Showcasing a study on a Cu/Zn bimetallic thermally regenerative ammonia-based battery (Cu/Zn-TRAB) for harvesting low-grade thermal energy by Dr Weiguang Wang and Prof. Hua Tian and Gequn Shu at Tianjin University.

A bimetallic thermally regenerative ammonia-based battery for high power density and efficiently harvesting low-grade thermal energy

Bimetallic thermally regenerative ammonia-based batteries (B-TRABs), using different metals (such as Cu, Zn, Ag, Co and Ni) that can form complexes with ammonia, efficiently convert low-grade thermal energy into electricity with high power density, realizing high-voltage discharge and low-voltage charge at room temperature.

As featured in:
A bimetallic thermally regenerative ammonia-based battery for high power density and efficiently harvesting low-grade thermal energy†

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A bimetallic thermally regenerative ammonia-based battery (B-TRAB) using inexpensive materials efficiently converts low-grade thermal energy into electricity with high power density. Through thermal regeneration of the anolyte, the B-TRAB system realized high-voltage discharge (1.38 V) with redox couples [Cu(II)/Cu and Zn(NH3)42+/Zn] and low-voltage charge (0.72 V) with Zn(II)/Zn and Cu(NH3)42+/Cu. Adding 2 M NH3 to the anolyte of a Cu/Zn-TRAB produced a peak discharge power density of 525 W m⁻²-electrode (120 W m⁻²-membrane), and the voltage (or current) and peak power could be doubled by connecting two cells in series (or parallel). In successive regeneration cycles, a maximum power density of 115 W m⁻²-electrode (26 W m⁻²-membrane) and a net energy density of 714 Wh m⁻³ were produced at a constant current density of 100 A m⁻². The power density was enhanced to 515 W m⁻²-electrode (118 W m⁻²-membrane) and maintained in successive cycles by adding acid to the regenerated catholytes, with a net energy density of 299 Wh m⁻³ (discharged at a constant load of 12 Ω and charged at a constant current density of 100 A m⁻²). A thermal-electricity conversion efficiency of 0.95% (10.7% relative to the Carnot efficiency) was achieved.

Introduction

A tremendous amount of low-grade thermal energy globally exists in various industrial processes, the environment, and solar thermal and geothermal sources.1–3 Residual heat generated from power plants and industry amounts to more than 8000 TW h per year in the US alone, and it is estimated that more than 50% of this energy is low-grade waste heat due to process inefficiency.4,5 In the UK, significant economic benefits with low-grade waste heat (up to 14 TW h) recovery reach £100s of millions per annum and simultaneously reduce the greenhouse gas up to 100s of ktCO₂ per year.6 China is the largest energy consumer and CO₂ emitter in the world, and the waste heat produced by primary energy sectors is estimated to range from 15% to 40% of the total fuel input, and the low-grade waste heat potential of cement, ironmaking and glass sectors is about 197 TW h in 2012.7

Despite the abundance of low-grade heat, it is generally difficult to extract energy efficiently from potential sources due to both the distributed nature and the small available temperature difference of these heat sources. High power production, scalability, high efficiency and low cost must be considered for thermal-to-electricity conversion technologies.8,9 The solid-state thermoelectric generator (TEG) and organic Rankine cycle (ORC) have been actively pursued for utilizing low-grade heat but face their own challenges of inefficiency, expensive material and/or operational costs, low power density, inability to store energy, and a relatively complex system.8,9,11 New liquid-based thermoelectrically converted batteries or systems may be more effective than previous methods for harvesting low-grade thermal energy. Among these new technologies, thermally regenerative electrochemical cycles (TRECs),12 thermally regenerative ammonia-based batteries (TRABs)13 and thermo-osmotic energy conversion (TOEC) systems14 are the most promising mainly owing to their high power densities and thermal-to-electricity conversion efficiencies. Specifically, TRECs achieve the highest thermal-to-electricity energy conversion efficiency of \( \eta_t = 0.52–5.7% \) with a temperature difference of 30 °C,12,13,16 and TOEC systems also have a higher efficiency of \( \eta_t < 4.1% \).17 However, these two technologies failed to produce a higher power density (a power density of 0.5 W m⁻² estimated between 10 and 80 °C by a TREC12 and TOECs14,18 generated a power density of <3.5 W m⁻²). Except for efficiency, the power density is also a critical index to evaluate the
conversion of low-grade thermal energy to electricity.\textsuperscript{5,19} The highest power density $P = 12$ W m\textsuperscript{-2} of thermo-electrochemical cells (TECs) was obtained by using optimized electrolyte and electrode materials, but with a lower Carnot-relative efficiency of $\eta_{DC} = 0.4%.\textsuperscript{20}$ TRABs have produced significantly higher power densities (80–120 W m\textsuperscript{-2}-electrode area) than the past technologies, with a thermal efficiency of $\eta_{DC} = 3.1–7%.\textsuperscript{12,21-23}$ Based on the above analyses of efficiency and power generation, the TRAB approach may have better practical application possibilities and value, but the voltage and power density of TRABs are still relatively low, and further improvements and developments are necessary.

Considering the lower power density of TREC\textsuperscript{s} and TOEC\textsuperscript{s} systems and the lower voltage of previous TRABs, here we report a bimetallic thermally regenerative ammonia-based battery (B-TRAB), achieving high-voltage discharge and low-voltage charge at the same temperature. The power density is significantly improved due to a large redox potential difference in the discharge process, and thermal energy was used to regenerate the anolyte and shift the redox couples to a low potential for charging, and then net energy was produced. In a B-TRAB, the electrodes are made of two different metals that can form ammine complexes, and the metal M\textsubscript{1} (such as zinc) that has a more negative redox potential of $M\textsubscript{1}(\text{NH}_3)_{2}\text{sq}^{+/M\textsubscript{1}}$ is the negative electrode and the metal M\textsubscript{2} (such as copper) that has a more positive redox potential of $M\textsubscript{2}\text{sq}^{+/M\textsubscript{2}}$ is the positive electrode (Fig. 1A). A closed-loop battery cycle consists of a discharge process, a charge process and two thermal regeneration processes (Fig. 1B). During the discharge, the Zn was oxidized to Zn(\text{NH}_3)\textsubscript{4}^{2+} with ammonia in the anode and the Cu\textsuperscript{2+} was reduced to Cu in the cathode, realizing high voltage discharge, as shown by the electrode reactions:\textsuperscript{24}

Cathode: Cu\textsuperscript{2+} (aq) + 2e\textsuperscript{-} $\rightarrow$ Cu (s) $E^0 = +0.34$ V

Anode: Zn (s) + 4 NH\textsubscript{3} (aq) $\rightarrow$ Zn(\text{NH}_3)\textsubscript{4}^{2+} (aq) + 2e\textsuperscript{-} $E^0 = -1.04$ V

After discharging, waste heat was used to regenerate the anolyte effluent in the distillation column for ammonia separation (Zn(\text{NH}_3)\textsubscript{4}^{2+} (aq) $\rightarrow$ Zn\textsuperscript{2+} (aq) + 4NH\textsubscript{3} (g)). This distilled ammonia was then passed into the spent catholyte, which made the spent cathode chamber the anode chamber. During the charge, the Cu was oxidized to Cu(\text{NH}_3)\textsubscript{4}^{2+} with ammonia in the anode and the Zn\textsuperscript{2+} was reduced to Zn in the cathode, realizing low voltage charge, as shown by the electrode reactions:\textsuperscript{24}

Cathode: Zn\textsuperscript{2+} (aq) + 2e\textsuperscript{-} $\rightarrow$ Zn (s) $E^0 = -0.76$ V

Anode: Cu (s) + 4 NH\textsubscript{3} (aq) $\rightarrow$ Cu(\text{NH}_3)\textsubscript{4}^{2+} (aq) + 2e\textsuperscript{-} $E^0 = -0.04$ V

Similarly, after charging, the anolyte was regenerated by waste heat (Cu(\text{NH}_3)\textsubscript{4}^{2+} (aq) $\rightarrow$ Cu\textsuperscript{2+} (aq) + 4NH\textsubscript{3} (g)) and then the distilled ammonia was passed into the spent catholyte, and the cathode and anode chambers were switched again. Deposition and corrosion reactions occur cyclically at the Zn and Cu electrodes during successive charge and discharge processes, so the electrode materials are not lost theoretically. Thermal energy in waste heat is saved in the distilled ammonia, which is used to shift the redox couples for charging at lower voltage and stored in the battery as chemical energy. When needed, this stored chemical energy can be converted into electric energy by discharging.

A variety of B-TRAB systems can be constructed using different metals (such as Cu, Zn, Ag, Co and Ni) that can form complexes with ammonia (Fig. 1A). For instance, the Ag/Zn-TRAB, Cu/Zn-TRAB, Ag/Cu-TRAB, Ni/Co-TRAB, and the like also belong to the category of B-TRAB. Although the B-TRAB requires external electricity for charging compared to the previous single metallic TRAB,\textsuperscript{13} the charging voltage is much lower than the discharging voltage and this voltage difference is higher than the highest cell voltage of the single metallic TRAB (0.45 V for the Ag-TRAB\textsuperscript{13}). Here, we present a cost-effective and high-performance Cu/Zn-TRAB for harvesting low-grade thermal energy by employing solid copper as the positive electrode and solid zinc as the negative electrode in an aqueous electrolyte (Fig. 1B). In this work, we mainly concentrated on the discharge and charge processes of the Cu/Zn-TRAB. The experimental results illustrated that the Cu/Zn-TRAB system had good scalability and energy output performance, and produced the highest power density among the existing liquid-based thermal-electrical conversion technologies.

Results and discussion

**Charge and discharge characteristics**

Except for thermal regeneration, the B-TRABs need to be charged, which is different from the single metallic TRAB. The charge and discharge characteristics of the Cu/Zn-TRAB were examined using fresh electrolytes instead of the regenerated electrolytes in this section. The combination of a high concentration of ZnSO\textsubscript{4} and (NH\textsubscript{3})\textsubscript{2}SO\textsubscript{4} formed a double salt (NH\textsubscript{3})\textsubscript{2}Zn(SO\textsubscript{4})\textsubscript{2}, which had a relatively low solubility at room temperature and existed as a precipitate. The precipitate could also be dissolved to form the zinc ammonia complex after adding excessive ammonia. During the discharge, there was a peak power density (Fig. 2A). In the charging process, because the reduction potential of the hydrogen evolution reaction (2H\textsuperscript{+} + 2e\textsuperscript{-} $\rightarrow$ H\textsubscript{2}, $E^0 = 0$ V) is more positive than the potential of the cathode reaction ($Zn\textsuperscript{2+} + 2e\textsuperscript{-} \rightarrow$ Zn, $E^0 = -0.76$ V), theoretically, the hydrogen evolution reaction occurs preferentially in acidic solution. However, the actual overpotential of the hydrogen reduction is very high at the Zn electrode, so the deposition efficiency of Zn\textsuperscript{2+} in weakly acidic solutions is nearly 100%.\textsuperscript{36,37} The Cu/Zn-TRAB was charged at different current densities for 30 min, and the current efficiency was higher than 90% (94%, 100 A m\textsuperscript{-2}; 97%, 200 A m\textsuperscript{-2}; 98%, 400 A m\textsuperscript{-2}). Larger current densities were more conducive to higher current efficiency, but the SEM images of the zinc electrode showed that more and larger crystalline dendrites were generated during the zinc deposition at large currents (see Fig. S2†). The growing of the dendrites is the main cause for the limited performance of the zinc electrode. It also exists in other promising high-energy-
density batteries (such as zinc–air batteries) and is a major obstacle to improving cycle performance and application development. However, many meaningful studies on the enhancement of zinc electrode performance were presented. Circulation of electrolytes in a flow battery can greatly alleviate the formation of dendrites. Structural modification of electrode materials by electrodeposition and advanced casting (such as 3D electrode structures), and modification of components by additives or chemical doping have proven to be feasible solutions for improving the performance of the zinc electrodes.
addition, back-side-plating is a new method to avoid short circuits due to zinc dendrites,22,23 but some structural optimizations should be made for reducing extra added resistance.

The charging voltage was less than the discharging voltage when the current density was lower than 400 A m\(^{-2}\), and then the charging voltage increased rapidly with increasing current densities (Fig. 2A). This increase was mainly due to the fact that the cathode potential shifted negatively with growing current densities (Fig. 2B), indicating that some side reactions (Zn(OH)\(_2\) + 2e\(^-\) \rightarrow Zn + 2 OH\(^-\) or Zn(NH\(_3\))\(_4\)^{2+} + 2e\(^-\) \rightarrow Zn + 4NH\(_3\), \(E^{0} = -1.25\) V) may be appear as a result of increased pH near the Zn electrode. These results manifested that the metal zinc could be used as the negative electrode of B-TRABs for high battery voltage and power productions.

**Power production at different NH\(_3\) and Cu(II)/Zn(II) concentrations during discharge**

Power density is significant for thermoelectric conversion, because high power density (or large current outputs) means that the transfer and storage of the produced electrical energy are more efficient and convenient. Consequently, the performance of the Cu/Zn-TRAB was inspected with various NH\(_3\) and Cu(II)/Zn(II) concentrations in a 1 M (NH\(_4\))\(_2\)SO\(_4\) supporting electrolyte. When the anodic NH\(_3\) concentration increased from 1 M to 2 M (the actual concentration of ammonia is greater than this value (concentration of ammonium hydroxide)), the maximum power density was improved from 370 W m\(^{-2}\)-electrode (85 W m\(^{-2}\)-membrane) to 525 W m\(^{-2}\)-electrode (120 W m\(^{-2}\)-membrane, Fig. 3A), primarily owing to both the promotion of anode performance and the reduction of cathode overpotentials (Fig. 3B). The more negative anode potentials at increased NH\(_3\) concentrations (based on the Nernst equation, see eqn S(2))† (Fig. 3A and B). A slightly decreased power density of 478 W m\(^{-2}\)-electrode (109 W m\(^{-2}\)-membrane) was achieved by increasing the Cu(II)/Zn(II) concentration to 0.2 M (Fig. 3A and B), which reduced the cathode performance but the anode potentials were not evidently affected (Fig. 3B). Moreover, appropriately reducing the initial Zn(II) (namely Zn(NH\(_3\))\(_4\)^{2+}) concentration could slightly improve the power densities and a higher NH\(_3\) concentration was beneficial for using higher Cu(II) concentrations (see Fig. S3†), which were in accord with the simulation results obtained using a flow-electrochemical cell coupled model for a thermally regenerative ammonia-based flow battery (Cu-TRAFB).22

**Power production with a range of concentrations of the supporting electrolyte during discharge**

By changing the (NH\(_4\))\(_2\)SO\(_4\) concentration, the influence of the supporting electrolyte concentration was inspected with 0.1 M Cu(II)/Zn(II) and 2 M NH\(_3\). Increasing the (NH\(_4\))\(_2\)SO\(_4\) concentration from 0 to 2 M commonly promoted the maximum power density (53 W m\(^{-2}\)-electrode, 0 M; 340 W m\(^{-2}\)-electrode, 0.5 M; 525 W m\(^{-2}\)-electrode, 1 M; 558 W m\(^{-2}\)-electrode, 2 M) (Fig. 3C), due to the increase of electrolyte conductivities (see Fig. S4†). Nevertheless, power production was more unstable at higher (NH\(_4\))\(_2\)SO\(_4\) concentrations, especially in the 2 M tests. To minimize this concentration polarization, the catholyte was stirred for achieving high power densities during all the tests. Moreover, the power production was not observably enhanced when the (NH\(_4\))\(_2\)SO\(_4\) concentration increased from 1 to 2 M. Increasing the concentration of (NH\(_4\))\(_2\)SO\(_4\) had a more appreciable influence on the anode potentials than the cathode potentials, because the concentrated NH\(_4\)^{+} restrained the dissociation of ammonia and improved the activities of ammonia, resulting in more negative anode potentials (Fig. 3D).
Battery scalability

In order to evaluate the scalability of the Cu/Zn-TRAB system during discharge, power density, voltage and electrode potentials were examined using two Cu/Zn-TRABs connected in series and parallel. The maximum discharge power density reached 1090 W m\(^{-2}\)-electrode (249 W m\(^{-2}\)-membrane) with two cells in series or parallel, and this value was about twice as much as that obtained with a single cell (525 W m\(^{-2}\)-electrode (120 W m\(^{-2}\)-membrane)) (Fig. 4A). The battery voltage was increased from 1.42 to 2.85 V with two cells in series operation, while the maximum current density was increased from 1016 to 1921 A m\(^{-2}\) with two cells in parallel operation, and this value was about twice as much as that obtained with a single cell (525 W m\(^{-2}\)-electrode (120 W m\(^{-2}\)-membrane)) (Fig. 4B). The electrode performance with the two cells in a series configuration was similar to that obtained with a single cell, and the cathode potential of the second cell (near the positive electrode side of the whole battery) was first attenuated at larger current densities. The electrode performance with the two cells in a parallel configuration was better than that of a single cell, and the electrode potentials of the two single cells were identical (Fig. 4C). Therefore, the Cu/Zn-TRAB system can be scaled up for boosting the whole battery voltage, current and power production.

Cycling performance and thermal efficiency

The stability of the battery performance over multiple successive cycles is significant for efficiently converting low-grade thermal energy into electricity. Thus, power and net energy productions by the Cu/Zn-TRAB were investigated using regenerated electrolytes over three successive cycles [0.1 M Cu(II) and 1 M (NH\(_4\))\(_2\)SO\(_4\) in the catholyte and 0.1 M Zn(II), 1 M (NH\(_4\))\(_2\)SO\(_4\) and 2 M NH\(_3\) in the anolyte before the first discharge cycle]. The power and energy densities can’t be promoted at the same time, so the cell performance was analyzed under different conditions. Cells were operated at constant current densities (100 and 200 A m\(^{-2}\)) and a constant load of 12 Ω (an especial case for maximum power production), and the discharging cycle ended when discharge voltage was <0.6 V and the charging cycle terminated when the charge capacity was equal to discharge capacity (see Fig. S5, S8 and S9). The thermal efficiency was calculated from the ratio of the net energy density to the required thermal energy in the thermal regeneration process. For the thermal regeneration process, the method of constant temperature heating was used in the preliminary experiments instead of the decompression distillation. The required thermal energy was estimated using a distillation column model (see Fig. S10).

In the first discharge cycle of 100 A m\(^{-2}\), the voltage and cathode potential dramatically decreased at the end of the cycle with initial fresh electrolytes, since the depleted Cu\(^{2+}\) affected the deposition reaction (see Fig. S5†). The peak discharge power density and maximum net energy density in this initial cycle were 132 W m\(^{-2}\)-electrode (30 W m\(^{-2}\)-membrane) and 714 W h m\(^{-2}\), respectively (Fig. 5). The coulombic efficiency of the cathode (based on the mass change of the copper cathode) during discharge was 85 ± 5%, which was lower than ~100% achieved by a Cu-TRAB using nitrate as the electrolyte. There are two main reasons for explaining this. Firstly, the anion is different. Cyclic voltammetry curves show that the reduced peak potential is more negative than in the case of SO\(_4^{2-}\) solutions, which means that the reduction of Cu\(^{2+}\) is more difficult. In addition, the adsorption effect of SO\(_4^{2-}\) also makes the cathodic peak current lower. Secondly, compared to the NH\(_4\)NO\(_3\), the pH of the solution (~2.4 to ~3.9) is increased using (NH\(_4\))\(_2\)SO\(_4\) as the electrolyte. At the end of discharge, the pH further increased to ~8.9 due to the consumption of Cu\(^{2+}\) and the

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**Fig. 3** (A) Power density and (B) electrode potentials with different NH\(_3\) and Cu(II)/Zn(II) concentrations in the discharge process, using 1 M (NH\(_4\))\(_2\)SO\(_4\) as the supporting electrolyte; (C) power density and (D) electrode potentials with (NH\(_4\))\(_2\)SO\(_4\) at various concentrations as the supporting electrolyte in the discharge process, using 0.1 M Cu(II) in the catholyte and 0.1 M Zn(II) and 2 M NH\(_3\) in the anolyte.
migration of NH$_3$ and OH$^-$ through the AEM (the catholyte turned dark blue at the end of discharge), which meant that Cu(NH$_3$)$_n^{2+}$ was reduced to Cu instead of Cu$_2^+$. The deposition efficiency of Cu(NH$_3$)$_n^{2+}$ is relatively low due to the presence of Cu(NH$_3$)$_n^+$ during the deposition process.$^{25}$ An anodic coulombic efficiency of 70 ± 5% was obtained, indicating that excess zinc leached into the anolyte but it was much higher than the efficiency of 35–37% in the Cu-TRAB,$^{13,21}$ likely due to the black passive film formed on the zinc surface that inhibited the oxidation of the zinc electrode. The SEM images and corresponding EDS analysis confirmed that the black film mainly consisted of nano-scale zinc and a small amount of zinc oxide particles (see Fig. S6†). After the discharge, the anolyte effluent was heated for evaporating ammonia (simulating distillation), and the catholyte effluent was added to concentrated ammonia for the charging cycle. The pH of the anolyte effluent decreased from ~10.3 to ~7.1 after thermal regeneration, during which there was precipitate formation in the solution as a result of the hydrolysis of Zn(NH$_3$)$_4^{2+}$. X-ray diffraction (XRD) analysis showed that this precipitate was mainly basic zinc sulfate Zn$_4$(SO$_4$)(OH)$_6$$^5$H$_2$O (see Fig. S7†). The charging voltage (~0.82 V, see Fig. 1A) with the regenerated electrolytes was higher than that with fresh electrolytes (~0.73 V, see Fig. 1A), likely because the reduction potential of Zn$_4$(SO$_4$)(OH)$_6$$^5$H$_2$O/Zn was more negative. Practically, the combination of two reduction reactions [Zn$_4$(SO$_4$)(OH)$_6$$^5$H$_2$O + 8e$^-$ + 4Zn(s) + 6OH$^-$/SO$_4^{2-}$ + 5H$_2$O and Zn$^{2+}$ + 2e$^-$ → Zn(s)] induced this higher charging voltage. In the charging cycle, the coulombic efficiency of the zinc cathode was 107.5%, indicating that almost no side reactions occurred as expected for Zn$^{2+}$ reduction. The coulombic efficiency of the copper anode was 49 ± 5% and no passivation film was observed on the surface of the copper mesh, making the copper more susceptible to corrosion. Dissolved oxygen in the solution may accelerate the corrosion process, as the reaction [Cu(s) + 1/2 O$_2$ + 4NH$_3$·H$_2$O → Cu(NH$_3$)$_4^{2+}$ + 2OH$^-$ + 3H$_2$O].$^{13}$ In the second and third closed-loop cycles, ammonia was separated from the Cu(NH$_3$)$_4^{2+}$ anolyte after charging and the
spent catholyte was added to concentrated ammonia for the next discharge cycle. The pH of the anolyte effluent dropped from \~{}10.4 to \~{}6.4. Similarly, a precipitate formed during this process due to the hydrolysis of the Cu(NH)\textsubscript{2}\textsuperscript{+}, and the XRD tests showed that this precipitate was mainly basic copper sulfate Cu\textsubscript{4}(SO\textsubscript{4})(OH)\textsubscript{6} (see Fig. S7†). For the two successive regeneration cycles, due to the existence of this precipitate for more negative electrode potential of Cu\textsubscript{4}(SO\textsubscript{4})(OH)\textsubscript{6}/Cu, the peak discharge power density was reduced but relatively steady, averaging 115 W m\textsuperscript{-2}-electrode (26 W m\textsuperscript{-2}-membrane) [132 W m\textsuperscript{-2}-electrode (30 W m\textsuperscript{-2}-membrane), cycle 1; 116 W m\textsuperscript{-2}-electrode (27 W m\textsuperscript{-2}-membrane), cycle 2; 114 W m\textsuperscript{-2}-electrode (26 W m\textsuperscript{-2}-membrane), cycle 3] (Fig. 5). The combination of two reduction reactions \(\text{Cu}_4\text{(SO}_4\text{)}\text{(OH)}_6 + 8 e^- \rightarrow 4\text{Cu (s)} + 6\text{OH}^- + \text{SO}_4^{2-}\) and Cu\textsuperscript{2+} + \(2e^-\rightarrow\text{Cu (s)}\) was the reason for the lower discharge power density when using regenerated electrolytes.

The maximum net energy density was also reduced in the second cycle (714 W h m\textsuperscript{-3}-electrode, cycle 2; 589 W h m\textsuperscript{-3}-electrode, cycle 2; 838 W h m\textsuperscript{-3}-electrode, cycle 3) (Fig. 5). The improvement of net energy density in the third cycle was due to the accumulation of charge or capacity in the previous cycles, which was consistent with higher Cu\textsuperscript{[n]} and Zn\textsuperscript{[n]} concentrations in the regenerated catholyte on the account of lower coulombic efficiencies of the copper and zinc anodes. This excess electrode corrosion could be relieved by removing the O\textsubscript{2} dissolved in the electrolyte, and recovered by some electrodeposition technologies.\textsuperscript{11} In future work, the electrodes need to be modified to improve coulombic efficiency and cycle performance, such as nanostructure synthesis on carbon substrates. Recently, carbon-silver electrodes have been used in the Ag\textsuperscript{-TRAB}, resulting in high coulombic efficiency close to 100\% and good stability over 100 cycles.\textsuperscript{29} Moreover, some catalysts should also be used to promote efficiency and performance. Similar to the first cycle with fresh electrolytes, the depletion of Cu\textsuperscript{[n]} [i.e. Cu\textsuperscript{2+} and Cu\textsubscript{4}(SO\textsubscript{4})(OH)\textsubscript{6}] in the catholyte markedly reduced the cathode potential at the end of the second or third discharge cycle. After discharging, the anolyte was regenerated for the next charging process. Peak discharge power densities were comparatively stable in the two continuous regeneration cycles, demonstrating good repeatability over successive cycles. Although the results provided here demonstrated that cycles are reproducible in a short term, long-term cyclability still needs to be developed in the future.

For a large current density of 200 A m\textsuperscript{-2}, the peak discharge power densities [246 W m\textsuperscript{-2}-electrode (56 W m\textsuperscript{-2}-membrane), cycle 1; 202 W m\textsuperscript{-2}-electrode (46 W m\textsuperscript{-2}-membrane), cycle 2; 205 W m\textsuperscript{-2}-electrode (47 W m\textsuperscript{-2}-membrane), cycle 3] were improved with an average value of 204 W m\textsuperscript{-2}-electrode (47 W m\textsuperscript{-2}-membrane) in the two successive regeneration cycles, but the maximum net energy density (400 W h m\textsuperscript{-3}) in the initial cycle was greatly reduced (Fig. 5). More seriously, the maximum net energy density in the second and third successive cycles dropped below 100 W h m\textsuperscript{-3}, mainly due to more negative cathode potentials in the discharge, indicating that the reduction potentials of Cu\textsubscript{4}(SO\textsubscript{4})(OH)\textsubscript{6}/Cu were more negative at large current densities (see Fig. S87).

In order to achieve the maximum power density and a higher net energy density, cells were discharged at a constant load of 12 \(\Omega\) (external resistance) and charged at a lower constant current density of 100 A m\textsuperscript{-2}, with the discharging cycle terminating when the voltage was \<{}0.6 V and the charging cycle terminating when the charge capacity reached the discharge capacity (see Fig. S9†). Simultaneously, some waste sulphuric acid was used to dissolve the Zn\textsubscript{4}(SO\textsubscript{4})(OH)\textsubscript{6}·5H\textsubscript{2}O and Cu\textsubscript{4}(SO\textsubscript{4})(OH)\textsubscript{6} precipitates in the regenerated catholytes. The results showed that the maximum power densities [515 W m\textsuperscript{-2}-electrode (118 W m\textsuperscript{-2}-membrane), cycle 1; 515 W m\textsuperscript{-2}-electrode (118 W m\textsuperscript{-2}-membrane), cycle 2] were achieved and maintained in the successive cycles, and the maximum net energy density (299 W h m\textsuperscript{-3}-electrode, cycle 1; 484 W h m\textsuperscript{-3}, cycle 2) did not decrease in the second cycle (Fig. 5). These results indicated that inexpensive acids could be used for achieving and maintaining a better battery performance.

Based on a distillation model developed using the software Aspen HYSYS,\textsuperscript{31,32,35} the thermal energy required for NH\textsubscript{3} separation from the anolyte (2 M) in one cycle was estimated to be 372 kW h m\textsuperscript{-3}-anolyte (see Fig. S10†). The simulating parameters for separation of 2 M NH\textsubscript{3} were similar to those of previous studies, with a condenser temperature \(T_\text{C}\) of 43 °C, a reboiler temperature \(T_\text{R}\) of 70.9 °C, an inlet temperature \(T_\text{in}\) of 27 °C, and an inlet pressure of 0.244 atm for a single distillation column.\textsuperscript{31,32,35} With a net energy density of 838 W h m\textsuperscript{-3} obtained at a current density of 100 A m\textsuperscript{-2}, the thermal energy efficiency was 0.45\% (3.5\% relative to the Carnot efficiency), which was lower than 7\% relative to the Carnot efficiency obtained with a Cu-TRAB using a poly(phenylene oxide) based AEM. The main reason is the B-TRAB needs two thermal regeneration processes in one closed cycle, which doubles the heat duty and reduces the thermoelectric conversion efficiency. But this efficiency was much higher than 0.25\% with a carbon-nanotube-based TEC.\textsuperscript{28} An increase of the inlet temperature from 27 to 40 °C slightly improved the thermal energy efficiency (from 0.45\% to 0.51\%) because the heat duty for distillation decreased from 372 to 327 kW h m\textsuperscript{-3}-anolyte, while that relative to the Carnot efficiency (from 3.5\% to 5.7\%) had a relatively appreciable improvement due to the obvious decrease of the Carnot efficiency from 13\% to 9\%. However, with an inlet temperature of 40 °C, a lower condenser temperature could significantly promote the thermal energy efficiency (from 0.43\% to 0.95\%) and that relative to the Carnot efficiency (from 5.7\% to 10.7\%) owing to the reduction of heat duty (from 327 kW h m\textsuperscript{-3}-anolyte (43 °C) to 88 kW h m\textsuperscript{-3}-anolyte (25 °C)). Additionally, the Carnot efficiency, calculated with a column reboiler temperature of 70.9 °C and an inlet temperature of 27 or 40 °C, did not change with decreased condenser temperatures.

**Performance comparison with other technologies**

The concentration-optimized Cu/Zn-TRAB achieved a maximum power density of 515 W m\textsuperscript{-2}-electrode (118 W m\textsuperscript{-2}-membrane) over multiple successive closed cycles, which was the highest in liquid-based thermoelectric conversion batteries or systems reported to date. This result was significantly higher than the previous TECs produced with activated carbon cloth and MWNT electrodes (<12 W m\textsuperscript{-2}),\textsuperscript{20,36} and about fourfold as...
much as the peak power density obtained with the single metallic Cu-TRAB (∼120 W m⁻²-electrode or 27.4 W m⁻²-membrane). A poly (phenylene oxide) based AEM⁶ and replacing ammonia with ethylenediamine as the ligand⁴ could be applied for further enhancing the power density of the Cu/Zn-TRAB.

The maximum net energy density of 714 W h m⁻³ for the Cu/Zn-TRAB (obtained with a constant current of 100 A m⁻²) was also higher than that of a Cu-TRAB (453 W h m⁻³) at room temperature.⁹ The flow system used for the single metallic TRAB improved the energy density to 500 W h m⁻³ (Ag-TRAFB³) and 630 W h m⁻³ (Cu-TRAFB³) based on the total electrolyte volume, which were lower compared to that in this work. By increasing the Cu[n]/Zn[n] concentrations in the electrolytes and using lower current densities, the net energy density could be markedly promoted. Besides, the flow battery system could also be used in the Cu/Zn-TRAB for higher energy density.

The energy conversion efficiency was 0.45% (3.5% relative to the Carnot efficiency) herein, which was in the range of 2–5% relative to the Carnot efficiency for commercial feasibility.³⁷ This Carnot-relative efficiency was greatly higher than 0.4% reported by a TEC with a power density of 12 W m⁻²,⁰ but lower than those obtained by a TREC (38%)²² and a TOEC process (34%).⁷ However, the methods of increasing the energy density described above can be used to improve the energy conversion efficiency of the Cu/Zn-TRAB, and additionally, optimizing the distillation parameters in the thermal regeneration process helps to enhance the efficiency. For example, an efficiency of 0.95% (10.7% relative to the Carnot efficiency) was realized through decreasing the condenser temperature from 43 to 25 °C and increasing the inlet temperature from 27 to 40 °C. The higher efficiency (34%) of TOEC needed a hydraulic pressure above 50 bar, but the first experiment only reached 13 bar.¹⁷ Besides, the calculation of another higher efficiency (38%) of the TREC considered a heat recovery efficiency of 50%;¹² however, we did not use heat recovery components (such as heat exchangers) in the ammonia separation process, indicating that the energy conversion efficiency of the B-TRAB could be further promoted by optimizing the thermal regeneration process.

Conclusions

The original Cu/Zn-TRAB presented herein is a cost-effective and practical approach for high power production and harvesting low-grade thermal energy. A maximum power density of ∼515 W m⁻²-electrode (118 W m⁻²-membrane) was achieved over successive regeneration cycles, and this value was the highest among the reported liquid-based thermal-electrical conversion technologies. The efficiency of thermo-electric conversion was 0.45% (3.5% relative to the Carnot efficiency) with a net energy density of 838 W h m⁻³ (obtained in the third cycle at a current density of 100 A m⁻²), and it could be substantially improved by enhancing energy density and optimizing the thermal regeneration process.

Despite the Cu/Zn-TRAB needing to be charged, its development, preparation and operation are uncomplicated, and the global reserves of copper and zinc are extremely abundant. The Cu/Zn-TRAB system has not been optimized, and thus modifications for single metallic TRABs could be used for higher power and net energy densities or better cycling performance. Potentially, there are some other promising B-TRAB systems, such as the Ag/Zn-TRAB that has the highest discharging voltage of 1.84 V (this means that greater power density could be achieved), Ag/Cu-TRAB that has the lowest theoretical charging voltage of 0.03 V (the minimum ratio between charge and discharge voltages means that greater net energy density and efficiency could be obtained), and Co/Ni-TRAB that is charge-free.

Experimental

Cu/Zn-TRAB development and operation

A single Cu/Zn-TRAB was developed using positive and negative electrode chambers (polycarbonate, 4 cm long and 3 cm in diameter) divided by an anion exchange membrane (AEM, Selemion AMV, 4 cm × 4 cm) [See Fig. S1†]. A copper positive electrode (50 × 50 mesh, McMaster-Carr; 0.8 cm × 2 cm, weight of 0.2160 ± 0.0005 g) and zinc negative electrode (0.2 mm thick sheet, McMaster-Carr; 0.8 cm × 2 cm, weight of 0.2400 ± 0.0005 g) were inserted into the chambers and connected by copper or zinc wires to an external resistance (discharge) or power source (charge) (Fig. 1B). Besides, polycarbonate end-plates and fluororubber gaskets were used to fix and seal the cell reactor with bolts and nuts. Two Ag/AgCl reference electrodes (+208.2 mV versus SHE at 20 °C, R0303, aida, 2 cm away from the electrode) were put into the electrolytes for monitoring the electrode potentials (see Fig. S1†). An egg-shaped stir bar (6.4 × 15.9 mm, VWR, 500 rpm) was only used in the cathode chamber for fully mixing the catholyte.

In the experiments, different concentrations of CuSO₄/ZnSO₄ (Alfa Aesar; 0.05 M–0.3 M), (NH₄)₂SO₄ (Alfa Aesar; 0–2 M) and ammonium hydroxide (Aladdin, AR, 25–28%; 1–3 M) were prepared for the electrolytes using ultrapure water. The electrolyte conductivity and pH were measured using a multi-parameter tester (S470, METTLER TOLEDO) (see Fig. S3†).

For the purpose of investigating the performance of the Cu/Zn-TRAB comprehensively over multiple cycles, the battery was operated at constant discharging and charging current densities (100 and 200 A m⁻²) in a cycle or was discharged at a constant load of 12 Ω (external resistance) and charged at a constant current density of 100 A m⁻², with the discharging cycle terminating when the voltage was <0.6 V and the charging cycle terminating when the charge capacity was equal to discharge capacity. After the charge and discharge, the electrolytes were collected separately, and the anolyte was heated at a constant temperature of 50 °C for distilling NH₃ out and regenerating a new catholyte for the next process. This distilled NH₃ (in the form of NH₃·H₂O) was put into the collected catholyte to generate a new anolyte. All experiments were conducted at room temperature (20–30 °C).

Measurements and calculations

Polarization tests were performed using battery testing equipment (Arbin Instruments, BT-G) connected to a personal...
In the discharge tests, current \((I, A)\) scanning with a rate of 1 mA s\(^{-1}\) started from open circuit \((0 \text{ A})\) to zero voltage. While the current scan stopped when the voltage reached 1.8 V during the charge tests. Battery voltage \((U, V)\) and electrode potentials relative to the respective Ag/AgCl reference electrode were recorded at each time interval. Current density was calculated and normalized to an projected electrode area of 1.6 \(\times 10^{-4}\) m\(^2\). Area-averaged power density \((P, W \text{ m}^{-2})\) was calculated using the projected electrode area \((1.6 \times 10^{-4} \text{ m}^{2},\text{ P}-\text{ electrode})\) for comparing with the previous single metallic TRABs and using the projected membrane area \((7 \times 10^{-4} \text{ m}^{2},\text{ P}-\text{ membrane})\) for contrasting with other technologies, such as TECs, TRECs and TOEC. Before the tests, the quiet time was set as 30 seconds, and the open circuit potential was recorded every 10 seconds.

In the successive regeneration cycle experiments, the amount of charge accumulated during discharging or charging was obtained as \(Q = \int i dt\), and discharge or charge energy was computed using the formula of \(W = \int U dt\). The volume-normalized net energy density was obtained through dividing the produced net energy in one cycle \((W_a - W_d)\) by the total electrolyte volume of 56 mL. The cathode and anode coulombic efficiencies (CCE and ACE) were calculated as the ratio between the actual accumulated charge and theoretical amount of charge in terms of the electrode mass change, as follows:

\[
\text{CCE}_d = \frac{(m_{\text{Cu},c} - m_{\text{Cu},d})}{Q_d M_{\text{Cu}}} n F \times 100
\]

\[
\text{ACE}_d = \frac{Q_d M_{\text{Zn}}}{(m_{\text{Zn},d} - m_{\text{Zn},c})} n F \times 100
\]

During the charge:

\[
\text{CCE}_c = \frac{(m_{\text{Zn},c} - m_{\text{Zn},d})}{Q_c M_{\text{Zn}}} n F \times 100
\]

\[
\text{ACE}_c = \frac{Q_c M_{\text{Cu}}}{(m_{\text{Cu},d} - m_{\text{Cu},c})} n F \times 100
\]

where \(m_d\) and \(m_i\) denote the electrode masses before and after the discharge or charge tests and are measured using an analytical balance, \(F\) (96 485 C mol\(^{-1}\)) is the Faraday constant, \(n\) \((n = 2\) for Cu and Zn\) is the number of electrons involved in the electrode reaction, \(Q_d\) and \(Q_c\) are the total charge transferred and subscripts \(d\) and \(c\) represent the discharge and charge processes, respectively, and \(M_{\text{Cu}}\) and \(M_{\text{Zn}}\) are the molecular weight of the metals \((\text{Cu, 63.55 g mol}^{-1}; \text{Zn, 65.38 g mol}^{-1})\).

The B-TRAB system needs four steps to complete the thermoelectric conversion. At first, the battery discharges with higher voltage. And then waste heat is used to regenerate the spent anolyte and shift the redox couples to a lower potential for charging. The battery is charged at lower voltage and net energy is produced, and then waste heat is used to regenerate the anolyte again and shift the redox couples to a higher potential for the next discharging cycle. Therefore, the thermal-electricity conversion efficiency is determined as the ratio between the net energy and the required thermal energy for two regeneration processes \((\eta_e = \text{net energy/demanded thermal energy})\). Usually, the energy conversion efficiency relative to the Carnot efficiency \((\eta_{\text{C}} = 1 - T_i/T_H)\) \((\eta_{\text{C}} = \text{net energy}/[\text{required thermal energy} \times (1 - T_i/T_H)])\) was reported for comparing with other techniques, in which \(T_i\) is the inlet temperature \(T_{\text{in}}\) and \(T_H\) is the reboiler temperature \(T_{\text{H}}\). Ignoring the separation energy of copper and zinc ammine complexes,\(^{13}\) the column thermal energy required for NH\(_3\) distillation from the anolyte was estimated by establishing a simplified model (that treated the anolyte as a mixture of NH\(_3\) and H\(_2\)O) with Aspen HYSYS (see Fig. S10†). In this model, the reboiler temperature was set at 70.9 °C, and the inlet pressure of the electrolyte is 0.244 atm.\(^{13,25,35}\) Previous simulation results indicated that over 97% of ammonia could be recovered.\(^{13,22,35}\) Different inlet temperatures (27 and 40 °C) and condenser temperatures (43 and 25 °C) were used to analyze the factors of thermal energy efficiency. Because only the anolyte needed to be thermally regenerated, this thermal energy consumed in the column was based on the anolyte volume of 28 mL.

A scanning electron microscope (SEM) was used to analyze the zinc electrode after 30 min of the constant-current charge tests, confirming that the zinc was deposited and the morphology was related to current density (see Fig. S2†). Besides, the SEM images and corresponding EDS (Energy dispersive spectrum) analysis (see Fig. S6†) of the zinc anode after discharging indicated that the nano-passivation film on the surface of the zinc anode may be the cause for the higher anodic coulombic efficiency than copper. X-ray diffraction (XRD) was performed for exploring the composition and structure of the precipitates produced during the thermal regeneration processes (see Fig. S7†).

**Conflicts of interest**

There are no conflicts to declare.

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