

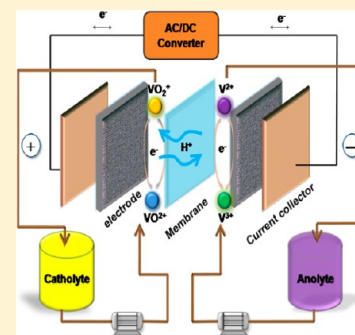
Vanadium Flow Battery for Energy Storage: Prospects and Challenges

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ABSTRACT: The vanadium flow battery (VFB) as one kind of energy storage technique that has enormous impact on the stabilization and smooth output of renewable energy. Key materials like membranes, electrode, and electrolytes will finally determine the performance of VFBs. In this Perspective, we report on the current understanding of VFBs from materials to stacks, describing the factors that affect materials' performance from microstructures to the mechanism and new materials development. Moreover, new models for VFB stacks as well as structural design will be summarized as well. Finally, the challenges, the overall cost evaluation, and future research directions will be briefly proposed.

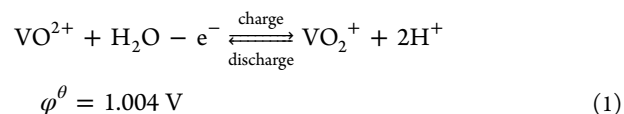


As the crisis of fossil fuel increases, renewable energy becomes the central topic of our times. However, the random and intermittent nature of renewable energy resources like solar and wind induces a low-quality output electricity and further affects their stability in the grid. The electricity energy storage technique (EES), which could provide a temporary medium to store and release electricity as needed, therefore, becomes a valid solution to solve these problems.¹ In combination with renewable resources, EES can increase the quality and the stability of photovoltaic (PV) and wind-generated electricity. To date, different kinds of energy storage techniques have been developed for different applications.² Each technology has its own advantages and limitations and is suitable for a limited range of applications. Considering the performance requirement and cost, electrochemical systems or rechargeable batteries are becoming an ideal option for EES due to their advantages,³ such as not being limited by geographical requirement, the ability to be installed anywhere, the quite large control window for power rate and capacity and the fast response time and low environmental footprint.

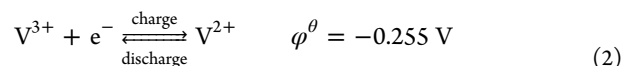
Simply, batteries are devices that can convert chemistry energy into electricity by the electron exchange via the oxidation or reduction of active species. This process could be reversed, allowing the system to be used for both energy storage and electricity delivery. Normally, batteries from different active species could meet specific EES applications according to their range requirement of power rate and capacity (Figure 1). For large-scale energy storage systems, the flow battery (FB) is emerging as an effective technique due to its attractive features like flexible design, high efficiency, high safety, and long cycle life. It employs dissolved active species in different oxidation states to store chemical potential energy. According to the types of active species and electrochemical

potential involved, a number of FBs including Fe/Cr, all-vanadium, Zn/Br₂ flow batteries (ZBBs), and polysulfide/Br₂ flow batteries have been successively proposed and developed. Among them, the all-vanadium flow battery (VFB) uses the same element in both half-cells, which avoids cross-contamination of the two half-cell electrolytes and, therefore, becomes the most promising technology for large-scale energy storage.⁴ Figure 2 indicates the principle and the basic structure of a VFB, where two electrolyte tanks and a battery stack are included. V(II)/V(III) and V(IV)/V(V) couples in sulfuric acid solution were used as negative and positive electrolytes, respectively, which cyclically pumped in the stacks. The electrochemical reactions during charge and discharge were listed as follows:

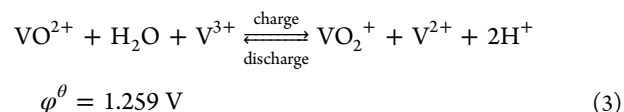
Positive electrode reaction:



Negative electrode reaction:



Overall electrochemical reaction of cell:



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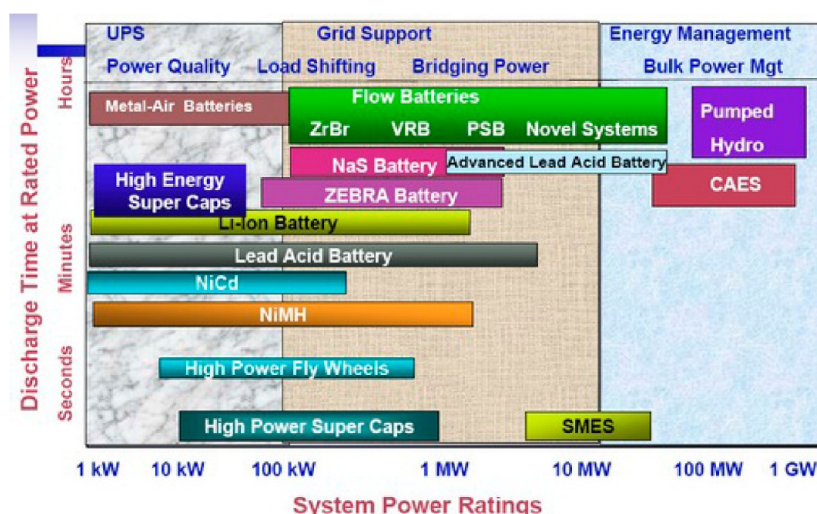


Figure 1. Basic characteristics of different energy storage techniques. Reprinted with permission from ref 2. Copyright 2010, Electric Power Research Institute, Inc.

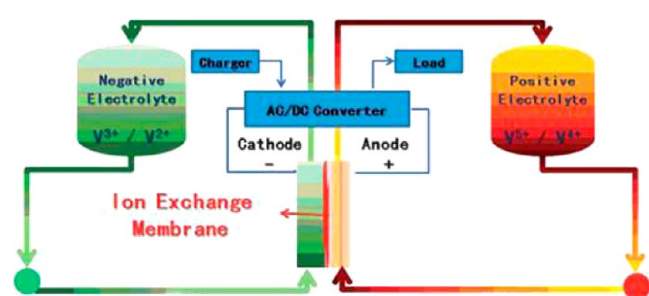


Figure 2. The principle of VFB. Reprinted with permission from ref 5. Copyright 2011, The Royal Society of Chemistry.

The characteristic “non-participating electrode” structure of VFB allows the independent design of power rating and storage capacity. The area of stacks determines the power rate, while the electrolyte’s volume and concentration will offer the battery with storage capacity. A VFB battery cell is normally composed of two half-cells, two solid electrodes, and a membrane separator. The key materials of VFBs including membranes, electrodes, and electrolytes will finally determine the cell performance. However, the circumstance of VFB is quite complicated, which is a concern for electrochemistry, materials science, and physical chemistry, and so forth. There are quite a lot of factors that can affect the properties of key materials. In this Perspective, the development of key materials will be summarized, and the factors that affect key materials will be discussed in detailed. Afterward, the main challenge of VFB and a possible solution will be provided.

Simple Introduction of Membrane. The membrane separator is a key component of VFB, playing the role of isolating electrolytes (vanadium ions) while still transferring ions (protons, SO_4^{2-}) to complete the circuit. The ideal membranes should possess high ion selectivity, ion conductivity, and good chemical and mechanical stability. The membranes traditionally used in VFB are perfluorinated sulfonic acid polymers such as Dupont’s Nafion. Although they show both high proton conductivity and chemical stability, the extremely high cost and low ion selectivity of these membranes (high vanadium crossover) have limited their further commercialization. Hence, alternative ion exchange membrane (IEM) materials are being sought. Quite recently, different kinds of IEMs including anion or cation exchange and even blend

membranes were investigated in VFB applications, summarized previously.^{5,6} Herein, we give a quite simple description on different membranes and some discussion on their perspective.

The current research is mainly focused on two critical issues of VFB membrane separators. One is mainly devoted to increasing membrane selectivity, while the other important task will be focused on improving membrane stability. The selectivity of membranes in the VFB is largely determined by the membrane morphology. Two regions normally coexist in traditional IEMs, a hydrophilic and a hydrophobic one.⁷ The distribution of these two regions will largely affect membrane properties like ion selectivity, ion conductivity, and mechanical and chemical stability. Various factors could affect the microphase-separated morphology of IEMs, among which, the nature of polymer chains could be one of the most important ones. The structure of currently used Nafion membranes consists of a flexible hydrophobic backbone and a side chain with highly hydrophilic terminal sulfonic acid functional groups ($-\text{SO}_3\text{H}$). In this structure, the hydrophobic Teflon backbone provides a membrane with excellent mechanical and chemical stability, while the hydrophilic zone, originating from the assembled sulfonated groups, ensures the membrane conductivity. The flexible long ionic side chain and perfluorinated backbone of Nafion could form continuous networks of ionic channels through the Nafion membrane. Different models were put forward to interpret the morphology of Nafion, among which the cluster-network model (Figure 3) was the most classical one.⁸ This model

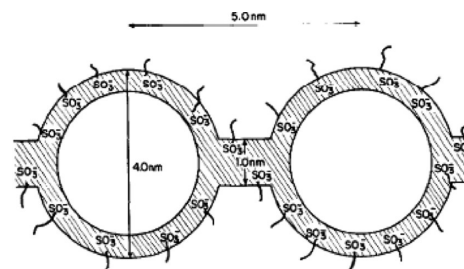


Figure 3. Cluster-network model for the morphology of hydrated Nafion. Reprinted with permission from ref 8. Copyright 1983, Elsevier.

consists of an equal distribution of sulfonated ion clusters (also described as inverted micelles) with a 40 Å (4 nm) diameter held

within a continuous fluorocarbon lattice. Narrow channels of about 10 Å (1 nm) interconnect the clusters, which forms the proton transport channels. Thus, Nafion membranes exhibit quite high proton conductivity; however, due to their higher swelling and larger cluster radius, the resistant capacity to vanadium ions of them is too low to ensure their ion selectivity. Therefore, most of the researches were focused on improving the ion selectivity of Nafion by blocking the hydrophilic clusters.

Modification of Nafion. Inorganic particles like SiO_2 , TiO_2 , and zirconium phosphate could be introduced into the Nafion to improve membrane selectivities.^{9–11} For example, the introduction of SiO_2 nanoparticles could effectively reduce the crossover of vanadium ions for Nafion membranes, and as a result, the coulombic efficiency (CE) of the membranes would be greatly improved after introduction of nanoparticles.⁹ An organic component can be introduced in perfluorinated membranes as well to decrease their vanadium ion permeability. Polyvinylidene (PVDF) can effectively suppress the swelling of Nafion due to its high crystallite nature. By introducing PVDF in Nafion, the CE of the battery improves due to its higher ion selectivity, while the energy efficiency increases as well.¹² Acid–base membranes like SPEEK, (sulfonated poly(ether ether ketone)) and PSf-ABIm (polysulfone-2-amide-benzimidazole) are another very good way to improve membrane selectivity by using the interactions between sulfonated acid and amide basic groups.^{13,14} Apart from the blend membranes mentioned above, composite membranes with a thin vanadium resistant layer could be another choice. For example, a positively charged polyethylenimine (PEI) layer was successfully introduced on the surface of a Nafion membrane by Luo et al. to increase the ion selectivity.¹⁵ Other polymers layers like polypyrrole¹⁶ or a multilayered polyelectrolytes complex (PEC)¹⁷ can be used as well to increase the ion selectivity of Nafion.

Nonperfluorinated Polymer Membranes. Another type of substitute membrane is based on the idea of changing the nature of the polymer chain to tune its selectivity and conductivity. Most recently, the cation and anion exchanged aromatic polymers received wide attention in the VFB. The choice of aromatic polymers instead of perfluorinated polymers is mainly based on their low cost and high selectivity. These polymer membranes often possess much higher ion selectivity than Nafion due to their distinctly different microstructures and the acidity of the sulfonic acid functional groups. As mentioned above, Nafion normally combines an extremely hydrophobic perfluorinated backbone and an extremely hydrophilic and flexible sulfonic acid side chain. Under the VFB operating condition, the hydrophobic/hydrophilic nanoseparation could easily occur, and the side sulfonic groups can easily aggregate and form well-connected hydrophilic domains, which are beneficial for transporting protons, for vanadium ions as well. For aromatic polymers, the rigid and less hydrophobic polymer chain together with the less acidic sulfonic groups leads to a low degree of hydrophilic/hydrophobic phase separation (Figure 4). These results can be confirmed from the results of small-angle X-ray scatter (SAXS) and the transform electron microscope (TEM).¹⁸ For example, for hydrated SPEEK membranes, a broadened ionomer peak at higher scattering angle could be found compared with Nafion, which indicated a smaller characteristic separation length with a wider distribution and a larger internal interface between hydrophobic and hydrophilic domains for SPEEK membranes.¹⁸ Therefore, their resistant capacity to vanadium ions could be improved greatly; as a result, their CE in the VFB could be much higher than that of commercial Nafion.

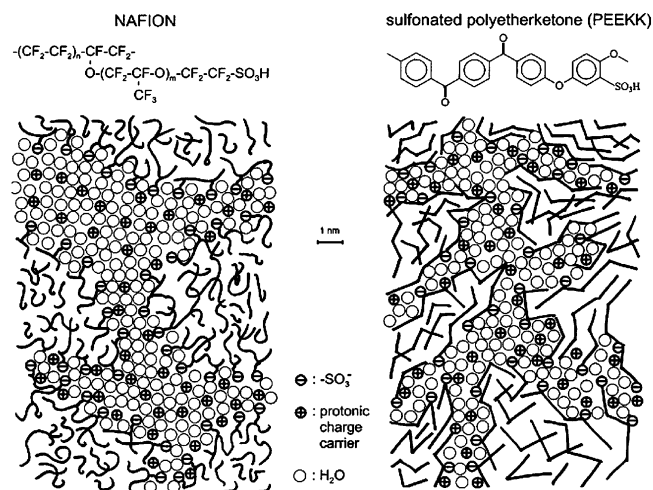


Figure 4. The schematic phase-separated structures of Nafion and SPEEK membranes. Reprinted with permission from ref 18. Copyright 2001, Elsevier.

Most of the sulfonated aromatic polymer membranes show much higher CE than the currently used Nafion due to their high selectivities. Other CEMs with different structures like sulfonated poly(arylene thioether ketone),¹⁹ sulfonated poly(fluorenyl ether thioether ketone),²⁰ poly(arylene ether sulfone),²¹ and sulfonated poly(tetramethyldiphenyl ether ether ketone)²² based membranes were then investigated by different researchers. As discussed above, most of these membranes showed much lower VO_2^+ permeability and higher CE than Nafion due to their high selectivity. Anion exchange membranes raised quite high attention due to their repellent effect to positive vanadium ions, which seems to be one of the most efficient methods to minimize the vanadium cross mixing.^{23–26} Recently, anion conductive membranes based on quaternarized poly(tetramethyldiphenyl ether sulfone) (QAPES) were fabricated by our groups; these membranes showed an impressive suppression effect on vanadium ions. The recorded vanadium permeability is 2 orders of magnitude lower than that of Nafion115.²⁷ The VFB assembled with the membrane shows outstanding performance, which carries much higher CE and EE at different current densities than that of Nafion115.

Even though most of the above-mentioned polymer membranes show quite high ion selectivity, their chemical stability is one of the most critical issues to affect their final application in VFBs. Especially the introduction of ion exchange groups in hydrocarbon membranes could accelerate the membrane degradation. Normally, VO_2^+ is regarded as a strong oxidant that could cause membrane degradation. The VFB operating condition is quite complicated; apart from the strong oxidized VO_2^+ , the electrical field could possibly have some effect on the degradation behavior of the membranes. Therefore, the currently available characterization techniques are also quite limited, which we summarized in our previous review.⁵ However, it is interesting to find that the anion exchange membranes could have better oxidation stability than the cation exchanged ones with a similar main chain due to their quite different interactions with VO_2^+ ions. As proposed by Vijayakumar and Kim,^{28,29} VO_2^+ would attach to $-\text{SO}_3^-$ in CEM and weaken the stretch intensity of sulfonated groups, whereas the positively charged ion exchange groups in anion exchange membranes are highly repellent to vanadium ions, which might, reasonably, hinder the approach of VO_2^+ and prevent the oxidation attack (Figure 5).

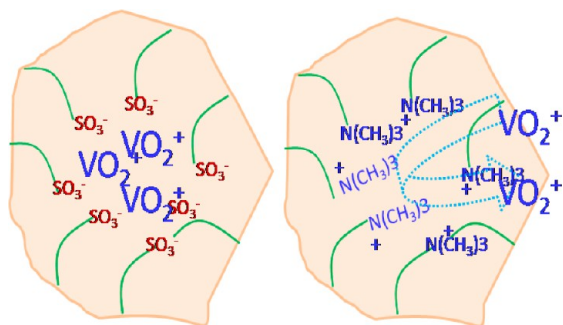


Figure 5. Oxidation stability of IEMs.

The concept of the porous membrane overcomes the stability restriction caused by ion exchange groups from traditional ion exchange membranes.

Porous Membrane Separators. As mentioned above, the introduction of ion exchange groups in a hydrocarbon polymer could induce membrane degradation, thus affecting their membrane stability in the VFB. To solve these problems, porous separators were introduced in the VFB recently.³⁰ The idea of separating vanadium ions from protons via pore size exclusion was realized (Figure 6). This concept successfully overcomes the restriction caused by ion exchange groups from traditional IEMs. The porous membranes successfully separated vanadium ions (V(II), V(III), V(IV), and V(V)) from protons due to their difference in radius, charge density, and specific interactions with the electrolyte and membranes. The first reported porous nanofiltration membrane for VFBs is made from hydrolyzed polyacrylonitrile (PAN-H). The membranes show good prospects in VFBs by achieving a CE up to 95% and an EE of 76% at the operating condition of 80 mA/cm².³⁰

More recently, part of the work on the VFB porous membrane separator is focused on solving the conflict between membrane selectivity and ion conductivity. Normally, membranes with larger pores are preferred in VFBs to reduce the loss of energy from ohmic polarization. On the other hand, membranes with a smaller pore size distribution are yet preferred to suppress the vanadium ion cross-mixing (i.e., enhance the ion selectivity). Therefore, improving the ion selectivity while still keeping the proton conductivity of membranes becomes quite a critical issue in this field. To solve this problem, some research was carried out via introducing silica oxide into the pores and on the surface to block the pores and further improve their ion selectivities.³¹ Another effective way is to design membranes with a specific morphology.

For example, a highly symmetric, sponge-like porous membrane with positively charged groups was fabricated, and the membranes perfectly combined excellent V-ion rejection with high proton conductivity, which showed overall better performance than commercial Nafion membranes.³²

In summary, the modified Nafion membranes could provide an efficient way for improving their selectivity. However, their internal high cost will be the biggest challenge. Even though nonfluorinated polymer membranes show a quite promising performance, the lack of long-term experiments still renders the stability of nonfluorinated membranes susceptible. It is regarded that a higher ion exchange capacity, that is, a larger amount of fixed ionic groups, of a nonfluorinated IEM would enhance its ion conductivity while being adverse to its chemical stability. Therefore, porous membrane separators could be a better option because ion exchange groups are no longer needed in this system. Even some critical issues still need to be further clarified, for example the transport mechanism of different ions in porous membranes, the conflict between the membrane selectivity and ion conductivity, and so forth.

Electrolyte. The electrolytes of VFBs serve as the medium to store and release energy, whereas the volume and the concentration of the electrolyte determine the energy of the battery.³³ As a carrier of electric energy, the stability of the electrolyte has a significant influence on the performance and cycle life of the battery. To improve the energy density and the cycle life of a VFB, it is indispensable to ensure the solubility and stability of electrolyte.

In a VFB, the electrolyte is composed of active species (vanadium ions with different valence states) and supporting electrolytes (e.g., sulfuric acid,³⁴ hydrochloric acid,³⁵ methane sulfonic acid,³⁶ and a mixed acid of the above³⁷ or an organic electrolyte).³⁸ The criterion for the selection of the supporting electrolyte is based on electrochemical kinetics of the active species at the electrode–electrolyte interface, the electrolyte solubility, and minimal cross-contamination of the active electrolytes.³⁹

Taking the most common supporting electrolyte, sulfuric acid, as an example, the supporting acid provides protons, making the equilibrium cell potential pH-dependent. In a VFB, the V(II)/V(III) redox couple serves as the anolyte, whereas the V(IV)/V(V) redox couple serves as the catholyte. Due to the use of two soluble redox couples, solid-state reactions with their accompanying morphology changing at the electrodes are absent. By employing the same element of four valences as the active couples, the issue of cross-contamination during long-term use is significantly diminished.⁴

During operation, active species undergo oxidation or reduction reactions when they are in contact with or close proximity to the current collector.¹ Electrochemical reactions within the battery stack change the valency of the vanadium ions. The concentration of vanadium is a function of the

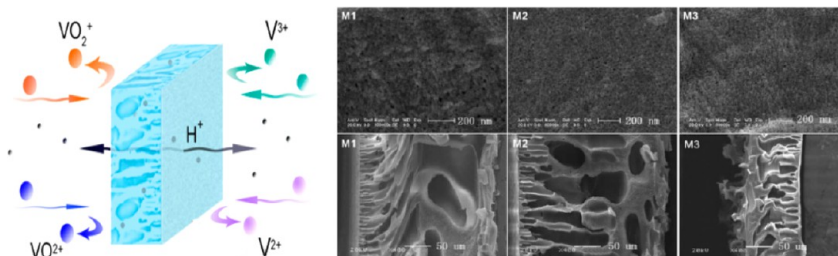


Figure 6. The porous membranes for the VFB separator. Reprinted with permission from ref 30. Copyright 2011, The Royal Society of Chemistry.

saturation solubility of the different oxidation states that are formed during charging and discharging in the positive and negative half-cell solutions.⁴⁰

To improve the energy density and the cycle life of VFBs, it is indispensable to ensure the solubility and stability of the electrolyte.

The chemical nature of vanadium is of great magnitude to track the internal factors (e.g., the transport mechanism of vanadium ions, the stability of electrolytes) that affect the VFB performance in depth.⁴¹ Vanadium in its V oxidation state exhibits a rich aqueous chemistry because the detected species are strongly dependent upon the pH and vanadium concentration (Figure 7).⁴²

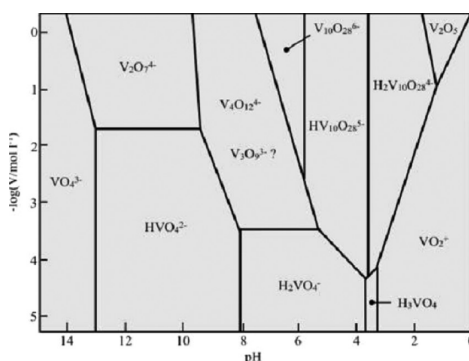


Figure 7. Stability domains of various vanadates and polyvanadates as a function of the pH and vanadium concentration. Reprinted from ref 42. Copyright 2007, American Chemical Society.

The real existence form of vanadium ions under the operating medium of VFB is quite complicated and blurry. The dissolved states of V(IV) and V(V) in concentrated sulfuric acid (H_2SO_4) solutions were investigated via spectroscopic and dynamic electrochemical methods.

The existence forms of the vanadium species in highly acidic conditions were studied by Raman spectroscopy. The results showed that the major existing species of vanadium ions are VO_2^+ , VO_2SO_4^- , $\text{VO}_2(\text{SO}_4)_2^{3-}$, $\text{V}_2\text{O}_3^{4+}$, VO_2HSO_4 , and so forth, the amount of which depends upon the actual V(V) and total sulfate concentrations and their ratio. At higher sulfate concentration, $\text{V}_2\text{O}_3^{4+}$, $\text{VO}_2(\text{SO}_4)_2^{3-}$, and their polymers tend to be formed, which are beneficial for stabilizing the positive electrolyte in the VFB.⁴³

The dissolved active species in various concentrations of H_2SO_4 have been investigated by means of various electrochemical methods such as cyclic voltammetry and chronopotentiometry.⁴⁴ The diffusion coefficients (D), Stokes radii, and existence form of related V(V), V(IV), V(III), and V(II) species⁴⁴ are listed in Table 1.

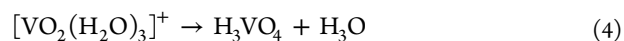
It is revealed that in concentrated H_2SO_4 solutions, V(IV) forms complex species with neither SO_4^{2-} nor HSO_4^- . The relatively large Stokes radii and the characteristic multistep reduction waves of V(V) were observed at a lower H_2SO_4 concentration region ($<7\text{ M}$), both suggesting that V(V) species exist in a certain polymeric form.⁴¹

The structure and stability of VO_2^+ in aqueous solution were studied by Car–Parrinello simulations,⁴² which concluded that $\text{VO}(\text{OH})_3$ was the most stable structure at 227°C in an acid

Table 1. Parameters of V Species in Electrolyte with Concentrated Sulfuric Acid and V Species

V species	existence form	diffusion coefficient/ (cm^2/s)	Stokes radius/ (nm)
V(II)	$\text{V}(\text{H}_2\text{O})_6^{2+}$	1.1×10^{-6}	0.32
V(III)	$\text{V}(\text{H}_2\text{O})_6^{3+}$	0.57×10^{-6}	0.32
V(IV)	VO^{2+}	1.0×10^{-6}	0.21
V(V)	VO_2^+	1.0×10^{-6}	0.28

medium. Vijayakumar et al. further illustrated that the V^{5+} species existed as hydrated pentacoordinated vanadate ions, that is, $[\text{VO}_2(\text{H}_2\text{O})_3]^+$ by nuclear magnetic resonance (NMR) and density functional theory (DFT).⁴⁵ This unstable hydrated structure will change into a neutral H_3VO_4 molecule via a deprotonation process at an elevated temperature and subsequently lead to V_2O_5 precipitation in the electrolyte.



The precipitation can be avoided by preventing the deprotonation process. Therefore, a simple way to prevent the deprotonation process is to increase the supporting acid concentration.

The conclusions about the dissolving state of vanadium are somehow a bit tricky due to the complicated medium of the VFB. However, the discrepancies for the results interpretation are acceptable because they are associated with different analytical techniques even under different chemistry circumstances.⁴³

Thermal Stability Behavior of the Electrolyte. Even though quite a lot of demonstrations of VFB systems have been carried out already,³ the current technology is still not ready for broad market penetration due to their internal limitation of energy density ($<25\text{ W h/kg}$). One of most critical issues that affect their energy density could be derived from the low solubility and the stability of the electrolyte solutions.³⁷ Moreover, increasing the concentration of vanadium ions can reduce the initial capital investment and the operation cost as well. Therefore, investigation on the stability of the electrolyte is of great significance for the development of the VFB.

Factors like the concentration of vanadium ions, the temperature, the concentration of sulfonic acid, the density, the viscosity, the state of charge (SOC), the conductivity, and the electrochemical behavior of electrolytes could strongly affect the VFB performance,⁴⁶ among which the concentration and thermal stability are of great importance. V(II), V(III), and V(IV) are inclined to form precipitation under a relatively low temperature (below 10°C), while the fully charged positive electrolyte solution displays poor stability at elevated temperatures (above 40°C) and also at high vanadium concentrations ($>2\text{ M}$).⁴⁵ As explained earlier, this poor stability is witnessed as hydrated V_2O_5 precipitation. The precipitation may cripple the pump circulation and severely reduce the charge/discharge efficiency of the battery and further lead to energy loss and failure of the battery.⁴⁷ Thus, it is important to optimize the operating conditions to improve the stability of the electrolyte, especially for the catholyte.

In the past years, there have been great efforts to increase the stability of vanadium species in sulfuric acid solutions, aimed at developing an electrolyte of high concentration and improving the energy density for VFB systems. The stability of the electrolytes for VFBs was investigated with ex situ heating/cooling treatment and in situ flow battery testing methods.⁴⁵

Several works have been reported on preventing and delaying the precipitate formation in the positive electrolyte of the VFB.

Although the thermal stability of V(V) can be dramatically enhanced by increasing the sulfuric acid concentration to more than 6 M,³³ this would have a negative impact on the solubility of the V(II), V(III), and V(IV) ions. As the acid concentration increases, the solubility of active species could decrease due to the common ion effect.⁴⁶ On the other hand, the acid concentration increase means higher cost and higher corrosive durability requirements for materials.

Besides, other approaches to inhibit the precipitation of V(V) under high temperature were studied by researchers, one of which is adding some organic or inorganic chemicals as stabilizing agents.^{40,48–51}

The stabilizers (1–3%) like alcohols with ring or chain structures can increase the solubility of V(II)–V(V) ions in the solution, stabilize the electrolyte, and reduce the vanadium precipitation in the electrolyte.⁵⁰ It is worth noting that most of organic chemicals with the functional groups of C=C, –OH, CHO, and C=O are not stable and are easily oxidized by the V(V) ions in the solutions.⁴⁸ They could participate in the electrochemical reaction and change the valency of V(V) in the solution, consequently resulting in capacity loss.⁵⁰

Among all of the studied chemicals, K₂SO₄,⁴⁰ sodium hexametaphosphate (SHMP),⁴⁰ poly(acrylic acid) (PA) and its mixture with CH₃SO₃H,⁴⁸ D-sorbitol,⁴⁹ and Coulter IIIA dispersant⁵⁰ proved to be promising to stabilize the positive electrolyte. The exact mechanism of stabilization by these additives has not been clearly clarified yet. It is expected that additives could be adsorbed on the surface of any nuclei and block the active sites to further reduce the rate of crystal growth.⁴⁰ Several organic additives, which contain one or more of –OH, =O, –NH₂ or –SH groups or combinations of these groups, are believed to encapsulate the hydrated pentacoordinated vanadate ion and inhibit precipitation formation.⁵² Another hypothesis for the surfactant cationic additive is based on the fact that the synergy of Coulomb repulsion and steric hindrance may reduce the aggregation of vanadium ions into V₂O₅.⁵⁰

The addition of stabilizing agents above can merely improve the stability of the electrolyte for a certain longer time in a relatively wider range of temperatures (–5–40 °C), and it is difficult for all four types of vanadium oxidation states to be stabilized at their corresponding high levels with the same additives.

For the purpose of increasing the solubility and stability of the electrolytes, another strategy was proposed by the group of Gary Yang, that is, employing chloride supporting electrolytes³⁵ or a sulfate–chloride mixed acid system³⁷ instead of pure sulfonic acid solutions. Chloride supporting electrolytes are capable of dissolving 2.3 M vanadium at varied valency states and shows excellent thermal stability.³⁵ The improved stability may be attributed to the formation of a vanadium dinuclear [V₂O₃·4H₂O]⁴⁺ or a dinuclear–chloro complex [V₂O₃Cl·3H₂O]³⁺. Recently, Li et al. used sulfate–chloride mixed electrolytes to increase the solubility of vanadium to 2.5 M with 6 M HCl,³⁷ which increased the energy capacity by 70% compared with the current sulfate system.

Except for the introduction of chloride as the supporting electrolyte, several organic electrolytes have also been proposed. The vanadium concentration can be increased up to 2 M by using 1.5 M CH₃SO₃H and a 1.5 M H₂SO₄ mixed acid solution.³⁶ Liu et al. developed a nonaqueous system, yielding an open-circuit potential (OCP) of 2.2 V and a CE of near 50%.³⁸ The wider potential window helps to raise the cell voltage and further increase the energy storage capacity.

However, the low conductivity of the organic electrolyte could be the most critical issue that needs to be solved further.

Electrode. VFB electrodes play the role of providing the proper sites for electrochemical reactions, but they do not take part in the electrochemical reaction directly. To obtain the high energy efficiency, the electrode materials should carry the following characteristics: high electrochemical activity and reversibility for redox couples to reduce the electrochemistry polarization; good conductivity to reduce the ohmic polarization; a stable 3D structure with a high active specific area, providing smooth channels for the electrolyte, increasing the mass-transfer rate and decreasing the concentration polarization; and excellent chemical, mechanical, and electrochemical stability and reasonable cost to meet the demands of large-scale production.

Mechanism of Electrode Reaction. Redox reactions can normally be divided into inner-sphere or outer-sphere electron-transfer reactions by modern quantum chemical theory. For outer-sphere reactions, the electron transfer occurs between two species without bonding between them, that is, electron tunneling from one species to the another, probably across a solvation layer, while for inner-sphere reactions, the electron transfer occurs in an activated complex, where a ligand is shared between the donor and acceptor molecules (and where the bridging ligand may or may not be transferred during the reaction).^{53–55}

Similar to the Fe³⁺/Fe²⁺ reaction, the V³⁺/V²⁺ reaction in the negative electrode is a simple one-electron-transfer reaction, which is commonly considered to be the prototypical outer-sphere reaction. However, Yamamura et al. proposed that it is not necessarily an outer-sphere reaction, even though strong stabilization of the divalent state gives nearly close metal–ligand distances for d³–V²⁺ and d²–V³⁺ ions.⁵⁶ Oriji et al. also suggested that some chemical step precedes the electron transfer.⁴⁴ However, the detailed reaction mechanism has not been very well studied.

The VO₂⁺/VO²⁺ reaction in the positive electrode is a multistep reaction that involves an oxygen transfer reaction before or after an electron-transfer step. Gattrell et al. proposed a model to predict their different mechanisms.^{57,58} As shown in Figure 8, the results

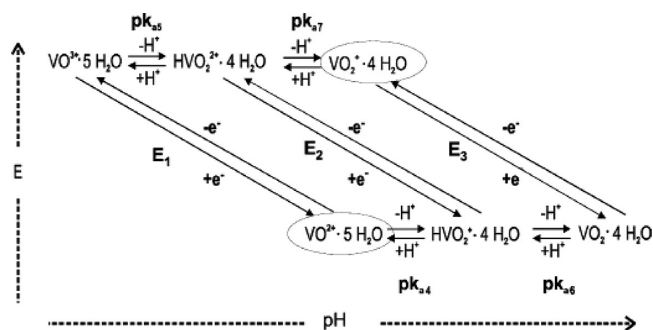


Figure 8. Schematic of the possible reaction pathways for the electrochemical reactions between VO²⁺ and VO₂⁺. Reprinted with permission from ref 57. Copyright 2004, The Electrochemical Society.

were consistent with a model, which combines a multistep CEC mechanism at low overpotentials with a multistep EC mechanism at higher anodic or cathodic overpotentials. Yamamura et al.⁵⁶ thought that this reaction proceeds by the outer-sphere mechanism (self-exchange between HVO²⁺ and HVO₂²⁺) rather than by the “rapid” inner-sphere mechanism (including a very rapid pre-equilibrium between VO₂⁺ and VO²⁺ to form a mixed-valence V₂O₃³⁺ species, which undergoes rapid electron exchange with VO²⁺) usually observed in the homogeneous reaction according to the Marcus equation.

Usually, we can distinguish between inner-sphere and outer-sphere reactions experimentally because outer-sphere reactions are generally rather insensitive to the nature of the electrode material,⁵⁵ whereas inner-sphere reactions depend very strongly on the electrode material. Table 2 summarizes the standard rate

Table 2. Standard Rate Constants (k_0) and Diffusion Constants (D) of V^{3+}/V^{2+} and VO_2^+/VO^{2+} Reactions on Various Electrodes

redox couple	k_0 (cm/s)	D (cm ² /s)	electrode	reference
V^{3+}/V^{2+}	1.7×10^{-5}	1.41×10^{-6}	GC	59
V^{3+}/V^{2+}	5.5×10^{-4}	4.0×10^{-6}	PG(c plane)	56
V^{3+}/V^{2+}	5.3×10^{-4}	2.4×10^{-6}	PFC	56
V^{3+}/V^{2+}	1.1×10^{-3}	4.0×10^{-6}	CP	60
VO_2^+/VO^{2+}	7.5×10^{-4}	1.4×10^{-6}	GC	59
VO_2^+/VO^{2+}	1.3×10^{-4}	2.4×10^{-6}	PG(c plane)	56
VO_2^+/VO^{2+}	8.5×10^{-4}	3.9×10^{-6}	PFC	56
VO_2^+/VO^{2+}	1.0×10^{-3}	2.4×10^{-6}	CP	60

constants (k_0) and diffusion constants (D) of V^{3+}/V^{2+} and VO_2^+/VO^{2+} reactions on various electrodes. As shown in Table 2, the electrode material has a large influence on the redox reactions of both V^{3+}/V^{2+} and VO_2^+/VO^{2+} . Therefore, a large amount of research has been carried out on the exploration and modification of electrode materials.

Electrode Material. VFB electrode materials can be mainly divided into two types, metal and carbon materials. A range of metal electrode materials such as Pb, Au, Pt, platinumized titanium (Pt–Ti), and iridium oxide dimensionally stable electrodes (DSAs) have been evaluated for VFBs.⁶¹ It was found that the electrochemical reversibility for the VO_2^+/VO^{2+} redox couple was not sufficient on the Au electrode, while the Pb and Ti electrodes were easily passivated in the potential range where the VO_2^+/VO^{2+} redox couple reactions occur, with a passivation film covering the surface, which leads to an increase in electric resistance.⁶¹ The problem of the passivation film is successfully avoided when using Pt–Ti and DSA as electrodes. However, their high cost limits them from being widely used.

Carbon materials are ideal VFB electrode materials for their wide operation potential range, high chemical stability, and reasonable cost.⁶² Various carbon materials such as carbon felt, graphite felt, carbon paper, and graphite powder have been investigated as the electrodes for VFBs.^{63–66} Among them, carbon felt and graphite felt are preferable electrode materials due to their better three-dimensional network structures and larger specific surface area, as well as high conductivity and chemical and electrochemical stability.

In recent years, carbon nanomaterials such as carbon nanotube,⁶⁷ graphite oxide,^{68,69} and graphene oxide (GO) nanosheets^{70,71} have attracted many researchers' attention. Han et al.⁷⁰ treated GO nanosheets at various temperatures, and the treated GO nanosheets demonstrated excellent electrocatalytic activity toward VO_2^+/VO^{2+} and V^{3+}/V^{2+} redox couples, which was attributed to their relatively high active surface area and the presence of a large amount of hydroxyl and carboxyl acid active groups on basal planes and sheet edges. However, electrodes based on single GO nanosheets suffered from low rate capability because of their rather poor electrical conductivity; thus, the energy efficiency and power capability were severely limited. Therefore, in order to improve the electron- and ion-transport capability, a GO nanosheets/multiwalled carbon nanotubes (GO/MWCNTs) hybrid was fabricated on a glassy carbon electrode (GCE)

(Figure 9) by an electrostatic spray technique after efficient ultrasonic treatment.⁷¹ The GO/MWCNTs hybrid combines

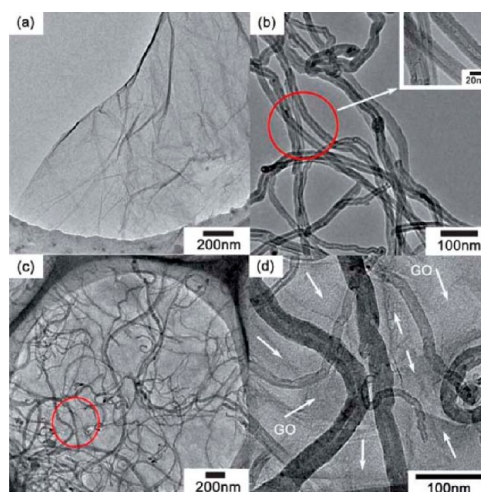


Figure 9. TEM images of (a) GO nanosheets, (b) MWCNTs, (c) GO/MWCNTs, and (d) a detailed view of the red circled area in (c). Reprinted with permission from ref 71. Copyright 2011, The Royal Society of Chemistry.

the catalytic activity of GO and the electronic conductivity of MWCNTs together and forms an electrocatalytic membrane with a mixed conducting network, which not only facilitates the rapid ion diffusion but accelerates the electron transport produced by the redox reaction of the VO_2^+/VO^{2+} couple. Therefore, compared with the pure GO nanosheets and MWCNTs, the GO/MWCNTs hybrid exhibited a much better electrocatalytic redox reversibility toward VO_2^+/VO^{2+} redox couples. The cathodic and anodic peak potential separation was only 0.15 V under a scan rate of 5 mV/s, and the value of I_{pa}/I_{pc} almost remained constant at about 1.20 in the range between 5 and 100 mV/s, which is close to the value of unity for the reversibility.

Modification of carbon electrode materials includes oxidation treatment, nitrogenization treatment, and introduction of an electrocatalyst.

Even though carbon electrodes themselves have some catalytic activity, the modification of the electrode materials is still necessary in order to enhance the reversibility of the electrode reaction as well as increase the electrocatalytic activity. A variety of modification methods have been carried out,^{72–84} which can be classified as oxidation treatment, nitrogenization treatment, and introduction of an electrocatalyst.

Oxidation Treatment. In a VFB, the oxygen-containing functional groups can facilitate improving the electrocatalytic activity of carbon electrode materials, and therefore, oxidation treatment becomes one of the effective modification methods.

Sun and Skyllas-Kazacos^{72,73} studied the effect of thermal and acid treatments of carbon and graphite felts on their electrochemical activity for VFBs. Graphite felt with a large amount of chemisorbed oxygen on the surface was fabricated by treating the graphite felt in 400 °C air or boiling them in concentrated sulfuric acid. Significant improvement in energy efficiencies were observed in cell

charge–discharge cycling tests after thermal or acid treatment of the graphite felt. The cell resistance apparently dropped after treatment. The increased electrocatalytic activity of the treated graphite felt was thus attributed to the increased concentration of C–O and C=O functional groups on the surface.

Other oxidation methods like electrochemical oxidation, mild oxidation, plasma treatment, and γ -ray irradiation^{74,75} were developed as well, and the battery performance was improved due to the introduction of oxygen-containing functional groups compared with the untreated carbon materials.

Nitrogenization Treatment. Apart from oxygen-containing functional groups, nitrogenous groups can also improve electrocatalytic activity of carbon electrode materials for the vanadium redox reactions. This is because carbon atoms adjacent to nitrogen dopants possess a substantially high positive charge density to counterbalance the strong electronic affinity of the nitrogen atom. The “positively charged” carbon atoms can work as the active sites for the oxidation reaction, while the five valence electrons of nitrogen atoms contribute extra charge to the bond in graphene layers, which enhances the basicity of carbon and the electrical conductivity of nitrogen-doped carbon. This is beneficial for the reduction process.⁷⁶

Shao et al.⁷⁶ prepared nitrogen-doped mesoporous carbon materials (N-MPC) by heat-treating mesoporous carbon in NH_3 . The electrocatalytic kinetics and the reversibility of the redox couple $\text{VO}_2^+/\text{VO}^{2+}$ were significantly enhanced on the N-MPC electrode compared with that for MPC and graphite electrodes. They thought nitrogen doping could facilitate the electron transfer on the electrode/electrolyte interface for both oxidation and reduction processes.

The experimental results of Wu⁷⁷ and Wang et al.⁷⁸ also confirmed this phenomenon. Furthermore, nitrogen doping can also make carbon materials more hydrophilic to increase the electrochemically active sites.

Electrocatalyst. The introduction of electrocatalyst on the surface of carbon felt to reduce the reaction overpotential of vanadium ion redox couples is another effective way. Sun and Skyllas-Kazacos⁷⁹ prepared the metallized graphite fiber electrode by impregnation or ion exchange with solutions containing Pt^{4+} , Pd^{2+} , Au^{4+} , Mn^{2+} , Te^{4+} , In^{3+} , and Ir^{3+} . The cyclic voltammetry results showed that the electrode modified by Ir^{3+} exhibited the best electrochemical behavior for the various vanadium redox species, while electrodes modified by Pt^{4+} , Pd^{2+} , and Au^{4+} are unsuitable because the high hydrogen evolution rates were promoted. The electrodes treated with Mn^{2+} , Te^{4+} , and In^{3+} also exhibited the significantly improved electrochemical activity compared with the untreated fiber electrode.

In addition, nano Bi^{81} and CuPt_3 ⁸² modified carbon electrode materials have also been investigated as the positive electrode for VFBS. The excellent electrochemical activity and reversibility toward the $\text{VO}_2^+/\text{VO}^{2+}$ reaction were attributed to the much higher electroactive area. However, the high cost of noble metal catalysts limited their commercial application. In this regard, advanced catalysts with low cost and high catalytic activity are in quite urgent need.⁸³ Recently, Yao et al.⁸⁴ prepared a carbon paper electrode coated with supported tungsten trioxide via an impregnation method, which resulted in improved electrocatalytic activity toward both $\text{VO}_2^+/\text{VO}^{2+}$ and $\text{V}^{3+}/\text{V}^{2+}$ redox reactions and an improved performance in terms of CE and EE of the VFB.

As mentioned above, the detailed reaction mechanisms of $\text{VO}_2^+/\text{VO}^{2+}$ and $\text{V}^{3+}/\text{V}^{2+}$ redox reactions have not been well-established yet, especially for the practical working circumstance of the VFB. Most research on the electrode was focused

on the improvement of the electrocatalytic activity of electrode materials, while the effect on the ohmic and concentration polarization was seldom the focus. For example, the nano-carbon material electrode delivers high electrocatalytic activity due to the large surface area, while the pore channels in this electrode are almost on the nanometer size scale, which is inconvenient for the transfer of electrolyte and leads to the increase of concentration polarization. Therefore, the reaction mechanism of both $\text{VO}_2^+/\text{VO}^{2+}$ and $\text{V}^{3+}/\text{V}^{2+}$ redox reactions in the VFB should be clarified further. The effect of the concentration of vanadium and H_2SO_4 should be investigated as well. Moreover, besides the electrocatalytic activity, the conductivity and the pore structure should also be considered to develop a high-performance electrode that enables the high power density to decrease the size and cost of a VFB.

Construction and Design of the Cell Stack. In real applications, the batteries are assembled from several single cells to form a battery stack. Electrodes are situated on either side of a bipolar plate, which separates each cell from the next one. The assembly of a cell stack is a straightforward mechanical process. Electrodes, membranes, and bipolar plates are manufactured to form a stack. Large steel end plates provide mechanical integrity. The cell size can be determined from the desired power rate, but in practice, cell size is driven by many other factors, such as mechanical strength, thermal stability, the dimension of the components, the shunt current, and so forth. The construction of a cell stack is shown in Figure 10. Most cell stacks are constructed

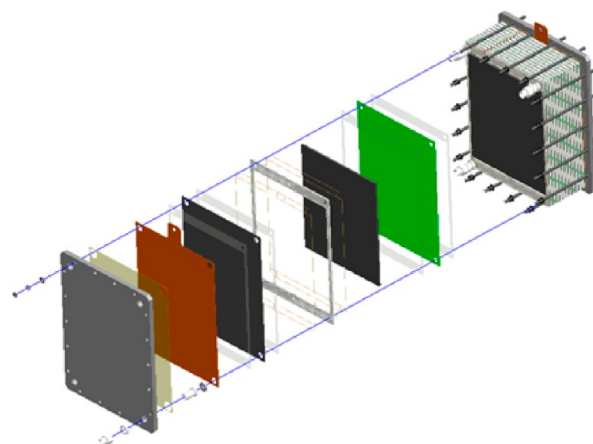


Figure 10. The assembly of a cell stack.

in a parallel-feed design, in which the cells are connected electrically in series and the electrolytes are pumped into all cells in parallel. The uniformity of the single-cell performance is largely determined by the distribution of the electrolyte.

The flow field is a critical factor in the design of a cell stack. It decides the uniformity of the electrolyte in the electrode and even directly determines the uniformity of the current density. Excessive local current density is the main factor to induce the stack performance decline. Therefore, clarifying the distribution of electrolyte velocity in the electrode and the location of the excessive local current density is essential to optimize the construction of the flow field and further improve the uniformity of the current density. However, little research is focused on this issue currently, and a mathematical model including more details about the configuration of the cell or stack is expected to attract more attention. Up to now, most of the existing models were based on the fundamental transport and chemical reaction kinetics

to predict cell performance. The following section will introduce more details about these models.

Most of the existing models were based on the fundamental transport and chemical reaction kinetics to predict cell performance and to control the cell stack and system.

Mathematical Modeling. The VFB has been one of the most often modeled flow batteries in the past decade. Most of the existing models are based on the kinetics of redox reactions and transport phenomena. The kinetics of redox reactions plays an important role in fundamental electrochemistry. In the model, the reaction kinetics determines the source terms of different vanadium ions and protons, which also relate to the charge and mass conservation. For VFBs, the precise multistep reaction mechanism is not known yet, and a one-electron redox reaction is used in the existing models. The Butler–Volmer equation is generally used for calculating the transfer current density in the electrode compartment, which describes the electrochemical reactions taking place on the surface of the porous carbon electrode.

There are two methods determined by different treatment of the reactants and products in a battery to deal with the mass conservation. The first is the lumped parameter method, which means that the concentrations of the reactants and products in the whole battery are treated as an integer. The concentrations only change with time and have no relationship with dimensions. This method was widely used to study the cell response because of its simple, rapid, economical characteristics. In order to study the relationship between the resistance in series and the state of the charge and further predict the performance of the VFB, Enomoto⁸⁵ and Hikiyama et al.⁸⁶ both proposed a zero-dimension transient model, which was based on the chemical reactions and circuit response. A transient thermal model developed by Tang et al.⁸⁷ was used to predict the battery temperature as a function of time under different operating conditions on the basis of the energy conservation. These models were not feasible to control and monitor the battery system, while Shah et al.⁸⁸ developed a transient control-oriented model for a unit cell system that could rapidly and accurately capture the battery performance and variation of important parameters.

Despite numerous advantages of the lumped parameter method, the variation of the temporal and spatial distributions of reactants or the current density could only be shown by using a more complex and detailed method. Therefore, a distributed parameter method was employed to investigate the operational mechanism in a cell by expanding modeling dimensions. In two- or three-dimension models, especially inside of a cell, the flow characteristic of the electrolyte plays an important role in affecting the concentration polarization in the electrode. Computational fluid dynamics (CFD) is introduced to model the electrolyte flow in the channel and electrode. The flow through the channel and porous electrode is governed by the continuity and momentum equations (Navier–Stokes equation and Brinkman equation). When coupled with the Nernst–Planck equation, the distribution of concentration of species can be calculated.

It is useful to study the operational mechanism in the cell. You et al.⁸⁹ presented a two-dimensional mathematical model for a flow-through porous electrode, in which the effects of mass transfer, ohmic resistance, and electrode reaction kinetics on the performance of the porous electrode were investigated. A transient, isothermal two-dimensional model for a single battery was put forward by Shah et al.,⁹⁰ which illustrated the effect of variation in concentration, electrode porosity, and electrolyte flow rate on the performance of the cell. Afterward, the nonisothermal effect⁹¹ and oxygen and hydrogen evolution^{92,93} were further considered in this model by adding an energy equation and gas-evolving side reactions. On the basis of the dynamic model developed by Shah, You et al.⁹⁴ developed a simplified stationary model by using the same mathematical framework. As an efficient supplement, the model predicted the effects of applied current density and the state of the charge on the battery performance (Figure 11). To further simplify the

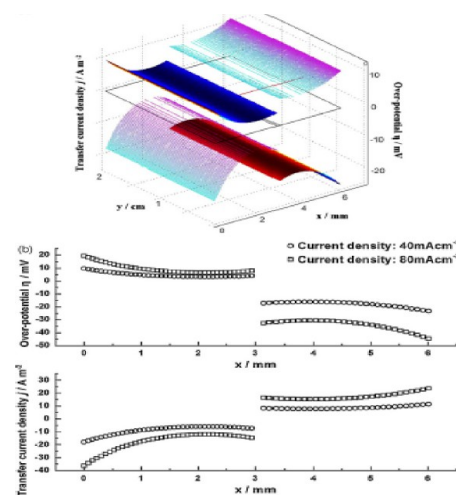


Figure 11. Distribution curves of the overpotential and transfer current density at 50% SOC for applied current densities of 40 and 80 mA/cm² along the direction of thickness during charge in the model of You et al. Reprinted with permission from ref 94. Copyright 2009, Elsevier.

model proposed by Shah et al., scaling and asymptotic methods were used.⁹⁵ Ma et al.⁹⁶ developed a 3D stationary model for a negative half-cell that included an inlet/outlet channel and electrode. The effect of velocity on the distributions of concentration, overpotential, and transfer current density in the sections that are perpendicular and parallel to the applied current was investigated. Figure 12 shows contour plots for distributions of the velocity, the V³⁺ concentration, the overpotential, and the transfer current density on the electrode/current collector interface.⁹⁴

It was reported that the electrode microstructure has quite a high impact on the VFB performance. The factors, for example, the surfaces area, porosity of the electrode, and electrolyte flow condition, have serious impact on the species' transport. As opposed to volumetric models, in which the computational regions such as the electrode and electrolyte are treated as a single continuum, the pore-scale resolved model is not based on the assumption of the electrode microstructure but obtains a configuration by X-ray-computed tomography. Therefore, it can offer a more accurate and detailed comprehension coupled with fluid flow, species transport, and electrochemical reactions

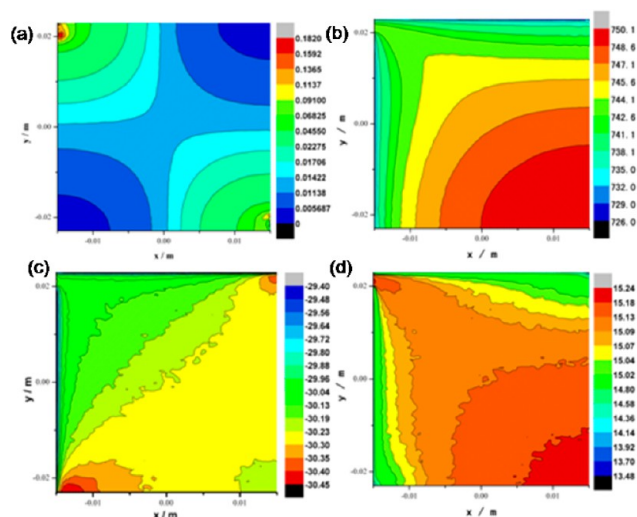


Figure 12. Contour plots for distributions of velocity (a), V^{3+} concentration (b), overpotential (c), and transfer current density (d) on the electrode/current collector interface. Reprinted with permission from ref 96. Copyright 2011, Elsevier.

occurring locally inside of a cell. Qiu et al.^{97,98} established a 3D isothermal, transient, pore-scale resolved model in succession, where a novel method was introduced to simulate the transport mechanism of flow, species, and charge at the pore scale in the electrode. The effect of electrode microstructure properties and operation under various conditions on the performance of the battery was investigated.

Although the models discussed above have provided a rapid and efficient method to analyze the cell characteristics, some limitations still exist to hinder them to predict the performance and distributions accurately. One is variation of protons and the Donnan potential across the membranes, which was not considered in the Nernst equation. It may cause about a 131–140 mV discrepancy between the calculated value and experimental value. To address this issue, a more complete version of the Nernst equation was proposed, and the error was effectively decreased from 8.1% to 1.2%.⁹⁹

Another limitation is derived from membrane separators. In the current model, the membrane is treated as a perfectly selective separator. Besides protons, other ions, for example, the vanadium ions and SO_4^{2-} ions, are absolutely isolated from the membranes. In reality, different positively and negatively charged species could partly pass through the membranes and further lead to capacity loss. To overcome the limitations, the lumped parameter method and distributed parameter method have been developed to simulate the capacity loss by adding an ion transportation mechanism. Skyllas-Kazacos and co-workers^{100–102} developed a transient, isothermal model to predict the expected capacity loss as a function of time, which was potentially incorporated into control system, later even taking into account the heat released from self-discharge reactions in both half-cells caused by diffusion of the vanadium ions across the membrane. You et al.¹⁰³ used a convection–diffusion equation to describe the transfer of vanadium ions in the membrane. The diffusion coefficient, the partition coefficient, and the concentration gradient between two half-cells mainly impacted the diffusion rate of the vanadium ions. Knehr et al.¹⁰⁴ found that osmotic and electro-osmotic convections in the membrane are major mechanisms contributing to species crossover by using a two-dimensional transient model. Figure 13 shows the average convective flow rate across the

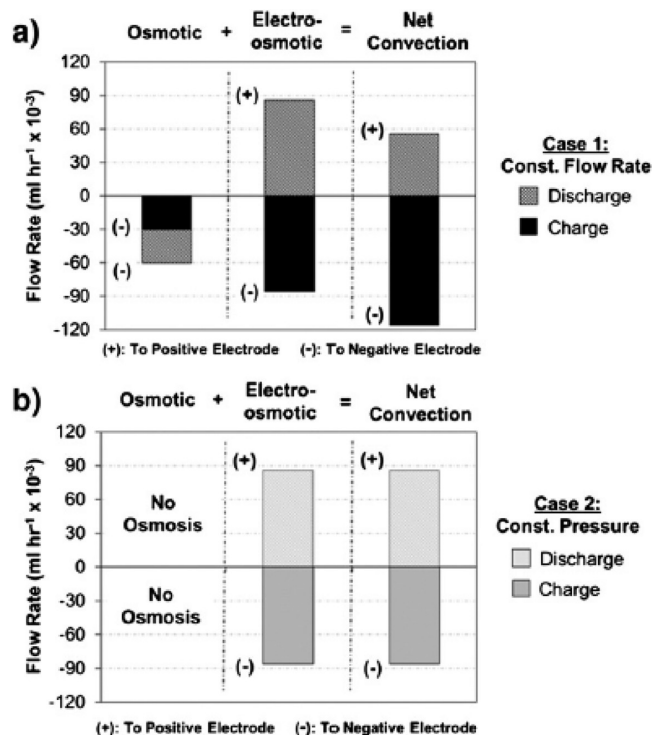


Figure 13. Average convective flow rate across the membrane during the 35th cycle at 50% SOC in the case of constant flow rate (a) and constant pressure (b) in the model of Knehr et al. Reprinted with permission from ref 104. Copyright 2012, Elsevier.

membrane during the 35th cycle at 50% SOC in the case of constant flow rate (a) and constant pressure (b) in the model of Knehr et al.¹⁰⁴ The model only focuses on the diffusion and convection mechanism. Many species such as water, protons, and bisulfate are not considered. Knehr et al.¹⁰⁵ make a good extension on the basis of the model proposed by Shah et al.⁹⁰ to consider all of the transport mechanisms, such as diffusion, convection, and migration, of all of the species across the membrane. The velocity was given by an alternative form of Schlogl's equation.¹⁰⁶ With a more complete version of the Nernst equation, this model offered more accurate predictions of cell voltage and capacity loss.

The existing models can be used to improve the cell designs such as optimized heat management, power density, and electrolyte utilization. The electrolyte flow in a cell is crucially important, which can be well-described by using a 3D model because of the real geometry of the cell. Such a 3D model could provide effective and optimized strategies to form an even distribution of reactant concentration and prevent the appearance of a stagnant region. The maintenance of high velocity in the electrode is the key design, especially for stacks with a large electrode area. Most importantly, there is an urgent requirement to establish a model to study the mechanism when enlarging the cell stack to a higher power level. An even distribution of current density may keep the performance of the stack at a high level. Meanwhile, a model including sufficient detailed mass, charge, and fluid transfer incorporated with the heat or electric circuit is vitally necessary to control and monitor the medium- or large-scale system.

Remaining Challenges and Outlook. Even though quite a lot of demonstrations were carried out to further push VFB commercialization, there are still some remaining challenges that need to be further solved. One of the most critical issues would be the cost. The current VFB cost is roughly \$500–600 per kW h,

which is too high for broad market penetration.³⁵ To realize the commercialization of VFBs, the capital and cycle life costs of VFBs need to be substantially lowered.³ There are several ways to reduce the cost, among which, improving the power density of the VFB stacks and exploring materials with lower cost could be the most effective ones. If we look at the cost map of VFB stacks,⁶² the membrane part occupies nearly 41% of the total cost. Therefore, novel membranes with advanced structures, low cost, and excellent stability should be developed in order to efficiently diminish the battery cost and extend the operational life span. However, without understanding the underlying basic science of the chemical stability problem for membranes, no significant progress in either improving the lifetime or lowering the cost of VFBs can be made.⁶ The desire to use hydrocarbon-based membranes and the approach to use microporous separators would be also tremendous cost-saving measures. Another important “high cost part” is attributed to the large amount of expensive vanadium electrolytes used. Moreover, the poor stability and low solubility of electrolyte induces the low energy density of the VFB, therefore significantly increasing the overall operating costs. Extra measures, such as periodic electrolyte remixing or electrochemical rebalance, can be used to recover the lost capacity in long-term cycling, which, however, increases the capital and/or operational cost.¹⁰⁷ New electrodes with low resistance and high electrochemical performance are particularly important to improve the power density and finally bring about considerable reduction in stack size as well as cost. Apart from the materials, modifying the cell architecture can also enhance system performance by several folds, and this is an area that warrants greater attention in the future. It is important that the architecture/design of the system is optimized so as to minimize the shunt current and to also improve other performance parameters in order to reduce the overall system cost.¹⁰⁸

Recently, our groups did quite a lot of work on decreasing the cost of VFBs. Our work involves materials modification (including membranes with higher conductivity and selectivity, electrodes with higher electrochemical activity, and electrolytes with higher stability and solubility) and optimization of the cell architecture design. The main idea is devoted to increase the operating current densities via combining the materials advancement and cell architecture design. Now, the current density of a single battery cell was successfully enhanced from 80 to 200 mA/cm², while their energy efficiency was kept higher than 80%. However, improving the power density of VFBs is still the most important research topic for VFBs in the near future.

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Author Contributions

The Perspective was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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