Seawater Flow Battery as Technology Platform

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ABSTRACT

Grid-level storage of renewable energy using electrolytes from seawater is a platform technology with multiple byproducts and use-case scenarios. The core application is to provide load-leveling for intermittent sources such as wind and solar. Membranes which conduct sodium to a cathode for energy storage yields chlorine gas, which can be sold. Discharging stored sodium produces electric power, and also sodium hydroxide and hydrogen gas. Hydrogen can be sold, or combined with stored chlorine gas in a H_2-Cl_2 fuel cell to boost the round-trip energy efficiency of the seawater flow battery system. Sodium hydroxide can be used in alkaline exchange membrane fuel cells. The brine from conventional desalination can be processed to produce sodium metal plus fresh water which can be released into the marine environment. Sodium metal extracted from the cathode can be used as an energy vector which, when combined with water, produces hydrogen on-demand for use in variable load applications such as fuel cell vehicles.

Keywords: sodium, flow, battery, seawater, low-cost, multi-purpose, hydrogen.

1 INTRODUCTION

Water is critical to the sustainability of our society and economy. With the global population increasing, the demand for desalinated water for irrigation and human consumption is on the rise. Current technologies include vacuum distillation and reverse osmosis, which have shortcomings such as high energy consumption and low flow rate, respectively. Superior technologies which can address these disadvantages and have a favorable economic model are needed. In addition, utilization of renewable energy sources such as solar and wind in desalination is desired to help mitigate the negative environmental impact, however, energy generation from these sources is intermittent in nature. Introducing energy storage, such as batteries, to the desalination system can overcome this issue. An integration system of desalination and batteries using renewable energies is a promising model with significant economic potential.

One potential byproduct of desalination is salt. Brine discharged from desalination systems stresses the environment. Damage to marine ecosystems is an externality not always included in project finance. If the sodium from salt could be harvested as a pure metal and used for a hydrogen-on-demand system like fuel cells, it has higher probability of improved economics and is likely more commercially viable. Fuel cells are promising technologies for mobile and stationary backup power supplies. A highly integrated system to simultaneously: (i) store renewable energy such as solar and wind; (ii) produce desalinated water; and (iii) create portable, salable energy storage as an additional byproduct is highly desirable. A system meeting these multi-faceted needs would be of considerable value. What is proposed herein builds upon this first-ever capability, and provides even more benefits besides.

2 TECHNICAL APPROACH

Energy storage and water desalination are accomplished simultaneously with a novel, patent pending device called the Seawater Flow Battery (SWFB), as shown in **Fig. 1** (see page 4). The system consists of two cells (electrolysis cell on the left and discharge cell on the right) which have a common sodium metal electrode immersing in nonaqueous liquid electrolyte working as cathode for the electrolysis cell and anode for the battery cell on the right, respectively. The nonaqueous chamber is separated by two sodium ion-conducting solid-state electrolytes from the seawater. The working principle is: seawater is supplied to the charge cell with the electrical energy generated from solar or wind to produce a valuable byproduct of chlorine gas and sodium metal which is deposited on the cathode as a form of energy storage. At the same time, seawater is desalinated and discharged from the electrolysis cell. As energy is demanded, the discharge cell starts to consume sodium metal anode and seawater to produce electricity and a byproduct of hydrogen for fuel cells. At the same time, sodium hydroxide as a valuable product is formed and discharged from the discharge cell. The chlorine and hydrogen gases produced can also be used as fuels in H_2-Cl_2 fuel cells, providing extra energy as demanded.

In conventional electrolysis of seawater or concentrated sodium chloride solution (brine), chlorine gas can be easily generated on the anode, while sodium metal cannot be produced on the cathode because water is more easily reduced. The advance of the SWFB technology is to separate the anode in aqueous electrolyte and cathode in nonaqueous electrolyte by the solid sodium ion conductor in the electrolysis cell, so that metallic sodium can be produced on the cathode. Similarly, the anode (Na) and cathode in the discharge cell are separated by the solid sodium ion conductor which allows on-demand generation of electricity energy and production of hydrogen gas. The key component in this system is the sodium ion conductor.

A NASICON ceramics with a composition of $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ($x = 2$) will be used in both cells because of its stability toward aqueous solution and sodium metal, and high ionic conductivities.[1,2] Such NASICON has been successfully used in a dual-electrolyte Na/Air battery by Hayashi *et al.* recently.[3] High ionic conductivities of 1.2×10^{-3} S/cm at 25 ° and 2×10^{-3} S/cm at 50 °C have been obtained, which can promise high current operations and energy efficiencies of the electrolysis cell.

The SWFB has been demonstrated recently at the lab bench scale at IUPUI, providing technical feasibility of the essential concept. A pending project will expand upon this work and build the essential elements of a system with the following features:

1. Produces desalinated water from seawater or brine – the saltier, the better.
2. Stores energy AS IT'S PRODUCING CLEAN WATER!
    a. Energy can come from intermittent renewables
    b. Energy could also come from the grid, if needed
    c. Energy can come from daughter storage devices (see below)
3. Generates hydrogen upon discharge of the SWFB
    a. A fungible, portable commodity – available for sale off-site
    b. Can be used in fuel cells to produce electric power
4. Harvests sodium metal ($Na_{(s)}$) which reacts with water electrochemically in the discharge cell, makes hydrogen (H_2)
    a. Can be sold as commodity for vehicles, homes, generators
    b. Spent caustic (NaOH) converts to brine with collected chlorine (Cl_2)
5. Chlorine generated during charging can be used to:
    a. Reprocess brine to make more $Na_{(s)}$.
    b. Mix with H_2 in H_2-Cl_2 fuel cells to produce electric power.

The prototype will be designed to demonstrate feasibility of the entire concept; however, the project itself will focus on the core technology of the SWFB membrane, electrolytes, and electrode configurations for both charge and discharge processes.

Research activities will begin with the established NASICON membrane materials. Improved materials, combinations or layers of materials, and geometrical configurations will be developed cognizant of the maritime environment where considerations such as biofouling and multiple salt species, are a concern. The production of desalinated water has a tradeoff with energy storage rate. To make ultra-pure water requires longer times; therefore the rate of energy storage becomes diminishingly small as the water becomes more pure. Characterizing this trade space will help in the development of economic use case models for evaluation of commercial viability.

The liquid electrolyte within which the sodium metal is collected is expected to require additional development. Ethylene carbonate (EC) is commonly used, and performed well in the early lab proof-of-concept tests. However, conductivity of EC is relatively low, which may limit the ultimate size of a SWFB; therefore, blends of various electrolytes containing other carbonate solvents (*e.g.*, propylene carbonate (PC)) and ether solvents (*e.g.*, tetraethylene glycol dimethyl ether (Tetraglyme)) will be tested for their combined performance against an array of solid NASICON membranes.

Temperature will increase conductivity, but is limited to well below 100 °C for water applications. The use of heating to boost both clean water production and energy storage will be explored in the design of the bench top apparatus. The rig to be design and built will include instrumentation for quantifying the production of byproducts such as chlorine, hydrogen, and sodium.

3 H_2/Cl_2 FUEL CELLS

The byproducts of chlorine and hydrogen gases generated in the electrolysis and discharge cells, respectively, can be used directly as fuels in H_2-Cl_2 fuel cells. Although H_2/Cl_2 fuel cells are not as popular as H_2-O_2 fuel cells, the product of HCl in H_2-Cl_2 fuel cells (as shown in Equation 1) is much more valuable than water.[4] In addition, the chlorine electrode process is much faster than that of the oxygen reduction process.[5]

$$H_2 + Cl_2 \rightarrow 2HCl \quad E^0 = 1.36V \tag{1}$$

The potential low-cost chlorine and hydrogen gases produced from SWFBs could make the product of HCl more competitive than those from other processes such as HCl gas produced from chlorine which is generated in the electrolysis of salt solution in the chlor-alkali industry.

H_2-Cl_2 fuel cells work as much a chemical reactor an electric generator.[6] One particular challenge with H_2-Cl_2 fuel cells is the hydroscopic byproduct of HCl which can remove most water from proton conducting membranes, e.g., Nafion®. To maintain the hydration of membranes and proton conductivity, chlorine gas can be dissolved in aqueous solution of HCl; however, the acid can corrode systems and cell performance. Alternative membranes, such as phosphoric acid doped PBI, could be used in H_2-Cl_2 fuel cells, but the removal of water by HCl can result in polymerization of phosphoric to form pyrophosphoric acid or higher oligomers.[6] Recently Liu et al.[7,8] demonstrate anhydrous membranes containing protic ionic liquids (e.g., porous nanofiltration membranes (NF) membranes containing trimethylammonium phosphate) in nonhumidified high temperature H_2-Cl_2 fuel cells, as shown in **Fig. 2**. The non-conducting polymers provide the mechanical support and protic ionic liquids form proton conducting pathways. This approach could overcome the issues with H_2-Cl_2 fuel cells and holds great promise.

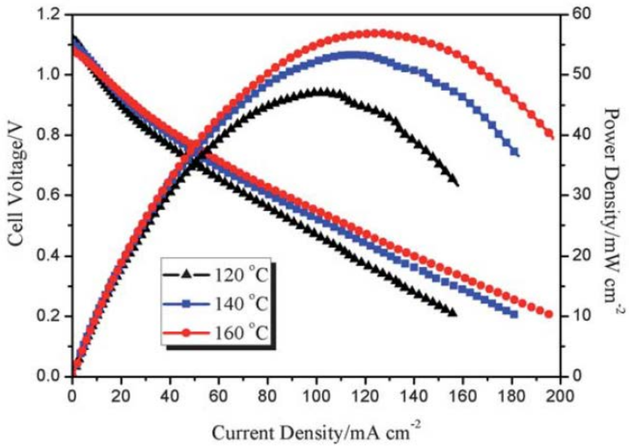

Figure 2: *Single-cell H_2-Cl_2 fuel cell performance of porous nanofiltration membranes (NF) membranes containing trimethylammonium phosphate operated at different temperature.*[7]

4 CONCLUSION

The SWFB promises low-cost, high-capacity electrochemical energy storage suitable for grid applications or for mobile use. A system of renewable energy using solar or wind power in conjunction with the SWFB provides load-leveling to meet demand 24 hours per day. Applications include cold ironing of ships at port, with the benefit of reducing air pollution from the current practice of running shipboard diesel generators.

While proven at the lab bench scale, the SWFB is ready for scale-up to a prototype. The Lugar Center for Renewable Energy is seeking partners and funding to advance this work towards commercial development.

End users of the SWFB can maximize their return on investment by selecting which byproduct provides the greatest monetary value at a given time. In this way, fiscal resilience is maximized at the same time that multiple needs are met flexibly, depending on the present need.

5 ACKNOWLEDGEMENTS

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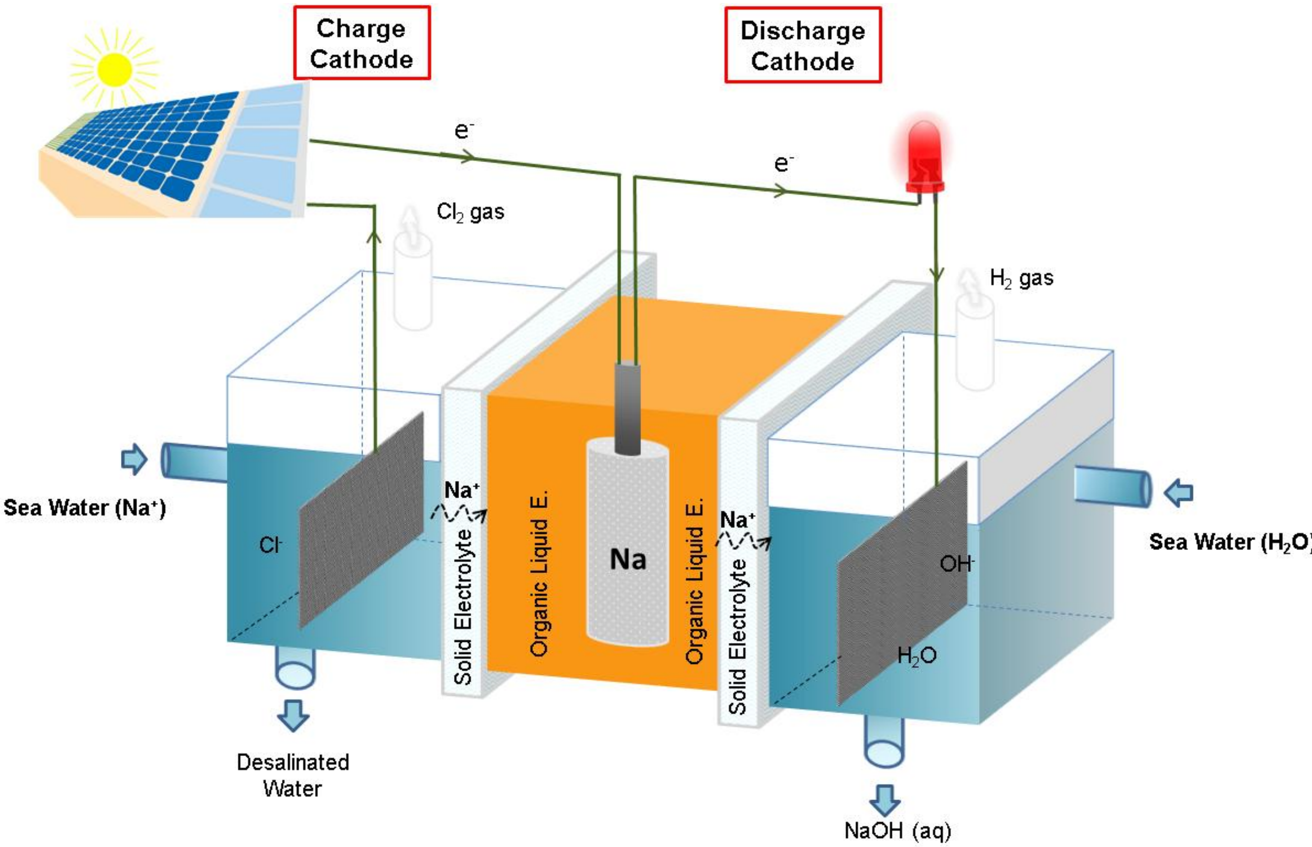

Figure 1: *Seawater Flow Battery (SWFB) stores intermittent solar power for discharge later.*

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