

## Redox flow batteries: a review

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**Abstract** Redox flow batteries (RFBs) are enjoying a renaissance due to their ability to store large amounts of electrical energy relatively cheaply and efficiently. In this review, we examine the components of RFBs with a focus on understanding the underlying physical processes. The various transport and kinetic phenomena are discussed along with the most common redox couples.

**Keywords** Flow battery Redox Regenerative fuel cell Flow cell Vanadium

### List of symbols

$a_{k,p}$  Interfacial surface area between phases  $k$  and  $p$  per unit volume ( $\text{cm}^{-1}$ )  
 $c_i$  Concentration of species ( $\text{mol}/\text{cm}^3$ )  
 $d_f$  Fiber diameter (cm)  
 $D_i$  Fickian diffusion coefficient of species in a mixture ( $\text{cm}^2/\text{s}$ )

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Standard cell potential (V)  
Equilibrium cell potential (V)  
Faraday's constant, 96487 C/equiv  
Superficial current density ( $\text{A}/\text{cm}^2$ )  
Exchange current density ( $\text{A}/\text{cm}^2$ )  
Transfer current density of reaction  $i$  per interfacial area between phases  $k$  and  $p$  ( $\text{A}/\text{cm}^2$ )  
 $k$  Permeability ( $\text{m}^2$ )  
 $k^0$  Standard rate constant, varies  
 $m$  Valence state  
 $n$  Valence state or number of electrons transferred in a reaction  
 $N_i$  Superficial flux density of species ( $\text{mol}/\text{cm}^2 \text{ s}$ )  
 $p$  Pressure (Pa)  
 $r_{l,k-p}$  Rate of reaction  $l$  per unit of interfacial area between phases  $k$  and  $p$  ( $\text{mol}/\text{cm}^2 \text{ s}$ )  
 $R$  Ideal-gas constant, 8.3143 J/mol K  
 $R_{g,k}$  Rate of homogenous reaction in phase  $k$  ( $\text{mol}/\text{cm}^3 \text{ s}$ )  
 $R_{i,j}$  Resistance of resistor  $j$  in Fig. 10 where  $ct$  stands for charge-transfer ( $\Omega \text{ cm}^2$ )  
 $s_{i,k,l}$  Stoichiometric coefficient of species in phase  $k$  participating in reaction  $l$   
 $t$  Time (s)  
 $T$  Absolute temperature (K)  
 $u_i$  Mobility of species  $i$  ( $\text{cm}^2 \text{ mol}/\text{J s}$ )  
 $v$  Superficial velocity ( $\text{cm}/\text{s}$ )  
 $x$  Stoichiometric coefficient  
 $y$  Stoichiometric coefficient  
 $z_i$  Valence or charge number of species

### Greek

$\alpha$  Transfer coefficient  
 $a_i$  Transport coefficient of species  $i$  ( $\text{mol}^2/\text{J cm s}$ )  
 $\epsilon$  Porosity

$\epsilon_0$	Permittivity (F/cm)
$n$	Electroosmotic coefficient
$q$	Density (g/cm <sup>3</sup> )
$q_c$	Charge density (C/cm <sup>2</sup> )
$r$	Conductivity of the electronically conducting phase (S/cm)
$g$	Overpotential (V)
$j$	Conductivity of the ionically conducting phase (S/cm)
$l$	Viscosity (Pa s)
$l_i$	(Electro)chemical potential of species $i$ (J/mol)
$\Phi_k$	Potential in phase $k$ (V)
$w_i$	Permeation coefficient of species $i$ (mol/s cm bar)

#### Super/subscripts

*	Reference state
0	Solvent
1	Electronically conducting phase
2	Ionically conducting phase
O	Oxidant
R	Reductant

## 1 Introduction

Renewable-energy sources, such as solar and wind, are being deployed in larger numbers than ever before, but these sources are intermittent and often unpredictable. These characteristics limit the degree to which utilities can rely upon them, and, as such, renewables currently comprise a small percentage of the primary power sources on the US electrical grid. Analysis suggests that an electric grid couldn't become destabilized if non-dispatchable renewable energy exceeds 20% of the energy-generation capacity without energy storage [1]. However, many utilities are mandating renewable portfolios approaching this level of deployment, thus there is a pressing need for storage technologies that complement and enable renewable standards. Other than capacitors, however, there is no way to store electrical energy as such. Instead, if electricity is to be stored, it must first be converted to some other form of energy. There are some technologies that enable practical storage of energy at their current levels of deployment, but only a very small fraction of North American power plants employ such technology [2]. To ensure that renewable energy succeeds in delivering reliable power to US consumers, the nation needs cost effective and reliable storage at the grid scale. Conventional rechargeable batteries offer a simple and efficient way to store electricity, but development to date has largely focused on transportation systems and small systems for portable power or intermittent backup power; metrics relating to size and volume are far less critical for grid storage than in portable or transportation applications.

It therefore stands to reason that optimizing battery performance over a different set of variables might result in an implementation that delivers superior performance for reduced cost. Batteries for large-scale grid storage require durability for large numbers of charge/discharge cycles as well as calendar life, high round-trip efficiency, an ability to respond rapidly to changes in load or input, and reasonable capital costs [3]. Redox flow batteries (RFBs) or redox flow cells (RFCs), shown schematically in Fig. 1, promise to meet many of these requirements [4].

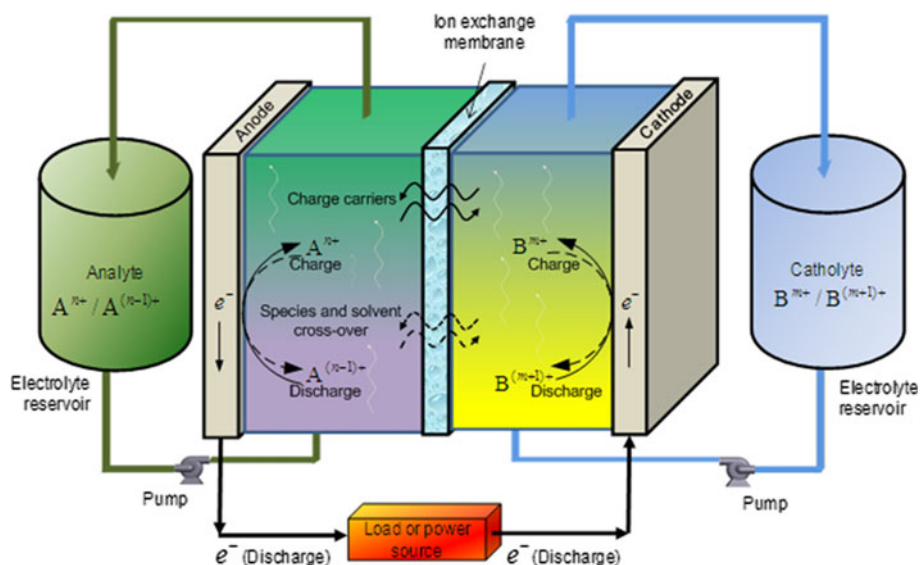
As shown in Fig. 1, a key component of RFBs is the ability to separate power and energy. The power is controlled by the stack while the energy is stored within the separated reactants. Thus, one can optimize over a greater range of variables and storage can be increased with relatively ease and minimal cost compared to the stack, which is typically the most expensive system component. To examine the technologies that are under development to meet the cost requirements of the marketplace and enable wide-scale storage, we consider the existing portfolio of RFB storage technologies and the possibilities of each. To that end, we introduce the various technologies and discuss in more depth the general attributes and concerns facing RFBs. The overall purpose of this review is to examine systemic issues for the field of RFBs, and not just to examine a specific chemistry or the various proposed RFBs. Excellent reviews of these latter issues and energy storage for the grid in general can be found in the literature [5–8]. The structure of this paper is as follows.

After an introduction and short overview of the various major RFBs, the kinetic and transport issues are examined. Next, some overall electrode/cell modeling and designs are reviewed. Finally, some comments about future research needs are made. It should be noted that this review is focused on cell-level issues and RFB chemistries, therefore issues of system integration and components are not examined in depth, although they can be critically important for system commercialization. Before discussing the various RFB chemistries, it is worthwhile to examine their current major applications.

### 1.1 Grid-storage needs

The present electric grid constitutes an enormous physical infrastructure, with a near-instantaneous transmission of value from primary power sources and generation assets to end users and with almost no storage capability. Because of this dearth of storage, the existing grid must conform to fluctuations in customer demand, resulting in the construction of power plants that may only operate for 100 h a year or less and can account for up to 30 MWh in capacity [9]. These generators are dispatched to respond to small oscillations in demand over very short time scales of

Fig. 1 A schematic diagram of a redox flow battery with electron transport in the circuit, ion transport in the electrolyte and across the membrane, active species crossover, and mass transport in the electrolyte



less than 1 h. They are also turned on and sped up to meet anthropogenic global warming gas emissions from a policy increasing load during the peak time of the day, and, at the other extreme of wastefulness, brought on by the lack of storage. For example, wind energy is wasted because of the inability to dispatch wind power at night when wind generation is at a maximum but customer demand is at a minimum; thus, there is a significant value added by the incorporation of storage [10]. Similarly, photovoltaics and solar-energy implementation will also require arbitrage intermittent generation assets or storage. In addition to improvements in resiliency that can enable increased renewable-energy generation, integration of storage into the smart grid also promises to enable greater system efficiency, even with existing generation control and maintenance of the electric grid. To date, however, energy storage comprises only about 2% of the installed generation capacity in the U.S. Because of differences in government policy and more favorable economics, storage plays a larger role in Europe and Japan, 10 and 15%, respectively [1].

The current worldwide electric generation capacity was estimated to be about 20 trillion kilowatt hours in 2007 [2]. More than two-thirds of the current mix is from some form of fossil fuel, with most of the balance coming from nuclear and hydroelectric power generation; at present, only about 3% comes from renewable-energy technologies. Furthermore, developing economies and electrification of the transportation sector both point to strong year-over-year growth in terms of electrical demand. While coal is already the primary source of power in the US electricity sector, there are concerns that it will become a larger portion of electricity production as increased global demand competes for cleaner resources like natural gas. Coal is, of course, the most carbon-intensive resource used in this sector; however, the debate continues about how to address

and life-cycle costs. Because of the decoupling of energy and power in RFB configurations, we can consider both, albeit without specification of duration or sizing. A 2008 estimate of RFB costs suggested nearly \$2500/kW, and power in RFB configurations, we can consider both, albeit without specification of duration or sizing. Regardless of detail, however, significant cost reduction and the cost per unit of energy-storage capacity (\$/kWh) must be achieved: technological improvements, material development, and economies of scale must be achieved to ensure success in the marketplace. We note that the cost per unit energy storage is not the incremental cost of producing or storing that energy, but the cost per unit of energy-storage capacity. In addition to costs, robust system lifetimes of ~10 years, high efficiency, and cyclic durability are necessary for grid-level storage.

Different applications have different acceptable costs, and the total power and total duration of storage provided will differ from application to application. As such, it is difficult to target a single metric that can concisely address the ultimate cost target for grid-based storage. Table 1 shows a generic RFB system. In the discharge mode, an anolyte solution flows through a porous electrode and reacts to generate electrons, which flow through the external circuit. The charge-carrying species are then transported to a separator (typically an ion-exchange membrane (IEM)), which serves to separate the anolyte and catholyte solutions. The general reactions can be written as follows:  $A^{n+} + xe^{-}$  (charge) and  $A^{n+} + xe^{-}$  (discharge). Current estimates of costs for conventional batteries and flow batteries are significantly higher than the required targets and

Table 1 Key performance targets for grid-storage applications, from Ref. [1]

Application	Purpose	Key performance targets
Area and frequency regulation (short duration)	Reconciles momentary differences between supply and demand within a given area	Service cost: \$20/MW Roundtrip efficiency: 85–90% System lifetime: 10 years Discharge duration: 15 min–2 h Response time: milliseconds
Renewables grid integration (short duration)	Offsets fluctuations of short-duration variation of renewables generation output Accommodates renewables generation at times of high grid congestion	Roundtrip efficiency: 90% Cycle life: 10 years Capacity: 1–20 MW Response time: 1–2 s
Transmission and distribution upgrade deferral (long duration)	Delays or avoids the need to upgrade transmission and/or distribution infrastructure Reduces loading on existing equipment to extend equipment life	Cost: \$500/kWh Discharge duration: 2–4 h Capacity: 1–100 MW Reliability: 99.9% System life: 10 years
Load following (long duration)	Changes power output in response to the changing balance between energy supply and demand Operates at partial load (i.e., increased output) without compromising performance or increasing emissions	Capital cost: \$1,500/kW or \$500/kWh Operations and maintenance cost: \$500/kWh Discharge duration: 2–6 h
Electric energy time shift (long duration)	Stores inexpensive energy during low demand periods and discharges the energy during times of high demand (often referred to as arbitrage)	Capital cost: \$1,500/kW or \$500/kWh Operations and maintenance cost: \$250–\$500/kWh Discharge duration: 2–6 h Efficiency: 70–80% Response time: 5–30 min

$B^{mp}$  ye  $\overset{\text{charge}}{!} B^{\overset{\text{charge}}{\Delta}mp}$  ybb and  $B^{\overset{\text{discharge}}{\Delta}mp}$  ybb  $\overset{\text{discharge}}{!} B^{mp}$  ye

for the anode (negative electrode) and cathode (positive electrode), respectively.

The key transport mechanisms are shown in Fig. 1 for this generic system. The dominant losses in these systems other than charge-transfer reaction kinetics, are related to the charge and mass transport in the electrolyte and separator, which are each discussed in turn in later sections of this review. Additionally, a key factor in many of these systems is crossover of species through the separator, which is dependent on current and membrane permeability. A sample RFB cell performance is shown in Fig. 2, where the charge and discharge are at different rates or current densities. One can see that similar to a fuel-cell polarization curve, there can be ohmic, mass-transport, and/or kinetic losses. The first part of the curves is dominated by kinetic overpotential, especially on charge. The middle part of the curves is dominated by ohmic or ionic-conduction losses, and the last part of the curves is typically a signature of reactant mass-transport limitations.

The reactor in Fig. 1 consists of a stack of individual cells, where each cell contains the sites where electrochemical charge-transfer reactions occur as electrolyte flows through them, as well as a separator (either an electrolyte-filled gap or a selective membrane) to force the electrons through the external circuit. The arrangement of a typical cell is shown in Fig. 3, and individual cells can be arranged in series to increase the overall stack voltage. Generally, stacks are arranged in a bipolar fashion so that current flows in series from one cell to the next.

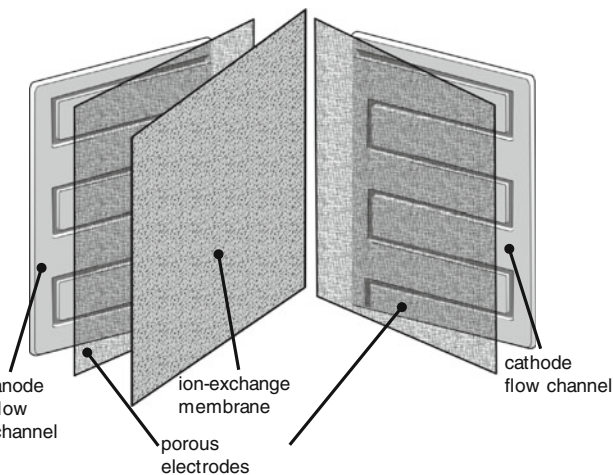


Fig. 3 Schematic diagram of standard RFB cell construction

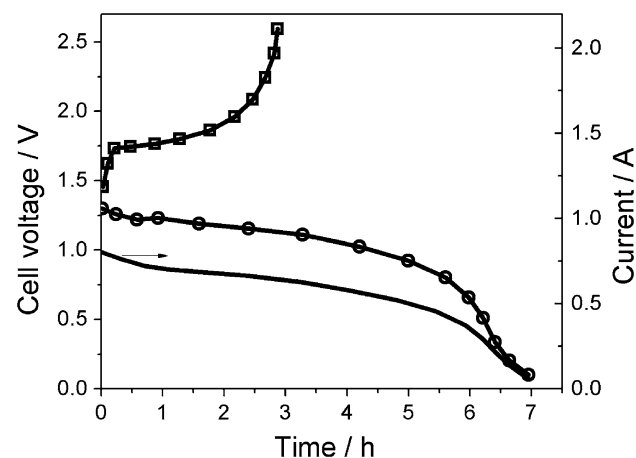


Fig. 2 Charge/discharge curves of an all vanadium RFB using 0.5 M  $VOSO_4$  in 2 M  $H_2SO_4$  and sulfonated polyethylene membrane. Electrode area = 90  $cm^2$ ; charging current density = 15  $mA\ cm^{-2}$ ; The discharge process used a 21 resistor and the average discharge current density = 6  $mA\ cm^{-2}$ . Adapted from Ref. [6] with permission

One of the key attributes of RFBs that suggests significant promise for stationary applications is the fact that, for many configurations, there is no physical transfer of material across the electrode/electrolyte interface. While there are some configurations that can be categorized as flow batteries only in the sense that the active material flows from outside of the cell to the electrode surface, most flow-battery systems under development utilize reversible solution-phase electrochemical couples on two electrodes to store chemical energy. Instead of storing the electrochemical reactants within the electrode itself, as with metal/metal alloy or intercalation electrodes, the reactants are dissolved in electrolytic solutions and stored in external tanks. Both the oxidized and reduced form of each reactant are soluble in the electrolyte, so they can be carried to/from the electrode surface in the same phase. Only the relative concentrations of oxidized and reduced forms change in each stream over the course of charge and discharge.

The electrodes in most RFB configurations are not required to undergo physical changes such as phase change or insertion/deinsertion during operation because the changes are occurring in the dissolved reactants in the solution phase adjacent to the solid-electrode surfaces. Though there are exceptions to this formulation, as mentioned in the next section, this feature generally affords the opportunity to simplify the electrode design considerably. As a consequence of the charge-transfer characteristics, the cycle life of a RFB is not directly influenced by depth-of-discharge or number of cycles the way that conventional rechargeable batteries are. Side reactions can, of course, complicate design and operation, but if the reactions proceed as intended, degradation of the electrode surface need not proceed as a matter of course. The decoupling of storage and reaction in RFB systems is an advantage in terms of flexibility, but it complicates their designs relative

to conventional batteries, and adds a mechanical balance of-plant element for pumping the often highly corrosive liquid electrolyte; as a result, their specific mass and volumetric energy densities are much lower than conventional batteries. A RFB configuration can nevertheless exceed the performance of other grid-storage technologies and does not require specific geographical siting, as pumped hydroelectric and compressed-air energy storage (CAES) do. Figure 4 shows some basic redox couples, charge-transfer, and ion-carrier-migration modes in various specific RFBs.

Additionally, RFBs offer the important advantage that power and energy outputs are independent variables since the power is determined by the reactor size and the amount of energy stored depends on the reactants chosen, their concentration, and the size of the reactant tanks. The amount of energy that can be stored in a conventional sealed battery is generally limited by the effective lengths for diffusion and migration in the direction normal to the current collector; making an electrode thicker will add to the amount of active material, but one experiences diminishing returns in terms of energy extraction because of diffusional and ohmic losses in these systems.

As shown in Fig. 1, most RFB systems currently require two separate electrolyte tanks: one for the anolyte and another for the catholyte. This ensures that the potentials at each electrode are close to the reversible potential for each of the half-cell reactions, and side reactions or competition from the other half-cell reactions are minimized. This does, however, add to the size and cost of the system, and it also requires a uniform delivery of the dissolved species to the entire surface area as oftentimes most of the convective flow is parallel to the electrode surface rather than being flowed directly through it. Details of ion transport and flow configurations are discussed more thoroughly in a subsequent section.

The key costs of RFBs are the active material stored in the electrolyte and the electrochemical cell itself. The construction costs of the cell scale with the total power requirement of the application, but these costs are directly related to the specific power of the device itself, i.e., how effectively the materials are utilized. While RFBs ought to be able to operate at relatively high current densities, as convection can be employed to deliver reactants to the electrode surface, RFBs have typically been operated at current densities consistent with conventional batteries without convection. It is anticipated that electrolyte management and cell design can deliver significant improvements in power density, thereby reducing considerably cell material costs.

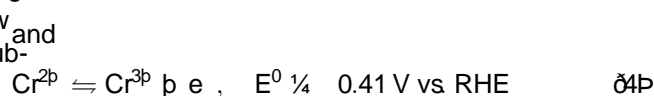
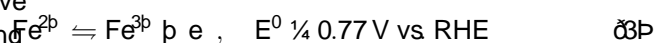
## 2.1 Redox-flow-battery chemistries

Several battery technologies have been considered for grid-based storage in recent decades. Traditional rechargeable

batteries have been modified and optimized for grid-based storage and are being deployed in some installations, including lead-acid, nickel-based, and lithium-ion batteries; but we turn our attention to RFBs, which have been demonstrated on the order of 100 kW to 10 MW. RFBs are generally categorized based upon the anolyte and catholyte that comprise the form of energy storage of the system. Figure 4 shows some basic redox couples, charge-transfer, and ion-carrier-migration modes in various specific RFBs. As shown in Fig. 4, configurations with the same species but different oxidation states (such as all-vanadium) as well as different active species in the anolyte and catholyte are used. In this section, we introduce the various important RFB types and briefly some of the advantages, disadvantages, and challenges of each.

### 2.1.1 Iron/chromium

Modern development of what we might term a RFB began with the development of an iron/chromium system (Fe/Cr) in the 1970s at NASA, which demonstrated a 1 kW/1.3 kWh system for a photovoltaic-array application [9, 20]. The Fe/Cr system is based upon an aqueous solution of a ferric/ferrous redox couple at the positive electrode ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ ); the negative electrolyte is a mixture of chromic and chromous ions ( $\text{Cr}^{2+}/\text{Cr}^{3+}$ ); most systems use hydrochloric acid as the supporting electrolyte. The charge-transfer reactions at each electrode are

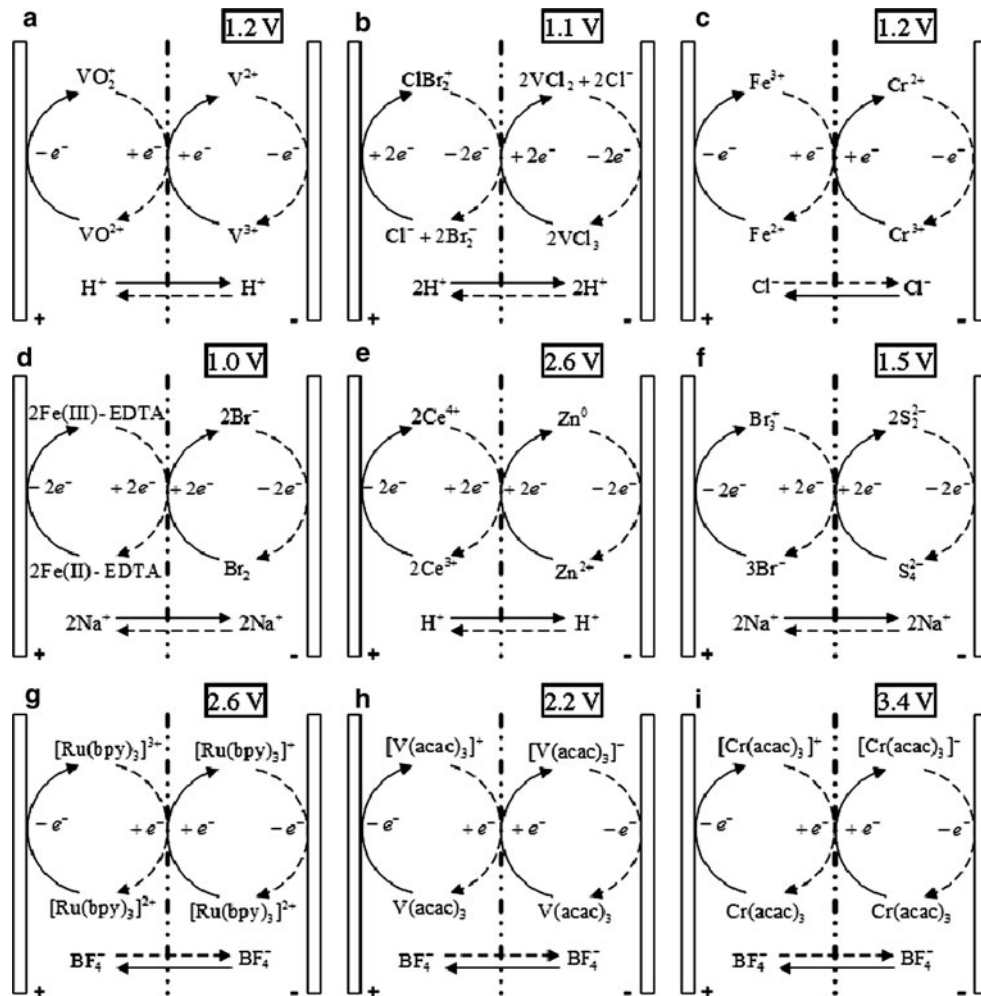


The system can operate with an IEM/separator and low-cost carbon-felt electrodes. Both charge-transfer reactions require only a single-electron transfer, which is expected to simplify charge transfer and result in reasonable surface overpotentials without specific electrocatalysts. Indeed, the iron redox couple is highly reversible on carbon or graphite electrodes, but the chromium redox couple has significantly slower kinetics and does require electrocatalysts. This system has a relatively low open-circuit potential (between 0.90 and 1.20 V), and designers must endure crossover of iron to the chromium stream and vice versa. Some Japanese companies built similar batteries by licensing the NASA patents, but have not shown improvement in the low output voltage and efficiency [21].

### 2.1.2 Bromine/polysulphide

The bromine/polysulphide RFB was patented by Remick [16] then extensively studied by Regenesys Technology

Fig. 4 Schematic of charge transport in various redox-flow systems (the values give the potential of the redox couple). a All vanadium, b vanadium/bromine, c iron/chromium, d Fe-EDTA/bromine, e zinc/cerium, f bromine/polysulphide, g nonaqueous ruthenium/bipyridine, h nonaqueous vanadium/acetylacetonate, i nonaqueous chromium/acetylacetonate



[22] from 1993 until 2006 when it was acquired by VRB Power Systems [5]. To date, three series of bromine/polysulphide RFB systems have been developed, including 5, 20, and 100 kW class systems. A commercial-size 15 MW system was successfully demonstrated. This plant used up to 120 modules, and 200 bipolar electrodes with an energy storage capacity up to 12 MWh and two 1800 m<sup>3</sup> electrolyte storage tanks [23].

In the bromine/polysulphide system, the positive electrolyte is sodium bromide, and the negative electrolyte is sodium polysulphide, though, the counter-ion could be replaced with another cation. The key attributes of this system are that the species that comprise the two electrolytes are abundant and reasonably inexpensive; furthermore, they are highly soluble in aqueous electrolytes which reduces the volume of electrolyte that is required to store a given quantity of charge. At the positive electrode three bromide ions combine to form the tribromide ion  $3\text{Br}^- \rightleftharpoons \text{Br}_3^- \quad \text{p} \quad 2e^- \quad E^0 \quad \frac{1}{4} \quad 1.09 \text{ V vs RHE}$

At the negative electrode, the sulfur in solution is shuttled between polysulphide and sulphide

$2\text{S}_2^{2-} \rightleftharpoons \text{S}_4^{2-} \quad \text{p} \quad 2e^- \quad E^0 \quad \frac{1}{4} \quad 0.265 \text{ V vs RHE}$  [26]. In this system, all of the electroactive species are anions, so a cation-exchange membrane is needed to prevent mixing of the anolyte and catholyte streams. Charge is carried via sodium ions through the membrane. When activated carbon/polyolefin composite electrodes were used in this system, the voltage increased from 1.7 to 2.1 V during the charging process due to adsorption of bromine in the activated carbon [24]. This system is prone to crossover and mixing of the electrolytes, however, which can lead to precipitation of sulfur species and the formation of H<sub>2</sub>S and Br<sub>2</sub>.

### 2.1.3 All-vanadium

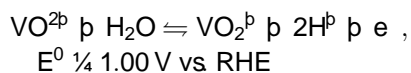
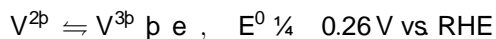
In both of the systems described above, a chief concern and liability is the incompatibility between, and sensitivity of, the two electrolyte streams to contamination from the other. If a species crosses over and reacts irreversibly with elements in the opposite stream, it comprises not just an efficiency loss on that particular charge/discharge cycle,

but a loss of capacity and degradation in the overall electrolyte stream and precipitation can occur; the performance of the system, which may result in expensive solubility limits depend upon both acid concentration and electrolyte separation and reactant recovery. To this end temperature [49].

it is helpful to develop a system with more than two oxidation states of the same element, wherein crossover only

represents an efficiency loss as no species are irreversibly consumed or removed from their reactive electrolytic

Because there are limits to how much vanadium can be stored in solution in the VRB system, some of the same V(III) redox couple at the negative electrode and these researchers who pioneered the work on the VRB cell noted V(IV)/V(V) redox couple at the positive electrode, generally identified to exist in the form of  $VO_3^-$  and  $VO_2^+$



In this case, the current is maintained by the migration of vanadium ions and protons across the membrane separator. While it is normally the change in the oxidation state of vanadium on either side of the membrane that stores and releases charge, there is a change in the pH of the solution over the course of a charge and discharge cycle. While crossover of the different oxidation states of vanadium comprises an efficiency loss, the proper forms can be regenerated electrochemically, which eases the stringency of maintenance requirements.

While exploratory research on vanadium as a redox couple began at NASA [8], the all-vanadium redox battery (VRB) was invented and developed by Maria Skyllas-Kazacos and her co-workers at the University of New South Wales [16, 25, 26]. Research has continued on this technology since that time. As a promising technology for storing intermittent renewable energy, VRB systems have received perhaps the most attention of all RFBs [36, 27-39]. In fact, prototypes up to the range of MW in power and MWh in energy-storage capacity have been demonstrated [3, 35, 40-47]. Figure 5 shows the 5-10 kW VRB stack developed by Skyllas-Kazacos group along with its general efficiencies.

stack developed by Skyllas-Kazacos group along with its general efficiencies.

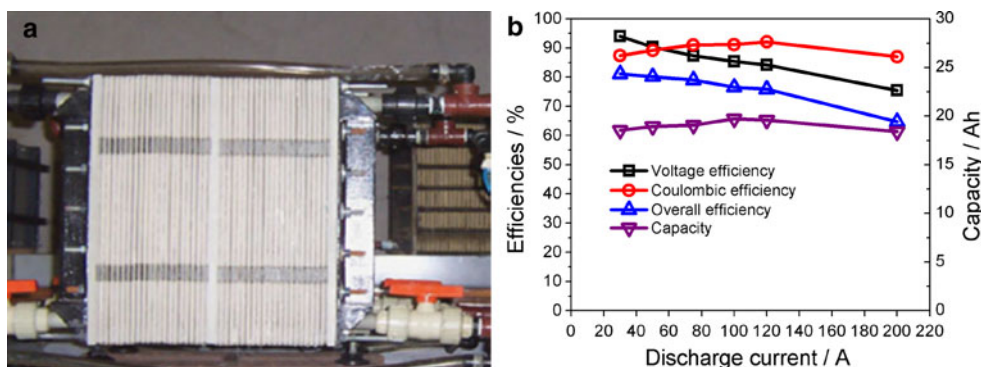
While energy density is not necessarily a primary concern for stationary, grid applications, nonetheless, the VRB energy density is limited by the solubility of vanadium in (typically air) and produces electricity and water. For a fuel

2.1.4 Vanadium/bromine  
 Because there are limits to how much vanadium can be stored in solution in the VRB system, some of the same V(III) redox couple at the negative electrode and these researchers who pioneered the work on the VRB cell noted V(IV)/V(V) redox couple at the positive electrode, generally identified to exist in the form of  $VO_3^-$  and  $VO_2^+$  of halide ions. In this case, during charging the bromide ions in the positive half-cell undergo oxidation to what is assumed to be the polyhalide ion  $2Br^-$ ; the formal potential of this couple is about 1.3 V more positive than the V(II)/V(III) couple [48, 50, 51]. The researchers were able to show significantly higher solubilities in this system:

vanadium-bromine solutions with nearly twice the solubility on a molar basis relative to vanadium sulfate solutions were demonstrated. The higher solubility of vanadium bromine results in higher energy densities (35-70 Wh/L) compared to the VRB systems (25-35 Wh/L). However, the potential concern of vanadium/bromine redox systems is toxic bromine-vapor emissions during operation, and thus Skyllas-Kazacos also used bromine complexing agents including tetrabutylammonium bromide, N-methyl-N-ethyl morpholinium bromide, and N-methyl-N-ethyl pyrrolidinium bromide to decrease or eliminate bromine-vapor emissions during operation [38]. Shown in Fig. 6 is a typical series of charge-discharge curves using a charge-discharge current density of 20 mA/cm<sup>2</sup> [48]. Generally, the coulombic efficiency increases with increasing current density due to lower self-discharge through the membrane; however, it decreases as temperature increases due to more rapid diffusion of vanadium and polybromide ions through the membrane.

2.1.5 Hydrogen-based systems

Fig. 5 a 5-10 kW VRB stack. b Stack efficiencies and capacity versus stack discharge current. Adapted from Ref. [48] with permission





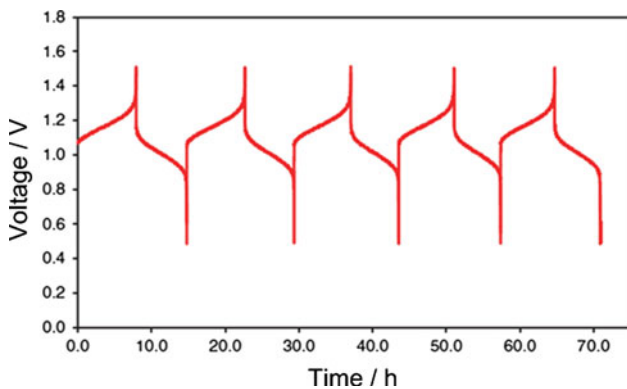


Fig. 6 A series of charge-discharge curves for vanadium-bromine redox cells using 2.5 M vanadium bromide electrolyte with the charge-discharge current density  $20 \text{ mA cm}^{-2}$  and  $T = 30 \text{ C}$ . Adapted from Ref. [48] with permission. These curves do not correspond to the same stack operating conditions as shown in Fig.

to, or removed from, the electrochemical cell without disassembling the cell structure, but which do not store all of the active material in a liquid or gaseous form per se. As such, we might consider them semi-flow cells with electrochemical reactions that are more complicated than simply shuttling between the oxidation states of a single species.

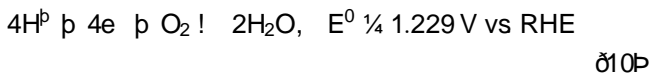
2.1.6.1 Zinc/bromine The prototypical hybrid or semi-flow RFB is the zinc/bromine system [60]. In this system, electrolyte solutions containing the reactive species are stored in external tanks and circulated through each cell in the stack, but the zinc reaction does not only involve dissolved species in the aqueous phase. At the positive electrode, bromide ions are transformed to bromine and back, see Eq. 11. It is important to note that the bromide ions can combine with bromine molecules to generate the tribromide ion [61]



cell, hydrogen oxidizes at the anode according to the reaction



and, at the cathode, oxygen is reduced

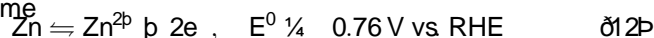


which occurs primarily in liquid bromine. In this system, relatively high concentrations of  $\text{Br}_2$  and  $\text{Br}_3^-$  can be utilized, enhancing both reaction kinetics and energy density. The toxicity of  $\text{Br}_2$  and the highly complexing/corrosive character of concentrated  $\text{HBr}$  are limitations however. The toxicity of  $\text{Br}_2$  can be mitigated by the use of complexing agents [62], but the effect of complexing agents on kinetics has not been studied quantitatively, particularly in strongly acidic supporting electrolyte.

If one were to design a system where the fuel cell acts in both the charge and discharge directions (i.e., a reversible or regenerative fuel cell), then a RFB system would exist.

Such a RFB system has been examined both with the same and different stacks for charge and discharge [55]. This system is inherently different from the RFBs discussed above since the reactants are in the gas and not liquid phase, which enhances mass transfer at the expense of a storage tank volume, and thus hydrogen compression and novel hydrogen-storage materials are needed. Although mass transfer is typically rapid, the oxygen reactions are known to be very sluggish and result in very large overpotentials [66], thereby rendering the overall efficiency of the system to be relatively low. To enhance as well as drive down the cost of the hydrogen/oxygen system, strategies including looking at alkaline media, high temperatures, and closed systems with oxygen and not air. Also, because of the difficulty associated with finding robust and effective oxygen reduction/evolution catalysts, different oxidants have been examined including bromine and chlorine, both of which react rapidly on carbon surfaces [59].

At the negative electrode, zinc metal is dissolved and redeposited,



To prevent self-discharge by combination of zinc and bromine, separate flowing streams of aqueous zinc bromide and bromine circulate in separate loops, separated by an OEM or a microporous PIm [63]. The metal negative electrode allows for a compact electrode, thus increasing the energy density. In addition, the zinc/bromine system has a high cell voltage, good efficiency, and expectations of low material costs. However, the demonstration of zinc/bromine has been limited due to material corrosion, dendrite formation and electrical shorting, high self-discharge rates, low energy efficiencies, and short cycle life. RedFlow Ltd. successfully demonstrated a zinc/bromine RFB unit up to MW size with an energy efficiency of nearly 74% in Australia [64]. The cell architecture was designed to optimize plating and deplating efficiency of zinc during charging and discharging operations. Derivatives of the zinc/bromine system include other halogens such as zinc/chlorine, which typically have similar performance and issues [65].

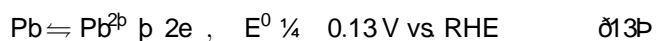
### 2.1.6 Hybrid redox-flow batteries

There are other battery configurations that share a development heritage and some common issues with what we would classify as RFBs in that the active material can be introduced

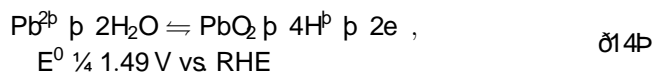
to a battery has also been considered [6]. The charge-transfer

2.1.6.2 Soluble lead acid A soluble form of the lead-acid battery has also been considered [6]. The charge-transfer

reactions as written are the same as in a traditional sealed-lead-acid battery configuration. Lead-acid batteries do not shuttle the same ion between the negative and positive electrode; that is,  $Pb$  is introduced and removed from solution at the negative electrode as lead is dissolved and plated,

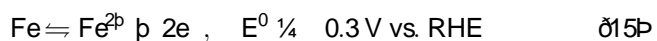


but at the positive electrode, lead ions combine with water to produce lead dioxide and protons,



As lead ions are produced in the oxidation step at the negative electrode and produced in the reduction step at the positive electrode on discharge, there is not a risk of crossover lowering the overall efficiency of the system. As long as the solid forms of lead and lead dioxide are maintained at the negative and positive electrodes, circulation of electrolyte can maintain the open-circuit potential of the battery and allow greater specific cell performance than with sealed or flooded lead-acid cells, assuming minimal weight and volume of the external storage tank. As with other semi-solid flow configurations, there are risks associated with maintaining the morphology of the solid phase as material can detach or grow across the separator gap to cause short-circuit problems.

**2.1.6.3 All iron** Similar to the all-vanadium RFB, the all-iron system [66, 67] involves only a single element, where on one electrode iron(II) goes to iron(III), and on the other plating of iron occurs

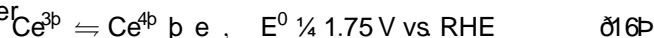


Due to the single species, crossover is not as much a concern although it is still a current inefficiency. This system yielded an open-circuit potential of 2.6 V, with system has some of the same issues as the other hybrid batteries including getting uniform plating of the metal, thereby necessitating precise pH control and supporting electrolyte; however, iron does not have the extensive dendrite problems of zinc. The benefits of the cell are also that the materials are nonhazardous and inexpensive. These are balanced by the fact that the overall cell voltage is relatively low and hydrogen generation can occur, although iron is a poor hydrogen-evolution catalyst.

### 2.1.7 Non-aqueous redox-flow batteries

The use of non-aqueous electrolytes in RFB configurations has been considered because of the higher cell potentials that are possible when one is not concerned by the breakdown of the aqueous electrolyte. In addition, many couples and reactants are much more soluble in non-aqueous

solvents. However, the challenges of low electrolyte conductivities, stability, and cost limit the development of non-aqueous RFB systems. As an example, the zinc/cerium cell has been worked on by Plurion Limited. As with the zinc/bromine cell, the negative electrode dissolves and plates zinc, and at the positive electrode, cerium is shuttled between Ce(III) and Ce(IV)



The developers claim a cell potential of approximately 2.5 V on charging, but it drops below 2 V during discharge with an energy density of 37.5 to 120 Wh/L [68, 69].

The high operating potential window is achieved by using methane sulfonic acid rather than pure water as the solvent, thus minimizing decomposition of water into hydrogen and oxygen, as well as aiding in zinc plating. The redox reaction of Ce(III)/Ce(IV) is kinetically slow and Ce(III) has a somewhat low diffusivity [70, 71]. High acid strength facilitates the solubility of Ce(IV); however, the solubility of Ce(III) decreases at higher acid concentrations. Other electrochemical couples including zinc/chlorine [72], zinc/ferricyanide [69], and vanadium/cerium [73] have been considered. While non-aqueous electrolytes generally imply higher costs than aqueous electrolytes and must be vetted for environmental and chemical compatibility, the expansion of the operating potential window is attractive, as the cell potential difference has a direct impact on the amount of power that can be delivered for a specified current density.

Other examples of nonaqueous RFBs include that of Matsuda et al. [74] who demonstrated a redox system based on  $[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^{3+}$  (bpy is bipyridine) as the anolyte and  $[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^{3+}$  as the catholyte in acetonitrile (CH<sub>3</sub>CN) with tetraethylammonium tetrafluoroborate (TEABF<sub>4</sub>) as the supporting electrolyte. This system yielded an open-circuit potential of 2.6 V, with an energy efficiency of 40%. Chakrabarti et al. evaluated a redox system based on a ruthenium acetylacetonate, obtaining a cell potential of 1.77 V [75]. Yamamura et al. [76] studied a non-aqueous system which used various uranium beta-diketonates with the cell potentials of about 1 V. Recently, Thompson and co-workers demonstrated a redox-flow system using  $M(acac)_3$  ( $M = V, Cr$  or  $Mn$ , and  $acac$  is acetylacetonate) with at least three different oxidation states [77, 79]. The vanadium and chromium acetylacetonate systems showed higher open-circuit potentials, 2.2 and 3.4 V, respectively, compared to around 1.26 V for the aqueous VRB system. However, crossover and ohmic losses due to the large distances between positive and negative electrodes limited the coulombic efficiency. Although the  $Mn(acac)_3$  system shows a lower open-circuit potential (1.1 V) than that of  $V(acac)_3$  and VRB, it exhibits better reversibility both for  $Mn(II)/Mn(III)$  and

Mn(III)/Mn(IV) redox couples, with a coulombic efficiency approaching 97% in a static H-type cell. Shinkle et al. studied the degradation mechanisms in the non-aqueous V(acac)<sub>3</sub> redox systems [80], and showed that environmental oxygen and water are associated with side reactions that affect the long-term charge/discharge response of the battery.

### 2.1.8 Other configurations

There is recent interest in the development of the lithium-air battery, which operates with a static lithium negative electrode, as might be found in a lithium-ion or lithium-polymer battery. Lithium ions combine with oxygen from air to form lithium oxide at the positive electrode on discharge; oxygen is regenerated during charging. Kraatz et al. and Ein-Eli provide an overview of the technology [91]. There are many challenges with such a battery system, such as ensuring proper isolation of the negative electrode from oxygen and water crossover and ensuring an electrode structure that provides for facile oxygen transport and reversible oxide formation and stripping. However, the promise for high energy density and low material costs suggest tremendous research opportunities.

Another recent flow-cell concept was invented by Yet-Ming Chiang's group at MIT and described by Duduković et al. [82, 83]. They proposed using typical intercalation and electrode materials as active materials for a lithium-sulfur rechargeable battery, but providing the active material in a slurry that can be mechanically pumped into and out of a reaction chamber. In the paper describing the concept, they note that they will be able to store much higher concentrations of active material in the solid component of the slurry than can be stored as ions dissolved in electrolyte (up to 24 M), thereby increasing the energy density well beyond what could be achieved in traditional RFBs.

### 3 Kinetics of redox reactions

The study of the kinetics of redox reactions occupies a central place in fundamental electrochemistry. Most important concepts in the theory of electrode reactions were developed from the consideration of redox reactions. The simplest form of a redox reaction is a one-electron transfer of an electron to or from an electrode to an ion in solution, written generally as



where O is the oxidized state and R the reduced state of the ion. In the simplest type of redox reaction, there are no changes in the ion other than the valence state and relaxation of the solvent around the ion. The prototypical example of such a reaction is the ferrous/ferric reaction

solutions of sulfuric acid (meticulously free of chloride ion, as discussed in more detail below). The reactions become more complex, and the theory more involved, when the anions are complexed with neutral or other anions that do not participate in the electron transfer directly (i.e., it does not change valence or state of charge), but are part of the relaxation of solvating ligands or assist the transfer of the electron from the electrode surface, termed mediated electron transfer. Ferri-/ferrocyanide and ferric/ferrous would be examples, respectively, of such redox couples. There are also reactions involving multi-atom ions and reactions where one state is a neutral molecule that are termed redox reactions. There are no hard criteria for what is or is not a redox reaction, but a common feature is that it involves electron transfer that is at least measurably reversible. For the purposes here, we will discuss only the more well-studied reactions that have some promise as RFB couples as mentioned above.

Most of the fundamental principles for the kinetics of electron transfer can be found in two classic texts in electrochemistry, and those form the basis of the principles reviewed here. The first is the text by Vetter [84], which contains an interesting and unique description of the history of the development of the fundamental theory of electrode kinetics, including the familiar names of Butler-Volmer, but less recognized (in this context) names such as Gurney, Erdey-Gruz and Vetter himself. This text also reviews experimental results for more than 25 redox couples, all from original papers published before ca. 1960, but these references remain in some cases as the best source of quantitative kinetic parameters versus more recent but qualitative (or less rigorous) measurements.

Another important resource is the text by Bard and Faulkner [85], more accessible than the Vetter text, with notation and terminology that is more contemporary. Following the notation in Bard and Faulkner, the Butler-Volmer model of the kinetics of reaction produces the essential current (i) versus overpotential ( $\eta$ ) relationship as

$$i = i_0 \left[ \left( \frac{c_O}{c_R} \right) \exp\left(\frac{aF}{RT} \eta\right) - \left( \frac{c_R}{c_O} \right) \exp\left(-\frac{aF}{RT} \eta\right) \right] \tag{18}$$

where  $\eta$  is the overpotential, defined as the difference between the electrode potential under current flow and the rest (zero current) potential

$$\eta = \Phi_k - \Phi_p - E_{eq} \tag{19}$$

where  $\Phi_k$  is the potential in phase k, and  $E_{eq}$  is the Nernst potential, which is related to the concentrations of the oxidized ( $c_O$ ) and reduced ( $c_R$ ) species by

$$E_{eq} \approx E^0 + \frac{RT}{F} \ln \left( \frac{C_O}{C_R} \right)$$

Eq. 20

where  $i_0$  is the exchange current density,  $\alpha$  is the transfer coefficient (or the symmetry factor in transition state theory), and  $R$ ,  $T$  and  $F$  have their usual meaning. This form of the Butler-Volmer equation is important for both fundamental (experimental) kinetic studies and for modeling practical devices, since in both cases one needs to consider the contribution of mass transport of the ions from the bulk solution to the electrode surface.

The essential kinetic parameters determined experimentally are the exchange current density and the transfer coefficient. The exchange current is the magnitude of the partial anodic and cathodic currents which are equal at equilibrium, and are in turn related to the bulk concentrations by the standard rate constant,

$$i_0 \approx F k^0 C_O^{\alpha} C_R^{1-\alpha}$$

Eq. 21

Since the exchange current density varies with the concentration of the redox species, the more fundamental measure of kinetics for redox reactions is the kinetic parameter  $i_0$  is an important quantity to confirm experimentally. The transfer coefficient is usually measured from the slope of  $\log i$  vs.  $\eta$  in the so-called Tafel region, where the back-reaction is negligible and the relationship between overpotential and current density reduces to

$$i \approx i_0 \left( \frac{C_O}{C_R} \right)^{\alpha} \exp \left( \frac{\alpha n F}{RT} \eta \right)$$

Eq. 22

and the experimental current is either obtained under conditions where  $C_O \approx C_R$  or accurate mathematical correction can be made to the experimental value, for example, the solution of the convective-diffusion equation for the rotating-disk electrode [85]. Likewise, the value of  $i_0$  can be obtained by extrapolation of the Tafel plot to  $\eta = 0$ . However, for fast kinetics, or where a second electrochemical reaction (e.g. hydrogen or oxygen evolution), occurs near the equilibrium potential, a linear Tafel plot may not be obtained and neither  $i_0$  nor  $\alpha$  may be obtained by this method. There are a number of other methods that may be used to obtain  $i_0$  indirectly. In those cases, the concentration dependence of the exchange current density may be used to obtain

Following the pioneering theoretical framework introduced by Gerischer [86], modern quantum chemical theory of redox kinetics at electrode surfaces has focused on the distance of the redox ion from the electrode surface [87]. Modern theory typically distinguishes redox reactions as either "inner-sphere" or "outer-sphere", the latter referring to reactions where the redox ion is "inside" the plane of the inner Helmholtz ionic layer and the former "outside" [88].

Practically, this distinction is important in that inner-sphere reactions typically have a very large dependence of the reaction kinetics on the electrode material, in many cases by orders of magnitude; the hydrogen electrode is perhaps the most dramatic in this respect. For outer-sphere reactions, the kinetic effect of different electrode materials is much less, but not insignificant. However, this distinction in electrode-material dependence is not essential, and there are examples where inner-sphere reactions have a relatively small dependence on the electrode material, e.g. the  $Br_2/Br^-$  reaction. The detailed discussion of the effect of electrode materials on the kinetics is beyond the scope of this review.

One can estimate the rough order of magnitude that the kinetic rate must be for a practical RFB. For example, using some of the metrics in Table 1 (i.e., a RFB must have high electrical efficiency, e.g. at least 80% round-trip, or 90% in each direction) and assuming a typical cell voltage of 1.5 V, then the kinetic overpotential must be less than 150 mV throughout the charge/discharge cycle. Assuming a minimum practical current density of at least 50 mA/cm<sup>2</sup> (a roughness factor of 10, i.e. 10 cm<sup>2</sup> surface per unit electrode geometric area, and a transfer coefficient of 0.5, the exchange current density must be greater than 0.3 mA/cm<sup>2</sup> (real) throughout the charge/discharge cycle. Assuming 1 M solutions at 50% state of charge, and assuming 90% utilization of the redox ions in the cycle, the minimum value of the standard rate constant is ca. 10<sup>5</sup> cm/s. If the rate constant is significantly less than this value, some compromises must be made to achieve a practical device which may increase cost and/or utility. For example, higher surface area/porosity electrodes will compromise a simple flow-by/through design. Reduced current density will reduce power density and result in larger electrodes and more material per unit volume in the RFB. The estimated value above can be compared to those in literature as shown in Table 2.

The results in Table 2 show that of all the redox couples recently or currently in use in practical RFBs, only the  $VO^{2+}/VO_2^+$  couple has a clear kinetic limitation and, in fact, is clearly problematic. This is not surprising since this redox is not a simple one-electron transfer reaction, but is in modern terminology an oxygen transfer reaction as shown in Eq. 8. As discussed in detail recently by Gattrell et al. [91], this reaction is a multi-step reaction in which oxygen transfer (a chemical step) may precede or follow an electron-transfer step, denoted in modern terminology as a CE or EC mechanism. Such reactions usually have current-potential relations which differ significantly from the ideal Butler-Volmer form, and that is the case here. The kinetic data from Gattrell et al. were obtained using a graphite RDE, which should be directly applicable to practical cells which use carbon-felt electrodes. Although the quantitative data

Table 2 Kinetic parameters for redox reactions used in flow batteries

Redox couple	$\alpha$	$k_0$ (cm/s)	Electrode	Reference
$\text{Fe}^{3+}/\text{Fe}^{2+}$	0.59	$2.29 \cdot 10^{-5}$	Au(poly)	[89]
	0.55	$1.29 \cdot 10^{-5}$	Au(111)	[62]
$\text{Cr}^{3+}/\text{Cr}^{2+}$	$\sim 0.5$	$29 \cdot 10^{-4}$	Hg	[90]
$\text{VO}_2^+/\text{VO}^{2+}$	0.42	$3.09 \cdot 10^{-7}$	Graphite	[91]
	0.3	$1.09 \cdot 10^{-6}$	Carbon	[92]
$\text{V}^{3+}/\text{V}^{2+}$	$\sim 0.5$	$49 \cdot 10^{-3}$	Hg	[90]
$\text{Ce}^{4+}/\text{Ce}^{3+}$	$\sim 0.5$	$1.69 \cdot 10^{-3}$	Pt	[84]
$\text{Br}_2/\text{Br}^-$	0.35	$1.79 \cdot 10^{-2}$	Pt(poly)	[93]
	0.46	$5.89 \cdot 10^{-4}$	Vitreous carbon	[94]

Supporting electrolyte in most cases is 1 M  $\text{H}_2\text{SO}_4$  or  $\text{HClO}_4$ ; concentration of redox species is  $10^{-3}$  to  $10^{-2}$  M

in Table 2 was obtained using a Hg electrode, the presence of even trace amounts of chloride ion enhances the experimental rate of electron transfer by at least two orders of magnitude, probably by a mediated or bridging transfer of the electron via adsorbed chloride anions. While the dependence of the  $\text{VO}_2^+/\text{VO}^{2+}$  couple on electrode material has not been proven conclusively that the chloride effect is exclusive to Pt and Au, theoretical considerations and co-workers [92] reported somewhat larger exchange-current densities for less well-characterized carbon-based electrodes than Gattrell et al. and suggested it is possible to enhance kinetics by surface treatment of carbon-based electrodes.

The dependence of the  $\text{VO}_2^+/\text{VO}^{2+}$  couple on electrode material has not been very well-studied. Skyllas-Kazacos and co-workers [92] reported somewhat larger exchange-current densities for less well-characterized carbon-based electrodes than Gattrell et al. and suggested it is possible to enhance kinetics by surface treatment of carbon-based electrodes. Zhong et al. fabricated conducting polyethylene (PE) composite electrodes with low resistivities by mixing PE with conducting fillers (carbon black, graphite and Pber) [92]. The chemical treatment of graphite based composite polymer electrodes with chromic acid was shown to enhance the surface reactivity for the electrode reactions. Carbon-polypropylene (PP) composite electrodes modified with rubber showed better mechanical properties, better impermeability and better overall conductivity compared to the PE composite electrodes [95]. A voltage efficiency as high as 91% was obtained for the VRB with the carbon-PP composite electrodes. Graphene oxide nanoplatelets (GONPs) demonstrated a more favorable electrocatalytic activity for V(V)/V(IV) and V(III)/V(II) redox couples than pristine graphite for the VRBs. It is found that the V(III)/V(II) redox reaction strongly depends on the formation of surface active functional groups of  $\text{C}=\text{OH}$  and  $\text{COOH}$  [96]. However, it is not clear that using an electrode material other than graphite/carbon would be cost effective.

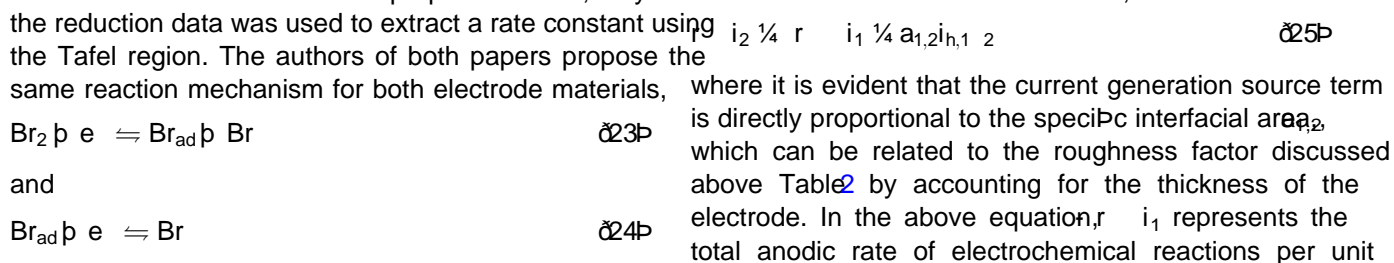
In contemporary studies of heterogeneous electron transfer reactions, the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  reaction is still considered to be the prototypical outer-sphere reaction amenable to quantitative quantum chemical treatment using modern ab initio methods. The data shown in Table 2 are relatively recent measurements using sulfuric-acid solutions purified specifically of chloride ion (to ppb levels). Following the pioneering work by Nagy et al. [97], it is now widely recognized that with Pt and Au electrodes, of dissociating the  $\text{Br}_2$  molecule to form an adsorbed state

Like the  $\text{VO}_2^+/\text{VO}^{2+}$  couple, the  $\text{Br}_2/\text{Br}^-$  is a multi-step reaction with at least one chemical step, that of breaking/making the  $\text{Br}-\text{Br}$  bond, either preceding or following electron transfer. The chemical step is, however, much simpler than the oxygen transfer step in the  $\text{VO}_2^+/\text{VO}^{2+}$  reaction. The kinetics of this reaction are not nearly as dependent on electrode material as, for example, the hydrogen electrode, to which it is mechanistically similar [84]. The data for Pt and vitreous carbon shown in Table 2 illustrate this fact well, with the difference in rate constant being only a factor 30, whereas for the hydrogen electrode the difference would be several orders of magnitude. The reason for this difference can be explained rather easily qualitatively by considering the bond energies involved in the possible/probable chemical steps, for example, that of dissociating the  $\text{Br}_2$  molecule to form an adsorbed state

of Br, analogous to the Tafel step in the hydrogen electrocatalysis, chemical stability and durability in the reaction environment. Carbon and graphite materials meet both these requirements, though metal foams and meshes are also candidates [105, 106]. The search for improved electroactive materials for RFBs will no doubt continue to be actively pursued.

Similar considerations apply in the anodic direction, where the proton is much more strongly solvated than the bromide ion (by about a factor of 10 [99]),

meaning much weaker chemical interaction with the electrode. The above kinetic constants and equations (e.g., (18)) are for rates per unit catalyst area. As mentioned, one way to compensate for a slower reaction is to increase the roughness factor or catalyst surface area per unit geometric area. For example, ignoring double-layer charging and assuming electroneutrality, one can write a current balance Butler-Volmer relation. For the purposes of Table 2, only the reduction data was used to extract a rate constant using the Tafel region. The authors of both papers propose the same reaction mechanism for both electrode materials,



The first step above is not an elementary step, and electron transfer must either precede or follow dissociation. From the energetic considerations above, it seems reasonable to suggest that on carbon electrodes the electron transfer precedes dissociation, consistent with relatively weak adsorption of  $\text{Br}_2$  on this surface. In many ways, the  $\text{Br}_2/\text{Br}^-$  couple is the ideal redox electrode for RFBs. The reaction is relatively facile, and the kinetics are not strongly dependent on electrode material, such that carbon and graphite electrodes provide reasonable performance, as demonstrated in zinc/bromine RFBs [60]. This material flexibility is a significant advantage in practical electrode design.

Before examining surface-area effects, a mention should be made about typical RFB electrode materials. As noted above, graphitic or vitreous carbon materials are widely used in RFBs [7, 28, 30, 100], such as graphite, carbon felt, carbon fiber, thermal and acid treated graphite, carbon polymer composite materials, carbon nanotubes, Ir-modified carbon felt and graphene-oxide nanoplatelets. In general, RFB couples are chosen for the facile kinetics and highly active catalytic materials are not necessary. Nonetheless, it has been found that various surface treatments can lead to improved reaction kinetics on carbon electrodes. Chemical etching [101], thermal treatment [102], chemical doping [11], carbon nanotube addition [103], and addition of metallic catalyst sites to the carbon fiber [104] have all been attempted. Aside from catalytic activity, the main criteria for electrode materials are electrical

$$a_{1,2} \approx \frac{4\delta l}{d_f} \frac{e\rho}{d_f} \quad (26)$$

Figure 7 shows the variation of total surface area as a function of fiber diameter for an 80% porous material.

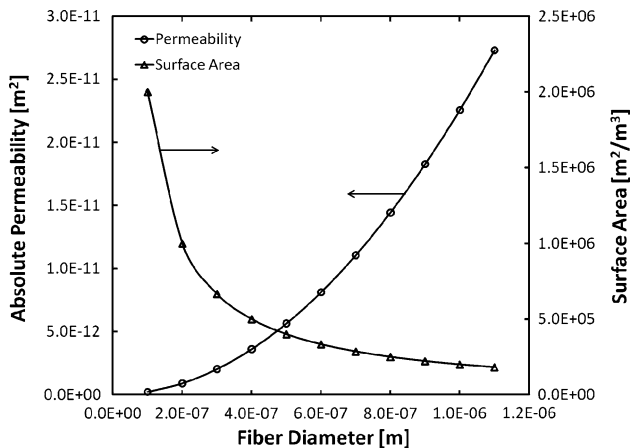


Fig. 7 Permeability and surface area of a porous material with a porosity of 0.8 as a function of fiber diameter. Permeability was calculated using the Carman-Kozeny model and surface area was estimated using the Plament analogue model

The actual surface area in a real fiber bed may be less than this value since fibers contact and overlap each other, or more if the fibers are not truly cylindrical but rough or ridged. In terms of a roughness factor, using a typical fiber properties and a thickness of a few millimeters, a value of around 50 is obtained. Also shown in Fig. 7 is the absolute-permeability change expected as calculated from the Carman-Kozeny equation [108], which has been shown to adequately describe the variation of permeability with porosity due to compression in porous materials [139] and is assumed to apply here.

Clearly, the fiber diameter dramatically impacts both aspects and unfortunately in opposing directions. Increasing the fiber diameter from 10 to 100 μm improves the permeability by a factor of 100, but reduces the surface area by a factor of 10. The same general trend would be true for other random electrodes such as particulate beds. Efforts to increase active surface area in a flowing electrolyte by using particles with microporosity have been reported [8], but, not surprisingly, this additional surface area does not contribute significantly to the electrochemically active area since such internal surfaces are highly diffusion limited. Attempts to increase the roughness of the electrode surface could be beneficial, but typically it is more profitable to modify the surface for increased kinetic or catalytic behavior rather than just surface area.

Another aspect of the active solid surface area that must be considered is the intimacy of the solid/electrolyte contact [18, 36]. Carbon and graphite materials have a neutral wettability to water [110] which prevents the spreading of electrolyte over the electrode surface. The trapped air pockets resulting from incomplete wetting reduce the electroactive surface area owing to the Cassie-Baxter effect. Such incomplete wetting would be exacerbated

on roughened surfaces. Sun and Skyllas-Kazacos found that certain electrode pretreatments intended to improve catalytic activity also lead to somewhat improved wettability behavior [36]. Litster et al. [111] report that briefly heating carbon fiber materials at 300 °C in an air environment rendered them fully hydrophilic, and Yan et al. [112] review various treatment procedures for altering carbon wettability. The presence of a gas phase at the solid/electrolyte interface could be due to residual air trapped during initial flooding of the electrode, or could appear due to evolution of gases such as the parasitic evolution of hydrogen and/or oxygen [8, 113].

#### 4 Transport phenomena

There are various mechanisms of transport that occur within a RFB. Typically, electron flow is not limiting due to the use of conductive additives or just carbon materials.

This transport is adequately described by Ohm's law,

$$j = \sigma \nabla \phi$$

where  $\sigma$  is the electronic conductivity. The other major transport issue is that of the reactants and products. Typically, this can be separated into two different regions, namely, that of the electrode and that of the membrane or separator. These two regions often have different properties; their transport species and mechanisms are discussed in turn below. For the electrolyte in the electrodes, diffusion is often the most important process while conduction

is for the membrane. Table 3 shows a summary of the charge-carrying species across the membrane, open circuit potential, and diffusivities of active ions. While dilute-solution theory does not necessarily strictly apply in the electrolyte systems of interest, diffusivities of the ions give a good indication of the relative motions of the relevant ions. Cation-exchange membranes (mainly  $\text{H}^+$  and  $\text{Na}^+$ ) are widely used in the aqueous RFBs due to their high ionic conductivity. Anion exchange membranes are used in many non-aqueous systems to be compatible with the supporting electrolytes used and suppress unwanted crossover. Generally, the open-circuit potential of an aqueous system is constrained to be lower due to the low electrochemical stability window of  $\text{H}_2\text{O}$  compared to that of non-aqueous RFBs, in which organic solvents (such as acetone) with a higher electrochemical stability voltage window are used. The diffusivities of active species in all systems listed in Table 3 are in the range of 1.6 to  $12.9 \times 10^{-6} \text{ cm}^2/\text{s}$  except for V(IV) ( $17709 \times 10^{-6} \text{ cm}^2/\text{s}$  in 6.4 M HBr and 2 M HCl). Finally, while there are some other, less critical issues such as thermal management and heat transport within the cell, such a discussion is beyond the scope of this review.

Table 3 Summary of different thermodynamic and transport parameters for various RFBs

RFB	Membrane charge carrier	Open-circuit potential (V)	Diffusivity, D (10 <sup>-6</sup> cm <sup>2</sup> /s)	Reference
All vanadium	H <sup>+</sup>	1.26	VCl <sub>3</sub> ? H <sub>2</sub> SO <sub>4</sub> /Na <sub>2</sub> SO <sub>4</sub> , glassy carbon electrode	1.50 (pH= 4.0) [29]
				1.34 (pH= 2.0)
Vanadium/bromine	H <sup>+</sup>	1.1	V <sub>2</sub> O <sub>5</sub> ? 1.8 M H <sub>2</sub> SO <sub>4</sub> /Na <sub>2</sub> SO <sub>4</sub> , glassy carbon electrode	1.16 (pH= 1.0)
				1.41 (pH= 0.0)
Iron/chromium	Cl <sup>-</sup> /H <sup>+</sup>	0.77	V(IV) ? 6.4 M HBr, 2 M HCl solution	5.7 [29]
			Fe(III)	1770 [50]
Zinc/bromine	H <sup>+</sup>	1.85	Cr(III)	6 [19]
			Zn <sup>2+</sup>	6
Zinc/cerium	H <sup>+</sup>	2.2	Ce(III) ion in methanesulfonic acid	7.54 [58]
				0.27
Bromine/polysulphide	Na <sup>+</sup>	1.54	Br <sup>-</sup>	0.72 [117]
			Br <sub>3</sub> <sup>-</sup>	12 [22]
			S <sub>2</sub> <sup>2-</sup>	5
			S <sub>4</sub> <sup>2-</sup>	6
Fe(III)/Fe(II) triethanolamine/bromine	Na <sup>+</sup>	1.0	N/A	5
Non-aqueous vanadium acetylacetonate	BF <sub>4</sub> <sup>-</sup>	2.2	V(acac) <sub>3</sub>	1.63 [64]
				1.8
				2.9 [66]

4.1 Electrolyte flow

$$D_i \approx \frac{1}{4} RT u_i$$

30

Within the electrode, the flux of the various species can be described using the Nernst-Planck equation assuming that dilute-solution theory holds [14]

$$N_i = -\frac{1}{4} z_i u_i F \nabla c_i + D_i \nabla c_i - c_i v$$

28

The first term in the expression is a migration term, representing the motion of charged species that results from a potential gradient. The migration flux is related to the potential gradient  $-\nabla \Phi$  by a charge number,  $z_i$ , concentration,  $c_i$ , and mobility,  $u_i$ . The second term relates the diffusive flux to the concentration gradient. The final term is a convective term and represents the motion of the species as the bulk motion of the solvent carries it along. For noncharged reactants and products (e.g. H<sub>2</sub>O), the same equation can be used with the migration term set to zero, resulting in the equation of convective diffusion [15]. Dilute-solution theory considers only the interactions between each dissolved species and the solvent, and thus one can consider the conductivity of the solution to be given by

$$\kappa = \frac{1}{4} F^2 \sum_i z_i^2 c_i u_i$$

29

The motion of each charged species is described by its transport properties, namely, the mobility and the diffusion coefficient. These transport properties can be related to one another at infinite dilution via the Nernst-Einstein equation [114, 116, 117]

For more complicated systems than binary electrolytes or where the interactions between species are important and/or non-ideal, concentrated-solution theory can be used as discussed by Newman and Thomas-Alyea [4]. In this approach, the transport coefficients of merit include the conductivity of the solution, and the transference numbers and diffusivities of the ions. It should be noted that many RFBs operate at higher concentrations such that concentrated-solution theory may be required; however, the use of supporting electrolytes does mitigate this to a certain extent in that detailed speciation is not required to predict cell performance fairly well.

The total current in the electrolyte can be expressed as

$$i = \frac{1}{4} F \sum_i z_i N_i$$

31

and the ionic conductivity of the electrolyte can be related to the above transport properties [14].

For most RFB applications, the system is one phase (liquid) and so complicated expressions for multiphase flow are unnecessary, in stark contrast to low-temperature fuel cells [118]. Thus, for the convective flow one can use the Navier-Stokes equations [15]

$$\nabla \cdot \tau = \rho \nabla p - \rho \nabla \cdot v$$

32

where  $p$  is the pressure, and  $\eta$  and  $\rho$  are the viscosity and density of the liquid, respectively. Since most RFB



electrodes are porous, the above equation can be extended by using various methodologies such as Brinkman [108, 115, 119], or even replaced by Darcy's law [108]

$$v \propto \frac{k}{\tau} r p$$

Flowing electrolyte through porous electrodes presents a number of challenges, both at the single-cell and full-stack level. At the pore scale within each electrode there will be significant differences in the interstitial flow rate in each pore (owing to size differences, with flow largely confined to the largest pores in the medium). Such pore-scale-channeling behavior provides convective mass transport at a limited number of surfaces, while dead zones of relatively stagnant flow and localized limiting currents would exist elsewhere throughout the electrode. Fibrous materials are the favored porous-electrode substrate for several reasons because high porosity can be achieved while still maintaining electrical conductivity and percolation in the solid phase due to bridging between long fibers. As discussed above, high porosity is advantageous since (a) there is a strong positive correlation between porosity and permeability, thereby resulting in reduced pressure drop and associated pumping costs; and (b) the effective ionic conductivity of the electrolyte is directly proportional to porosity and inversely proportional to tortuosity which tends to increase with decreasing porosity [113].

Due to the wide spread use of porous electrodes for various applications, a number of studies have looked at mass transfer in carbon-fiber electrodes [121, 124]. Schmal et al. [6] compared mass transfer at single fibers to fiber assemblies (bundles and felts) and found that per unit length of fiber the mass transfer to a single fiber was significantly higher. This was attributed to channeling within the fiber assemblies causing dead-zones or stagnant regions, effectively reducing the active area for reaction. A porous material with very uniform pore-size distribution would help alleviate this problem, but such materials may be impractical. Saleh [25] studied the effectiveness factor in packed bed electrodes and found that ohmic resistance which is a combination of fluid properties and bed geometry, also played a key role in determining the extent to which the porous electrode was utilized.

Another cell-scale issue arising from the convective flow in porous electrodes is large scale heterogeneities due to assembly tolerances or uneven thermal expansion, which could lead to bypassing of large sections of a cell. Moreover flow through porous electrodes presents major manifold issues at the stack-scale since each cell must have nearly identical permeability. This would be difficult to achieve since stacks may be compressed significantly when assembled. This situation is analogous to interdigitated flow fields proposed for low-temperature fuel cells, which showed very

promising performance results in single-cell tests, but the inevitable differences in permeability from cell to cell in a stack created uneven flow distribution among cells [126].

To enhance flow and electrolyte utilization during deep discharge where high flow rates are required, physical barriers or roughened electrode materials can be used

inside the cell to promote turbulence and mass transport. Lessner et al. designed a flow-through porous electrode for bromine/polysulphide RFBs [24]. To ensure uniform flow distribution and prevent channeling, quartz particles (with diameter of 0.5 to 1.0 mm) were placed 0.5 cm above the inlet. Based on the results, the relationship between dimensionless mass transfer rate (Sherwood number,  $Sh$ ) and Reynolds number ( $Re$ ) for their geometry was obtained

as  $Sh \propto 14.29 Re^{0.348}$  [34]. This functional dependence is in excellent agreement with Sioda [127] and Cano and Bohm [28] findings. Leung et al. also investigated the effect of the mean linear flow velocity of the electrolyte on the cell performance both under constant current charge and discharge [79]. Figure 8 presents the effect of the mean linear flow velocity on the discharge voltage with different constant discharge current densities. It is shown that there is a maximum cell voltage at the mean linear flow velocity of 3.9 cm/s.

4.1.1 Reactant concentration effects

The issue of reactant solubility in the flowing electrolyte solution can be important. The energy density of a RFB system is set by the concentration of dissolved species, but the maximum concentration in any stream is limited by the

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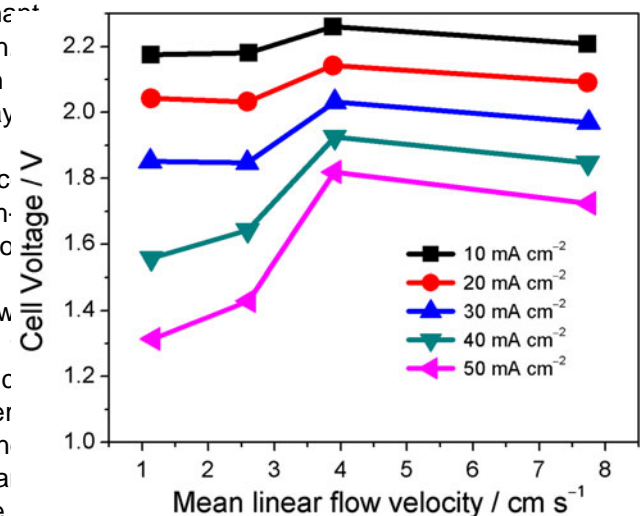


Fig. 8 Effect of the mean linear flow velocity of the electrolyte on the cell voltage of the Zn/Ce RFB. Adapted from Ref. [79] with permission

solubility of the least soluble species. Precipitation of battery configuration in which cells are configured in series, reactants or products in the porous electrode is calamitous, it is intended for all of the current to flow in the electrolytic phase via ionic conduction from one negative electrode to the adjacent positive electrode, and in the process impacts the power density and cell efficiency as well. Lower concentrations mean reduced mass-transfer rates and current density, thus increasing concentration polarization and/or pumping power. Solubility is a function of temperature as well, which must be factored into cell design. For instance, it is observed that at elevated temperature, limiting the operating temperature to the range of 10 to 40 °C [37, 129]. Li et al. improved this situation with the development of a vanadium redox flow battery using a vanadium concentration up to 2.5 M over a temperature range of -5 to 50 °C [46]. However, temperature excursions in an operating cell could cause a precipitation event and lead to cell failure [18].

Other issues regarding concentrations include the fact that for many systems increasing the concentration of the reactants can lead to more complexing and lower diffusivities and perhaps even more viscous solutions. For example, recent data measured at LBNL show that the diffusivity of HBr is increased from 1 to 7 M [30]. Such tradeoffs require optimization for the specific system. Another ubiquitous issue present in flowing reactors of all types concerns the extent of reactant conversion, sometimes referred to as utilization or stoichiometry. The difficulty is determining the optimum reactant concentration at the outlet of the electrode. It is desirable or necessary that the electrode near the outlet is not starved of reactant to preclude parasitic reactions such as gas evolution or electrode corrosion. On the other hand, fully consuming or utilizing the reactants means recovery of the maximum amount of energy stored in the solution. For many systems, the stoichiometry is high for single-cell studies (typically over 10) and it is not clear as to how this can be translated into actual systems where such performance would necessitate multiple passes through the electrodes. One such approach would be to have a cascade of reactors that are tailored to specific operating points and concentrations [131].

Of particular concern in flow batteries is the development of shunt currents via the liquid electrolyte. While shunt currents can develop in the liquid phase in conventional fuel-cell and battery designs [33, 134], the restriction of the primary electrolyte to the region between each pair of current collectors minimizes most obvious paths for current flow, at least in the electrolytic phase. While fuel cells do distribute fluids from one cell to another via the manifold, the effective conductivities of liquid-feed fuels and of most coolants are much lower than the conductivities of RFB electrolytes [8].

Because RFBs involve the circulation of electrolyte to each of the individual cells, there is an obvious ionic current path from one cell to another. The currents that flow in the circulating electrolyte from one cell to another via the electrolyte flow manifolds are best managed by increasing the effective resistance of the flow path, either by increasing the effective path length between cell flow inputs and outputs in the manifold, or by reducing the cross-sectional area of the ports. Unfortunately, increasing the resistance in such a way to minimize shunt currents also works to increase the requirements for parasitic power to circulate the electrolyte through the system; this complicates system design and increases both capital and operating costs. Several researchers have investigated the design implications for flow batteries for particular systems, though optimization will be required for specific electrolyte and cell configurations [35, 137].

#### 4.1.2 Shunt currents

One of the challenges of stack design that must be given particular attention in RFB configurations is protection against shunt currents. Generally speaking, a shunt current refers to a condition in which current deviates from the intended path, via a parallel path with a sufficiently low resistance to divert a portion of the current. In general, the path of least resistance in a cell or stack is designed to follow the direction of intended current flow. In a flow

4.2 Separators

There are two main types of RFB separators. The first is a microporous separator that can allow for exchange of

liquids between the anolyte and catholyte compartments of Henry's law and a transport coefficient such as a permeability. Such an approach is akin to the discussion above concerning a porous region. Because of this ability to mix, microporous separators often lead to higher rates of reactant and product crossover, and thus lower coulombic efficiencies. For this and other reasons, most RFBs use an ionically conducting membrane as a separator.

The IEM is one of the most critical components in RFBs. In terms of transport, the dual and opposing needs to enhance the desired charge transport while limiting undesired crossover of reactant, product, and other species is an unresolved engineering issue. There are a number of IEMs which have been used in RFBs, with the most common one being NaPon, a perfluorosulfonic acid membrane that binds cations to its sulfonic acid sites. NaPon is the membrane of choice in many RFBs due to its high proton and sodium conductivities and its proven stability in chlor-alkali industry. It has a conduction mechanism that includes both hopping and vehicular modalities.

Since most IEMs are single ion conductors (see Table 3), transport within them can often be described using Ohm's law (Eq. 7). If there are other interactions such as electroosmotic flow, this description can be modified; for example, for proton conduction in NaPon the following expression can be used [39, 140]

$$i_2 \approx j r \Phi_2 \frac{jn}{F} r l_0 \tag{35}$$

$$N_0 \approx \frac{jn}{F} r \Phi_2 \left( a + b \frac{jn^2}{F^2} \right) r l_0 \tag{36}$$

where  $n$  is the electroosmotic coefficient,  $j$  is the ionic conductivity,  $l_0$  is the chemical potential of the solvent, and  $a$  is the transport coefficient of the solvent through the membrane. If there are other ions in the solution that penetrate the membrane, it is easiest to describe this motion using a Poisson-Nernst-Planck (PNP) framework where the Nernst-Planck equations are used (Eq. 8) along with Poisson's equation,

$$r^2 \Phi_2 \approx \frac{q}{\epsilon_0} \tag{37}$$

where  $\epsilon_0$  is the permittivity and  $q$  is the charge density. This methodology accounts for non electroneutrality conditions that exist due to the small charged pathways inside the membrane for conduction. In the above PNP treatment, dilute-solution theory is used and if interactions between species and non-dilute behavior is expected, one can use concentrated-solution theory, which complicates the expressions, requires more knowledge of the transport properties, and is beyond the scope of this paper (for example, see Delacourt and coworkers [1, 142]). In terms of reactant and product crossover, the easiest way is to use a permeation coefficient, which is a combination

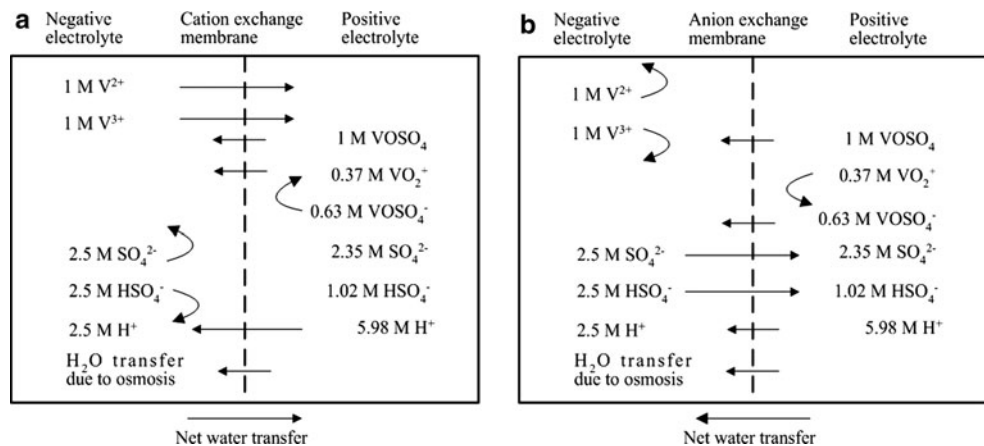
Membrane design should consider the following properties: ion conductivity, ion selectivity, permeability, chemical stability, and mechanical properties. A detailed summary of the recent progress of IEM for VRBs can be found in the review by Li et al. [4] and we use the VRB as the example for discussing IEMs and transport; Table 4 shows some IEMs used for the VRB example case. Skylas-Kazacos et al. used the Amberlite CG 400 composite membrane in the VRBs. The membranes showed a good stability of more than 4000 h. Zhang et al. found that the current efficiency of 94 and 91% are achieved for NaPon115 and 112 membranes used in VRBs, respectively [5]. However, the NaPon membranes suffer from heavy active ion crossover and low ion selectivity. By incorporation of inorganic species (such as SiO<sub>2</sub>, TiO<sub>2</sub>, and ZrP) into NaPon, the crossover of vanadium ions can be effectively reduced [43, 144, 152]. The ion selectivity can be enhanced using the organic/NaPon hybrid membranes fabricated with interfacial polymerization and directly blending methods. Xi et al. prepared NaPon/SiO<sub>2</sub> hybrid membranes using in situ sol-gel method, and showed that the vanadium crossover was effectively reduced due to the polar clusters of the original NaPon [144]. The maximum energy efficiency of the VRB using this membrane was nearly 80% at 20 mA/cm<sup>2</sup>. Luo et al. modified NaPon117 membrane using interfacial polymerization method for VRB application [53]. Sulfonated poly(tetramethyldiphenyl ether ether ketone) (SPEEK) membrane showed one order of magnitude of vanadium ion permeability lower than that of NaPon115 [145]. In the multiple-cycle tests, the SPEEK40 membrane shows high stability and high coulombic efficiency above 98%. Generally, IEMs prepared with interfacial grafting, blend, radiation, non-fluorinated and hybrid membranes show lower ion permeability than that of NaPon membrane. However, when V<sup>5+</sup> crossover is blocked, the protonic conductivity is also decreased which results in relatively low conductivity. So it is still a critical challenge for IEM development that ion selectivity is enhanced with high ionic conductivity. VaPadis and Skylas-Kazacos assessed a range of IEMs in vanadium/bromine RFBs considering ion-exchange capacity, conductivity, vanadium ion diffusion, water content, and chemical stability [6]. In addition to ion transfer, electroosmotic flow can cause the transfer of water from one half cell to the other one during the charge-discharge cycles. The direction and magnitude of the transport is affected by the membrane used. Mohammadi et al. studied the water transfer behavior of anion- and cation-exchange membranes in the VRB [66].

Table 4 Summary and comparison of ion-exchange membranes used in all-vanadium RFB (VRB)

Membrane	Approach	Thickness (μm)	IEC (mmol/g)	Permeability (ppm)			Ionic conductivity (mS/cm)	Liquid uptake (wt%)	Reference
				V <sup>3+</sup>	VO <sup>2+</sup>	VO <sub>2</sub> <sup>+</sup>			
NaPon /SiO <sub>2</sub>	Hybrid	204	0.96	<134	<82	<17.8	56.2	21.5	[143]
ModiPek NaPon 117	Interfacial polymerization	201	0.88	∅	34.6	∅	15	∅	[144]
SPEEK	Blend	88	1.76	∅	12.4	∅	7.5	28.6	[145]
PVDF-g-PSSA-co-PMAC	Radiation grafting	70	1.95	11.2	0.73	1.1	100	22	[146]
AIEM	Two-step radiation-induced grafting	42	0.97	∅	22	∅	31	25.4	[147]
SPFEK	Non-fluorinated	∅	1.92	∅	<125	∅	34.8	20.5	[148]
SFPEK	Non-fluorinated	151	1.59	∅	94	∅	2.2	36	[149]
SPTK	Non-fluorinated	∅	1.29	∅	12	∅	10.5	11.9	[150]
SPTKK	Non-fluorinated	∅	1.91	∅	31	∅	13.6	19.3	[150]
NaPon 117	PFSA	178	0.94	<600	<550	<120	58.7	26.0	[151]
NaPon 115	PFSA	127	0.91	∅	79.5	∅	13.4	26	[145]

IEC ion exchange capacity

Fig. 9 Various fluxes across cation exchange membrane (a) and anion exchange membrane (b) for the vanadium electrolyte solutions [44]

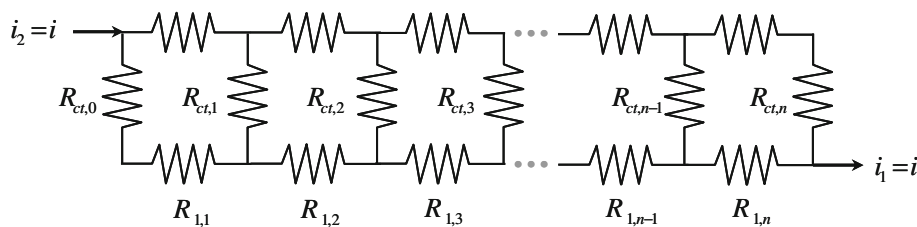


As shown in Fig.9, a significant amount of water is transferred from the negative-half-cell electrolyte to the positive half cell in a VRB using a cation-exchange membrane such as NaPon. This movement is attributed to the hydration shells of V<sup>2+</sup> and V<sup>3+</sup> ions which carry a large amount of water and can easily permeate through cation-exchange membranes. For anion-exchange membranes, the permeation of V<sup>2+</sup> and V<sup>3+</sup> co-ions are restricted. However, there is a net water transfer from the positive half cell to the negative half cell because of the neutral VOSO<sub>4</sub> and negative VOSO<sub>4</sub><sup>-</sup> in the positive half cell that can readily permeate through the membrane [44].

### 5 Cell modeling and design

The above two sections describe transport and kinetic processes that occur at the interface between the electrolyte and the electronically conducting phase (denoted as phase k and the electronically conducting phase (denoted as

Fig. 10 Steady-state resistor-network representation of porous-electrode theory

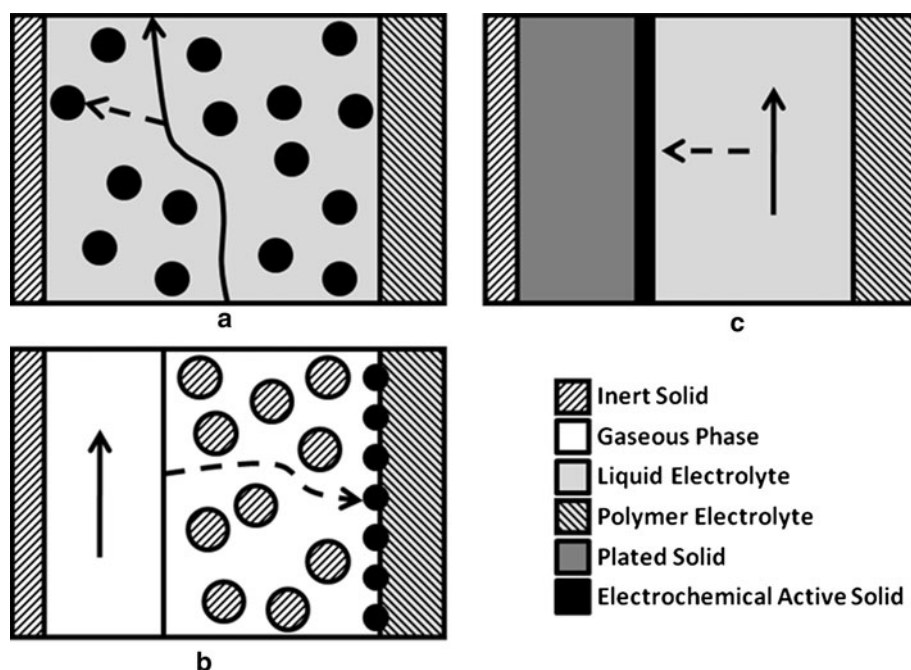


phase 1). The second summation accounts for all other phenomena involved to help minimize transport losses and interfacial reactions that do not include electron transfer facilitate optimized material design and architectures. The and the  $\beta n a l$  term accounts for homogeneous reactions in models help lead to optimized porous-electrode structures, phase  $k$ . In the above expression,  $\epsilon$  is the porosity of the which are crucial in increasing RFB performance and domain,  $s_{i,k}$  is the stoichiometric coefficient of species hence reducing cost. These issues are explored in more phase  $k$  participating in heterogeneous reaction,  $i_{i,p}$  is the detail in this section. rate of the heterogeneous reaction per unit of interfacial area with phase  $p$ .  $R_g$  is the rate of a strictly homogenous 5.1 Electrode structure reacting per unit volume.

The key component in a RFB is the porous electrode. RFB can have two basic electrode configurations: flow where the reactions occur. The fundamentals behind porous through a porous 3D electrode or flow past a planar electrodes are well established by the work of Newman and electrode. These are shown schematically in Fig. a, b coworkers [14, 154]. A porous electrode can be visualized respectively. Naturally, these two configurations are often as a resistor network as shown in Fig. 10. referred to as flow-through and flow-by electrodes, but

In Fig. 10, the total current density,  $i$ , flows through this terminology is somewhat confusing since these two the electrolyte phase (2) and the solid phase (1) at each terms are also occasionally used to describe flow parallel respective end. In between, the current is apportioned and perpendicular to the direction of the current flow based on the resistances in each phase and the charge transfer resistances. The charge-transfer resistances can be flow-through a porous electrode and flow-by a planar nonlinear because they are based on kinetic expressions electrode. Thus, the reaction will proceed depending on what is Whether a flow-through or a flow-by electrode can or limiting. Since kinetics are typically facile in RFB systems, must be used depends on a number of factors including the main issues are reactant and ion movement to and away physical state of the flowing reactant (i.e. gas or liquid), from the reaction site. For example, if the mass-transfer of the electrode reaction occurring (e.g. plating of solid or a reactant is limiting, then the reaction will proceed near electron transfer in solution) and the conductivity of the the inlet, whereas if ion conduction is limiting, then it will electrolyte phase. For instance, in the prototypical or occur near the separator; a uniform reaction rate is rarely ventional RFB [57, 58] the reactants and products on both achieved without some kind of mass-transfer control the anode and cathode are dissolved ions, and a porous 3D (e.g., a microporous layer limiting flow of a reactant). An flow-through electrode, as shown in Fig. 10a, is typically interesting issue is that one cannot diagnose what is based on both sides. In this configuration the liquid elec- limiting purely from a polarization curve, since even trolly flows through a porous matrix of electrochemically mass-transfer limitations can appear to be ohmic ones. For active solids, usually carbon fibers with appropriate cata- example, due to reactant mass-transfer limitations, a reaction-lytic surface properties. The ions produced by the reaction tion may proceed at the electrode surface near the flow migrate through the electrolyte phase toward the opposing inlet yet the performance will look as if it is ohmically electrode and the electrons move through the network of limited due to the distance the ions have to travel from the carbon fibers to the current collector. The flow-through separator to the reaction site. Because of this and other electrode is well suited to reactions of flowing liquid-phase reasons, mathematical modeling is often used to understand species for a number of reasons. First, the diffusivity of the limiting phenomena and processes in a RFB; yet liquid-phase species is quite low so forced convection relative to the experimental and demonstration system through a porous electrode provides enhanced mass-transfer development, analytical and computational modeling of rates. Second, the concentration of reactive ions is generally RFBs has trailed, which may be due to the era in which low due to solubility limits so forced mass transfer helps they were heavily researched. Advanced modeling is maintain higher current densities. Finally, the flowing needed to understand fully the various physiochemical electrolyte will generally have a high ionic conductivity,

Fig. 11 Schematic diagrams of a flow through electrode, b flow-by electrode with active surface near the current collector (left) and near the membrane separator (right), and c flow-by electrode used in solid-plating cells. Solid arrows indicate convective flow of reactants and dashed arrows represent diffusive paths



which is necessary to avoid ohmic polarization losses by Pletcher, Wills and co-workers [2, 71] uses a solid over the long transport lengths created by the 3D electrode on both the anode and cathode where Pb and PbO are stored as plated solids. Ion conduction through the configuration.

The planar electrode is most commonly used when flowing electrolyte phase to the opposing electrode is at a gaseous reactant is involved. A common example is the maximum distance in this configuration so ohmic losses are hydrogen/bromine cell [71] which uses a liquid mixture of high. Also, the surface area for reaction is at a minimum bromine and aqueous hydrobromic acid on the cathode and equal to the geometric area of the cell. Consequently, with a flow-through electrode (Fig. 1a) and gaseous this type of flow-by electrode is only used when absolutely hydrogen on the anode, with a flow-by electrode as shown necessary, as is the case of the aforementioned solid-plating in Fig. 11b. In this configuration a gaseous species flows in parallel to the electrode and diffuses laterally to the essentially planar electrode surface. (In reality there are reactants to demonstrate the viability of RFB technology electrode surface is a 3D porous zone of catalyst particles is not uncommon in research papers on the subject and immobilized electrolyte phase, but it behaves essentially as a planar surface on the scale of the electrode surface area and long ion-transport distances, would assembly.) The porous region of inert solid between the flow channel and the reactive surface acts to distribute gas uniformly to the catalyst and conduct electrons from the Thaller [42], the possibility of using porous, 3D electrodes electrode to the current collector. The flow-by electrode is well suited to gaseous reactants for two reasons. First, the geometric placements and concerns can be found in the literature, including the pioneering work of Trainham and reaction must happen at or near the electrolyte phase. Newman [156, 158] who examined optimum electrode Second, the diffusivity of gaseous species are 3 to 4 orders of magnitude higher than liquid-phase species so diffusive resistances in Fig. 10.

mass transfer is able to supply reactants to the electrode at a sufficient rate. Another variant of the flow-by electrode is shown in Fig. 11c, which is used when a solid is electrochemically plated out or dissolved as in the hybrid RFBs.

## 5.2 Cell modeling of certain chemistries

### 5.2.1 Iron/chrome

Because the electrode grows during plating, it is not feasible to use a porous electrode as it would become plugged by the plating solid. The so-called single-flow cell reported by Redkiw and Watts developed a mathematical isothermal model to describe the operation of a single anode-

separator-cathode Fe/Cr cell based on electrode theory, redox kinetics, mass transfer, and ohmic effects. The parasitic hydrogen reaction was also considered. It is found that the separator ohmic resistance is the dominant resistance followed by the electrolyte ohmic resistance. The kinetic resistance was determined to be negligible at reasonable flow rates. It was predicted that countercurrent electrolyte flow improves global cell performance due to a more uniform current distribution. Decreasing the electrode area tended to decrease the cell current but resulted in high velocity and enhanced mass transfer within the penetration thickness and increased current. This model also provided a method of determining a charge/discharge protocol that obtained the maximum chromium conversion and minimized hydrogen evolution at the same time. Finally, Codina et al. [135] examined the issue of shunt currents when a cell is scaled up to larger sizes and stacked.

### 5.2.2 All vanadium (VRB)

Not surprisingly, the VRB is the most often modeled RFB, especially recently [161-167]. Shah et al. developed a two-dimensional transient model validated against the experimental diurnal data to study the effects of variation on concentration, electrolyte flow rate, and electrode porosity on the performance of VRBs by dynamic modeling [162, 164, 165]. As shown in Fig. 12, numerical simulation demonstrates good agreement with the experimental data [162].

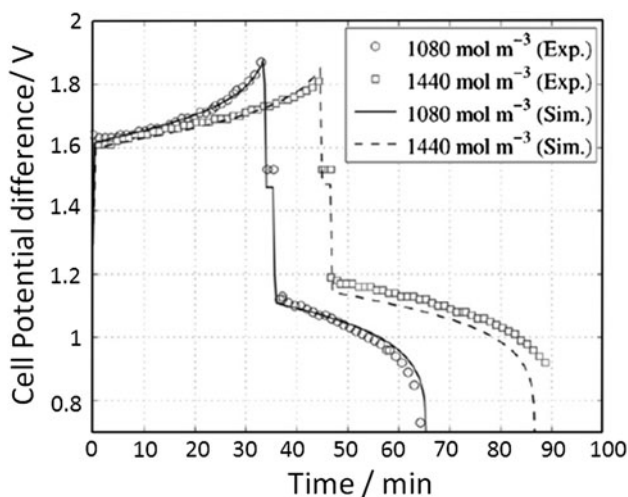
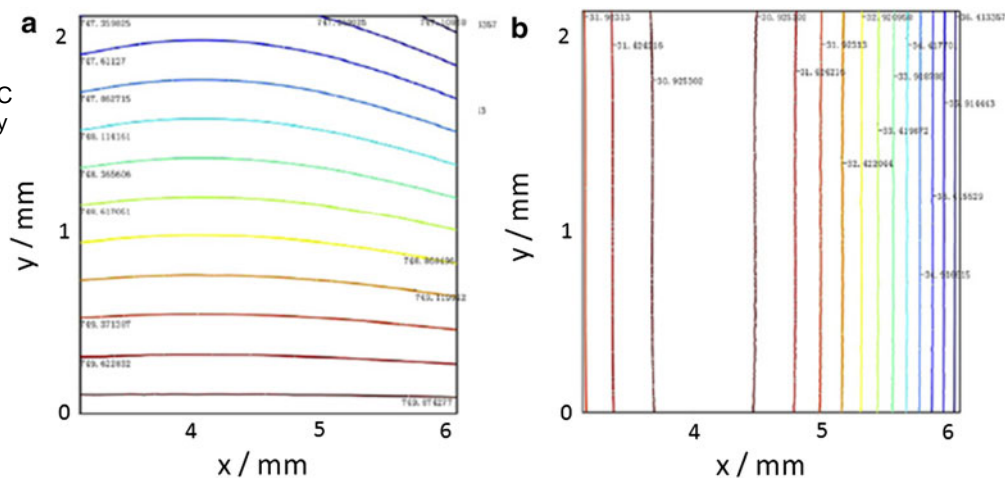


Fig. 12 A comparison between simulated and experimentally obtained cell potential difference. Adapted from Ref. [162] with permission

Fig. 13 Profiles of  $V^{3+}$  concentration (a), and overpotential (b) inside in the negative electrode at 50% SOC with the applied current density of 40 mA/cm<sup>2</sup>. Adapted from Ref. [167] with permission

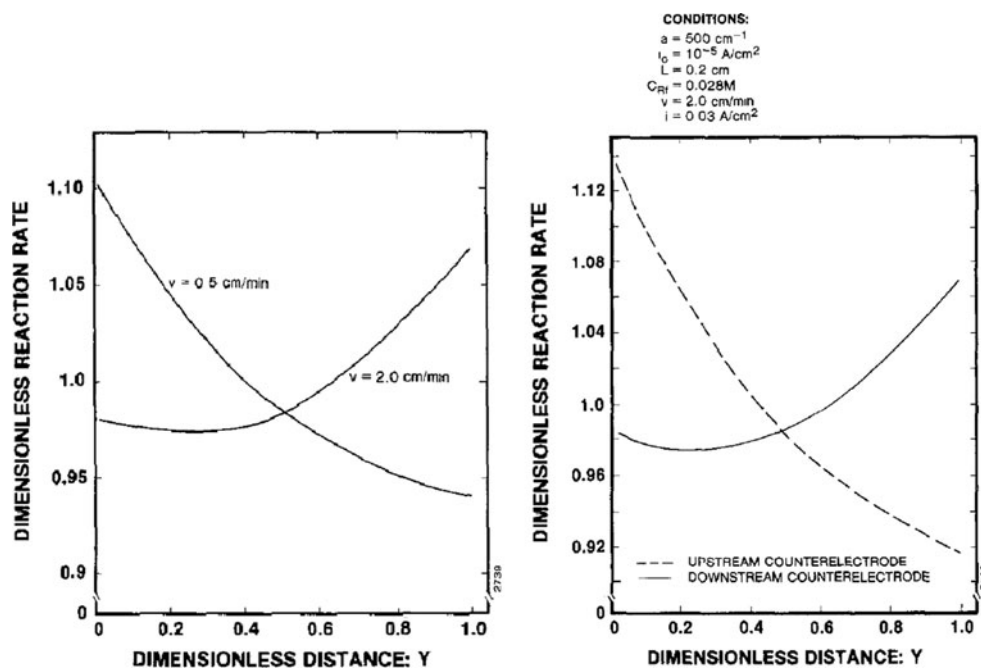


Evolved H<sub>2</sub> and O<sub>2</sub> in the form of bubbles on the negative and positive electrodes, respectively, impact performance through partial occlusion of the electrolyte flow, reduction in the active surface area for reaction, and reduced mass- and charge-transport coefficients. You et al. built a two-dimensional stationary model to describe a single VRB flow cell [167]. They found the decrease in the mass transfer coefficient almost has no effect on the distribution of V<sup>3+</sup> concentration and overpotential, as shown in Fig. 13. Li and Hikiyama developed a model considering the transient behavior in a VRB and the model was also examined based on the tests of a micro-RFB [169]. They found that the chemical reaction rate is restricted by the attached external electric circuit and the concentration change of vanadium ions depends on the chemical reactions and electrolyte flow.

### 5.2.3 Bromine/polysulphide

Scamman et al. developed a numerical model that can be used for the design and optimization of large-scale bromine/polysulphide RFBs [170, 171]. They used the Butler-Volmer equation to estimate overpotential losses. The crossover of active species and self-discharge was also considered. This model is able to predict the concentration

Fig. 14 Reaction-rate profiles for a Cl<sub>2</sub> discharging electrode in a Zn/Cl<sub>2</sub> RFB at different flow velocities and electrode placement. Adapted from Ref. [176] with permission



and current variation along the electrode and determine various efficiencies, energy density, and power density in the charge-discharge processes. It is found that the electrochemical rate constants of the bromide and sulphide are  $4.9 \cdot 10^{-5}$  and  $39 \cdot 10^{-6} \text{ cm/s}$ , respectively.

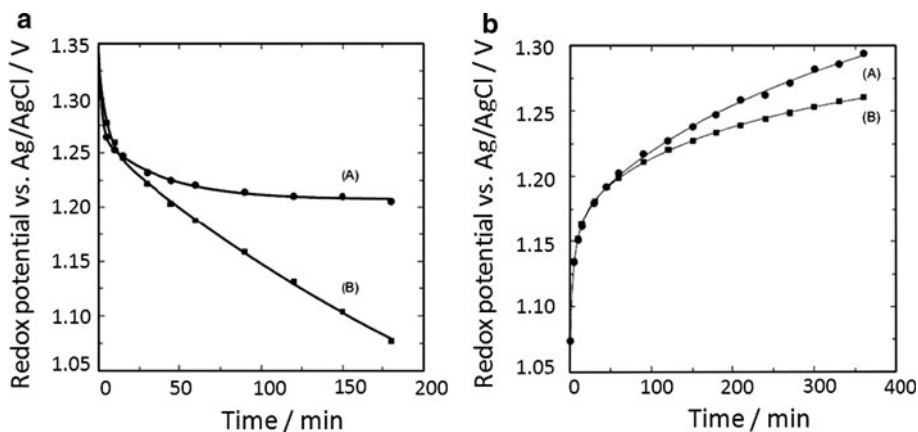
### 5.2.4 Zinc/bromine

Several models of Zn/B have been developed to understand the physical phenomena and to determine how cell performance can be improved. These models have been used to investigate the species transport, secondary electrode reactions, and chemical reactions in the bulk electrolyte, including issues during the plating of zinc.

Putt [173] and Lee and Selman [174] developed thin diffusion-layer models. These models include electrolyte convection with Butler-Volmer kinetics. Mader and White [61] developed a mathematical model for the cell mainly to predict performance of the cell as a function of architecture and operating conditions. They also used their model to determine the effects of the mass transfer and electrokinetics in the porous bromine electrode on the round-trip performance of the cell. It was found that the cell efficiency increases with the porous electrode thickness. Jorne and coworkers [175, 176] also developed models for the chlorine electrode in a Zn/Cl cell. This electrode is very similar to the bromine one and they showed that the flow from the gap to the zinc electrode can impact the current density and reaction-rate distribution significantly, as well as the placement of the electrode as shown in Fig. 14.



Fig. 15 a Redox potential versus time for the reduction of 0.043 M of Ce(IV) in 1 M H<sub>2</sub>SO<sub>4</sub> for both experimental (A) and calculated (B) values. b Redox potential versus time for the reduction of 0.127 M Ce(III) in 1 M H<sub>2</sub>SO<sub>4</sub> and 0.046 M of Ce(IV). Adapted from Ref. [177] with permission



are needed through combined experimental and analytical or computational modeling:

- € Charge transport and electrochemical reaction at and near the electrode surface.
- € The complex charge transport and nonidealities in the various RFB couples and electrolytes used.
- € Species charge transport and crossover in ionic exchange membranes. For many systems, the membranes represent a key limiting component in system feasibility. Low-cost, low-permeability membranes with good ion selectivity, stability, high conductivity, and suitable mechanical properties are required.
- € The fluid mechanics and transport of electrolyte through the various electrode and cell architectures including coupled reaction rates and flow distribution to determine optimal electrode structures and properties.

To enable more complete studies in these areas, a new class of RFB diagnostics will also be needed. Another topic requiring future study as the systems with the greatest potential become defined is performance degradation. As in other, more studied, electrochemical-power-conversion systems, many modes of material degradation will likely be associated with transport processes that can be better optimized to promote longevity.

Finally, throughout this review not much mention has been made concerning other components within the RFB system. In particular, the typical solvents and chemistries are inherently highly corrosive due to their high ionic and perhaps protonic concentrations. Their nature makes sealing and material selection for pumps, flow fields, pipes, etc. very difficult and expensive; pending solutions to these issues is necessary for RFB systems to gain entrance to the market.

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