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A numerical model for a thermally-regenerative ammonia-based flow battery using for low grade waste heat recovery

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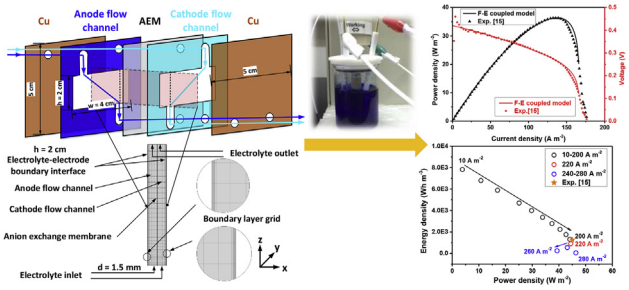
HIGHLIGHTS

- A stationary and a transient two-dimensional models were firstly developed for a TR-AFB.
- Parameters of electrode reaction kinetics were investigated.
- Appropriately reducing the initial Cu $(NH_3)_4^{2+}$ concentration promotes power and energy densities.
- The relation between the energy and power densities was given.

GRAPHICAL ABSTRACT



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ABSTRACT

A stationary and a transient two-dimensional models, based on the universal conservation laws and coupled with electrochemical reactions, are firstly applied to describe a single thermally-regenerative ammonia-based flow battery (TR-AFB), and emphasis is placed on studying the effects of reactant concentrations, physical properties of the electrolyte, flow rates and geometric parameters of flow channels on the battery performance. The model includes several experimental parameters measured by cyclic voltammetry (CV), chronoamperometry (CA) and Tafel plot. The results indicate that increasing NH_3 concentration has a decisive effect on the improvement of power production and is beneficial to use higher Cu^{2+} concentrations, but the endurance of membrane and self-discharge need to be considered at the same time. It is also suggested that appropriately reducing the initial Cu $(NH_3)_4^{2+}$ concentration can promote power and energy densities and mitigate cyclical fluctuation. The relation between the energy and power densities is given, and the models are validated by some experimental data.

1. Introduction

Harvesting the low-grade waste heat has drawn increasing attentions as it is a huge energy resource generated at many daily industrial processes [1]. Because the traditional solid-state devices for direct thermal-electric energy conversion are expensive and inefficient, liquid-based thermally regenerative batteries or cycle systems have gradually become potential technologies in recent years. According to the working principle, these technologies can be divided into the following three kinds: (1) Liquid-based thermal-electric energy conversion system based on the Seebeck effect, the typical examples are thermal-electrochemical cells using the redox couple [$Fe(CN)_6^{3-}$/ $Fe(CN)_6^{4-}$] [2–4] and thermally regenerative electrochemical cycle (TREC) [5–7]. (2) Energy conversion system from salinity differences at different

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temperatures, the typical examples are mixing entropy batteries (MEBs) [8,9] and distiller-electrochemical cell system [10]. (3) Thermo-osmotic energy conversion system, the typical example is steam membrane battery using the pressure difference at a given temperature difference [11]. The above-mentioned liquid-based thermally regenerative battery techniques allow a carbon neutral approach for the storage and conversion of low-grade waste heat into electrical power, with potentially low material cost and high efficiency. Moreover, these techniques are suitable for a large number of low-grade waste heat conversions on fixed devices, which benefits by the advantages of long-term stability and damage prevention. Despite great progress has been made in recent years, however, these batteries or cycle systems still produce low power densities. A maximum power density of 6.6 $W m^{-2}$ was produced in a thermal-electrochemical cell using the [$Fe(CN)_6^{3-}$/$Fe(CN)_6^{4-}$] redox couple and carbon nanotube aerogel sheet electrodes at a temperature difference of 51 °C (Carnot-relative efficiency of 3.95%) [3]. The use of ionic liquids enabled operation at higher temperatures (130 °C), but the maximum power density reached only 0.5 $W m^{-2}$ with a cobalt(II/III) tris(bipyridyl) ionic liquid and Pt black-coated electrodes [12]. A relatively high heat-to-electricity energy conversion efficiency of 5.7% was obtained by a thermally regenerative electrochemical cycle (TREC) between 10 and 60 °C, but the power density was estimated only about 0.5 $W m^{-2}$ when operated between 10 and 80 °C [5]. Mixing entropy batteries (MEBs) [8], distiller-electrochemical cell [10] and steam membrane battery [11] operate only with physical changes inside the system and without the formation of new substance, which limits their power densities about 6.3 $mW m^{-2}$ ~ 3.53 $W m^{-2}$.

An original concept of thermally regenerative ammonia-based battery (TRAB) [13] has recently been proposed for low-grade waste heat energy recovery. In the TRAB, the potential difference is generated from the ammonia concentration gradient between the anolyte and catholyte, and the charging process is the regeneration of ammonia from the anolyte by waste heat. There is no loss of electrode materials theoretically in the TRAB system, and the ammonia can be recycled. Besides, the battery system has lower costs, and it is possible to connect multiple cells in series or parallel for boosting voltage and power production. By optimizing the operating temperatures, TRAB yielded the maximum power and energy densities of 236 $W m^{-2}$ and 650 Wh m^{-3}, respectively [14]. To further enhance battery performance, a thermally-regenerative ammonia-based flow battery (TR-AFB) has been developed, achieving a maximum energy density of 1260 Wh m^{-3} and a thermal energy efficiency of 0.7% (5% relative to the Carnot efficiency) [15].

Establishing a reasonable numerical model is meaningful for optimized design and commercial development of the TR-AFB. However, compared to conventional batteries such as the lead-acid and lithium-ion batteries [16–19], there is not yet a model in the published literature to describe the TR-AFB during discharge. Only models (stationary or dynamic) of redox-flow batteries (RFBs), especially for the all-vanadium system, can be found and referenced for TR-AFB model establishment. Example for the all-vanadium redox-flow battery is a transient 2D model developed firstly by Shah et al. [20] until 2008. Recently, some 2D stationary [21,22] and non-isothermal [23–25] models were presented for studying the effects of electrode porosity, operating temperature, electrolyte viscosity and flow field on the battery performance and distributions of concentration and current. Besides, several 3D models [26–28] have been developed and the simulation results can provide the information in more details, especially the spatial distributions of velocity, concentration, overpotential and transfer current density. But most of the electrode kinetic parameters in these models are assumed or estimated. The essences of cathode and anode reactions in the ammonia-based flow battery are the deposition and corrosion of copper, respectively, but the electrolyte system involves high concentrations of NO_3^- and NH_4^+, which has fundamental differences compared with the common systems containing SO_4^{2-} or Cl^-. Therefore, some key data of the electrode reaction kinetics are also not referenced.

In this paper, two-dimensional stationary and transient models of the AFB were developed on the basis of an actual test reactor. It relies on the mass, charge and momentum conservation principles, flow-electrochemical coupling and some experimental parameters (such as kinetic parameters of electrode reactions, electrolyte conductivity and density). In order to be consistent with experimental conditions and verify the accuracy of the model, the porous electrode was not applied. There are three main purposes in this study, and firstly, we need to obtain the key parameters of electrode reaction kinetics. Then, we need to evaluate the precision of the stationary model, which is used for predicting the battery maximum power and current densities and optimizing the concentration and composition of electrolyte, geometry parameters of the reactor and flow field. Finally, the transient model is mainly used to detect the battery discharge performance on the time scale and forecast the achievable energy density and limiting factors.

2. Model developments

2.1. Working principle of the TR-AFB

A schematic representation of the thermally-regenerative ammonia-based flow battery is given in Fig. 1. Similar to the traditional flow battery structure, the external part is mainly composed of reservoirs, peristaltic pumps and power load. The battery module consists of copper electrodes (both the anode and cathode are copper plates, and also as the collectors), electrolyte flow channels, and an anion exchange membrane (AEM). In particular, the AFB only works in the discharging phase (as shown in the red dotted box). At cathode-catholyte interface, reduction of Cu^{2+} occurs as the reaction (1). The ammonia corrodes the copper at anode-anolyte interface as the reaction (2). No corresponding inverse reactions happen during charging. The electrode reactions [29] are as follows:

During the discharge:

$$\text{Cathode:} Cu^{2+} + 2e^- \rightarrow Cu \quad E^\circ = +0.34V \tag{1}$$

$$\text{Anode:} Cu + 4NH_3 \rightarrow Cu(NH_3)_4^{2+} + 2e^- \quad E^\circ = -0.04\,V \tag{2}$$

During the charge:

$$Cu(NH_3)_4^{2+} \overset{\Delta}{\rightarrow} Cu^{2+} + 4NH_3 \tag{3}$$

After the discharge, the waste heat can be used to heat the anolyte, then the anolyte becomes catholyte as a result of the evaporation of NH_3(aq). The ammonia vapor NH_3(g) is added into the catholyte, which turns into the anolyte, namely the thermal regeneration process (charging phase, as shown in the black dotted box). Therefore, by reversing the function of electrodes in the next discharge stage, theoretically, there is no net loss of copper. This paper focuses on the discharge phase that determines the battery power and energy densities.

2.2. Model geometry and assumptions

The actual flow paths of the ammonia-based flow battery and the two-dimensional geometric model with details on the meshing elements are shown in Fig. 2 (a) and (b), respectively. The two-dimensional geometric model is the *X-Z* plane of the flow reactor, and it contains five domains or boundaries: anolyte-anode interface boundary, anode flow channel, anion exchange membrane (AEM), cathode flow channel and catholyte-cathode interface boundary. The catholyte consists of $Cu(NO_3)_2$ and NH_4NO_3, and the anolyte is formed by adding a certain amount of $NH_3{\cdot}H_2O$ into the catholyte. These electrolytes are pumped into the flow channels from external reservoirs and react with copper electrodes, which generates the electricity. The main geometric dimensions of the model are marked in Fig. 2 and summarized in Table 1.

The model couples the flow field and electrochemical reactions, and each species is transported under the influences of diffusion, electro-