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Energy storage by reversible electrodialysis: The concentration battery

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ABSTRACT

Reverse electrodialysis has long been recognized as a tool for harnessing free energy from salinity gradients but has received little attention for its potential in energy storage applications. Here we present the experimental and modeled performance of a rechargeable electrodialytic battery system developed for the purpose of energy storage. Experimental round-trip energy efficiency ranged from 21.2% to 34.0% when cycling the system between 33% and 40–90% state of charge. A mass transport model based on chemical thermodynamics is also proposed to describe the system's performance. Results indicate that, upon model calibration, the model effectively predicts experimental values. Experimental and modeled results suggest that the membrane resistance and osmosis are the primary sources of ohmic and faradaic energy losses, respectively. The results demonstrate that a functioning battery can be constructed using typical reverse electrodialysis stack components. Future improvements in membrane technology and optimization of the system chemistry offer promising avenues to improve the power density, energy density, and round-trip energy efficiency of the process.

1. Introduction

Renewable energy sources such as wind and solar power provide a pathway to a lower-carbon energy future. However, the inconsistent and/or cyclical nature of these supplies limits their value to electric utilities because periods of peak renewable energy output do not necessarily coincide with periods of peak demand for electricity. As such, the ability to store tens or hundreds of MWh of energy is becoming increasingly important to the reliability of electric grids around the world. By storing renewable energy when it is available (e.g. during daytime or periods of strong winds) and releasing it when demand for electricity is the highest, large-scale rechargeable batteries would support the dispatchability of renewable energy supplies as well as the overall stability and reliability of the electric grid. Energy storage technologies will thus play a significant role in modernizing the electrical systems of developed countries and lowering the barriers to electrification for less developed countries or regions. It is predicted that the global demand for large-scale energy storage technologies will exceed 40 GW by 2022 [1].

While numerous technologies exist that are capable of storing such quantities of energy, few have achieved the combination of low capital cost, long operating life, and high round-trip energy efficiency that are required to make a compelling economic case for widespread deployment [2–5]. Battery systems in particular must often employ either rare, expensive, and/or hazardous materials (e.g. lithium, vanadium, lead, sulfuric acid) and/or highly specialized manufacturing techniques, both of which result in high system cost.

In this paper we propose a rechargeable concentration battery which stores energy in the form of an ionic concentration (i.e., chemical potential) difference between two electrolyte solutions. The battery is charged by using electrical energy to perform electrodialysis (ED) on the solutions, creating a concentration difference. The system can later be discharged by reverse electrodialysis (RED), which reconverts the chemical potential energy into direct current electricity. To the authors' knowledge, this paper presents the first experimental results of this type of concentration battery in the peer-reviewed literature.

Electrodialysis (ED) uses direct-current electricity and a stack of alternating anion exchange membranes (AEMs) and cation exchange membranes (CEMs) to move ions from a feed solution to a concentrated solution. ED has been employed for several decades in applications such as desalination of drinking water, food processing, and the treatment of industrial wastes [6,7]. The reverse process (reverse electrodialysis, RED) was proposed in the 1970s as a means of harnessing electrolyte concentration differences in e.g. seawater and river water to produce renewable electricity [8]. In

Abbreviations: AEM, anion exchange membrane; CEM, cation exchange membrane; ED, electrodialysis or energy density; *OCV*, open circuit voltage; PD, power density; RED, reverse electrodialysis; *SOC*, state of charge

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the last decade, RED has become an active area of research [9–19], but remains challenged by three primary sources of energy loss: the low conductivity of the dilute solution (generally river water), fouling by natural materials in the feed water, and performance limitations of the ion exchange membranes (i.e. high resistance, low selectivity, insufficient power density) [12,14,15,20–22].

As long as a reversible electrode system is used, both ED and RED can be performed using the same apparatus. Several such electrode systems have been described in the literature [23–25]. As such, it is possible to construct a rechargeable battery system that uses ED to charge the battery by converting electrical energy into chemical potential energy in the form of a concentration difference, and RED to discharge the battery by converting said chemical potential energy back into electricity. While there has been some research of closed-loop RED for generating energy from low-grade heat [26–28] (in which the solutions are continuously regenerated by thermal means), the use of a *rechargeable concentration battery* represents a novel approach to the problem of energy storage which may offer several distinct advantages over traditional battery systems.

From a materials standpoint, the electrolyte may be selected from a variety of non-toxic, environmentally benign salts (such as sodium chloride). This flexibility would allow the system to benefit from existing economies of scale in certain electrolytes such as road de-icing salts and well completion fluids. Furthermore, the design is inherently safer than that of a traditional battery since the position of the electrodes within the electrodialysis stack virtually eliminates the risk of thermal runaway. Finally, the power capacity (membrane area) and the energy capacity (electrolyte volume) can be independently scaled to suit different application requirements; a characteristic currently offered only by redox flow batteries [5].

Given these potential advantages, the first objective of this study was to build and test a laboratory-scale prototype of a rechargeable electrodialytic concentration battery. The second objective was to develop a mathematical model based on chemical thermodynamics to describe the performance of the system. The model combines established concepts and equations in electrodialysis, reverse electrodialysis, and battery systems. The modeling results provide insight into the relative impact of various design and operating variables on the round-trip energy efficiency, power density, and energy density of the system.

2. Formulation of model to describe battery performance

2.1. Overview of battery operation and corresponding phenomena to be modeled

At its core, the concentration battery is a closed-loop (reverse) electrodialysis, (R)ED, system as illustrated in Fig. 1. In the system, an (R)ED stack comprising alternating CEMs and AEMs separates two electrolyte solutions stored in tanks, which may initially be at the same concentration. The solutions are circulated through the (R)ED stack by pumps in a closed loop. Working electrodes at either end of the stack (the battery terminals) allow electricity from a power source to be transferred into the solutions as ionic current. To charge the battery, an electric current is applied to the stack to cause ED, resulting in a net movement of ions out of one of the solutions and into the other. As the charging process continues, a concentration gradient develops between the two solutions, and a chemical potential difference is established across the membrane stack. When the externally-applied electric current through the system is stopped and the circuit is kept open, the system is effectively storing energy as a salinity gradient. When the circuit is closed by connecting it to an electrical load, the chemical potential drives a current in the reverse direction through RED, discharging the system and eventually returning it to the initial state in which both electrolyte concentrations are equal. Thus in theory, a closed-loop (R)ED system can be charged with electrical energy by ED to later discharge the stored energy by RED.

The theoretical energy storage capacity of the system is given by the Gibbs free energy of mixing between the solutions, ΔG_{mix},

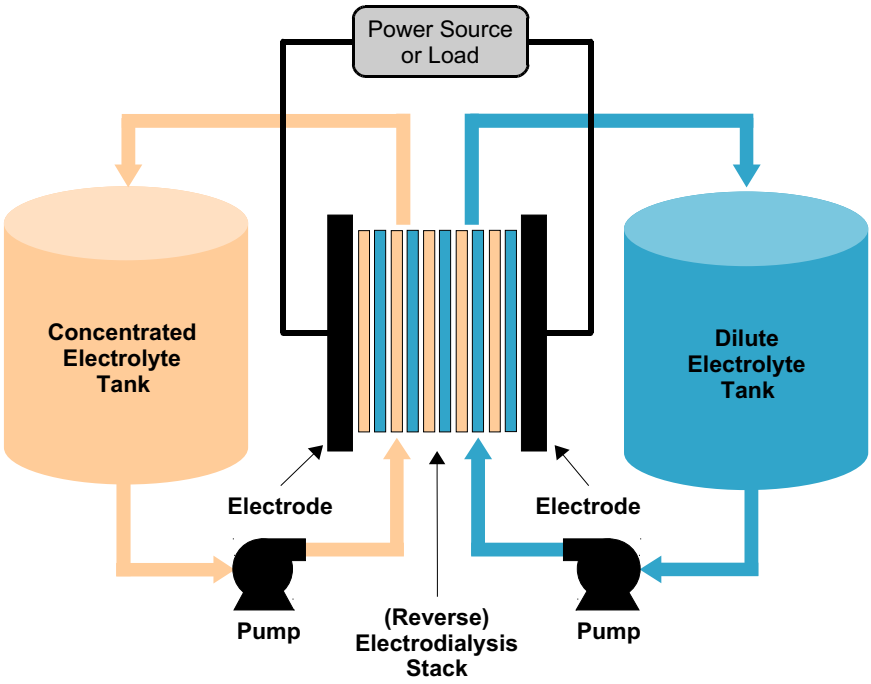

Fig. 1. Schematic diagram of closed-loop electrodialytic energy storage system – the concentration battery. During charging by ED, ions migrate from the dilute to the concentrated electrolyte. When discharging by RED, the direction of electrical current is reversed and ions move back from the concentrated to the dilute electrolyte, eventually restoring the initial concentrations. (See Figs. 2 and 4 for details of the interior of the (reverse) electrodialysis stack.)