Section 5.2.

The power required for separation for a n stage RO process, as shown in Fig. 3, can be estimated by finding the work consumed and recovered in the components used as

$$\dot{W}_{ro} = \dot{W}_{pump_1} + \dot{W}_{booster\text{-}pump} + \Sigma_{i=2}^{n}\dot{W}_{pump_i} + \dot{W}_{turbine_1} \tag{6}$$

where the respective pumps and turbine are labelled in Fig. 3. The work required for pump is defined as

$$\dot{W}_{pump} = \frac{1}{\eta_p}\dot{V}^p \Delta P^p \tag{7}$$

where η_p is the efficiency of the pump, $\dot{V}^p$ is the volumetric flow of the stream pressurized in the pump, and ΔP^p is the pressure difference of the stream before and after being pressurized. The work recovered in a turbine is defined as

$$\dot{W}_{turbine} = \eta_t \dot{V}^t \Delta P^t \tag{8}$$

where η_t is the efficiency of the turbine, $\dot{V}^t$ is the volumetric flow of the stream being depressurized, and ΔP^t is the pressure difference of the stream before and after being depressurized.

We insert the pump and turbine work equations, Eqs.(7),(8) in Eq.(6), and use Eq(s).(4),(5), to simplify the work requirement,

$$\dot{W}_{ro} = \frac{1}{\eta_p} A\dot{V}_{sw_1}(P_0 - P_1^r) + \frac{1}{\eta_p}(1-A)\dot{V}_{sw_1}(-\delta P) + \Sigma_{i=2}^{n}\frac{1}{\eta_p}\dot{V}_{sw_{i-1}}(1 - X_i)(P_{i-1}^r - P_i^r) + \eta_t(1-A)\dot{V}_{sw_1}(P_n^r - P_1^r - \delta P) \tag{9}$$

where P_i^r for all membrane modules, $i = \{1, n\}$, is defined in Supplementary Information Section 1, along with the detailed mathematical model for multistage RO.

Once all stream properties and hydraulic pressures are solved in terms of the known variables, we optimize for the minimum work required for separation, for a particular set of system parameters and component properties. The variable that is used for optimization is the X_i ratio for each mm_i. The X_i values correspond to the hydraulic pressures required in that particular membrane module. The hydraulic pressure P_i^r for the i^{th} membrane module (mm_i) is described with all the known variables and the optimizing variable X_i, as shown in Supplementary Information Section 1, Eq. 9.

The system parameters include salty water properties, number of stages,n, fresh water recovery ratio, A, and other factors that can be altered, we study the effects of such alterations on energy density and roundtrip efficiency in Section 6. Component properties include membrane module effectiveness (i.e., $\eta_{mm} = 0.90$, see Section 5.2); pump efficiency (i.e., $\eta_p = 0.95$ [34]); turbine efficiency (i.e., $\eta_t = 0.95$ [35]) and PEX's pressure loss (i.e., $\delta P = 0.5\ bar$ [36]). The component properties are kept consistent when optimizing the system energy denisty and roundtrip efficiency, discussed in Section 6. However, the component properties are varied when their influence on the OES system is studied in Section 5.

Similar modelling is done for PRO as described next.

4 Recovering Energy: Multistage Pressure Retarded Osmosis (MPRO)

When there is a demand for electricity, the chemical potential is converted back into electrical work by mixing the brine (br) and fresh water (fw) streams using PRO. The br and fw streams were a result of separation from the RO stage. This section presents the mathematical model for multistage PRO. As discussed before, the model accounts for losses in the membrane module and the mechanical components. The pressure loss in the pipes and membrane modules is ignored in this model, due to it's insignificance when compared with other losses.

Fig. 3-bottom shows an n-stage PRO process, with n membrane modules (mm), where the pressure of the brine (br) stream entering the first membrane module (mm_1) is P_1^p (superscript 'p' is used to denote PRO, to separate

this pressure variable from RO's). The hydraulic pressure of the br stream is decreased gradually from the first to the last membrane module, according to the osmotic pressure of the br stream, using turbines and hence producing work. The exiting salty water (sw) stream from the n^{th} membrane module (mm_n) is at a pressure of P_n^p bar. The hydraulic pressures are set after optimization and the method of finding them will become clear in this section.

As labelled in Fig. 3-bottom, a pressure exchanger (PEX) is equipped to exchange the pressure of the $\dot{V}_{sw}''$ stream exiting the n^{th} membrane module (mm_n) with the brine (br) stream $\dot{V}_{br_1}$, which is entering the first membrane module at P_1^p. In a single stage PRO process, the pressure of the exiting salty water (sw) stream is equal to the entering br stream, hence PEX placement is trivial. In multistage PRO, the pressures are different in each membrane module, hence the pressure of the sw stream is increased from P_n^p to $(P_1^p + \delta P)$, using a pump, where δP is the pressure loss in the PEX, hence must be added to the stream before it enters the PEX, to accomodate the loss. The benifits provided by the PEX in comparison to a pump-turbine pair and the reason behind the specific positioning of the PEX will be explained in Section 5.1.

The brine (br) and fresh water (fw) streams enter the PRO part of the OES system at volumetric flows of $\dot{V}_{br}$ and $\dot{V}_{fw}$, respectively; both streams enter at environmental pressure P_0. As the PEX requires equal volumetric flow on each side, the sw stream is split into $\dot{V}_{sw}''$ and $\dot{V}_{sw,p}'$, where $\dot{V}_{sw}''$ is equal to the volumetric flow of the br solution and $\dot{V}_{sw,p}'$ is equal to the volumetric flow of the remainder. $\dot{V}_{sw}''$ stream is pressurized in a pump to match the pressure required in the first membrane module and to overcome the PEX pressure loss δP, before it is sent to the PEX, to exchange pressure between the br stream $\dot{V}_{br_1}$. The presssure of the other $\dot{V}_{sw,p}'$ stream is dropped using a turbine to P_0 bar and is then mixed back with the $\dot{V}_{sw}''$ stream, to make $\dot{V}_{sw}$.

After being pressurized to P_1^p, the brine (br) stream $\dot{V}_{br_1}$ enters the first membrane module (mm_1) on the draw side, along with the fresh water (fw) stream (which is at environemntal presure P_0) on the feed side. The osmotic pressure difference between the streams causes some of the fresh water (fw) from the feed side to cross the membrane layer and dilutes the br stream. The amount of fw water crossing the membrane is controlled by the hydraulic pressure difference ΔP_1^p between the two streams, defined in Supplementary Information Section 2.

We define a fresh water (fw) mixing ratio Y_i for the i^{th} membrane module (mm_i) which describes how much fw is mixed with the brine (br) stream entering the membrane module. All of the membrane modules have their own separate fw recovery ratio Y_i. The fw recovery ratio for mm_i is defined as

$$Y_i = \frac{\dot{V}_{br_{i+1}}}{\dot{V}_{br_i}} = \frac{\dot{V}_{br_i} + (\dot{V}_{fw_i}^p - \dot{V}_{fw_{i+1}}^p)}{\dot{V}_{br_i}} = 1 + \frac{\dot{V}_{fw_i}^p}{\dot{V}_{br_i}} - \frac{\dot{V}_{fw_{i+1}}^p}{\dot{V}_{br_i}}. \tag{10}$$

Further we can describe the outgoing brine and fresh water streams in terms of the incoming streams as

$$\dot{V}_{br_{i+1}} = Y_i \dot{V}_{br_i} \tag{11}$$

$$\dot{V}_{fw_{i+1}}^p = \dot{V}_{fw_i}^p - (\dot{V}_{br_{i+1}} - \dot{V}_{br_i}) = \dot{V}_{fw_i}^p - \dot{V}_{br_i}(Y_i - 1) \tag{12}$$

where the brine (br) stream entering the i^{th} membrane module (mm_i) on the draw side is labelled as $\dot{V}_{br_i}$; $\dot{V}_{fw_i}^p$ is the fw stream entering mm_i on the feed side; $\dot{V}_{br_i}$ is the diluted br stream exiting mm_i on the draw side and $\dot{V}_{fw_{i+1}}^p$ is the left over fw stream exiting mm_i on the feed side. The fw mixing ratio for PRO is defined such that Y_i for any PRO membrane is always larger or equal to 1. A Y_i value close to 1 indicates no fw crosses the membrane layer, on the other hand, a higher Y_i value, for instance $Y_i = 2$ would indicate that the amount of fw mixed results in twice the amount of the br stream.

The multistage PRO process as shown in Fig. 3 has n membrane modules where each membrane module gradually decreases the salinity of the draw stream. For the sake of understanding, these diluted draw streams are referred with a subscript 'br', with an incremental numbering. In the same fashion, the fw streams are numbered with respect to the membrane module they are permeating from. The diluted brine (br) stream exiting the last membrane module is the resulting sw_p stream, $\dot{V}_{sw_p}$. Note that this stream has a lower volumetric flow than that of the salty water (sw) stream used in RO. The reason for this is that the membrane module is unable to uptake all the fresh water from the feed side. Ideally, by the end of the PRO process, we want all of the fw to mix with the br stream, so that all the useful work can be recovered. However, for the n^{th} membrane module (mm_n) the quantity of fw mixed into the br stream depends on the uptake capacity of the membrane module.

The loss due to the lack of uptake is felt significantly in the last membrane module, as the freshwater (fw) stream entering the last membrane module (mm_n) has built up a high salt concentration from the reverse salt flux (explained later in this section) in the previous membrane modules. In terms of recovering energy, it is not useful to draw water from this fw stream ($\dot{V}_{fw_{n-1}}^p$) which is at relatively high osmotic pressure. Consequently, the leftover stream, which the membrane is unable to uptake, leaves the last membrane module (mm_n) as the flush stream ($\dot{V}_f^p$), on the feed side. We define the membrane uptake ratio ϕ such that the flush and the incoming streams are related, as

$$\dot{V}_f^p = \dot{V}_{fw_n}^p = (1-\phi)\dot{V}_{fw_{n-1}}^p\,, \tag{13}$$

where $\dot{V}_{fw_{n-1}}^p$ is the feed stream entering the last membrane module (mm_n) and $\dot{V}_{fw_n}^p$ is the feed stream exiting the last membrane module, which is also referred as the flush stream $\dot{V}_f^p$. A ϕ value equal to 1 indicates that all fw is drawn to the br side, which indicates least entropy generation. In the same way, if ϕ is equal to 0, none of the fw crosses the membrane and all of it exits as the flush stream. The uptake ratio is implicitly accounted by the membrane effectiveness factor. The uptake ratio depends on how well the membrane can draw the feed water stream when operating with lower water flows on the feed side. As shown in the OES process diagram (Fig. 3) the flush stream is mixed, irreversibly, with the draw stream from the last membrane module to make the sw stream that can be used again in RO, as

$$\dot{V}_{sw} = \dot{V}_f^p + \dot{V}_{sw}^p = \dot{V}_{fw_n}^p + \dot{V}_{br_{n+1}}. \tag{14}$$

OES is designed as a closed loop system: the streams mixed in PRO are used again in RO and no external salt or water is required. As discussed in the previous section, while optimizing such a system, it is important to constrict the water flow according to the closed-loop constrains (optimization parameters are discussed later in Section 5). The authors found that using the fw mixing ratio Y_i for modelling and optimization was more straightforward, than using hydraulic pressures which lead to implicit equations and makes flow management complicated. The hydraulic pressure is the actual parameter used in a PRO plant for operations, it is directly related with the fw mixing ratio Y_i (Supplementary Information Section 2) and can be easily found after the optimized Y values are known. Similar to what was done in the RO model, we take this reverse approach as it is easier to work with different Y values.

Ideally, in PRO mixing, the fresh water (fw) stream, as the name suggests, is desired to have no salt. However, with current membranes this is not possible, some of the salt from the salty water (sw) side diffuses into the fw side. The reverse salt diffusion increases the osmotic pressure of the fw stream and consequently decreases the osmotic pressure of the sw stream. This reduces the amount of energy retrievable from the streams, hence it is key to reduce the reverse salt diffusion in the membrane module. The losses associated with this crossflow are discussed in Section 5.2.

The power recovered in a n stage PRO process as shown in Fig. 3 is estimated by finding the work consumed and recovered in the components used as

$$\dot{W}_{pro} = \dot{W}_{booster-pump} + \dot{W}_{pump_1} + \Sigma_{i=1}^{n-1}\dot{W}_{turbine_i} + \dot{W}_{turbine_n} \tag{15}$$

where the respective pumps and turbines are labelled in Fig. 3.

With work for pump and turbines given by Eqs. (7), (17), and with Eq(s). 10 and 11, the work Eq. (15) becomes

$$\dot{W}_{pro} = \frac{1}{\eta_p}\dot{V}_{br_1}(-\delta P) + \frac{1}{\eta_p}\dot{V}_{br_1}(P_3^p - P_1^p - \delta P) + \Sigma_{i=1}^{n-1}\eta_t Y_i \dot{V}_{br_{i+1}}(P_i^p - P_{i+1}^p) + \eta_t(Y_n\dot{V}_{br_n} - \dot{V}_{br_1})(P_n^p - P_0^p) \tag{16}$$

where P_i^p for all membrane modules, $i = \{1, n\}$, is given in Supplementary Information Section 2, along with the detailed mathematical model for multistage PRO.

Once all stream properties and hydraulic pressures are solved in terms of the known variables, we optimize for the maximum work recoverable while mixing, for a particular set of system parameters and component properties. The variable that is used for optimization is the Y_i ratio for each mm_i. The Y_i value corresponds to the hydraulic pressures required in that particular membrane module. The hydraulic pressure P_i^p for mm_i is described with all the known variables and the optimizing variable Y_i, as shown in Supplementary Information Section 2.

The system parameters include salty water properties, number of stages, n, fresh water recovery ratio, A, and other factors that can be altered, we study the effects of such alterations on energy density and roundtrip efficiency in Section 6. Component properties include membrane module effectiveness (i.e., $\eta_{mm} = 0.90$, see Section 5.2); pump efficiency (i.e., $\eta_p = 0.95$ [34]); turbine efficiency (i.e., $\eta_t = 0.95$ [35]) and PEX's pressure loss (i.e., $\delta P = 0.5\ bar$ [36]). The component properties are kept consistent when optimizing the system energy denisty and roundtrip efficiency, discussed in Section 6. However, the component properties are varied when their influence on the OES system is studied in Section 5.

5 Influence of different components on OES performance

The OES system comprising of RO and PRO is designed by assembling different components, where each component has a specific task. In this section we will study how these components can affect the OES system's overall performance.

We can define various parameters to study OES's perfomance; however from a thermodynamic standpoint, round trip efficiency and energy density are the obvious choices, since they are key to study and compare OES's performance with other energy storage technologies.

Round trip efficiency, η_s, is defined as the ratio of the power generated while mixing in PRO, to the amount of power consumed to separate the solutions in RO,

$$\eta_s = \frac{\dot{W}_{pro}}{\dot{W}_{ro}} \tag{17}$$

Energy density, ε, is defined as the amount of energy that can be stored in the OES system per m^3 of salty water (sw) stored. In other words, the amount of energy that is recovered in the PRO process per m^3 of sw, i.e. the power produced per m^3 of sw, integrated over time for the whole PRO cycle,

$$\varepsilon = \frac{\int \dot{W}_{pro} dt}{\int \dot{V}_{sw} dt} = \frac{W_{pro}}{V_{sw}} \quad \left[\frac{kWh}{m^3}\right] \tag{18}$$

where V_{sw} is the volume of the salty water (sw) stored in the OES system and W_{pro} is the net work produced in PRO.

Influence of the components on OES's performance is studied in the next few subsections. The first subsection focuses on the mechanical devices and the second section focuses on the membrane modules. Both sections discuss how the OES performance can be improved by identifying where losses occur.

5.1 Mechanical Devices

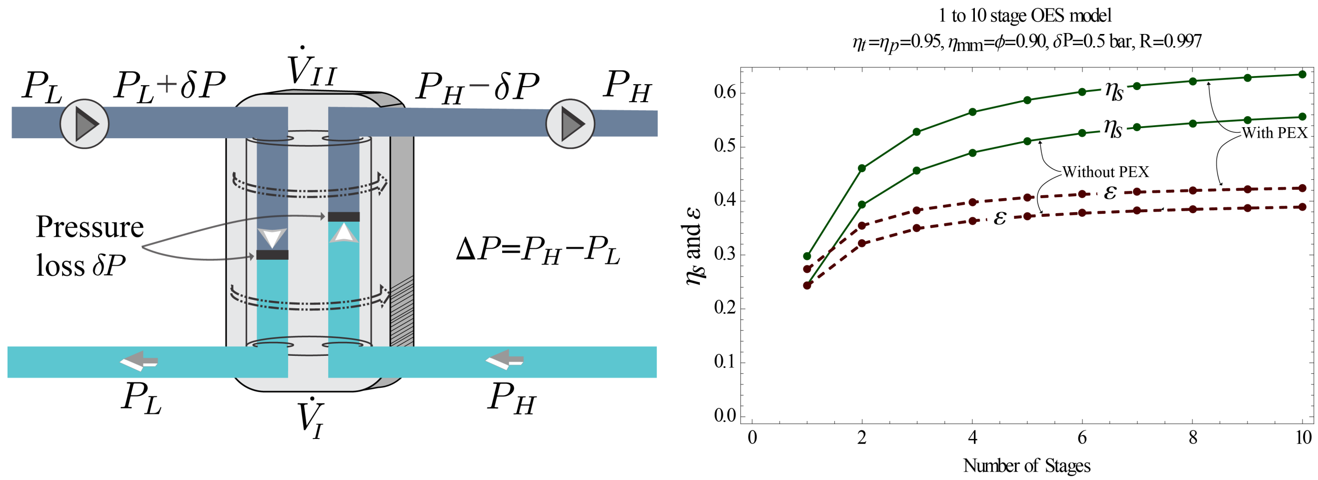
All the components used in OES (pumps, turbines etc.) have irreversibilities which contributes to the overall losses in the OES system. Incorporating higher efficiency components improves OES's performance. However, current off-the-shelf pumps and turbines have efficiencies of 85-95%[34][35], and there are quite a few of these components required in the multi-stage OES process, hence the losses add up.

To improve performance, we replace some of the lower efficiency pressure transfer mechanisms, i.e., pump-turbine pairs, with pressure exchangers (PEX). Unlike a single stage membrane process, in a n–stage system we have to drop and increase the pressure n times on the feed and draw sides in RO and PRO, respectively. This requires multiple pump-turbine pairs, which decreases the systems performance. Our previous research on MPRO plants showed that having a pressure exchanger (PEX) replace a pump-turbine (P-T) combination can increase systems performance [33]. A feed and a booster pump are required to compensate for pressure losses in the PEX. Due to the constant pressure loss in a PEX, such an arrangement is beneficial only when there is a requirement of exchanging pressure between two streams that have a sufficiently large pressure difference. The loss factor of a pressure exchanger (shown in Fig. 4(a)) is typically defined as [33]

$$\gamma_{pex} = \frac{2\delta P}{P_H - P_L}, \tag{19}$$

where δP is the pressure loss in the PEX; P_H is the hydraulic pressure of the stream entering the pressure exchanger at relatively high pressure and P_L is the hydraulic pressure of the stream which is entering the PEX at lower pressure, as shown in Fig. 4(a). With the pressure loss for a particular PEX being approximately constant, the loss factor decreases drastically with increasing pressure difference. PEX are broadly used in RO, where the pressure difference between the streams, $\Delta P \approx 60$ bar, so that - with $\delta P = 0.5$ bar - the loss factor is only 1.7%. Whereas, for a lower pressure difference, say $\Delta P \approx 15$ bar, the loss factor is about 6.7%. The pressure exchangers loose their advantage over pump-turbine pairs, for situations where the pressure difference is relatively small.

To improve OES process's performance, the pump-turbine (P-T) pairs are replaced with pressure exchangers (PEX), as shown in Fig. 3. The placement of the pressure exchanger (PEX) is key, hence, only the pump-turbine pairs which had more losses than the alternative (PEX) were replaced. Such a scenario is mathematically modelled in the previous sections.



(a) (b)

Figure 4: OES's performance is studied when a pressure exchanger is applied. (a) represents a generic pressure exchanger(PEX) where stream I is exchanging pressure with stream II. Both streams are at a pressure difference of ΔP. There is a pressure loss of δP bar on both arrays of the PEX. A specific PEX has a constant pressure loss, (b) shows how OES's performance, in terms of energy density, ε, and roundtrip efficiency, η_s, is affected when a PEX is equipped, compared to an OES system without a PEX. The components efficiencies are consitent to other simulations as labelled on the graph.

Using the work equations defined in Eqs. (9), (16), and the performance parameter described in Eqs. (17), (18), we simulate the performance of the OES system - with and without pressure exchangers - varying the number of stage, n, from 1 to 10. The simulation considers current off-the-shelf pumps, turbines and a PEX with a pressure loss of $\delta P = 0.5$ bar. The graph shown in Fig.4(b) shows the simulation results, where a OES system equipped with pressure exchangers exibits ∼20% higher roundtrip efficiency than an OES system without PEX, the benefit in performance is significant. From a thermodynamic standpoint, it is clear that having pressure exchangers in the appropriate configurations, reduces entropy generation in the system and improves OES's performance.

5.2 Membrane Modules

The key component in the OES system is the membrane module. The membrane module with its semipermeable properties allows for the controlled separation and mixing, which is the basis of OES's working.

RO desalination has more than half a century of industrial operational experience. The RO industry is mature and much older than PRO. Consequently, there has been extensive work to produce robust membranes which have made RO desalination profitable; however, there is still ample room for improvement towards salt rejection, water permeability and anti-fouling properties [37][38]. OES is modelled and simulated with current off-the-shelf RO membranes and similar to RO desalination, there are multiple prospects of the membrane that can be modified to directly improve OES's performance, which we discuss later through Fig. 5.

Fouling and concentration polarization are some of the major issues faced in river-seawater PRO [39]. A closed loop system like ours uses clean solutions which assists with the issue of fouling and improves membrane performance for both PRO and RO, in that respect [29][40]. The other irreversibility in the membranes is the undesired salt flow, which, on the contrary, has a greater negative effect on a closed loop system [41]. Reverse salt diffusion in OES results in a salty fresh water (fw) stream out of RO, which is used again in PRO (as it is closed loop). The salt in fw limits the available chemical potential that can be recovered in PRO, hence drastically affects OES's performance. However, more R&D towards membranes with higher salt rejection capabilities, thinner support layers, higher water permeability coefficients and increased anti-fouling properties can and will directly improve OES's performance (see Fig. 5) [30][39].

To find out how the membrane properties affect OES's performance, we analyze the systems roundtrip efficiency and energy density over a range of membrane performance values- i.e. different membrane uptake values (ϕ), salt rejection coefficients (R) and membrane module effectiveness factors (η_{mm}). The simulation results are presented in

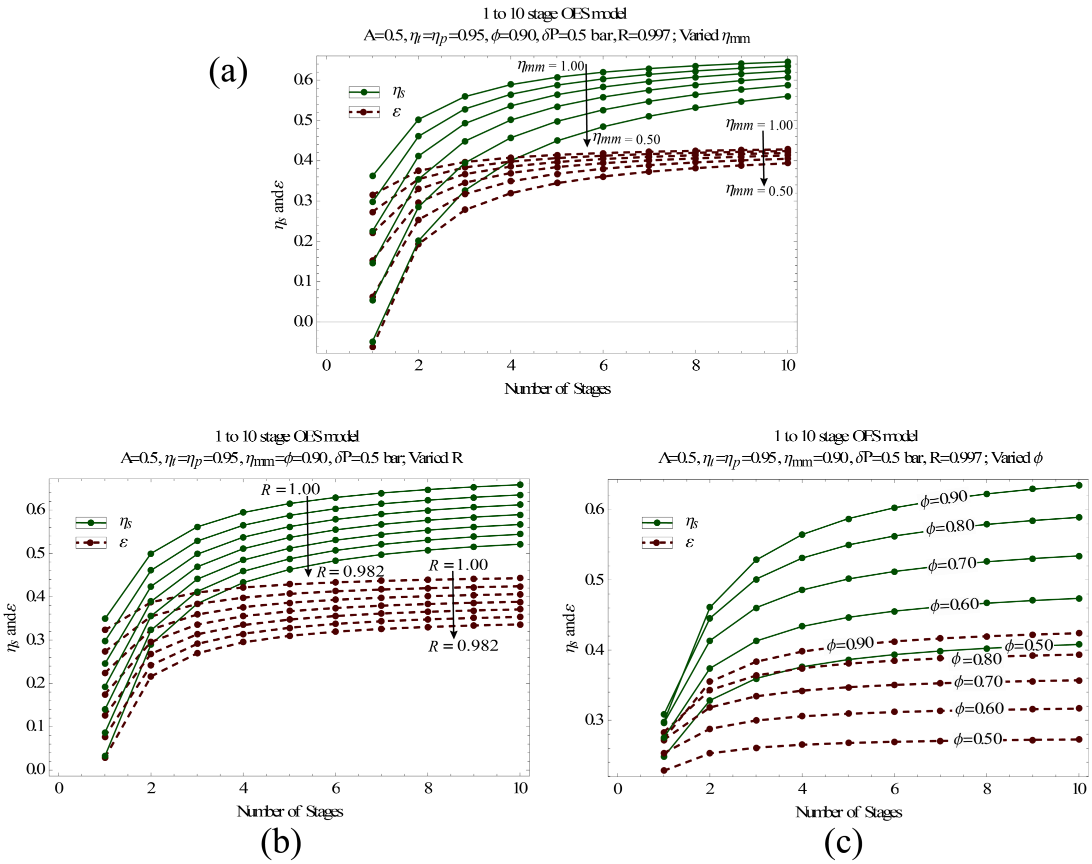


Figure 5: OES's performance, in terms of η_s and ε, is simulated with varying membrane properties. Green line represents the round trip efficiency, η_s, and the dashed-red line represents energy density $\varepsilon\left[\frac{kWh}{m^3 \text{ of } sw}\right]$. (a) shows the affect of different membrane effectiveness factor, (b) shows the affect of different salt rejection coefficients and (c) shows the affect of different uptake ratio on η_s and ε values.

Fig. 5.

Fig. 5(a) shows the effect on OES's performance with different membrane effectiveness factors, η_{mm}. This factor is a parameter that accounts for majority of the losses inside a membrane module, it is explained in detail in the Supplementary Information (available with this paper) Section 1 and 2, for RO and PRO, respectively. In a few words, a membrane with a higher membrane effectiveness indicates that the difference in osmotic pressure of the streams exiting a membrane module is relatively closer to the hydraulic pressure difference between the streams. A perfect membrane module with a 100% effectiveness factor i.e. $\eta_{mm} = 1$, would have the exiting stream's osmotic pressure difference equal to the hydraulic pressure difference between them. Alternatively, a fully irreversible membrane module ($\eta_{mm} = 0$) would show no change in the osmotic pressure of the streams on either side of the membrane. It is important to undestand that the effectivenss of a membrane module depends on the operating conditions, there is no single value of effectiveness that can describe a module [33]. One may intentionally desire to operate a membrane module at lower effectivess factors, by using short membranes, so that the water flux accross the whole membrane area is maximized. As a lower η_{mm} value indicates a relatively larger difference in osmotic and hydraulic pressures between the exiting streams (hence a larger driving force, Eq 1), which would have been minimized if η_{mm} value was closer to 1. However, this would mean that some of the chemical potential is lost, which can be acceptable in the case of river-ocean PRO, as the target might be to optimize for membrane power denisty. But in a closed loop system like ours, such chemical potential loss can cause major penalties in roundtrip efficiency and power denisty, as discussed in this paper, using the flush stream. From Sindey Loeb's analysis for PRO in [42], one can conclude a value of $\eta_{mm} \approx 0.83$. This was achieved, while targeting high membrane power density, instead one could achieve higher membrane effectiveness by changing the volumetric flows and hydraulic pressures. We assume a membrane effectiveness of 90% (i.e., $\eta_{mm} = 0.90$) for simulations in the next section. Achieving η_{mm} values of 0.90 are possible, however they might reduce membrane power density and hence require more membrane area to generate equivalent amount of energy. In the case of mixing brine with fresh water [via PRO], such may be acceptable as optimum power densities of 13-22 W/m^2 are achievable [24][43], hence there is plenty room for sacrificing power density, while still being above the 5 W/m^2 mark [44].

As the membrane effectiveness factor considers the difference in osmotic pressure between the entering and exiting streams on the draw and feed side, it implicitly accounts for the entropy generated due to reverse salt flux and lack of water uptake in PRO. To explicitly calculate and understand how these properties individually affect OES's performance, we simulate the effect of the salt rejection coefficient R (Supplementary Information Section 1 & 2) and the membrane uptake ratio ϕ (Eq. (13)) in Figs. 5(b) and (c).

Each of the parameters reflect a particular membrane performance capability, theoretically ranging from 0% (completely incapable) to 100% (perfect capability). Obviously, OES's overall performance varies with membrane performance; as indicated in Fig. 5, all three membrane performance parameters affect both energy density, ε, and roundtrip efficiency, η_s.

The simulation results, apart from showing the potential of achieving high ε and η_s values, also show the extent of membrane irreversibilities an OES system can sustain without sacrificing on energy density and roundtrip efficiency. When using membranes that have lower η_{mm} values - which among other increased irreversibilities, corresponds to high concentration polarization in the membrane - decreases the roundtrip efficiency. However, due to the multistage configuration, an OES system with membranes performing at a 60% effectiveness factor can still provide a round trip efficieny of ∼40% with 3 stages, instead of only ∼5% with a single stage. Note that in this case, for both 3 stage and single stage OES, equal amount of fresh water is separated and mixed. Having multiple stages does not correspond to relatively higher membrane area, it infact corresponds to using less membrane area for the same task. As in multistage the membrane is operated at optimum hydraulic pressures, see Sec. 2 and refer to [33] for more detailed explanation.

The losses due to low ϕ and R values directly decrease the chemical potential and may not be possible to mitigate by modifying the process design. Lower R value increases the fresh water (fw) stream's osmotic pressure, that increases the work needed for separation and decreases the work obtainable in PRO. This loss can only be mitigated by improving the salt rejection coefficient. Currently, commecial thin-film composite membranes operate at around 99.6 to 99.8% salt rejection [13][45]. We assume a salt rejection of 99.7% (i.e., $R = 0.997$) for simulations in the next section.

At first glance, one might say that the graphs in Fig. 5, show an improvement in OES performance with higher stages, for constant R (and ϕ) values. That is true, however, the improvement in OES's performance does not directly indicate that the irreversiblities caused by reverse salt flux (and lack of water uptake), are being reduced with higher stages. It is actually the decrease in other reducable irreversibilites, as explained in Sec. 2, that improves OES's performance (see Fig. 1).

It is also key to note that due to reverse salt flux, approaching water uptake (ϕ) values close to 100% is not possible. As salt accumulation (due to reverse salt flux) and loss of water (due to water flux from the feed to draw side) creates high osmotic pressure on the feed side, which on its own constricts water cross-flow, as explained by Eq. 1. Hence, the reverse salt flux in a way restricts the membrane from reaching high water uptake values (ϕ), regardless of the membranes hydrophilic properties. If the reverse salt flux is minimized, one could work towards increasing membranes hydrophilic properties which would enable higher water uptake values. As it is well accepted that increasing the membranes hydrophilicity, increases the water flux, because it promotes the wetting of all available pores [46][47]. To conclude, reaching ϕ values close to 1 is important to utilize all the chemical potential, but is impossible to achieve without having higher salt rejection properties in both RO and PRO stage membranes.

Overall, to achieve high roundtrip efficiency and high energy density, we need to have membranes which can benefit from closed loop operation and operate at high salt rejection (R) and high membrane effectiveness (η_{mm}) values. In the next section we optimize the OES process and discover that high pressure resistance is another key property required for improved performance.

6 Varying plant parameters for improved performance

So far we have analyzed the n-stage OES system which recovers 50% of the fresh water (fw) from a salty water (sw) stream, i.e., at an osmotic pressure of π_{sw} =30 bar. This operational process is similar to that of the standard sea water desalination process. OES is a closed loop system and depending on what gives the desired optimum performance, several sw concentrations and fw recovery ratios can be applied. We now study the three basic parameters that can be altered directly to improve OES's energy density, ε, and roundtrip efficiency, η_s. They are:

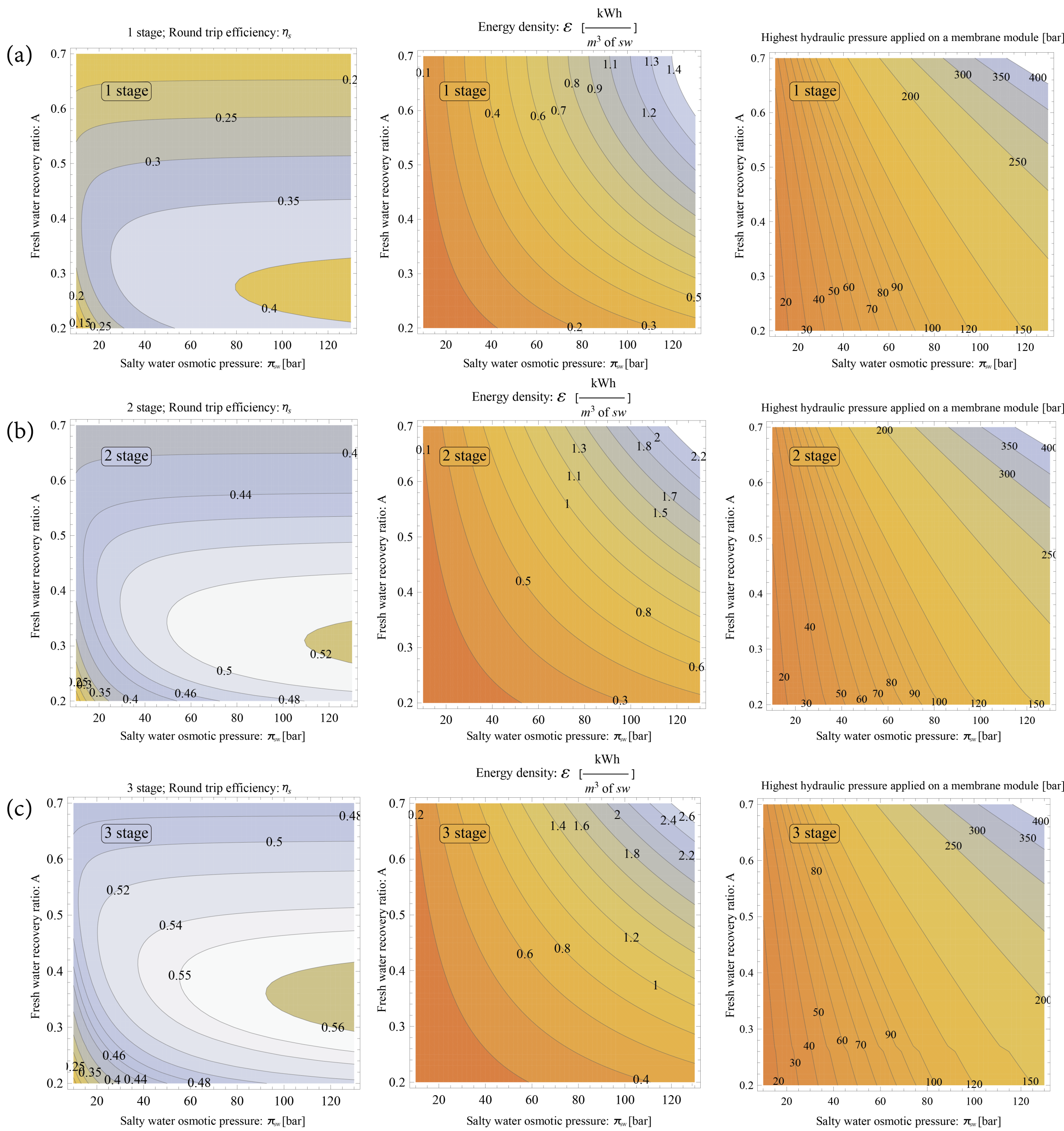


Figure 6: OES system is studied with varying fw recovery ratio and sw osmotic pressure. The affect of different A and π_{sw} values on round trip efficiency of 1-stage (left-a), 2-stage (left-b) and 3-stage (left-c) OES systems is simulated. The centre column shows the affect on energy density where the rows are arranged in increasing stage order of n, from 1 to 3. Right column shows the highest hydraulic pressure applied in a membrane module (experienced at the RO stage), for that particular A, π_{sw} and n value. The component efficiencies are consistent with other simulations, where $\eta_{mm} = \phi = 0.90$, $\eta_t = \eta_p = 0.95$, $\delta P = 0.5bar$ and $R = 0.997$.

1. Number of stages, n
2. Fresh water (fw) recovery ratio, A
3. Osmotic pressure (alternatively, the salt concentration) of the salty water stream, π_{sw}.

By now it is clear that having higher number of stages improves the roundtrip efficiency and energy density of the system. To understand how different A and π_{sw} values affect system performance, we simulate three different OES systems for n = 1, 2 and 3 (process diagram for n stage OES is shown in Fig. 3) in Figs. 6(a), (b) and (c) respectively. The effect on η_s and ε is studied, when A and π_{sw} values are varied for each n value, as shown in Figs. 6-left and centre coloumns, respectively. Along with the performance graphs, we have recorded and presented the highest hydraulic pressure applied to a membrane module for that particular A, π_{sw} and n value, as shown in Figs. 6-right coloumn. The membrane module that experiences the highest hydraulic pressure in OES (in a n-stage system) is during the RO process, at the n^{th} stage; which is shown in Figs. 6-right coloumn.

The behaviour of η_s and ε with varying A and π_{sw} values has a similar trend for 1, 2 and 3 stage OES systems, however the performance and magnitude is better at higher stages. We choose to study the behaviour for a 3 stage OES system as it presents promising results. The reasoning behind the trend and behaviour is consistent for all three OES systems with different n values.

The graphs (Fig. 6c-left and centre) hint at a relationship between A and π_{sw}, complementing each other. Higher π_{sw} value gives higher energy density and efficiency (shown in Fig. 6(c)-left and centre coloumns). However, the problem is that higher osmotic pressure calls for even higher hydraulic pressures for separation. A membrane module can only withstand certain hydraulic pressures without fracturing its structure. This is where a lower fw recovery ratio, A, can reduce the hydraulic pressure required for separation, as less fw is squeezed out at lower A values. At the same time, low A values give high efficiency as shown in Fig. 6(c)-left. Ideally, having high osmotic pressures and lower recovery ratios allows the OES system to perform at high efficiencies, while still operating at reasonably low hydraulic pressures.

Membrane modules in a typical seawater RO desalination plant operate at pressures of 50-60 bars. With current RO membranes this is not possible. To achieve high energy density, we need to operate at higher hydraulic pressures. In a recent study, in which operating pressures of 100 to 175 bars were tested on off-the-shelf RO membranes, the membranes exibited excellent rejection rates of upto 99.62% (when operating at 172 bar). On the contrary, water permeability of the membrane modules was shown to drastically drop at such high pressures [48]. This means that due to lower water flux, more membrane area (at the 3^{rd} RO stage) would be required to accomplish the same separation task when operating at such high pressures. Although still far from commerical application, nanoporous graphene membranes have shown possibility of extreemely high water permiability and salt rejection, as well as the possibility of operating at extreeme high pressures (1000-5000 bar), without fracturing the graphene monolayers [49][50][51].

High roundtrip efficiencies of ∼55% can be achieved when the hydraulic pressure in the 3^{rd} stage RO membrane is only 80 bar. However, if the goal is to achieve high energy density, one can achieve so by operating at high fresh water recovery ratios (A). At a hydraulic pressure close to 175 bar, both high energy density (∼1.2 $\frac{kWh}{m^3}$) and high roundtrip efficiencies (∼55%) can be achieved. Note, both energy densities and roundtrip efficiencies increase with higher n values, but with added capital costs.

It is straightforward to cut-off the impractical regions on the graph by considering what pressures a membrane module cannot sustain. However, choosing between high η_s, ε and n can be complicated. Many factors affect the optimization goals of an energy storage plant, such as economics, location of the plant, space availability, charge duration, etc. This paper is focused on introducing the concept and technology of storing energy through multistage osmotic process; detailed optimization that incorporates these factors is beyond the scope of this paper.

To have a better understanding of the scale for energy density, we can take an example of an energy storage plant built by BC hydro in Field, BC, Canada. The plant was built to improve the reliability and response times to outages which are abundant in this remote location [52]. This energy storage plant is capable of storing upto 6 MWh of electricity. If an OES system was built to provide similar electrical demand, it would have to hold 5,000 m^3 (for reference- an olympic swimming pool holds around 2,500 m^3 to 3,750 m^3 of water) of total solution (i.e., water and salt) at an energy density of 1.2 $\frac{kWh}{m^3}$. Such amount of liquid storage is not unheard of in the water storage industry, where standard sized tanks for potable water and brine storage can range form 75 m^3 to 22,700 m^3 [53]. However, this is on the lower end of the spectrum for energy storage densities, where battery technologies have energy storage densities ranging from 50-500 $\frac{kWh}{m^3}$ and fuel cells have energy density of 500-3,000 $\frac{kWh}{m^3}$ [11]. Depending on the available space and economics, storing large amount of liquid might or might not be an issue. In the case of the 6 MWh energy storage plant in Field, BC, being a remote location there is a lot of available land currently unused. On the contrary, if we consider another storage facility in Toronto, Canada[54], where the city required small and compact energy storage units that can provide 0.25 MWh of electricity storage in an urban setting, OES would not be well suited.

On the larger end, i.e. a GWh scale of energy storage, which is currently dominated by pumped hydro, an OES plant would require storing atleast 10^6 m^3 of liquid. Pumped hydro (PH) has comparable energy density to OES[11], however PH takes the advantage of giant open reservoirs. In this paper we have discussed how OES can benifit from a closed loop system, having open brine and fresh water reservoirs like PH would give away that advantage. Every cycle may require some type of pretreatment that would consume energy and with evaporation more water might be required regularly. Although, without an economical and feasibility study, we cannot say that storing 1000 million litres of water in enclosed tanks might be impractical (there are few examples of tank farms storing oil at similar amounts), but it is safe to say that such a size for energy storage [using OES] would require a lot of land and cause additional losses in the system.

7 Conclusion

The data presented in this paper demonstrates that an osmotic energy storage system can be viable for storing electrical energy. Previous studies on storing energy using osmosis have shown a competing relationship between roundtrip efficiency and energy density. With multistage operation we have discovered that both energy density and roundtrip efficiency can together be improved. The OES system has shown that it can approach practical efficiencies of 50-60% or higher, using the modified RO and PRO approach. The simulations were done assuming co-current flow in PRO for simple explanations; a counter-current flow configuration would, however, have higher roundtrip efficiencies, energy densities and operate at higher membrane power densities [55].

OES itself, has the potential to incorporate a thermolytic solution and operate as a hybrid RO-distillation set-up for separation. When waste heat is available, such a hybrid system can achieve higher roundtrip efficiency by separating some of the salty water (sw) solution, while mitigating the losses caused by reverse salt flux.

The OES process showed that it could approach realistic energy densities close to $1.2\frac{kWh}{m^3}$, which is approximately equal to a 500 meter high pumped hydro energy storage system (i.e. operating at 80% efficiency). A pumped hydro process is known to perform at 10-20% higher efficiency than OES; however, it is geographically constrained. An OES system on the other hand can be constructed in any type of geography and would occupy storage space similar to a 500 meter high pumped hydro plant that would have been restricted to hilly regions.

OES system is operated in a fashion that has a potential of storing energy for long durations and operating at variable power capacities. OES system has shown to perform better when it operates under its peak capacity. This is better explained with an example. Let's assume a 4 MW peak capacity OES plant, operated with 4 arrays of 3-staged PRO processes, at a 1MW capacity each. In a scenario where the demand for electricity is at half the peak capacity, the OES system can transform from 4 arrays (with 3 stages in each array) to a double array with 6 staged PRO process in each array. Such a shift and complete utilization of components, increases plant roundtrip efficiency and energy density.

Ideally, the OES system would operate with membrane modules that can be used for both RO and PRO. Having such a compact system would clean the membrane when the water flux is in the opposite direction, save space, and possibly decrease capital costs. There has been some work towards surface modification of thin film composite membrane with polydopamine that enables using RO membranes for PRO at certain pressure range [56]. However, to realize the realistic feasibility of the OES system, there needs to be further work to develop commercial membranes. Membranes that can either work as both RO/PRO membranes, or, themselves (separately) offer higher water permeability and salt rejection, while operating at high hydraulic pressures.

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