The Critical Role of Supporting Electrolyte Selection on Flow Battery Cost

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Redox flow batteries (RFBs) are promising devices for grid energy storage, but additional cost reductions are needed to meet the U.S. Department of Energy recommended capital cost of $150 kWh\(^{-1}\) for an installed system. The development of new active species designed to lower cost or improve performance is a promising approach, but these new materials often require compatible electrolytes that optimize stability, solubility, and reaction kinetics. This work quantifies changes in RFB cost performance for different aqueous supporting electrolytes paired with different types of membranes. A techno-economic model is also used to estimate RFB-system costs for the different membrane and supporting salt options considered herein. Beyond the conventional RFB design incorporating small active species and an ion-exchange membrane (IEM), this work also considers size-selective separators as a cost-effective alternative to IEMs. The size selective separator (SSS) concept utilizes nanoporous separators with no functionalization for ion selectivity, and the active species are large enough that they cannot pass through the separator pores. Our analysis finds that SSS or H\(^+\)-IEM are most promising to achieve cost targets for aqueous RFBs, and supporting electrolyte selection yields cost differences in the $100's kWh\(^{-1}\).

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Energy storage has emerged as a key technology for improving the sustainability of electricity generation\(^1\) by improving the efficiency of existing fossil-fuel infrastructure through load-leveling or price arbitrage;\(^2\) alleviating the intermittency of renewables (i.e., solar, wind) to promote their broad implementation,\(^3\) and providing price arbitrage,\(^2\) alleviating the intermittency of renewables (i.e., solar, wind) to promote their broad implementation,\(^3\) and providing back-up power.\(^4\) Redox flow batteries (RFBs) are promising devices for low-cost grid energy storage due to decoupled capacity and power scaling, long operational lifetime, easy thermal management, and good safety features.\(^2,4–9\) Unlike enclosed batteries (i.e., lithium-ion, nickel-metal hydride), RFBs implement soluble redox active species dissolved in liquid electrolytes, which are stored in large, inexpensive tanks. Specifically, the electrolyte is comprised of a supporting electrolyte, which contains solvent (e.g., water) and a supporting salt (e.g., sulfuric acid, sodium chloride), and the redox active species (e.g., bromine). The electrolyte is pumped through an electrochemical stack where the active species are oxidized or reduced to charge or discharge the battery. The size of the electrochemical stack determines the power rating, while the tank volume determines the energy capacity, enabling scalability unique to the RFB architecture. A variety of RFB chemistries have been researched in recent years,\(^7,10–12,15\) with many examples of successful commercial deployment, such as zinc-bromine (e.g., Redflow,\(^13\)) Primus Power\(^14\), zinc–iron (e.g., ViZn Energy Systems\(^15\)), and organometallics (e.g., Lockheed Martin\(^16\)). The all-vanadium redox flow battery (VRFB) has been the most successful chemistry,\(^17,18\) and several companies (e.g., Sumitomo Electric Industries,\(^19\) Vionx Energy,\(^20\) Gildemeister,\(^21\) UniEnergy Technologies\(^22\)) are presently commercializing the technology at grid scale. The success of the VRFB has hinged on its facile engineering, given that all relevant redox couples lie just within the practical electrochemical window of the sulfuric acid (H\(_2\)SO\(_4\)) based electrolyte, enabling high cell potential without dissociating water. Additionally, since the positive and negative electrolytes utilize the same parent species (vanadium sulfate), crossover does not irreversibly degrade cell performance.\(^18\) Despite the technological success of the VRFB and other aqueous redox flow battery (AqRFB) chemistries, RFB costs in 2014 exceeded $500 kWh\(^{-1}\)\(^23–25\), well above the U.S. Department of Energy (DOE) recommended capital cost target ($150 kWh\(^{-1}\)) for an installed energy storage system with 4-h discharge at rated power.\(^2\)

The introduction of new redox chemistries is a strategy for substantially lowering the electrolyte (energy) cost contribution to the total battery cost via increased solubility and increased electrolyte energy density.\(^23,26\) Key active species characteristics in determining the RFB electrolyte cost are the solubility (M), molar mass (kg mol\(^{-1}\)), number of electrons transferred per molecule (\(-\)), material cost ($ kg\(^{-1}\)), and cell potential (V). The latter two characteristics have an especially significant impact on total RFB cost.\(^23,28\) Raising cell potential, by identifying active species with more extreme redox potentials,\(^26\) is a particularly effective approach to reducing RFB costs because increasing cell potential decreases both the electrolyte and reactor (power) cost contributions.\(^23,26\) Battery cost is also sensitive to active material cost,\(^26\) and as such, many recent studies have sought to identify active species that could serve as cheap replacements for the incumbent RFB chemistries. Abundant inorganic active species (e.g., metal polysulfides,\(^27–29\)) can be inherently inexpensive. Further, redox-active organic molecules (ROMs) are comprised of earth-abundant elements (i.e., hydrogen, carbon, oxygen, nitrogen, sulfur) and their cost is not determined by production rates of raw materials or material reserves.\(^31\) New organometallic active species,\(^32–36\) as well as ROMs, show promise through the addition of functionalizing ligands, enabling rational molecular design. Typically when a new active material is discovered, the supporting electrolyte must simultaneously be tuned to facilitate its implementation. Key technical considerations when designing a supporting electrolyte are the active material solubility, chemical stability, reaction kinetics, and safety. Numerous experimental examples of such electrolyte development campaigns can be found in literature. As a solubility example, 2,6-dihydroxyanthraquinone is only sufficiently soluble (>0.5 M) in alkaline electrolytes,\(^37\) and anthraquinone disulfonic acid (AQDS) is more soluble in the protonated state, as opposed to the sodium form.\(^38,39\) Regarding charge transfer kinetics, modifying the supporting electrolyte composition, without adding catalysts or pretreating electrodes, has been shown to dramatically affect the electrochemical reaction rates for both metallic and organic...
active species.\textsuperscript{40-42} Considering chemical stability, charged methyl viologen\textsuperscript{11,43,44} is known to react with molecular hydrogen, making it unsuitable for use in acidic electrolytes where hydrogen evolution is a likely side reaction.\textsuperscript{45} Finally, as for safety, metal polysulfides\textsuperscript{27} or ferrocyanide\textsuperscript{27,37} can undergo chemical decompositions in acid to produce toxic hydrogen sulfide or cyanide gases, respectively. While designing a new supporting electrolyte may be beneficial for enhancing the electrochemical behavior of a new active material, other cell-level performance metrics, such as area specific resistance (ASR) or cell potential, can suffer as a consequence; these cell-level performance metrics are often overlooked when developing a cost-effective alternative to the state-of-the-art VRFB. For example, neutral and alkaline RFBs tend to exhibit significantly lower power densities than VRFB,\textsuperscript{46-48} due to more resistive membranes. Moreover, many new proposed chemistry combinations exhibit theoretical open-circuit potentials (OCP) well below that of the VRFB (1.4 V).\textsuperscript{18,30,31,38,39,43,49}

This study explores how variations in RFB performance due to supporting electrolyte and membrane selection impacts system cost. We focus on aqueous electrolytes, as opposed to nonaqueous electrolytes,\textsuperscript{12,50,51} due to the higher technology-readiness level of AqRBs and, consequently, the larger amount of associated device information for grid-relevant operation. First, we identify governing physical parameters, namely the membrane ASR, electrolyte conductivity, electrolyte viscosity, and cell potential, which significantly impact RFB cost. Membrane ASR can vary drastically with membrane type, working ion, or electrolyte pH.\textsuperscript{52-54} The latter two factors can also impact electrolyte conductivity and viscosity. A typically overlooked characteristic, electrolyte viscosity is of critical importance as it directly impacts mass transfer rates in the porous electrodes of a RFB, as well as required pumping power through the entire battery.\textsuperscript{55-57} As mentioned before, cell potential is a key parameter that affects the power and energy density of the RFB, both of which define RFB cost.\textsuperscript{52,56} Second, to link these materials properties to RFB cost, full-cell ASR is calculated by implementing a one-dimensional porous electrode model that solves for electrode polarization as a function of electrolyte resistivity, charge-transfer kinetics, and convective mass transfer rate. The electrode ASR contribution is combined with ASR values of ion-exchange membranes (IEMs)\textsuperscript{27,31,59} and newly proposed size-selective separators (SSS)\textsuperscript{59-65} in various supporting electrolytes. Third, we develop a techno-economic model to estimate RFB capital cost as a function of electrolyte composition and cell potential, among other detailed device parameters. The reactor cost contribution is calculated by leveraging prior literature,\textsuperscript{23,25,26} as well as developing new and more nuanced descriptions of the electrolyte cost, which enable consideration of cost differences from various supporting salts and specific inclusion of tank costs. We also implement a new estimate of balance of plant (BOP) costs, which accounts for variations in pumping costs with changes in electrolyte flow rate and viscosity, as well as reactor geometry. Combining the reactor, electrolyte, and BOP costs, as well as literature estimates of unit cost less materials,\textsuperscript{23,25} permits evaluation of variations in RFB capital cost for different AqRFB supporting electrolytes. Through this dual analysis of electrochemical performance and techno-economics, we have found that changes in supporting electrolyte or membrane selection can yield battery cost differences in the $100’s kWh\textsuperscript{-1}.

### Estimating Materials Parameters

**Ion-exchange membrane and electrolyte conductivities.** Conductivities of IEMs implemented with new RFB electrolytes are rarely reported and can vary drastically depending on the working ion\textsuperscript{52} and the properties of the surrounding supporting electrolyte.\textsuperscript{64} As such, we derive membrane ($\kappa_{\text{mem}}$) and electrolyte ($\kappa_{\text{electrolyte}}$) conductivities from a limited amount of available literature data (Table I). For H\textsuperscript{+}-IEMs, we assume the conductivity of a membrane employed in a state-of-the-art VRFB,\textsuperscript{50} and the associated electrolyte conductivity is taken as an average of VRFB electrolyte conductivities across all states-of-charge (SOCs).\textsuperscript{18} For Na\textsuperscript{+}- and Cl\textsuperscript{−}-IEMs, we estimate membrane conductivity from the high-frequency intercept of full-cell impedance measurements from published flow cells employing these membranes.\textsuperscript{53,51} As thick membranes ($\geq 120 \mu m$) were employed in the relevant studies, the high-frequency intercept on the experimental Nyquist plot is dominated by the membrane resistance. The conductivity of a NaCl-based RFB electrolyte is taken as an average value from a recent literature study.\textsuperscript{31} Although a K\textsuperscript{+}-IEM has been utilized in two experimental RFB studies,\textsuperscript{37,65} the associated conductivity has not been measured, and no impedance data is available to derive an experimental estimate. In the present work, we estimate the conductivity of K\textsuperscript{+}-IEM by scaling the conductivity of the H\textsuperscript{+}-IEMs by the ratio of ionic conductivities of the two membranes without active species present.\textsuperscript{52} In a similar fashion, we estimate the conductivity of a KOH-based electrolyte by scaling the conductivity of an average VRFB electrolyte by the ratio of the peak ionic conductivities\textsuperscript{66} of H\textsuperscript{2}SO\textsubscript{4} and KOH. From prior systematic studies of Naion conductivity with various working ions in supporting electrolyte (no active species), we anticipate that cation-exchange membrane conductivity will decrease in the following order: H\textsuperscript{+} > Na\textsuperscript{+} > K\textsuperscript{+}. Similarly, from prior data reporting on the conductivity of various acid and salt solutions, we anticipate that the electrolyte conductivity should decrease as: H\textsubscript{2}SO\textsubscript{4} > KOH > NaCl.\textsuperscript{56} The membrane conductivities reported in Table I are converted to a membrane ASR ($\Omega_{\text{mem}}$, $\Omega$m\textsuperscript{2}), where Figure 1a denotes the relationship among $\Omega_{\text{mem}}$, the working ion, and the membrane thickness.

| Membrane | Ion   | Salt          | $\kappa_{\text{mem}}$ (mS cm\textsuperscript{-1}) | $\kappa_{\text{electrolyte}}$ (mS cm\textsuperscript{-1}) |
|----------|-------|---------------|-----------------------------------------------|--------------------------------------------------|
| Naion    | H\textsuperscript{+} | H\textsubscript{2}SO\textsubscript{4} | 21\textsuperscript{b} | 280\textsuperscript{b} |
| Naion    | Na\textsuperscript{+} | NaCl          | 7.9 \textsuperscript{+}2.7 | 150\textsuperscript{+}1 |
| Naion    | K\textsuperscript{+} | KOH           | 3.2 \textsuperscript{+}0 | 200 \textsuperscript{+}0 |
| AEM     | Cl\textsuperscript{−} | NaCl          | 5.3 \textsuperscript{+}3.1 | 150\textsuperscript{+}1 |
| SSS\textsubscript{Na} | H\textsuperscript{+} | SO\textsubscript{4}\textsuperscript{2−} | 110 \textsuperscript{+}c | 280\textsuperscript{+}b |
| SSS\textsubscript{Na} | Na\textsuperscript{+} | NaCl          | 41 \textsuperscript{+}c | 150\textsuperscript{+}1 |

*\textsuperscript{a}Estimated from experimental impedance data in the associated reference.*

*\textsuperscript{b}Estimated by scaling H\textsuperscript{+}/K\textsuperscript{+} conductivity without active species.\textsuperscript{52,66}

*\textsuperscript{c}Estimated from Bruggeman relation (Equation 1).
for blocking oligomeric or polymeric active species in RFBs.\(^6\) The relationship between diffusion coefficient and electrolyte viscosity is plotted (Figure 1b) for both solvated radii, indicating that larger active species will exhibit slower transport rates. While this analysis does not explicitly consider the case of transport for large redox-active polymers\(^6\) (RAPs) in AqRFBs, the case of a high viscosity electrolyte, with large active species, likely mimics their transport rates, assuming Newtonian flow behavior.

\[
D = \frac{k_B T}{6 \pi \mu r}
\]  

The diffusion coefficient of an active material describes transport in the absence of forced convection and must be mathematically connected to a description of mass transport within a flow-through porous electrode. The total effective mass transfer rate \((k_m, \text{m}^{-1})\), in a porous carbon electrode, can be described in two steps (Equation 3), including the macro-scale mass transfer rate from the flow-field channel to the electrode pores \((k_p, \text{m}^{-1})\) and the pore-scale mass transfer rate \((k_m, \text{m}^{-1})\):\(^7\)

\[
k_m = (k_p^{-1} + k_p^{-1})^{-1}
\]

The macro-scale transport rate is provided in Equation 4, where \(\alpha\) and \(\beta\) \((\text{m s}^{-1})\) are constants specific to the porous electrode, and \(v_e\) is the intra-electrode electrolyte velocity \((\text{m s}^{-1})\).\(^7\) \(\alpha\) and \(\beta\) values for transport to a carbon fiber electrode are available in Ref. 78.

\[
k_p = \beta v_e \alpha
\]

We employ an empirical relationship (Equation 5) for the pore-scale mass transfer rate (Figure 1c), measured for the case of vanadium transport in a porous carbon-felt electrode,\(^3\) where \(d_j\) is the electrode fiber diameter \((\text{m})\) and Re is the Reynolds number \((-)\) for the electrolyte within the porous electrode. For this work, the electrode fiber diameter is assumed to be that of SGL 25AA \((d_j \approx 7 \mu \text{m})\).\(^7\) Note that the diffusion coefficient is not constant in the present analysis and has a dependence on the electrolyte viscosity (Equation 2).

\[
\frac{k_p d_j}{D} = 2 + 1.534 \text{Re}^{0.912}
\]

The Re associated with the porous electrode, sometimes referred to as the Blake number, is similarly defined as in the case of a packed particle bed reactor (Equation 6). In Equation 6, \(\rho\) is the electrolyte density \((\text{kg m}^{-3})\) and \(\varepsilon\) is the electrode porosity \((-)\). For this work, the electrolyte density is assumed to be that of water \((\rho = 1000 \text{ kg m}^{-3})\), and the electrode porosity is that of SGL 25AA carbon paper under \(\approx 20\%\) compression \((\varepsilon = 0.75)\).\(^7\) The intra-electrode velocity \((v_e)\) is calculated as the mean velocity over the rib of an interdigitated flow field (IDFF) from a typical high performance VRFB experiment \((v_e = 0.025 \text{ m s}^{-1})\).\(^8\) All relevant electrode and transport properties are listed in Table II.

\[
Re = \frac{\rho v_e d_j}{\mu \varepsilon}
\]

**Computing Cell Area Specific Resistance**

The full-cell ASR \((R_{DC}, \Omega \text{ cm}^{-2})\) can broadly be described as the summation of membrane \((R_{mem})\), contact \((R_{contact})\), and electrode resistances \((R_{electrode})\) in the cell (Equation 7). Contact resistances assume a fixed experimental value of 35 mΩ cm\(^2\) for SGL 25AA carbon paper under 20% compression on a typical carbon composite bipolar plate with an IDFF.\(^8\) The membrane resistances are derived from Figure 1a, assuming an optimistically thin membrane of 25 μm, the dry thickness of Nafion N211.\(^8\)

\[
R_{DC} = 2(R_{contact} + R_{electrode}) + R_{mem}
\]
The electrode resistance model.—The electrode resistance contribution to $R_{DC}$ is computed using a one-dimensional, steady-state porous electrode polarization model from a recent publication, and this model was validated with experimental flow cell polarization data employing various flow fields and electrolyte flow rates. The model calculates individual electrode polarization, accounting for overpotential losses due to the convective mass transfer, Butler-Volmer reaction kinetics, and the electrolyte resistivity in the pore-phase of the porous electrode. Importantly, this steady-state model assumes that variations in active species concentration in an electrode are negligible in the directions parallel to the separator, which holds true when the electrolyte flow rate is very high relative the rate of change in battery SOC (i.e., low reactant conversion per pass). This assumption aligns with high power RFB cell design, where typically the mass transfer increases afforded by pumping the electrolyte faster lead to improvements in power density that vastly outweigh the pumping losses associated with the faster flowing electrolyte. To briefly summarize the full derivation and analysis available in Ref. 82, Equations 8 through 16 describe how the overpotential distribution and, subsequently, the current distribution in the porous electrode are computed, using all dimensionless parameters.

The second derivative of the overpotential distribution $d^2\tilde{\eta}/d\tilde{x}^2$ with respect to the position in thickness of the electrode is proportional to the overall electrochemical reaction rate (Equation 8), which is a function of several dimensionless parameters. Equation 8 is specifically derived for an electrode at 50% SOC, with transfer coefficients $a_m = a_c = 0.5$, and the solid-phase electrode conductivity ($2200 \pm 2700$ mS cm$^{-1}$)[68] is much higher than the electrolyte conductivity (see Table I).

$$\frac{d^2\tilde{\eta}}{d\tilde{x}^2} = \frac{2\nu^2 \tanh(\frac{\tilde{x}}{2})}{1 + 2\nu \tanh(\frac{\tilde{x}}{2})}$$  \[8\]

$\tilde{\eta}$ is the dimensionless overpotential, which is defined as the overpotential ($\eta$, V) normalized by the thermal potential ($RT/F$, V), where $R$ is the gas constant ($8.314$ J mol$^{-1}$ K$^{-1}$) and $F$ is the Faraday constant (96485 C mol$^{-1}$):

$$\tilde{\eta} = \frac{\eta}{RT/F}$$  \[9\]

$\tilde{x}$ is the dimensionless position in the porous electrode, where $x$ is position (m) and $L_e$ is the electrode thickness (m):

$$\tilde{x} = \frac{x}{L_e}$$  \[10\]

$\tilde{c}$ is the dimensionless concentration, which is defined as the active species concentration ($c$, mol m$^{-3}$) normalized by the reference concentration ($c^r$, typically $1000$ mol m$^{-3}$):

$$\tilde{c} = \frac{c}{c^r}$$  \[11\]

$\nu^2$ is the dimensionless exchange-current density (Equation 12), where $a$ is the electrode area per volume (m$^2$ m$^{-3}$), $i_0$ is the exchange-current density (A m$^{-2}$) and $\kappa_{eff}$ is the effective electrolyte conductivity in the porous electrode (S m$^{-1}$). Physically, $\nu^2$ represents the ratio of charge-transfer and ion-conduction rates in the porous electrode.

$$\nu^2 = \frac{Fa_iL^2}{\kappa_{eff}RT}$$  \[12\]

$\theta$ is the dimensionless limiting current (Equation 13), defined as the ratio between the exchange and limiting current densities ($i$, A m$^{-2}$). Physically, $\theta$ represents the ratio of charge-transfer and mass transfer rates in the porous electrode.

$$\theta = \frac{i_0}{i}$$  \[13\]

The limiting current density relates to the mass transfer coefficient (Equation 14), where $n$ is the number of electrons transferred per active molecule (-).

$$i_t = nFc_{k_{as}}$$  \[14\]

The dimensionless overpotential distribution in the electrode can be determined by setting a constant overpotential boundary condition at the membrane-electrode interface ($\tilde{\eta} = 0$) and a zero ionic current boundary condition at the electrode-current collector interface ($\tilde{x} = 1$). Once the overpotential distribution has been solved numerically, the dimensionless current density ($\nu^2$) passing through the membrane can be derived (Equation 15).

$$\delta = -\frac{1}{2} \left( \frac{d\tilde{\eta}}{d\tilde{x}} \right)_{\tilde{x}=0}$$  \[15\]

The geometric cell current density ($J$, A m$^{-2}$) is related to $\nu^2$ by Equation 16.

$$J = 2\theta \frac{\kappa_{as}RT}{L_eF}$$  \[16\]

Now that current density can be related to the overpotential at the membrane-electrode interface, we can generate polarization curves that describe the current-voltage characteristic of RFB electrodes at 50% SOC. Relevant values of the $\theta$ parameter can be computed by relating $\theta$ to $k_{as}$ (Figure 1c). The effective electrolyte conductivity in the porous electrode ($\kappa_{as}$) is found by using the Bruggeman relation (Equation 1) and the relevant electrolyte conductivity (Table I). The electrode area per unit volume ($a$, m$^2$ m$^{-3}$) is estimated using Equation 18 and listed in Table II.[83] Given these relations, values of $\theta$ can be generated as a function of experimentally measured mass transfer coefficients and the dimensionless exchange current density ($\nu^2$).

$$\theta = \frac{\kappa_{as}RT}{F a L e^2 F c_{k_{as}}}$$  \[17\]

$$\nu^2 = \frac{4(1 - \epsilon)}{d_f}$$  \[18\]

Figure 2a illustrates electrode polarization for various Re with optimistically fast reaction kinetics ($\nu^2 = 2$) and a large active species ($r = 3$ nm), with a H$_2$SO$_4$-based electrolyte. Polarization calculations are performed assuming 1.5 M total active species concentration, a target value for AqRFBs.[23] Varying active species concentration is a commonly explored electrolyte design parameter, so, to focus on the underreported role of supporting electrolyte composition and viscosity, the present study does not vary active species concentration. Further, while the 50% SOC model assumption does not capture ASR variations due to changes in active species concentration that may affect charge or mass transfer resistances, the ASR at 50% SOC represents the average cell performance throughout the battery’s discharge; at high SOC (>50%), cell ASR for discharge will be smaller, whereas at low SOC (<50%), ASR for discharge will be larger. Incorporating a SOC-dependent ASR model would require knowledge of a characteristic discharge profile, which would also narrow the applicability.
An overpotential of 60 mV aligns with voltaic efficiency targets (91.6%)[29] during both charge and discharge for AqRFBs, assuming a large cell potential of 1.5 V;[23,29] hence, during typical operation, a RFB electrode at 50% SOC should be polarized by a maximum of ≈ 60 mV.

Figure 2b plots $R_{\text{electrode}}$ as a function of $R_e^{-1}$ for three values of the dimensionless exchange current density (small active species, $r = 1$ nm, H$_2$SO$_4$-based electrolyte), highlighting the critical role of reaction kinetics in defining $R_{\text{electrode}}$. Increasing $\nu$ can deliver significant reductions in $R_{\text{electrode}} (>0.25 \, \Omega \, \text{cm}^2)$, while varying Re changes $R_{\text{electrode}}$ by as much as 0.03 $\Omega \, \text{cm}^2$ across the range of Re under consideration for the small active species. As $\nu$ increases, $R_{\text{electrode}}$ becomes more sensitive to Re because the relative contribution of charge-transfer losses shrinks. Since one motivation for implementing a new active material or supporting electrolyte in a RFB is improved reaction rates,[30] all subsequent calculations will incorporate optimistically large exchange current densities. While the kinetic rate constant of an electrochemical reaction is an important factor in determining overall cell performance and cost, reaction kinetics within RFBs has been studied extensively, with many reports identifying new catalysts or electrode treatments to reduce activation polarization losses.[3,5,8] Moreover, in a previous report, Darling et al. contemplate the cost implications of active species with varying kinetic rates.[24] Thus, the present report focuses on the case of optimistically fast kinetics (i.e., $\nu = 2.0$) to highlight the cost implications of underreported factors: charge carrier identity, salt cost, and electrolyte viscosity. Our value of $i_0$ is estimated by first assuming that cells with even the highest electrolyte conductivities (i.e., H$_2$SO$_4$-based supporting electrolyte) will be ohmic-limited. As such, the H$_2$SO$_4$-based electrolyte is assigned a $\nu = 2.0$, corresponding to $i_0 = 7.26 \, mA \, \text{cm}^{-2}$, and this exchange current is fixed in all subsequent analyses. For reference, our estimated value of $i_0$ is similar to that of AQDS on carbon paper (12.3 $mA \, \text{cm}^{-2}$),[39] which is known to exhibit rapid kinetics in H$_2$SO$_4$-based electrolytes.[39,34]

Figure 2c shows electrode resistances as a function of $R_e^{-1}$ for H$_2$SO$_4$-, NaCl-, or KOH-based electrolytes with small active species ($r = 1$ nm), as well as H$_2$SO$_4$- or NaCl-based electrolytes and large active species ($r = 3$ nm). All resistance curves in Figure 2c employ the high value of exchange current density previously mentioned. As the electrolyte conductivity decreases (i.e., H$_2$SO$_4$ to KOH), the electrode resistance increases due to a larger ohmic loss through the porous phase of the electrode. This phenomena is especially apparent in the limit of infinitely fast mass transfer (Figure 2c, y-intercept), where the variation in $R_{\text{electrode}}$ among the three supporting electrolytes is strictly imposed by differences in the electrolyte conductivity. Between the H$_2$SO$_4$ and NaCl electrolytes, changes in the electrolyte conductivity can increase the total electrode resistance by a small value of 0.04 $\Omega \, \text{cm}^2$; this difference will be exacerbated if thick (i.e., $> 300 \, \mu m$) porous electrodes are selected. Further, the sensitivity of electrode resistance to changes in Re increases as the active species size increases; the large active species ($r = 3$ nm) induces a change in $R_{\text{electrode}}$ of 0.10 $\Omega \, \text{cm}^2$ across the range of Re considered, while the small active ($r = 1$ nm) species causes an increase of only 0.03 $\Omega \, \text{cm}^2$. The larger active species exhibits lower diffusion coefficients (Figure 1b), invoking slower mass transport rates (Figure 1c) and subsequently causing greater electrode sensitivity to Re (Figure 2c).

**Full cell area-specific resistance.**—One can now estimate the full-cell ASR ($R_{\text{DCC}}$. Figure 3) of an AqRFB employing various working ions, membranes (IEMs or SSS), or electrolyte viscosities by incorporating the values of $R_{\text{electrode}}$ (Figure 2c) into Equation 7. Note that the present analysis considers a fixed IEM or SSS thickness of 25 $\mu m$, and lower (or higher) ASR values could be achieved if the thickness were further reduced (or increased). Estimates of $R_{\text{DCC}}$ for IEM-based RFBs assume transport rates for small active species ($r = 1$ nm) with H$_2$SO$_4$-, NaCl-, or KOH-based supporting electrolytes, whereas estimates for SSS-based RFBs assume transport rates for large active species ($r = 3$ nm) with H$_2$SO$_4$- or NaCl-based supporting electrolytes. Changing the type of ion passing through a membrane leads to a linear increase of our modeling efforts. Such a model and necessary experimentation would not exhibit the transparency and computational efficiency of the polarization model used here. Fixing the SOC at 50% in the present analysis permits mathematical simplification, offers a reasonable estimate of cell performance throughout discharge, and provides multiple parameters to analyze.

For all Re in Figure 2a, as the current density through the cell increases, the overpotential drop across the electrode increases, but, as $R_e$ increases, a smaller overpotential is required to drive the same current through the electrode. This trend occurs because increasing Re correlates with a higher rate of convective mass transfer (i.e., smaller viscosity, increased flow rate), yielding lower mass transfer resistances. Re = $\infty$ represents the case of infinitely fast mass transport, where the electrode experiences losses only due to charge-transfer and electrolyte resistivity. The low overpotential regime ($\leq 60 \, mV$) of the polarization curves is linearized to derive a value $R_{\text{electrode}}$ for each Re.

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Figure 2. (a) Electrode polarization for multiple Re values with $\nu = 2.0$, $r = 3 \, \text{nm}$, and H$_2$SO$_4$-based electrolyte. (b) Computed values of $R_{\text{electrode}}$ as a function of $R_e^{-1}$ for multiple $\nu$ values, $r = 1 \, \text{nm}$, and H$_2$SO$_4$-based electrolyte. (c) Computed values of $R_{\text{electrode}}$ as a function of Re$^{-1}$ for the various electrolytes under consideration ($\nu = 2.0$).
or decrease in $R_{DC}$ due to variations in membrane conductivity, while increasing Re (lower $Re^{-1}$) decreases $R_{DC}$ due to a higher rate of convective mass transfer. When considering the SSS case, both the NaCl and H$_2$SO$_4$ systems offer the lowest $R_{DC}$ at high Re, however, at sufficiently low Re, the H$^+$-IEM outperforms both SSS options. While we do not explicitly consider the effects of temperature on ASR, the resistance contribution plots (e.g., Figure 1a, Figure 2b, Figure 2c, Figure 3) can illustrate the role of increasing temperature on decreased cell ASR; raising temperature will increase charge and mass transfer rates, as well as electrolyte and membrane conductivities, all of which will decrease cell ASR.

Figure 3 illustrates a critical balance in membrane and supporting electrolyte selection, where the membrane conductivity and electrolyte viscosity must be optimized to deliver the lowest $R_{DC}$ possible. The Na$^+$-, Cl$^-$-, and K$^+$-IEMs afford much higher ASR (up to 3.1×) than the H$^+$-IEM or SSS. Multiple techno-economic analyses have recommended a target $R_{DC}$ $\approx$ 0.5 $\Omega$ cm$^2$ for cost-effective AqRFBs, indicating that only a few of the membrane and working ion combinations presented in Figure 3 could achieve DOE cost targets, in the regime of high Re. The next section uses a techno-economic model to estimate complete RFB capital costs for the different membrane and supporting salt options under consideration here, so that the reader may better appreciate the cumulative cost impact of all the RFB components.

**Pressure Drop and Pump Power Requirement**

**Pressure drop.—** We assume that AqRFBs will employ state-of-the-art IDFFs, which have been shown to balance excellent electrochemical performance with an acceptable pressure drop. Antony and Perry described a series of analytical equations to calculate the pressure drop through an IDFF for flow batteries using a formulation and Perry described a series of analytical equations to calculate the pressure drop through an IDFF for flow batteries using a formulation and Perry described a series of analytical equations to calculate the pressure drop through an IDFF for flow batteries using a formulation and Perry described a series of analytical equations to calculate the pressure drop through an IDFF for flow batteries using a formulation.

The pressure drop through a channel within the IDFF is computed according to Equation 20, where $v_{ch}$ is the electrolyte velocity in the channel (m s$^{-1}$), $L_{ch}$ is the channel length (m), and $d_h$ is the channel hydraulic diameter (m).

$$\Delta P_{ch} = \frac{32\mu v_{ch} L_{ch}}{d_h^2}$$  \hspace{1cm} [20]

Since a rectangular channel is assumed, the $d_h$ can be calculated in Equation 21, where $w_{ch}$ is the channel width (m), and $h$ is the channel height (m). In this work, $w_{ch}$ and $h$ have fixed dimensions of 0.00117 m and 0.00076 m, respectively, based on a recent experimental RFB study employing IDFFs.

$$d_h = \frac{2w_{ch}h}{w_{ch} + h}$$  \hspace{1cm} [21]

The channel velocity is defined in Equation 22, where $N$ is the number of inlet channels in the flow field (−), and $Q$ is the electrolyte flow rate through one side of a single cell (m$^3$ s$^{-1}$).

$$v_{ch} = \frac{Q}{N w_{ch} h}$$  \hspace{1cm} [22]

The channel and intra-electrode velocity for the IDFF are related, as shown in Equation 23.

$$\frac{v_{ch}}{v_{rib}} = \frac{w_{ch} h}{L_{ch} w_{rib}}$$  \hspace{1cm} [23]

The geometric factor, $\zeta$, in Equation 19 is defined in Equation 24, where $k$ is the electrode permeability (m$^2$), Table II and $S$ is the mean path length of the electrolyte through the electrode and over the rib (m).

$$\zeta = \frac{128L_{ch}^2 k L_e}{S d_h^2 w_{ch} h}$$  \hspace{1cm} [24]

While $S$ can be numerically computed for the IDFF, such a calculation is beyond the scope of this work. We estimate $S$ as given in Equation 25, where $w_{rib}$ is the width (m) of the rib in the IDFF, $w_{rib}$ has a fixed dimension of 0.00089 m, based on a recent experimental RFB study employing IDFFs.

$$S \approx w_{ch} + w_{rib} + L_e$$  \hspace{1cm} [25]

Later estimates of pump cost will consider cells with a total width ($W$) of 26 cm and $L_{ch} = 31.2$ cm ($L_{ch}/W = 1.2$), which are similar dimensions to k-W-scale flow cells, resulting in a cell active area of 811 cm$^2$. For fixed channel and rib widths, $W$ defines the number of inlet channels and ribs in the IDFF (for $W = 26$ cm, $N_{ch} = 80$). To briefly illustrate how pressure drop varies with cell aspect ratio ($L_{ch}/W$), consider Figure 4a, which plots the pressure drop through a single side of one cell against inverse mass transfer coefficient within the porous electrode, both of which are functions of electrolyte flow rate. Figure 4a illustrates the tradeoff between pressure drop and mass transfer rate for a small (r = 1 nm) active species. As expected, larger convective mass transfer rates (smaller $k_m$) will require higher pressure drops. Further, as the aspect ratio increases (higher $L_{ch}/W$), a larger pressure drop is required to sustain the same mass transfer rate, due to a larger flow rate requirement to sustain the same intra-electrode velocity.

**Pump power requirement.—** The required pump power ($P$, W) to pass electrolyte through a single side (positive or negative electrolyte) of a RFB can be computed as shown in Equation 26, where $\eta_{pump}$ is the pump efficiency (−), and $N_{cells}$ is the number of cells in the electrochemical stack (−).

$$P = \frac{\Delta P Q N_{cells}}{\eta_{pump}}$$  \hspace{1cm} [26]

The primary goal in evaluating pump power requirement here is to account for the capital cost of appropriately sized pumps for an aqueous RFB stack, however, the importance of designing a RFB with
sufficiently low pump power requirement, relative to the stack output power, should not be overlooked. The pump power requirements plotted in Figure 4 align with state-of-the-art system efficiencies at lower transport rates for our assumed stack geometry. A stack with 1.4 V OCP, 0.4 \text{s} m^{-1} is the assumed upper transport rates for our assumed stack geometry. A stack with 1.4 V OCP, 0.4 \text{s} m^{-1} ASR, 91.6% voltage efficiency, aspect ratio of 1.2, and 60 cells delivers a total power of \approx 18.3 kW, indicating that \approx 0.92 kW of pump power, for two electrolyte streams, can be afforded to maintain \approx 5% system efficiency loss. In subsequent cost calculations, we will assume an optimistic system efficiency of 94%, which accounts for energy losses due to pumping, power electronics, and thermal management equipment. Critically, when designing a specific, new electrolyte, the pump power requirement must be compared with the nominal battery power output to ensure high system efficiency. For example, a battery with relatively low cell potential, high viscosity, poor flow field design, and low mass transfer rates (e.g., high viscosity, poor flow field design) could engender a RFB design where the pump power actually exceeds the power output from the electrochemical stack. Identifying the viable regions of the efficiency design space is outside the scope of the present analysis, but must be considered when evaluating new, specific RFB chemistries.

Techno-Economic Modeling

The following sections describe the integration of the flow battery ASR model and pump power requirement calculation with a techno-economic model that evaluates RFB cost as a function of many design, chemical, and cost input parameters. Benchmarking the quality of a techno-economic model is challenging considering the lack of available detailed engineering designs, costs, and profit margins for commercially available RFBs. In an attempt to validate the techno-economic model, we input literature parameters for state-of-the-art RFB component costs and performance,\textsuperscript{18,23,25,58} and we subsequently compared our cost estimate to a few other recent published values (Table III). Note that each of the literature values in Table III were computed with different models and may not incorporate the same capital cost considerations; for example, unlike Darling and Gallagher et al., Viswanathan et al. did not consider a profit margin in their RFB cost calculations. In particular, while we have utilized the reactor cost model from Darling and Gallagher et al., all other cost components in the present analysis are computed using new models.

Reactor cost.—To begin bridging membrane and supporting electrolyte selection to RFB cost, the full-cell ASR can be incorporated into a description of RFB reactor cost. In the present analysis, RFB reactor cost \(C_{reactor} (\$ \text{kW}^{-1})\) is defined similarly to prior literature (Equation 27),\textsuperscript{23,26} where \(U\) is the cell potential (V), \(\varepsilon_{sys}\) is the system efficiency (-), and \(\varepsilon_{v}\) is the voltaic efficiency (-). Additionally, \(c_{stack}\) is the areal cost of the electrochemical stack materials ($ m^{-2}$), including bipolar plates, gaskets, electrodes, and current collectors, and \(c_{mem}\) is the areal membrane (or separator) cost ($ m^{-2}$). \(\varepsilon_{sys}\) is the system efficiency (-), and \(\varepsilon_{v}\) is the voltaic efficiency (-). Additionally, \(c_{stack}\) is the areal cost of the electrochemical stack materials ($ m^{-2}$), including bipolar plates, gaskets, electrodes, and current collectors, and \(c_{mem}\) is the areal membrane (or separator) cost ($ m^{-2}$).

\[
C_{reactor} = \frac{(c_{stack} + c_{mem})R_{DC}}{\varepsilon_{sys}(1 - \varepsilon_{v})U^{2}}
\]

Note that in the present analysis, we separate the stack hardware cost from the membrane cost to offer a more flexible framework for incorporating various membranes. This treatment contrasts prior studies that lump these two costs into one term.\textsuperscript{23,26} We also consider present and future-state areal reactor and membrane costs, since these material costs are anticipated to decrease with bulk purchasing required for future large-scale manufacturing, which will be described later (see Unit cost less materials section). Estimates of the electrochemical stack costs and IEMs are adapted from prior literature for present and future-state (Table IV).\textsuperscript{23,24} Note that emerging IEM technologies, such as hydrocarbon-based options,\textsuperscript{29} could reduce membrane costs relative to Nafion. Estimates for present and future-state areal reactor and membrane costs, since these material costs are anticipated to decrease with bulk purchasing required for future large-scale manufacturing, which will be described later (see Unit cost less materials section). Estimates of the electrochemical stack costs and IEMs are adapted from prior literature for present and future-state (Table IV).\textsuperscript{23,24} Note that emerging IEM technologies, such as hydrocarbon-based options,\textsuperscript{29} could reduce membrane costs relative to Nafion. Estimates for present and future-state areal reactor and membrane costs are extracted from Figure 3. Hence, the reactor cost is described as a function of the full-cell ASR. As \(R_{DC}\) increases, a larger area electrochemical stack is required to drive the same total current at the same voltaic efficiency, yielding a more expensive reactor overall.

Table III. Comparison of recent VRFB capital cost estimates and reports, as compared to the value generated by the present model.

| Report                     | Year | VRFB Capital Cost ($ kWh\textsuperscript{-1}) |
|----------------------------|------|---------------------------------------------|
| Viswanathan et al.\textsuperscript{24} | 2014 | 489                                         |
| Darling and Gallagher et al.\textsuperscript{23} | 2014 | 185                                         |
| Lazard’s Levelized Cost of Storage\textsuperscript{26} | 2016 | 430 to 1010                                 |
| Vionx Radio Interview\textsuperscript{20} | 2017 | 400                                         |
| Present Model              | 2017 | 469                                         |

Figure 4. (a) Calculated pressure drop through one side of a single RFB cell employing an IDFF, with a total width of 26 cm. (b) Calculated pump power requirement for a single electrolyte stream passing through a RFB stack, where \(N_{cells} = 60\). The legend numbers denote the \(L_{d}/W\) ratio.
volumes due to implementation of the relatively inexpensive separator, as compared to the IEM.

Again considering Equation 27, as the combined stack and membrane cost ($c_{\text{stack}} + c_{\text{mem}}$) per unit area decreases, the total reactor cost ($C_{\text{reactor}}$) becomes less sensitive to differences in $R_{\text{DC}}$. Figure 5b explicitly illustrates how the total reactor cost grows as a function of $c_{\text{stack}} + c_{\text{mem}}$, for the different membrane/working ion configurations, where larger values of $R_{\text{DC}}$ necessitate that the reactor cost grows more quickly with larger $c_{\text{stack}} + c_{\text{mem}}$. This sensitivity to the stack and membrane costs indicates that RFBs with more expensive cell components must offer lower cell ASR to keep reactor costs down. Considering that present-day stack and membrane costs are much higher than their anticipated future-state costs at mass-scale production, engineering low ASR cells today via rational selection of membranes and supporting salts is of the utmost importance in facilitating early adoption of RFBs. Given that SSS are anticipated to be more than an order-of-magnitude less expensive than IEMs, assuming present cost estimates, the SSS is an attractive option to pursue when reactor costs (ca, $\text{s/m}^2$) are high.

**Electrolyte cost.**—Equation 28 describes the total electrolyte cost normalized by the energy delivered upon discharge ($C_{\text{electrolyte}}$, $\text{S/kWh}^{-1}$) with the following parameters: $\epsilon_{\text{ct}}$ is the coulombic efficiency (-), $F$ is the Faraday constant (0.0268 kAh), $M$ is the molar mass of the active material (kg mol$^{-1}$), $s$ is the stoichiometric coefficient of the discharge reaction (-), $\chi$ is the depth-of-discharge (-), $n_r$ is the number of electrons stored per mole of active material (-), $c_m$ is the active species cost per unit mass ($\text{S/kg}^{-1}$), $r_{\text{salt}}$ is the arithmetic mean ratio of moles of salt per mole of active species across both electrolytes (-), $M_{\text{salt}}$ is the molar mass of the supporting salt (kg mol$^{-1}$), $c_{\text{salt}}$ is the salt cost per unit mass ($\text{S/kg}^{-1}$), $c_r$ is the tank cost per unit volume ($\text{S/L}^{-1}$), and $\bar{\epsilon}$ is the mean active species molarity across both sides of the cell (M). Note that the present model explicitly accounts for the salt and tank cost contributions to the electrolyte cost, in contrast with prior reports. The plus/minus subscripts denote the positive/negative sides of the battery, respectively. The cost of water as a solvent is neglected in this estimate as the cost contribution of deionized water ($\approx$ $0.001 \text{S/kg}^{-1}$) is at least one order-of-magnitude lower than all other electrolyte components. Tank cost is fixed at $0.15 \text{S/L}^{-1}$ for all electrolytes under consideration since inexpensive polypropylene or polyethylene tanks should be chemically compatible across all pH. Additionally, the coulombic efficiency and allowable SOC range are set to 97% and 80%, respectively.

$$C_{\text{electrolyte}} = \frac{1}{\epsilon_{\text{ct}}F} \left[ \frac{s_r M c_{m, r}}{n_r \bar{\epsilon} X_r} + \frac{s_r M c_{m, r}}{n_r \bar{\epsilon} X_r} + 2 \left( r_{\text{salt}} M_{\text{salt}} c_{\text{salt}} + c_r \right) \right] \ [28]$$

Since one motivation for designing a new AqRFB electrolyte is to leverage inexpensive active materials, we assume an optimistically low cost for the active material of $\text{S/kg}^{-1}$. Precursors to some proposed ROMs come close to this value today. For example, anthraquinone is a precursor to multiple proposed ROMs and costs $\approx$ $4.40 \text{S/kg}^{-1}$. For comparison, vanadium sulfate costs $\approx$ $22 \text{S/kg}^{-1}$ and sulfur (S$_8$) costs $\approx$ $0.20 \text{S/kg}^{-1}$. The active species molecular weight is another key parameter that defines electrolyte cost because the molecular weight normalized by the number of electrons

| Modeling Parameter | IEM + Small Active Species | SSS + Large Active Species |
|--------------------|-----------------------------|-----------------------------|
|                    | Present | Future | Present | Future |
| Stack cost per unit area, $c_{\text{stack}}$ | $\text{S/m}^2$ | $\text{S/m}^2$ | $\text{S/m}^2$ | $\text{S/m}^2$ |
| Membrane cost, $c_{\text{mem}}$ | $\text{S/m}^2$ | $\text{S/m}^2$ | $\text{S/m}^2$ | $\text{S/m}^2$ |
| OCP, $U$ | 1.4 V | 1.5 V | 1.4 V | 1.5 V |
| Discharge time, $t_d$ | 5 h | 5 h | 5 h | 5 h |
| System discharge efficiency, $\epsilon_{\text{sys}}$ | 0.94 | 0.94 | 0.94 | 0.94 |
| Voltage discharge efficiency, $\epsilon_{r}$ | 0.916 | 0.916 | 0.916 | 0.916 |
| Round-trip coulombic efficiency, $\epsilon_{\text{ct}}$ | 1 | 1 | 1 | 1 |
| Stoichiometric coefficient, $s$ | 0.80 | 0.80 | 0.80 | 0.80 |
| Allowable state-of-charge range, $\chi$ | 100 g mol$^{-1}$ | 100 g mol$^{-1}$ | 125 g mol$^{-1}$ | 125 g mol$^{-1}$ |
| Equivalent weight, $M_r$ | $\text{S/kg}^{-1}$ | $\text{S/kg}^{-1}$ | $\text{S/kg}^{-1}$ | $\text{S/kg}^{-1}$ |
| Actives cost per unit mass, $c_m$ | $\text{S/kg}^{-1}$ | $\text{S/kg}^{-1}$ | $\text{S/kg}^{-1}$ | $\text{S/kg}^{-1}$ |
| Mean molar salt ratio, $n_r$ | 1 | 1 | 1 | 1 |
| Mean active Species Molarity, $\bar{\epsilon}$ | 1.5 M | 1.5 M | 0.15 L$^{-1}$ | 0.15 L$^{-1}$ |
| Tank Cost, $c_r$ | $\text{S/L}^{-1}$ | $\text{S/L}^{-1}$ | $\text{S/L}^{-1}$ | $\text{S/L}^{-1}$ |
transferred (equivalent weight (g mol\(^{-1}\))) specifies the mass of active material that must be purchased to store a certain amount of charge. In the present analysis, we assume a moderate equivalent weight of 100 g mol\(^{-1}\) for small active species.\(^{26}\) For comparison, the equivalent weight of vanadium is 51 g mol\(^{-1}\), whereas AQDS has an equivalent weight of 184 g mol\(^{-1}\), assuming that AQDS has 2e\(^{-}\) transfer capability.\(^{39}\) In the case of RFBs with SSS, we estimate that the active species equivalent weight must be \(\approx 1.25 \times \) that of a small active species, paired with an IEM, to successfully implement size exclusion; this equivalent weight increase is similar to that of the added molecular weight imposed by linkers between redox-active centers on oligomerized ROMs.\(^{60}\) Finally, the active-species concentration is set to 1.5 M, for consistency with previous cell polarization calculations, in determining RFB cost.\(^{26}\) The molar masses and costs for H\(_2\)SO\(_4\), NaCl, and KOH are listed in Table V. Figure 6 shows how electrolyte cost varies as a function of \(r_{\text{salt}}\) for the salt types listed in Table V for small active species with H\(_2\)SO\(_4\), NaCl, or KOH as the supporting salt, or large active species with H\(_2\)SO\(_4\) or NaCl. \(r_{\text{salt}}\) represents the number of moles of salt per mole of active species on one side of the RFB, and typical \(r_{\text{salt}}\) values for VRFB electrolytes can vary between 0.7–2.\(^{39,97}\) For comparison, recent studies on new AqRFB active species experimentally illustrated that by employing multifunctional, ionic active species, the need for a separate supporting salt can be eliminated.\(^{30,98}\) The slopes of the electrolyte cost curves in Figure 6 are defined by the salt costs (\(\$ \text{kg}^{-1}\)), and the y-intercepts (Figure 6) represent the cost contributions from the tanks and active species. As such, the higher equivalent weight active species yield a larger electrolyte cost in the limit of zero salt. Overall, variations in electrolyte cost with supporting electrolyte type and amount are relatively small in comparison to other cost contributions for AqRFBs.

**Balance of plant.**—The balance-of-plant (BOP) costs (\(C_{\text{BOP}}, \$ \text{kW}^{-1}\)) for RFBs typically comprise costs associated with ancillary equipment, normalized by the power output of the RFB stack. In the present work, the BOP cost accounts for thermal-management systems (e.g., heat exchangers), controls, and pumps. Note that this work does not consider power-conditioning equipment (e.g., inverters) or installation costs.\(^{26}\) Since we do not anticipate the cost of thermal management or controls to vary significantly with supporting electrolyte composition, we assume that their cost (\(C_{\text{control}}\)) is \$60 kW\(^{-1}\), as estimated in a recent RFB techno-economic analysis.\(^{23}\) Note that in the particular case of thermal management equipment, an analysis of the thermal balance of a RFB is presently unavailable, and additional research is required to define the size, design constraints, and costs associated with this equipment. Electrolytes that are tolerant to large temperature variations, unlike the VRFB,\(^{18}\) could reduce the controls cost contribution to the BOP. The total \(C_{\text{BOP}}\) is calculated as shown in Equation 29,\(^{23}\) where \(N_{\text{pump}}\) is the number of pumps required to operate the RFB and \(C_{\text{pump}}\) is the pump cost per power (\(\$ \text{kW}^{-1}\)). Since the BOP cost is normalized by the RFB stack power, \(N_{\text{pump}} = 2\) because each electrolyte stream will require one pump.

\[
C_{\text{BOP}} = C_{\text{controls}} + N_{\text{pump}} C_{\text{pump}} \tag{29}
\]

Pump cost (\(c_{\text{pump}}, \$\)) is estimated using the cost correlation in Equation 30,\(^{91}\) where \(P\) is the required pump power (kW). The pump cost (\(\$\)) as a function of required pump power is depicted in Figure 7a.

\[
c_{\text{pump}} = -1100 + 2100 \cdot P^{0.66} \tag{30}
\]

We normalize the pump cost by the power capability of the electrochemical stack (Equation 31). The variations in battery energy efficiency with changes in pumping energy requirements are typically small\(^{8,67}\) and would also require details of the battery’s thermal management system. Thus, for simplicity, we choose to hold \(k_{\text{sys}}\) constant at 94%.\(^{23}\) Figure 7b shows how pump costs (\(\$ \text{kW}^{-1}\), left axis) vary as

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**Table V. Supporting salt cost parameters used in electrolyte cost calculations.**

| Working Ion | Salt   | Molar Mass (g mol\(^{-1}\)) | \(c_{\text{salt}}\) (\(\$ \text{kg}^{-1}\)) |
|------------|--------|-----------------------------|------------------------------------------|
| H\(^+\)    | H\(_2\)SO\(_4\) | 98.1                        | 0.075\(^{26}\)                           |
| Na\(^+\)/Cl\(^-\) | NaCl     | 42.4                        | 0.055\(^{26}\)                           |
| K\(^+\)    | KOH    | 56.1                        | 0.30\(^{90}\)                            |

---

**Figure 6.** Electrolyte cost as a function of \(r_{\text{salt}}\) (the number of moles of salt per mole of active species on one side of the RFB) for different salt types and active species equivalent weights. \(U = 1.4 \text{ V}\) and \(c_m = 55 \text{ kg}^{-1}\).
a function of cell potential for the upper and lower \( \text{Re} \) values considered in this work. As the reactor performance improves via increased cell potential, the effective pump cost decreases because less total pumping power is required to deliver a certain power upon discharging the battery. Additionally, the high \( \text{Re} \) case (e.g., low viscosity) has a much weaker dependence of pump cost on cell potential because of a small pressure drop and improved mass transfer rates. Note that when normalizing the pump cost by discharge time (\( \$ \text{kWh}^{-1} \)), Figure 7b (right axis), the pump cost is \( \approx \$2 \text{kWh}^{-1} \) for nearly all design conditions, indicating that pump costs are small as compared to reactor (Figure 5) and materials costs (Figure 6) in the target discharge duration time. Thus, although varying electrolyte viscosity will impact pumping costs, the overall contribution to battery cost will be relatively small; viscosity has a significantly larger impact on cell ASR, which affects the reactor cost contribution.

\[
C_{\text{pump}} = \frac{\epsilon_{\text{pump}} R_{\text{DC}}}{\epsilon_{\text{sys}} (1 - \epsilon_t)^{U^2 L I_{\text{dc}} W}}
\]

**Unit cost less materials.**—The final cost contributions to consider for estimating RFB capital cost are termed unit cost less materials (\( C_{\text{UCLM}} \)), which is also sometimes referred to as additional costs.\(^{23,26,101} \) The unit cost less materials accounts for all RFB costs excluding purchased goods. Purchased goods refers to all RFB parts manufactured by specialty firms and implemented in the electrochemical stack, electrolyte, or BOP.\(^{25} \) For instance, carbon-paper electrodes are an example of a purchased good that will be used in the electrochemical stack, but the manufacturing cost of implementing the carbon paper in the stack falls under the unit cost less materials. The unit cost less materials in this work specifically accounts for depreciation, research and development, sales, administration, variable overhead, direct labor, and warranty costs.\(^{25} \) Note that the present analysis excludes an estimate of profit margin, which has been incorporated in prior analyses.\(^{23,25,26,101} \) As such, this work considers battery cost, as opposed to battery price.

The unit cost less materials depends on the production volume of RFB components. As production volume increases, the unit cost less materials will decrease due to increased utilization of capital-intensive manufacturing infrastructure. As before, we first consider a present-day estimate of unit cost less materials at the low RFB production volumes at the time of publication. We also consider a future-state estimate of unit cost less materials, assuming that RFB annual production achieves the volume to store \( \approx 1\% \) of the world’s energy consumption in 2013 for 5 h (2 GW, 10 GWh).\(^{25,102} \) The present-day estimate of unit cost less materials is taken to be \$1550 kW\(^{-1} \), which was originally computed by engaging a gap analysis between present-day costs of RFB materials and costs of energy storage systems in the field.\(^{25} \) For the future-state estimate, we assume values calculated by Ha and Gallagher, which are listed in Table VI for convenience.\(^{25} \)

**Battery cost.**—Now that the reactor, electrolyte, BOP costs, as well as the unit cost less materials, have been computed for all membranes and supporting electrolytes under investigation, these cost contributions can be combined in Equation 32 to describe the battery cost. The total RFB cost (\( C_{\text{battery}} \), \( \$ \text{kWh}^{-1} \)) is defined as the total cost of the battery normalized by the energy delivered upon discharge. Since the reactor, BOP, and additional costs are all defined in units of \( \$ \text{kWh}^{-1} \), their costs are normalized by a total discharge time (\( \tau_d \)) of 5 h. The DOE target capital cost of \$1.50 kW\(^{-1} \) includes the costs of power conditioning equipment and installation, which has been estimated to be \( \approx \$250 \text{kW}^{-1} \),\(^{23} \) so the \$1.50 kW\(^{-1} \) DOE target translates to a battery cost of \( \approx \$100 \text{kWh}^{-1} \) in the present analysis.\(^{25} \) Further, note that the DOE target cost is an aggressively low value that would enable ubiquitous adoption of an energy storage technology for nearly all grid-level services. Some grid-level energy storage services are more valuable than others (e.g., frequency regulation), and estimated affordable costs of energy storage for specific grid services are available in market reports, such as Lazar’s Levelized Cost of Energy Storage.\(^{22} \)

\[
C_{\text{battery}} = \left( \frac{C_{\text{reactor}} + C_{\text{BOP}} + C_{\text{UCLM}}}{\tau_d} + C_{\text{electrolyte}} \right)
\]

Figure 8 shows battery costs as a function of cell potential for the membrane and supporting salt combinations under consideration, along with a low and high value of \( \text{Re} \) number, corresponding to a 10 \( \times \) viscosity change. Present-day (Figure 8a) and future-state estimates (Figure 8b) illustrate how changes in stack and membrane cost with production volume impact battery cost. Along with Figure 8, Table VII highlights select RFB design iterations, varying cell potential, salt identity, membrane type, and electrolyte viscosity to quantitatively illustrate the range of impact on ASR, \( C_{\text{electrolyte}}, C_{\text{reactor}}, \) and \( C_{\text{battery}} \). For present-day, differences in the RFB performance and electrolyte costs can manifest as cost differences \( \approx \$100 \text{kWh}^{-1} \), in the limit of low cell potentials (< 1 V). At high cell potentials (i.e., 1.4 V), the differences are smaller, but still reaches \( \approx \$100 \text{kWh}^{-1} \) between the SSS and K\(^{+} \)-IEM designs (Table VII). Viscosity changes can induce

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**Table VI.** Cost contributions used in the estimate of future-state unit cost less materials.\(^{25} \)

| Contribution          | Cost ($ kW\(^{-1} \)) |
|-----------------------|-----------------------|
| Warranty              | 50.6                  |
| Sales & Administration | 30.0                  |
| Research & Development| 23.7                  |
| Depreciation          | 7.9                   |
| Direct Labor          | 4.7                   |
| Variable Overhead     | 3.2                   |
| \( C_{\text{UCLM}} \) | 120                   |

---

**Figure 8.** Battery cost as a function of cell potential with (a) present-day and (b) future-state costs, for various working ion/membrane types and two extreme values of \( \text{Re} \). This analysis assumes 5 h discharge time.
a difference in battery cost as high as $30 \text{ kwh}^{-1}$ for designs with higher $R_{DC}$ and low cell potential. Surprisingly, however, a 10-fold variation in electrolyte viscosity has a relatively small impact on RFB cost, as quantitatively indicated in Table VII.

For present-day costs, RFBs implementing SSS have an advantage over the IEM options. The separator cost is much lower than that of an IEM; we calculate that the SSS options are least expensive across the design space. The use of the higher conductivity electrolyte (H₂SO₄) with the SSS offers marginally better cost performance due to reduced ASR. When the stack and IEM costs decrease, as assumed for future state, SSS options with high electrolyte viscosity perform worse than IEMs with H⁺ or Na⁺ charge carriers due to the slower transport and higher materials cost associated with large active species.

The future-state cost estimates (Figure 8b) only show the high Re variation in electrolyte viscosity has a relatively small impact on RFB performance (Figure 5b). In future state estimates, variations in reactor performance (Figure 5b). In future state estimates, variations in reactor performance (Figure 5b). In future state estimates, the H⁺-SSS option yields a lower ASR than the H⁺-IEM and is anticipated to be less expensive, the SSS requires utilization of larger active materials, with higher molecular weights, than the IEM-based designs. Hence, in the future state cost projections, the higher chemical cost associated with the larger active material results in the H⁺-SSS being marginally more expensive than the H⁺-IEM according to future state costs. Finally, despite substantial cost future state cost reduction, battery costs only surpass the $100 \text{kwh}^{-1}$ guideline for cell potentials $>1.2 \text{ V}$, and the H⁺-IEM offers the best opportunity to exceed the benchmark cost, whereas the K⁺-IEM only reaches the benchmark cost with precisely a 1.5 V cell.

## Conclusions

RFBs are promising electrochemical devices for grid-scale energy storage, but their capital costs must be reduced for ubiquitous adoption. As such, recent reports have investigated new active species for RFBs geared toward lower cost or improved performance. The identification of a promising active material typically involves tailoring the supporting electrolyte to optimize stability, solubility, and reaction kinetics. The choice in electrolyte composition, however, can have a significant impact on the low cost potential of a new redox chemistry, which, to date, has yet to be systematically evaluated.

This work quantifies changes in RFB cost performance for different supporting electrolytes paired with ion-selective membranes and size-selective separators. Membrane ASR is derived from RFB reports employing cation or anion exchange membranes with various charge-carriers (H⁺, Na⁺, $\text{Cl}^-$, and K⁺) in concentrated electrolytes. The ASR contribution of the RFB electrodes is quantified by implementing a steady-state, one-dimensional porous-electrode model that describes cell overpotential as a function of current density, incorporating losses from the electrolyte resistivity, Butler-Volmer reaction kinetics, and convective mass transfer. The consideration of mass transfer losses allows us to link the description of electrode resistance to the electrolyte viscosity through a mass transfer coefficient power law correlation. The physical description of cell ASR is then integrated into a techno-economic model that estimates RFB cost for the different membrane and supporting electrolyte options under consideration, accounting for the reactor, electrolyte, BOP, and additional costs. Variations in cell performance due to the working ion selection and electrolyte viscosity can yield battery cost differences in the $100's \text{kwh}^{-1}$, and this analysis allows for quantification of cost performance changes by selecting certain electrolyte characteristics. The battery cost curves in Figure 8 can also be used to quantify how much extra cell potential is required to overcome a performance loss due to selecting a less mobile ion or more viscous electrolyte.

Beyond the conventional RFB design incorporating small active species and an IEM, this work also considers the combination of nanoporous separators, with no functionalization for ion selectivity, and larger active species that cannot pass through the separator pores. Supporting electrolyte ions, however, can pass freely through the SSS, imparting higher ionic conductivities that their IEM counterparts. Drawbacks of the SSS concept are that the larger active species will exhibit slower transport rates and will have higher active material costs, but these performance setbacks are offset by the lower cost associated with the SSS. With the benchmark performance and cost values assumed in this analysis, the H⁺-IEM option offers the best opportunity to achieve the ultimate DOE target capital cost at cell potentials $>1.2 \text{ V}$, however, for present costs, SSS combined with low cost active materials and electrolytes are an attractive design option.

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## List of Symbols

| Symbol | Description | Units |
|--------|-------------|-------|
| $a$    | Electrode area per unit volume | $\text{m}^2 \text{m}^{-3}$ |
| $b$    | Bruggeman coefficient | - |
| $c$    | Concentration | $\text{mol} \text{m}^{-3}$ |
| $c^b$  | Standard-state concentration | $\text{mol} \text{m}^{-3}$ |
| $c^d$  | Dimensionless concentration | - |
| $c_{\text{act}}$ | Active species cost | $\text{S kg}^{-1}$ |
| $c$    | Mean active species molarity | $\text{mol} \text{L}^{-1}$ |
| $c_{\text{mem}}$ | Membrane (or separator) cost per unit area | $\text{S m}^{-2}$ |
| $c_{\text{pump}}$ | Pump cost | $\text{S}$ |
| $c_{\text{ealt}}$ | Supporting electrolyte cost | $\text{S kg}^{-1}$ |
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Greek

Symbol Description Units

α Mass transfer correction exponent -

β Mass transfer correction pre-factor m s⁻¹

δ Dimensionless geometric current density -

ε Electrode porosity -

νpump Pump efficiency -

νq Round-trip coulombic efficiency -

ρ System discharge efficiency -

δ Voltage discharge efficiency -

ζ Dimensionless geometric factor -

η Overpotential V

η Dimensionless overpotential -

κeff Effective conductivity S m⁻¹

κelectrolyte Electrolyte conductivity S m⁻¹

κmem Membrane (or separator) conductivity -

μ Viscosity Pa s

ν² Dimensionless exchange current density -

ρ Electrolyte density kg m⁻³

θ Ratio of exchange to limiting current -

χ Allowable state-of-charge -

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