



A thermally regenerative ammonia battery with carbon-silver electrodes for converting low-grade waste heat to electricity



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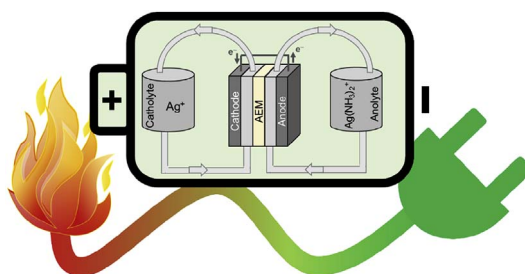
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HIGHLIGHTS

- A battery based on a ligand and silver salts was developed to produce electricity.
- Carbon paper or cloth loaded with silver particles were used as the electrode.
- Silver battery showed a higher performance compared to copper battery.
- The power density of silver battery was enhanced by up to 64%.
- The silver battery produced a stable power over a hundred charge/discharge cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

Thermally regenerative ammonia batteries (TRABs) have shown great promise as a method to convert low-grade waste heat into electrical power, with power densities an order of magnitude higher than other approaches. However, previous TRABs based on copper electrodes suffered from unbalanced anode dissolution and cathode deposition rates during discharging cycles, limiting practical applications. To produce a TRAB with stable and reversible electrode reactions over many cycles, inert carbon electrodes were used with silver salts. In continuous flow tests, power production was stable over 100 discharging cycles, demonstrating excellent reversibility. Power densities were 23 W m^{-2} -electrode area in batch tests, which was 64% higher than that produced in parallel tests using copper electrodes, and 30 W m^{-2} (net energy density of 490 Wh m^{-3} -anolyte) in continuous flow tests. While this battery requires the use a precious metal, an initial economic analysis of the system showed that the cost of the materials relative to energy production was \$220 per MWh, which is competitive with energy production from other non-fossil fuel sources. A substantial reduction in costs could be obtained by developing less expensive anion exchange membranes.

1. Introduction

Low-grade waste heat (temperature $< 130 \text{ }^\circ\text{C}$) generated by industrial plants and geothermal and solar-based systems is estimated to be major sustainable energy source for the future [1–3]. Low-grade waste heat generated at industrial plants in U.S.A contains

approximately half of the current energy demand of this country ($2.9 \times 10^{13} \text{ kWh}$ in 2013) [4], and recovering even a fraction of this energy would be a major step towards developing a more sustainable energy infrastructure [5–9]. Technologies to convert low-grade waste heat to electricity must produce high power densities and be efficient, scalable, and cost-effective [1,10], but so far no approach has met all

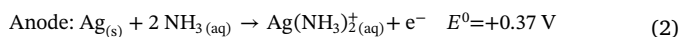
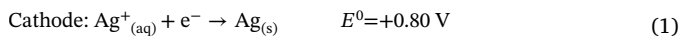
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these goals. For example, solid-state thermoelectric devices based on p- and n-type semiconductor materials have high material costs, lack the capacity for energy storage, and have relatively low power densities [1,11,12]. Liquid-based thermoelectrochemical cells (TECs) could potentially provide a more cost effective and scalable approach, but power densities have generally been in the range of only 0.5–6.6 W m⁻² [13–15]. One TEC produced 12 W m⁻², with an inter-electrode temperature difference of 81 °C, but the efficiency relative to the Carnot cycle was only 0.4% [16], which was low compared to other approaches (efficiencies of 1.4–4.0%) [13–15]. As a result of these relatively low power densities and thermal-electrical inefficiencies, solid state and TECs have not yet been commercialized [17].

Recently, a new approach for converting low-grade waste heat to electricity, called a thermally regenerative ammonia battery (TRAB), was shown to produce significantly higher power densities than TECs or other approaches [18]. A flow TRAB with copper electrodes and salts produced a maximum power density of ~25 W m⁻² (normalized to a single electrode area), with an estimated Carnot thermal-electrical conversion efficiency of 5% [19]. TRABs generate electrical power from electrochemical potentials produced by adding a ligand to one electrolyte chamber, with the two chambers separated by a membrane. The first TRAB used copper mesh electrodes and a copper nitrate electrolyte (Cu-TRAB), with ammonia as the ligand [18]. When ammonia is added to one electrolyte chamber it becomes the anode chamber, due to formation of a copper ammine complex. When the potential difference between the electrodes is discharged, the anode undergoes oxidative dissolution, and aqueous copper ions are reductively deposited on the cathode (Eqn. S1, S2). After discharging, the ammonia is separated from the anolyte using conventional separation technologies, such as distillation or air stripping, using low-grade waste heat [18,20]. The separated ammonia is then added to the former cathode chamber, so that the function of the chambers is switched, ideally achieving a closed-loop cycle with no net loss of copper from the electrode. In order to provide stable operation over many cycles, metal deposition on the cathode must be balanced with metal removal in the next cycle. However, the conversion of the copper anode into current in the Cu-TRAB was only 35% (i.e., approximately three times as much copper dissolves from the electrode as would be expected) [18–20]. This irreversible loss of copper from the anode limited the number of possible cycles using this copper and ammonia-ligand system. The use of an alternative ligand (ethylenediamine) reduced, but did not eliminate, irreversible losses of copper from the anode [21].

A new type of TRAB was developed here based on using carbon electrodes and solutions containing dissolved silver to avoid losses of the metal to reaction with the electrolyte and enable fully reversible charging cycles. The open circuit voltage using silver (0.45 V) is very similar to that of copper (0.44 V), but the anode and cathode potentials are much more positive than those for copper, with half-cell reactions of:



where E^0 is the standard reduction potential (vs. SHE) [22]. For copper, the cathode E^0 value is +0.34 V and the anode E^0 value is -0.04 V vs. SHE (Eqn. S1, S2) [23]. To demonstrate the feasibility of silver-based TRAB (Ag-TRAB), power production was examined in single cycle tests (fed batch conditions) using silver nitrate solutions and carbon paper electrodes, and compared to power generated using a Cu-TRAB containing copper mesh electrodes and a copper nitrate solution. Power production was then examined in a continuous flow system with carbon paper or carbon cloth anodes, with the reversibility and stability of the carbon cloth electrodes studied by cycling the battery one hundred times. The morphology of the silver electrodeposited on the carbon electrodes was examined using a scanning electron microscope (SEM), and the cost of electricity produced was evaluated on the basis of the

cost of the materials used in the continuous flow system.

2. Materials and methods

2.1. Silver electrodeposited electrode preparation and characterization

Commercially available carbon cloth and paper (AvCarb Material Solutions) were treated to improve surface hydrophilicity and reaction with silver, by soaking overnight at room temperature in a mixed solution of concentrated sulfuric and nitric acids (v:v = 3:1) [24,25]. The materials were then thoroughly rinsed and then stored in DI water prior to use. Silver was electrodeposited onto the carbon electrodes (cloth or paper) in a cubic reactor (4 cm long and 3 cm in diameter) with platinum mesh (AMETEK Inc.) as the counter electrode. The electrolyte was mixed using a magnetic stirrer (6.4 × 15.9 mm; VWR) at 500 rpm. A current density of 7 mA cm⁻² was applied for 60 min to deposit silver onto the carbon electrodes. Based on the amount of silver deposited on the carbon materials (calculated by measuring the weight of the substrate before and after the electrodeposition), the coulombic efficiencies were > 90% for silver deposition ($\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}^0$) (Table S1). The electrolyte was 0.1 M AgNO₃ with a 5 M NH₄NO₃.

Silver deposited electrodes were examined using scanning electron microscopy (SEM; NanoSEM 630, FEI, Hillsboro, OR) to observe the morphology and size of the silver particles. Energy-dispersive X-ray spectra (EDS; NanoSEM 630, FEI, Hillsboro, OR) were used to identify composition of the particles formed on the carbon substrate.

2.2. TRAB construction and operation

Power densities and anodic coulombic efficiencies of the Ag-TRAB were first evaluated in a fixed volume battery (no flow conditions) that had sufficient room for reference electrodes to monitor electrode potentials, constructed as previously described [23,26]. Briefly, the cell consisted of a cathode and an anode chamber, each 4 cm long and 3 cm in diameter, separated by an anion exchange membrane (AEM; Selemion AMV, Asahi Glass, Japan), producing an electrode area per volume of reactor of 25 m² m⁻³. Two silver electrodeposited carbon papers were used as the electrodes, with each electrode placed at the end of the reactor. To monitor the electrode potentials, two Ag/AgCl reference electrodes (+0.211 V vs. SHE; RE-5B; BASi) were inserted 1 cm away from each electrode (Fig. S1). The power production and coulombic efficiency of Ag-TRAB were also compared to those of the Cu-TRAB. The same reactor configuration was used for the Cu-TRAB but the electrodes were copper mesh (50 × 50 mesh; McMaster-Carr, OH), consistent with previous tests [21,23].

The remaining tests were conducted using a compact, custom-built flow cell with a design similar to our previous tests [27,28]. The flow cell consisted of two thin circular channels (diameter = 3 cm; thickness = ~100 μm) separated by an AEM that were fed with either the electrolyte containing ammonia (anolyte) or plain electrolyte, with an electrode packing density of 10,000 m² m⁻³. The electrodeposited silver-carbon electrodes were placed in each channel, and graphite foil behind the electrodes was used as a current collector. The symmetrical cell was sealed using two end plates (Fig. 1).

The electrolytes were prepared using 0.1 M of either AgNO₃ (Sigma-Aldrich; Ag-TRAB) or Cu(NO₃)₂ (Sigma-Aldrich; Cu-TRAB) with 5 M NH₄NO₃ as the supporting electrolyte to increase conductivity. Ammonium hydroxide (2 M final concentration; 5 N solution, Sigma-Aldrich) was added only to one chamber (anolyte) to form the metal ammonia complex and create a potential difference between the anode and cathode chambers. The electrolyte composition was chosen based on the optimum values previously reported [18].

2.3. Cell performance evaluation

Polarization tests were performed using a potentiostat (model

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