JES Focus Issue on Redox Flow Batteries–Reversible Fuel Cells

Advanced Redox-Flow Batteries: A Perspective
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Redox-flow batteries are entering a period of renaissance, buoyed by both the increasing need for affordable large-scale energy-storage solutions, as well as leveraging the advancements in flow-cell technology, mainly in polymer-electrolyte fuel cells. This perspective highlights the research-and-development avenues and opportunities for redox-flow-battery cells and materials.

The focus of this perspective article is on promising technological advancements in redox-flow batteries (RFBs) that were first developed by NASA during the energy crisis of the 1970’s. Unlike traditional batteries, RFBs utilize redox couples that can be stored in independent tanks and only brought together when power is needed through an energy-conversion cell stack as shown in Fig. 1.1 It has long been recognized that stationary EES systems could save substantial quantities of energy, as well as provide other potential benefits, such as improved reliability and reduced emissions. However, to date, most electrical grids utilize minimal storage since EES technologies have not been economically viable or proven. There is a growing need for grid- and urban-scale EES, as demonstrated in Fig. 1.1

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The competing technology that dictates cost is essentially rapid-response power generation, such as spinning reserves of various gas turbines. Grid-scale EES must still reach lower cost in order to be widely deployed. The cost targets for grid-scale EES are typically more aggressive than those for portable or transportation applications; however, the typical size of the EES system is also orders of magnitude larger, as shown in Fig. 2. Clearly, an EES technology that can scale up in a cost-effective manner is highly desirable and necessary.

RFBs are inherently well suited for large applications since they scale-up in a more cost-effective manner than other batteries. Since the energy and power capacities of a RFB system are independent variables, the required capacities for any application can be met using correctly-sized energy and power modules. RFBS also possess other compelling attributes for stationary EES applications, especially long-duration applications. For example, the RFB architecture enables long lifetimes since the electrodes are not inherently required to undergo physiochemical changes during charge/discharge cycles. Because of the growing demand for grid-scale EES and the inherent attractive attributes of RFBs, the technology appears to be undergoing a renaissance period. This growth in RFB research is readily evident in Fig. 3 showing the total number of publications, as well as in the number of recent review articles on RFB technology.1-6 However, although interest is growing, the absolute number of RFB papers is still small relative to those on PEFCs or conventional batteries (e.g., Li-ion batteries). A wide variety of RFB system installations have effectively demonstrated the inherent capabilities of the technology. However, further technological improvements are necessary to achieve the aggressive cost targets required for widespread commercialization. Since there has been a relatively small amount of R&D investment in RFB technology, to date, there is a large potential for substantial improvements. The focus of this perspective article is on promising technological pathways to further reduce RFB cost. The most obvious route to reduce cost is to utilize materials with inherently lower cost (i.e., reduce the average $/kg). However, one can also realize higher performance (i.e., reduce the kg/kWh). A good example of this approach has been the recent dramatic improvements in RFB power density ($/m²) using the same basic set of materials utilized in previous RFB cells with improved flow-field and electrode designs.7-13 The effectiveness of this approach is illustrated in Fig. 4, which illustrates how cell cost (i.e., $/m²) strongly depends on power density. The assumed areal costs ($/m²) are typical for the three major repeat parts in a RFB cell stack: 1) separator, 2) electrodes, and 3) bipolar plates at modest production volumes (e.g., ≈100 MWh/yr), which are highly relevant for new product targeted for a developing market. The lower cost ($500/m²) is realistic for cells that utilize a low-cost porous separator, while the higher cost is more likely for cells that include fully-fluorinated ion-exchange membranes, such as perfluorinated sulfonic-acid (PFSA) membranes.

This perspective highlights potential pathways employing approaches of both new materials and improved cell power densities. In either case, it will be difficult to achieve the desired cost targets for a complete RFB system if the non-active cell materials alone cost approximately $100/kWh. This perspective is limited to the cell-stack components and the active materials because the remaining required parts of a RFB system are typically composed of commercial off-the-shelf components, where there are much fewer opportunities for substantial cost reductions, as discussed in a recent techno-economic analyses.6,15

Next-Generation RFB Active Chemicals

The first-generation of RFB chemistries have been based on single-element active materials dissolved in aqueous electrolytes. The most

Figure 1. Schematic of a RFC system. (Reproduced from Reference 1).
common of these being transition metals (e.g., Fe, Cr, V) since these metals often have multiple oxidation states and one, or more, of the transitions between these oxidation states occurs at a desirable standard reduction potential (SRP) that is within the kinetically favorable stability window of water.2 Other single-element reactants have also been used (e.g., H₂ and some halogens, especially Br₂ or Cl₂), although this approach enables only a small set of RFB chemistries due to SRP compatibility. A number of research groups have begun to develop new RFB chemistries, which are promising because they often employ whole new approaches than enable a much larger number of options.6

The next-generation of RFB chemistries are likely to be engineered molecules or complexes, since this approach enables one to shift the SRP to a more desirable potential. One approach that has been utilized to do this is ligand-modified transition metals, which shift the SRP to a more desirable potential. One approach that has been utilized to do this is ligand-modified transition metals, which is actually analogous to the first approach. Namely, the SRP of known redox couples (e.g., the quinone family) are shifted by tailoring the organic molecules that include one or more of these redox couples. One can also utilize functionalization (e.g., hydroxyls and/or sulfonate groups) to alter both the SRP and the solubility of these organic complexes.25 Both positive and negative reactants have been demonstrated in aqueous22,23 and non-aqueous solutions.24 One can also utilize more complex solvent solutions to potentially improve redox-couple solubility, such as the aqueous mixed-acid solution proposed for vanadium RFBs (VRFBs).25

As noted above, both aqueous and non-aqueous options are being pursued because non-aqueous electrolytes enable a broader window of electrochemical stability, which is obviously advantageous from both an energy-density and cell-voltage perspective. However, non-aqueous electrolytes also have significant disadvantages, such as higher solvent costs, higher viscosities, and lower ionic conductivities. A detailed techno-economic analysis recently quantified these trade-offs and concluded that complete RFB systems utilizing advanced RFB chemistries based on either aqueous or non-aqueous electrolytes also have significant disadvantages, such as higher solvent costs, higher viscosities, and lower ionic conductivities. A detailed techno-economic analysis recently quantified these trade-offs and concluded that complete RFB systems utilizing advanced RFB chemistries were inherently more complex and may therefore require an electrocatalyst to enable the required roundtrip efficiencies.

Advanced Electrodes and Electrocatalysts
To enable the high roundtrip energy efficiencies required to minimize the major operational costs of an EES system, highly reversible more expensive cell stacks. There are undoubtedly more risks with development of non-aqueous electrolytes, such as the relatively high active-material solubilities required (to minimize electrolyte cost), solutions and separators with sufficiently high ionic conductivity (to minimize stack size), and compatibility of the reactants and/or solvents with air and/or water (eliminating air exposure is challenging in flow systems). Therefore, if the realistic projected end points are essentially identical, one may reasonably conclude that the aqueous path appears to be more attractive. In any case, the most attractive future RFB chemistries are likely to be ones that offer multi-electron redox reactions per active-species molecule, since this can enable high energy densities at modest concentrations, especially since pumping losses (i.e., solution viscosity) and perhaps ion-exchange-membrane conductivity are enhanced for dilute solutions.36 However, such reactions are inherently more complex and may therefore require an electrocatalyst to enable the required roundtrip efficiencies.
redox reactions are required. Many first-generation RFB chemistries are able to utilize simple carbon electrodes because many of these simple redox reactions are facile and involve outer-sphere electrocatalysis. However, the fundamental reaction kinetics of even some relatively mature RFB chemistries are not well understood. For example, the literature on the kinetics of VRFB reactions is full of conflicting data. The reason why the simple $V^{2+/3+}$ redox reaction on some carbon surfaces is actually less facile than more complex $V^{4+/5+}$ reaction (which includes the production of water during the reduction) has not been explained.\textsuperscript{27} Additionally, pre-oxidation of the carbon electrodes generally results in improved performance, but the actual mechanism(s) responsible for this improvement are still being debated (e.g., improvements in hydrophilicity, and/or an increase in adsorption of $V$ species, and/or an increase in edge-plane sites, etc.). Improved understanding of kinetic fundamentals should enable the development of higher performance RFB electrodes. A major contributing factor to the complexity of RFB reactions on carbon electrodes is the fact that carbon is an extremely complex material. There are many types of carbons, and pretreatments of even the same carbon material can yield very different surface species, which can dramatically impact catalytic activity. Additionally, carbon itself is electrochemically active in the potential window of interest for most RFBs (and all aqueous RFB chemistries). Therefore, an even better understanding of fundamental carbon properties is required for RFB cells that rely on carbon as a catalyst relative to fuel cells, where carbon is simply a catalyst support and/or a structural component with acceptable electrical conductivity and stability. A major conclusion of a recent review article on carbon materials in RFBs was that additional studies on degradation mechanisms are needed.\textsuperscript{28}

Conventional RFB electrodes have not been highly optimized, especially carbon-based electrodes that typically consist of a single, homogeneous layer of porous carbon fibers (e.g., carbon felt or carbon paper). Multiple-layer electrodes offer a path to higher performance than single-layer electrodes. For example, utilizing micro-porous layers between the separator and adjacent macro-porous layers can potentially enable improved roughness factors without necessarily increasing the pressure drops of flow-through electrodes. The macro-porous layer can be optimized to minimize both flow resistance and mass-transport losses, while the micro-porous layer can be optimized for enhanced surface areas with highly kinetically-active surfaces. These micro-porous layers may even include supported electrocatalysts (i.e., analogous to fuel-cell electrodes).

Catalyst materials for redox reactions, beyond carbon, deserve more attention. The most challenging requirement for RFB electrocatalysts is that they must not promote undesirable side reactions (e.g., electrolysis of water in aqueous RFB chemistries). Cost is actually less of a concern, since even a relatively expensive catalyst material may be worthwhile at reasonable catalyst loadings and high cell power densities. For example, if one assumes a platinum-group-metal (PGM) alloy catalyst that costs $50/g, then with 0.1 mg/cm$^2$ material may be worthwhile at reasonable catalyst loadings and high cell power densities. Some of the different technology-commercialization advancements opportunities proposed here are complementary, which could potentially facilitate the pace of development. For example, it is likely that the next-generation of RFB systems will be composed of significantly different materials than those being used today. A primary focus for R&D should be on pathways that enable lower costs; both the use of inherently lower-cost materials, as well as materials that can enable significantly higher energy densities (Wh/L) and/or power densities (W/m$^2$). Some of the different technology-advancement opportunities proposed here are complementary, which could potentially facilitate the pace of development. For example, it is likely that the next-generation of RFB chemistries shall utilize larger active-species molecules, which can facilitate the development of simple porous separators with acceptable ionic selectivity. Additionally, advanced electrocatalysts can potentially enable a broader set of compelling next-generation RFB chemistries. All of these potential advancements can be facilitated by improved understanding of RFB fundamentals (e.g., redox kinetics and impact of carbon surface species, multicomponent transport of various ions and water in membranes, etc.), with RFB chemistries, etc.)

Finally, while this perspective has focused mainly on performance, especially since many of the improvements suggested for RFBs are at a nascent stage, one should also note that stationary EES applications
typically require long lifetimes (e.g., 10 to 20 years but with operation around half the time, e.g., a 4–5 h discharge and 5–6 hour charge per day). Thus, one must be cognizant of durability concerns to minimize cost due to stack or electrolyte replacements. While performance data from RFB systems that have been operating for extended periods in real-world applications have not generally been publically reported, it is apparent that the high oxidizing potentials, impacts of changing state of charge (i.e., material concentration changes), and need for both operation in discharge and charge mode with a single technology material set, make assessing lifetime and durability challenging. However, as demonstrated for fuel cells, one should consider degradation mechanisms while considering new materials, and there is a critical need to establish operation protocols and accelerated stress tests (ASTs) to enhance the key stressors expected during operation and quickly probe materials and cell durability. Such an effort requires a good fundamental understanding of the degradation mechanisms.

Overall, the maturation level of RFB technology is nowhere near that of many conventional batteries or fuel cells, and this provides a rich set of R&D opportunities. These improvements in fundamental understanding, and the resulting improvements in the performance/lifetime/cost of RFBs, will require many different skill sets, similar to those that have successfully advanced fuel-cell and conventional-battery technologies over the past decades.

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