Electrical power production from low-grade waste heat using a thermally regenerative ethylenediamine battery

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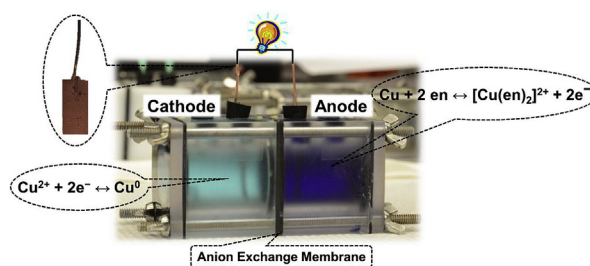[b] Dipartimento dell'Innovazione Industriale e Digitale, Ingegneria Chimica, Gestionale, Informatica, Meccanica, Università degli Studi di Palermo, Viale delle Scienze, 90128, Palermo, Italy
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HIGHLIGHTS

- A battery based on a ligand and copper salts was developed to produce electricity.
- Ethylenediamine as the ligand showed a higher performance than ammonia.
- The ethylenediamine battery produced higher power 68% than an ammonia battery.
- The energy production was 1.5 times higher than ammonia.
- Anodic coulombic efficiency improved to 80% for the ethylenediamine battery.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Thermally regenerative ammonia-based batteries (TRABs) have been developed to harvest low-grade waste heat as electricity. To improve the power production and anodic coulombic efficiency, the use of ethylenediamine as an alternative ligand to ammonia was explored here. The power density of the ethylenediamine-based battery (TRENB) was 85 ± 3 W m^{-2}-electrode area with 2 M ethylenediamine, and 119 ± 4 W m^{-2} with 3 M ethylenediamine. This power density was 68% higher than that of TRAB. The energy density was 478 Wh m^{-3}-anolyte, which was ~50% higher than that produced by TRAB. The anodic coulombic efficiency of the TRENB was $77 \pm 2\%$, which was more than twice that obtained using ammonia in a TRAB (35%). The higher anodic efficiency reduced the difference between the anode dissolution and cathode deposition rates, resulting in a process more suitable for closed loop operation. The thermal-electric efficiency based on ethylenediamine separation using waste heat was estimated to be 0.52%, which was lower than that of TRAB (0.86%), mainly due to the more complex separation process. However, this energy recovery could likely be improved through optimization of the ethylenediamine separation process.
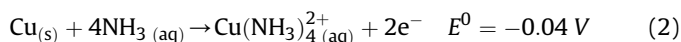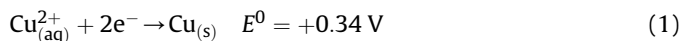
1. Introduction

A vast amount of low-grade thermal energy (temperature < 130 °C) is available globally at industrial plants and

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from solar and geothermal sources [1–3]. Converting this low-grade heat into electrical power has drawn increasing attention due to its wide availability and energy potential [4–8]. Different types of thermoelectrochemical systems (TESs) are being investigated to convert low-grade waste heat to electrical power [9–12]. Most of the reported TESs rely on using a chemical that has temperature-dependent reduction and/or oxidation potentials in aqueous solutions, but the performance of these TESs needs to be improved in terms of electrical power densities and thermal-electric conversion efficiencies [11,13]. For example, a maximum power density of 1.5 W m^{-2}-electrode area with a Carnot efficiency of 1.4% was achieved in a TES operated with a ferrocyanide/ferri-cyanide redox solution and carbon nanotube electrodes when operated with a temperature difference of 60 °C [14]. The power density was increased to 6.6 W m^{-2}-electrode area (Carnot efficiency of 3.95%) using carbon nanotube aerogel sheets with a 51 °C temperature difference, but this required the use of platinum [15]. Even though this system could be viable due to the relatively high Carnot efficiencies [16], the systems still has a relatively low power density and it required the use of a precious metal.

An alternative approach to convert waste heat to electricity, called a thermally regenerative battery (TRB) based on using ammonia (TRAB), was recently shown to be capable of producing a significantly higher power density of ~80 W m^{-2}-electrode area, with a Carnot thermal-electric conversion efficiency (6.2%) that was greater than previous systems [17]. Unlike TESs which rely on reversible redox couples, TRBs operate using chemical potentials obtained by adding ligands into a metal salt solution [17–19]. In a TRAB, copper ammine complexes are produced when ammonia is used as the ligand in the anolyte, but not in the catholyte. Copper reduction occurs at the cathode while copper oxidation proceeds on the anode immersed in the ammonia ligand solution, according to:

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \quad E^0 = +0.34 \, V \tag{1}$$

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

where E^0 is the standard reduction potential (vs. a standard hydrogen electrode, SHE) [20]. After discharging the electrical power, the ammonia is separated from the anolyte using conventional technologies such as distillation and low-grade waste heat. The extracted ammonia is then added to the other chamber so that the former anode electrode functions as the cathode for the next discharge cycle (Fig. S1). This alternating cycle of electrode disso-lution/deposition allows the Cu electrodes to be operated in closed-loop cycles as long as the mass lost and gained on the electrodes is balanced in each cycle. While the cathodic deposition of copper is efficiently regained from the current (i.e., the increase in mass of the electrode is equal to the expected value based on the number of electrons transferred), the conversion of anode copper into current of TRABs is only 35% (i.e., approximately three times as much copper dissolves from the electrode as would be predicted based on the numbers of electrons transferred) [17–19]. This low conversion of anode copper into current (i.e., anodic columbic efficiency, ACE) of TRAB would limit its use in closed-loop cycles as there would be a net loss of anode copper into solution for each cycle, eventually requiring the electrodes to be replaced.

The use of ethylenediamine as an alternative ligand to ammonia was explored here as a method to increase the power production as well as improve ACE. In theory, the anode open circuit potential of a TRB can be improved by using a ligand in which the complexation reaction (Cu + n L → [Cu(L)$_n$]$^{2+}$ + 2e$^-$; L: ligand) has a higher standard reduction potential than the copper ammonia complex

(Eq. (2); −0.04 V). For the complexation reaction of copper and ethylenediamine (en), the anode standard reduction potential is −0.12 V, as [21]:

$$Cu_{(s)} + 2en_{(l)} \rightarrow Cu(en)^{2+}_{2 \, (aq)} + 2e^- \quad E^0 = -0.12 \, V \tag{3}$$
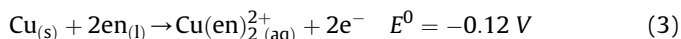
The performance of a thermally regenerative ethylenediamine-based battery (TRENB) was examined in terms of power and energy densities, electrode coulombic efficiencies and compared to that of the previously developed ammonia-based system using copper electrodes and copper nitrate electrolytes.

2. Materials and methods

2.1. TRB construction and operation

The cells used for all tests were constructed as previously described for TRABs [17,22]. The cells 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, Asashi Glass, Japan) with a projected surface area of 7 cm^2. Two 0.8 ± 0.05 cm $\times$ 2 ± 0.05 cm pieces of copper mesh (50×50 mesh; McMaster-Carr, OH) connected by copper wire were used as the electrodes, with each electrode placed 1 cm from the membrane (Fig. S2). 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 (2 cm away from the membrane). To facilitate the mass transfer of ions to the electrode, the catholyte was mixed using a magnetic stirrer (6.4×15.9 mm; VWR) at 600 rpm [17].

The electrolytes were prepared by dissolving 0.1 M of Cu(NO$_3$)$_2$ (Sigma-Aldrich) in deionized water with 5 M NH$_4$NO$_3$ as the sup-porting electrolyte to increase conductivity. Either ammonium hydroxide (for TRAB; 2 M final concentration; 5 N solution, Sigma-Aldrich) or ethylenediamine (for TRENB; ReagentPlus$^{\circledR}$, $\geq$99%, Sigma-Aldrich) was added only to the anolyte to form the copper complex and create the potential difference between the cathode and anode chambers.

2.2. TRB performance evaluation

Polarization tests were performed using a potentiostat (model 1470E, Solatron Analytical, Hampshire, England) to measure the cell voltage (U) and each electrode potential at room temperature (~23 °C). External resistances were switched every 4 min from open circuit to a minimum of 1.4 Ω. Both current density ($i=U/RA$, A m^{-2}; i: current density, U: voltage, R: external resistance, A: surface area), and power density ($P=U^2/RA$, W m^{-2}) were normalized to a single electrode projected surface area (1.6 cm^2) [23]. The total charge transferred over the entire cycle was calculated by integrating the current−time profile $Q = \int I \, dt_s$, where Q is the total charge (C), I the current (A), and t_s time (s). The energy density, normalized to the total electrolyte volume (E, Wh m^{-3}), was calculated as $E = \int U I \, dt_h/V$, where U is the voltage (V), I the current (A), t_h the cycle time (h), and V the total volume (2×28 mL).

The discharging energy efficiency (η_d) was calculated as the ratio between actual energy density produced in the experiments and the theoretical energy density stored in the solutions. The theoretical energy density was calculated using the equation $\Delta G=nFE$, where F is Faraday's constant (96485 C mol^{-1}) and E the measured open-circuit potential (V). The ΔG calculated for TRENB was 110 kJ mol^{-1}, while that of TRAB with the same concentration of ligand (2 M) was 89 kJ mol^{-1}. The ΔG of TRENB further enhanced by increasing the ligand concentration to 116 kJ mol^{-1} (3 M) and 124 kJ mol^{-1} (4.5 M). Thermal energy efficiency (η_t) was calculated as the ratio between the actual energy density produced and the