

Performance of an all-aqueous thermally regenerative flow battery using CNT/carbon cloth composite electrode

Si Li^{1,2}, Yichao An^{1,2}, Jieyu Jia^{1,2}, Liang Zhang^{1,2*}, Jun Li^{1,2}, Qian Fu^{1,2}, Xun Zhu^{1,2}, Qiang Liao^{1,2}

1 Key Laboratory of Low-grade Energy Utilization Technologies and Systems, Chongqing University, Ministry of Education, Chongqing, 400030, China

2 Institute of Engineering Thermophysics, School of Energy and Power Engineering, Chongqing University, Chongqing, 400030, China
(*Corresponding Author: liangzhang@cqu.edu.cn)

ABSTRACT

All-aqueous thermally regenerative battery (ATRB) is a promising technology for converting low-grade waste heat into electricity while the low specific surface area of electrodes limits its performance. In this study, a porous composite electrode by modifying carbon cloth with carbon nanotubes (CNT/CC) is developed to promote battery performance, and the effect of CNT loading amount is analyzed. The results indicate that the porous composite electrode has a significantly larger specific surface area, resulting in a 37.4% increase in battery performance compared to ATRB with the traditional carbon cloth (CC) electrode. In addition, ATRB performance initially rises and then declines with the increasing carbon nanotube loading. The optimal loading (4 mg) induces a peak power density of 492.6 W/m², which is competitive for future practical applications of ATRBs.

Keywords: All-aqueous thermally regenerative flow battery, composite electrode, specific surface area, energy systems for power generation, environment and carbon nanotube loading

NONMENCLATURE

Abbreviations

ATRB	All-Aqueous Thermally Regenerative Battery
CNT/CC	Carbon Nanotube/Carbon Cloth
CC	Carbon Cloth
TRB	Thermally Regenerative Battery
NMP	N-methyl-2-pyrrolidone
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy

EIS	Electrochemical impedance spectroscopy
CV	Cyclic voltammetry

1. INTRODUCTION

In industrial production, a significant quantity of low-grade thermal energy (temperature <130 °C) is produced [1]. Transforming this thermal energy into electricity is conducive to reducing carbon emissions and alleviating the energy crisis [2]. Currently, there are different technologies available to convert low-grade thermal energy to electricity. These include solid-state thermoelectric systems [3, 4], organic Rankine cycle systems [5, 6], and thermo-osmotic energy conversion systems [7, 8]. However, these techniques are relatively expensive and intricate, limiting their practical application and development.

Thermally regenerative ammonia-based battery (TRB) is a new technology that converts low-grade thermal energy into electricity [9]. In order to improve TRB performance, some researchers have directed their attention toward enhancing electrode structures. A three-dimensional porous foam copper electrode has been proposed to increase electrode surface area and power generation. This led to a 38% increase in maximum power density compared to conventional copper plate electrodes [10]. A Cu/Ni composite electrode with a high specific surface area and structural stability has been introduced to enhance electrode stability and anode coulomb efficiency. In comparison to TRB with foam copper electrodes, this innovation resulted in an 82% improvement in maximum power density [11]. To improve TRB power generation performance, a porous composite electrode was fabricated using biomass waste. Due to its higher specific

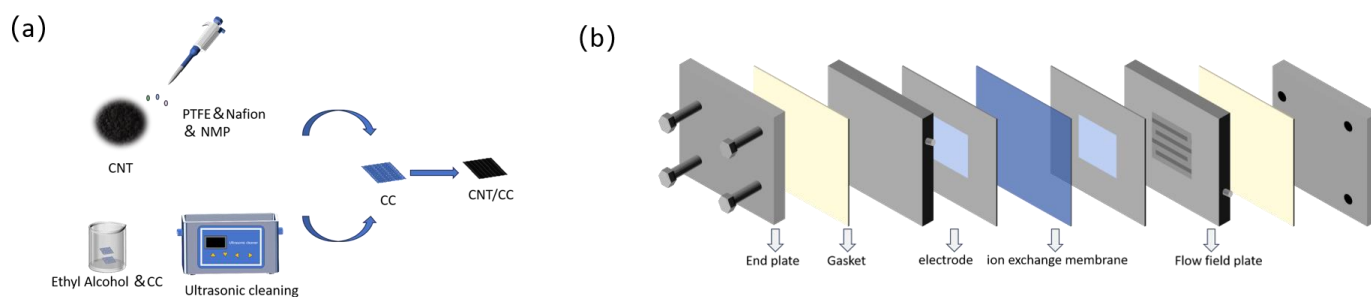


Fig. 1. Schematic diagram of electrode preparation (a) and compact reactor (b)

surface area and a stratified porous structure conducive to mass transfer, this approach achieved a peak TRB power density of 81.6 W/m^2 [12].

Additionally, the investigation of reactor structures was explored. The operational parameters of TRBs had a significant impact on performance. Within a certain range, reducing the electrode spacing diminished the ohmic resistance, thereby enhancing TRB performance [13]. In the pursuit of enhancing reactor efficiency, a new compact reactor design was developed that utilized a stacked structure of solid copper plates, spacers, and membranes to achieve a closely packed arrangement. In comparison to preceding TRB configurations, this compact reactor achieved a higher power density of 45 W/m^2 [14]. To improve cell voltage and power density, a study was conducted on a compact copper/zinc bimetallic thermally regenerative ammonia fuel cell. A single cell could achieve a peak power density of up to 280 W/m^2 due to the reactor's compact structure and elevated voltage. High specific surface area electrodes and compact reactor designs are advantageous for TRB performance.

However, traditional thermally regenerative batteries relied on thermodynamically unstable reactions involving the deposition and dissolution of copper metal, making recycling difficult and reducing coulomb efficiency, thus imposing limitations on practical applications. To address these challenges, all-aqueous thermally regenerative batteries (ATRB) were proposed. In the ATRB design, ligands are employed to stabilize Cu(I) and Cu(II) ions within the electrolyte. This innovation leads to enhancements in coulomb efficiency, open-circuit voltage, and power density. Using carbon cloth as an electrode in the ATRB yielded a maximum power density of 350 W/m^2 [15]. Currently, the specific surface area of the electrodes remains relatively low, which limits the ATRB performance.

Therefore, for enhancing ATRB performance, it is imperative to design electrode materials with high specific surface areas. In this regard, carbon nanotubes

offer distinct advantages due to their expansive specific surface area and exceptional conductivity. Carbon cloth emerges as a frequently utilized current collector due to its cost-effectiveness and stable electrochemical attributes. Loading carbon nanotubes on the carbon cloth can effectively increase the specific surface area of the electrode, thus improving the performance of ATRB.

This study employs a compact reactor and a CNT/CC composite electrode with a high specific surface area to enhance the performance of ATRB. The microstructure of the electrode was characterized, the feasibility of electricity generation was studied, and the preparation parameters (carbon nanotube loading amount) were optimized.

2. MATERIALS AND METHODS

2.1 Preparation of CNT/CC composite electrode

In this experiment, carbon cloth was used as the base material. Initially, the carbon cloth was trimmed to dimensions of $2 \text{ cm} \times 2 \text{ cm}$, and then underwent multiple rounds of ultrasonic cleaning using anhydrous ethanol, followed by rinsing with deionized water to ensure the elimination of surface impurities from the carbon cloth. Subsequently, the dried carbon cloth was designated as CC.

Carbon nanotubes, acetylene black, PTFE, and nafion solutions were mixed in N-methyl-2-pyrrolidone (NMP) at a mass ratio of 7:2:0.5:0.5, then coated onto treated carbon cloth and dried at 80°C overnight to obtain CNT/CC (Fig. 1a).

2.2 Construction and operation of TRAB

The compact reactor used for the full battery performance test consisted of titanium plates with serpentine flow field plates, aluminum end plates, CNT/CC composite electrodes, a proton exchange membrane, and gaskets (Fig 1b). In the test, the electrolyte was consistently pumped through the flow channel and circulated into the battery, subsequently

returning to the reservoir at a steady flow rate. For the half-cell testing, a three-electrode system was adopted, including a calomel reference electrode, a platinum counter electrode, and the CNT/CC composite electrode. A battery was also fabricated using carbon cloth under the same conditions to facilitate comparison.

The cathode electrolyte was formulated using a solution containing 5 M ammonium bromide and 0.5 M copper bromide. In the anode electrolyte, the inclusion of 5 M ammonia in the mixture of 5 M ammonium bromide and 0.5 M cuprous bromide established a potential difference.

2.3 Characterization and measurements

To understand the properties of CNT/CC composite electrodes, various material characterizations were conducted. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to understand the electrode morphological characteristics. The physical adsorption method is to analyze nitrogen adsorption-desorption profiles and the specific surface area of the electrode.

For polarization testing, linear sweep voltammetry was executed employing the Biological electrochemical workstation. In order to calculate the battery power density, the projected area (4 cm²) underwent normalization. The electrochemical impedance spectroscopy (EIS) assessment was conducted within the 100 kHz to 0.1 kHz frequency range. Cyclic voltammetry (CV) was performed at an electrochemical workstation.

3. RESULTS AND DISCUSSION

3.1 Electrode characterization

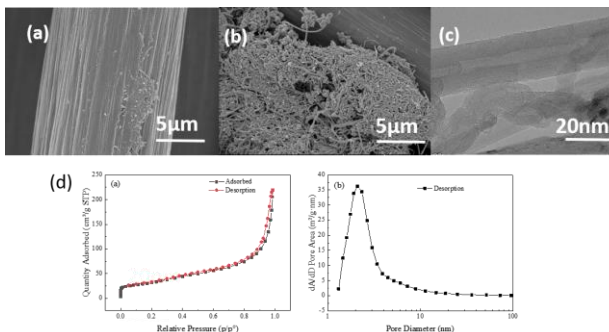


Fig. 2. SEM images of CC electrode (a) and CNT/CC composite electrode (b) TEM image of CNT (c) physical adsorption

In this study, the CNT/CC composite electrode was fabricated through the application of a scraping-coating method. To examine the surface microstructure of this composite electrode, a comparative analysis was

performed using SEM to contrast the morphology of the CC electrode with that of the CNT/CC composite electrode. The CC electrode, predominantly composed of carbon fibers, exhibited a sleek surface texture on the carbon cloth fibers (Fig 2a). Conversely, in the CNT/CC composite electrode (Fig 2b), an aggregation of carbon nanotubes was apparent on the carbon fiber surface, the nanotubes intertwined and interconnected, forming a diverse and rich porous structure. Furthermore, a detailed examination through TEM revealed the well-defined linear hollow tubular structure of the carbon nanotubes (Fig 2c), which facilitated substance transport channels. Simultaneously, to determine the specific surface area and pore size distribution of the CNT/CC composite electrode, the physical adsorption method was conducted (Fig 2d). The results showed that the specific surface area of the CNT/CC composite electrode is 115.4 m²/g, which was significantly higher than that of the CC electrode. The adsorption and desorption curve was a type II curve. At high relative pressures, gas molecules entered pores rapidly and occupied them, while at low relative pressures, the pores gradually become saturated, indicating the presence of a mesoporous structure. According to the pore size distribution of the CNT/CC composite electrode, the mesoporous structure with pore size mainly between 2-4 nm provided more reaction sites and facilitated mass transfer. The above results showed that the CNT/CC composite electrode has a high specific surface area, which was expected to improve the ATRB performance.

3.2 Construction and operation of TRAB

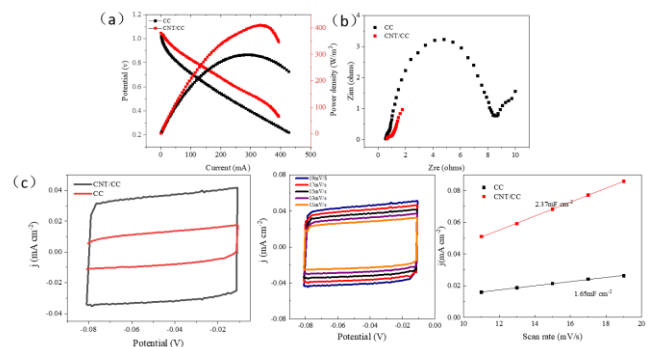


Fig. 3. Power generation (a), Nyquist plots of the whole-cell impedance (b), and CV test (c) of the ATRB-CNT/CC and ATRB-CC.

To study the performance of the CNT/CC composite electrode at ATRB, the polarization test was conducted on the CNT/CC composite electrode (carbon nanotube load =5 mg, flow rate =30 mL/min), and the ATRB performance was compared with that of the CC electrode. As shown in Fig 3a, The ATRB with two

electrodes had a close open circuit voltage (1 V), however, the polarization curve of the ATRB-CNT/CC showed a smaller polarization loss than the ATRB-CC, and the lower voltage drop indicated a faster reaction kinetics and a smaller ohmic loss. The ATRB-CNT/CC exhibited a notable increase in maximum power density, reaching 409.6 W/m², which is 37.4% higher than that of ATRB-CC (298.1 W/m²). Concurrently, the EIS test presented in Fig 3b indicated a substantial reduction in ohmic internal resistance for ATRB with the CNT/CC composite electrode. The outcomes of the CV test (Fig 3c) revealed that the CNT/CC composite electrode yielded a higher current than the CC electrode, which indicated that the CNT/CC composite electrode had excellent electrochemical performance of charge and discharge. In addition, the double layer capacitance of the CNT/CC composite electrode was 2.37 mF/cm², which was 43.6% higher than that of the CC electrode (1.65 mF/cm²), indicating that the CNT/CC composite electrode had a higher active specific surface area.

The above results indicated that the electricity generation performance of ATRB-CNT/CC was higher than ATRB-CC, and could be further optimized to improve battery performance.

3.3 Effect of carbon nanotube loading amount

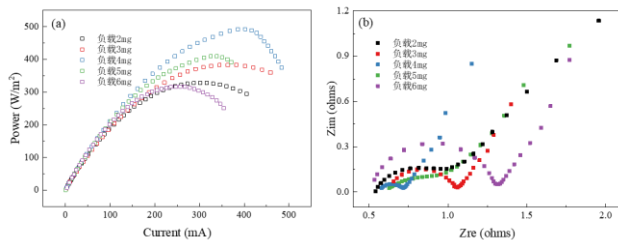


Fig. 4. Power generation (a), Nyquist plots of the whole-cell impedance (b) of different carbon nanotube loading amount

CNT/CC composite electrodes with different loading capacities were prepared and tested to investigate the effect of carbon nanotube loading on ATRB. The power curves of ATRB under different loading amounts were depicted in Fig. 4, revealing a trend of performance enhancement followed by a decline with increasing loading. As the load increased from 2 mg to 4 mg, the maximum power density of ATRB increased from 316.0 W/m² to 492.6 W/m², indicating a performance improvement of 55.9%. This enhancement was due to the increase of the carbon nanotubes on the CC, resulting in more reaction sites and reduced ohmic internal resistances, consequently improving ATRB performance. However, with a further increase in loading to 6 mg, the maximum power density of ATRB decreased to 317.0

W/m². This decline can be attributed to the accumulation and aggregation of carbon nanotubes caused by excessive carbon nanotubes coated on the carbon cloth, leading to a detrimental effect on battery performance. Hence, the optimal CNT loading was determined to be 4 mg, at which ATRB achieved its peak performance.

4. CONCLUSIONS

In order to enhance the performance, a CNT/CC composite electrode was constructed, and the effects of carbon nanotube loading amount on the performance of batteries were studied. The main research findings can be outlined as follows:

- (1) The CNT/CC composite electrode had a high specific surface area (115.4 m²/g) and abundant mesoporous structure.
- (2) The maximum power density of ATRB-CNT/CC (409.6 W/m²) was 43.6% higher than that of ATRB-CC.
- (3) At a loading level of 4 mg, the battery performance was further improved, yielding the highest power density of 492.6 W/m².

ACKNOWLEDGEMENT

This work was supported by the National Natural Science Foundation of China (No. 51976018), Innovative Research Group Project of the National Natural Science Foundation of China (No. 52021004), Natural Science Foundation of Chongqing, China (CSTB2022NSCQ-MSX1596), and Scientific Research Foundation for Returned Overseas Chinese Scholars of Chongqing, China (No. cx2021088).

DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

REFERENCE

- [1] Yu B, Duan J, Cong H, et al. Thermosensitive crystallization-boosted liquid thermocells for low-grade heat harvesting. *Science* 2020;370:342.
- [2] He Y, Li T, Chen Q, et al. A novel pump-free organic Rankine cycle with the efficient utilization of unsteady low-grade heat. *J Clean Prod* 2021;313.
- [3] Cheng H, He X, Fan Z, et al. Flexible Quasi-Solid State Ionogels with Remarkable Seebeck Coefficient and High Thermoelectric Properties. *Adv Energy Mater* 2019;9.
- [4] Zabek D, Morini F. Solid state generators and energy harvesters for waste heat recovery and thermal energy harvesting. *Therm Sci Eng Prog* 2019;9:235-47.

- [5] Lin C, Hsu P, He Y, et al. Investigations on experimental performance and system behavior of 10 kW organic Rankine cycle using scroll-type expander for low-grade heat source. *Energy* 2019;177:94-105.
- [6] Li D, He Z, Wang Q, et al. Thermodynamic analysis and optimization of a partial evaporating dual-pressure organic rankine cycle system for low-grade heat recovery. *Appl Therm Eng* 2021;185.
- [7] Li J, Zhang Z, Zhao R, et al. Stack Thermo-Osmotic System for Low-Grade Thermal Energy Conversion. *ACS Appl Mater Inter* 2021;13:21371-8.
- [8] Li W, Liu Y, Zhang Z, et al. Thermo-osmotic ionogel enabled high-efficiency harvesting of low-grade heat. *J Mater Chem A* 2021;9:15755-65.
- [9] Zhang F, Liu J, Yang W, et al. A thermally regenerative ammonia-based battery for efficient harvesting of low-grade thermal energy as electrical power. *Energ Environ Sci* 2015;8:343-9.
- [10] Zhang L, Li Y, Zhu X, et al. Copper Foam Electrodes for Increased Power Generation in Thermally Regenerative Ammonia-Based Batteries for Low-Grade Waste Heat Recovery. *Ind Eng Chem Res* 2019;58:7408-15.
- [11] Shi Y, Zhang L, Li J, et al. Cu / Ni composite electrodes for increased anodic coulombic efficiency and electrode operation time in a thermally regenerative ammonia-based battery for converting low-grade waste heat into electricity. *Renew Energ* 2020;159:162-71.
- [12] Chen P, Zhang L, Shi Y, et al. Biomass waste-derived hierarchical porous composite electrodes for high-performance thermally regenerative ammonia-based batteries. *J Power Sources* 2022;517.
- [13] Shi Y, Zhang L, Li J, et al. Effect of operating parameters on the performance of thermally regenerative ammonia-based battery for low-temperature waste heat recovery. *Chinese J Chem Eng* 2021;32:335-40.
- [14] Zhu X, Rahimi M, Gorski CA, et al. A Thermally-Regenerative Ammonia-Based Flow Battery for Electrical Energy Recovery from Waste Heat. *Chemsuschem* 2016;9:873-9.
- [15] Springer R, Cross NR, Lvov SN, et al. An All-Aqueous Thermally Regenerative Ammonia Battery Chemistry Using Cu (I , II) Redox Reactions. *J Electrochem Soc* 2021;168.