



# The concentration gradient flow battery as electricity storage system: Technology potential and energy dissipation



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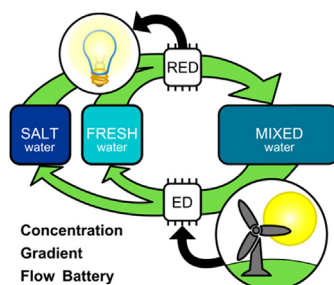
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## HIGHLIGHTS

- A novel environmental friendly concentration gradient flow battery is proposed.
- High power dissipation due to water and co-ion transport occurs at  $m_c > 1$  M NaCl.
- Charge and discharge show different mass transport and thermodynamic efficiency.
- At high salt concentrations water transport is the major power dissipation source.
- At low salt concentrations internal resistance is the major power dissipation source.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Unlike traditional fossil fuel plants, the wind and the sun provide power only when the renewable resource is available. To accommodate large scale use of renewable energy sources for efficient power production and utilization, energy storage systems are necessary. Here, we introduce a scalable energy storage system which operates by performing cycles during which energy generated from renewable resource is first used to produce highly concentrated brine and diluate, followed up mixing these two solutions in order to generate power. In this work, we present theoretical results of the attainable energy density as function of salt type and concentration. A linearized Nernst-Planck model is used to describe water, salt and charge transport. We validate our model with experiments over wide range of sodium chloride concentrations (0.025–3 m) and current densities ( $-49$  to  $+33$  A m<sup>-2</sup>). We find that depending on current density, charge and discharge steps have significantly different thermodynamic efficiency. In addition, we show that at optimal current densities, mechanisms of energy dissipation change with salt concentration. We find the highest thermodynamic efficiency at low concentrate concentrations. When using salt concentrations above 1 m, water and co-ion transport contribute to high energy dissipation due to irreversible mixing.

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## 1. Introduction

Due to the intermittent nature of renewable energy sources

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such as sun and wind, implementation of large scale electrical energy storage (EES) in the electricity grid is considered as a feasible solution to match power supply and demand. Additionally, EES is useful for preventing power outages and load leveling of the electricity grid [1–11]. Currently, 99% of the worldwide large scale electricity storage capacity is installed in pumped hydroelectric systems (PHS) with a total capacity of 127 GW [3]. PHS store and recover energy by pumping water into an elevated reservoir and by flowing water down through a turbine. The energy density of PHS is determined by the height of the reservoir and is about  $0.27 \text{ kWh m}^{-3}$  for each additional 100 m in height. A main limitation of PHS is the need for appropriate geographical conditions [1]. By contrast to PHS, battery storage is a new market development. Batteries are characterized by much higher energy densities and are suitable for mobile application. However, for large scale electricity storage batteries are less suitable due to high costs, safety issues and environmental concern caused by usage of toxic and scarce compounds [2]. Therefore an opportunity exists for a storage system that is environmentally safe and can also be used in flat terrains.

Until now, Pressure Retarded Osmosis (PRO) which makes use of water flux through a semi-permeable membrane, and Reverse Electro Dialysis (RED) which uses the ion flux through ion-exchange membranes to produce power have been extensively studied [12]. Here, we study an energy storage system based on using two salt solutions of different concentrations not unlike the combination of RED and electro dialysis (ED) proposed in Ref. [13]. Fig. 1 shows a typical RED configuration used for extracting power by controlled mixing of two solutions. The same cell design can be used to split the previously mixed solution back into two solutions with different concentrations. By operating the proposed system, first in RED mode (discharging step) and then in ED mode (charging step) a closed-system battery is created. This system we call the “concentration gradient flow battery” (CGFB). Advantages of the CGFB are that it is scalable and can be used in small households as well as in large scale grid storage. Moreover, the energy-containing solutions can be made of cheap, environmentally friendly and abundant materials and the CGFB systems can be installed at any

location and are very safe

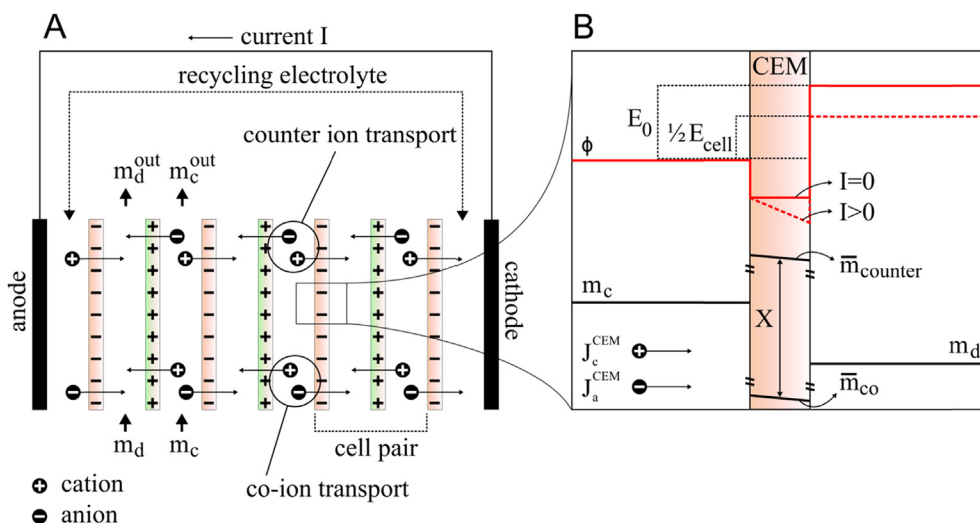
In this work we choose to work with NaCl salt, because of its high theoretical energy density (see the results section), and because it is one of the safest, cheapest, and most abundant salts on our planet. For an ideal solution the chemical potential of salt in a concentrated solution (concentrate) is higher than in a diluted solution (diluate). Interestingly, this difference of chemical potential across ion-exchange membranes (IEMs) can be utilized to extract power by transferring salt from concentrate to diluate. This is possible because IEMs allow passage of either positively charged ions (using a cation-exchange membrane, or CEM) or negatively charged ions (using an anion-exchange membrane, AEM), giving rise to a membrane potential when the salt concentration is different between the two sides. When AEMs and CEMs are combined such that half of the flow channels are fed by a concentrated solution, while the other half of the channels has a flow of diluate, an energy as high as  $0.21 \text{ kWh per m}^3$  of mixed sea and river water solution can be extracted (see Fig. 1) [14].

In case of an ideal IEM, the membrane potential can be calculated using the Nernst equation [15],

$$E_m = \frac{RT}{zF} \ln \left( \frac{\gamma_c m_c}{\gamma_d m_d} \right) \quad (1)$$

where  $E_m$  is the membrane potential (V),  $R$  the universal gas constant ( $\text{J K}^{-1} \text{ mol}^{-1}$ ),  $z$  charge of the ion,  $F$  is Faraday’s constant ( $\text{C mol}^{-1}$ ) and  $\gamma$  and  $m$  are the activity coefficient and molality of solution respectively. Subscripts  $c$  and  $d$  describe concentrate and diluate stream.

In case of a CGFB, a difference in chemical potential between concentrate compartment and diluate compartment leads to power release when salt is transported from the concentrate to the diluate solution. As a result of salt transport, the concentration difference between the two solutions will decrease. In order to recharge the CGFB, one needs a technology that can restore the original salt concentration difference. In this study we use ED to restore the original concentration difference. The regeneration step is carried out by applying a higher potential than the membrane potential.



**Fig. 1.** LEFT (A): Discharging step of a concentration gradient flow battery (CGFB). Due to a chemical potential difference between ingoing solutions, counterions are transported from the concentrate ( $m_c$ ) to the diluate ( $m_d$ ) solution, resulting in ionic current. Please note that the membrane fixed charge is denoted by black minus (–) and plus (+) signs. Two IEMs and two adjacent compartments are called a cell pair. This figure describes a stack with 3 cell pairs. Osmotic flow of water is always in the direction of the concentrate. Electro-osmosis goes in the direction of co-ion and counterion transport. For charging mode of operation, Fig. 1A is identical, except for the direction of current and counterion transport which is reversed, and both electrodes change their polarity. RIGHT (B): Illustrative picture of potential ( $\phi$ ) and concentration ( $m_i$ ) profiles over one IEM [15] in discharge mode. Diffusion boundary layers, diffusion potentials and potential drop in solutions are not depicted. Fixed membrane charge density is denoted as  $X$ . During charging mode Fig. 1B is identical except for the fact that counterion transport ( $J_c^{\text{CEM}}$ ) reverses its direction and potential increases.

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