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Review

Harnessing Interfacial Electron Transfer in Redox Flow Batteries

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SUMMARY

Redox flow batteries (RFBs) have garnered increasing attention for their potential to enable the widespread adoption of renewable electricity. However, a critical need associated with the continued development of this technology involves designing electrode-electrolyte interfaces that exhibit rapid, stable electron transfer kinetics. This targeted review outlines key challenges associated with measuring and enhancing the electron transfer kinetics of established and emerging flow battery active materials. We discuss several promising opportunities for advancing flow battery science and technology using the tools of applied electroanalysis and catalysis science. These challenges and opportunities are broadly relevant for future research directed at advancing the commercial adoption of RFBs for grid-scale energy storage.

INTRODUCTION

Electrochemical energy storage (EES) technologies are becoming increasingly important as a means to buffer between the demand and supply of electricity.[1,2] While primary and secondary batteries have been commercially available for over a century, the last several decades have seen sustained growth in the scale and impact of EES.[3–5] This growth period began with the development and commercialization of Li-ion batteries for portable electronics beginning in the early 1990s.[6–8] Research and development of EES technologies continue to be driven by applications in portable electronics and, more recently, in transportation electrification. Currently, Li-ion and "beyond Li" technologies form the major emphasis of energy storage research for these applications.[9–13] However, we are also beginning to see a third, emerging growth area for EES that involves the use of secondary batteries to grow the supply of renewable energy technologies on the electric grid. Owing to the intermittent nature of renewables, large-scale energy storage is vital to establish a continuous supply of low-carbon electric power.[14–16] Accordingly, this application presents unique challenges and opportunities for further development of EES technologies.

The redox flow battery (RFB) is promising as an alternative to Li-ion and other secondary battery technologies for grid-scale EES (Figure 1).[17–21] In particular, the distinct design characteristics of RFBs make them especially suitable for large-scale fixed installations. A typical RFB charges and discharges through reduction and oxidation reactions involving liquid-phase redox couples over a centralized electrode assembly referred to as a charge-discharge stack. Many such stacks can be coupled to control the maximum power output of the battery up to the MW scale. The liquid-phase electroactive species are stored in external reservoirs of arbitrary size and pumped through the stack only when necessary for charge and discharge. This is a key contrast to conventional secondary batteries where the charge-storing

Context & Scale

Redox flow batteries (RFBs) are uniquely suited to mitigating the intermittency of renewable energy sources, such as solar and wind power by storing large quantities of electricity at a modest cost. However, the most technologically mature flow battery systems are still limited in several key performance metrics, including round-trip energy-conversion efficiency and capital cost per unit capacity. Ongoing work in RFB research is directed toward developing novel materials—particularly soluble redox-active molecules for advanced electrolytes. However, another very important consideration in improving the performance of RFBs involves understanding the kinetics of electron transfer between electrolytes and electrodes in the charge-discharge stack. In this targeted review, we outline the challenges associated with translating laboratory measurements of interfacial electron transfer into enhanced practical battery performance, and we highlight several key opportunities for developing advanced RFB electrodes and electrolytes using the tools of catalysis science.

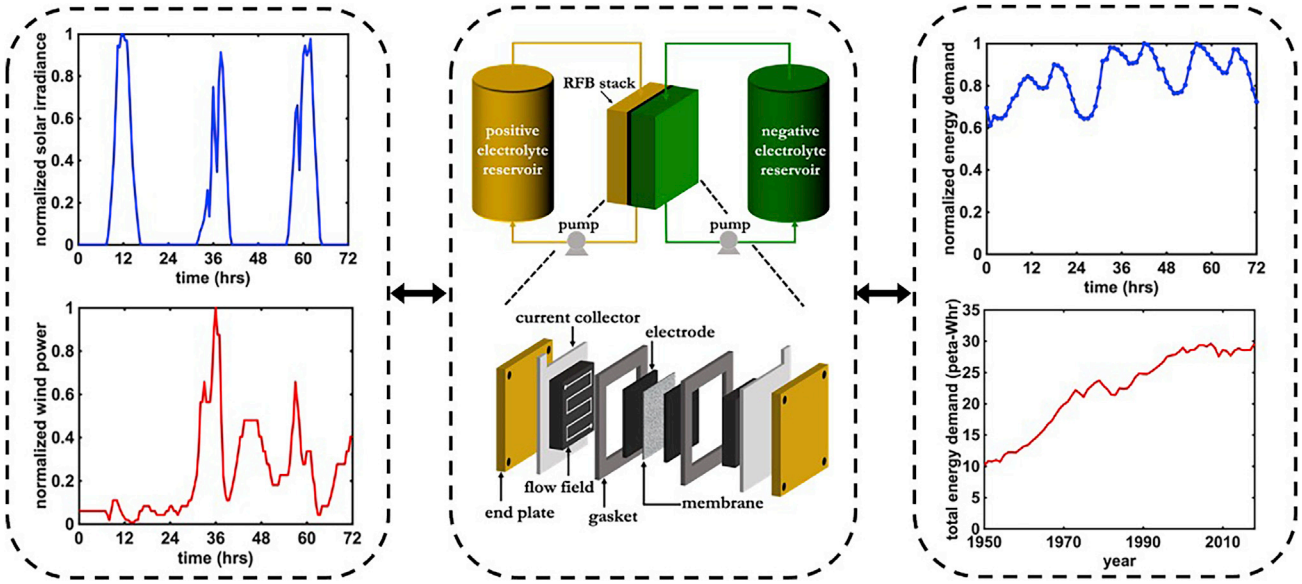

Figure 1. Value proposition for redox flow batteries

Redox flow batteries are designed for large-scale energy storage, including as a means to transduce between the supply of renewable energy (left) and energy demand (right). Representative depictions of available solar and wind power are presented based on publicly available data collected over a 3-day time span in the region near Bend, Oregon, USA.[22,23] Solar irradiance, wind power, and energy demand data are normalized to their respective maxima.

components are fixed in place with electrodes and separators using permanent packaging. The modular design of RFBs decouples the design specifications for battery power (primarily dictated by the stack) from the total system capacity (dictated by the electrolytes and storage tanks). Moreover, the stack, tank, and pump systems are generally not packaged together, so they can be accessed individually for service or replacement, potentially enabling reduced maintenance, replacement, and recycling costs compared with fully integrated battery modules.

RFBs have seen a significant technological development since the first demonstrations in the 1970s.[24] Early work was focused on using transition-metal coordination compounds of iron, chromium, and titanium in highly acidic aqueous electrolytes as the charge-storage media.[25–27] However, these designs suffered from challenges associated with keeping dissimilar molecules separated across a semipermeable membrane. This challenge motivated the development of the all-vanadium redox flow battery (VRFB), which has since become the most popular and technologically mature electrolyte chemistry.[28–33] Despite the success of the VRFB, recent work has refocused heavily on electrolyte design, in part to address the relatively high cost of vanadium precursors and stack components.[34–36] Significant interest is currently centered on organic and organometallic redox couples, due in part to the ability to tune key physicochemical properties such as reduction potential and solubility.[37–44] These electrolytes have shown excellent promise in laboratory studies and are undergoing initial deployment in early-stage commercial devices.

In solid-state secondary batteries, and particularly Li-ion systems, gravimetric energy density is widely regarded as the most important figure of merit. This stems from the overriding importance of the footprint of the battery pack in portable electronics, electric vehicles, and the like. By contrast, grid-scale energy storage installations are not constrained by space or weight limitations in the same way.

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Accordingly, the practical performance of RFB systems is better described via the interplay between efficiency, lifetime, and cost.

The overall efficiency of a secondary battery is simply the total energy that can be discharged from the cell relative to the energy that is required to charge it. Current-generation RFBs generally achieve efficiencies on the order of 70% after accounting for all losses, including those for ancillary components such as fluid pumps.[19,45–49] One way to achieve increased energy-conversion efficiency is to operate at reduced areal power density; however, this strategy reduces the cost advantage of RFBs relative to solid-state batteries, as it requires larger charge-discharge stacks for a given rated power output.[35,50,51] For example, Jiang et al. very recently demonstrated a VRFB operating at a very high peak power density of 2.78 W/cm^2, but the energy-conversion efficiency of this cell was <70% even at a much lower operating power density.[52] Conversely, González et al. reported a VRFB with 95.8% energy-conversion efficiency but only when operating at ~35 mW/cm^2 power density.[53] This tradeoff between power density and energy-conversion efficiency results directly from kinetic limitations in vanadium redox couples as well as transport limitations in membrane separators. By contrast, the practical lifetime of RFB active materials and devices is expected to significantly exceed that of the solid-state secondary batteries. This advantage is attributable in part to the ability to access very high and low states of charge without degrading the active components,[17,54] as well as the ability to perform maintenance on electrolyte and stack components throughout the lifetime of the battery. Moreover, flow battery stacks can be completely drained of the electrolyte when the system is not under operation.[21,55] This suppresses degradation from unwanted side reactions when the electrode and electrolyte are in contact, which is not achievable in a conventional battery.

System cost is often touted as a major advantage for RFBs over established secondary batteries such as Li-ion in grid-scale energy storage.[56–58] This primarily results from the fact that increasing the capacity of a flow battery simply requires the use of more electrolyte. Accordingly, RFBs are especially suited for long-duration storage (i.e., more than a few hours), and these applications will become increasingly important as intermittent renewables make up a larger fraction of the total generation capacity.[59–61] Nonetheless, these anticipated cost advantages have not yet been fully realized in practical RFBs, as the most well-developed all-vanadium cells still suffer from relatively high electrolyte and stack costs.[35,56,62–69]

In view of the rapidly developing research landscape, this review is focused on challenges and opportunities associated with one important and often overlooked characteristic of RFBs—interfacial electron transfer kinetics. First, we outline the role that electron transfer kinetics play in dictating the practical performance of RFBs. We then critically analyze a representative (but not exhaustive) subset of prior work aimed at elucidating electron transfer rates and reaction mechanisms in RFB active materials. Finally, we present several opportunities for future research in which the tools of electrochemical catalysis can be used to understand and ultimately improve RFB performance.

The Importance of Electron Transfer in Flow Batteries

Interfacial electron transfer kinetics have a significant impact on several key RFB performance characteristics. The most readily apparent of these is efficiency. RFBs suffer from characteristically lower round-trip energy-conversion efficiencies than solid-state intercalation batteries primarily due to reduced voltage efficiency, which is the ratio of the discharge voltage to the charge voltage, $\frac{V_{discharge}}{V_{charge}}$.[47,48] The voltage

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efficiency of an RFB is influenced by the kinetic, resistive, and transport losses in the system, which collectively result in overpotentials (voltage in excess of the thermodynamic equilibrium voltage) that are required for the charge and discharge reactions.[70,71] Ohmic losses from porous electrodes and current collectors can be reduced through appropriate cell compression and cell architectures that minimize the distance between electrodes; however, losses attributable to membrane resistance still poses a significant challenge.[72,73] Accordingly, the ability to achieve high power densities by maximizing the rate of mass transport is one of the main considerations for driving down the cost of these systems.[74,75] Generally, mass transport in an RFB depends on a range of parameters such as the diffusivity, viscosity, state of charge, and solubility of active species, as well as the geometry of flow fields in the charge-discharge stack.[76,77] Finally, charge-transfer losses result from sluggish reaction kinetics on the electrode of interest.

Figure 2 compiles a series of mathematical simulations that illustrate the influence of electron transfer kinetics on RFB efficiency. Complete simulation details are provided in the Supplemental Information; the parameters were adapted from recent reports on VRFB research cells.[70,72,73,78] As illustrated in panels A and B of Figure 2, kinetic limitations manifest as overpotentials that are required to initiate the generation of an appreciable current density in an RFB (tens of mA cm^{-2} or greater). At even larger current densities, additional contributions to overpotential are dominated by electric resistance and mass transfer. Figure 2C shows that electron transfer kinetics also play a major role in determining the maximum power density that can be achieved in an RFB while maintaining a target voltage efficiency. The operating power density in turn contributes critically to device cost, because increasing the power density enables the use of a smaller charge-discharge stack (which generally contains the most expensive hardware) for a specified total power output.

These simulations show that, for RFBs operating at current densities up to several hundred mA/cm^2, the *effective* heterogeneous electron transfer rate constant, k^0_{eff}, must be at least 10^{-2} cm/s to minimize kinetic contributions to overpotential. These values are characteristic of rapid "outer-sphere" electron transfer reactions and "inner-sphere" reactions that are efficiently catalyzed at the electrode surface.[79,80] Increasing the electrode surface area (e.g., by using porous carbon cloth or paper) can also increase k^0_{eff}, even for an electrode reaction that exhibits an intrinsic heterogeneous electron transfer rate constant, k^0, that is smaller than 10^{-2} cm/s. However, surface area alone cannot be expected to improve reaction rates by more than a factor of 10–100 without incurring additional transport losses.[72,73] Accordingly, as a general benchmark, we propose establishing a value of $k^0 > 10^{-4}$ cm/s as a minimum viable electron transfer rate constant for efficient RFB systems.

Another key parameter in the overall efficiency of a flow battery is its coulombic efficiency (CE), which is the ratio of total charge, Q that can be extracted relative to the total charge that is stored, $\frac{Q_{discharge}}{Q_{charge}}$. The primary contributors to CE losses are self-discharge processes and side reactions.[81–84] Self -discharge mainly occurs via diffusion of the redox-active species in the electrolyte across the semipermeable membrane that separates the positive and negative electrode compartments in the RFB stack. This results in direct charge transfer between the molecules, which releases energy as heat rather than useful electric power. While self -discharge was found to be a major loss mechanism in early RFBs, the magnitude of this loss has been reduced with the development of superior electrolytes and ion-selective membranes.[85–88] Notably, recent demonstrations of aqueous RFBs based on organic

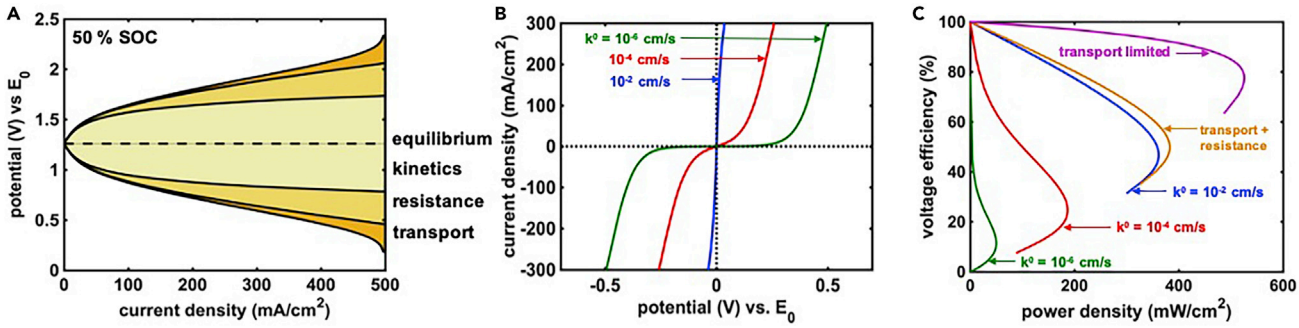

Figure 2. Numerical simulations illustrating the influence of electron transfer kinetics on the performance of a redox flow battery

(A) Simulated charge-discharge curve for a prototypical VRFB at 50% state of charge, highlighting contributions of kinetics, resistance, and mass transport to the total overpotential losses during charge and discharge.

(B) Simulated VRFB polarization curves at 50% state of charge encompassing the expected range of electron transfer rate constants for sluggish versus facile reaction kinetics.

(C) Simulated voltage efficiency versus power density for a hypothetical VRFB illustrating efficiency losses associated with transport, electrical resistance, and reaction kinetics.

molecules such as quinones and viologens have displayed remarkably low rates of self-discharge resulting in CEs greater than 99.99% per cycle.[89–91]

Whereas self-discharge primarily depends on transport processes in an RFB, side reactions are strongly influenced by the fundamental thermodynamics and kinetics of electron transfer. Side reactions comprise redox reactions that do not involve the intended active species, such as electrolysis of the battery solvent as well as over-oxidation or over-reduction of the charge carriers. In many cases, these reactions lead to reduced capacity due to irreversible changes to the electrolyte composition. For example, water electrolysis constitutes a problematic pair of side reactions (hydrogen and oxygen evolution) that fundamentally limit the maximum feasible voltage of aqueous RFBs to values somewhat larger than 1.25 V. However, this voltage limit is highly sensitive to the catalytic properties of the electrode materials.[92–95] Hence, while precious metals such as Pt, Ir, and Ru are used as electrocatalysts in many electrochemical energy-conversion technologies, they are undesirable in aqueous RFBs as they efficiently catalyze hydrogen and/or oxygen evolution. By contrast, aqueous Pb-acid batteries operate at voltages in excess of 2 V because Pb-based electrodes exhibit exceptionally slow electron transfer kinetics for hydrogen and oxygen evolution.

While solvent decomposition is problematic in RFB systems, it generally does not result in permanent capacity loss because the reaction products (i.e., H_2 or O_2 gas in the case of water) are easy to remove and the electrolyte can often be restored to a pristine state via rebalancing.[96,97] More problematic are irreversible side reactions that involve degradation of the active species. The dynamics of these processes depend critically on the associated thermodynamics and electron transfer kinetics, as illustrated in Figure 3. Here, we simulated the steady-state current-voltage behavior of a hypothetical RFB half-reaction involving a positive electrolyte that undergoes the desired oxidation reaction at $E_1^0 = 0$ V (versus an arbitrary reference voltage) followed by a second oxidation at $E_2^0 = 0.3$ V that results in rapid irreversible decomposition (see Supplemental Information for complete simulation details). Critically, the partial current density of the degradation reaction is small but nonzero even at applied potentials corresponding to the onset of the desired oxidation reaction; this is a result of the Nernst equilibrium relationship $E_{eq} = E^0 - \frac{RT}{nF}\ln\frac{[red]}{[ox]}$, which dictates that the oxidative decomposition reaction will proceed in the forward direction far negative of its standard equilibrium potential

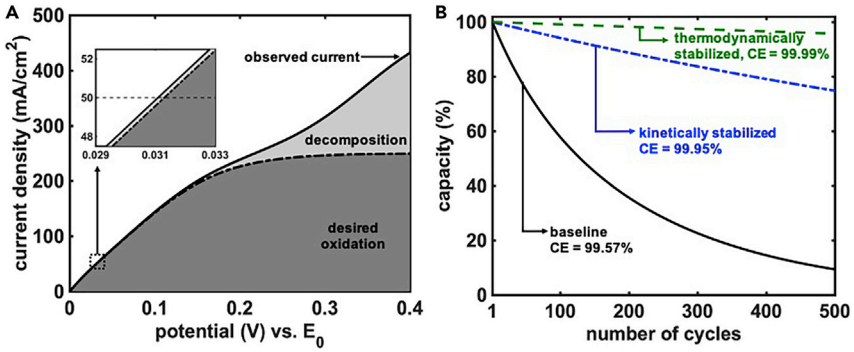

Figure 3. Numerical simulations illustrating the influence of kinetic and thermodynamic parameters on RFB electrolyte degradation by over-oxidation

(A) Simulated polarization curves for the oxidation of a hypothetical RFB positive electrolyte, where the desired oxidation is followed by an undesired over-oxidation reaction that results in irreversible decomposition.

(B) Simulated capacity retention data for three cases: the "base case" corresponding to the parameters depicted in (A); thermodynamic stabilization, where the equilibrium potential for the decomposition reaction was shifted positive by 0.1 V; and kinetic stabilization, where k^0 for the decomposition reaction was decreased by a factor of 10.

since the product concentration [ox] remains very small. Thus, irreversible degradation associated with over-oxidation or over-reduction occurs even when the RFB is operated at what seems to be a "safe" range of potentials.

It is likely that many RFB redox couples of interest are ultimately susceptible to degradation by over-oxidation or over-reduction, as even the strongest covalent bonds are thermodynamically unstable under highly oxidizing or reducing conditions. Notably, recent work by Aziz has clearly shown that the type of over-oxidation process shown in Figure 3 limit the cycle life of quinone-based RFB redox couples in aqueous solutions.[98] Moreover, reactions of this type may result simply from storing electrolytes in their charged state, which illustrates the importance of considering RFB degradation rates in terms of both cycle life (degradation rate per cycle) and calendar life (degradation rate per time).[34,99] Accordingly, one way to enhance the long-term stability of RFB electrolytes is to destabilize the over-oxidized product, which brings about a more positive shift in its equilibrium potential and decreases the partial current density under operating conditions—this constitutes a thermodynamic stabilization strategy. Another strategy involves kinetic stabilization, where the electron transfer rate constant for decomposition reaction is suppressed relative to the desired reaction; this type of kinetic selectivity is a hallmark of well-designed catalyst materials.

Kinetically inhibited electron transfer also translates into large overpotentials required to induce electron transfer reactions, resulting in a need to access extreme voltages. This again leads to the possibility of decreased stability due to the emergence of undesired side reactions (involving the RFB redox couple itself or the supporting electrolyte) as an indirect result of sluggish reaction rates. Thus, a general correlation can be inferred between slow electron transfer kinetics and decreased stability of RFB electrolytes. However, more work is warranted to determine the extent to which accelerating electron transfer kinetics for an otherwise unstable redox couple (e.g., by introducing a catalytic electrode) translates into improved stability.

Challenges and Opportunities in Understanding Electron Transfer in RFBs

Figure 4 schematizes a conceptual workflow wherein flow battery research can be organized into three distinct phases: (1) materials discovery; (2) applied

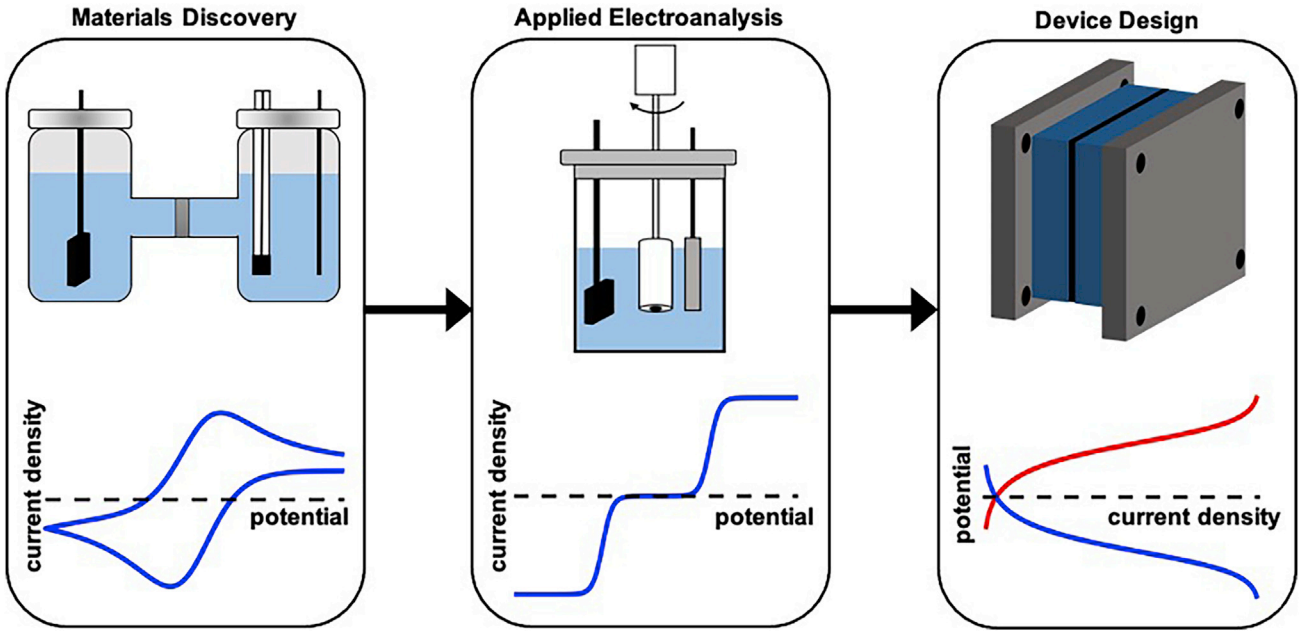

Figure 4. Phases of redox flow battery research
Schematic Representation of a Scientific/Engineering Workflow that Describes Ongoing Work on RFB Systems

electroanalysis; and (3) device design. Notably, the majority of flow battery research over the past several decades can be classified in the materials discovery and device design phases.[17–19] Initial discovery and characterization of redox-active molecules and electrodes is often carried out under analytical conditions,[100–110] and the most promising redox couples are then immediately deployed into model devices to establish performance parameters.[111–121] However, the lack of effort in applied electroanalysis to understand the fundamental behavior of RFB active materials makes it difficult to transition from discovery based on heuristics toward the directed design of improved batteries.

The Challenge of Making Good Measurements

Understanding, and ultimately controlling, interfacial electron transfer in RFBs fundamentally depends on the ability to accurately measure reaction rates as a function of applied potential and to interpret the results in the context of RFB operation. There already exists a large body of work in the physical and analytical electrochemistry literature dedicated to understanding the dynamics of interfacial electron transfer in many molecules of interest for RFBs.[80,122–127] While such studies provide valuable insights, these types of measurements are generally executed using conditions that are quite different from practical RFB operation. For instance, flow batteries are operated at high concentrations of active and supporting electrolytes—usually in excess of 1 M. By contrast, electroanalytical experiments are usually performed with concentrations of the electroactive analytes in the mM range or lower.[128,129] Additionally, routine electroanalytical experiments are usually carried out with planar electrodes in quiescent solution or under well-defined hydrodynamic conditions.[130–132] Conversely, RFBs employ porous electrodes, usually constructed from conductive carbon fibers, under forced convection in turbulent flow.[114,127] For redox couples whose electron transfer mechanisms involve explicit interactions with the electrode, it can also be difficult to relate kinetics data collected from model electrodes, such as glassy carbon, to technologically relevant electrodes, such as carbon felt, which are not guaranteed to exhibit the same surface chemistry. These

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Table 1. Compiled Kinetics Data for Aqueous RFB Redox Couples at Various Types of Carbon Electrodes

Redox Couple	Electrode Material	Rate Constant, k^0 (cm/s)	Measurement Technique	Supporting Electrolyte	Conc. of Active Species	Ref.
$Fe^{3+/2+}$	glassy carbon	7.3×10^{-5}	RDE	2 M H_2SO_4	1 M	Yang et al.[133]
	glassy carbon	2.3×10^{-3}	RDE	0.2 M $HClO_4$	5 mM	McDermott et al.[138]
	glassy carbon	1.5×10^{-4}	RDE	0.5 M HCl	5 mM	Sawant and McKone[139]
	oxidized glassy carbon	1.8×10^{-3}	RDE	0.5 M HCl	5 mM	Sawant and McKone[139]
	pyrolytic graphite	1.0×10^{-3}	CV	1.5 M HCl	1 M	Hollax and Cheng[140]
$V^{3+/2+}$	glassy carbon	1.0×10^{-6}	PP	4.2 M H_2SO_4	1.6 M	Oriji et al.[130]
	glassy carbon	1.4×10^{-4}	EIS	4.5 M H_2SO_4	1.5 M	Bourke et al.[141]
	electrochemically-activated graphite	1.1×10^{-6}	CV	2 M H_2SO_4	2 M	Liu et al.[129]
	carbon felt	1.4×10^{-6}	LSV	0.1 M H_2SO_4	150 mM	Li et al.[134]
	carbon felt	1.5×10^{-5}	CV	1 M H_2SO_4	50 mM	Agar et al.[135]
	carbon paper	1.1×10^{-3}	CV	1 M H_2SO_4	50 mM	Wu et al.[126]
VO^{2+}/ VO_2^+	glassy carbon	2.2×10^{-6}	PP	4.2 M H_2SO_4	1.6 M	Oriji et al.[130]
	glassy carbon	4.5×10^{-5}	EIS	4.5 M H_2SO_4	1.5 M	Bourke et al.[141]
	electrochemically-activated graphite	8.2×10^{-4}	CV	2 M H_2SO_4	2 M	Liu et al.[129]
	carbon nanotubes	1.8×10^{-6}	CV	1 M H_2SO_4	100 mM	Friedl et al.[142]
	carbon paper	1.0×10^{-3}	CV	1 M H_2SO_4	50 mM	Wu et al.[126]
	carbon-polymer composite	8.5×10^{-4}	CV	1 M H_2SO_4	50 mM	Yamamura et al.[143]
AQDS/ AQS	glassy carbon	7.2×10^{-3}	RDE	1 M H_2SO_4	1 mM	Huskinson et al.[37]
	glassy carbon	1.5×10^{-4}	RDE	1 M H_2SO_4	1 mM	Yang[136]
	glassy carbon	4.8×10^{-4}	CV	1 M H_2SO_4	10 mM	Lantz et al.[137]
	glassy carbon	1.5×10^{-4}	RDE	2 M H_2SO_4	1 M	Yang et al.[133]

(RDE, rotating disk electrode voltammetry; CV, cyclic voltammetry; LSV, linear sweep voltammetry; EIS, electrochemical impedance spectroscopy; PP, potentiostatic polarization).

differences lead to one of the biggest current challenges for the field: how do we design and interpret analytical measurements that give the most relevant information for practical operating RFBs?

To illustrate the need for high-quality electroanalysis that is specifically directed at RFB operation, we have compiled in Table 1 a representative set of electron transfer rate constants, k^0, that have been reported for four popular aqueous RFB redox couples using several types of carbon electrodes. These data were collected from some studies that were directed at RFB operation and others that were directed at the fundamental chemistry and physics of interfacial electron transfer. Accordingly, only a subset of these values include accompanying measurements of RFB figures of merit,[37,133–137] which in turn makes it challenging to contextualize differences in kinetics in terms of device-level performance. Furthermore, the large spread in these data clearly shows that electron transfer processes, even for these established RFB active materials, remain rather poorly understood. Some of the ambiguity likely results from differences in the conditions under which the measurements were executed—varying electrolyte concentrations, characterization techniques, and

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electrode pretreatment protocols. However, differences in k^0 of 10-fold or more have been reported for these electrolytes even while keeping one or more of these variables constant. Moreover, the use of k^0 as a kinetic descriptor implies direct knowledge of the fundamental electron transfer rate (and associated reaction mechanism), which should not vary with measurement technique or with small differences in electrolyte concentration. Thus, there remains a clear need to develop and validate robust characterization methods that can be readily deployed for established and emerging RFB active materials.

At least three different types of electroanalytical techniques are currently used to understand electron transfer in flow battery systems. The first comprises classical analytical electrochemistry methods such as static and hydrodynamic voltammetry, potential and current-step techniques, and electrochemical impedance spectroscopy.[130,141,144–147] These techniques can be further adapted for electrodes and electrolytes resembling those used in RFBs—e.g., by using high electrolyte concentrations or technologically relevant electrode materials. As an illustrative example, Savinell et al. reported a series of studies using rotating-disk electrode voltammetry to understand the influence of carbon electrode composition and surface preparation on the kinetics of VRFB active materials.[141,148] They found that the electron transfer kinetics of $V^{3+/2+}$ redox couple was enhanced or inhibited by anodic and cathodic electrochemical pretreatment, respectively, whereas that of the $V^{5+/4+}$ redox couple was enhanced by cathodic pretreatment and inhibited by anodic pretreatment; these enhancement factors ranged from 10 to 25 for the $V^{3+/2+}$ redox couple and from 5 to 10 for $V^{5+/4+}$.[104] The advantage of these electroanalytical techniques is the ability to obtain credible estimates of electron transfer rates using equipment and supplies that are readily available in most electrochemistry laboratories. However, the main drawback of these methods is their dissimilarity to practical RFB operation.[149–155] Moreover, it is challenging to execute these types of measurements under simulated RFB cycling conditions, which would require ancillary equipment to charge and discharge the electrolyte of interest while maintaining minimal interference from the counter electrode. Accordingly, classical electroanalytical methods are excellent for making precise measurements of several key physicochemical properties of RFB active materials—including kinetic parameters such as k^0—but care must be taken when using these data to make specific inferences about the performance of a particular electrode or electrolyte in a battery.

A second category of RFB analytical measurements comprises those that are executed using fully functional flow cells. This type of measurement can be accomplished using a small-scale RFB stack with electrodes and electrolytes that are otherwise identical to those used in a practical device. Additional analytical precision can be obtained by incorporating a reference electrode to isolate the behavior of individual half-cells. Zawodzinski et al. made excellent use of this type of lab-scale RFB to understand the influence of electrode pretreatments on overpotential and CE losses in VRFBs.[73,156,157] They found that the negative half-cell, comprising the $V^{3+/2+}$ redox couple, is responsible for ~80% of the total overpotential of the system. Additionally, they found that heat treating the carbon-paper electrodes resulted in an increase in the wetted surface area and improved overpotential performance by >100 mV. Similarly, Brushett and co-workers have used small-scale flow cells to execute analytical measurements on aqueous and nonaqueous RFB active materials.[66,77,155,158] For example, they characterized the performance of a model nonaqueous redox-active organic molecule based on a 2,2,6,6,-tetramethylpiperidine-1-oxyl (TEMPO) derivative, which yielded a current efficiency of 99.4% and a capacity retention of 92.6% over 20 charge-discharge cycles.[159] These figures of merit

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are useful for setting a performance baseline for organic electrolyte development but they remain well below the minimum requirements for technological viability. The main benefit of deploying full flow cells for RFB electroanalysis is the ability to use the results to directly inform the design of larger prototypes. However, these measurements are difficult to execute as they require specialized equipment that is neither as readily available nor as well standardized as most analytical electrochemistry tools. It can also be difficult to extract quantitative information about the properties of interest (e.g., electron transfer rate constants) from full RFB-cell measurements, as the data often include significant contributions from complex diffusion/convection behavior, membrane crossover, heterogeneous current distributions across porous electrodes, and other convoluting factors. Nonetheless, full device measurements should be considered the gold standard for validating specific hypotheses about the effects of electron transfer kinetics on the practical behavior of RFBs.

A third category of analytical methods comprises electrochemical tools that are dissimilar to practical flow battery configurations but offer unique advantages for understanding interfacial electron transfer behavior. Perhaps the most popular of these are micro- and nano-electrochemical techniques.[160–162] Ultramicroelectrode (UME) voltammetry, for example, offers the ability to measure electron transfer kinetics even at very high current densities due to the reduced influence of mass-transfer limitations and series resistance losses.[163–165] Specifically, as the dimensions of a working electrode approach the sub-mm scale, the mass transport of electroactive species changes from linear to hemispherical diffusion, which allows significantly enhanced mass transfer even under quiescent conditions.[166–168] Moreover, current densities at UMEs are characteristically smaller than those at macroelectrodes, which significantly decrease measurement errors associated with uncompensated solution resistance.[169,170] Hence, UMEs have been used to good effect to measure the electron transfer kinetics of both aqueous and nonaqueous RFB electrolytes.[171–173] Furthermore, the same types of mathematical analyses (e.g., least-squares regressions on the Butler-Volmer equation) can be used to extract electron transfer rates from UME voltammetry just as with macroelectrode voltammetry, except that the UMEs exhibit characteristically larger mass-transfer rates, making it easier to operate under pure kinetic control. Scanning electrochemical microscopy (SECM) takes micro/nanoelectrochemistry a step further by offering the ability to control mass-transport conditions using feedback mechanisms and to spatially resolve variable electron transfer rates across an electrode surface.[174,175] Accordingly, this technique has been used to excellent effect to evaluate electron transfer kinetics for RFB redox couples and electrode materials.[176,177] For instance, Ritzert et al. used SECM to evaluate the electron transfer rate constants of 10 different redox mediators on graphene electrodes in water, acetonitrile, and dimethylformamide solvents.[178] They found that the kinetics of quasi-reversible mediators, such as Fe(EDTA) and $[Ru(CN)_6]^{4-}$, were substantially accelerated in the presence of minute quantities of a surface-adsorbed Os complex, thereby illustrating the significant impact of impurities and dopants on electron transfer kinetics.

Recent work has also demonstrated the value of executing *in situ* measurements of RFB materials. Several methods, such as conductivity measurements, spectroscopic monitoring, and cell potential measurements have been used to measure the state of charge of redox flow batteries during operation.[179–183] Spectroscopic techniques are especially useful for studying RFB active materials because changes in oxidation state often give rise to characteristic changes in optical absorption spectra.[181,184–188] The particular benefits of optical spectroscopy include high

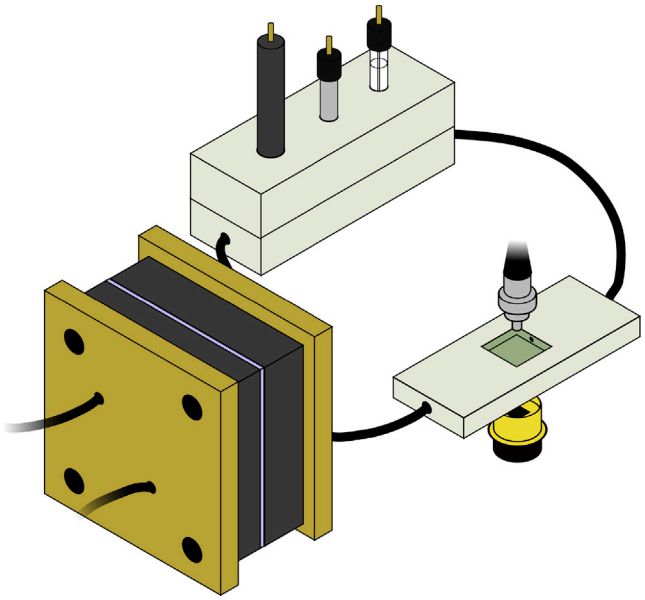

Figure 5. A Sensorized Redox Flow Battery

Conceptual Schematic of a Set of Real-Time Analytical Capabilities Based on Ultramicroelectrode Voltammetry (Top) and Spectroelectrochemistry (Right) that Can be Directly Interfaced with an Operating RFB Cell (Lower Left)

precision—high-quality spectrophotometers can detect absorbance changes on the order of 0.1% or less over timescales of hours to days—and the ability to measure the state of charge without directly perturbing the oxidation state of the active species.

While UME and spectroscopic techniques cannot be used to directly predict the practical performance of a fully scaled RFB system, they may offer additional valuable insights via deployment as *in situ* analytical tools for flow battery metrology. Figure 5 presents a conceptual schematic of a micro-electrode flow cell and an online optical spectrophotometer integrated into the flow loop of a functional RFB half-cell. These types of integrated, real-time analytical tools can be used to measure key parameters such as state of charge, electrolyte degradation, and perhaps even temporal changes in reaction kinetics (if the analytical electrode could be designed to adequately resemble the actual RFB electrode), all at a modest cost and with minimal perturbation of the associated RFB device. Thus, micro-electrochemical methods and *in situ* spectroscopy each provide opportunities to advance battery design and operation by "sensorizing" RFB devices.

Opportunities to Leverage Catalysis Science

Continued efforts to improve the performance of RFBs would greatly benefit from insights and design strategies adopted from electrochemical catalysis. Recent theoretical and experimental advances in this field have resulted in a versatile set of design rules for catalytic interfaces based on stabilization or destabilization of surface-bound intermediates.[189–192] Applying this type of analysis to RFB chemistry leads to an important conclusion: because flow battery electrolytes generally involve redox reactions comprising only one or two electron transfers, the associated reaction mechanisms likely require no more than one adsorbed intermediate. Accordingly, it should be possible to design catalytic interfaces with near optimal binding energetics—directly analogous to that of the hydrogen evolution reaction (HER) at a Pt electrode in acid solution. This means it should be possible to virtually eliminate

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kinetic losses in any RFB redox couple that features $\leq$2 electron transfer reactions. Nonetheless, much work remains to realize this outcome in functional RFBs.

The all-vanadium flow battery provides an excellent case study regarding the need to design effective electrocatalysts for RFBs. Despite the relative simplicity of its redox chemistry (both the negative and positive redox couples require only one electron transfer), the VRFB suffers from remarkably sluggish kinetics at unmodified carbon electrodes.[128,193] To address this limitation, a variety of electrode and electrolyte modifications have been used to accelerate the associated redox reactions.[141,194–197] However, these strategies have been developed mainly through trial-and-error methods and have not yet been successful at fully eliminating kinetic losses. Additionally, there is still active debate as to the molecular basis of enhanced catalysis at pretreated carbon electrodes, as well as whether the positive ($V^{5+/4+}$) or negative ($V^{3+/2+}$) redox couple exhibits faster kinetics.[102,135,145,193,198] Finally, the stability of these electrode treatments over long-term operation remains poorly understood. Renewed efforts to understand the mechanism of vanadium redox chemistry at well-defined electrode materials would be extremely valuable in guiding the design of efficient catalysts.

Quinone-based electrolytes provide an intriguing counterpoint to vanadium in that their redox chemistry is generally observed to be fast at carbon electrodes despite the fact that they undergo two-proton, two-electron transfer reactions in acid.[37,133,136,199] Hence, it is plausible that graphitic and/or fullerene-like carbon surfaces could behave as excellent electrocatalysts for aqueous quinone redox chemistry. This is consistent with prior analytical studies showing that some quinones strongly adsorb on clean carbon electrodes, which enables a "self-catalytic" mechanism wherein the surface-adsorbed quinone stabilizes transition state(s) associated with proton-coupled electron transfer to solution-phase quinones.[200] This may also help explain the wide range of rate constants that have been reported for quinones in RFBs, as electrode surface preparation is likely to have a strong influence on surface adsorption. Further work to understand the fundamental mechanism of quinone redox catalysis at carbon electrodes would be valuable—especially efforts to understand the long-term stability of these spontaneously generated catalytic interfaces under RFB reaction conditions.

An increasingly popular strategy for RFB electrolyte development involves designing molecules (especially organics and organometallics) that exhibit inherently fast, outer-sphere electron transfer reactions. These reactions are characterized by minimal changes in the structure and bonding of the reactant upon oxidation or reduction, which eliminates the need for specific interactions with the electrode surface to stabilize intermediates or transition states. Examples include organics such as viologens and TEMPO derivatives as well as transition-metal complexes such as metallocenes.[173,201–203] This molecular design strategy is indeed attractive but it suffers from several key limitations. First, it is difficult to achieve outer-sphere reactivity using redox couples with more than one electron transfer reaction, which in turn makes it difficult to design kinetically facile RFB electrolytes with high volumetric energy densities. Second, the inherently fast kinetics of these molecules makes them promiscuous electron transfer reagents—they readily undergo redox reactions with solvent, impurities, or stack components that are susceptible to galvanic corrosion. Accordingly, using kinetically facile redox couples may result in excellent voltage efficiencies at the expense of reduced long-term stability for these batteries. This consideration is especially important for emerging nonaqueous RFBs, which are touted for their potential to achieve very large cell voltages—of the order of 3 V or larger. This goal is often rationalized by analogy to the use of nonaqueous solvents in Li-ion battery

systems.[6,158,204] However, this analogy may in fact be inaccurate, as Li-ion systems are mainly stabilized by passivation layers that form on the solid electrodes due to transient decomposition of solvent and supporting electrolyte.[205–210] This passivation effect is not readily translatable to RFBs, and in fact, kinetically facile redox couples that readily transfer electrons to or from solvent species will likely degrade rapidly in this type of environment.

Based on the analysis above, an ideal RFB redox couple would exhibit multi-electron transfer chemistry at an extreme reduction potential (up to several hundred mV beyond the thermodynamic stability limit of the solvent and supporting electrolyte) and would also exhibit generally *sluggish* electron transfer kinetics except in the presence of a highly catalytic electrode material. Interestingly, VRFB electrolytes would fit this description well if improved electrocatalysts could be developed. Water-soluble quinones also satisfy most of these requirements, which helps explain why they are among the most promising contenders for next-generation RFB active materials.[37,137,211,212] Nonetheless, there likely remains a large unexplored parameter space for RFB active materials that can achieve large cell voltages, long-term stability, and highly efficient operation all through careful control of interfacial electron transfer. Working toward this goal will require research strategies that consider electrode and electrolyte materials together. This increases the complexity of experimental design for RFB materials discovery, but it also enables a higher degree of tuneability via modifications of the electrode and electrolyte in tandem.

SUMMARY AND OUTLOOK

The rapid growth of renewable energy globally presents a massive opportunity for grid-scale energy storage and RFBs. Despite significant progress, laboratory and commercial development of RFB technologies remain at a relatively early stage. Hence, there are a myriad of valuable research opportunities available in developing fundamental insights related to flow battery electrodes and electrolytes, and many of these insights will be immediately applicable to advancing RFB technology. We advocate for increased efforts to understanding interfacial electron transfer in RFBs using a framework of applied electroanalysis, which can act as a bridge between novel materials discovery and device design.

Moving forward, there are specific opportunities in designing molecules with the ability to perform multi-electron transfer reactions alongside the development of efficient and selective electrocatalysts. Research in RFBs will also greatly benefit from a deeper understanding of kinetic stabilization strategies to increase cell voltage. These will likely be necessary for nonaqueous RFBs that are as stable as Li-ion batteries, and they may be equally useful for aqueous systems. Finally, developing robust empirical correlations between analytical and device-level measurements—e.g., how electron transfer rates observed from rotating disk electrode voltammetry translate into overpotential losses in practical flow cells—would be especially useful to guide the down-selection of novel electrolyte and electrode materials. Recent recommendations by Wang et al. for kinetics measurements and by Brushett, Aziz, and Rodby on electrolyte stability are promising in this regard.[34,213] Advances in these areas will ultimately support improved battery efficiency, stability, and cost, which will be integral to the long-term value of RFB technology.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.joule.2020.11.022.

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AUTHOR CONTRIBUTIONS

T.V.S. initiated this critical review, generated the figures as well as drafted, edited, and revised the manuscript; C.S.Y., T.J.H., and D.M.M. assisted in literature review, provided input for discussion and editorial feedback; J.R.M. supervised the preparation of this review, formulated mathematical models, and drafted, edited, and revised the manuscript.

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