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 \(\text{Cu} (\text{NH}_3)_4^{2+}\) 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 \(\text{NH}_3\) concentration has a decisive effect on the improvement of power production and is beneficial to use higher \(\text{Cu}^{2+}\) 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 \(\text{Cu} (\text{NH}_3)_4^{2+}\) 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 \([\text{Fe(CN)}_6^{3-} / \text{Fe(CN)}_6^{4-}]\) \[2–4\] 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 $\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}$ 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$^{-2}$ $\sim$ 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. 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 essence 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 $\text{NO}_3^-$ and $\text{NH}_4^+$, which has fundamental differences compared with the common systems containing $\text{SO}_4^{2-}$ or $\text{Cl}^-$. 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 $\text{Cu}^{2+}$ 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:
\[
\text{Cathode:} \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \quad E' = +0.34 V \quad (1)
\]
\[
\text{Anode:} \text{Cu} + 4\text{NH}_3 \rightarrow \text{Cu} (\text{NH}_3)^{2+} + 2e^- \quad E' = -0.04 V \quad (2)
\]

During the charging:
\[
\text{Cu} (\text{NH}_3)^{2+} \overset{\Delta}{\rightarrow} \text{Cu}^{2+} + 4\text{NH}_3 \quad (3)
\]

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 $\text{NH}_3(aq)$. The ammonia vapor $\text{NH}_3(g)$ 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 $\text{Cu(NO}_3)_2$ and $\text{NH}_4\text{NO}_3$, and the anolyte is formed by adding a certain amount of $\text{NH}_3\cdot\text{H}_2\text{O}$ 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-
migration and convection. All the species in the electrochemical reactions satisfy the mass, charge and momentum transport and conservations, therefore, the whole numerical model is highly non-linear. For the purpose of simplification within a reasonable scope, the following assumptions have been made in the present study:

1. The effects of the thickness of the copper electrode are ignored, so the electrode is replaced by the electrolyte-electrode interface boundary. Similarly, the thickness variations caused by copper deposition and corrosion are smaller compared to the size of the reactor and also could be neglected.
2. The electrolyte flow is treated as incompressible flow.
3. An isothermal condition (298.15 K) is assumed for all domains, and physical properties of electrode, electrolyte and membrane are isotropic and homogeneous.
4. The viscosity of the electrolyte does not vary as the concentrations continuously change with the progress of electrode reactions.
5. Side reactions such as the formation of complexes with different

Fig. 1. Schematic representation of the TR-AFB to convert waste heat into electricity.

Fig. 2. (a) Configuration of each plate and flow paths. (b) Two-dimensional representation of the AFB used for the model with details on the meshing elements.
coordination numbers \((\text{Cu(NH}_3)_3^{2+}, \text{Cu(NH}_3)_2^{2+} \text{ and Cu(NH}_3)_3^{2+})\) and ionization of ammonia are not considered.

(6) The self-discharge phenomenon that a small quantity of NH3 and OH\(^-\) react with the catholyte is neglected.

2.3. Model development

In this section, the stationary and transient numerical models for the ammonia-based flow battery have been put forward. The main discrimination between them is that the stationary model can obtain a series of the steady-state physical quantities at a certain initial concentration and an applied current density, but the transient model describes the changes of the battery performance and concentration at the time scale. Moreover, there are some differences in the model structure. The stationary model does not include the pumps and reservoirs, and the inlet concentration of each species is constant. The transient model needs to consider the pumps and reservoirs, and the concentrations of the reactants in the reservoirs decrease and the concentrations of the products increase as the reactions progress. Therefore, the inlet concentrations vary continuously in the transient model, and this change is related to the flow rate of pump and the volume of electrolyte in the reservoirs.

2.3.1. Steady model

2.3.1.1. Control equations for electrolyte flow. The flow of liquid electrolyte through the channel is governed by the incompressible Navier-Stokes equations and the continuity equations [30]:

\[
\begin{align*}
\rho (\nabla \cdot \vec{u}) \vec{u} &= -\nabla p + \mu \nabla^2 \vec{u} \\
\nabla \cdot \vec{u} &= 0
\end{align*}
\]

(4)

(5)

where \(\vec{u}\) is the electrolyte velocity field, \(p\) is the pressure of the electrolyte, \(\rho\) is the density and \(\mu\) is the dynamic viscosity of the electrolyte. Both \(\rho\) and \(\mu\) are measured and calculated as constant values.

2.3.1.2. Conservation equations for mass transport. In the electrolyte flow channel, the transport of each species \(i\) is governed by the modified Nernst-Planck equation [32]:

\[
\vec{N}_i = -D_i \nabla c_i - \frac{z_i c_i D_i F}{RT} \nabla \phi_e + c_i \vec{u}
\]

(6)

Let \(c_i\) denotes the concentration of species \(i\) in the electrolyte, where \(i = \text{Cu}^{2+}, \text{NH}_3^+\) and \(\text{NO}_3^-\) in the catholyte and \(i = \text{Cu(NH}_3)_3^{2+}, \text{NH}_4\text{aq}, \text{NH}_4^+\) and \(\text{NO}_3^-\) in the anolyte. Where \(\vec{N}_i\) is the flux of species \(i\), \(D_i\) (see Table 2) and \(z_i\) are the diffusion coefficient and valence, respectively, \(\phi_e\) is the ionic potential within the electrolyte, \(T\) is the temperature of the electrolyte, and \(F\) and \(R\) are the Faraday and gas constant. The electrolyte is considered to be electrically neutral and governed by condition [20,21]:

\[
\sum_i z_i c_i = 0
\]

(7)

which is used to calculate the concentration of \(\text{NO}_3^-\). In the steady model, the concentration of each species \(c_i\) does not change with time \(t\), which can be described as follows [30]:

\[
\nabla \cdot \vec{N}_i = 0
\]

(8)

2.3.1.3. Conservation equations for charge. The total current density in the electrolyte can be calculated, using the electroneutrality condition, as follows [21]:

\[
j_e = -\kappa \nabla \phi_e - F \sum_i z_i D_i \nabla c_i
\]

(9)

The potential gradient \(\nabla \phi_e\) can be yielded and the electrolyte conductivity \(\kappa\) is given by Ref. [20]:

\[
\kappa = \frac{F^2}{RT} \sum_i z_i^2 D_i c_i
\]

(10)

In the electrolyte flow channel, the porosity is set to 1. A charge balance sets the divergence of the electrolyte current density to zero leading to [23,22]:

\[
\nabla \cdot j_e = 0
\]

(11)

In the membrane, the secondary current distribution is applied:

\[
j_e = -\kappa_m \nabla \phi_e
\]

(12)

where \(\kappa_m\) represents the electrolyte conductivity in the membrane and is considered as a constant.

2.3.2. Transient model

In the transient model, the concentration of each species \(c_i\) changes with time \(t\), which can be described as follows [33]:

\[
\frac{\partial c_i}{\partial t} + \nabla \cdot \vec{N}_i = 0
\]

(13)

As a first approximation, the Cu concentrations on the cathode and anode surface (electrolyte-electrode boundary interface) are assumed to be uniform and vary with time \(t\) according to the following mass balances [33]:

\[
\frac{\partial c_{\text{Cu}}}{\partial t} = \frac{j_c}{2F}
\]

(14)

\[
\frac{\partial c_{\text{Cu}}}{\partial t} = -\frac{j_c}{2F}
\]

(15)

where \(j_c\) refers to the faradaic current density in the cathode and anode associated with the deposition/reduction of \(\text{Cu}^{2+}\) and the corrosion/oxidation of \(\text{Cu}\), respectively, and \(\text{"−"}\) denotes the corrosion of \(\text{Cu}\) in the anode surface.

Table 1

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel height (m)</td>
<td>(h)</td>
<td>0.02</td>
</tr>
<tr>
<td>Channel width (m)</td>
<td>(w)</td>
<td>0.04</td>
</tr>
<tr>
<td>Channel thickness (m)</td>
<td>(d)</td>
<td>1.5e-3</td>
</tr>
<tr>
<td>Electrode height (m)</td>
<td>–</td>
<td>0.05</td>
</tr>
<tr>
<td>Electrode width (m)</td>
<td>–</td>
<td>0.05</td>
</tr>
<tr>
<td>Electrode thickness (m)</td>
<td>–</td>
<td>5e-4</td>
</tr>
<tr>
<td>Membrane height (m)</td>
<td>–</td>
<td>0.05</td>
</tr>
<tr>
<td>Membrane width (m)</td>
<td>–</td>
<td>0.05</td>
</tr>
<tr>
<td>Membrane thickness (m)</td>
<td>–</td>
<td>1.3e-4</td>
</tr>
<tr>
<td>Height of electrolyte-electrode boundary interface (m)</td>
<td>–</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Quantity</th>
<th>Catholyte</th>
<th>Anolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D_{\text{Cu}^{2+}})</td>
<td>Cu(^{2+}) diffusion coefficient ((\text{m}^2\text{s}^{-1}))</td>
<td>(1.5 \times 10^{-9})</td>
<td>–</td>
</tr>
<tr>
<td>(D_{\text{Cu(NH}_3)_3^{2+}})</td>
<td>Cu(NH(_3))(^{2+}) diffusion coefficient ((\text{m}^2\text{s}^{-1}))</td>
<td>–</td>
<td>(0.6 \times 10^{-9})</td>
</tr>
<tr>
<td>(D_{\text{NH}_3})</td>
<td>NH(_3) diffusion coefficient ((\text{m}^2\text{s}^{-1}))</td>
<td>(1.7 \times 10^{-9})</td>
<td>–</td>
</tr>
<tr>
<td>(D_{\text{NH}_4^+})</td>
<td>NH(_4^+) diffusion coefficient ((\text{m}^2\text{s}^{-1}))</td>
<td>(0.95 \times 10^{-9})</td>
<td>(0.95 \times 10^{-9})</td>
</tr>
<tr>
<td>(D_{\text{NO}_3^-})</td>
<td>NO(_3^-) diffusion coefficient ((\text{m}^2\text{s}^{-1}))</td>
<td>(0.9 \times 10^{-9})</td>
<td>(0.95 \times 10^{-9})</td>
</tr>
</tbody>
</table>

\(^{a}\) Calculated based on mechanism experiment.
\(^{b}\) Estimated based on the CRC Handbook of Chemistry and Physics [31].
2.4. Boundary conditions

2.4.1. Steady model

The electrolytes enter the channels with a prescribed average velocity \( \bar{u}_m \) (in the \( z \) direction) in laminar form and with a constant concentration \( c_i = c_i^0 \) in each species. No-slip conditions (\( \tau = 0 \)) are applicable for the electrolyte at the electrolyte-electrode interfaces and electrolyte-membrane interfaces. The pressure \( p \) as well as the flux of all of the species \( (-\overrightarrow{n} \cdot D_i \overrightarrow{\nabla} c_i) \) are set to zero at the outlets.

The source terms for each species enter through the boundary conditions, applied at the electrolyte-electrode boundary interfaces, which depend on their local faradaic current density at these interfaces. At catholyte-cathode boundary interface:

\[
- \overrightarrow{n} \cdot \overrightarrow{N}_{\text{Cu}^2+} = -\frac{j_0}{2F}
\]  

(16)

At the anolyte-anode boundary interface:

\[
- \overrightarrow{n} \cdot \overrightarrow{N}_{\text{NO}_3^-} = -\frac{j_0}{2F}
\]  

(17)

\[
- \overrightarrow{n} \cdot \overrightarrow{N}_{\text{NH}_4^+} = -\frac{2j_0}{F}
\]  

(18)

For the species (\( \text{NH}_4^+ , \text{NO}_3^- \)) that are not involved in the electrode reactions:

\[
- \overrightarrow{n} \cdot \overrightarrow{N}_i = 0
\]  

(19)

where \( \overrightarrow{n} \) is the normal vector of the electrode surface oriented toward the electrolyte.

The simplest descriptions of the redox reactions taking place at the electrode surfaces are the Butler-Volmer expression for charge transfer kinetics:

\[
j^+ = i_0 \left[ \exp \left( \frac{\alpha^+_{\text{Cu}^2+} nF \eta}{RT} \right) - \exp \left( -\frac{\alpha^+_{\text{Cu}^2+} nF \eta}{RT} \right) \right]
\]  

(20)

\[
j^- = i_0 \left[ \exp \left( \frac{\alpha^-_{\text{NH}_4^+} nF \eta}{RT} \right) - \exp \left( -\frac{\alpha^-_{\text{NH}_4^+} nF \eta}{RT} \right) \right]
\]  

(21)

where \( \alpha^+ \) and \( \alpha^- \) are charge-transfer coefficients in the oxidation and reduction direction (\( \alpha^+ + \alpha^- = 1 \)); \( n \) is the number of electron involved in the reaction (\( n = 2 \)); while \( \eta \) is the reaction overpotential, and \( i_0 \) is the exchange current density. The exchange current densities are defined by:

\[
i_0^+ = nFk_d^0 (c_{\text{Cu}^2+}^0)^{\alpha^+_{\text{Cu}^2+}}
\]  

(22)

\[
i_0^- = nFk_d^0 (c_{\text{NH}_4^+}^0)^{\alpha^-_{\text{NH}_4^+}}
\]  

(23)

\( c_{\text{Cu}^2+}^0 \) and \( c_{\text{NH}_4^+}^0 \) are the concentrations of the species at the electrolyte-electrode boundary interfaces, and \( c_{\text{Cu}^2+} \), \( c_{\text{NH}_4^+} \) are the concentrations of the species in the electrolyte bulk. The overpotentials are defined by:

Table 4

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Quantity</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T )</td>
<td>Operating temperature (K)</td>
<td>298.15</td>
</tr>
<tr>
<td>( c_{\text{Cu}^2+}^0 )</td>
<td>Initial ( \text{Cu}^2+ ) concentration (mol L(^{-1}))</td>
<td>0.2</td>
</tr>
<tr>
<td>( c_{\text{Ni(NO}_3^-)}^0 )</td>
<td>Initial ( \text{Ni(NO}_3^- ) concentration (mol L(^{-1}))</td>
<td>3</td>
</tr>
<tr>
<td>( c_{\text{Cu(NH}_4^+)}^0 )</td>
<td>Initial ( \text{Cu(NH}_4^+ ) concentration (mol L(^{-1}))</td>
<td>0.2</td>
</tr>
<tr>
<td>( \phi_0 )</td>
<td>Electrolyte volume in reservoir (m(^3))</td>
<td>( 2 \times 10^{-5} )</td>
</tr>
<tr>
<td>( \phi_0 )</td>
<td>Equilibrium potential (V): reaction (1)</td>
<td>0.34 [27]</td>
</tr>
<tr>
<td>( \phi_0 )</td>
<td>Equilibrium potential (V): reaction (2)</td>
<td>-0.04 [27]</td>
</tr>
</tbody>
</table>

Consistent initial conditions are prescribed for the concentrations and potential (see Table 4), as follows:

In the electrolyte flow channels and membrane (concentration differences are ignored in the membrane):

\[
c_i = c_i^0
\]  

(24)

\[
\phi_e = -E_{\text{th}} + E_{\text{cell}}
\]  

(25)

At the catholyte-cathode boundary interface:

\[
c_i = c_i^0
\]  

(26)

\[
\phi_e = 0
\]  

(27)

At the anolyte-anode boundary interface:

\[
c_i = c_i^0
\]  

(28)

\[
\phi_e = 0
\]  

(29)

\[
\phi_{e-a} = 0
\]  

(30)

2.4.2. Transient model

In the transient model, the movement of the electrolytes through the

Table 3

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Quantity</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_d^+ )</td>
<td>reaction rate constant (m s(^{-1})): reaction (1)</td>
<td>( 5 \times 10^{-6} )</td>
</tr>
<tr>
<td>( k_d^- )</td>
<td>reaction rate constant (m s(^{-1})): reaction (2)</td>
<td>( 7 \times 10^{-7} )</td>
</tr>
<tr>
<td>( n_i )</td>
<td>Cathodic transfer coefficient: reaction (1)</td>
<td>0.36</td>
</tr>
<tr>
<td>( \alpha^+ )</td>
<td>Anodic transfer coefficient: reaction (1)</td>
<td>0.5</td>
</tr>
<tr>
<td>( \alpha^- )</td>
<td>Cathodic transfer coefficient: reaction (2)</td>
<td>0.64</td>
</tr>
<tr>
<td>( \alpha^a )</td>
<td>Anodic transfer coefficient: reaction (2)</td>
<td>0.5</td>
</tr>
</tbody>
</table>

* Calculated based on mechanism experiment.

* Fitted parameter.
channels, pumps and reservoirs alters the inlet concentrations with time as the real system. It is essential to capture the main features of this process because the flow rate is the main variable used to control the distribution of the electrolyte, and variations in $u_{in}$ can markedly affect the battery performance.

Assuming instantaneous mixing and neglecting reaction in the reservoir, the inlet concentrations are approximated from the following mass balance equation:

$$ V \frac{dc_{in,i}}{dt} = \int (\overline{n} \cdot \overline{N}_i) \, dS - \int (\overline{n} \cdot \overline{N}_i) \, dS $$

where $V$ is the total volume of flowing electrolyte in the reservoir, $h$ is the height of the flow channel, and $c_{in,i}$ is the inlet concentration (i denotes the Cu$^{2+}$, NH$_4^+$, Cu(NH$_3$)$_4$H$^{2+}$ and NH$_3$(aq)).

In the simulation of transient model, the energy density $W$ during discharge was calculated:

$$ \frac{dW}{dt} = \int_0^b V \frac{dE_{vib}}{dx} $$

Compared to the stationary model, the main difference of the transient model is that the inlet concentrations of reactants and products vary continuously as the reactions progress. Therefore, some equations in the stationary model could also be applied to the transient model expect for equations (13)–(15), (33) for the description of the concentration over time. Accordingly, where $j^i$ is derived from equation (20) and the inlet concentrations of species are approximated from mass balance equations (13) and (33); where the battery voltage $E_{vib}$ is calculated by equation (28).

### 2.5. Numerical details

The model is implemented in Comsol Multiphysics (version 5.0), which is an intuitive computational software and particularly appropriate for models that involve several physics to be solved simultaneously.

The fluid dynamics equations (4) and (5) were implemented in the flow channels by the Laminar Flow toolbox. The Tertiary Current Distribution toolbox was used for mass transport equations (6) and (8) and electrolyte current and potential equations (9) and (11). In the transient model, the inlet concentration of each species and energy density were defined by means of the global ordinary differential equations. Then, the geometry was meshed using the physics-controlled mesh tool, setting the element size in standard. At the electrolyte-electrode boundary interfaces, boundary layer grid was applied for charge transfer kinetics, which result in dramatic changes in concentration (see Fig. 2 (b)).

Due to the unidirectional coupling between fluid dynamics and mass transport (the electrolyte convection influences the transport of ionic species in solution but the opposite is false), it is not necessary to solve all of the equations simultaneously. Instead, the flow equations were solved independently and then the velocity vector injected in the mass transport equations, which are solved all together with the electrolyte current and potential equations, leading to a considerable saving in the computational time. Fully coupled non-linear solvers were employed each time. Direct linear solvers were employed, namely the PARDSO solver for fluidic equations and the MUMPS solver for electrochemical equations. The convergence criterion ($\epsilon < 10^{-3}$) is reached typically after 6 s and five iterations for the resolution of the velocity field while the electrochemical variables are solved within a few minutes involving ten to fifty iterations.

### 3. Experimental results for the model parameters

The physical properties of the catholyte and anolyte (such as the conductivity $\kappa$, the density $\rho$, the pH, and the viscosity $\nu$) were measured over a range of electrolyte compositions by a multi-parameter analyzer (DZS-708L, INESA) and an ubbelohde viscometer, as shown in Table 5. A typical three-electrode cell (see Fig. S1) was applied for the electrochemical experiments of cyclic voltammetry (CV), chronopotentiometry (CA) and Tafel plot based on a rotating disk electrode (GC-RDE, RRDE-3A, ALS). These electrochemical measurements were carried out for the estimation of several parameters that were used in the model equations: the ion diffusion coefficient $D$ and the other kinetic parameters $\alpha_1$, $\alpha_2$, and $k_b$ associated to charge transfer at each electrode, as shown in Table 6. For the cathode reaction (1), the diffusion coefficient of Cu$^{2+}$ at basic electrolyte condition is determined to be (9.32–15.8) $\times$ 10$^{-10}$ m$^2$ s$^{-1}$ at 298 K with different electrochemical technologies (Figs. S2–S4). The value of cathodic diffusion coefficient $\alpha_1$ is 0.385 at the scan rate of 100 mV s$^{-1}$ (Fig. S2 (a)) and the cathodic reaction rate constant $k_2$ is evaluated to be (4.98–11.68) $\times$ 10$^{-6}$ m$^{-1}$ s$^{-1}$ (Fig. S2 (c)). For the anode reaction (2), due to the interaction between newly deposited copper and NO$_3^-$, a disproportionation reaction of copper with Cu(NH$_3$)$_4$H$^{2+}$ and a self-corroded reaction of copper with ammonia (Fig. S5), the experimental data cannot be used to calculate related kinetic parameters of the anode reaction. The diffusion coefficient of Cu(NH$_3$)$_4$H$^{2+}$ is determined to be $5.5 \times 10^{-10}$ m$^2$ s$^{-1}$ at a switching potential of $-0.6$ V with the redox couple [Cu(NH$_3$)$_4$]$^{2+}$/Cu

### Table 5

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<td>Potential of hydrogen</td>
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<tr>
<td>$\nu$</td>
<td>Kinematic viscosity (mm$^2$ s$^{-1}$)</td>
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<td>0.985</td>
<td>0.847</td>
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### Table 6

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<th>transfer coefficient $\alpha_1$</th>
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<td>$8.52$ (5.71–11.68) $\times 10^{-6}$</td>
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<td>Anode reaction</td>
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<td>-</td>
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<tr>
<td>Cyclic voltammetry (CV)</td>
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(NH$_3$)$_2$$^+$) (Fig. S6).

4. Results and discussion

4.1. Stationary model

4.1.1. Validation of the model

The numerical solutions were validated against the experimental data in our published literature [15]. Battery power was measured based on a constant current $I$. The battery voltage $E_{cell}$ was recorded by a potentiostat, and the power was calculated by $P = E_{cell}I$. The area-normalized power density $P_a$ of single cell pair was obtained using the projected electrode area $A_e$ ($8 \times 10^{-4}$ m$^2$). During the simulation, an area-normalized current density $i_{app}$ was given, and then the battery voltage and power density could be determined. Fig. 3 (a) shows the comparison of the simulated power density and voltage values by the flow-electrochemical (F-E) coupled model with the experimental data at basic electrolyte condition (Catholyte: 0.2 M Cu(NO$_3$)$_2$, 3 M NH$_4$NO$_3$; Anolyte: 0.2 M Cu(NO$_3$)$_2$, 3 M H$_3$·H$_2$O and 3 M NH$_4$NO$_3$) and a flow rate of 1 mL min$^{-1}$. It was observed that the model captured the trend well. The small discrepancies in the power density between the numerical results and the experimental data at high current densities may be caused by the presence of side reactions, which are not accounted in the present study.

4.1.2. Effects of the electrolyte flow

First simulations were performed to characterize the distribution of electrolyte flow in the channels, as shown in Fig. 3 (b). The volume flux $Q_{in}$ (mL min$^{-1}$) can be converted to the average velocity $u_{in}$ (m s$^{-1}$) at the inlet by the equation: $u_{in} = Q_{in}/60wd$. The relevant Reynolds number at a flow rate of 1 mL min$^{-1}$ in the channels is about 0.55 ($Re = \frac{u_{in}d \rho}{\mu}$), and we can assume that the flow is in the laminar regime ($Re < 2000$). The line ($x = 0$, $y = 0$–2) represents the anolyte-anode interface boundary, and the other side is the catholyte-cathode interface boundary. As it can be observed, the velocity distributions of the catholyte and anolyte are homologous. The velocity near the wall (electrodes or membrane) is very small and the largest velocity is in the center of the channel, and the distribution of the flow field is symmetrical. Compared to the average velocity $u_{app}$, there is an acceleration in the center of the channel, which enhances the mass transfer. While near the electrode surfaces, the smaller velocity extremely limits the convective diffusion of the reactants and products. As a result of the discrepancy in density and viscosity of the catholyte and anolyte, the velocity and gradient in the cathode flow channel are significantly larger than in the anode flow channel. Although the density of the catholyte is slightly large, but the main reason is the difference of the viscosity. Fig. 3 (c) shows the variations of the power density and pressure drop with different flow rates using electrochemical model (the velocity is evenly $u_{app}$ all the flow channel, including near the wall) and flow-electrochemical (F-E) coupled model. As it can be seen, the calculated power density by the electrochemical model is superior to the results of the flow-electrochemical coupled model, which illustrates that the two-dimensional plate electrode has a poor utilization for the mass transport compared with the porous electrode and that the uniformity of the velocity distribution is also significant. The power density does not increase in any case when the flow rate reaches a higher value. The errors between the simulation and experiment are ignorable at lower flow rates, but the simulation results have a large difference with experimental data when the flow rate is greater than 8–10 mL min$^{-1}$. The possible reasons are that first of all, the model is two-dimensional and the actual flow channel is three-dimensional, and the electrolyte has more contact surfaces and pipe orifices. Therefore, kinetic energy is consumed due to a lot of friction loss, especially at higher flow rates. Secondly, it is observed during the experiment that bubbles are generated in the flow channel when the anode (Cu electrode) is corroded,
which disturbs the laminar flow. Furthermore, when the battery is tested at different flow rates, the electrochemical surface of the copper electrode will undergo large changes with increasing flow rates, which will delay the reaction kinetics. Finally, the presence of some side reactions also affects power production, especially during the anode process. Besides, higher flow rates create larger pressure drop and can’t effectively enhance the velocity in the boundary layer near the electrode surfaces. Thus, it is essential to consider the balance between the power production and the pressure drop.

4.1.3. Effects of the NH$_3$ concentration

The performance of the AFB was examined over a range of NH$_3$ concentrations in the anolyte, as shown in Fig. 4 (a). It was found that the achieved limiting current density was independent of the anodic NH$_3$ concentration, but the anodic NH$_3$ concentration had a great effect on the power production. The anodic kinetic parameters at different NH$_3$ concentrations did not change in the present model. Decreasing the anodic NH$_3$ concentration from 3 M to 2 M seriously weakened the power production and voltage, which was consistent with the test results. While increasing the anodic NH$_3$ concentration from 3 M to 4 M mildly improved the battery performance, which was agreed with the discussion of the previously proposed TRAB [13], but the experimental data of the AFB revealed that all the power production and voltage had a certain decline [15]. So as to further explore the reason for this deviation, the average overpotentials and electrode potentials of the anode at various NH$_3$ concentrations and 0.2 M Cu$^{2+}$ at a flow rate of 1 mL min$^{-1}$, using 3 M NH$_4$NO$_3$ as the supporting electrolyte. (c) Distributions of anodic NH$_3$ concentration and cathodic Cu$^{2+}$ concentration at the maximum current density $i_{app} = 166$ A m$^{-2}$ when the initial NH$_3$ concentration is 4 M.

overpotential is relatively tiny and not the main factor. Improved anode performance was consistent with the Nernst equation (26) as the anode potentials were more negative at increased NH$_3$ concentration. Under the experimental condition, the pH of the anolyte and the quantity of OH$^-$ from the ammonia ionization increased as increasing NH$_3$ concentration, and the NH$_3$ concentration near the membrane was still high at the end of discharge (as shown in Fig. 4 (c)). The ion of OH$^-$ and NH$_3$ molecules may permeate to the catholyte and react with the Cu$^{2+}$ [34], which is the self-discharge and may be the cause of battery performance degradation in the AFB. Fig. 4 (c) shows the distributions of anodic NH$_3$ concentration and cathodic Cu$^{2+}$ concentration at the maximum current density $i_{app} = 166$ A m$^{-2}$ when the initial NH$_3$ concentration is 4 M. It was observed that the depleted Cu$^{2+}$ concentration in the catholyte-cathode interface boundary restricted the increase of the limiting current density. However, the Cu$^{2+}$ concentrations in the middle of the channel and near the membrane were almost not consumed, which led to low mass availability and uneven distribution of the concentration. Likewise, the distribution of NH$_3$ concentration was also inhomogeneous and the gradient of NH$_3$ concentration diminished from the inlet to the outlet. The NH$_3$ concentration in the anolyte-anode interface boundary was excessive against with the cathodic Cu$^{2+}$ concentration.

4.1.4. Effects of the Cu$^{2+}$ concentration

The performance of the AFB was examined over a range of Cu$^{2+}$ concentrations in catholyte, as shown in Fig. 5 (a). It was noticed that the Cu$^{2+}$ concentration not only determined the achieved limiting current density, but also had a markedly impact on the power production. From Fig. 5 (a), there was an optimal Cu$^{2+}$ concentration for
maximizing the power density with 2 M anodic NH₃ concentration. The main reason is that high Cu(NH₃)₄²⁺ (namely the Cu²⁺ in the anolyte) concentration leads to the decrease of the anodic NH₃ concentration, which restricts the increase of limiting current density and power production. For example, reducing the anodic Cu(NH₃)₄²⁺ concentration to 0.2 M clearly improved the limiting current density and power production when the cathodic Cu²⁺ concentration was 0.3 M. Despite some deviations between the simulation and experiment, the variation tendency of the predicted battery performance is accordant with the experiment, and the numerical results are still within acceptable range taking into account the existence of experimental errors (as shown in Fig. 5(c)). Increasing the Cu²⁺ concentration to 0.3 M did not deteriorate the battery performance when the anodic NH₃ concentration was 3 M, as shown in Fig. 5 (b). It is concluded that the higher NH₃ concentration can promote the optimal Cu²⁺ concentration, but the NH₃ concentration cannot be excessively increased during the actual operation. This limits the increase of Cu²⁺ concentration, and the power production is also limited accordingly.

The cathodic Cu²⁺ concentration and the anodic Cu(NH₃)₄²⁺ concentration are consistent to ensure the cycle stability. However, more copper electrode is corroded by the anolyte at a large discharge current density, which increases the anodic Cu(NH₃)₄²⁺ concentration after the discharge. This means that the cathodic Cu²⁺ concentration is far greater than the anodic Cu(NH₃)₄²⁺ concentration in the next discharge cycle, which brings about the cyclical fluctuation and affects the continuity of the power production. Therefore, appropriately decreasing the initial anodic Cu(NH₃)₄²⁺ concentration according to the discharge current density is beneficial to boost the battery performance and reduce the cyclical fluctuation (see Fig. 5 (d)), which is parallel to the effects of increasing the NH₃ concentration.

4.1.5. Effects of the NH₄NO₃ concentration

The NH₄NO₃ as the supporting electrolyte plays an important role in enhancing the electrolyte conductivity and reducing the resistance, while not bringing other ions and polluting the electrolyte. The concentrated NH₄NO₃ affects the viscosity, ohmic resistance and reaction resistance, balances the pH, inhibits the dissociation of the ammonia and improves the ammonia activities simultaneously. In the present model, the viscosity, conductivity and density changes of the electrolyte were measured at different NH₄NO₃ concentrations (see Table 5), and these changes would directly affect the distributions of the flow field. The ohmic resistance, namely the conductivity, was mainly determined by the concentration and diffusion coefficient of all species in the electrolyte using equation (10). The reaction resistance was generally neglected due to the lack of enough experimental data. Fig. 6 shows the effects of NH₄NO₃ concentration on the power production and voltage. Increasing the concentration of NH₄NO₃ from 1 M to 3 M increased the power production, but the power production had a slight drop when increasing the NH₄NO₃ concentration from 3 M to 5 M. Changes in the...
viscosity of the electrolyte may be the main reason for this phenomenon. In addition, a lower NH₄NO₃ concentration favors a higher limiting current density. There are two possible reasons to explain this phenomenon: on the one hand, the higher NH₄NO₃ concentration is beneficial to reduce the ohmic resistance of the battery, but the reaction resistance increases at the same time and the total resistance is greater than the lower concentrations [13]; on the other hand, transport loss is a major cause of the sharp reductions of the power and voltage at higher current densities, so the transport of Cu²⁺ may be more difficult at higher NH₄NO₃ concentrations.

4.1.6. Effects of the flow channel geometry

The effects of the geometric parameters (such as thickness, height-width ratio and cross-sectional area) of the flow channel on the battery performance were analyzed in this section. From Fig. 7 (a), the power production and limiting current density were improved significantly when the channel thickness decreased from 1.5 mm to 1 mm, which was owing to the increase of the local velocity and mass transfer flux at the same flow rate. However, the pressure drop in the channel increased intensely with the reduction of the channel thickness, which resulted in more additional power consumption. Fig. 7 (b) displays the distributions of cathodic Cu²⁺ concentration with different channel thicknesses at a current density of 120 A m⁻². It was found that in spite of the analogous distributions of the Cu²⁺ concentration, the concentration gradient near the cathode surface increased as the channel thickness decreased, which was thanks to the promoted mass transfer. Meanwhile, the Cu²⁺ concentration increased at the cathode surface as the channel thickness decreased under the same discharge current density, which accelerated the process of the electrode reaction and enhanced the battery performance. Fig. 7 (c) shows the effects of different channel height-width ratios (2:9, 1:2 and 2:1) and cross-sectional areas (2, 8 and 18 cm²) on the battery performance.

4.2. Transient model

4.2.1. Discharge energy characteristics

Fig. 8 shows the variations of the power production, voltage, energy density and ion inlet concentration with discharge time at various discharge current densities. From Fig. 8 (a), the power production and voltage rapidly drop at the beginning of the discharge, that is, activation loss, resulted from the low kinetics or small reaction area; the power production and voltage maintain a relatively high value at this stage; the power production and voltage sharply reduce at the end of the discharge, that is, transport loss, occurring due to the reactant transport from the center of the channel to the electrode surface. It was seen that at the current density of 220 A m⁻², the power density
reached the maximum value, which was similar to the results of the stationary model. The relationship between the energy and power densities at different discharge current densities was shown in Fig. 8 (b), and it was observed that the energy density and its variation degree decreased with increasing discharge current density. The power density increased at first and then decreased, reaching a maximum at a current density of 220 A m\(^{-2}\). The energy density at maximum power density was 961 Wh m\(^{-3}\), which had little difference compared to the experimental value. A larger energy density can be achieved when the discharge current density is very small, but the power density is severely lost. Thus, it is essential to compromise between the energy and power densities based on the practical energy demands. At the same time, the situation that an excessive current should be avoided in the actual discharge process, giving rise to the decreasing energy and power productions. Fig. 8 (c) demonstrates the variations of the inlet concentrations of the cathodic Cu\(^{2+}\) and anodic Cu(NH\(_3\))\(_4^{2+}\) during the discharge. It was found that the inlet cathodic Cu\(^{2+}\) concentration decreased and the inlet anodic Cu(NH\(_3\))\(_4^{2+}\) concentration increased with the discharge. The anodic Cu(NH\(_3\))\(_4^{2+}\) concentration after the discharge is the initial cathodic Cu\(^{2+}\) concentration in the next discharge cycle, likewise, the cathodic Cu\(^{2+}\) concentration after the discharge is the initial anodic Cu(NH\(_3\))\(_4^{2+}\) concentration in the next discharge cycle. The distinctions of the initial concentrations in successive discharge cycles will cause the cyclical fluctuation, as above sections described.

### 4.2.2. Effects of the inlet concentration of Cu(NH\(_3\))\(_4^{2+}\)

Fig. 8 (c) and (d) shows the effects of the initial Cu(NH\(_3\))\(_4^{2+}\) concentration on the inlet concentrations, power and energy densities in the transient model. In the stationary model, reducing the initial Cu(NH\(_3\))\(_4^{2+}\) concentration can make the initial inlet Cu\(^{2+}\) concentration in the next discharge cycle consistent with the last cycle, and the mount of the reduction is determined by the discharge current and the depth of the discharge. From Fig. 8 (d), it was detected that reducing the initial Cu(NH\(_3\))\(_4^{2+}\) concentration was beneficial to the promotion of both the power and energy productions, and the fundamental reason was indirect increase of the anodic NH\(_3\) concentration.

### 5. Conclusions and future development

Based on the experiments of reaction mechanisms and the measurements of physical properties of electrolyte, a stationary and a transient two-dimensional numerical models of the TR-AFB during the discharge have been developed. The stationary model primarily focuses on the variations of power and energy densities with discharge time. The simulation results were well consistent with experimental data. The following conclusions can be drawn based on the results:

(I) The viscosity of electrolyte and geometric parameters of the flow channel have great effects on the distribution of flow field, which is a significant factor affecting the power production. A larger flow rate helps to promote the battery performance, while it cannot be further improved at excessive flow rates. The velocity of catholyte is markedly larger than the anolyte, which is ascribed to the increase of viscosity of the anolyte after adding ammonia. Reducing the thickness and increasing the cross-sectional area of the flow channel can improve the battery performance, while there is...
almost no improvement of power production with different channel height-width ratios.

II. The production and battery voltage are improved with increased anodic NH3 concentration, mainly due to the more negative anode potentials. However, a higher NH3 concentration will aggravate the burden of anion exchange membrane (AEM) and facilitate the ionization of OH\(^-\). The OH\(^-\) and NH3 may permeate to the catholyte and react with the Cu\(^{2+}\), which results in self-discharge and degradation of battery performance. Both the achieved limiting current density and power production are markedly elevated as the Cu\(^{2+}\) concentration increases, however, this effect is restricted by the anodic NH3 concentration. The effects of NH4NO3 concentration on battery performance is mainly due to the influence on the kinematic viscosity of the electrolyte.

III. Reducing the initial anodic Cu(NH3)\(_4\)^{2+} concentration from 0.2 M to 0.1 M promotes the maximum power density by 6.6% and energy density by 3.5% when the NH3 concentration is 3 M and cathodic Cu\(^{2+}\) concentration is 0.2 M. Meanwhile, the initial concentrations of anodic Cu(NH3)\(_4\)^{2+} and cathodic Cu\(^{2+}\) in next discharge cycles are consistent when the discharge current density is 200 A m\(^{-2}\) and the depth of the discharge is 91%. The discharge current density, power and energy densities need to be balanced on the basis of actual energy demands.

The following two recommendations are helpful for improving the performance of TR-AFB in future modeling and experimental studies: (i) the 2D plate electrode should be replaced with 3D (porous or fibrous) copper electrode, which benefits the increase of electrode surface area and electrolyte utilization. (ii) increase the ammonia concentration as much as possible without leading to the self-discharge, which requires the comprehensive consideration of ion exchange membrane, electrolyte and channel structure.

Acknowledgements

The authors would like to thank Dr. Xiuping Zhu for useful discussions. This work was supported by the National Natural Science Foundation of China (No. 51676133). The authors gratefully acknowledge them for support of this work.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2018.03.070.

Symbols

Latin letters

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<td>( A_c )</td>
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<td>concentration (mol m(^{-3}))</td>
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<td>( d )</td>
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\( \vec{N} \) | molar flux (mol m\(^{-3}\) s\(^{-1}\)) |
| \( p \) | pressure (Pa) |
| \( P \) | power (W) |
| \( P_a \) | area-normalized power density (W m\(^{-2}\)) |
| \( Q_v \) | volume flux (mL min\(^{-1}\)) |
| \( R \) | molar gas constant (J mol\(^{-1}\) K\(^{-1}\)) |
| \( t \) | time (s) |
| \( T \) | temperature (K) |
| \( \eta \) | electrolyte velocity vector (m s\(^{-1}\)) |
| \( V \) | electrolyte volume in reservoir (m\(^3\)) |
| \( w \) | Channel width (m) |
| \( W \) | energy density (Wh m\(^{-3}\)) |

Subscript

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Superscript

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<td>initial value</td>
</tr>
<tr>
<td>( \infty )</td>
<td>bulk solution value</td>
</tr>
</tbody>
</table>

References