

# Recent Progress in Redox Flow Battery Research and Development

Wei Wang,\* Qingtao Luo, Bin Li, Xiaoliang Wei, Liyu Li, and Zhenguo Yang

With the increasing need to seamlessly integrate renewable energy with the current electricity grid, which itself is evolving into a more intelligent, efficient, and capable electrical power system, it is envisioned that energy-storage systems will play a more prominent role in bridging the gap between current technology and a clean sustainable future in grid reliability and utilization. Redox flow battery technology is a leading approach in providing a well-balanced solution for current challenges. Here, recent progress in the research and development of redox flow battery technology, including cell-level components of electrolytes, electrodes, and membranes, is reviewed. The focus is on new redox chemistries for both aqueous and non-aqueous systems.

The capricious nature of the power from renewable sources poses a serious caveat to the current aging grid, as integration of more than 20% intermittent renewables could endanger the stability of the grid without required storage.<sup>[4]</sup> In this regard, an electrical energy-storage system (EES) would offer a well-established, value-added approach for improving the reliability and overall usage of the entire power system (i.e., generation, transmission, and distribution). From a historical perspective, the current electric grid, which features near-instantaneous transmission and distribution of electricity, has an extreme scarcity of storage. For example, in the United

## 1. Introduction

The perils of fossil fuel depletion, the detrimental long-term environmental effects of greenhouse gas emissions, and the growing sense of urgency toward energy security compel an imminent transition from hydrocarbon fuels to renewable and environmentally sustainable energy sources. Renewable energy technologies have therefore attracted much scientific and public interest in recent years. Among the available renewable energy sources, solar and wind are probably the most abundant and readily accessible, characteristics that are increasingly being recognized as essential components of future global energy production.<sup>[1]</sup> Although technology advancements are still warranted to efficiently and economically harvest the inexpensive energy from renewable energy sources, rapid growth in implementation of solar and wind energy generation devices has spread in many countries around the world. Globally, a total of 74.3 GW and 94 GW of wind power generation capacity were installed in 2006 and 2007, respectively.<sup>[2]</sup> The World Energy Council estimates that new wind power capacity worldwide will total up to 474 GW by 2020.<sup>[1]</sup> Likewise, the expansion of photovoltaic module installations currently is increasing by 40% per year worldwide.<sup>[3]</sup>

States, only  $\approx 2\%$  of the electricity is dispatched through storage systems.<sup>[5]</sup> As such, the grid relies heavily on thousands of generators to smooth out discrepancies between power supply and demand. These generators often are brought online in response to temporary fluctuation in demand, but they usually are idle, which results in an extreme waste in electricity generating resources.<sup>[6]</sup> Simple examples of renewable resources are solar and wind power that only function when the sun is shining or the wind is blowing, conditions that cannot be coordinated with customer demand. The power generated during off-peak time often is wasted because of the lack of demand. The mismatch between power generation and demand thus requires energy arbitrage that is achieved mainly by using a storage system to efficiently reap the inexpensive, yet abundant, solar and wind power. Incorporating energy storage thus adds significant value to the solar and wind power technology,<sup>[6,7]</sup> which is one of many high-value applications for energy storage recently identified that range from renewable energy integration to grid optimization.<sup>[8]</sup> In a broader perspective, an energy storage system would enable a time domain in the operational dimension of the grid, thus granting the control and regulation agent paramount flexibility to move electricity to meet demand not only over distance but also over time. As illustrated in **Figure 1**, there is an increasing recognition that energy storage will play a more conspicuous role in the future grid, providing many grid services in addition to renewable energy integration (e.g., frequency regulation and load following (the aggregated term most often used is balancing services), cold-start services, contingency reserves, and energy services that shift generation from peak to off-peak periods).

Bearing witness to these considerations is the recent renaissance in research and development (R&D) focused on stationary energy storage. These R&D efforts also underline the eagerness

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and anticipation in the utility industry to find solutions for the traditional grid, which is currently undergoing fundamental changes. Performance requirements of EES for stationary use depend on application markets that are broad and varied in power and energy ratings, the ratio of power to energy, the discharging time, etc. However, cost, quick response, durability, and safety are among common requirements for stationary energy-storage systems. A number of technologies are potential candidates for renewable energy and utility applications. As shown in **Figure 2**, these technologies can be classified into two groups based on the storage mechanism. The first group of technologies store electricity directly as electrical charges, typically as capacitors or supercapacitors. Alternatively, electrical energy can be stored by converting electrical energy to another form of energy. Typical examples of energy forms involved in electrical energy conversions include kinetic energy (flywheels), potential energy (pumped hydro and compressed air energy storage), and chemical energy (electrochemical storage systems primarily various battery techniques).

In general, electrochemical energy storage offers additional advantages over other storage systems, such as standalone modular design, no geographical requirement, high efficiency, fast response, etc. Of particular interest is the redox flow battery technology, which is widely considered suitable for large-scale energy storage and has recently attracted considerable research interest because of several attractive features including long calendar life, simple design, and capability to withstand fluctuating power supply. Several excellent recently published reviews have presented in-depth assessments of redox flow battery (RFB) technology including its individual components and its use for energy storage for stationary applications in general.<sup>[1,6,7,10–12]</sup> Therefore, our survey is not another exhaustive historical review on this subject, but is limited to recent breakthroughs and developments, with a focus on new chemistries reported since 2010. Following is a short introduction and overview of the RFB technology and common RFB chemistries; recent R&D of aqueous RFB cell-level components, namely electrolytes, electrodes, and membranes (or separators) are discussed. Research in the emerging field of non-aqueous RFBs is reviewed next, including various redox chemistries and new battery configurations. Finally, we discuss the future direction and perspectives of RFB technology. It should be noted that the review is limited to R&D focused on cell-level components, which exclude stack and system studies such as flow-field simulations, shunt-current analysis, and bipolar plate development.

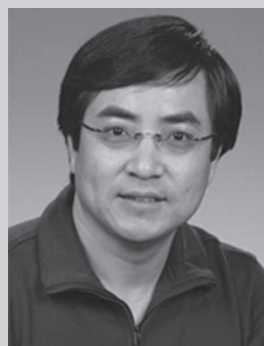
## 2. Redox Flow Battery Technology

### 2.1. Overview

An RFB, shown schematically in a generic form in **Figure 3**, is a type of energy-storage device capable of providing reversible conversion between electrical and chemical energy, typically in two soluble redox couples contained in external electrolyte tanks sized in accordance with application requirements. Unlike traditional batteries that store energy in electrode materials, RFBs are sometimes referred to as regenerative fuel cells as energy is



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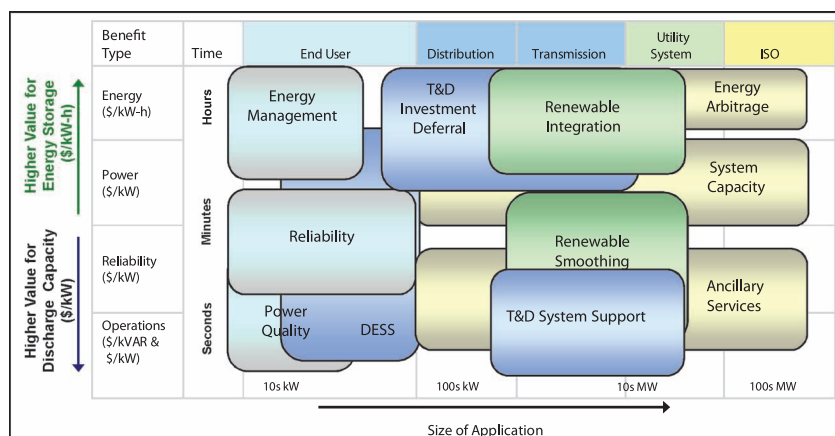


**Dr. Liyu Li** received his B.S. degree in Applied Chemistry from Peking University in 1989 and received his Ph.D. in chemical engineering from the China Institute of Atomic Energy in 1995. He has broad experience in the fields of clean coal and biomass technologies, CO<sub>2</sub> capture, flow batteries for large-scale energy storage, inorganic adsorbents, hydrogen storage materials, heterogeneous catalysts, inorganic ion exchangers, and glass and ceramic nuclear waste forms.



**Dr. Zhenguo (Gary) Yang** is the co-founder and chief executive officer of UniEnergy Technologies, LLC, a Seattle-based clean energy company with a focus on scale-up and commercialization of advanced EES technologies. Previously, Dr. Yang was a Lab Fellow at Pacific Northwest National Laboratory, where he led extensive efforts in research and development of varied electrochemical energy storage technologies. Dr. Yang received his Ph.D. in materials science and engineering from the University of Connecticut.

stored in the incoming fuels in the form of two dissolved redox pairs that convert into electricity at the electrodes. More like their solid-state battery relatives, however, is the fact that the redox reactions are reversible, which qualifies the RFB as a secondary battery system. The conversion between electrical energy and chemical (or electrochemical) energy occurs as the liquid electrolytes are pumped from storage tanks to flow-through electrodes in a cell stack. The electrolytes flowing through the cathode and anode often are different and are referred to as the anolyte and the catholyte, respectively. Between the electrodes is



**Figure 1.** Power and discharge duration (or energy) requirements for varied applications. Reproduced with permission.<sup>[9]</sup> Copyright 2010, Electric Power Research Institute, Inc.

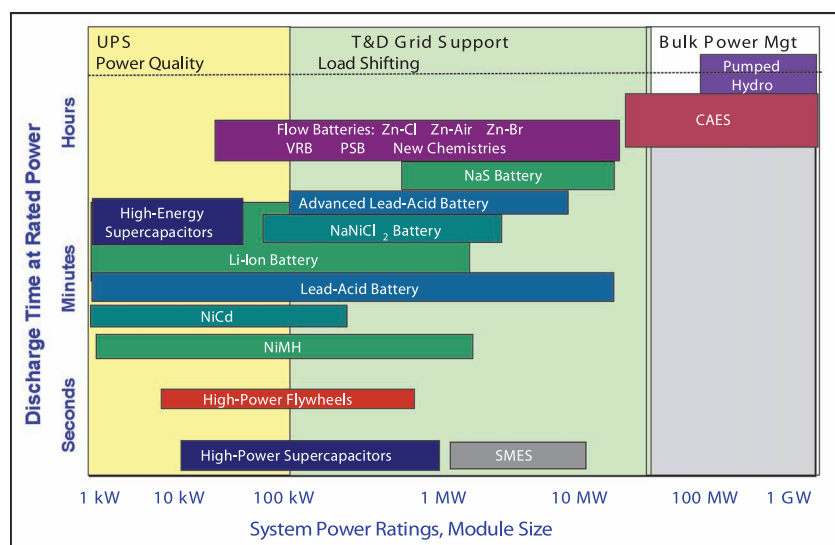
an ionic conducting membrane or separator that keeps the two electrolytes from mixing while allowing transport of the charge-carrying ions (e.g.,  $H^+$ ,  $Cl^-$ ) to maintain electrical neutrality and electrolyte balance.

The unique working mechanism of the RFB provides several desirable features. First is its ability to store large amount of power and energy up to multi-megawatts (MW) and megawatt-hours (MWh). The flexible modular design allows the RFB to be sized for a wide spectrum of power and energy storage, ranging from utility-scale storage (MWh) such as energy wholesale service to an end-user application such as home power backup (kilowatt-hours [kWh]). With the electrolyte and electroactive materials stored externally, the most prominent advantage of RFBs is that their power and energy are not coupled as is the case for other battery systems. In an RFB, the system energy capacity is controlled by the size of the electrolyte reservoirs, while the size of the stack dictates the system power capability. The decoupling of the power and energy requirements gives considerable design latitude to individually tailor the

constituent is a liquid (e.g., water for aqueous RFBs) and the reactive materials are stored separately, RFBs are an inherently safe energy-storage system. A catastrophe resulting from internal shorting is very unlikely. In a flow battery, the flowing electrolytes carry away the heat generated during the redox reaction, thus circumventing the serious heat dissipation issue facing solid-state batteries that are targeted for large-scale applications. Moreover, the liquid electrolyte and dissolved redox species in an RFB are in intimate proximity with the electrodes, making quick response (on the order of sub-seconds) possible for utility applications. Often neglected are the unparalleled advantages of manufacturing ease and system configuration of RFBs. The unique mechanism of the RFB significantly simplified its manufacturing into modular production of stacks, electrolyte containers, plumbing, and electrical systems, thus bypassing the cell-making process, which is the most expensive, complicated, and capital-intensive step in solid-state battery (e.g., Li-ion and NiMH) production. In a practical solid-state battery, such as a 18650 Li-ion cell, active materials count for less than

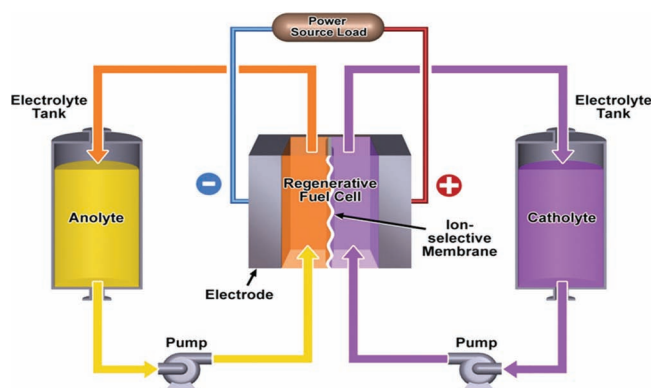
50 vol% of the cell and even less in weight percentage because of the need to accommodate other inactive parts (e.g., binders, additives, and packaging) in the cell assembly.<sup>[14]</sup> These inactive parts largely attenuate the energy density of the battery at the cell and system levels. The unique RFB configuration provides a simple design that can limit the negative impact of inactive materials on the system energy density because the volume of the energy-bearing electrolyte can be independently scaled up.

With these unique advantages, the RFB technique is poised to be one of the most promising technologies for stationary energy storage, aside from the current relatively high capital cost (\$/kW and \$/kWh) and a life-cycle cost that depends on performance, maintenance, etc. Both materials and components as well as performance parameters, including energy density, cycle/calendar life, energy efficiency, etc., contribute to the



**Figure 2.** Power ratings and discharge times (i.e., energy ratings) of varied technologies. Reproduced with permission.<sup>[9]</sup> Copyright 2010, Electric Power Research Institute, Inc.





**Figure 3.** Schematic of the structure of a redox flow battery. Reproduced with permission.<sup>[13]</sup>

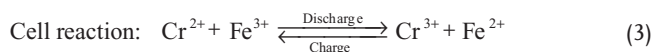
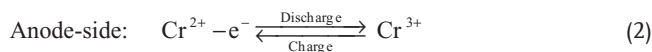
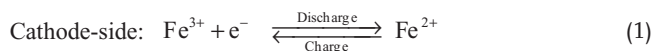
current high cost of RFBs. Regarding materials, expensive vanadium resources and high priced Nafion-based membranes are the two factors that inflate the capital cost of all-vanadium RFBs (VRBs). In terms of system performance, which is limited by the cell operation voltage and active materials concentration, the RFB is, in general, a low energy density system ( $<25 \text{ Wh L}^{-1}$  in most true flow battery systems). Because of the limitation of the electrolyte temperature stability, some RFBs also require active temperature management, which further lowers the energy efficiency by parasitic losses. While efforts have been made to search for new redox couples and electrolytes that can lead to new RFBs with improved energy density and performance over existing technologies, it also is critical to further optimize materials and develop advanced materials, along with cell/stack engineering and design, to further reduce cost and improve performance.

## 2.2. Existing Redox Flow Battery Technologies

Modern RFBs were invented in the 1970s by Lawrence Thaller at the National Aeronautics and Space Administration (NASA).<sup>[15]</sup> Since then, RFB technology has undergone continuous development. The first true RFB used a ferric/ferrous ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ ) halide solution electrolyte in the positive half-cell and a chromic/chromous ( $\text{Cr}^{2+}/\text{Cr}^{3+}$ ) halide solution electrolyte in the negative half-cell, but soon encountered severe cross-contamination that resulted in dramatic capacity decay. The effort to mitigate the cross-contamination led the invention of two important RFB systems in the 1980s including Generation (GEN)-2 Fe/Cr redox flow batteries (ICBs), which employ a mixed electrolyte as both positive and negative electrolyte,<sup>[16]</sup> and all-vanadium flow batteries that enlist the same element in both positive and negative electrolytes.<sup>[17–20]</sup> Since then, a number of other RFB chemistries were reported or developed.<sup>[6,12]</sup> Depending on the active redox species in the anolyte and catholyte, these RFBs can be classified as follows: polysulphide/bromine flow batteries (PSBs),<sup>[21,22]</sup> zinc/bromine flow batteries (ZBBs),<sup>[23,24]</sup> vanadium/cerium flow batteries, soluble lead-acid batteries, etc. Among different RFBs, VRBs, ZBBs, ICBs, and PSBs have been demonstrated at a few hundred kW power levels and even multi-MW power levels. A brief overview of existing flow battery chemistries follows.

### 2.2.1. Fe/Cr Redox Flow Batteries

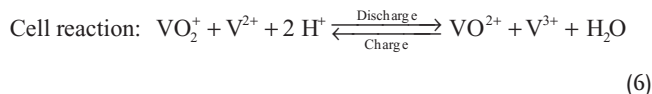
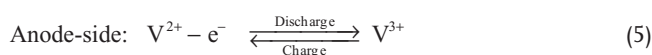
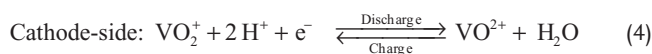
The first true RFB, the Fe/Cr redox flow battery invented and primarily developed at NASA, employed the following electrode and cell reactions:



The cell reaction offers a standard voltage of 1.18 V. The ICB operates with either a cation or anion exchange membrane/separator and typically employs carbon fiber, carbon felt, or graphite as electrode materials. The  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple exhibits a very high reversibility and fast kinetics on the carbonaceous electrodes (carbon or graphite). In comparison, the low electrochemical activity of the  $\text{Cr}^{2+}/\text{Cr}^{3+}$  redox reaction requires catalyst loading on the electrode. The Fe/Cr system usually operates at elevated temperature ( $\approx 65^\circ\text{C}$ ) with an active heat management system to further facilitate the  $\text{Cr}^{2+}/\text{Cr}^{3+}$  redox reactions, resulting in significant parasitic energy loss,<sup>[25]</sup> system complexity, and increased cost. On the other hand, the low potential ( $-0.41 \text{ V}$ ) of the  $\text{Cr}^{2+}/\text{Cr}^{3+}$  redox reaction often is accompanied by  $\text{H}_2$  evolution during charging, which limits fuel use ( $\approx 60\%$ ), and lowers the coulombic efficiency. An  $\text{H}_2$  rebalance cell is often required to manage the gas evolution. An outstanding issue with early ICBs was the cross-transport of iron and chromium active species. A significant reduction in the cross-transport was achieved by using mixed electrolytes at both the cathode and anode sides.<sup>[16]</sup>

### 2.2.2. All-Vanadium Redox Flow Batteries

The VRB is probably the most important and promising technology of RFBs; it capitalizes on four different oxidation states of vanadium ions to form two redox couples separated as the anolyte and the catholyte with only one active element in both sides. As such, the cross-transport of the active component (i.e., vanadium) in VRBs might be controlled. In a VRB, the energy conversions are realized via changes in vanadium valence states through the following electrode reactions:



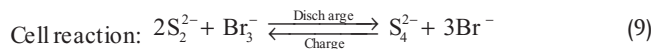
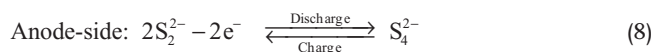
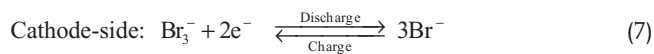
The overall electrochemical reaction gives a cell voltage of 1.26 V at  $25^\circ\text{C}$  and unit activities (i.e., standard voltage).

Invented and pioneered by Skllyas-Kazacos and co-workers at the University of New South Wales in the 1980s,<sup>[17–20,26]</sup> the VRB has since been the focus of increasing R&D effort around the world. While significant progress was made in advancing RFBs with the demonstration of multi-MWh VRB systems,<sup>[12,25]</sup>

the current technology cannot meet all of the performance and cost-requirement matrices for broad market penetration. Traditional sulfuric-acid-based VRB technology is significantly hindered by the vanadium ion solubility and stability in electrolyte solutions over a certain temperature window, which limits the system not only to a low energy density of  $<25 \text{ Wh L}^{-1}$  ( $<1.7 \text{ M}$  of active vanadium concentration), but also to a narrow operational temperature range between 10 and  $40^\circ\text{C}$ .<sup>[27–30]</sup> In many cases, an active heat management system is necessary during operation of the VRB stack, which inadvertently lowers the system efficiency because of parasitic energy losses. High V(V) corrosiveness, low fuel utilization ratio to suppress the gas evolution, and the need for relatively expensive membranes are among the issues that have plagued the traditional VRB system.

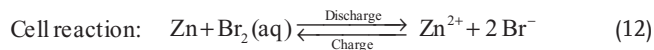
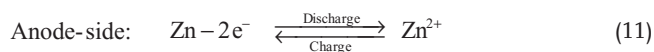
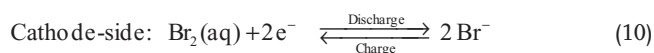
### 2.2.3. Other Systems

PSBs employ sodium bromides and sodium polysulfides as electrolytes.<sup>[31]</sup> A standard cell voltage of 1.36 V is given by the following electrochemical reactions:



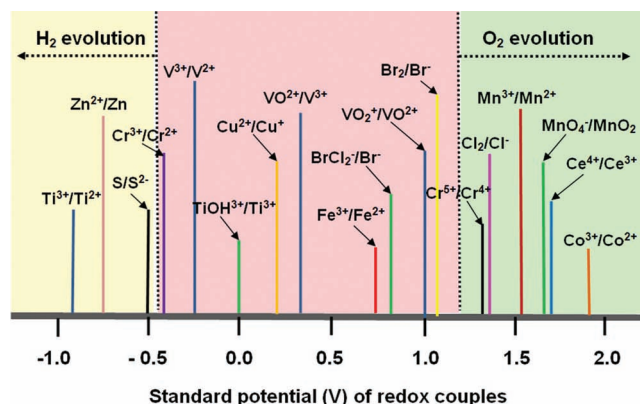
These chemicals are abundant, soluble in aqueous media, and are of reasonable cost, which is a key attribute of the system. However, the system is suffered from severe crossovers that lead to precipitation of sulfur species and the formation of  $\text{H}_2\text{S}$  and  $\text{Br}_2$ .

The ZBB hybrid flow battery system, often classified in the RFB category, employs the zinc metal dissolution/plating redox reaction at the anode and bromine ion/bromine conversion at the cathode. The charge and discharge of ZBB cells proceed via the following electrode reactions:



The ZBB system usually delivers higher energy density than traditional RFBs such as VRBs and ICBs due to the elimination of one volume of the electrolyte and relatively higher voltage. ZBB system performance often is limited by its low energy efficiency and short cycling life. As is common with metal electrodes, the zinc anode constantly suffers from dendrite formation, which leads to electrical shorting. Furthermore, the bromine gas is very corrosive and hazardous, leading to health and environmental concerns.<sup>[23,24,32]</sup>

A number of other redox chemistries can be combined to construct an RFB. **Figure 4** compiles available metal redox couples and their standard potentials in aqueous systems (except the  $\text{H}^+/\text{H}_2$  couple, which is based on the over-potential of carbon electrodes). Bounded by hydrogen and oxygen evolution, the choices for a combination of two redox couples with useful



**Figure 4.** Standard potential (vs. the standard hydrogen electrode) of redox couples, except the  $\text{H}_2$  evolution potential, which is the over-potential at the carbon electrodes. Reproduced with permission.<sup>[1,40]</sup> Copyright 2011, American Chemical Society.

voltage and appreciable solubility is however greatly limited. Several other redox chemistries have been explored, including  $\text{V}^{2+}/\text{V}^{3+}$  vs.  $\text{Br}^-/\text{ClBr}_2$ ,<sup>[33–35]</sup>  $\text{Ce}^{4+}/\text{Ce}^{3+}$  vs.  $\text{V}^{2+}/\text{V}^{3+}$ ,<sup>[36]</sup>  $\text{Fe}^{3+}/\text{Fe}^{2+}$  vs.  $\text{Br}_2/\text{Br}^-$ ,<sup>[37]</sup>  $\text{Mn}^{2+}/\text{Mn}^{3+}$  vs.  $\text{V}^{2+}/\text{V}^{3+}$ ,<sup>[38]</sup>  $\text{Fe}^{3+}/\text{Fe}^{2+}$  vs.  $\text{Ti}^{2+}/\text{Ti}^{4+}$ ,<sup>[39]</sup> and others.<sup>[6,12]</sup> Presently, ICBs and VRBs remain the two most extensively studied chemistries and RFB systems, but their commercial success has been limited.

Innovation in the energy-storage field is always rare and hard-won, especially in RFB R&D. Despite continuous research effort, only marginal improvement has been achieved. Compared to the lithium-ion battery technology, whose energy density as a class has improved an average of  $\approx 8$  to 9% per year since the early 1990s,<sup>[41]</sup> the energy density of the major players in the RFB field have remained largely the same over the past 20 to 30 years. Accompanying the burgeoning field of stationary energy-storage research, there is, however, a revival in the development of RFB technology. Several recent reports have demonstrated considerable improvement holding great promise for advancing the performance of RFBs, especially their energy density.

## 3. Aqueous Redox Flow Batteries (RFB)

### 3.1. Electrolyte Chemistry

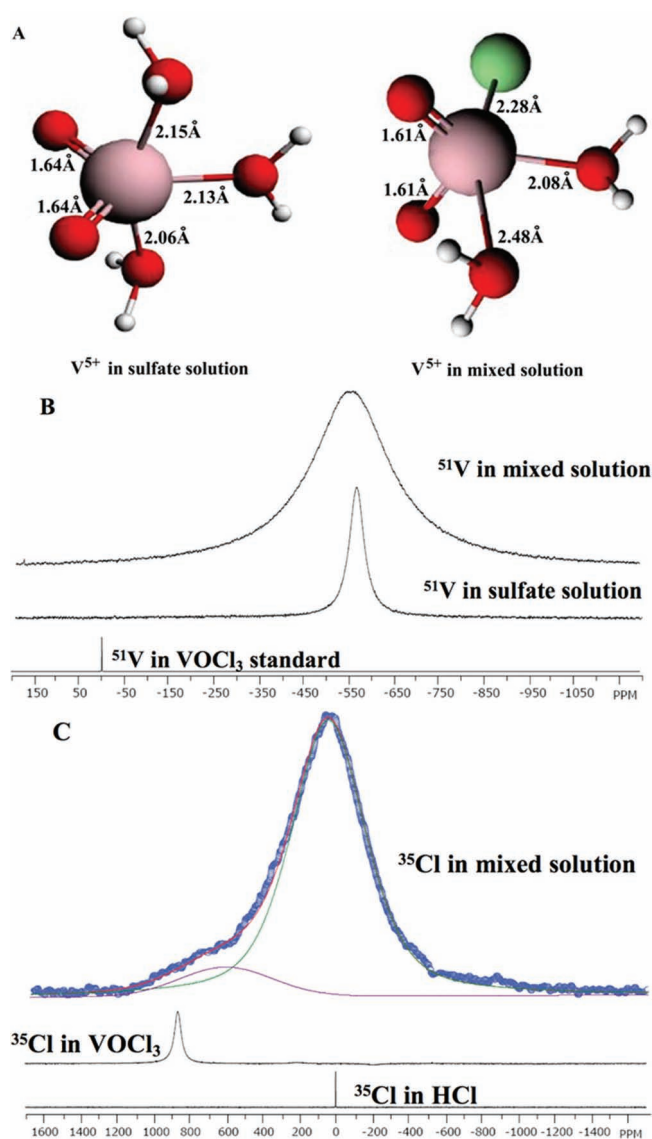
The electrolyte is the most important component of an RFB; its properties dictate overall battery performance. As the RFB uses two soluble agents as active materials, the concentration of the electrolyte will determine the system-specific energy density. Consequently, a higher solubility of all redox agents is always desired. Of equal importance is the temperature stability of the electrolyte, which defines the temperature window for the RFB operation. It is worth noting that the electrolyte needs to be stable over the entire state of charge (SOC), especially for  $\approx 0\%$  and  $\approx 100\%$  SOC, which usually represent the most adverse conditions during cell operation and electrolyte storage. Although the voltage window is usually limited by the water electrolysis potential in an aqueous RFB, it is an important parameter to consider for a non-aqueous RFB. The redox reaction potential

needs to be within the stable electrolyte potential range to avoid electrolyte breakdown or decomposition. The electrolyte also needs to possess adequate ionic conductivity to provide a decent rate capability. Viscosity usually is not an issue in the aqueous system, but one needs to take into consideration the high pressure drop due to high viscosity when designing a non-aqueous RFB system. The properties of the electrolyte, such as the acidity, air sensitivity, flammability, etc., also significantly affect the system design and integration in terms of materials selection, chemical compatibility, etc. In this section, several recently reported new electrolyte chemistries for aqueous RFBs are reviewed. Electrolyte development in the non-aqueous RFB area is discussed in a later section.

### 3.1.1. Mixed-Acid Vanadium Redox Flow Batteries

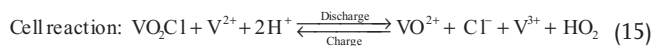
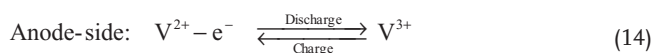
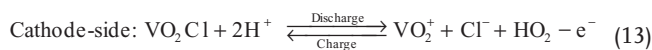
Researchers at Pacific Northwest National Laboratory (PNNL) recently revisited the solution chemistry of the vanadium electrolyte. It was found that the <1.7 M concentration limit of the vanadium sulfate electrolyte is a compromise between the low solubility of  $\text{VOSO}_4$  at low temperature (0 °C) and the precipitation of  $\text{V}_2\text{O}_5$  at higher temperature (40 °C).<sup>[13]</sup> Using advanced nuclear magnetic resonance (NMR) spectroscopy and density functional theory based computational modeling, the structure and kinetics of vanadium (IV)<sup>[42]</sup> and vanadium (V)<sup>[43]</sup> species were revealed further. The vanadium (IV) species appears as hydrated vanadyl ion ( $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ ) forming an octahedral coordination with vanadyl oxygen in the axial position with the remaining positions occupied by water molecules. An increase in the sulfate acid concentration leading to an increase of sulfate anion in the second-coordination sphere of the vanadyl ion results in increased reorientation activation energy that makes the vanadyl ion less mobile; this explains previous experimental results of decreased  $\text{VOSO}_4$  solubility with increased sulfate acid concentration.<sup>[44]</sup> On the other hand, the vanadium (V) species was identified as hydrated penta coordinated vanadate ion  $[\text{VO}_2(\text{H}_2\text{O})_3]^{1+}$ , which is not stable at elevated temperature and changes into neutral  $\text{H}_3\text{VO}_4$  molecule via a de-protonation process, subsequently leading to the  $\text{V}_2\text{O}_5$  precipitation.

Advances in understanding the vanadium species structure and interaction with solvent ions led to exploration on the solubility and stability of vanadium ions in different acid-supporting electrolyte systems, which successfully led to the discovery of a mixed sulfate and chloride electrolyte that effectively stabilizes all four vanadium cations at a 2.5 M concentration within the temperature range of −5 to 50 °C.<sup>[13]</sup> The addition of chloride acid achieves two purposes: solubility of the V (III) and V (IV) ions improved because of the decrease in the sulfate ion concentration and the chloride ion improved the stability of V(V) ions at elevated temperatures, which is attributed to the formation of a soluble neutral species  $\text{VO}_2\text{Cl}(\text{H}_2\text{O})_2$  at temperature >20 °C. The formation of  $\text{VO}_2\text{Cl}(\text{H}_2\text{O})_2$  was first predicted using the Amsterdam density functional (ADF) program and later evidenced in the different chemical shift and width of  $^{51}\text{V}$  and  $^{35}\text{Cl}$  in a pure sulfate acid electrolyte and a mixed solution, respectively, by the NMR study shown in Figure 5. Performance of the mixed-acid VRB cell also was reported to have demonstrated more than 70% increase in the energy density and broadening the operational temperature range from ≈10 to 40 °C to −5 to

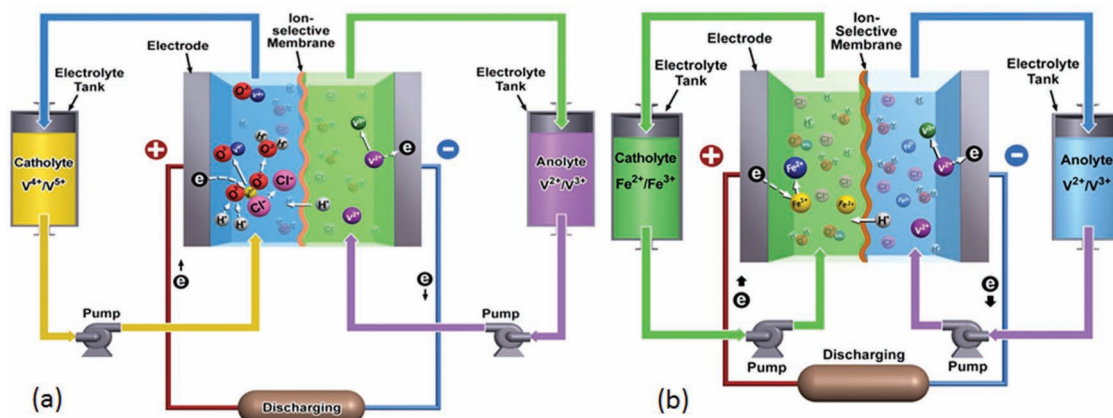


**Figure 5.** Structures of vanadium sulfate-chloride mixed electrolyte. A) The structures of  $\text{V}^{5+}$  complexes in the sulfate and the sulfate-chloride mixed solutions, as predicted by quantum calculation. The pink, green, red, and white spheres represent vanadium, chloride, oxygen, and proton ions, respectively. The numbers are the calculated bond lengths. B)  $^{51}\text{V}$  NMR spectra of a mixed sulfate-chloride solution (20 °C, 2.5 M  $\text{V}^{5+}$ , 2.5 M  $\text{SO}_4^{2-}$ , 6 M  $\text{Cl}^-$ , and 7.25 M  $\text{H}^+$ ) and a sulfate solution (20 °C, 2 M  $\text{V}^{5+}$ , 5 M  $\text{SO}_4^{2-}$ , and 9 M  $\text{H}^+$ ). C)  $^{35}\text{Cl}$  NMR spectra of the mixed solution in B). Reproduced with permission.<sup>[13]</sup>

50 °C.<sup>[13]</sup> Based on the formation  $\text{VO}_2\text{Cl}(\text{H}_2\text{O})_2$  species, the cell reaction can be rewritten as the following at the temperature >20 °C as shown schematically in Figure 6a during a discharge process. The mixed-acid all vanadium RFB technology has been licensed for commercial scale-up production.



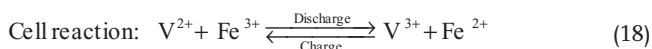
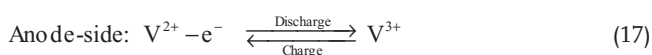
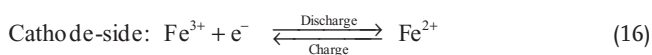




**Figure 6.** a) Schematic of a mixed-acid VRB during the discharge process using a mixed sulfate-chloride acids supporting electrolyte at room temperature. Reproduced with permission.<sup>[13]</sup> b) Schematic of an iron-vanadium redox flow battery (during discharging) using a chloride acid supporting electrolyte.

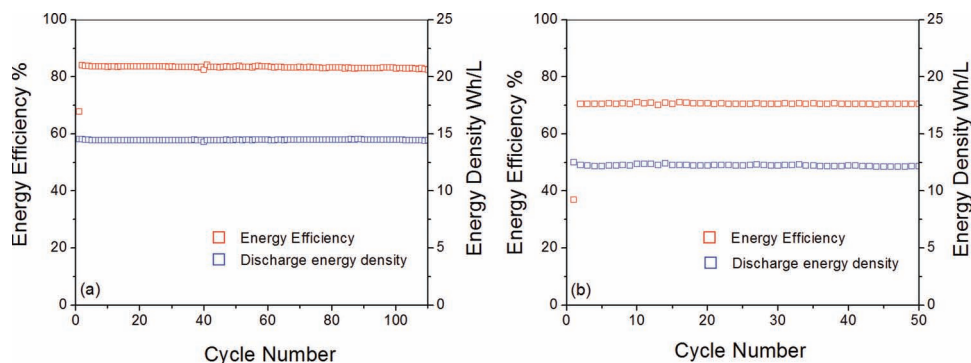
### 3.1.2. Fe/V Redox Flow Batteries (IVBs)

Accompanying the debut of the mixed-acid vanadium redox flow battery is the Fe/V redox flow battery (IVB), which was proposed and investigated by the same group at PNNL<sup>[45]</sup> with the goal of combining the advantages of the ICB and VRB systems and avoiding their drawbacks. Inspired by the development route of the ICBs, the mixed electrolyte approach was adopted to cope with capacity fade. Based on the following redox reactions occurring at the positive and negative electrodes, respectively, a standard voltage of 1.02 V can be obtained. The GEN1 IVB used pure chloride acid as a supporting electrolyte as illustrated in Figure 6b; the chloride acid was soon replaced by a mixed sulfuric and chloride acids supporting electrolyte in the GEN2 IVB system, which increased the system discharge energy density by 25%.<sup>[46]</sup>



In essence, the IVB system is a combination of the ICB cathode with the VRB anode. By substituting the  $Cr^{2+}/Cr^{3+}$

reaction with  $V^{2+}/V^{3+}$  redox couple, the IVB system was able to overcome the sluggish kinetics of the  $Cr^{2+}/Cr^{3+}$  reaction achieving 80% energy efficiency without any catalyst loading at room temperature. On the other hand, the lower potential of the  $Fe^{2+}/Fe^{3+}$  couple at the positive electrode of the IVB reduces its corrosive strength relative to the VRB, allowing inexpensive membranes to be employed and reducing cost significantly. Gas evolution often seriously endangers the long-term cycling of both ICBs and VRBs, but it is significantly limited in the IVB system because of the substantially higher potential of  $V^{4+}/V^{5+}$  compared to  $Cr^{2+}/Cr^{3+}$  and the replacement of oxygen evolution with  $V^{4+}/V^{5+}$  redox reaction as the over-charge protection at the positive electrode. **Figure 7** shows that the GEN2 IVB demonstrated excellent capacity retention using both a Nafion 212 membrane and a Daramic microporous separator.<sup>[46]</sup> This excellent capacity performance can possibly be attributed to the fact that there is no proton generation in the redox reaction, therefore minimal water transfer during the cell redox reaction, and the successful suppression of gas-producing side reactions. Compared with the ICB and the traditional VRB, the energy density of the IVB is lower because of the  $\approx 200$  mV decrease in cell voltage, which is largely compensated by an improvement in the active materials concentration and the high SOC operation. Compared to the mixed-acid VRB, however, the tradeoff between high energy density and



**Figure 7.** Cycling performance of the IVB at room temperature using a) NR212 and b) Daramic microporous separator as the membrane at a current density of  $50 \text{ mA cm}^{-2}$ . Reproduced with permission.<sup>[46]</sup>

an inexpensive membrane must be taken into consideration in system development.

### 3.1.3. Other New Redox Chemistries

Limited by the water electrolysis window and the availability of the redox couples, it is a great challenge in an aqueous system to find new soluble redox couples to form an RFB because the new redox chemistries need to simultaneously satisfy many requirements, such as meaningful voltage, appreciable solubility, facile kinetics, and adequate electrochemical activity. Consequently, there is a renewed interest in “hybrid” RFBs, in which one of the half-cell redox reactions involves reactants in a non-liquid form. Revisiting the ZBBs, Zhang and co-workers at the Dalian Institute of Chemical Physics (DICP) recently proposed a zinc/polyhalide battery (ZPB).<sup>[47]</sup> Using  $\text{ZnBr}_2$  and  $\text{ZnCl}_2$  as both positive and negative electrolytes, the ZPB is essentially a combination of a ZBB with its analog zinc/chlorine battery, and it exhibited a slightly higher voltage and energy density than traditional ZBBs. Similar challenges and issues that face the ZBB and its derivatives, namely material corrosion, dendrite growth, etc., can be expected for the development of ZPB system.

Another hybrid system that has recently garnered some interest is the vanadium/air redox flow battery, which uses  $\text{V}^{2+}/\text{V}^{3+}$  solution as the anolyte and  $\text{H}_2\text{O}/\text{O}_2$  as the cathode-side redox couple.<sup>[48,49]</sup> Researchers at the University of Twente in The Netherlands have reported a limited number of charge/discharge cycling of a  $\text{V}/\text{O}_2$  RFB, which suffered from low voltage efficiency. A similar issue has been encountered by the Li-air battery system, indicating the poor reversibility. Research interest in the “hybrid” RFB stems from the expectation of higher energy densities because one volume of the liquid redox couple is eliminated. The future of the “hybrid” RFB, however, is far from certain given current performance and complicating challenges.

## 3.2. Membrane and Separator Development

The membrane or separator in an RFB system is a key component that separates the cathode and anode compartments while allowing the transport of charged ions ( $\text{H}^+$ ,  $\text{SO}_4^{2-}$ , etc.) to complete the circuit. The membrane first needs to be stable in the electrolyte across the full spectrum of SOC operation range. To minimize resistance and power loss, the membrane must have a high ionic conductivity, which normally requires the membrane to be hydrophilic at the interface between the liquid electrolyte and solid membrane surface to ensure a fast ion transfer. In addition, the fast ionic transport must be highly selective; the transport of active species must be minimized to reduce capacity and energy losses. Water transport across the membrane should be limited as well to maintain catholyte and anolyte balance and simplify maintenance. A membrane that is inexpensive and exhibits high stability and excellent conductivity is critically important for commercializing RFB technology.

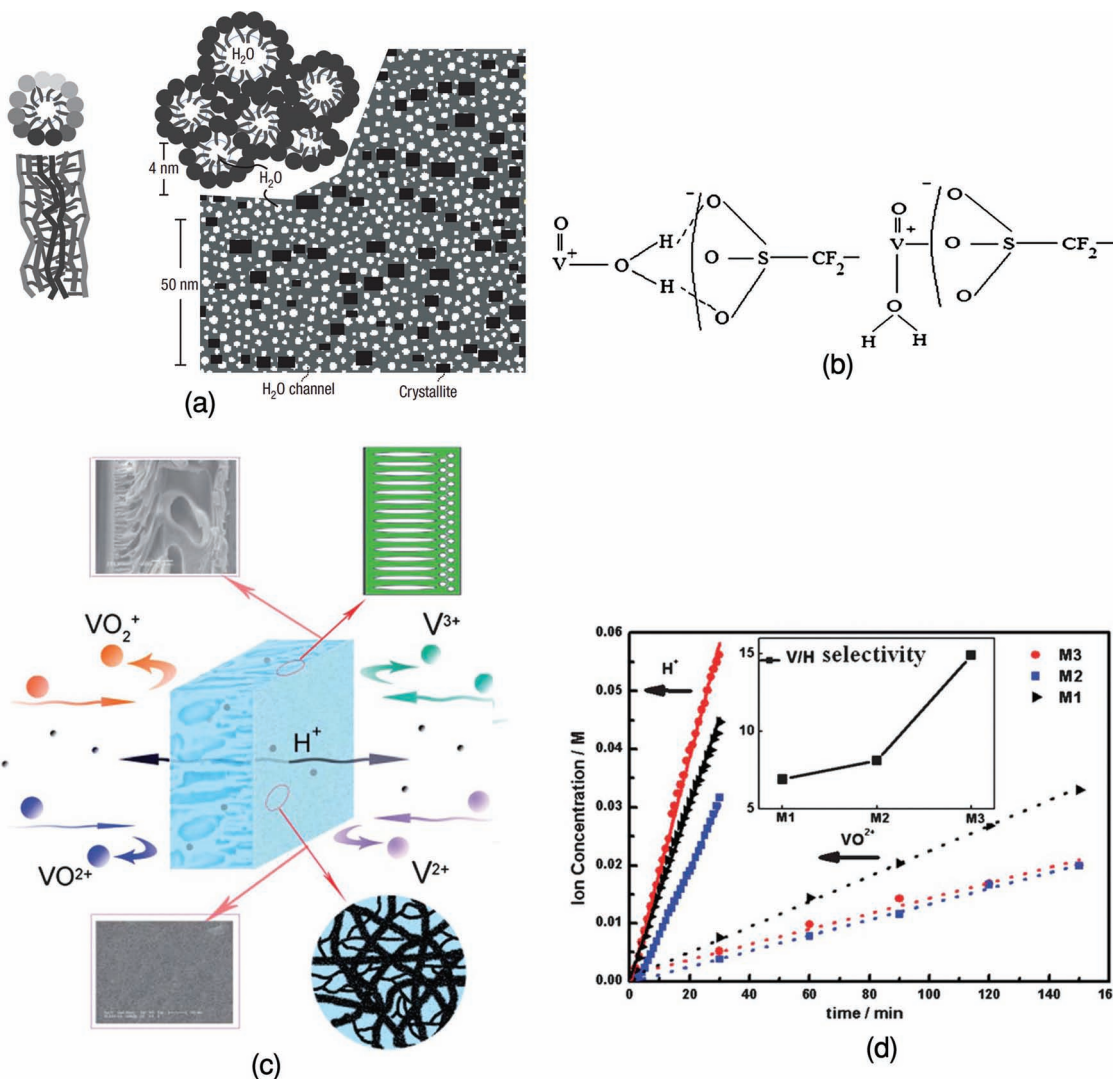
Traditionally, VRBs almost exclusively use perfluorinated polymer membranes (such as Nafion) to withstand the strong acidic environment and highly oxidative  $\text{VO}_2^+$  ions in the positive half-cell electrolyte. For RFBs with less corrosive active

materials, such as ICBs and IVBs, hydrocarbon-based membranes and separators can be a sensible choice to significantly reduce the capital cost of the systems. Current membrane development often follows the design idea and materials selection of proton exchange membrane fuel cells and direct methanol fuel cells. Most of the membrane research has focused on the VRB system in efforts to replace expensive Nafion membranes, which accounts for  $\approx 40\%$  of the cell stack cost.<sup>[25]</sup> Comprehensive reviews on the development of ion-selective membranes (IEM) for VRB system have been published.<sup>[10,11]</sup> This section provides a short overview of recent progress in membrane development. First, we review membrane research targeting VRB applications and then separator development, which has attracted more and more interest recently because of its extremely low cost. Later, we evaluate the capacity decay issue, which is closely related to the transport phenomena with membranes and is of vital importance in the long-term operation of the RFBs.

### 3.2.1. Membrane Development for VRBs

Nafion, a perfluorinated polymer membrane, has been the preferred membrane for the VRB system. The morphology of Nafion is a hydrophobic and hydrophilic two-phase structure, in which the tetrafluoroethylene (i.e., Teflon) forms the hydrophobic backbone while the sulfonate groups, terminated by pendant vinyl ether side chains, make up the hydrophilic region. The proton transport mechanism inside Nafion is usually explained using a water channel model as shown in Figure 8a. In this model, the sulfonic acid functional groups are arranged into long, parallel, randomly parked water channels with diameters between 1.8 and 3.5 nm, which affords excellent proton conductivity.<sup>[50]</sup> The most attractive characteristics of Nafion for the VRB application, however, are its excellent chemical and mechanical stabilities provided through the Teflon backbone against the strong oxidant  $\text{VO}_2^+$  in the acidic environment because most other polymeric membranes cannot survive. It is worth noting that the Nafion membrane was designed and widely researched for fuel cell applications, which obviously operate in a drastically different working environment than RFBs. Consequently, there is very limited understanding of the fundamental properties of the Nafion membrane under RFB operating conditions, which suggests a need for greater understanding of many important issues related to the Nafion membrane itself with the RFB electrolyte, such as chemical identity environment of the cation ions and their interaction with sulfonic acid groups inside the channel network. A recently reported spectroscopic study of cation absorption inside the membrane materials revealed that hydrated  $\text{V(IV)}$  cations can become bound to the sulfonic acid groups through water molecules and, therefore, can enter and accumulate inside the Nafion channels as shown in Figure 8b.<sup>[51]</sup> Although the structure of the Nafion remained intact upon exposure to the vanadium electrolyte, the absorption and accumulation of cations may be responsible for the significant decrease in proton conductivity, which will lead to performance degradation over time. The study thus emphasized the importance of conducting a fundamental study on the RFB relevant membrane mechanism and properties. Such a study hopefully would provide clues on





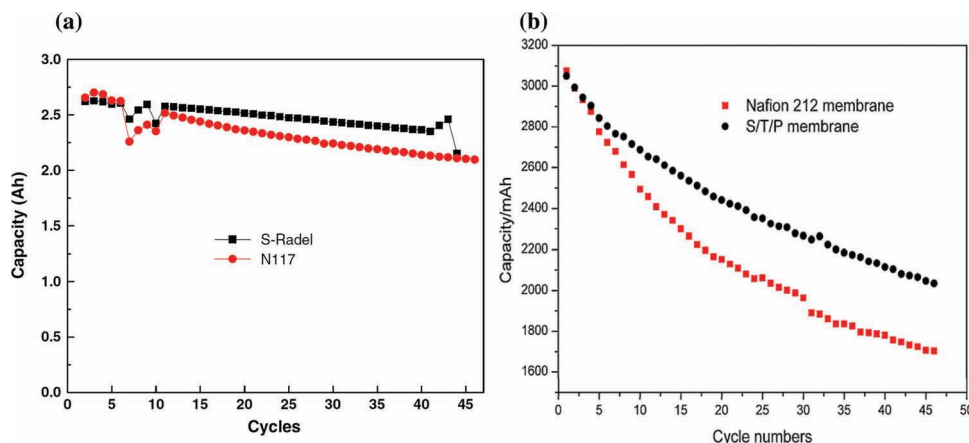
**Figure 8.** a) Water channel model of the Nafion structure show parallel channels for water diffusion and proton transport. Reproduced with permission.<sup>[50]</sup> Copyright 2008, Nature Publishing Group. b) Two possible mechanisms on the binding of V ions to the sulfate groups of Nafion. Reproduced with permission.<sup>[51]</sup> Copyright 2011, Elsevier. c) Schematic of nanofiltration membranes. Reproduced with permission.<sup>[66]</sup> Copyright 2011, Royal Society of Chemistry. d) Different transport time for V ions and proton in nanofiltration membrane (M represents samples with different percentages of volatile co-solvent during preparation). Reproduced with permission.<sup>[66]</sup> Copyright 2011, Royal Society of Chemistry.

how to improve the membrane structure and chemistry, and also RFB operation.

Despite the excellent chemical stability and proton conductivity, high vanadium ion permeability remains a concern for Nafion membranes, as cross-contamination severely diminishes the available active materials. Chemical and physical modification of Nafion membranes to improve ion selectivity therefore receives continuous research interest. Following previous reports published by Qiu's group,<sup>[52,53]</sup> Another group has reported continuous work on Nafion/SiO<sub>2</sub> and Nafion/organically modified silicate (ORMOSIL) membranes. Trogadas and co-workers reported a low-SiO<sub>2</sub> loading Nafion/SiO<sub>2</sub> and Nafion/TiO<sub>2</sub> membrane prepared by the solvent-cast method; their membrane lowered the vanadium permeability by ≈80 to 85%.<sup>[54]</sup> They observed that V(IV) ion diffusion through their membranes was about half that reported by

Qiu's group.<sup>[52,53]</sup> However, neither of these reports provided VRB cycling test data. A Nafion/organic hybrid blend membrane also was reported by Zhang's group at DICP; in that membrane, highly crystalline hydrophobic polyvinylidene fluoride was blended with Nafion to reduce the swelling of the Nafion and improve ion selectivity.<sup>[55]</sup> Cross-over of the different valence vanadium ions may be controlled by other methods, the importance of developing highly ion-selective membrane may be diminished.

The desire to use hydrocarbon-based membranes in VRBs is mostly driven by cost-reduction efforts. Recently, the development of non-fluorinated membranes has focused on sulfonated aromatic polymers in a hope that the rigid chain and less connected ionic cluster will prevent vanadium ion crossover. Meng's group has published several papers on the synthesis and characterization of sulfonated poly(arylene thioether),<sup>[56]</sup> sulfonated



**Figure 9.** Reported capacity fading during cycling for vanadium cells with various membranes: a) S-Radel (sulfonated Radel) and Nafion 117 membrane. Reproduced with permission.<sup>[69]</sup> Copyright 2010, Elsevier. b) S/T/P and Nafion 212 membrane. Reproduced with permission.<sup>[63]</sup> Copyright 2010, Elsevier.

poly(fluorenyl ether ketone),<sup>[57]</sup> sulfonated poly(fluorenyl ether ketone) with embedded  $\text{SiO}_2$ ,<sup>[58]</sup> sulfonated poly(arylene ether sulfone),<sup>[59]</sup> and sulfonated poly(fluorenyl ether thioether ketone)<sup>[60]</sup> membranes. In addition, Zhang's group reported on a sulfonated poly(tetramethyldiphenyl ether ether ketone) (SPEEK) membrane.<sup>[61]</sup> In general, these membranes demonstrated better columbic efficiency in the VRB cell test, indicating lower vanadium ion permeability. However, the long-term durability of these membranes in the V(V) electrolyte remains unknown. Another popular approach for reducing the use of Naion is a composite membrane, which started with a Nafion/SPEEK-layered composite membrane.<sup>[62]</sup> Recent reports describe SPEEK/TPA/polypropylene (PP)<sup>[63]</sup> and polysulfone/polyphenylenesulfidesulfone/TPA<sup>[64]</sup> composite membranes. Sandwich-type composite membranes are prone to delamination over prolonged cycling and their cycling stability has yet to be validated.

### 3.2.2. Microporous Separator as RFB Membranes

Another type of membrane that potentially can be employed for RFB applications is the microporous separator, which has recently garnered some renewed interest because of their significantly lower price compared to Nafion. Microporous separators have been widely used in Li-ion batteries and flooded lead acid batteries and also in waste water treatment to remove polyvalent ions. It also has been used as the membrane in VRBs as reported previously.<sup>[65]</sup> As shown in Figure 8c, the microporous separator clearly has a different structure than that of the Nafion and most hydrocarbon membranes, which usually have much bigger pore sizes and thicknesses (i.e., both at the micrometer-size level). The microporous separator capitalizes on the different transport speed of the different ionic species in the liquid electrolyte to achieve separation of the ions. For example, in a VRB cell, the protons and vanadium ions have different Stokes radii and charge densities. As a result, there is significant difference in the time they needed to diffuse through the separator as is shown in Figure 8d. This characteristic can be exploited to accomplish decent ion selectivity. For this reason, the combination of pore size and thickness of

the separator is particularly important for the specific RFB electrolyte to ensure that the redox reaction can be finished with satisfactory columbic and energy efficiency.

Zhang's group at DICP has reported nanofiltration membranes for VRB application,<sup>[66]</sup> while the PNNL flow battery team has studied the electrochemical cycling performance of the IVB cell with Daramic microporous separators.<sup>[67]</sup> In both reports, RFB cells equipped with microporous separators demonstrated acceptable cycling performance. In comparison with the Nafion membranes, the porous separators generally possess lower ionic conductivity and selectivity, which often results in a flow cell energy efficiency approximately 5 to 10% lower than that of the Nafion. One can expect strategies similar to those used to improve the Nafion and hydrocarbon membranes can be applied directly to the microporous separator. Such strategies might include adding organic/inorganic fillers to reduce the pore size to improve the ion selectivity and coating an ionic exchange polymer to increase the conductivity.<sup>[65,68]</sup> Although the long-term stability of microporous separators in VRBs still needs experimental validation, the tantalizing advantage of significantly lower cost makes porous separators attractive for future development.

### 3.2.3. Capacity Decay During RFB Operation

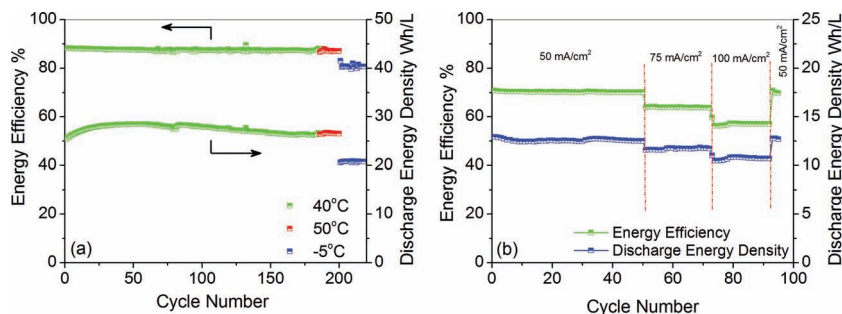
There is a haunting issue with VRB operation that is highly relevant to ion-transport behavior across membranes. This issue is the substantial capacity decay during cycling that is not well understood yet is critically important to the long-term operation of VRBs. Capacity or energy-density data for VRBs along cycling are rarely reported. As shown in Figure 9, very few papers have reported capacity decay during cycling of VRB batteries with a wide selection of various membranes, including S-Radel (sulfonated Radel),<sup>[69]</sup> S/T/P (SPEEK/TPA/PP),<sup>[63]</sup> Nafion 117<sup>[69]</sup>, and Nafion 212<sup>[63]</sup> membranes. In a membrane stability study, researchers at the University of New South Wales also reported a significant capacity decrease for a VRB cell using a GORE SELECT membrane.<sup>[70]</sup> Although the capacity fading mechanism is not entirely understood by the VRB research community, the

fact that VRB cells with different membranes and test setups by different groups all fade in capacity might suggest that capacity fading is intrinsic to the VRB system. This phenomenon may relate directly to the same element design of the VRB system and, therefore, may be indifferent to membrane selection and experimental conditions.

Unlike solid-state-batteries, in which capacity fading often indicates irreversible materials structure deterioration or crystallographic phase alteration, the lost capacity in a VRB often can be recovered through certain techniques. Extra measures, such as periodic electrolyte remixing, electrolyte transfer, or electrochemical rebalance, also can be used to alleviate the problem to some extent. These extra measures, however, not only complicate the system, but also increase the capital and/or operational cost. Regardless of the methods, any electrolyte rebalancing sacrifices energy whether it is externally supplied or it is the chemical energy that has been stored in the reactants, which will further lower the system energy efficiency.

It is true that various reasons, such as gas evolution or oxidation of V(II) ions, can cause capacity fading as previously reported.<sup>[12]</sup> Under well-controlled experimental condition, however, capacity fading reveals a more serious issue: the differential crossover of vanadium ions across the membrane. The net transfer of vanadium ions has been experimentally verified through the long-term accumulated effect of vanadium ion transport during cycling.<sup>[71]</sup> It is imperative for the VRB research community to achieve a better understanding of vanadium-ion transport across Nafion during electrochemical cycling. On one hand, precipitation may occur if the vanadium-ion concentration in one half-cell electrolyte continues to increase as a result of the imbalanced net transfer of vanadium ions, which will be devastating to the long-term operation of the VRB system. On the other hand, a clearer apprehension of vanadium-ion transport phenomena across the Nafion membrane will enable modeling or simulation to predict the time required for the electrolyte maintenance to achieve long-term optimal operation.<sup>[72]</sup>

Limited by the poor understanding of the concentrated electrolyte solution, it is a challenging task to establish a sound model for simulating the capacity loss of a VRB. Difficulties include a lack of accurate diffusion coefficients with coupling effects to the chemical entities of VRB electrolytes and the complexity of establishing the vanadium concentration profile within the Nafion membrane. The reactions between transported vanadium ions and native vanadium ions make the study of vanadium-ion transport across a Nafion membrane very challenging. Recently, Luo and co-workers at PNNL carried out an in situ investigation of vanadium-ion transport in VRB using  $\text{VO}^{2+}/\text{VO}^{+2}||\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $\text{Fe}^{2+}/\text{Fe}^{3+}||\text{V}^{3+}/\text{V}^{2+}$  flow batteries to mimic the VRB environment.<sup>[73]</sup> Although the diffusion environment and electric field strength within the test flow batteries are clearly different from those in a true VRB, this innovative method undoubtedly affords a new avenue for exploring the ion-transport behavior of the VRB and for RFBs in general.

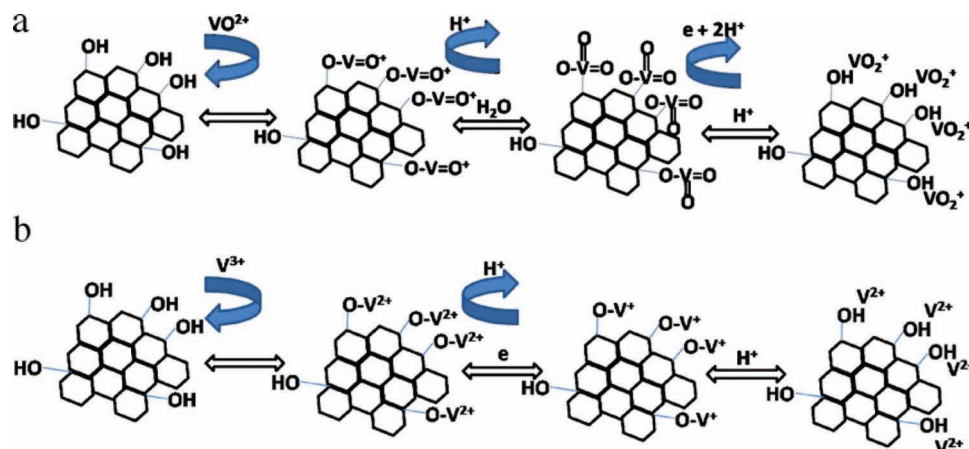


**Figure 10.** a) Long-term cycling performance of the optimized mixed-acid RFB at different temperatures and a current density of  $50 \text{ mA cm}^{-2}$  with Nafion 115 as the membrane. b) Long-term cycling performance of the IVB using Daramic microporous separator at different current densities.

Inspired by the results of this work, researchers at PNNL were able to stabilize VRB cycling over three months (>200 cycles) of continuous operation without any electrolyte maintenance as shown in Figure 10a.

For RFBs using microporous separators, such as the ICBs and IVBs, the capacity fading mechanism is completely different from that of the VRB. The low-potential (i.e.,  $-0.41 \text{ V}$ ) of the  $\text{Cr}^{2+}/\text{Cr}^{3+}$  redox reaction often is accompanied with hydrogen evolution during charging, which contributes to the capacity decay in ICB systems. For the IVB system, however, this gas-evolution issue is negligible. Considering the significantly larger pore size within the separator, convection plays a bigger role in ion-transport behavior. As a result, the capacity loss usually comes from the imbalanced electrolyte volume change driven by hydraulic pressure. A recently published report documented that the active materials concentration change is only at minimal with an IVB flow battery after long-term cycling with significant volume change.<sup>[67]</sup> Therefore, for RFBs with separators as membranes, it is important to maintain a desired hydraulic pressure on both sides of the separator to minimize volume changes. The hydraulic pressure inside the flow battery is not only associated to the properties of the electrolyte and the flow battery system design and configuration, but also can be affected by the external environment, such as temperature fluctuations. Various factors, such as the viscosity of the electrolyte, the porosity of the electrode, and the friction of the plumbing route, may well affect the hydraulic pressure of electrolyte flowing by a separator. As an example, through optimization of the electrolyte viscosity within the whole SOC operation range, researchers at PNNL were able to achieve stable cycling with an IVB flow battery using a Daramic microporous separator at various current densities as shown in Figure 10b. They also reported that the capacity decay in an IVB separator flow cell after an induced temperature change can be stabilized through simple operational parameter adjustments such as implementation of differential flow rates on each half-cell.<sup>[67]</sup> The ability to re-establish stable cycling through a simple operation parameter adjustment after temperature fluctuation gives the IVB system critical operational latitude in maintaining stable cycling during practical use in environments that will inevitably encounter the climate changes. In this regard, microporous separators offer an appealing advantage over Nafion membrane.





**Figure 11.** The possible catalytic mechanism of GO materials to facilitate the a)  $\text{VO}_2^+/\text{VO}_2^{+}$  and b)  $\text{V}^{3+}/\text{V}^{2+}$  redox reactions. Reproduced with permission.<sup>[80]</sup> Copyright 2011, Elsevier.

### 3.3. Electrode Research

The electrodes in a RFB battery must have a high surface area, suitable porosity, low electronic resistance, and high electrochemical activity toward the reactions between redox species for optimized performance. Because of the commonly acidic and corrosive environment in an RFB, choices of electrode materials are rather limited. Inert, high-surface-area, graphite- or carbon-based materials in forms such as felt or porous structures have been the most common electrode materials. Certain types of RFBs, such as ICBs, will require catalyst loading to facilitate redox reactions having inadequate electrochemical activity. Compared with the electrode in solid-state batteries, the electrode in an RFB is greatly simplified and needs mostly to provide an electrochemically active surface.

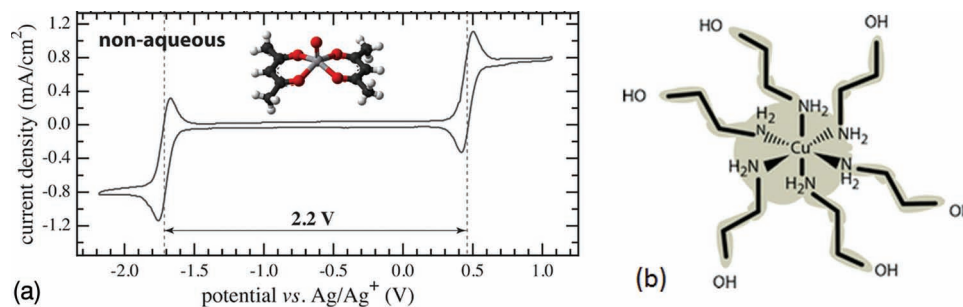
In a VRB system, common graphite- or carbon-based electrodes often exhibit inadequate electrochemical activity and kinetic reversibility toward the electrochemical reactions between the vanadium species. In early research, various approaches were employed to optimize the graphite or carbon electrodes for improved electrochemical activity, including heat treatment,<sup>[74]</sup> chemical treatment,<sup>[75]</sup> electrochemical oxidation,<sup>[76]</sup> and doping or depositing other metals on carbon fibers.<sup>[77]</sup> Among these, heat treatment is probably the simplest yet most effective way to activate the carbon-based electrode. The increased activity was attributed to the increased surface hydrophilicity and the formation of the functional groups of C–O–H and C=O on the surface of the graphite felt. Sun and co-workers suggested that the C–O groups on the electrode surface behave as active sites and catalyze the reactions of vanadium species.<sup>[74]</sup>

In recent years, influenced by the rapid development of carbon-based nanomaterials such as carbon nanotubes and graphene, there have been a number of publications on the application of carbon based nanomaterials as the VRB electrode. Considering the potential catalytic effect of the surface functional group on the redox reaction between vanadium ions with different valences as discussed above, graphene oxide (GO) has spurred some research interest. GO nanosheets have a quasi-two-dimensional layered structure with a large number of hydroxyl and carboxyl acid active groups attached

on the edges, which possibly provide active sites to facilitate the vanadium redox reactions. Cui and colleagues first reported improved electrocatalytic activity of GO nanosheets towards the  $\text{V}^{4+}/\text{V}^{5+}$  and  $\text{V}^{2+}/\text{V}^{3+}$  redox couples compared with pristine graphite, which was attributed to the formation of surface active functional groups of C–OH and COOH.<sup>[78]</sup> However, the poor electrical conductivity of the GO limited the voltage efficiency of the VRB cell. A subsequent publication reported an electrode of GO nanosheets/multiwalled carbon nanotubes (MWNTs) electrode, which demonstrated better electrocatalytic redox reversibility towards the positive  $\text{V}^{4+}/\text{V}^{5+}$  couple than either GO nanosheets or MWNTs themselves.<sup>[79]</sup> In a similar design, Yan et.al. reported a graphite/GO composite electrode for VRB with improved electrochemical activity.<sup>[80]</sup> The catalytic mechanism of the GO composite electrode is similar to that of heat treatment. As shown in **Figure 11**, it is believed that the surface functional groups, such as oxygen, tethered on the basal planes and the edge of the GO sheet function as active site to bridge the active vanadium species and catalyze the electron-transfer process. Meanwhile, nitrogen doping has also been found to facilitate the reaction kinetics and reversibility of the  $\text{V}^{4+}/\text{V}^{5+}$  redox couple.<sup>[81]</sup> Despite the reported increased electrochemical activities with electrodes modified by various methods, whether those improvements can be translated into RFB cell-cycling performance remains unknown. Nevertheless, it is believed that the surface properties of the carbon-based porous electrode are of importance to the vanadium-redox reaction. A surface functional group seems a viable way to improve the electrochemical activity of the carbon electrode. However, how to immobilize the functional group in a flowing acidic environment for long-geivity remains a challenge.

## 4. Non-Aqueous RFBs

Limited by the water electrolysis potential window and the active materials' concentrations, traditional aqueous RFBs are, in general, low-energy-density systems ( $<25 \text{ Wh L}^{-1}$  in most true flow battery systems). In pursuit of high-energy-density systems for energy-storage applications, a non-aqueous RFB system is



**Figure 12.** a) The  $V(acac)_3$  structure (insert) and cyclic voltammogram of 0.01 M  $V(acac)_3$  and 0.1 M  $TEABF_4$  in acetonitrile on glassy carbon at  $10 \text{ mV s}^{-1}$  scan rate. Reproduced with permission.<sup>[83]</sup> Copyright 2011, Elsevier. b) Schematic of the metal based ionic liquids (MetILs). Reproduced with permission.<sup>[92]</sup> Copyright 2011, Royal Society of Chemistry.

attractive because it offers the expansion of the operating potential window that has a direct impact on the system energy and power density. Expansion of cell operational voltage is considered the primary advantage of non-aqueous RFBs over the aqueous RFBs, which also increases choices of available redox couples. Another way to increase the system energy density is to employ multi-electron-transfer redox reactions to further improve the system energy density. Although efforts have been made to utilize multiple redox couples in aqueous RFBs,<sup>[82]</sup> this approach is limited by the narrow potential window. The wider potential window and more available redox couples with non-aqueous RFBs, however, renders much more flexibility in design an RFB system making use of multiple redox couples. Additional potential advantages may include higher solubility and better stability of the redox couples in the non-aqueous solution.

Nevertheless, the non-aqueous RFB R&D is in its emerging state, which has attracted a great deal of research interest recently. Current reported results on non-aqueous systems cannot possibly compete with state-of-art aqueous RFBs. In general, non-aqueous RFBs with operating voltages higher than 2.0 V have been demonstrated in various non-aqueous chemistries. However, the solubility of the active materials is poor ( $<0.1 \text{ M}$  of active materials in most cases) compared with aqueous systems in which VRBs demonstrated active-material concentrations of  $>2.0 \text{ M}$ . Reported cycling performances of non-aqueous RFBs is often cycled at much smaller current densities than those of aqueous RFBs and accompanied by poor voltage and energy efficiencies and significant degradation over cycling. One can expect that low electrolyte conductivities, temperature stability, and high cost could be challenges that, among others, limit the development of non-aqueous RFB systems. At the cell component level, little research has been done on electrodes and membranes for non-aqueous RFBs. Major efforts are concentrated on electrolyte development focusing on identifying suitable redox couples with compatible supporting electrolyte. This section therefore will provide a short review of research on various non-aqueous redox chemistries.

#### 4.1. Metal-Coordinated Redox Couples

Metal-coordinated complexes are attractive active species for non-aqueous RFBs. In a metal coordinated redox agent design, the metal center usually dictates the redox reaction

potential, while the choice of ligands affects the solution chemistry. Therefore, considerable design freedom is afforded to achieve higher redox potential and decent solubility. Schematic of  $V(acac)_3$  structure and the cyclic voltammogram spectrum of 0.01 M  $V(acac)_3$  and 0.1 M  $TEABF_4$  in acetonitrile on glassy carbon working electrode are shown in Figure 12a, which demonstrates an increase of approximately 0.8 V in the working voltage compared to that of the aqueous vanadium system.<sup>[83]</sup> Matsuda et al. first reported a redox system based on  $[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^{3+}$  (bpy stands for bipyridine) as the anolyte and  $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$  as the catholyte in acetonitrile ( $CH_3CN$ ) with tetraethylammonium tetrafluoroborate ( $TEABF_4$ ) as the supporting electrolyte.<sup>[84]</sup> Ruthenium-based active materials were investigated later by Chakrabarti et al. with ruthenium acetylacetonate ( $Ru(acac)_3$ ) redox couples in  $CH_3CN$  with  $1 \text{ M dm}^{-3}$   $TEABF_4$ .<sup>[85]</sup> The most studied non-aqueous system, however, is the zinc/cerium hybrid redox flow battery developed at Plurion Limited, which uses methanesulfonic acid supporting electrolyte.<sup>[86]</sup> More recently, Thompson and co-workers reported RFBs based on an  $M(acac)_3$  ( $M = V, Cr, \text{ or } Mn$ ; acac is acetylacetonate) redox couple.<sup>[87–89]</sup> An ionic liquid also was recently reported for RFB application by Li et al., using tetrabutylammonium hexafluorophosphate ( $TEAPF_6$ ) and 1-ethyl-3-methyl imidazolium hexafluorophosphate ( $EMIPF_6$ ) as the supporting electrolytes of a non-aqueous RFB based on vanadium acetylacetonate ( $V(acac)_3$ ) active species.<sup>[90]</sup> With the presently reported research, the solubility of the active species is still the major concern. Extensive matrix work is required to identify the suitable redox couple and supporting electrolyte solution offering high solubility and stability in a high operational voltage window. Another recent development in this direction is the synthesis of a new family of metal-based ionic liquids (MetILs) for use in flow battery applications reported by Sandia National Laboratory.<sup>[91,92]</sup> As shown in Figure 12b, the redox-active transition metal cations and ligands, which are ionically conductive materials serving as both supporting electrolyte and energy bearing active species. The unique concept and structure of the materials could offer opportunities for a high-energy-density flow battery. However, flow battery cycling data for MetILs has not been reported so far. It appears that the success of this material will depend on the design and modify the ionic liquid ligands that simultaneously satisfy the stability, conductivity, viscosity, and electrochemical activity requirements for a non-aqueous RFB electrolyte.

## 4.2. Total Organic Redox Flow Batteries

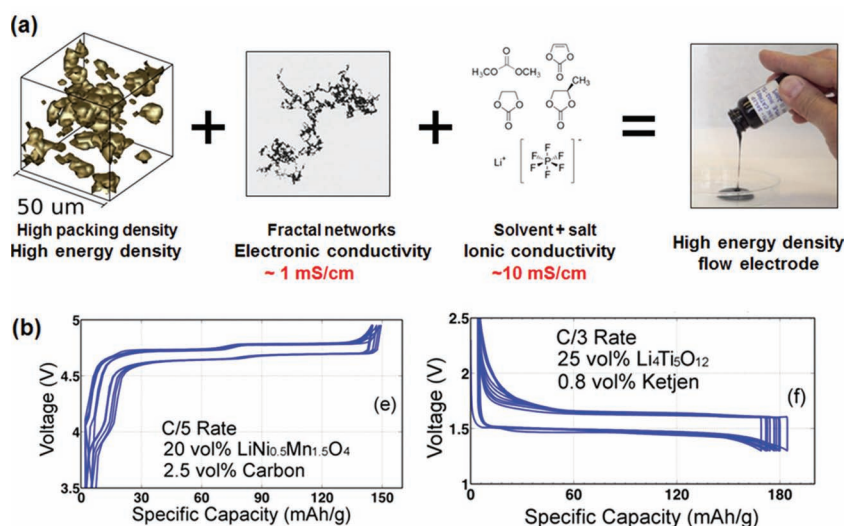
Inspired by the growing field of organic electrode materials for Li-ion batteries,<sup>[93]</sup> Liu and co-workers recently proposed and investigated a total organic redox flow battery (TORFB) system that uses metal-free organic redox reagents as electro-active materials in non-aqueous electrolytes,<sup>[94]</sup> in which 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and *N*-methylphthalimide were employed as active materials for the catholyte and anolyte, respectively. Sodium ions from NaClO<sub>4</sub> dissolved in the anhydrous acetonitrile supporting electrolyte were used as the charge carrier. In a more recent paper, Brushett et al. reported a similar all-organic RFB with 2,5-di-*tert*-butyl-1,4-bis(2-methoxyethoxy)benzene (DBBB) as the catholyte active species and a variety of molecules derived from quinoxaline as anolyte active materials.<sup>[95]</sup> Common electrolytes used in Li-ion batteries were used as the supporting electrolyte including lithium hexafluorophosphate salt in ethylene carbonate/ethyl methyl carbonate mixed solvent and lithium tetrafluoroborate salt in propylene carbonate solvent. In both of these reports, although the redox agent at the positive half-cell possesses a high voltage, TEMPO at 3.5 V and DBBB at 4.0 V vs. Li/Li<sup>+</sup>, the cells deliver a moderate voltage of <2.0 V, which revealed one of the major difficulties of the TORFB in identifying an organic redox active agent that possess a low enough redox potential to harvest the full potential of this design. In addition, the solubility of the active materials is still limited. The approach, however, merits further R&D because of the possible better compatibility between organic redox agents and organic solvents for higher solubility. In addition, TORFB offers environmental benefits, flexibility in structure design, high safety, and natural abundance, which may become critical in future large-scale applications.

## 4.3. Hybrid Non-Aqueous RFBs

Most recently, there have been several new approaches toward developing promising perspectives for future high-energy-density RFBs. Most of the approaches are “hybrid” in nature. For example, the semi-solid lithium rechargeable flow battery uses conventional Li-ion battery electrode materials in a form of suspension flowing through the flow battery cell configuration,<sup>[14]</sup> while the Li-RFB is based on hybrid electrolytes that are non-aqueous on the lithium side but aqueous on the other.<sup>[97,98]</sup> All of those new designs originate somewhat from the Li-ion battery field in an attempt to inherit its high energy density, while adopt a flow battery configuration that can achieve the unique flow battery advantages, such as the decoupling of the power and energy. It is obvious now that the synergy between the RFB and other battery chemistries has offered a fascinating new area for scientific research and has attracted more and more interest and effort.

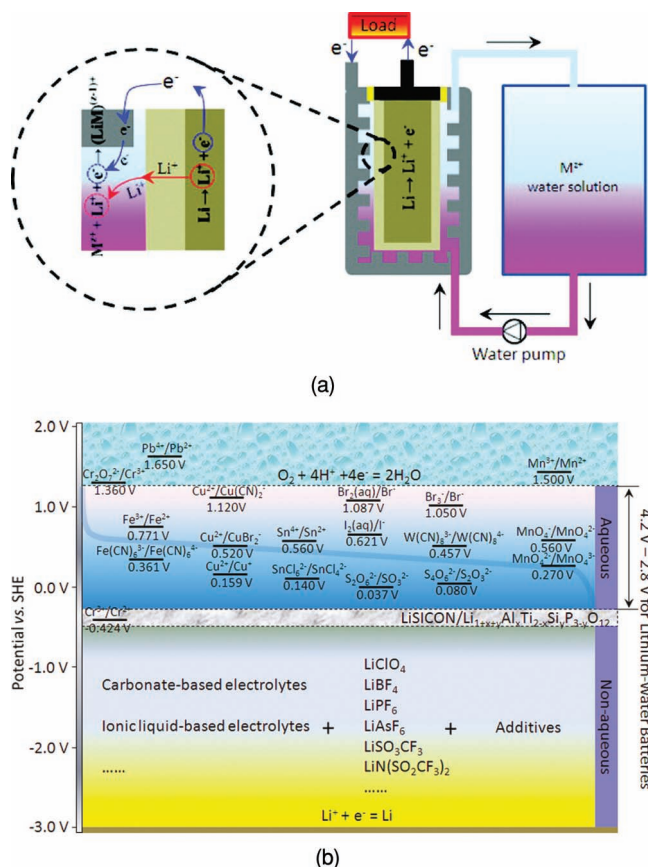
### 4.3.1. Semi-Solid Lithium Rechargeable Flow Batteries

Chiang's group at the Massachusetts Institute of Technology demonstrated a semi-solid lithium rechargeable flow battery in which the traditional Li-ion battery electrode solid materials (LiCoO<sub>2</sub> and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>) were suspended in a conductive gel circulating through each of the half-cells, which were separated by an Li-ion battery microporous separator.<sup>[14]</sup> The LiCoO<sub>2</sub>–Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> full-cell test produced an average 2.35 V discharge voltage with 397 Wh L<sup>−1</sup> of energy density. Presumably, other Li-ion battery intercalation chemistry compounds can be used by the same mechanism. The combination of high concentration and high voltage yields significant increases in energy density. The novelty in this approach is the use of particulates of a redox-active compound in suspensions rather than solutions. As a result, the energy density of the electrolyte is no longer constrained by the solubility limitation, but rather the allowed fraction of active material solids in the flowable suspension. In achieving the electronic charge transfer between the active materials particles and the current collector, another intriguing concept of “flowable electrodes” was developed, in which the particulate active materials and conductive additives (ketjen black) were dispersed in a typical Li-ion battery electrolyte solution to form a percolation nanoscale conductor network, as shown in Figure 13a.<sup>[96]</sup> The fractal-like network formed by the nanoscale conductor thus renders the electrolyte decent electronic conductivity. Figure 13b shows the voltage profile of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> suspension achieved in a flowable form.<sup>[96]</sup> In doing so, the charge transfer is no longer confined on the local surface area of the electrode; rather, it is extended to the whole electrolyte volume, which could be a revolutionary development for the RFB electrode. Although it is difficult to suspend the conductive particles in the aqueous RFB electrolyte because of the strong acidic environment, the



**Figure 13.** a) Formation of flowable electrode, where both the particulate active materials and nanoscale electronic conductors are suspended in common Li-ion battery electrolytes. b) Voltage profile achieved in a flowable form of 20 vol% LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> dispersed in 1 M LiPF<sub>6</sub> in ethylene carbonate/dimethyl carbonate and 25 vol% Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> dispersed in 1 M LiPF<sub>6</sub> dimethyl carbonate. Figure courtesy of Prof. Yet-Ming Chiang at the Massachusetts Institute of Technology.<sup>[96]</sup>





**Figure 14.** a) Schematic of the Li-redox flow battery. b) Choices of the catholyte redox couples and organic supporting electrolytes for lithium anode. Reproduced with permission.<sup>[99]</sup> Copyright 2011, American Chemical Society.

approach potentially can be expanded to other non-aqueous RFBs with the help of surface functional groups and the use of the surfactant.

#### 4.3.2. Li-Redox Flow Batteries

In 2011, Goodenough's group at The University of Texas and Zhou's group at the Advanced Institute of Science and Technology in Japan, both independently reported a hybrid system with an aqueous cathode operating as a true flow battery cathode and a lithium metal that functions as anode.<sup>[97,98]</sup> The schematic of the cell configuration is shown in **Figure 14a**. Although the reported cell is limited by the low cathode-active materials concentration (0.1 M K<sub>3</sub>Fe(CN)<sub>6</sub> in Goodenough's report and 0.1 M FeCl<sub>3</sub> in Zhou's report), a high cell voltage of 3.4 V was achieved with a stable cycling performance up to 20 cycles. The flow cell uses a Li-metal as anode with the organic electrolyte in the anode half-cell, while an aqueous solution containing redox couple as the catholyte in the cathode half-cell. A solid electrolyte separator (e.g., LISICON or NASICON) is thus required to completely separate the anode and cathode to prevent the violent reaction between lithium metal and water. The unique design capitalizes on the advantages of an RFB system on the cathode side while pinning down the anode with the

lithium redox potential to achieve high voltage. Because of the use of the solid lithium metal anode, the energy and power of the Li-redox flow battery, however, is not completely decoupled like that of the true RFBs. In a later report, Goodenough and co-workers summarized the available selection of the aqueous cathode as shown in **Figure 14b**.<sup>[99]</sup>

Obviously, the success of the Li-redox flow battery will hinge on the development of its key component, the solid-electrolyte that separates the organic and aqueous electrolytes. In addition to the requirements for membranes in aqueous RFB, such as high conductivity and stability in both organic solution and aqueous electrolyte with various pH values, the solid electrolyte should possess enough mechanical strength to prevent possible dendrite growth on the lithium anode from reaching the cathode. Judging from the current development status, the solid electrolyte may present difficulties in cost reduction and scalability for future large-scale applications. In addition, lithium anode protection and safety if internal shorting occurs remain concerns.

#### 4.3.3. Metal-Organic RFBs

As previously discussed, the voltage output of the current TORFB is limited because of the difficulty in identifying an organic redox agent that possesses a low enough potential. In this regard, researchers at PNNL have proposed and investigated a hybrid metal-organic RFB (MORFB).<sup>[100]</sup> The new MORFB system uses redox reactions between metal and organic electroactive molecular redox reagents, employs redox active organic molecules at the positive half-cell and metal or metal ions at the negative half-cell, or vice versa. The rationale for exploring the metal organic hybrid system is to capitalize on the differences in the redox potentials, solubilities, and stabilities of different material systems. The hybrid nature of the system renders greater flexibility in identifying two redox couples for the construction of an RFB with a designable voltage window. In their first proof-of-concept test, a non-aqueous, hybrid metal-organic redox flow battery based on a tailored anthraquinone structure is demonstrated to have an energy efficiency of ≈82% and a specific discharge energy density similar to those of aqueous redox flow batteries, which is due to the significantly improved solubility of the modified anthraquinone in supporting electrolytes.

In summary, development of non-aqueous RFBs is still in its infancy and would need extensive development effort before the technology could compete with current aqueous RFBs. Current R&D efforts are concentrated on the extensive search for and rational design of the redox species and compatible supporting electrolytes with desirable potentials, capacities, stabilities, and solubilities. Little effort has been made to design and synthesize the ion-conductive membrane and electrode for non-aqueous RFB applications.

## 5. Perspectives

Given the current trend towards reducing greenhouse gas emissions and increasing the penetration of renewable energy,

along with demands of high-quality power and implementation of smart grids, there appears to be general agreement on the need for EESs in the electrical grid. The demand for stationary energy storage has rapidly changed the worldwide landscape of energy system research, which recently brought the RFB technology into the spotlight. Deemed suitable for large-scale energy storage, the unique mechanism of RFBs does offer tremendous research opportunities, although current fundamental research is clearly outpaced by industrial prototype development. The recent invention of the mixed-acid VRB system highlighted the importance of advancing the essential understanding of electrolyte solution chemistry, while the lingering capacity fading issue in VRBs manifested the lack of comprehension of the redox reaction kinetics and transport phenomena. Concrete and comprehensive research is therefore urgently needed in this field on, but not limited to, the topics of complex charge transfer and redox reaction kinetics on the electrode surface, transport in membranes, and fluid mechanics through the electrode. The growing interest and worldwide R&D activities suggest a bright outlook for developing improved RFB technologies for the future electric grid.

A recent surge in research activities on non-aqueous RFBs reiterates a high level of interest in high-energy-density systems. This interest is also reflected in the development of Li-ion/RFB hybrid energy-storage systems. Although in the initial stage, these approaches open extraordinary new research avenues to adopt redox flow concepts onto other chemistries holding great promise to multiply the energy density of RFBs potentially for transportation applications. The complexity of the non-aqueous RFB system also offers tremendous opportunities in fundamental research in the area of materials design, organic synthesis, solution chemistry, kinetics, transport, etc. The hybrid nature of these new systems will require an interdisciplinary approach to successfully leverage our knowledge of existing battery chemistries with unique redox flow technologies.

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