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Reduction of the shadow spacer effect using reverse electrodeionization and its applications in water recycling for hydraulic fracturing operations

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ABSTRACT

Reverse electrodialysis (RED) is an electrically driven process for the extraction of usable energy from the Gibbs free energy of mixing. Past research efforts have focused on the improvement of power density through higher voltages, large cell numbers, and overall reduction of stack resistance, yet the process remains far from optimized. One of the principal problems is the shadow spacer effect where limited conductivity near the spacer decreases the amount of electrical transport. We have improved this technology by incorporating ion exchange wafers in each cell, shortening the diffusion pathways, limiting the shadow spacer effect, and obtaining net power densities of approximately 0.32 W/m^2 for reverse electrodeionization (REDI) compared to 0.01 W/m^2 for the RED case. Further, we have found that applying voltage to the system gives an increase in the overall power extraction efficiency due to wafer optimization and the non-ohmic behavior at low voltages. This is the first study incorporating electrodeionization techniques in RED systems. We also investigated the use of REDI in hydraulic fracturing and obtained a net power density of approximately 0.79 W/m^2 using produced water. This technology could be utilized for processing of produced water from hydraulic fracturing operations to provide some of the power used at the well site (when mixing with fresh water for re-fracking) with no greenhouse gas emissions. Using REDI at fracking sites, an industrial process that has been mired by environmental concerns can take positive steps toward developing and adopting sustainable practices.

1. Introduction

Recently, salinity-gradient energy sources have become competitive options in the alternative energy sector [1,2]. Salinity-gradient energy, or "blue energy" [3], is defined as the energy available from mixing two aqueous solutions of different salinities, and has a total global potential for power production of 1.4–2.6 TW or as many as 3000 coal fired power plants [2,4–10]. When "produced water" from fracking is returned to the surface, it contains a high concentration of salts, thus when 1 m^3 of salt water is mixed with 1 m^3 of fresh water for later reuse a maximum potential of 10 MJ is available to extract as usable power from Gibbs free energy of mixing [11–13]. However, no studies have been conducted relating this energy potential to the fracking industry. The fracking industry is an ideal application for reverse electrodialysis (RED) because brine solutions and freshwater are found in large quantities at each well site. Not only does our research focus on augmenting the RED process for improved power production, but also it takes this a step further by providing a sustainable solution some environmental hydraulic fracturing concerns.

1.1. Reverse electrodialysis

Reverse electrodialysis is an electrochemical process driven by the concentration difference between feed streams (diluate and concentrate) that are separated by ion selective membranes, creating an ion flux as cations and anions migrate across the membranes [1,3,14]. Through a redox reaction which occurs at the electrodes, this ion flux is converted directly into an electric current [3,15]. Several designs for RED systems have been considered, generally consisting of alternating cation and anion exchange membranes separated by spacers and terminated with an electrode at each end [14–16]. In multi-cell systems, a serial configuration is used to maximize voltage potential and power generation [17]. Homogeneous ion exchange membranes are used for their high permselectivity for ions with opposing charge while repelling ions

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Nomenclature

EDI	electrodeionization	$R_{electrode}$	electrode resistance
N	number of cells	R_{load}	load resistance
RED	reverse electrodialysis	R_{total}	total stack resistance
REDI	reverse electrodeionization	$V_{applied}$	applied voltage
R_{cell}	cell resistance	$V_{cell\ pair}$	voltage generated per cell pair

with like charge [18]. Previous research has found solutions to some limitations in RED including those for the spacer shadow effect [19–21], fouling [6], and resistance [10]. Balster et al. investigated the use of profiled membranes and spacer-free systems for increased mass transfer and reduced cell resistance [22,23]. Dlugolecki et al. found that the spacer shadow effect can reduce the overall energy recovered by 30–40%, representing a significant loss in total energy that must be recovered in order to make RED systems attractive for energy production [19].

In a traditional RED setup, the low conductivity of the liquid in the diluate chamber results in limited ionic transport. As a result, the electrical resistance in the diluate chamber is often the dominant restriction [24,25]. Therefore, the focus of this research is to provide a working solution to limited ion diffusion and energy production by applying principles of electrodeionization (EDI) [26–28] in hopes of reducing the shadow spacer effect and increasing the overall current density. A wafer is made by binding ion exchange resins with a polymer [26] and inserting it into an electrodialytic cell in place of a flow spacer to stimulate ionic transport. This concept can be used to not only reduce the spacer-shadow effect but also improve the ion transport restrictions caused by low solution conductivity. Thus, this study investigated the improvement of energy production and power density in an RED system through the use of ion exchange resin-wafers in solution compartments. This work differs than previous studies in that the wafer is used as a conductive spacer to reduce the spacer-shadow effect and cell resistance similar to the effects seen in EDI.

1.2. Technology implications for produced water from hydraulic fracturing

Hydraulic fracturing has become widely utilized as a means for extracting natural gas and oil previously thought unobtainable. Each well site is horizontally drilled, and injected with 12–16 million liters of "fracking fluid" (water with sand and chemical additives), under high pressure to crack the formation thus increasing the permeability of the surrounding rock enabling enhanced gas and oil flow to the well [29]. Following the fracturing process, 20–100% [11,29] of this fluid returns to the surface as "produced" water containing contaminants, mainly dissolved salts. Because of the high concentration of salts the produced water has little value and is commonly disposed of in deep injection wells. However, it is suspected that this has contributed to recent seismic events in addition to permanently removing water from the ecosystem [30–32]. As a result, the need for devising an alternative method for handling produced water has become both environmentally and economically pressing.

Although RED won't treat produced water, the potential power recovery is attractive to those in hydraulic fracturing. To begin produced water recovery in a system utilizing RED, a series of pretreatment regimens are implemented in order to remove non-ionic contaminants such as oil components, chemicals included in the fracking fluid, and foulants. Once these have been removed, RED technology can be used to harness the Gibbs free energy of mixing ions between this partially treated produced water and a freshwater feed with the purpose of replenishing the water that could not be recovered from water clean-up. This extracted energy can then be used to power ongoing processes or stored in a battery for later use in subsequent fracking process when needed. The resulting water solution output from the RED system can then be recycled back into the hydraulic fracturing process. This revolutionary approach allows for the recycle of water and production of energy.

2. Materials and methods

We designed an innovative reverse electrodeionization system (REDI) system that utilized EDI techniques to minimize system resistance. This system was tested with varying numbers of cell pairs (1-cell system, 5-cell system, 10-cell system). Membranes were separated by custom hybrid spacer-gaskets to minimize cell length. In a traditional EDI system, a flow spacer is used to move fluid across the membrane while a rubber gasket is placed between each spacer to ensure a water tight seal. For this study, we used a specialized plastic to act as both the flow spacer and sealing gasket to reduce overall cell thickness. Each one measured 500 μm thickness. Fumatech FKS-30 and FAS homogeneous ion exchange membranes were used for experimentation. A schematic of the general system configuration is shown below in Fig. 1.

2.1. Wafer casting

Ion exchange wafers used in experimentation were composed of both anion and cation exchange resins (Amberlite® IRA-400 (Cl^-) and Amberlite® IR120 (Na^+) form ion exchange resins), polymer (polyethylene powder, 500 μm), and sucrose. A custom iron cast

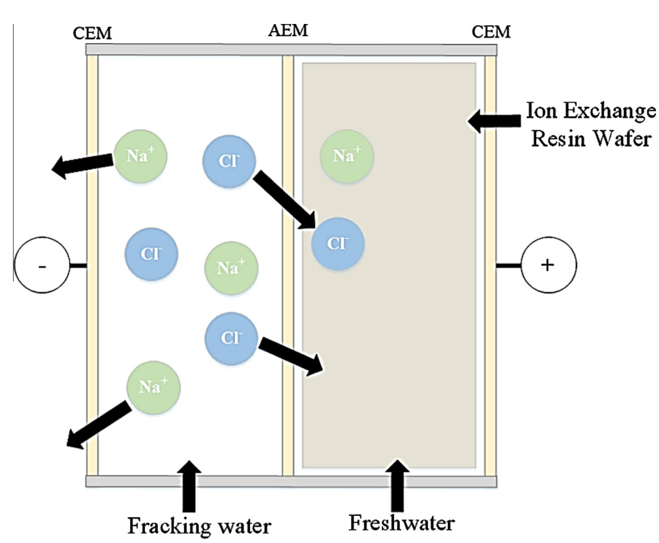

Fig. 1. Diagram of RED cell using resin technology. Membranes are spaced within the cell, and compartments alternate between freshwater and fracking/brackish water. Ion exchange resin wafers are placed in freshwater compartments to improve solution electrical conductivity. Rinse compartments not shown.