A bimetallic thermally-regenerative ammonia-based flow battery for low-grade waste heat recovery

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HIGHLIGHTS

- A B-TRAFB was presented for converting low-grade waste heat to electricity.
- The B-TRAFB realized high-voltage discharge and low-voltage charge at room temperature.
- The compact design enhanced the membrane and volume-averaged performance.
- A cost-effective Cu/Zn-TRAFB achieved a high power density of \( \sim 280 \, \text{W m}^{-2} \).
- The Cu/Zn-TRAFB showed good efficiency, scalability and cycle stability.

GRAPHICAL ABSTRACT

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ABSTRACT

Converting low-grade waste heat into electrical energy helps alleviate the increasingly tense energy crisis. Here, we present a feasible approach for low-grade waste heat recovery, called bimetallic thermally-regenerative ammonia-based flow battery (B-TRAFB), realizing high-voltage discharge and low-voltage charge at the same temperature. The performance of a cost-effective and structure-compact copper/zinc bimetallic thermally-regenerative ammonia-based battery (Cu/Zn-TRAFB) is investigated comprehensively. A peak power density of \( \sim 280 \, \text{W m}^{-2} \) is achieved by a single Cu/Zn-TRAFB cell, and with this case, the net energy density is about 1280 Wh m\textsuperscript{-3} with a thermoelectric conversion efficiency of 0.34\% (2.7\% of the Carnot efficiency). The power density obtained herein is much higher than those previously reported for ammonia-based batteries and other liquid-based heat-to-electricity technologies. The cell voltages, currents and power densities can be boosted by adding stacked cells in series or parallel. The energy conversion efficiency can be promoted to 1.64\% (27\% of the Carnot efficiency) by optimizing the thermal regeneration process.

1. Introduction

Due to the inefficiency of energy utilization and transformation, huge amounts of untapped energy exist in our daily life and industrial processes in the form of low-grade waste heat (< 100–130 °C), which is gradually recognized as a renewable energy source and converting it into useful electrical energy helps to ease the energy problems faced by humanity currently [1–3]. However, distribution characteristics and small temperature differences of these low temperature heat sources increase the difficulty of utilization and conversion [4,5]. Organic Rankine cycles and solid-state thermoelectric devices have been comprehensively examined for many years, but their high material or
operating costs, low power density and efficiency restrict the development of practical applications [6–10].

Recently, liquid-based thermal electrochemical cells or systems may have better prospects than the traditional technologies mentioned above for efficiently harvesting low-grade waste heat. Among them, thermally regenerative electrochemical cycles (TRECs) [4,5,11] and thermo-osmotic energy conversion (TOEC) process [12] achieved the highest thermoelectric conversion efficiency. For example, a high energy conversion efficiency of 3.7% was received by a TREC between 20 and 60 °C without heat recuperation [11], and the efficiency of TOEC process could up to 7% with a high operating pressure of 150 bar [12]. However, these two options still output low power densities to date (a TREC only produced a power density of 0.5 W m$^{-2}$ estimated by an average discharge voltage of 0.55 V, the theoretical electrolyte mass and the electrode area of 0.25 cm$^2$ between 20 and 60 °C [11], and the power density obtained by a TOEC preliminary experiment was 3.53 W m$^{-2}$ and it was reduced to ~1 W m$^{-2}$ with higher energy efficiencies [12,13]). In addition to efficiency, power density is another important parameter for evaluating thermoelectric conversion approaches [10,14]. At present, technologies achieved higher power densities are thermo-electrochemical cell (TEC) [14–17] and thermally regenerative ammonia-based battery (TRAB) [18–21]. The maximum power density reported by TECs was 12 W m$^{-2}$ with a temperature difference of 80 °C, but its Carnot-relative efficiency $\eta_{t/C}$ was only 0.4% [10,17]. The TRABs using the same metal as the electrodes achieved relatively high power density of 14–45 W m$^{-2}$ normalized to the membrane area with the Carnot-relative efficiencies between 3.1 and 7% [10,18–21], and the $\eta_{t/C}$ of TRAB could be improved to 13% by elevating the operating temperature [22]. The single metallic TRABs showed better performance, however, their power outputs were still

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**Fig. 1.** Bimetallic thermally-regenerative ammonia-based flow battery (B-TRAFB): (A) working principle representation of the Cu/Zn-TRAFB for converting waste heat into electric energy; (B) a single cell during discharging; (C) a single cell during charging; (D) two cells connected in parallel during discharging; (E) two cells connected in series during discharging; (F) construction of each part and details of flow paths; (G) a photograph of laboratory set-up for Cu/Zn-TRAFB system.
insufficient for viable application development due to their lower battery voltages (< 0.45 V).

Newly, we proposed a bimetallic thermally-regenerative ammonia-based battery (B-TRAB) for harvesting low-grade thermal energy, and it discharged at high voltage and was charged at low voltage with room temperature [23]. A low-cost Cu/Zn-TRAB generated the highest power density of 120 W m\(^{-2}\) in contrast to previous heat-to-electricity technologies [23]. In a Cu/Zn-TRAB, Cu with more positive electrode potential of Cu\(^{2+}\)/Cu was used as positive electrode, and Zn with more negative electrode potential of Zn(NH\(_3\))\(_4\)\(^{2+}\)/Zn was used as negative electrode. During discharging, Cu\(^{2+}\) was deposited on the Cu electrode and the Zn electrode was oxidized to Zn(NH\(_3\))\(_4\)\(^{2+}\), and the higher potential difference between Cu\(^{2+}\)/Cu and Zn(NH\(_3\))\(_4\)\(^{2+}\)/Zn was the discharge voltage, producing a high power density. After the discharge, the ammonia in the anolyte was separated by waste heat energy and then passed into the catholyte to complete the thermal regeneration of the electrolytes. During charging, the regenerated electrolytes were used, and Cu electrode was oxidized to Cu(NH\(_3\))\(_4\)\(^{2+}\) and Zn\(^{2+}\) was reduced on Zn electrode, and the lower potential difference between Cu(NH\(_3\))\(_4\)\(^{2+}\)/Cu and Zn\(^{2+}\)/Zn was the charge voltage. After the charge, waste heat was used again to regenerate the anolyte, and the next closed cycle repeated as described above. The discharge voltage was higher than the charge voltage to generate net energy, achieving thermoelectric conversion.

Compared to previous liquid-based technologies, B-TRABs increase the power density to a much higher level and have good efficiency and energy output performance. However, the previous B-TRAB system had some shortcomings that would greatly limit the battery performance, such as: I) the design of battery device was not convenient for continuous cycle operation, leading to intermittent power productions; II) the distance between the electrodes (20–25 mm) was large, which increased the battery internal resistance; III) a small ratio (0.23 m\(^2\) m\(^{-2}\)) of the electrode area to the membrane area lowered the availability of the membrane and increased the costs, and the membrane-normalized performance was also deteriorated; IV) a small ratio (5.7 m\(^2\) m\(^{-3}\)) of the electrode area to the electrode chamber volume weakened the volume-averaged performance. To avoid these shortcomings, we presented a bimetallic thermally-regenerative ammonia-based flow battery (B-TRABF) here that worked similarly to previous B-TRABs (Fig. 1A).

The main difference was that in this flow battery system, the electrolytes were stored in external reservoirs and continuously circulated through the battery by peristaltic pumps (Fig. 1A and G). The discharging and charging energy were determined by the electrolyte volume in the reservoirs, and the switching of the discharge and charge cycles only needed to replace the reservoirs. Moreover, the electrodes, flow channels, and membranes were stacked together, and this compact design allowed for a significant reduction of occupied space (Fig. 1B–F). The distance of two electrodes was narrowed to 3 mm, which helped to reduce the cell internal resistance. The ratios of the electrode area to the membrane area (1 m\(^2\) m\(^{-2}\)) and the electrode chamber volume (667 m\(^3\) m\(^{-3}\)) were greatly increased, improving the use efficiency of membrane, power and energy densities, and reducing the system costs. The flow battery system also could be applied to other B-TRABF systems using different metals (Ag, Cu, Co, Ni and Zn) as the electrode plates. In this work, we used the more economical metals (Cu and Zn) as electrodes to construct a Cu/Zn-TRABF, and the highest power density was obtained by optimizing the electrolyte concentrations and flow rates. With the maximum power density, the net energy density of the Cu/Zn-TRABF was tested, and the corresponding thermoelectric conversion efficiency was calculated. In addition, the series and parallel characteristics of two cells (Fig. 1D and E), the system stability, and the electrode reversibility were also evaluated.

2. Experimental methods

2.1. Cu/Zn-TRABF system configuration and operation

The construction of a single Cu/Zn-TRABF (Fig. 1B, C and 1F) was carried out by stacking a copper positive electrode (5 × 5 × 0.05 cm, McMaster-Carr), a zinc negative electrode (5 × 5 × 0.05 cm, McMaster-Carr), two flow channels (2 × 4 × 0.15 cm), High-Purity High-Temperature Silicone Rubber sheets, (McMaster-Carr), and an anion exchange membrane (AEM, 5 × 5 cm, Selion AMV). The two electrodes were respectively connected to the PTFE fixed blocks by an adhesive-back silicone rubber sheet, and then integrally embedded in two polycarbonate endplates with a groove (5 × 5 × 0.2 cm), and then fixed by bolts and nuts (Fig. 1G). The series and parallel connections of multiple cells only needed to increase the number of electrodes, flow channels and membranes and other fixing parts were unchanged, and two adjacent electrodes were separated by an insulating silicone gasket (Fig. 1D and E). Except for the battery module, the flow battery system also included catholyte and anolyte reservoirs, two peristaltic pumps, two reference cells and PTFE tubes (Fig. 1A and G). The position of the reference cell was between the pump and the battery inlet, and two reference electrodes (+204 mV versus SHE at 20 °C, R0305, Tianjin aida) were inserted into the reference cells to detect the electrode potentials (Fig. 1A and G). The PTFE tubes were connected to the internal thread on the PTFE fixed blocks by the external thread joints, and the electrolytes flowed into and out of the battery from the joints.

The electrolytes with different concentrations of (NH\(_4\))\(_2\)SO\(_4\) (0.5 M – 2 M, Alfa Aesar), CuSO\(_4\)/ZnSO\(_4\) (0.1 M – 0.5 M, Alfa Aesar) and ammonium hydroxide (1 M – 3 M, Aladdin, 25–28% AR) were prepared using ultrapure water and pumped into the battery system at different flow rates. All experiments were conducted at room temperature (20–30 °C).

2.2. Measurements and calculations

Battery performance tests were carried out by a computer-controlled battery tester (BT-G, Arbin Instruments). In the polarization tests, 20 mL of different concentrations of electrolytes were circulated in the system at different flow rates. During the discharge process, the current (I, A) was scanned from open circuit to zero voltage at a rate of 1 mA s\(^{-1}\), and the scan was turned off when battery voltage reached 1.5 V in the charge process. Battery voltage (U, V) and electrode potentials relative to the reference electrodes were measured and recorded. The electrode potentials reported in this work were converted to the potentials relative to the SHE. Power (P, W) was obtained by multiplying the current and voltage as P = UI. Based on the projected membrane area (8 × 10\(^{-4}\) m\(^2\)), the area-averaged current (I_\(\text{avg}\), A m\(^{-2}\)) and power (P_\(\text{avg}\), W m\(^{-2}\)) densities were received, and the volume-averaged power density (P_\(\text{avg}\), W m\(^{-3}\)) could be calculated by using the total reactor volume (2.4 × 10\(^{-5}\) m\(^3\)).

In the net energy density test, constant load (4Ω) discharge was performed firstly with optimized electrolytes (20 mL of catholyte with 0.4 M CuSO\(_4\) and 1 M (NH\(_4\))\(_2\)SO\(_4\), and 20 mL of anolyte with 0.4 M ZnSO\(_4\), 1 M (NH\(_4\))\(_2\)SO\(_4\) and 2 M NH\(_4\)OH) and flow rate (8 mL min\(^{-1}\)), and it was cut off when the voltage was lowered to 0.6 V. The accumulated charge Q and output energy \(E_Q\) during the discharge process were also recorded. After the end of the discharge, the spent anolyte was collected for thermal regeneration. In the initial experiment, a method of constant temperature heating (50 °C) on a magnetic stirrer was used to remove NH\(_3\) (simulating distillation process, as shown in Fig. S1), forming a regenerated catholyte for the next charge cycle [18]. The evaporated NH\(_3\) was not collected in the current experiment, and concentrated ammonia was added into the catholyte to form a new anolyte for charging. The regenerated catholyte produced a basic precipitate during thermal regeneration, and adding some waste sulphuric acid could dissolve this precipitate [23]. But because of the low
solubility of \((\text{NH}_4)_2\text{Zn(SO}_4)_2\), it still existed as a precipitate, so the catholyte was magnetically agitated with an egg-shaped stir bar (6.4 × 15.9 mm, VWR, 600 rpm) in the charge process. Constant current (50 \(\text{A m}^{-2}\)) charge was performed with the regenerated electrolytes, and the charging cycle was turned off when the charge capacity was equal to the discharge capacity. The accumulated charge \(Q_d\) and input energy \(E_t\) in the charge process were also recorded. The difference between the output energy and the input energy was the net energy \(E_n = E_d - E_t\) in one cycle, and the volume-averaged net energy density \(E_n = \frac{E_n \cdot \text{Wh m}^{-3}}{c}\) was calculated based on the anolyte volume (20 mL). The anode and cathode coulombic efficiencies could be obtained using the mass changes of electrodes and the actual accumulated charges \((Q_a\) and \(Q_c)\) [23].

Since a closed cycle of the Cu/Zn-TRAFB included a discharge process, a charge process and two thermal regeneration processes, the thermoelectric conversion efficiency \(\eta\) was calculated by the ratio of the net energy density in one cycle and the thermal energy required for the two thermal regeneration processes. The net energy density was obtained experimentally and the required thermal energy was estimated from a distillation model developed using Aspen HYSYS [18,23]. Based on a traditional simulation condition with an inlet temperature of 27°C, a reboiler temperature of 70.9°C and a condenser temperature of 43°C [18,22,24], the thermal energy needed to separate 2 M NH₃ from the anolyte twice in one cycle was about 372 kWh m⁻³. Over 97% of ammonia could be recovered using a vacuum distillation condition [18]. In order to make a fair comparison with other heat-to-electricity technologies, the Carnot-relative efficiency \(\eta_{\text{CR}}\) was also reported, and the Carnot efficiency \(\eta_{\text{C}} = 1 - \frac{T_c}{T_h}\) was calculated using the inlet temperature \(T_i\) and the reboiler temperature \(T_{r}\). In addition, the effects of different inlet temperatures and condenser temperatures on energy conversion efficiency were also analyzed.

In the system stability and electrode reversibility tests, a single Cu/Zn-TRAFB was discharged and charged every 15 min with a constant current of 16 mA, and a 5-min interval between the discharge and charge cycles was used to drain the electrolytes in the system and exchange the flow paths of the catholyte and anolyte. The same fresh electrolytes were used for each cycle (20 mL of catholyte with 0.1 M CuSO₄ and 1 M (NH₄)₂SO₄, and 20 mL of anolyte with 0.1 M ZnSO₄, 1 M (NH₄)₂SO₄ and 2 M NH₄OH were recycled at a flow rate of 1 mL min⁻¹ in the discharge cycle; 20 mL of catholyte with 0.1 M ZnSO₄ and 1 M (NH₄)₂SO₄, and 20 mL of anolyte with 0.1 M CuSO₄, 1 M (NH₄)₂SO₄ and 2 M NH₄OH were recycled at a flow rate of 1 mL min⁻¹ in the charge cycle). Battery voltage, power density and electrode potentials over time were recorded during the tests.

3. Results

3.1. Working characteristics of Cu/Zn-TRAFB

In order to confirm that the Cu/Zn-TRAFB system can realize high-voltage discharge and low-voltage charge, preliminary tests were carried out on the charge and discharge characteristics with fresh electrolytes and without thermal regeneration. Fig. 2A and B showed the discharge and charge voltages and corresponding electrode potentials as a function of current densities. The discharge voltage gradually decreased with increasing current density. The main reason for the rapid decline of the voltage at the end of discharge was the sharp decrease of the deposition potential of Cu²⁺ (Fig. 2A and B), due the depletion of the Cu²⁺ concentration on the electrode surface at higher current densities [25]. The charge voltage increased with increasing current density (Fig. 2A). The cathode potential during charging was around −0.82 V (Fig. 2B), demonstrating that deposition of Zn²⁺ occurred instead of hydrogen evolution reaction. This was mainly because of the high overpotential of the hydrogen evolution reaction on the Zn electrode, so the deposition efficiency of Zn²⁺ in neutral or weakly acidic solutions was nearly 100% [26,27]. Previous tests for Cu/Zn-TRAB have also shown that the deposition efficiency was close to 100% [23]. The open circuit voltages of the discharge and charge were about 1.4 V and 0.65 V respectively, so a voltage difference of 0.75 V can be used for net energy outputs (Fig. 2A). As the current density increased, the voltage difference gradually decreased (Fig. 2A). However, as long as the charging current density was small enough (< 50 A m⁻²), the Cu/Zn-TRAFB at most of the discharging conditions could achieve high-voltage discharge and low-voltage charge.

3.2. Optimization of electrolyte concentrations

The battery power density in the discharge process is a key parameter to evaluate the ability of a technology to convert waste heat into electrical energy. Therefore, the influences of the concentrations of (NH₄)₂SO₄, Cu²⁺/Zn²⁺ and NH₄OH on the power productions of a single Cu/Zn-TRAFB were investigated. (NH₄)₂SO₄ is used as the supporting electrolyte, and its main function is to promote the conductivity of the solution and reduce the internal resistance of the battery. But at the same time, its presence will produce a reaction resistance, which is bad for power outputs and limits the excessive increase in its concentration [18]. Additionally, ionized NH₄⁺ helps to inhibit the ionization of NH₄OH and enhance the activity of NH₃. Increasing the (NH₄)₂SO₄ concentration from 1 M to 2 M, the peak power density was reduced from 77 W m⁻² to 70 W m⁻² (Fig. 3A). When the concentration of (NH₄)₂SO₄ was lowered from 1 M to 0.5 M, the peak power density was improved from 77 W m⁻² to 84 W m⁻² (Fig. 3A). These results showed that the increase of ohmic resistance of the electrolytes had little effect on the power production, and the increasing reaction resistance at higher concentrations was the decisive factor. Increasing the concentration of Cu²⁺/Zn²⁺ from 0.1 M to 0.4 M significantly enhanced the peak power density (77 W m⁻², 0.1 M; 148 W m⁻², 0.2 M; 196 W m⁻², 0.3 M; 252 W m⁻², 0.4 M, Fig. 3B), which was mainly...
owing to improved cathode potentials with increasing Cu$^{2+}$ concentrations (Fig. S2). Continuing to increase the concentration of Cu$^{2+}$/Zn$^{2+}$ to 0.5 M did not further increase the peak power density (Fig. 3B). The cathode potential was no longer enhanced, but the concentration of free NH$_3$ in anolyte decreased at higher Zn$^{2+}$ concentration, making the anode potential shift positively and thereby limiting further improvement in power production (Fig. S2). When the concentration of NH$_4$OH was reduced from 2 M to 1 M, the peak power density decreased from 252 W m$^{-2}$ to 152 W m$^{-2}$, but a higher NH$_4$OH concentration of 3 M led to a slight deterioration of peak power density to 247 W m$^{-2}$ (Fig. 3C). Higher NH$_4$OH concentrations contributed to promote the anode performance, but ionized more OH$^-$, the OH$^-$ and NH$_3$ molecules could permeate through the anion exchange membrane and react with Cu$^{2+}$ in catholyte, resulting in self-discharge and weakening the power outputs [20].

Based on the above experimental results, the optimal combination of electrolyte concentrations for Cu/Zn-TRAB were 0.5 M (NH$_4$)$_2$SO$_4$, 0.4 M Cu$^{2+}$/Zn$^{2+}$, and 2 M NH$_4$OH, which was different from the results of Cu/Zn-TRAB (1 M (NH$_4$)$_2$SO$_4$, 0.1 M Cu$^{2+}$/Zn$^{2+}$ and 2 M NH$_4$OH). For (NH$_4$)$_2$SO$_4$, since the spacing of electrodes in flow battery was only 3 mm (compared to the 20–25 mm for previous Cu/Zn-TRAB [23]), a smaller supporting electrolyte concentration could be used without being affected by a larger ohmic resistance. However, 0.5 M (NH$_4$)$_2$SO$_4$ would cause the anolyte to ionize more OH$^-$, and some blue precipitates attached to the cathodic side of AEM after the test. Considering that the concentration of (NH$_4$)$_2$SO$_4$ had a relatively small impact on power output, 1 M (NH$_4$)$_2$SO$_4$ was selected as the supporting electrolyte in subsequent experiments. The ratios of electrode area to electrolyte volume (667 m$^2$ m$^{-3}$) and membrane area (1 m$^2$ m$^{-2}$) compared to previous battery device (5.7 m$^2$ m$^{-3}$ and 0.23 m$^2$ m$^{-2}$) had been improved substantially, so greater concentrations of reactants were required, especially the cathodic Cu$^{2+}$. The increase of anodic Zn$^{2+}$ concentration reduced the free NH$_3$ concentration, but it had less effect on the anode potentials (Fig. S2). For NH$_4$OH, when the NH$_4$OH concentration increased from 2 M to 3 M in the previous Cu/Zn-TRAB test, the peak power density decreased sharply [23]. But in the current flow battery tests, the power output of 3 M NH$_4$OH was slightly smaller than the case of 2 M, which indicated that the demand for NH$_4$OH concentration was increased. Besides, no precipitate formed after adding 1 M NH$_4$OH to a solution containing 0.4 M Zn$^{2+}$, demonstrating that zinc-ammonia complex Zn(NH$_3$)$_2$$^{2+}$ existed in various forms ($n = 1, 2, 3, 4$).

3.3. Effect of flow rate on power output

Fig. 4 showed the peak power density of a single Cu/Zn-TRAFB cell at different electrolyte flow rates. When the flow rate was increased from 1 mL min$^{-1}$ to 8 mL min$^{-1}$, the peak power density was improved from 252 W m$^{-2}$ to ~280 W m$^{-2}$, mainly due the accelerated mass transfer within the flow channels. But a further increase of flow rate to 20 mL min$^{-1}$, the peak power output was approximately the same, which was owing to the limitation of the reaction kinetic rate under sufficient mass transfer. In this flow battery system, the Reynolds number (Re) was about 11 at a flow rate of 20 mL min$^{-1}$, the electrolyte flows could be regarded as laminar flow. At large flow rates, the flow pressure drop increased, causing power loss. According to the formulas of pressure drop and power loss ($\Delta P = \frac{f \cdot \rho \cdot Q^2}{2d}$ and $P_{\text{loss}} = \frac{\mu Q}{d}$) [24], the pressure drop was only about 0.2 Pa at a flow rate of 20 mL min$^{-1}$ and the corresponding power loss was $7 \times 10^{-5}$ W m$^{-2}$, which was negligible. The reason for the smaller

![Fig. 3. Power outputs of a single Cu/Zn-TRAFB cell with different electrolytes at a flow rate of 1 mL min$^{-1}$. (A) (NH$_4$)$_2$SO$_4$ [0.1 M CuSO$_4$ in the catholyte, and 0.1 M ZnSO$_4$ and 2 M NH$_4$OH in the anolyte]; (B) CuSO$_4$/ZnSO$_4$ [1 M (NH$_4$)$_2$SO$_4$ in the catholyte, and 1 M (NH$_4$)$_2$SO$_4$ and 2 M NH$_4$OH in the anolyte]; (C) NH$_4$OH [0.4 M CuSO$_4$, and 1 M (NH$_4$)$_2$SO$_4$ in the catholyte, and 0.4 M ZnSO$_4$ and 1 M (NH$_4$)$_2$SO$_4$ in the anolyte].

![Fig. 4. Peak power density of a single Cu/Zn-TRAFB cell at various flow rates with 0.4 M CuSO$_4$ in the catholyte, and 0.4 M ZnSO$_4$ and 2 M NH$_4$OH in the anolyte, using 1 M (NH$_4$)$_2$SO$_4$ as the supporting electrolyte.](image-url)
pressure drop was that the thickness of the flow channel was 1.5 mm and relatively large. The peak power density of 280 W m\(^{-2}\) based on the membrane area was greatly enhanced compared to the 120 W m\(^{-2}\) previously obtained by a Cu/Zn-TRAB [23], which meant that with the same membrane area (or cost, because the cost of the membrane in this battery system was the highest), Cu/Zn-TRAFB could provide more than twice the power output. The maximum power density of a Cu-TRAFB with similar flow battery device was only 45 W m\(^{-2}\) (15 kW m\(^{-3}\)) [19], and Cu/Zn-TRAFB herein increased the power density by more than six times without extra costs. The peak power density achieved by Cu/Zn-TRAFB normalized to the reactor volume was 93 kW m\(^{-3}\), which had a significant improvement over the 1.5 kW m\(^{-3}\) obtained with Cu/Zn-TRAB [23], mainly attributed to the compact battery structure design.

3.4. Net energy production and energy conversion efficiency

The net energy density of the Cu/Zn-TRAFB at peak power output was examined with optimum electrolyte concentrations and flow rate (Fig. 5A and B). The cell was discharged at an external resistance of 4 \(\Omega\). The maximum voltage of 1.4 V, and the discharge power density of 50 A m\(^{-2}\) was applied in the charge process.

The peak power density reached \(~280\) W m\(^{-2}\) during discharging (Fig. 5B). The constant load discharge increased the discharge current and greatly reduced the battery voltage to 0.98 V, which extremely weakened the discharge energy density (Fig. 5A). As the discharge capacity increased, the discharge voltage gradually decreased. The charge voltage was 0.76 V with a constant current density of 50 A m\(^{-2}\) and increased with charge capacity. When the capacity was 240 mAh, the net energy density reached the maximum value of 1280 Wh m\(^{-3}\)\(\text{m}_{\text{anolyte}}\) \(^{-3}\), which was higher than 598 Wh m\(^{-3}\)\(\text{m}_{\text{total electrolyte}}\) \(^{-3}\) with the maximum power density of 120 W m\(^{-2}\) received by the Cu/Zn-TRAB [23], primarily due the higher Cu\(^{2+}\) concentration. Discharging with a lower current density can significantly boost the net energy density, but the power output will be reduced. In addition, a lower charging current density also helps lower the charge voltage and increase the net energy density.

By measuring the mass change of electrodes before and after the experiments, the cathodic and anodic coulombic efficiencies during discharging were calculated to be about 100% and 80%, respectively, which were similar to previous studies [23]. It was showed that there was no side reactions in the deposition process of Cu\(^{2+}\), and excess zinc was oxidized. The cathodic coulombic efficiency during the charge process was approximately 115%, and the anodic coulombic efficiency was about 32%. It indicated that the deposition of Zn\(^{2+}\) mainly occurred in the cathode, and the part higher than 100% may be due to the adsorption of a small amount of Zn(OH)\(_2\) on the surface of Zn electrode, resulting in slightly heavier electrode mass. As the OH\(^{-}\) and NH\(_3\) molecules passed through the membrane, some Zn(OH)\(_2\) was formed and absorbed on Zn electrode at the end of charge, and this phenomenon was observed after the test. The anodic coulombic efficiency of copper was lower, similar to that obtained by Cu-TRAB [18] and Cu-TRAFB [19], and the main reason was that Cu(NH\(_3\))\(_4\)\(^{2+}\) was partially reduced to Cu(NH\(_3\))\(_2\)\(^{2+}\) and Cu\(_2\)(NH\(_3\))\(_4\)\(^{2+}\) during the oxidation of copper [24]. As shown by cyclic voltammetry (CV) curves in Fig. S3, the first reduction peak had begun to form during the formation process of oxidation peak, and the occurrence of reduction current could offset a portion of the oxidation charge and led to a lower coulombic efficiency. The coulombic efficiency of Zn as the anode was much higher that of Cu anode. From the CV curves, it was found that there was no reduction peak near the potential of Zn oxidation peak (Fig. S9). However, the coulombic efficiency of Zn anode is not 100%, which is not unilateral and needs be explored in future studies.

Based on a distillation column model established in Aspen HYSYS (Fig. S1) [18,23], the thermal energy required to separate 2 M NH\(_3\) from the anolyte in a closed cycle was about 372 kW h m\(^{-3}\)\(\text{m}_{\text{anolyte}}\). The distillation column has an inlet temperature (T\(_{\text{in}}\)) of 27 °C, a reboiler temperature (T\(_{\text{r}}\)) of 70.9 °C and a condenser temperature (T\(_{\text{c}}\)) of 43 °C [18,22,24]. The calculated thermoelectric conversion efficiency was 0.34% (2.7% relative to the Carnot efficiency) in the case of maximum power output, which met the necessary condition for the commercial application of technologies to convert thermal energy into electricity (the Carnot-relative efficiency reached the range of 2% ~ 5%) [28]. At the maximum power output, the energy density is relatively small [25]. The method of enhancing the net energy density was also suitable for improving the thermal energy efficiency. Moreover, if the inlet temperature of distillation column was raised to 50 °C and the condenser temperature was lowered to 34 °C, the energy conversion efficiency could be increased to 1.64% (27% relative to the Carnot efficiency), indicating that the distillation parameters had a decisive effect.

3.5. Scalability of Cu/Zn-TRAFB

To examine the scalability of this flow battery system, the performance of two Cu/Zn-TRAFB cells connected in series and parallel were investigated (Fig. 6A and B). Fig. 1D and E showed the connections of two cells in parallel and series. The catholyte and anolyte flowed into the two cells separately through the peristaltic pumps, and the effluent electrolytes were collected and flowed back to the respective reservoirs (Fig. 1D and E). Two cells were connected in series for increasing the voltage of the entire battery system to 2.75 V, which was about twice the single cell voltage of 1.4 V, and the difference in maximum current was small (Fig. 6A). The parallel connection of two cells approximately...
It was seen from Fig. 7A that the minimum charge density were stable at 1.34 ± 0.02 V and 27 ± 1 W m⁻², respectively. The above results indicated that the system performance remained relatively stable in successive cycles. The maximum value of the deposition potential of the cathodic Cu²⁺ in discharge cycles was about 0.26 ± 0.01 V, and the most negative value of Zn anode potential was also around at −1.16 ± 0.01 V (Fig. 7B). Correspondingly in the charge cycles, the most positive values of the Zn²⁺ deposition potential and Cu oxidation potential were stable at −0.84 ± 0.005 V and −0.16 ± 0.01 V, respectively (Fig. 7B). These results demonstrated that the copper and zinc electrodes maintained good reversibility in the cyclic oxidation and reduction reactions.

4. Discussion

To avoid some of the shortcomings of previous B-TRAB devices, a cost-effective and structure-compact Cu/Zn-TRAFB was developed and investigated from several aspects, such as power and energy densities, efficiency and system stability. The Cu/Zn-TRAFB with optimal electrolytes and flow rate produced a peak power density of 280 W m⁻² based on the membrane area (93 kW m⁻³ based on the reactor volume), which was greater than that of reported by other liquid-based thermoelectric conversion batteries or systems up to now (Fig. 8). The previous Cu/Zn-TRAB (118 W m⁻² or 1.5 kW m⁻³) [23] and Cu-TRAFB (45 W m⁻² or 15 kW m⁻³) [19] had relatively excellent power output performance, but they were far less than that obtained here owing to their incompact reactor or low cell voltage. Using a new BTMA PPO-based AEM [20] or ethylenediamine as a ligand for metal ions [21] both could further increase the power density of Cu/Zn-TRAFB.

Under the condition of generating maximum power density, the Cu/Zn-TRAFB received a net energy density of 1280 Wh m⁻³, which was the highest compared to other methods. A relatively high energy density of 1260 Wh m⁻³ obtained by a Cu-TRAFB at a constant load of 2Ω was similar to the result herein, but its peak power density was only 20 W m⁻² and lower than the maximum (45 W m⁻²) it could reach [19]. A lower current density for charging and discharging can significantly enhance the net energy density, but decrease the power output at the same time.

An energy conversion efficiency of 0.34% (2.7% of the Carnot efficiency) was received herein in the case of maximum power density, which was lower than the 0.7% (5% of the Carnot efficiency) reported with a Cu-TRAFB [19], because the Cu/Zn-TRAFB needed two thermal regeneration processes in one closed cycle and consumed twice as much thermal energy, but the peak power density was promoted by more than ten times. This Carnot-relative efficiency of 2.7% was higher than that of 1.4% by a TEC using carbon multi-walled nanotube (MWNT) electrodes [15], but much lower than those obtained by a TREC (25%) [11] without heat recuperation and an optimized TOEC process (34%) [13] at a pressure of 50 bar. However, the TREC's Carnot-relative efficiency of 25% was calculated based on the theoretical electrolytes, electrodes mass and volume instead of the parameters of experimental battery device, which substantially reduced the heat absorption and increased the efficiency [11]. The efficiency of TOEC processes was directly determined by the working pressure and membrane performance, but it was impossible to achieve too high pressure under experimental conditions currently, and an efficient heat exchanger was needed for reaching such efficiency [12,13]. The Cu/Zn-TRAFB here did not need too strict working conditions, and no heat exchangers were used during the thermal regeneration process. In addition, the energy conversion efficiency of Cu/Zn-TRAFB could be improved by using the approaches described above for increasing the energy density and optimizing the thermal regeneration process. For example, the energy conversion efficiency could be enhanced to 1.64% (27% of the Carnot efficiency) by elevating the inlet temperature from 27 to 50°C and lowering the condenser temperature from 43 to 34°C. Moreover, among the B-TRAFBs, the Ag/Cu-TRAFB may obtain higher energy density and efficiency due to the lowest charging voltage theoretically.

3.6. System stability and electrode reversibility

The Cu/Zn-TRAFB system needs to work in a continuous mode of closed cycles, in which the catholyte and anolyte flow through the system circularly and copper and zinc electrodes also undergo cyclic oxidation and reduction reactions. Therefore, the stability of battery system performance and redox reversibility of the electrodes were investigated in 10 cycles (Fig. 7A and B). The cell was discharged and charged for 15 min alternately at a constant current of 16 mA, and there was 5 min interval between the discharge and charge cycles to drain the electrolytes in the system and exchange the electrolytes in the catholyte and anolyte. Previous studies [18,23] had demonstrated that the thermal regeneration process could be implemented and it also had been performed in energy testing experiments, so no regenerative electrolytes were used in this tests. Besides, in order to eliminate the influence of electrolyte concentration changes on voltage and power output, fresh and identical electrolytes were used for each discharge or charge cycle. In discharge cycles, the Cu²⁺ was deposited to Cu on copper electrode, and the zinc electrode was oxidized under the effect of NH₃. Both the maximum discharge voltage and the peak power density were stable at 1.34 ± 0.02 V and 27 ± 1 W m⁻² (Fig. 7A). The maximum values of discharge cycle 1 and 6 were slightly higher, because the flow paths were flushed with ultrapure water after the fifth charge cycle, excluding the impacts of residual NH₃. During the charge process, the copper electrode was oxidized and the Zn²⁺ was reduced on the zinc electrode. It was seen from Fig. 7A that the minimum charge voltage and input power were uniform at about 0.7 ± 0.02 V and 14 ± 0.5 W m⁻², respectively.

![Fig. 6. (A) Voltage and (B) power output of two Cu/Zn-TRAFB cells that were connected in series and parallel, compared with the single Cu/Zn-TRAFB cell operating at a flow rate of 1 mL min⁻¹ with 0.4 M CuSO₄ and 1 M (NH₄)₂SO₄ in the catholyte, and 0.4 M ZnSO₄, 1 M (NH₄)₂SO₄ and 2 M NH₄OH in the anolyte.](image-url)
5. Conclusions

The copper/zinc bimetallic thermally-regenerative ammonia-based battery (Cu/Zn-TRAFB) system developed in this work can convert low-grade waste heat energy into electrical energy with low material costs and good performance. The compact bimetal electrodes and flow channels stacked design realized high-voltage discharge and low-voltage charge at room temperature and overcame the shortcomings of the previous Cu/Zn-TRAB with large internal resistances and low membrane utilization rates. A peak power density of 280 W m\(^{-2}\) was obtained at optimum electrolyte concentrations and flow rates, achieving a significant improvement compared to previous liquid-based thermoelectric conversion systems. In the case of maximum power density, the net energy density of the battery was 1280 Wh m\(^{-3}\) anolyte, which was higher than those reported by ammonia-based batteries or systems under similar conditions. The thermoelectric conversion efficiency was 0.34\% (2.7\% relative to the Carnot efficiency). By elevating the distillation column inlet temperature and lowering the condenser temperature, the thermoelectric conversion efficiency could be further increased to 1.64\% (27\% relative to the Carnot efficiency). The Cu/Zn-TRAFB system also showed good scalability and cycle stability.

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Appendix A. Supplementary data

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References
