Transport Property Requirements for Flow Battery Separators

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Transport Property Requirements for Flow Battery Separators

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Flow batteries are a promising technology for storing and discharging megawatt hours of electrical energy on the time scale of hours. The separator between the positive and negative electrodes strongly affects technical and economic performance. However, requirements for separators have not been reported in a general manner that enables quantitative evaluation of new systems such as nonaqueous flow batteries. This gap is addressed by deriving specifications for transport properties that are chemistry agnostic and align with aggressive capital cost targets. Three key transport characteristics are identified: area-specific resistance $R_Z$, crossover current density $i_S$, and the coupling between crossover and capacity loss $\Psi$. Suggested maximum area-specific resistances are 0.29 and 2.3 $\Omega \cdot \text{cm}^2$ for aqueous and nonaqueous batteries, respectively. Allowable crossover rates are derived by considering the possible fates of active molecules that cross the separator and the coupling between Coulombic efficiency (CE) and capacity decline. The CE must exceed 99.992% when active species are unstable at the opposing electrode, while a CE of 97% can be tolerated when active molecules can be recovered from the opposing electrode. The contributions of diffusion, migration, and convection are discussed, quantified, and related to the physical properties of the separator and the active materials.

Energy storage can mitigate electrical transmission bottlenecks and provide ancillary services in addition to supplying stable and continuous power when coupled to inherently variable renewable energy sources or placed in remote regions or districts with unreliable grids.1,4 Redox flow batteries (RFBs) are a class of electrochemical devices that are suitable for storing energy for multiple hours as described in several recent review articles.3,5–8 In a flow battery, the reactants or active materials are stored in external tanks separate from the reactor, enabling independent scaling of energy and power. This segregation permits cost effective implementation of electrochemical couples with low energy density. The reactants are commonly ions dissolved in an electrolyte at concentrations near 1 mol/L. A conventional battery like lead acid or lithium ion utilizing active materials with such low volumetric capacity would incur tremendous cost, mass, and volume penalties because the amount of inactive material, principally current collectors and separators, scales with volumetric capacity in enclosed architectures.9 Appropriately designed flow batteries optimize the power density of the reactor, consequently minimizing the contributions of separators and current collectors to total system cost.

The primary functions of a separator are to prevent shorting of the electrodes while allowing ionic charge carriers to move freely.10 Any material that fulfills these basic functions is referred to as a separator in this work. The term membrane is reserved for a separator that selectively favors transport of a desired charge carrier, like protons, and thwarts transport of other components like redox molecules and solvents. The complexity of separators used in electrochemical storage and conversion devices varies dramatically. Early in the development of these devices, separators made from simple cloth or even wood were common.10 Today, sophisticated engineered materials are routinely used and research and development continues at a fast pace as ever more functionality is demanded. Some flow batteries rely on nanoporous (i.e. <100 nm pores) polyolefin separators, while others use ion-exchange membranes like DuPont’s Nafion. Despite being expensive, ion-exchange membranes like Nafion are favored in flow batteries because high hydraulic resistance and proton conductivity are desired in addition to electrical isolation and chemical stability.

The low production volumes needed to support existing industries including Chlor-alkali, electrolysis, and fuel cells have resulted in pricing levels on par with specialty chemicals.11 Techno-economic modeling for PEFCs projects that a substantial increase in production would result in an order-of-magnitude reduction in price12–14 Thus, reliance on membranes like Nafion should not present an insurmountable barrier to achieving future cost goals. However, moderate-to-high specific cost will be required in the mid-term to cover costs associated with scaling production if market demand rises.

Recent research into separators for vanadium RFBs has been reviewed by Schwenzer et al.15 The publications cover a broad range of materials including cation-exchange fluorocarbons, cation-exchange hydrocarbons, anion-exchange polymers, amphotheric polymers, and nonionic separators. Any new separator intended to supplant Nafion in aqueous RFBs must demonstrate a significant improvement in at least one key metric, like resistance or crossover, without sacrificing other critical aspects of performance. Porous separators with low hydraulic resistance and no selectivity are also employed in RFBs. The operative philosophy is to use inexpensive materials at the expense of technical performance and this approach can only be implemented when all active species are stable at both electrodes. This methodology has been applied to aqueous iron-chrome batteries where both reactants are added to both electrolytes during commissioning to minimize capacity loss. Low Coulombic efficiency (CE) is an unavoidable side effect of this approach.

Shin et al. recently reviewed the status of separators for nonaqueous flow batteries.16 Nonaqueous flow batteries may be regarded as a burgeoning concept at a considerably lower technology readiness than their aqueous counterparts. Anion-exchange membranes have been utilized to a great extent in nonaqueous cells because the majority of redox molecules have been positively charged. Nafion and similar cation-exchange membranes are expected to receive more interest as concerns about chemical costs compel research and development of negatively charged active species to avoid expensive counter-ions like PF$_6^−$. Doyle et al. systematically examined the behavior of perfluoro-sulfonic acid cation-exchange polymers in contact with a broad range of solvents in two papers focused on possible use in Li-ion batteries.17,18 These reports provide foundational information about the behavior of cation-exchange membranes in contact with nonaqueous solvents that might be used in future RFBs.
Mathematical Analysis

The purpose of this analysis is to derive electrochemical performance requirements that encompass separators for aqueous and nonaqueous flow batteries. Analyses of mechanical, manufacturing, stability, and compatibility demands are beyond the scope of this work. The key attributes examined are area-specific resistance (ASR) and parasitic crossover of active species. ASR targets are determined as a function of open-circuit voltage (OCV) using a Monte Carlo analysis that features an aggressive capital cost goal of $120/kWh and optimistic future component costs. Distinct targets are proffered for aqueous and nonaqueous environments. Allowable crossover currents are derived that consider both capacity loss and energy efficiency (EE). A set of equations describing transport of active species across the separator is presented and the consequences of different modes of transport on cell operation are discussed. The various terms in the transport equations are examined and classified as first or second order. Finally, separator requirements are presented in the form of measurable transport phenomena. Exemplary results for aqueous systems are used to illustrate and quantify phenomena where instructive. A companion manuscript detailing the status of membranes and separators for nonaqueous RFBs in light of the specifications determined here is planned.10

Area-specific resistance.—The capital cost of a flow battery may be expressed as the sum of reactor, chemical, auxiliary equipment, and other costs. The last category includes depreciation, labor, overhead, and margin. Installation costs are not considered in this work due to their inherently variable and site-specific nature. The contribution made by the reactor is:5

\[
p_r = \frac{\sum c_i \cdot \sum R_i}{\varepsilon_{sys,d} \cdot U^2 \varepsilon_{sys,d} (1 - \varepsilon_{sys,d})} \cdot \tau_d
\]

\[
\sum R_i = \frac{p_r \varepsilon_{sys,d} \cdot U^2 \varepsilon_{sys,d} (1 - \varepsilon_{sys,d}) \cdot \tau_d}{\sum c_i}
\]  

where \( p_r \) is the capital cost of the reactor in $/kWh, \( c_i \) is the cost of component \( i \) per unit area in $/m², \( R_i \) is the ASR of component \( i \) in Ω·m² (or more commonly Ω·cm²), \( \varepsilon_{sys,d} \) is the efficiency of the system supporting the battery when it discharges, \( U \) is the open-circuit voltage in V, \( \varepsilon_{sys,d} \) is the average voltage efficiency (VE) during discharge, and \( \tau_d \) is the discharge time in h. We introduce \( R_{sys} = \Sigma R_i \) and the resistance of the separator or membrane, \( R_{sep} \), to simplify notation. In our previous analysis, we allocated $60/kWh to the sum of the reactor and chemical costs in order to achieve a system cost of $120/kWh (see Figure 3 in Reference 9).

A Monte Carlo algorithm where values of \( p_r \), \( U \) and \( \{c_i\} \) were randomly selected from triangular probability distributions and introduced into Equation 1 was used to define distinct ASR requirements for aqueous and nonaqueous batteries. The remaining parameters, \( \varepsilon_{sys,d} \), \( \varepsilon_{sys,d} \) and \( \tau_d \) were treated as invariant specifications. The ASR was calculated for 5000 combinations of parameters. Table 1 shows the minimum, mode, and maximum for each probability distribution. Mean values, equal to one third of the sum of the minimum, mode, and maximum, are provided in the final column. The calculated nonaqueous ASR can be approximately corrected, for example, to a particular OCV, by multiplying by \((U/3.5)^2\), where 3.5 V is the mean OCV for nonaqueous flow batteries.

The reactor cost, \( p_r \), was found by fitting the ratio of reactor cost to the sum of reactor plus chemical costs estimated by Darling et al.9 to a triangular distribution function and multiplying the results by $60/kWh. The chemical or energy cost in a nonaqueous flow battery is approximately 2X to 9X more than the reactor or power cost according to the inputs in Table I. On average the reactor comprises 23% of the $60/kWh allocated to the sum of reactor plus chemicals. Identical values of \( p_r \) were used for aqueous and nonaqueous batteries to facilitate comparison. Separator costs were taken from a logarithmic curve fit to a projection done for thin ion-exchange membranes for PEFCs for automobiles; the relevant production volumes are shown in parentheses in the fifth row of Table I.12 The lower volumes are incompatible with the goal of storing 1% of global electricity production, but they serve to temper the optimism of the predictions and help to bridge the gap to product introduction. For the sake of comparison, reverse osmosis membranes range from 20 to 40 $/m²20 and polyolefin separators for lithium-ion batteries cost about 1 $/m².21 The remaining component costs are taken from our previous work and are intended to apply to a future state characterized by high production.9 The Monte-Carlo algorithm returns a truncated normal distribution for the ASR with a mean of 3.5 Ω·cm² and a standard deviation of 1.2 Ω·cm² for nonaqueous batteries. The requirement is set at the mean minus one standard deviation, 2.3 Ω·cm², which covers 84.1% of the simulations. The target ASR for nonaqueous batteries is ~10X larger than the best results reported for aqueous systems. For example, Cho et al. reported an ASR of 0.23 Ω·cm² for an aqueous H₂–Br cell with a 15 μm reinforced membrane.22 The Monte-Carlo simulations gave a mean of 0.45 Ω·cm² with a standard deviation of 0.16 Ω·cm², yielding a target of 0.29 Ω·cm² for aqueous batteries. The discharging current densities that coincide with the ASR targets at the prescribed OCVs and VE are 130 and 360 mA/cm² for nonaqueous and aqueous, respectively.

Figure 1a shows how required resistance varies with separator cost. Curves are shown for five open-circuit voltages. The remaining parameters were randomly selected from the probability distributions in Table I. Separator cost was selected as the independent variable because realistic estimates vary over a wide range. The two lowest OCVs, 1 V and 1.5 V, are characteristic of aqueous flow batteries, while the larger OCVs are characteristic of nonaqueous systems. The maximum allowable ASR is a strongly decreasing function of membrane cost. The figure and inset indicate that a nonaqueous flow battery at 3.5 V can tolerate an ASR that is roughly 5–6X larger than its aqueous counterpart at 1.5 V because of the benefits associated with higher voltage. Figure 1b shows the discharging current densities that are consistent with the ASRs in Figure 1a at a VE of 91.6%. The figure shows current density to be a linear function of membrane cost with a slope and intercept that both increase as OCV decreases.

The ASR of a separator depends on both thickness and the inherent conductivity of the material. Figure 2 depicts the trade between

### Table I. Parameters for Triangular Probability Distribution Functions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Minimum</th>
<th>Mode</th>
<th>Maximum</th>
<th>Mean</th>
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<tr>
<td>Reactor cost, $/kWh</td>
<td>( p_r )</td>
<td>6.0</td>
<td>14.4</td>
<td>21.0</td>
<td>13.8</td>
</tr>
<tr>
<td>Nonaqueous OCV, V</td>
<td>( U )</td>
<td>3</td>
<td>3.5</td>
<td>4</td>
<td>3.5</td>
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<tr>
<td>Aqueous OCV, V</td>
<td>( U )</td>
<td>1</td>
<td>1.25</td>
<td>1.5</td>
<td>1.25</td>
</tr>
<tr>
<td>Separator, $/m² (m²/y)</td>
<td>( c_m )</td>
<td>16 ((10^6))</td>
<td>50 ((10^6))</td>
<td>155 ((10^6))</td>
<td>74</td>
</tr>
<tr>
<td>Flow field, $/m²</td>
<td>( c_{fl} )</td>
<td>10</td>
<td>35</td>
<td>55</td>
<td>33</td>
</tr>
<tr>
<td>Electrode, $/m²</td>
<td>( c_e )</td>
<td>10</td>
<td>30</td>
<td>70</td>
<td>37</td>
</tr>
<tr>
<td>Frames and seals, $/m²</td>
<td>( c_s )</td>
<td>1</td>
<td>3</td>
<td>6</td>
<td>3.3</td>
</tr>
<tr>
<td>Discharge time, h</td>
<td>( \tau_d )</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>System efficiency on discharge</td>
<td>( \varepsilon_{sys,d} )</td>
<td>94%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge voltage efficiency</td>
<td>( \varepsilon_{sys} )</td>
<td>91.6%</td>
<td></td>
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conductivity and thickness for a separator when $R_D = 2.3 \, \Omega \cdot \text{cm}^2$. Lines obeying the equation $\kappa = 1/R_m$ are shown for $R_m/R_D = 1$ and $R_m/R_D = 0.5$. The optimistic condition $R_m/R_D = 1$ can be approached if the reactions are fast and the electrodes are made of very electronically conductive materials, thereby negating the importance of the conductivities of the electrolytes in the electrodes, and transport losses are minimized by operating at high intra-electrode velocities. The conductivities of lithium-exchanged Nafion 117 (N117) in combination with a thin ion-exchange membrane may be able to achieve the nonaqueous ASR target.

Parasitic transport of active species through the separator inevitably increases as thickness decreases. However, it is reasonable to expect that parasitic crossover will decrease in tandem with conductivity in many cases. That is, solvents that impart detrimental low conductivity may also impart beneficial low crossover. Doyle et al. used pure solvents in all cases. The presence of ions in the bulk solution is anticipated to alter the conductivity of the membrane. For example, Tang et al. showed that bathing N117 in sulfuric acid concentrations below 5 mol/kg enhanced conductivity relative to pure water, while higher concentrations diminished conductivity. The vertical series of data plotted as triangles at an arbitrary thickness consists of the conductivities of various lithium battery electrolytes containing carbonate solvents. The rightmost series denoted by diamonds at an arbitrary thickness is the data for the Li-ion electrolytes corrected to a porosity of 40% using the formula $\kappa = \kappa_{\text{bulk}} / \epsilon^{0.4}$. Commercial Celgard Trilayer separators for Li-ion batteries range from 12 to 38 $\mu$m thick. The substantial reduction in conductivity that occurs when an electrolyte is confined within a porous medium brings the conductivities in line with the best combinations of solvent plus Nafion. An ion-exchange membrane like Nafion may inhibit crossover of active species more than a conventional porous separator, which should be weighed against any conductivity differences.

Coulombic efficiency and capacity loss.— Undesired movement of active species through the separator to the opposing electrode is difficult to avoid in flow batteries. The need to minimize crossover depends, in part, upon what happens to active molecules at the counter electrode. At worst, active species may deposit on the surface of the...
the electrode becoming unavailable for energy storage and interfering with other essential processes. At best, the active species may be converted to species that participate effectively in energy storage at the invaded electrode. This best scenario describes aqueous vanadium redox batteries. In the worst case, separators or active molecules must be engineered to severely restrict crossover while maintaining high ionic conductivity. Alternatively, if active species that cross the separator retain the ability to store energy then it may be possible to use simple porous materials that allow substantial crossover and employ a scheme to return material to its origin (i.e. balance the electrolyte) periodically provided the attendant Coulombic inefficiency can be tolerated.

The energy efficiency of the reactor in a flow battery is the product of voltage and Coulombic or faradaic efficiencies. The EE of the reactor is multiplied by the efficiency of the system in order to calculate the overall efficiency of the battery. This portion of the analysis focuses on Coulombic inefficiency caused by passage of active species through the separator and assumes that shunt currents, electrical shorts, and side reactions like the formation of passive films and gas evolution can be neglected. The unwanted movement of active species through the separator also causes capacity to decline as the system is cycled. This second effect necessitates increasing the amount, and consequently cost, of active material stored within the system and leads to time-varying performance. The permissible flux through the separator can be set by either efficiency or capacity loss considerations. Energy efficiency is the dominant concern when crossover of the limiting reactant and capacity decline are weakly coupled, while capacity decline is dominant when the coupling is strong.

Coulombic inefficiency and capacity loss are linked because both depend on transport of active redox molecules across the separator. The goal of the derivations that follow is to understand and place bounds on the proportionality constant $\Psi$ in the equation:

$$\frac{dQ}{dt} = -AI_i \Psi$$

that relates capacity decline to crossover current density for the four illustrative cases depicted schematically in Figure 3. In Equation 2, Q is capacity in C (or A-h), $t$ is time in s, A is area in cm$^2$, and $i_i$ is crossover current density in A/cm$^2$. Both $i_i$ and $\Psi$ may vary over the course of extended cycling as the compositions of the electrolytes change; however these changes should be modest for small changes in capacity. Limits on $\Psi$ are derived assuming that the charged species at the negative electrode is the limiting component. This choice is arbitrary and the development can be revised to accommodate other possibilities if desired, however the bounds on $\Psi$ are robust to this choice. With reference to Figure 3, the letter A identifies the chemical formula of the active center on the negative side, while the letter B identifies the chemical formula of the active center on the positive side in Case 3. The letter j denotes the lowest oxidation state of A on the negative side, while the letter k denotes the lowest oxidation state of either A (Case 4) or B (Case 3) on the positive side. In Case 4, $k > j$. Only two oxidation states of A or B are permitted on either side of the separator in this analysis. Though not attempted, extending this study to species that exhibit more than two stable oxidation states at either electrode should be possible and dramatic changes in the nature of the results are not expected. Briefly, no crossover occurs in Case 1 so that the CE is always 100%, active molecules that cross the separator are destroyed in Case 2, in Case 3 active species that cross the separator survive and are converted to the oxidation state that is stable at the counter electrode, namely A(j+1) at the positive and B(k) at the negative, finally in Case 4 the active species on both sides of the separator are based on the same molecule or element. Case 3 is conceptually similar to an aqueous iron-chrome battery, while Case 4 is similar to an aqueous all-vanadium battery. While other cases may be conceived of, the four cases tracked in this work cover a broad range of behaviors that encompass many battery systems of interest.

Mole balances on the two oxidation states of active center A on the negative side are:

$$\frac{dN_{A(j)}}{dt} = -\frac{I}{F} - AS_{A(j)}$$

$$\frac{dN_{A(j+1)}}{dt} = -\frac{I}{F} - AS_{A(j+1)}$$

$N_i$ is the amount of species i in the negative electrolyte in moles, $t$ is the time in s, I is the current in A, F is the Faraday constant in C·mol$^{-1}$, A is the area in cm$^2$, and $S_i$ is the rate of disappearance of species i in mol/cm$^2$·s. Table II shows how $S_{A(j)}$ depends on the fluxes of A and B across the separator in the four cases. The fluxes of A(j) and A(j+1) are positive in the direction from negative electrode to positive electrode, while the fluxes of A(k) and A(k+1) and B(k) and B(k+1) are positive in the direction from positive electrode to negative electrode. In Case 3, B(k+1) that crosses the membrane reacts with A(j) to give A(j+1) and B(k) causing a net decrease in $N_{A(j)}$ and a net increase in $N_{A(j+1)}$. Similarly, $n_{A(k)}$ and $n_{A(k+1)}$ cause a net decrease in $N_{A(k)}$ and a net increase in $N_{A(k+1)}$ in Case 4. That is, species crossing from the positive to the negative in Cases 3 and 4 tend to consume the charged species A(j) and produce the discharged species A(j+1) causing the battery to self-discharge. Hence, for fluxes of similar magnitude $S_{A(j)}$ will tend to be larger than $S_{A(k)}$ in Cases 3 and 4. The coefficients multiplying $n_{A(k)}$ and $n_{A(k+1)}$ can be determined by simultaneously balancing moles and oxidation states. Other molecules, like protons and water in aqueous systems, are needed to completely describe the reactions. The self-discharge processes are assumed to proceed without coupling to side reactions that do not involve active species, like oxygen and hydrogen evolution in Cases 3 and 4. The current is a signed quantity that is positive when the battery discharges and negative when the battery charges. $N_{A(j)}$ decreases when the cell discharges, while $N_{A(j+1)}$ increases. The converse occurs when the battery charges. Both equations involve a single electron transfer because the reactants are one oxidation state apart.

The total amount of A on the negative side is found by summing Equations 3 and 4:

$$\frac{dN_{A}}{dt} = -A(S_{A(j)} + S_{A(j+1)})$$

**Table II. Rates of Disappearance.**

<table>
<thead>
<tr>
<th>Case</th>
<th>$S_{A(j)}$</th>
<th>$S_{A(j)} + S_{A(j+1)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>$n_{A(j)}$</td>
<td>$n_{A(j)}$</td>
</tr>
<tr>
<td>3</td>
<td>$n_{A(j)} + n_{B(k+1)}$</td>
<td>$n_{A(j)} + n_{A(j+1)}$</td>
</tr>
<tr>
<td>4</td>
<td>$n_{A(j)} + (k - j - 1)n_{A(k)} + (k - j)n_{A(k+1)}$</td>
<td>$n_{A(k)} + n_{A(j+1)} - n_{A(k)} + n_{A(k+1)}$</td>
</tr>
</tbody>
</table>
The sums of $S_{A(j)}$ and $S_{A(j+1)}$ are provided in the final column of Table II. Because $A(j+1)$ is present on the positive side of the separator in Case 3, $n_{A(j+1)}$ will tend to be suppressed relative to $n_{A(j)}$. Consequently, the net movement of $A$ across the separator, $n_{A(j)} - n_{A(j+1)}$, will tend to be suppressed in Case 3 compared to Case 2. Similarly, the net movement of $A$ from the negative electrode is suppressed in Case 4 by the countervailing movement of $A(k)$ and $A(k+1)$. For fluxes of similar magnitude, Case 2 should suffer the most rapid capacity decline, while zero capacity loss is conceivable for Cases 3 and 4. Case 1 captures an ideal that may be possible to approach with a very selective separator like an ion-conducting ceramic or large active molecules. Case 2 imposes stringent limits on crossover for a device intended to operate for years, Case 3 relies upon excess active material and solvent, while Case 4 retards crossover like Case 3 while requiring less excess material. Because the crossover rates of the various components usually differ in magnitude, batteries described by Cases 3 and 4 may become unbalanced with repeated cycling which may necessitate maintenance procedures.

Table III. Crossover Current Multipliers and Capacity Loss.

<table>
<thead>
<tr>
<th>Case Description</th>
<th>Perfect separation</th>
<th>Destructive crossover</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity loss coupling, $\Psi$</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Cycles before recovery</td>
<td>1250</td>
<td>1250</td>
</tr>
<tr>
<td>Allowable capacity loss (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relative charge time, $t_{q,rt}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coulombic inefficiency, $1-\epsilon_{q,rt}$</td>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>Normalized crossover current, $i_{x}/i_d$</td>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>$i_{x}/i_d$ @ $\tau_{ecsdl.org/site/terms_use}$ is 97%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The crossover current density is defined as:

$$i_x = F \bar{S}_{A(j)} = \phi F \bar{h}_{A(j)}$$ [6]

The overbar denotes averaging over a complete charge/discharge cycle. The crossover current density is related to the CE of the cell and can be regarded as a gross crossover of $A(j)$. The quantity $i_x$ is a combination of fluxes multiplied by the Faraday constant to facilitate comparison with applied current densities. The crossover process may, or may not, involve electron transfer across a solid/liquid interface. For example, active species in all-vanadium redox cells are converted by redox reactions in the electrolyte phase once they cross through the separator. For an all-vanadium redox cell, $j = 2$, $k = 4$ and $\phi$ would equal 4 if all fluxes were equal in magnitude.

The proportionality constant relating crossover current density and capacity decline can be found by manipulating Equations 2, 5, and 6:

$$\bar{S}_{A(j)} = \frac{\bar{h}_{A(j)}}{\bar{S}_{A(j)}}$$ [7]

$\Psi$ can be regarded as a ratio of net transfer of $A(j)$ plus $A(j+1)$ to gross transfer of the limiting component $A(j)$. Examination of Table II indicates that all flux contributions to $S_{A(j)}$ are positive as are the coefficients $(k-1)$ and $(k-j)$ so $S_{A(j)}$ is always positive. The sum $S_{A(j)} + S_{A(j+1)}$ displays more complicated behavior. $i_x$ is 0 by definition in Case 1, and the value of $\Psi$ is irrelevant. In Case 2 $\bar{h}_{A(j+1)}$ is positive and $S_{A(j)} + S_{A(j+1)} > S_{A(j)}$, so $1 < \Psi < 2$. In Case 3, $A(j+1)$ is present on both sides of the separator and $\bar{h}_{A(j+1)}$ can be positive or negative so $0 < \Psi < 2$. A complete examination Case 4 is more difficult because of the additional fluxes. However, it is easy to show that $\Psi = 0$ when $\bar{h}_{A(j)} = \bar{h}_{A(j+1)} = \bar{h}_{A(k)}$, which conveys the idea that the presence of the same active center on both sides of the separator will tend to minimize capacity loss. The parameter $\Psi$ should lie in the range $0 < \Psi < 2$ for all cases of interest.

The round-trip CE, $\epsilon_{q,rt}$, of a complete quasi stationary-state cycle can be found by integrating Equation 3 for charging and discharging half cycles:

$$\epsilon_{q,rt} = \frac{Q_s}{Q_t} \approx 1 - \frac{i_x}{i_d}$$ [8]

Here, the phrase stationary state is used to indicate that immediately preceding and following cycles yield essentially identical results and the word quasi is used as a modifier to indicate that slow capacity decay occurring as the battery cycles prevents the attainment of a true stationary state. The inability to obtain a true stationary state impacts error to the approximation represented by Equation 8. Equation 8 can be used to estimate $i_x$ from measured CE and could be modified to allow for different crossover rates on charge and discharge if warranted.

Table III shows required crossover rates for the four cases depicted in Figure 3. Rows 3 through 6 contain input parameters, while subsequent rows contain outputs. The presence of $A$ on both sides of the separator lowers the rate of capacity loss substantially, hence $\Psi = 0.1$ in Cases 3 and 4. However, practicing Case 3 will tend to increase electrolyte costs because it requires more active material, salt, and solvent for the same capacity. Two variants, (a) and (b), are introduced to admit the possibility of recovering active species that cross the separator in Cases 3 and 4. A battery that cycles every weekday for five years executes approximately 1250 cycles, Cases 1, 2, 3a, and 4a. A criterion of 50 cycles was arbitrarily selected for variants 3b and 4b to address the nuisance and expense of returning the active materials to the cell.

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All of the above inputs are meant to be representative and reasonable, but clearly a thorough economic analysis could be undertaken to discern a more optimal set of parameters. The crossover rates were calculated with a dimensionless form of Equation 2 integrated for constant $i_x$ and $\Psi$:

$$i_x = -\frac{\Delta \theta}{(1 + \tau)m\Psi}$$ [9]

All variables on the right are dimensionless. $\Delta \theta$ is the change in the ratio of present to initial discharge capacity which is a negative quantity, $\tau$ is the ratio of charge to discharge times, and $m$ is the number of cycles. The total operating time was approximated as $Q_s/\epsilon_{q,rt}$, which is appropriate for small changes in $t_c$. This formulation assumes that no crossover occurs when the battery is not operating.

The final three rows of Table III are calculated outputs. The seventh row shows Coulombic inefficiencies (1-CE), while the eighth row shows the normalized crossover current densities, $i_{x}/i_d$. Equation 8 is used to translate between CE and $i_{x}/i_d$. The last row gives the ratio $i_{x}/i_d$ needed to achieve a CE of 97%. This provides an upper limit on $i_x$ that becomes operative in Cases 3b and 4b. The acceptable level of crossover is 20X larger in Cases 3a and 4a than in Case 2. Clearly there is a large benefit associated with using an active material.
that is stable at the counter electrode. Furthermore, comparison of variants (a) and (b) shows the substantial relaxation of requirements obtained when periodic balancing of electrolyte is permitted. The ratio \(i_x/i_d\) increases by a factor of 25, which equals the ratio of cycle counts. The CE requirement of 97% taken from our previous work\(^9\) is more stringent than the capacity requirement in Cases 3b and 4b with \(\Psi = 0.1\).

Figure 4a depicts the relationship between the rate of capacity decline and the characteristic flux of active material across the separator. Curves are shown for three values of \(\Psi\). \(\Psi = 0.1\) represents situations where the active molecule is present on the opposite side of the separator as either a spectator or an active participant in the reaction on the opposing electrode, i.e., Cases 3 and 4. Simply put, the net crossover from positive to negative is 90% of the net crossover from negative to positive when \(\Psi = 0.1\). \(\Psi = 2\) represents situations where active species that cross the membrane are destroyed by reaction, i.e., Case 2. \(\tilde{\eta}_{xj} = \tilde{\eta}_{a/j+1}\) when \(\Psi = 2\) is an intermediate case. The rate of capacity decline is proportional to \(\Psi\) according to Equation 2. The requirements on \(i_x/i_d\) are stringent for Case 2 because a large number of cycles must be completed and the multiplier is large. The lines for \(\Psi = 0.1\) and 0.5 are dashed when \(i_x/i_d\) exceeds the value calculated at \(\tilde{\eta}_{xj} = 97\%\), which is approximately 0.01. Coulombic efficiency rather than capacity decline is controlling under these circumstances. Figure 4a was constructed assuming constant values of \(i_x/i_d\) and \(\Psi\), which is a reasonable first approximation for relatively small capacity changes. The round-trip CE, \(\tilde{\eta}_{xj}\), is shown on the right vertical axis.

Evaluation of data from cells.— The parameters \(R_\Omega\), \(i_x\), and \(\Psi\) can be fit to data obtained with single cells or multi-cell stacks. Allowances must be made for shunt currents when evaluating stack data. Figure 5 illustrates the Coulombic, voltage, and energy efficiencies of a small vanadium redox cell subjected to constant current cycling between 0.7 and 1.65 V. Both electrolytes contained 1.5 M vanadium and 4.1 M total sulfate. The cell had interdigitated flow fields, electrodes consisting of heat treated carbon papers, and a Nafion 212 membrane (NR212).\(^{32}\) The DC resistance of the cell before testing was >10 kΩ, indicating an absence of electrical shorts. The charge and discharge currents were always equal in magnitude and the data was taken from the second of two runs done at each condition. The symbols are measured values, while the lines are the curve fits described below. The CE was fit to the formula \(\tilde{\eta}_{xj} = (i - i_x)/(i + i_x)\) with a best value of \(i_x\) of 1.7 mA/cm\(^2\). The VE was fit to the equation \(\tilde{\eta}_{xj} = (U - i_x R_\Omega)/(U + i_x R_\Omega)\). The best value of \(R_\Omega/U\) was 0.421 cm\(^2\)/A. The average OCV was determined separately to be \(U = 1.416\) V which gives \(R_\Omega = 0.596\) mΩ/cm\(^2\). Kinetic losses lead to higher ASRs at low current densities and cause the deviation between model and experiment below 50 mA/cm\(^2\). This cell operates at 200 mA/cm\(^2\) at \(\tilde{\eta}_{xj} = 91.6\%\) hence \(i_x/i_d = 0.0085\) and \(\tilde{\eta}_{xj} = 98.3\%\) when \(\tau = 1\). The normalized capacity of the cell during repeated cycling at 150 mA/cm\(^2\) is plotted against the right ordinate. Time in hours was divided by 100 to enable representation of the data with the same absissa as the efficiencies. The dimensionless capacities cover the range 0.8 < \(\theta\) < 1. Fitting the data gives \(|d\theta/dt| = 0.50\) mA cm\(^{-2}\) near maximum capacity, which can be divided by \(i_x = 1.7\) mA/cm\(^2\) to yield \(\Psi = 0.3\) which is reasonably small as expected for a vanadium redox battery.

Flux.— The previous section addressed the fluxes of active species across the separator that can be tolerated in different circumstances.
This section examines the terms that contribute to these fluxes. Dilute-solution theory is used to describe transport of active species through the separator by diffusion, migration, and convection (see chapter 11 in Reference 27):

\[ n_i = -D_i \nabla c_i - z_i \mu_i F c_i \nabla \Phi + c_i \nu \]  

[10]

The subscript i identifies the component. \( n_i \) is flux in mol/cm²·s, \( D_i \) is the diffusion coefficient in cm²/s, \( c_i \) is concentration in mol/cm³, \( \mu_i \) is mobility in cm²·mol/J·s, \( F \) is the Faraday constant in C/mol·e⁻, \( \Phi \) is the potential in V, and \( \nu \) is the bulk velocity in cm/s. The bulk velocity is assumed to be equal to the solvent velocity, \( v_0 \). Invoking the Nernst-Einstein equation, \( \nu_i = D_i / RT \) where \( R \) is the universal gas constant and \( T \) is absolute temperature, eliminates the mobility and reduces the number of transport properties in Equation 10. Application of Equation 10 to solutions of high ionic strength, such as those encountered in most batteries, is approximate because it does not address all of the interactions present. Nevertheless, dilute-solution theory is commonly used because it is simple to apply and provides a sound basis for understanding many crucial behaviors.

The importance of the concentration is emphasized by its appearance in all of the flux terms. Concentrations are continuous at the boundaries between simple porous components. By contrast, the concentrations on either side of an interface between an ion-exchange membrane like Nafion and an adjacent bulk solution usually differ. An ion-exchange membrane tends to reject co-ions and accept different counter-ions at ratios that are dissimilar from those that prevail in the contacting bulk solutions. Steric effects become important when the sizes of separator pores and solvated molecules are similar. Thus, it is reasonable to expect that active species, especially large counter-ions, will be less concentrated in an ion-exchange membrane than in a simple separator in contact with the same bulk solution. As a first approximation, we assume that the major charge carriers obey Ohm’s law and that the active species contribute negligibly to the conductivity of the membrane. This allows further simplification of Equation 10 with the substitution: \( d\Phi / dx \approx -i / \kappa \).

**Diffusion and migration of active species.—** We begin our analysis by setting \( v_0 = 0 \) and focusing on the combined effects of diffusion and migration. The flux of \( A(j) \) from negative to positive through the membrane divided by the corresponding diffusive component of the flux is (see Appendix A):

\[ \frac{n_{A(j)}}{n_{A(j),diff}} = \frac{\beta (\bar{e}^j - \bar{\psi})}{(\bar{e}^j - 1)(1 - \bar{\psi})} ; \quad \bar{\psi} = c_2 / c_1 \]

[11]

\( c_1 \) is the concentration on the negative feed side of the separator, and \( c_2 \) is the concentration on the positive side, which is zero for \( A(j) \) in all cases. This equation can be applied to a galvanostatic half cycle to good approximation by using the average values of \( c_1 \) and \( c_2 \). The dimensionless number \( \beta \) is indicative of the relative importance of migration and diffusion. The parameters needed to define \( \beta \) are: valence \( z \), Faraday constant \( F \), current density \( i \), separator conductivity \( \kappa \), universal gas constant \( R \), and absolute temperature \( T \). The second equality uses a linear polarization equation to replace the current density. The relative importance of migration tends to increase with increasing OCV at fixed VE and with an increasing ratio of membrane to total resistance. Recall that the current is a signed quantity that is positive when the battery is discharging and negative when the battery is charging. Equation 11 is unbounded when \( \beta > 0 \), but subject to a minimum of zero when \( \beta < 0 \). Thus, the influence of migration is not symmetric.

**Figure 6** shows the normalized fluxes when diffusion and migration tend to move \( A(j) \) in the same direction, labelled allied, and when migration opposes diffusion, labelled majoring, \( c_2 / c_1 = 0 \) was assumed in both cases. The linear average of the two fluxes is also shown, labelled average. This describes the net movement over a complete cycle when the current densities during the two half cycles are equal in magnitude. As can be seen, the influences of migration during the charging and discharging half cycles do not completely cancel, and there is a net augmentation to diffusion when \( \beta > 1 \). For \( U = \{ 1.5, 3, 4 \}, \beta_2 = \{ 4.9, 9.8, 13.1 \} \approx n_{A(j)/n_{A(j),diff}} \) provided \( c_2 / c_1 = 0 \), \( T = 298.15 \) K, \( \epsilon_{vd} = 91.6 \)%, \( z = 1 \), and \( R_m / R_g = 1 \). Thus, migration should significantly influence the parasitic movement of active species across the separator in flow batteries operating near target conditions. Furthermore, migration should be more important in non-aqueous batteries because of the higher voltages and lower electrolyte conductivities.

The ratio of the total flux to the diffusive component of the flux averaged over a complete cycle is (see Appendix B):

\[ \frac{n_{A(j)}}{n_{A(j),diff}} = \frac{\beta}{1 + \tau} \left( \frac{1}{1 - e^{-\beta}} - \frac{1}{1 - e^{\beta}/t} \right) = g(\beta, \tau) \]

[12]

The overbars denote averaging over a complete charge/discharge cycle. The parameter \( \beta \), defined in Equation 12, is evaluated for discharging conditions. The parameter \( \tau \) is a ratio of charge time to discharge time. Figure 7 shows how the ratio of fluxes depends on \( \beta \) and \( \tau \). The contribution of migration increases with increasing \( \beta \) and decreases with increasing \( \tau \). Diffusion dominates at small \( \beta \) and large \( \tau \).

While crossover tests that measure diffusion through separators and membranes for energy-conversion systems such as direct methanol fuel cells, vanadium RFBs, and non-aqueous RFBs are routine, tests that assess migration are relatively rare. Equation 13 relates the diffuse flux to the maximum allowable crossover current density, \( \kappa \).

\[ n_{A(j),diff} = \frac{D_{A(j)} / \kappa_{A(j)}}{l} \leq \frac{i_k}{\phi Fg(\beta, \tau)} \]

[13]

Equation 13 can be used to link ex-situ diffusion measurements to in-situ crossover, thereby negating the need to execute a series of experiments to study the effect of current density on crossover. An all-vanadium flow battery provides a concrete example of how to apply this criterion. Representative performance parameters, \( U, R_m, \kappa, \Psi, \) and \( i_k \), were provided in connection with Figure 5. The ratio \( R_m / R_g = 0.16 \) assuming a 50.8 μm thick Nafion membrane with a conductivity of 52 mS/cm. \( \beta = 1.52 \) was computed for this set of parameters with \( z_k = 2 \) which gives \( n_{A(j)/n_{A(j),diff}} \approx 1.09 \) for \( \tau = 2 \).
c0 is the concentration of the solvent in the separator, D0 is the diffusion coefficient of the solvent, ξ is the drag coefficient, k is hydraulic permeability in cm², μ is solvent viscosity in Pa·s, and P is pressure in Pa. Osmotic drag can be neglected in porous separators with uncharged internal surfaces. The viscosity of a solvent confined within small pores inside a membrane can differ from the bulk viscosity, but we ignore this effect.

**Magnitudes of flux terms.**—Table IV lists representative properties for a Nafion 212 (NR212) membrane in contact with a typical electrolyte for an aqueous all-vanadium RFB. The electrolyte consists of VOSO4, denoted V4, in sulfuric acid. The diffusion coefficients D4,m and D0,m were calculated from fluxes and intra-membrane concentrations gathered from disparate literature sources. Thus, D4,mΔc4,m in row 2 was divided by c4,m in row 3 to give D4,m in row 4. The same procedure was used to find D0,m. Frequently, diffusion through Nafion is reported in terms of bulk, external concentration or activity differences because measuring the concentration in the membrane is difficult and empirically unnecessary in many situations. The hydraulic permeability of NR212 has been observed to decrease as the ionic strength of the contacting electrolyte increases (see Figure 6 in Reference 38, for example). Presumably this is because NR212 shrinks when exposed to electrolytes with high ionic strength.39 The final four rows contain bulk electrolyte properties and the permeability of a simple porous separator, kS, for the sake of comparison to the NR212 values.

Table V compares partial fluxes of V4 (multiplied by the Faraday constant) across NR212 and a hypothetical porous separator constrained to have the same ASR, 102 m²·cm⁻². The NR212 is 50.8 µm thick, while the separator is 79 µm thick. The electrolyte consists of 0.75 mol/L V4 (equivalent to 1.5 mol/L vanadium at 50% SOC) in 4.1 mol/L total sulfate to match the experiments reported in Figure 5. The resulting concentration of V4 in NR212 was estimated to be 21 mmol/L by interpolating the measurements of Cho et al.37 The porous separator was assumed to have a porosity of 40% and the bulk transport properties in Table IV were multiplied by ε² to correct for porosity and tortuosity. The driving forces used to make these estimates are listed in the third column. The flux components, with the exception of drag, are uniformly higher for the separator. The diffusive flux for the separator is 5X larger than for NR212. Roughly the same factor applies for migration, while solvent diffusion is 25X larger and pressure driven flow is 2100X larger. Clearly, the CE will be lower for the separator at the same current density. For example, if diffusion were the only term then a cell with NR212 that achieved 97% CE with a porous separator. The rate of capacity decline would increase in a similar fashion.

Migration alternately augments and hinders transfer during charge and discharge, as discussed previously. The ionic strengths of the...
electrolytes, and consequently the solvent activities, on either side of the separator continuously change as the battery charges and discharges because the different oxidation states of the active species have different valences. Consequently, the direction of solvent diffus-

In order to examine this phenomenon, a difference between the two flowing electrolytes will lead to a large unwanted flow of material. In order to examine this phenomenon, a simple pseudo three-dimensional capillary model, $k = \kappa d_p^2 / 96$, was assumed to adequately describe the relationship among pore diameter $d_p$, porosity $\epsilon$, and permeability $k$.

Figure 8 relates pore diameter to flux across a 79 μm separator for different pressure differences subject to the conditions listed in the plot. A simple separator that does not partition the electrolyte was assumed, consequently $c_{i,m} = 0.75$ M. The total pressure drop experienced by either electrolyte from inlet to exit in a stack will likely be between 10 and 1000 kPa. The pressure difference across the membrane should be no more than 10% of this number, which is the rationale for the values of $\Delta P$ in Figure 8. Fitting the permeability in Table IV to the capillary model gives a pore diameter of 3.1 nm for Nafion assuming a porosity of 40%. This gives $n_{V4}F = 6 \mu A/cm^2$ for a 10 kPa pressure difference, which is larger than the value reported in Table V because the concentration in the separator is equal to the bulk concentration of 0.75 mol/L, instead of 21 mmol/L. The volume fraction of solvent in Nafion varies with the osmotic pressure of the external solution. For a sulfuric acid solution, $a_0 = 1$ gives $\lambda = 20$ and $\xi = 40\%$, while $a_0 = 0.8$ gives $\lambda = 13$ and $\xi = 30\%$. Thus, resistance to solvent transport through the membrane should increase as the ionic strengths in the adjacent bulk solutions increase. The pores in a typical lithium-ion battery separator are ~30 nm in diameter, which yields 0.52 mA/cm² at 10 kPa. Clearly, maintaining high CE is more challenging with a separator having large pores.

Concentration in separator.— Pore sizes in the reverse-osmosis (RO) and nanofiltration (NF) range should inhibit transport of large active molecules. Table VII compares V4 diffusion through as-received NR212, a NF membrane (Dow NF Nanofiltration Membrane41), and a RO membrane (Dow XLE Reverse Osmosis Membrane42). The NF and RO membranes are both polyamide based, and are probably positively charged at low pH.43 The fluxes have been multiplied

### Table V. Partial Fluxes for NR212 and a Simple Separator with the same ASR.

<table>
<thead>
<tr>
<th>Flux contribution</th>
<th>Equation</th>
<th>Driving force</th>
<th>NR212, 50.8 μm</th>
<th>Separator, 80.5 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion</td>
<td>$n_i = \frac{D_i \Delta c_i}{RT}$</td>
<td>$\Delta c_{V4,bulk} = 0.75$ M, $\Delta c_{V4,NR212} = 21$ mM</td>
<td>1.0</td>
<td>5.1</td>
</tr>
<tr>
<td>Migration</td>
<td>$n_i = \frac{2F \rho_{m,i}}{RT}$</td>
<td>$i = 200$ mA/cm²</td>
<td>1.5</td>
<td>8.1</td>
</tr>
<tr>
<td>Solvent diffusion</td>
<td>$n_i = \frac{c_{i,m} D_i \Delta c_i}{RT}$</td>
<td>$\Delta \rho_{i} = 0.1$</td>
<td>0.22</td>
<td>5.6</td>
</tr>
<tr>
<td>Drag</td>
<td>$n_i = \frac{i c_{i,m}}{c_{F}}$</td>
<td>$i = 200$ mA/cm²</td>
<td>0.55</td>
<td>0</td>
</tr>
<tr>
<td>Pressure</td>
<td>$n_i = \frac{c_{i,m} D_i \Delta P}{\mu}$</td>
<td>$\Delta P = 10$ kPa</td>
<td>$2.5 \times 10^{-4}$</td>
<td>0.52</td>
</tr>
</tbody>
</table>

### Table VI. Properties of Different Classes of Membranes.

<table>
<thead>
<tr>
<th>Filtration</th>
<th>Pore size (nm)</th>
<th>Molecular weight cut off (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reverse osmosis (RO)</td>
<td>0.1</td>
<td>100</td>
</tr>
<tr>
<td>Nanofiltration (NF)</td>
<td>1</td>
<td>200</td>
</tr>
<tr>
<td>Ultrafiltration (UF)</td>
<td>3</td>
<td>2000</td>
</tr>
<tr>
<td>Microfiltration</td>
<td>100</td>
<td>200,000</td>
</tr>
<tr>
<td>Particle filtration</td>
<td>1000</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Figure 8. Flux across a separator as a function of pore diameter for various pressure differences.
Table VII. Fluxes of V4 through various separators.

<table>
<thead>
<tr>
<th>Separation</th>
<th>Molecular weight cut off (g/mol)</th>
<th>Barrier thickness (μm)</th>
<th>Pore radius (nm)</th>
<th>V4 diffusion (μA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR212 (untreated)</td>
<td>-</td>
<td>50.8</td>
<td>1.6</td>
<td>72</td>
</tr>
<tr>
<td>Dow</td>
<td>150 – 300</td>
<td>&lt; 0.1</td>
<td>0.36 and</td>
<td>0.12</td>
</tr>
<tr>
<td>NF</td>
<td></td>
<td></td>
<td>0.78</td>
<td></td>
</tr>
<tr>
<td>Dow Reverse</td>
<td>100</td>
<td>&lt; 0.2</td>
<td>0.42</td>
<td>0.008</td>
</tr>
<tr>
<td>Osmosis XLE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 9. Co-ion concentration in the membrane divided by the co-ion concentration in the bulk for a 1:1 salt when c5 = 1 mol/L and z5 = -1. The tendency for the membrane to reject anions quickly declines as the concentration of ions in the external solution surpasses the concentration of fixed acid sites in the membrane according to

$$K = \frac{c_{5,m}}{c_{5,b}} = \left( \frac{z_{5}c_{5,b} + z_{5}c_{5,m}}{z_{5}c_{5,m}} \right)^{-z_{5}/z_{5}}$$

The following equation describes diffusion and migration of a minor component in a dilute solution where the supporting charge carriers follow Ohm's law:

$$n_{i} = -D_{i} \frac{dx}{dx} + \frac{z_{i}F \psi_{i}}{RT} \; ; \; \psi(x = 0) = \psi_{0} \; ; \; \psi(x = l) = \psi_{l}$$

Figure 9. Electrolytes in flow batteries tend to be highly concentrated which implies that charge exclusion may be relatively weak. This prediction is crude because the electrolytes are assumed to be ideal, although they are highly concentrated.

**Conclusions**

Transport properties aligned with an aggressive capital cost target of $120/kWh were derived for separators for both aqueous and nonaqueous redox flow batteries. ASR targets of 0.29 and 2.3 Ω · cm² were determined using a Monte-Carlo model with a mean separator price of 74 $/m² for aqueous, 1.25 V, and nonaqueous, 3.5 V, batteries. These ASR targets translate to continuous current densities of 360 and 130 mA/cm². The required power density decreases when less expensive separators are used. Parasitic crossover, iᵢ, through the separator affects both Coulombic efficiency and capacity loss. The parameter $\psi$ was introduced to describe this coupling. Strong coupling between Coulombic inefficiency and capacity decline leads to $\psi \approx 2$, which necessitates $i_{d}/i_{a} \approx 2.7 \times 10^{-3}$ or CE 99.992% to achieve 1250 cycles with 20% capacity decline. The upper limit on $i_{d}/i_{a} \approx 10^{-2}$ is controlled by the minimum CE of 97% and is operative when coupling is weak, $\psi \approx 0$. Achieving lower crossover currents may be possible by utilizing separators with small pores that impede pressure driven flow and decrease mobility of active species while allowing for conduction of desired ionic species. Initial estimations suggest these pores should be in the reverse-osmosis or nanofiltration size range.

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The following dimensionless variables are defined to simplify notation: \( z = x \phi \), \( \psi = c_i/k_{i0} \), \( f = n_i/D_i c_{i0} \), and \( \beta = z_i F / R T \). Substitution yields the dimensionless first-order differential equation:

\[
\frac{df}{dx} + \beta f = \psi(x = 0) = 1; \quad \psi(x = 1) = \psi_1
\]

This equation is separable because the flux is constant and can be integrated to give:

\[
f = \psi_1 \left( \frac{e^\beta - \psi_1}{e^\beta - 1} \right)
\]

This equation can be divided by the flux when migration is absent, \( f = 1 - \psi_1 \), to give Equation 11.

**Appendix B**

The instantaneous flux across the separator was derived in Appendix A. When the concentration at the far side of the separator is 0, the dimensionless flux is:

\[
\frac{n_{diff}}{n_{diff}} = \frac{\beta}{1 - e^{-\beta}}
\]

The flux averaged over a full charge-discharge cycle is:

\[
\tilde{n} = \frac{n_{diff}}{1 + \tau} \cdot \frac{n_{diff}}{1 + \tau} = \frac{\beta}{1 - e^{-\beta}}
\]

Substituting in for the fluxes gives

\[
\tilde{n} = \frac{n_{diff}}{1 + \tau} \left( \frac{\beta}{1 - e^{-\beta}} + \frac{\beta}{1 - e^{-\beta}} \right)
\]

The values of the parameter \( \beta \) during the charging and discharging half cycles are related as follows:

\[
\beta_c = \beta_d \frac{i_c}{i_d} = \frac{\beta}{\tau}
\]

The negative sign appears because the charging current density is a negative quantity while the discharging current density is a positive quantity. Replacing \( \beta_c \) and rearranging gives:

\[
\frac{n_{diff}}{n_{diff}} = \frac{\beta}{1 + \tau} \left( \frac{1}{1 - e^{-\beta}} - \frac{1}{1 - e^{-\beta}} \right)
\]

**List of Symbols**

A formula for active chemical

Area, m²

ci cost per unit area of component i, $/m²

d diameter, nm

D_i diffusion coefficient of i (in solvent), cm²/s

Faraday constant, C/eq

Current, A

I_i current density, A/cm²

k permeability, cm²

l thickness, cm

m number of cycles

N molar amount, mol

n molar flux, mol/cm² · s

NF nanofiltration

P reactor cost, $/kWh

Q extrinsic capacity, C

q intrinsic capacity, C/cm²

r radius, nm

R universal gas constant, J mol⁻¹ K⁻¹

R_i area-specific resistance of component i, Ω · cm²

s_i rate of disappearance of i, mol cm⁻² · s⁻¹

t time, s or h

T temperature, K

U theoretical open-circuit potential, V

SOC state of charge

z valence

**Greek**

\( \beta \) dimensionless ratio relating migration and diffusion

\( \varepsilon \) efficiency or porosity

\( \phi \) concentration ratio

\( \psi \) coupling between inefficiency and capacity loss

**References**


