

Review

Modeling and Simulation of Non-Aqueous Redox Flow Batteries: A Mini-Review

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Abstract: Redox flow batteries (RFBs) have been widely recognized in the domain of large-scale energy storage due to their simple structure, long lifetime, quick response, decoupling of capacity and power, and structural simplicity. Because of the limited open circuit voltage (OCV) by hydrogen and oxygen evolution reactions, together with the relatively low solubility of active species, RFBs with aqueous electrolytes are challenging to reach high energy densities. Researchers have been trying to develop new solvent systems without water to remove the electrochemical window limitation of water and pursue higher cell potential. However, non-aqueous solvents are also hindered by some key problems, such as high viscosity and poor safety. Meeting these challenges require a comprehensive understanding of relevant structural design parameters and multi-variable operation in the non-aqueous flow battery (NAFB) system. Modeling and simulation are not only an effective way to understand the basic mechanism of flow batteries at different scales of size and time but also an ideal tool for optimizing the reaction process, battery assembly, and the whole flow battery installation. This review paper introduces the development of the non-aqueous flow battery, the challenges it faces, and the research progress of related modeling and simulation for verification or optimization. Finally, the future development prospects of the non-aqueous flow battery model are pointed out, especially for those systems and fields that have not yet been explored.

Keywords: large-scale energy storage; flow battery; non-aqueous solution; numerical simulation; high energy density; structure design parameter; multi-variable operation; electrochemical window limitation



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1. Introduction

With the development of the population and economy, the huge consumption of fossil energy has brought serious environmental pollution and energy unsustainability. To achieve the sustainable development of human society and the improvement of the ecology, many countries have proposed the “carbon neutral” commitment, in which the efficient development and application of renewable energy is the key. However, renewable energies represented by wind energy and solar energy are limited by various geographical environmental factors, which cannot guarantee the sustainability and stability of power output, seriously restricting their large-scale application. [1] A stable, safe, and efficient energy storage system is the best choice to settle the problem. Among the numerous energy storage systems that have been launched in succession, redox flow batteries (RFBs) stand out with their outstanding advantages and great potential. The concept of RFB was first proposed by Thaller [2]. It achieves the mutual conversion between electrical energy and chemical energy by the reversible redox reaction between a pair of redox electric pairs. The basic unit of the flow battery consists of two electrolyte tanks, two electrodes, and a membrane. The positive and negative electrolytes are pumped into the porous electrode from the electrolyte tanks, and the oxidation-reduction reaction occurs on the electrode surface, which is then transported back to the original tank to complete a

hydraulic cycle. The independent electrolyte storage scheme enables the power generation and energy storage capacity of the RFBs to be flexibly and independently adjusted to meet the demands of large-scale power reserves. This unparalleled flexibility gives the flow battery a promising future.

RFBs are usually classified according to the active species used. They are also named according to the corresponding species, such as an iron-chromium flow battery [3], a hydrogen-bromine flow battery [4], a zinc-bromine flow battery [5], an all-vanadium flow battery [6], a soluble lead-acid flow battery [7], and an organic flow battery [8]. Because it employs vanadium ions only in the cell to avoid cross contamination, the all-vanadium flow battery has received the most attention, which has matured and gradually moved towards industrialization and commercialization [9].

RFBs can also be classified by the type of electrolyte. The currently reported RFBs are still mainly based on aqueous electrolytes [10]. This type of flow battery is called an aqueous flow battery, and a flow battery that does not contain water in the electrolyte is called a non-aqueous flow battery. Aqueous RFBs were first widely studied because aqueous solutions are easy to prepare, are nonflammable or non-plosive, and are cheaper. However, restricted by the electrochemical window of the water, it is difficult for the voltage of the aqueous flow battery to reach over 2 V [11]. To solve this problem, non-aqueous electrolytes were introduced to design RFBs with higher voltages. The non-aqueous solvents used in RFBs mainly include organic solvents [12] and ionic liquids [13]. The solubility of metal ions in organic compounds is poor, so the non-aqueous RFBs using organic solvents generally choose metal coordination complexes [14] or organic compounds [15] as redox couples. For example, acetonitrile has been used many times in the development of non-aqueous RFBs because of its low viscosity, high dielectric constant, and good compatibility with supporting electrolytes [16]. In addition, organic solvents such as ethylene carbonate [17] and propylene carbonate [18] are often used in the liquid phase of semi-solid RFBs. Organic solvents can use different functional groups for directional synthesis to meet specific design requirements [19]. The disadvantages of organic solvents are their generally low conductivity because they usually do not exist in the form of ions in liquids. Organic solvents are also flammable and volatile, as well as expensive due to their design and synthesis [20]. Ionic liquids are another promising non-aqueous solvent that are composed of only ions. They can remain as liquids below 100 °C or even at room temperature owing to the weak coordination between ions [13]. It is worth mentioning that, as a novel type of ionic liquid, the deep eutectic solvent (DES) has gradually attracted the extensive attention of researchers, which will be elaborated on in the following chapters.

Currently, the limitations of non-aqueous RFBs are uniformly manifested in their low current density, energy efficiency, and cycle life. This is usually due to the excessive viscosity of the solvent or poor cycle stability. Secondly, the selection of membranes for non-aqueous RFBs is more stringent. Non-aqueous solvents, especially organic solvents, are easy to interact with membranes of specific materials, causing the membrane to dissolve or swell [21]. Therefore, how to maintain the stability of the membrane in non-aqueous solvents is also an issue that cannot be ignored.

The research on non-aqueous RFBs started relatively late, and non-aqueous electrolytes were widely selected, each with its advantages and characteristics. Therefore, most researchers focused on the development of new electrolyte systems [22–24] and carried out a series of electrochemical tests for the new systems to verify their feasibility and prospects. Some researchers have developed a mature system, based on which they further improve the design, optimize the key components such as the supporting electrolyte, electrode, and membrane, and enhance the synergy between the different parts to obtain higher performance [25].

As the performers of electrochemical reactions, ions play a decisive part in the performance and life of RFBs. Exploring the interaction mechanism of ions at the microscale and reflecting it on the macro-operation of the battery can point out a clear and constructive direction for the design of the battery system. Since the microscale ion transport behavior

is challenging to observe and evaluate with experiments, mathematical modeling, and numerical simulation methods have become an indispensable part of battery design. In addition, the mathematical model also has unique advantages in parameter optimization, idea verification, etc., which can greatly save the time and cost of system development [26]. From the end of the last century to the present, there have been quite a lot of excellent numerical simulation works in the field of aqueous RFBs, especially all-vanadium RFBs, which have played a good role in boosting the development of RFBs [27–31]. Mathematical modeling is also necessary for non-aqueous RFBs, especially considering the research status of non-aqueous RFBs. The current demand for numerical simulation work can be rated as urgent.

Based on previous work, this paper introduces the physicochemical process and operation parameter design of non-aqueous RFBs. It discusses the limitations of current research and summarizes the latest progress in exploring non-aqueous RFB through modeling and simulation. Finally, it points out future directions for modeling and numerical simulation of non-aqueous RFBs.

2. Design and Operation Parameters of Non-Aqueous Flow Batteries

Compared with the aqueous RFBs, the design features of the non-aqueous RFBs are mainly reflected in three aspects: redox couple design, solvent pairing and supporting electrolyte selection, and membrane selection. This section will specifically describe the design ideas of the non-aqueous flow battery from the above three perspectives.

2.1. Redox Couple Design

As the performers of electrochemical reactions, redox couples directly determine the performance and cost of the RFBs. The redox potential in the flow cell depends on the active materials selected in a given solvent. Enhancing the voltage is an effective method to bring the cost down and save the footprint of the battery under the defined power output. In addition, redox pairs should have a low melting point, high solubility, good reversibility, and chemical stability. For non-aqueous RFBs using organic solvents, the redox pairs used are usually organic. All organic, non-aqueous RFBs have more active materials on the anode (high potential) side and have been verified and developed in many battery systems, including RFBs (such as TEMPO [32]). On the cathode side, organic active materials are less developed and used. The concept of symmetrical redox couples provides novel ideas for the development of organic RFBs. Different high-potential and low-potential active species are synthesized by using the same organic matrix as the raw material. The advantage of the symmetrical design is particularly prominent because the fully discharged battery contains the same molecules on both sides. This design helps to ameliorate the cross-contamination and electrolyte imbalance of the flow battery and improve the cycle efficiency. Numerical modeling methods can be used to evaluate the performance of different redox couples in a flow battery by simulating their electrochemical behavior. This involves modeling the electron transfer reactions that occur between the redox couple and the electrodes, as well as the mass transport of the redox species through the electrolyte. This can help optimize the design of the redox couple for improved performance and efficiency.

2.2. Solvent Paring and Supporting Electrolyte Selection

In accordance with the law of “like dissolves like”, species with polar groups (such as organic molecules and metal ions) are easier to dissolve in aqueous electrolytes, while free radicals and organic molecules with non-polar groups tend to dissolve in non-aqueous electrolytes [33]. The type of solvent largely depends on the choice of redox couples—the dissolution of solute is the primary task of the electrolyte of RFBs, which is followed by the limitation of non-aqueous solvents. An excellent flow battery solvent should have high conductivity, low viscosity, good stability, and a wide liquid temperature range while ensuring high solubility of the solute. In reality, it is very difficult to develop such an ideal solvent. With the increase in functional requirements, the difficulty and cost of solvent

development will rise sharply. Therefore, the choice of non-aqueous solvents is often accompanied by trade-offs and sacrifices. It is our consistent idea to retain and give full play to the most valuable characteristics of solvents based on design requirements. The numerical simulation method greatly reduces the cost and time of this process. Through simulating the behavior of the ion migration in non-aqueous solvents and supporting electrolytes and evaluating their electrochemical performance, available solvent and supporting electrolyte combinations can quickly be found. This can help optimize the concentration and properties of the electrolyte for improved battery performance and stability.

2.3. The Choice of Membrane

As a critical component of RFBs, membranes can prevent the crossing of active substances and promote the ion transport of supporting electrolytes. It plays a key part in the stability and high performance of the flow battery. The membrane in non-aqueous RFBs should have high selectivity and ionic conductivity, low expansion and cost, and good chemical and mechanical stability in non-aqueous solvents. For several existing common membranes, Yuan et al. [34] proposed a hexagonal evaluation system (Figure 1) to comprehensively evaluate them from six aspects: ion selectivity, ionic conductivity, chemical stability, expansibility, and cost. At the end of the paper, it is pointed out that the membrane of non-aqueous RFBs can be designed from the aspects of surface modification, organic and inorganic composite materials, and the use of nanomaterials. In addition to selecting suitable ion exchange membranes through experience, numerical modeling can be used to study the transport of the active species through the membrane as well as the impact of the membrane properties on battery performance.

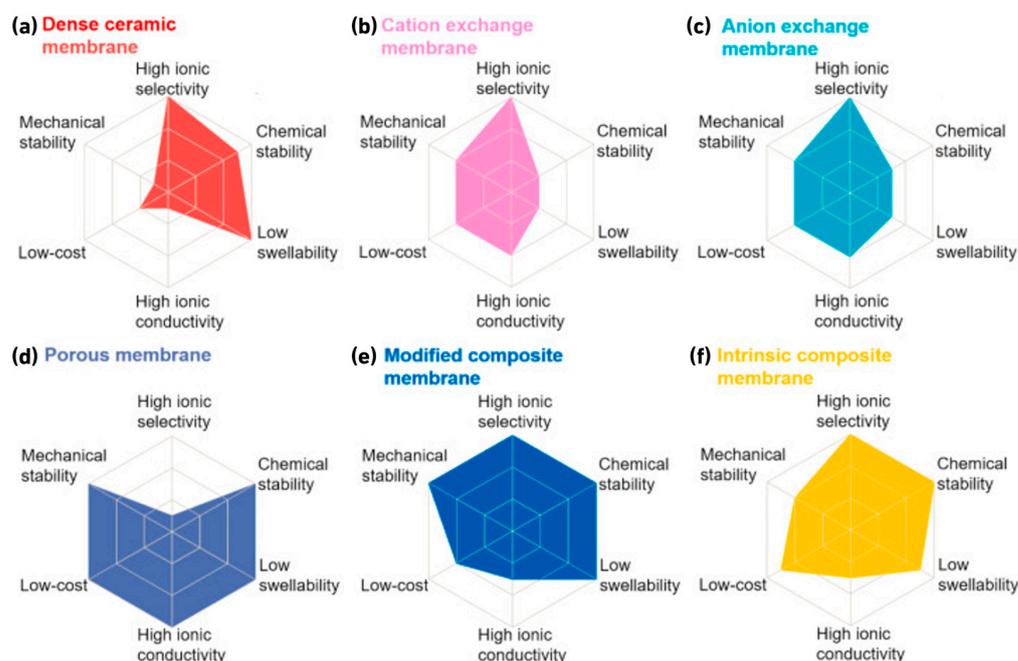


Figure 1. Radar charts of the performance parameters of different membranes [34].

3. Non-Aqueous Flow Batteries with Organic Solvents

3.1. Working Principle

There are three kinds of non-aqueous RFBs using organic solvents: organic RFBs, metal-ligand RFBs, and semi-solid RFBs. Organic molecules are typical uncharged substances without any net electron spin; their valence electrons pair as discrete molecular orbitals (MOs). However, free radicals can generate species with single-occupied molecular orbitals (SOMO) through bond homolysis with no difficulty [35]. Most free radicals are active because of their energetically advantageous spin, so radical coupling or dimerization is quite easy. Furthermore, the free radical reaction with spin molecules, through the abstract

or addition mechanism, may also lead to the diffusion of free radicals to other molecules and the occurrence of a free radical chain reaction.

3.2. Modeling Research

As a mature electrolyte component for lithium-ion batteries, organic solvents are gradually being explored in the field of flow batteries. In the early stages of the study, the semi-solid flow battery (SSFB) stands out as a new type of flow battery that combines the characteristics of a flow battery and a lithium-ion battery [18]. Drawing on experience from both, the research on SSFB has begun to take shape, including modeling and simulation. The modeling of SSFB can be carried out from the following perspectives:

1. Numerical simulation methods based on multi-physics field coupling. These methods include multi-physics field computational fluid dynamics (MPF-CFD) models, the finite element method (FEM), and multiscale simulation methods.
2. In terms of electrochemical reaction models, molecular simulation methods, such as molecular dynamics simulation, can be applied to simulate chemical reactions and diffusion phenomena inside the electrolyte. These methods can provide more accurate reaction mechanisms and reaction kinetics information, thus improving the reliability of simulation results.
3. In the flow model aspect, the non-Newtonian flow characteristics of SSFB should receive attention. Some studies have shown that the non-Newtonian flow characteristics of SSFB have a significant impact on battery performance and thus need to be taken into account.
4. With the continuous development of machine learning and artificial intelligence technology, these technologies can also be used in SSFB modeling. For example, machine learning methods can accurately predict the potential distribution and ion concentration distribution inside the battery, providing better guidance for optimizing design and operating parameters.

Brunini et al. [36] built a dynamic three-dimensional electrode model of a SSFB to calculate the electrochemical and hydrodynamic processes of a SSFB. The model couples ion flux, electron current, and hydrodynamics, and takes into account non-Newtonian flow. For incompressible non-Newtonian fluids, the Navier-Stokes equation and power law viscosity are usually used to model the active suspension flow:

$$\rho \left(\frac{\partial \vec{u}}{\partial t} + \vec{u} \cdot \nabla \vec{u} \right) = -\nabla p + \nabla \cdot \left(\mu \left(\nabla \vec{u} + \left(\nabla \vec{u} \right)^T \right) \right) \quad (1)$$

$$\mu = C \dot{\gamma}^{n-1} \quad (2)$$

where μ represents the viscosity, $\dot{\gamma}$ represents the shear rate, p represents the pressure, ρ represents the density of the electrolyte, t represents the time of the reaction, and \vec{u} represents the fluid velocity. C is a given constant. In their COMSOL Multiphysics® model, the suspension is regarded as a uniform domain with both solid and liquid phases. The potential and current distribution in the solid are combined by Ohm's law, and the current source term corresponding to the local electrochemical reaction rate:

$$\nabla \cdot (\sigma \nabla \phi_s) - F a_s j_n = 0 \quad (3)$$

where σ represents the electronic conductivity in the solid phase, ϕ_s represents the potential in the solid phase, F represents Faraday's constant, a_s represents the specific surface area of embedded particles, and j_n represents the reaction rate on the particle surface. In the liquid phase, the potential is described by:

$$\nabla \cdot \left(\kappa_{\text{eff}} \nabla \phi_e - \frac{\kappa_{\text{eff}} RT}{F} \left(1 + \frac{\partial \ln f_a}{\partial \ln c_e} \right) (1 - t_+^0) \nabla \ln c_e \right) + F a_s j_n = 0 \quad (4)$$

where κ_{eff} represents the effective ionic conductivity of the electrolyte, ϕ_e represents electrolyte potential, f_a represents the activity coefficient of dissolved salt species, c_e represents the salt concentration, and t_+^0 represents the number of electrolyte transference.

Owing to the high viscosity of semi-solid flow battery suspension, the state of charge (SOC) in the channel changes along the channel length. In the same electrode model, the article compares the steady-state current density and charge distribution along the channel in the SSFB of LiCoO_2 and LiFePO_4 particles (Figure 2). In contrast, LiFePO_4 shows a more well-distributed SOC and higher energy efficiency.

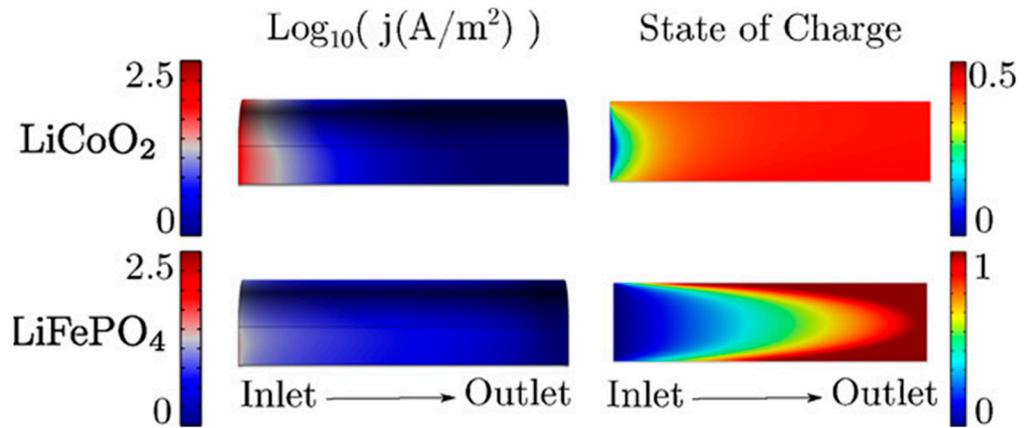


Figure 2. Comparison of the SOC and steady-state current density distributions along a flow channel in an SSFB, using LiCoO_2 and LiFePO_4 active particles [36].

Lacroix et al. [37] combined the work of Brunini to establish the three-dimensional model of the SSFB and simulated the diffusion of lithium-ion in LTO/LNCM particles and the SSFB liquid phase, as well as the electrochemical behavior and reaction kinetics in the SSFB at the micro- and macro-scale. The simulation results (Figure 3) show that changing the flow rate has barely any effect on the voltage drop in the channel. Combined with the deviation between the experimental data and the simulation results, it is pointed out that the battery channel should be as thin as possible to minimize the ohmic loss.

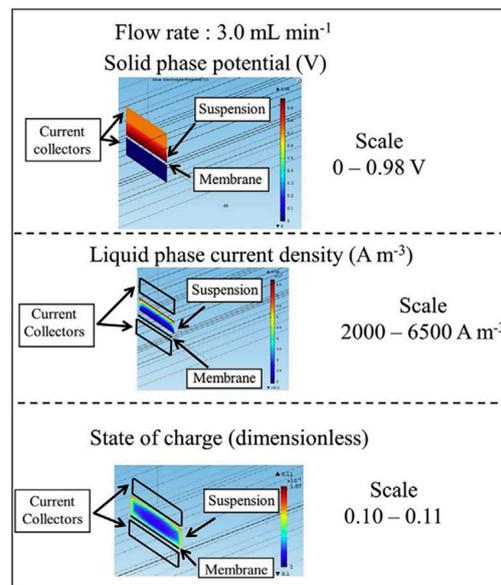


Figure 3. Model of the SSFB with a LTO-based suspension at a current density of 0.34 mA cm^{-2} and a 10% state of charge. The results of liquid phase current density, solid phase potential, and state of charge were shown in the form of a two-dimensional section [37].

Diffusion, as a major component of ion behavior in RFBs, has a significant impact on the efficiency, long-term performance, and capacity of the system. Exploring the diffusion behavior of ions in electrolytes can play a guiding part in the selection of active materials and the setting of operation parameters. In non-aqueous RFBs, electrolyte crossover has a significant effect on system stability. To this end, Lee et al. [38] built a 2D model of an all-vanadium acetylacetonate flow battery. The flow chart (Figure 4) of the model gives a clear view of the simulation logic. Through the variable-controlling method, the influence of the change of the vanadium ion diffusion coefficient in different valence states on the charge and discharge processes was studied. The relationship between the intersection of active species and battery performance was explored from the three perspectives of the battery operation cycle, system efficiency, and system capacity. The reaction equations of each half-cell are as follows:

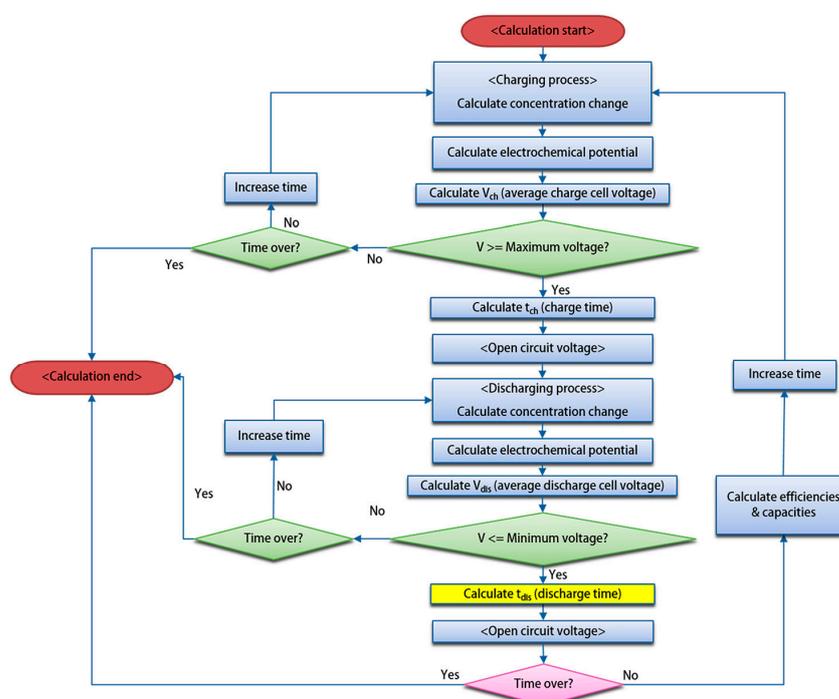
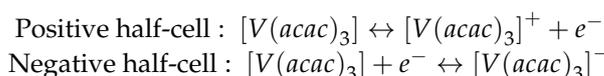


Figure 4. Flow chart of the VRFB simulation [38].

By trying different combinations of different diffusion coefficients of vanadium ions, the influence of the crossover of V_2^+ , V_3^+ , and V_4^+ was studied. The results show that the self-discharge caused by the crossover of V_2^+ and V_4^+ has a significant impact on cycle life length, but the crossover of V_3^+ remedies the imbalanced distribution of V_3^+ at the positive and negative electrodes. The results indicate the direction of searching combinations of diffusion coefficients of vanadium species, which is a guideline for the development of ion-exchange membranes for all-vanadium acetylacetonate RFBs.

Since SSFBs originate from lithium-ion batteries, they face similar obstacles. They have a simple flow pattern because of the viscous electrolytes, so the research focuses on optimizing the composition of organic electrolytes, both in the method of experiment and simulation. By using the macroscopic model of the flow channel, the flow of different electrolytes can be readily compared, along with the performance of the battery. In addition, these models can be easily established with engineering simulation software, such as COMSOL and ANSYS.

In regard to other non-aqueous flow batteries using organic electrolytes, there is still a long way to go before being put into official use. The modeling research can thereby be

carried out in many aspects and scales. For macroscale modeling work, the performance test of full-cell or half-cell in new organic solvents is valuable. Combined with the physical parameters measured in the experiment, the feasibility of the new system can be effectively verified. For microscale modeling, the diffusion of ions in organic solvents is a key aspect to consider. Through customized algorithms and models, the behavior of ions in the electrolyte or through the membrane is easy to obtain, which can also be reflected in macroscopic models to improve their accuracy.

4. Non-Aqueous Flow Batteries with Ionic Liquid Solvents

4.1. Working Principle

Ionic liquids have high ionic conductivity, low volatility, high electrochemical stability, and tunable solubility, polarity, and charge distribution, making them attractive as electrolytes. These properties are determined by the interactions between cations and anions, such as van der Waals and Coulomb forces, and the presence of Lewis acidity or basicity in their structures [13]. Deep eutectic solvents (DESs) have high conductivity, viscosity, and surface tension, making them attractive for electrochemical applications [39]. DESs can be made using inexpensive and biodegradable precursors such as oxalic acid and urea and have the potential for large-scale use.

Research into the mechanisms of electrochemical reactions in ionic liquids is an important aspect of numerical simulation studies of these liquids. Molecular dynamics simulations can be used to investigate issues such as electron transfer in ionic liquids, interactions between ions and electrodes, and chemical reaction pathways. Additionally, density functional theory and diffusion-reaction theory can be used to study the electrochemical reaction kinetics in electrochemical processes, including reaction rates, activation energies, and other parameters.

4.2. Modeling Research

After 2000, ionic liquids began to be applied in the field of electrochemistry. They were first used in the development of lithium-ion batteries and were then extended to RFBs. However, the numerical simulation study in RFBs has made slow progress. Since DESs have been applied to the field of RFBs, it has aroused the strong interest of some researchers, and a series of experiments and numerical simulations have been carried out.

Xu et al. [40] used a 2D model to find the influence of temperature on the performance of the vanadium flow battery with DES solvents. In the electrode, the transfer of species is governed by diffusion, electromigration, and convection. The expression is shown as:

$$\nabla \cdot \left(-D_i^{eff} \nabla c_i - Z_i \mu_i^{eff} F c_i \nabla \phi_i \right) + \vec{v} \cdot \nabla c_i = 0 \quad (5)$$

where c_i represents the concentration of the species i , F represents the Faraday constant, \vec{v} represents the fluid velocity, Z_i represents the charge number of the species i , ϕ_i represents the ionic potential, and μ_i^{eff} and D_i^{eff} are the effective ionic mobility and effective diffusion coefficient of species i respectively. The dynamic equation is given by the Butler-Volmer equation:

$$j_1 = i_1^0 \left[\frac{c_{Fe(III)}^s}{c_{Fe(III)}} \exp\left(-\frac{\alpha_{1,c} F \eta_1}{RT}\right) - \frac{c_{Fe(II)}^s}{c_{Fe(II)}} \exp\left(-\frac{\alpha_{1,a} F \eta_1}{RT}\right) \right] \quad (6)$$

$$j_2 = i_2^0 \left[\frac{c_{V(III)}^s}{c_{V(III)}} \exp\left(-\frac{\alpha_{2,c} F \eta_2}{RT}\right) - \frac{c_{V(II)}^s}{c_{V(II)}} \exp\left(-\frac{\alpha_{2,a} F \eta_2}{RT}\right) \right] \quad (7)$$

where j_1 and j_2 are the current densities of the positive and negative electrodes, respectively, and $c_{Fe(III)}^s$, $c_{Fe(II)}^s$, $c_{V(III)}^s$, $c_{V(II)}^s$ represents the surface concentrations of Fe^{3+} , Fe^{2+} , V^{3+} , and V^{2+} on the electrode.

The results (Figure 5) show that the SOC of the battery should be controlled between 10% and 85% to limit side reactions. In a certain range, increasing the temperature can lessen the power loss to ameliorate the performance of the flow battery. Due to the high viscosity of DES, the ion transfer in the electrolyte is slow, so the redox reaction is mostly concentrated in the area near the membrane.

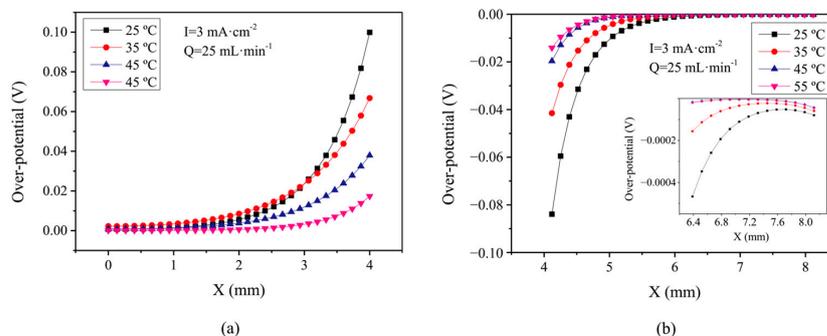


Figure 5. Distribution of over-potentials with different temperatures, where (a) and (b) represent the negative and positive electrode respectively [40].

In the research direction of DESs, some researchers have explored the complex mass transfer behavior of the electrode from a more microscopic point of view. In 2019, Ma et al. [41] used the lattice Boltzmann method to explore the flow, charge transfer of species, and electrochemical reaction behavior of the DES electrolyte in the electrode of all copper NAFBs. It is proven that temperature plays a significant part in the operation of NAFBs with DESs. The results (Figure 6) show that the decrease in porosity increases the depletion time of the species and improves the utilization efficiency of the electrolyte. With the temperature rising, the flow rate increased, and the average overpotential of DES electrolytes decreased significantly. This conclusion is especially applicable at a working temperature below 313 K.

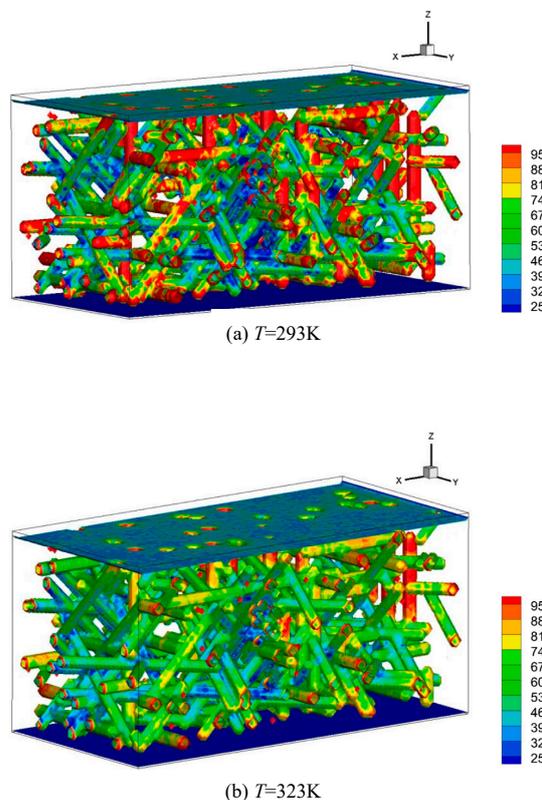
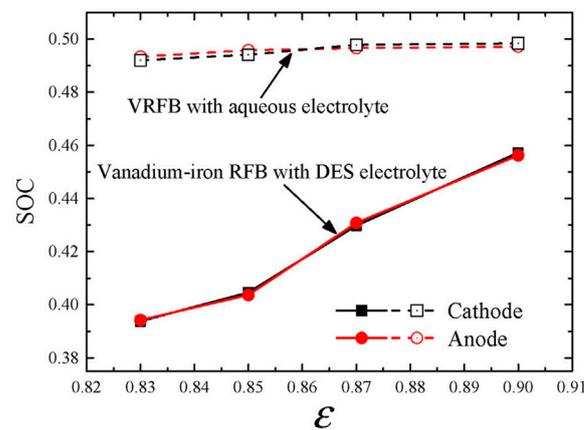
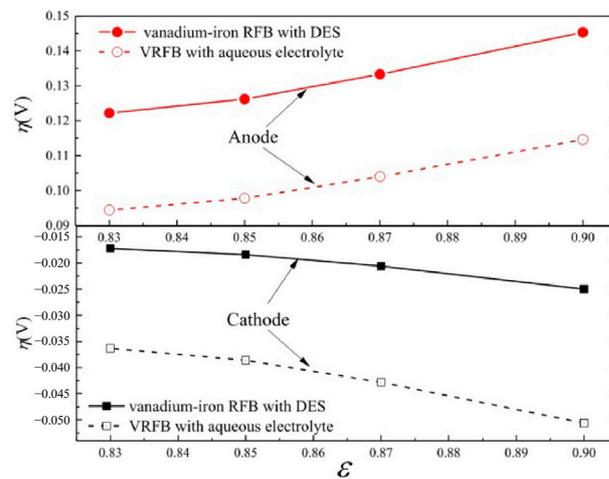


Figure 6. Contour showing the effect of operating temperature on current density ($\epsilon = 0.9$) [41].

In 2020, the lattice Boltzmann method was applied to iron-vanadium NAFB with DES [42]. The reaction mechanism of vanadium and iron ions in DES at the pore scale was explored by using the parameters from experimental data. The results (Figure 7) show that under the condition of constant current discharge and given pump power, electrodes with low porosity and small fiber diameter can make the reactants consume more time in DES electrolyte. At the same time, the larger the fiber diameter is, the wider the pore size distribution is, resulting in a larger, more obvious local current density inhomogeneity entering the porous electrode. In addition, the activation potential of the anode is higher than that of the cathode, which is due to the low transfer coefficient and diffusion coefficient of vanadium ions in DES.



(a)



(b)

Figure 7. Comparative investigation between vanadium-iron RFB with DES and VRFB with aqueous electrolyte. (a) Comparison of average SOC in the anode and cathode. (b) Comparison of overpotential in the anode and cathode [42].

Ionic solvents suffer from high viscosity, which limits their mass transfer capacity. There are three main ways to solve this problem: by imposing operating conditions, changing electrode structures, and improving electrolyte composition. All three of the above methods can be achieved efficiently and economically through modeling and simulation. Especially when it comes to the study of pore scale, mesoscopic simulation methods such as the lattice Boltzmann method play an irreplaceable role in the development of non-aqueous RFBs with ionic solvents.

5. Summary and Outlook

With their flexible design, controllable cost, continuous and stable power output, and high energy conversion efficiency, RFBs are the best scheme for renewable energy storage at present. All-vanadium flow batteries have been the focus of researchers for their high electrolyte utilization, fast response, long cycle life, and large energy storage. In contrast, RFBs of other systems generally have obvious shortboards, which is challenging to compete with the all-vanadium flow battery. Therefore, we should not relax on the development of new systems of RFBs, paying more attention to other flow battery systems to adapt to the gradually expanding flow battery market in the future as soon as possible. For NAFBs, most of the research is still in its infancy, and there are still a lot of gaps between mathematical modeling and real systems. It is the key link to push the theory into practice to improve the structure design, optimize the operating parameters, predict and improve the performance, improve the capacity, and find more combinations of materials with the help of mathematical models.

Among the RFBs using organic solutions as electrolytes, SSFB and vanadium NRFB were first explored through modeling and simulation methods. For SSFBs, it is particularly important to solve the lack of understanding of the influence of the slurry electrode phenomenon and electrode composition on conductivity. This indicates that new strategies are needed in element geometry modeling and material performance evaluation. To uncover the complexity of semi-solid RFBs and realize more accurate predictions, mathematical models of active species and suspension dynamics other than viscosity should be established, and some appropriate assumptions should be made, including the selection of collectors suitable for fluid flow. For improving the rheological and electrochemical performance of the battery, modeling studies can explore more operating characteristics, including the evaluation of mass transfer situations and flow field design majorization. For metal-based NRFBs, self-discharge caused by crossover is still one of the major problems. Therefore, modeling ion behavior through the membrane is still the top priority. Except for vanadium, other metal ions should also be studied in the NRFB systems. However, this requires a large amount of experimental data as a basis. Organic NAFBs still lack progress in modeling and simulation, and more characteristics and performances of organic RFB systems need to be predicted by modeling. This can be accomplished by stack and system modeling under different operating parameters, exploring stack design, simplifying structural design, and optimizing reaction conditions to minimize pump loss and shunt current and prolong cycling life. There is also a brand-new prospect of using the fast computing method [43] to quickly screen organic redox couples and solvents to meet the design requirements.

At present, the main problems of ionic liquids are their high viscosity, large mass transfer resistance, slow transfer of active substances, and a tendency to polarize. To solve these problems, people can try to optimize it using out-field coordination, artificial control of fluid flow, a change in the electrode porous structure, and so on. Because of their advantages of environmental protection, easy preparation, and high ionic solubility, DESs have been well studied in both experiments and numerical simulations. It will be very meaningful work to draw experience from the existing models and establish a formatted numerical simulation method that can be extended to other ionic liquid solvent RFB systems.

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