Energy extraction and water treatment in one system: The idea of using a desalination battery in a cooling tower

Barak Shapira, Izaak Cohen, Tirupathi Rao Penki, Eran Avraham*, Doron Aurbach

Department of Chemistry, Bar-Ilan University, Ramat-Gan 5290002, Israel

HIGHLIGHTS

- A flow battery comprising $Na_4Mn_9O_{18}$ (NMO) and Ag/AgCl was constructed.
- The temperature dependence of the NMO electrode potential was -0.63 mV/K.
- Energy extraction alongside with desalination was demonstrated at low C-rate.

GRAPHICAL ABSTRACT
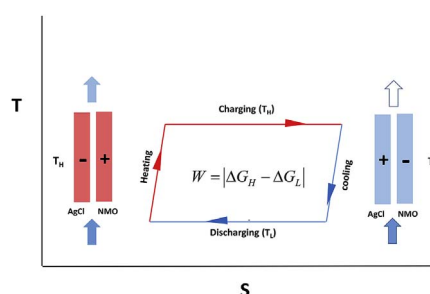
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ABSTRACT

The use of sodium manganese oxide as an intercalation electrode for water treatment was recently explored, and referred to as a "desalination battery" and "hybrid capacitive deionization". Here, we examine the feasibility of using such a desalination battery, comprising crystalline $Na_4Mn_9O_{18}$ as the cathode and $Ag/AgCl/Cl^-$ electrode as the anode, to extract energy from low-grade waste heat sources. Sodium manganese oxide electrode's material was produced via a solid-state synthesis. Electrodes were produced by spray-coated onto graphite foils, and showed a temperature dependence of the electrode potential, namely, $\partial E/\partial T$, of -0.63 mV/K (whereas, the Ag/AgCl/Cl$^-$ mesh electrode showed much lower temperature dependence, < 0.1 mV/K). In order to demonstrate ion-removal capabilities together with the feasibility of thermal-energy conversion, a flow battery system was constructed. Thermally regenerative electrochemical cycles (TREC) were constructed for the flow battery cell. The thermal energy conversion, in this particular system, was shown to be feasible at relatively low C-rate (C/19) with temperatures varying between 30 °C and 70 °C.

1. Introduction

The increasing shortage in accessible fresh water is one of the biggest challenges facing the global community. The consumption of fresh water is mostly associated with household consumers, however fresh water is frequently consumed in industry. Cooling towers are among the biggest consumers of water in industrial processes due to the use of large volumes of fresh water as makeup water in system [1,2]. The cooling process is based on water evaporation in order to obtain the

cooling effect. As the water evaporates, the salt concentration of the remaining water (blowdown water) increases. This blowdown water is usually dumped into the wastewater drain and, therefore, addition of make-up water is needed to compensate for the water loss. Many efforts have been made to mitigate fresh water consumption in cooling towers. For instance, the reverse osmosis method was considered for the treatment of a recirculating stream in the cooling tower [3]. Recently, a membrane capacitive deionization method for treating the recirculating water in cooling towers was suggested [4], demonstrating water saving

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by up to 28%.

Sodium intercalation compounds are, in most cases, investigated in the context of energy storage and conversion [5]. Sodium manganese oxides have been considered as a promising cathode materials since they were first reported in 1971, by Parant et al. [6]. Sodium manganese oxides, in particular $Na_4Mn_9O_{18}$, have been recently explored as a positive electrode material for an aqueous electrolyte in sodium-ion energy storage devices [7–9]. The solid-state synthesized $Na_4Mn_9O_{18}$ (also known informally as $Na_{0.44}MnO_2$) shows a specific capacity up to 45 mAh g^{-1} in aqueous solutions. A cell composed of $Na_4Mn_9O_{18}$ as a positive electrode and activated carbon as the negative electrode demonstrates over 1000 deep discharge cycles without loss in capacity [10]. The system sodium manganese oxide - in the form of crystalline $Na_2Mn_5O_{10}$ as the cation capturing electrode (positive electrode) and $Ag/AgCl/Cl^-$ as the anion capturing electrode (negative electrode) - was recently explored for purposes other than energy storage. For instance, another suggested approach is to utilize the $Na_2Mn_5O_{10}$ /Ag/ $AgCl/Cl^-$ system in order to extract sodium and chloride ions from feed water, referred therein as a "*desalination battery*" (reported by Ref. [11]). It was shown that a desalination battery may have some significant advantages over the conventional desalination process, Capacitive Deionization CDI [12,13], such as a higher salt adsorption capacity (SAC), and a lower self-discharge. Another interesting utilization for the $Na_2Mn_5O_{10}/Ag/AgCl/Cl^-$ system, as reported by Mantia et al. [14], is to extract energy from salinity differences, known as the "*mixing entropy battery*".

The idea of thermal energy conversion (from low-grade waste heat sources) to electricity by exploring the thermodynamic cycle, using an electrochemical system, as in thermomechanical engines, was recently reported by Lee et al. [15]. In this cycle, referred to as a thermally regenerative electrochemical cycle (TREC), the negative electrode has the characteristics of obtaining a positive shift in potential during heat absorption, whereas the positive electrode exhibits the opposite behavior. In general, the cycle comprises four processes: in the first process, the cell, initially held at low temperature at a certain voltage (usually open circuit voltage (OCV)), is heated, such that the entropy of the system increases. After the heat absorption process, the cell is charged by means of an external power supply. In the third process, the cell is disconnected and cooled to lower temperature (the entropy of the system decreases), and in the final process, the cell is discharged at a higher voltage through the external power supply. Because the charging voltage is lower than the discharging voltage, work can be extracted. The process is illustrated in Fig. 1 on a T-S diagram. Considering the Gibbs free energy, the net energy that can be obtained from the cycle is the difference between the free energy at high temperature, namely,

$\Delta G_H = \Delta H_H - T_H \Delta S_H$, and the free energy at low temperature, $\Delta G_L = \Delta H_L - T_L \Delta S_L$. Assuming that the heat absorbed and the heat released are the same, the area enclosed in the cycle is the net work.

The most crucial factor in such systems is the temperature coefficient, which is defined as the temperature dependence of the electrode potential, namely $\partial E/\partial T$, and is related to the change in partial molar entropy. For half-cell reaction A + ne$^-$ → B:

$$\alpha = \frac{\Delta S_{A,B}}{nF} \tag{1}$$

Where n is the number of electrons transferred in the reaction, F is Faraday's constant, and $\Delta S_{A,B}$ is the partial molar entropy change for the half-cell reaction in the isothermal condition.

Nevertheless, we should consider energy losses in electrochemical systems, which are mostly attributed to polarization effects during cell charging (or discharging). The energy losses can be higher than the energy that can be harvested from the conversion of the waste heat to energy. Therefore, electrodes with low polarization should be adopted. Alternatively, the charge-discharge C-rates may be compromised at the expense of the power density in such systems.

In cooling towers, there is a consistent need for water treatment, resulting in a sustainable source for waste heat (the industrial machinery, for instance). This waste heat is, in fact, carried by the recirculating water that comes out of the cooling tower, and is dissipated through evaporation. Alternatively, the heat that is carried by the recirculating water can be exploited. In this work, we aim at demonstrating the concept of a desalination system such as $Na_4Mn_9O_{18}//Ag/AgCl/Cl^-$, which is also utilized, in certain conditions, for the conversion of thermal energy.

2. Experimental

2.1. Synthesis of crystalline $Na_4Mn_9O_{18}$

The synthesis of manganese sodium oxide was similar to the procedure described by Lee et al. [16]. The sodium manganese oxide was synthesized using a solid-state reaction. Mn_2O_3 was ball-milled with Na_2CO_3 at a molar ratio of 0.484:1 (Na_2CO_3:Mn_2O_3) (all materials were obtained from Sigma Aldrich). The mixture was then heated at 500 °C for five hours under air conditioning, and the product was ball-milled again and heated at 800 °C for one hour under air.

2.2. Electrode preparations

Polytetrafluoroethylene (PTFE), carbon black, and the sodium manganese oxide were mixed, in a weight ratio of 7:7:86 in NMP (*N*-Methyl-2-pyrrolidinone) to obtain a slurry mixture (all materials were obtained from Sigma Aldrich). The mixture was then spray-coated onto a graphite foil (Graftech), which was placed on a plate at constant temperature of 120 °C. The thickness of the electrode was 100 μm (the electrode is shown in Fig. 2a). The $Ag/AgCl/Cl^-$ electrode was made of a silver mesh that was deeply anodized in a 0.1 M HCl solution to yield a thick AgCl layer. The charge stored in the AgCl layer was equivalent to more than twice the charge stored in the positive electrode.

2.3. Cell structure

The cell is defined as a "flow-through" battery, where the solution is forced to flow onto the electrodes. The cell components are enclosed between top and bottom polyvinyl chloride covers with distributors to ensure the homogeneous flow of the solution throughout the whole circular cross section of the cell. Glassy papers serve as separators, and a sealing gasket is formed by soaking silicon glue into the rims of the separator. A PTFE ring spacer forming a 1 mm gap is placed between the electrode and the separator. Flexible impermeable graphite papers with crescent-shaped slits serve as current collectors, to ensure the flow
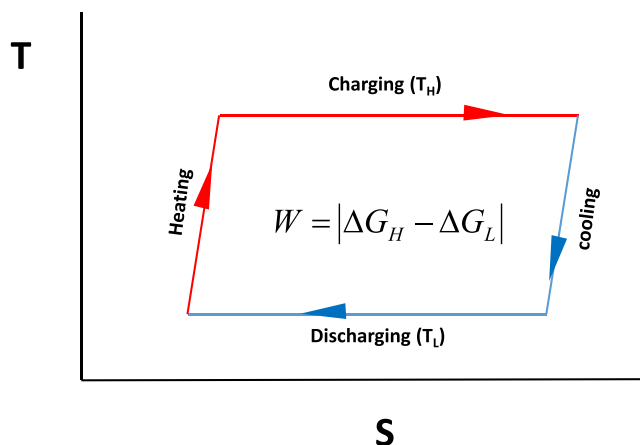

Fig. 1. Temperature–entropy (T–S) diagram for the thermal energy to electrical energy conversion process.

$$W = \left| \Delta G_H - \Delta G_L \right|$$