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Improved electrical power production of thermally regenerative batteries using a poly(phenylene oxide) based anion exchange membrane

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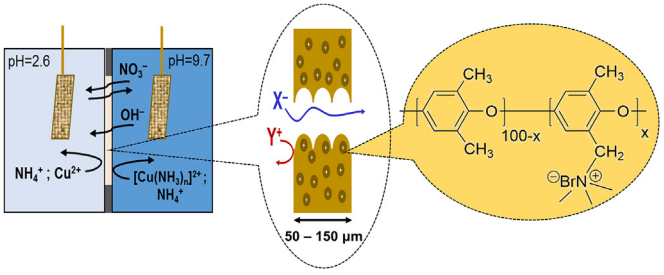
HIGHLIGHTS

- A battery based on ammonia and copper salts was used to produce electricity.
- Quaternary ammonium-based poly(-phenylene oxide) membranes were tested.
- The synthesized membranes had different ion exchange capacities and thicknesses.
- The power density of the BTMA membrane (40% DF, 50 μm thick) was 106 ± 7 W m^{-2}.
- Energy recovery was estimated to reach 7.0% relative to the Carnot efficiency.

GRAPHICAL ABSTRACT



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ABSTRACT

Thermally regenerative ammonia-based batteries (TRABs) can be used to harvest low-grade waste heat as electrical power. To improve TRAB performance, a series of benzyltrimethyl quaternary ammonium-functionalized poly(phenylene oxide) anion exchange membranes (BTMA-AEMs) were examined for their impact on performance relative to a commercial AEM (Selemion AMV). The synthesized AEMs had different degrees of functionalization (DF; 25% and 40%), and thicknesses (50, 100 and 150 μm). Power and energy densities were shown to be a function of both DF and membrane thickness. The power density of TRAB increased by 31% using a BTMA-AEM (40% DF, 50 μm thick; 106 ± 7 W m^{-2}) compared to the Selemion (81 ± 5 W m^{-2}). Moreover, the energy density increased by 13% when using a BTMA-based membrane (25% DF, 150 μm thick; 350 Wh m^{-3}) compared to the Selemion membrane (311 Wh m^{-3}). The thermal-electric conversion efficiency improved to 0.97% with the new membrane compared to 0.86% for the Selemion. This energy recovery was 7.0% relative to the Carnot efficiency, which was 1.8

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times greater than the highest previously reported value of a system used to capture low-grade waste heat as electricity.

1. Introduction

A significant amount of low-grade waste heat (temperature < 130 °C), approximately half of the current U.S.A energy demand (2.9×10^{13} kWh in 2013), is generated at industrial plants in the U.S. [1–4]. In recent years, harvesting low-grade waste heat as electrical power has drawn increasing attention due to its vast potential and availability often at locations where electrical power is needed [5–8]. One method of direct waste-heat-to-electricity energy conversion is solid-state thermoelectrics based on p- and n-type semiconductor materials [9–11], but high costs, long-term unreliability, and lack of capacity for energy storage have limited applications of these technologies [11]. Liquid-based thermoelectrochemical cells (TECs) that utilize the temperature dependence of electrochemical redox potentials to drive an electrochemical cell offer an alternative, potentially less expensive and scalable system for direct thermal-electric energy conversion, with opportunities for energy storage [12–14]. While a considerable amount of progress has been achieved during recent years in developing new types of TECs, their power densities and thermal-electricity energy conversion efficiencies need to be improved to make them commercially viable [15].

A thermally regenerative ammonia battery (TRAB) was recently developed as a new approach to harvest low-grade waste heat as electrical power that improved power densities compared to existing TECs [16]. In a TRAB, two copper electrodes are exposed to a copper(II) electrolyte, such as copper(II) nitrate. The two electrode chambers are separated by a membrane, as discussed below. Electrical power is produced by adding ammonia to the anolyte, but not to the catholyte (Fig. S1a). The ammonia complexes copper(II) and generates a potential difference between the electrodes according to the following reactions:

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}\ ;\ E^0 = +0.340\ V \quad (1)$$

$$Cu_{(s)} + 4NH_{3\ (aq)} \rightarrow CU(NH_3)^{2+}_{4\ (aq)} + 2e^-;\ E^0 = -0.04\ V \quad (2)$$

where E^0 is the standard reduction potential vs. the standard hydrogen electrode (SHE) [17]. After discharging the cell (Fig. S1b), ammonia is separated from the anolyte using conventional separation technologies, such as distillation, that utilize low-grade waste heat (Fig. S1c) [18,19]. The distilled ammonia is then added to the other electrolyte chamber for the next discharge cycle (Fig. S1d). By switching the compartment that contains ammonia, copper is re-deposited onto the formerly dissolved electrode, and the other electrode dissolves (Fig. S1e). This alternating cycle of electrode dissolution/deposition allows the Cu electrodes to be maintained in closed-loop cycles, and waste heat energy is converted to electricity through ammonia distillation (Fig. S2). A maximum power density of 80 W m^{-2}-electrode area with a thermal-electricity conversion efficiency of 0.86% (6.2% relative to the Carnot efficiency), has been achieved using a TRAB containing a commercial anion exchange membrane (AEM) [16,19,20].

In a TRAB, an AEM is used to separate the cathode and anode compartments and facilitate ion conduction to balance the internal charge transfer through transport of anions such as nitrate and hydroxide between the electrolyte chambers. In addition, the AEM minimizes self-discharge by reducing the transfer of either ammonia or positively-charged copper(II) amine complexes from the anolyte to the catholyte, and copper(II) ions from the catholyte to the anolyte (Fig. 1a). However, the transfer of hydroxide from the alkaline anode chamber (pH = 9.7) to the acidic cathode chamber (pH = 2.6) results in a shift in the NH_4^+/NH_3 acid/base equilibrium towards NH_3 formation in the cathode chamber (Eq. S(1)). This formation of NH_3 in the cathode chamber results in an unfavorable chemical consumption (Eqs. S2–S5) instead of electrochemical consumption of copper ions (Eq. (1); Fig. 1b). In previous TRAB tests using a commercial AEM (Selemion AMV), substantial self-discharge occurred that limited the electrical energy production [16,20]. In addition, in our recent study on copper removal from water using an adaption of a TRAB, it was shown that the cell self-discharge limited the effectiveness of copper removal at low initial concentrations of copper in the catholyte (<0.01 M) [21].

Here, we hypothesized that by varying the AEM's thickness and ion exchange capacity (IEC), we could reduce cell self-discharge and

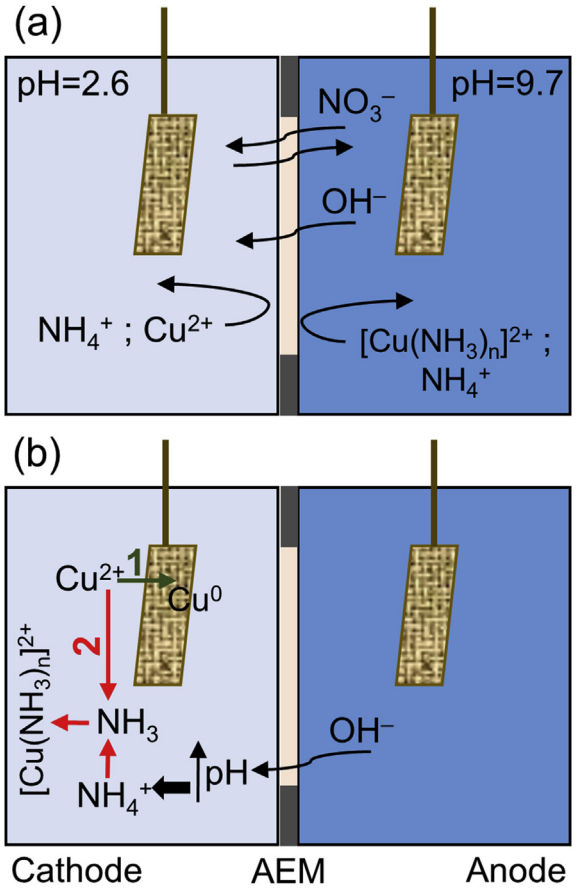

Fig. 1. Schematic of the TRAB with an anion exchange membrane (AEM): (a) AEM prevents transfer of both NH_3 and positively charged species, (b) higher transfer of OH^- through the membrane causes a higher rate of TRAB self-discharge by chemical consumption of copper ions (reaction 2; $Cu^{2+} + n\ NH_3 \rightarrow Cu(NH_3)^{2+}_n$).