Analysis of Crossover-Induced Capacity Fade in Redox Flow Batteries with Non-Selective Separators

Venkat Pavan Nemani 1,2,∗ and Kyle C. Smith 1,2,3,4,∗,z

1 Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, USA
2 Computational Science and Engineering Program, University of Illinois at Urbana-Champaign, Urbana, Illinois, USA
3 Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, USA
4 Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, Illinois, USA

Redox flow batteries (RFBs) are candidates for grid-scale energy storage. For RFBs mechanistic understanding of redox-active species crossover is needed to optimize electrolyte composition (both of inert salt ions and redox-active species) especially when low-cost separators are used instead of ion-selective membranes. We simulate these effects using a multi-component porous electrode model with Nernst-Planck fluxes and Marcus-Hush-Chidsey kinetics to predict capacity utilization and fade. The molar ratio of inert salt to redox species and the ratio of their diffusivities are used to parameterize different electrolytes in RFBs with non-selective separators. Irrespective of whether redox couples use a common charge-balancing counterion (rocking chair configuration) or not (salt splitting configuration) the molar ratio of inert salt to redox species must exceed 50% to cycle with substantial capacity. Using Damköhler numbers (characteristic scales of reaction rates to transport rates) for both inert salt and redox-active species we classify three RFB operating regimes: redox shuttle limited, ohmic polarized, and sufficient supporting electrolyte. In the sufficient supporting electrolyte regime capacity fade is found to scale inversely with a power of approximately 80% for Damköhler numbers smaller than 12.

© The Author(s) 2018. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0701813jes]

Manuscript submitted July 30, 2018; revised manuscript received September 7, 2018. Published October 4, 2018.

In 2017 about 60% of electricity in the USA was generated from fossil fuels whereas only ∼10% was generated using renewable energy sources such as wind and solar. However, the use of renewables (excluding hydropower) has grown by 15% in the USA over the past 10 years, and it is projected that by 2050 22% of total electricity generation in the USA will be produced by wind and solar power plants. Therefore, it is imperative to develop technologies to enable electrical energy storage (EES) from such renewable sources of energy that are intermittent in nature. Redox flow batteries (RFBs) are attractive EES solutions because of their ability to independently scale energy capacity and power density by way of scaling electrolyte volume and reactor area, respectively. Such a capability could enable the integration of renewable energy resources, as well as load leveling and peak shaving on the electric grid. The commercialization of RFB technology at grid-scale is currently challenged by high system prices. Accordingly, the United States Department of Energy has set an aggressive target price of $120/kWh for the commercialization of RFB EES.

A typical RFB is comprised of a reactor (electrode compartments separated by an electron insulating separator) and two tanks (electrolyte storehouse) connected through a network of pipes and pumps. The electrolyte is made by dissolving redox-active molecules in aqueous (AqRFB) or non-aqueous (NAqRFB) solvents along with inert salt. We note that charged redox-active molecules can be synthesized as salt wherein the particular redox-active molecule is crystallized together with an inert ion of opposite charge. Hereafter, we use “salt” to refer to the inert ions dissolved in solution, apart from those originally crystallized with as-synthesized redox-active molecules. Existing AqRFB chemistries include Fe/Cr, all vanadium, polysulfide/bromine, zinc/bromine, metalloenes, and organic redox molecules such as TEMPO, quinones, and redox-active polymers (RAPs). The development of NAqRFBs with non-aqueous electrolytes or even ionic liquids is motivated by the fact that these electrolytes provide a wider electrochemical stability window allowing higher energy density storage devices.

Separators electrically isolate the two electrolytes in RFBs and allow conduction of inert salt ions to maintain charge balance across the two electrolytes. Regardless of the types of RFB, ion-selective membranes are most commonly used as separators to prevent crossover of redox active species with non-zero oxidation state. However, these ion-exchange membranes have limited lifetime and are expensive, accounting for almost 20% of total battery cost. Alternatively, a non-selective separator can conceivably be used, albeit with inherent capacity loss due to crossover. Membrane-free RFBs such as hybrid RFBs, laminar flow RFBs, and immiscible electrolyte RFBs have been proposed. The scalability of these systems is challenging as they either use a solid electrode, flow in micro-channels or viscous ionic liquids respectively. In addition to membrane costs, the costs associated with supporting electrolyte are high particularly for NAqRFBs (~$5/kg) which use fluorinated derivatives as inert salt. The primary purpose of inert salt ions is to facilitate long-range ion conduction between electrodes while retaining redox-active species within their respective electrodes. Therefore controlling the usage of solvent and inert salt is vital for commercialization of RFBs. In this regard, a proof-of-concept NAqRFB omitting the use of inert salt was demonstrated by using redox species in their respective electrodes paired with a common inert counterion to facilitate long-range ion conduction.

The flowing electrochemistry in RFB reactors complicates their design, operation, and electrolyte development, and mathematical modeling of the transport phenomena therein can aid in linking RFB development to technical targets. As the initial simulations can be used to predict the equilibrium properties of RFB electrolytes, continuum simulations that predict the spatial and temporal distribution of each species and their reaction rates are needed to understand the influence of electrolyte properties on RFB performance. The first two-dimensional, transient model of a vanadium RFB was developed by Shah and co-workers following which several other models were developed particularly accounting for crossover through ion-exchange membranes. Other redox chemistries such as sodium/bromine, polysulfides, and organic/inorganic molecules have been modeled as well. Recently, we simulated a RAP-based NAqRFB using a non-selective separator and established the importance of maintaining a high flow rate to...
minimize the capacity losses inherent to the mixing processes in RFB tanks, the results of which were later used to assess the impact of electrolyte viscosity and ionic conductivity of redox-active polymer electrolytes on RFB performance. However, most previous models simulated specific redox chemistries with certain diffusion coefficients at certain concentrations of both inert ions and redox-active species, one notable exception is zero-dimensional, time-independent modeling that employed ad hoc flux equations with species conversion rules that were used to specify materials selection criteria for RFB separators.

In the current work, we use physics-based modeling to predict the capacity utilization and fade of RFB electrolytes with a range of diffusion coefficient values and concentrations in order to extract guidelines for the design of electrolytes and the operation of RFBs that minimize crossover rates. To predict crossover rates accurately, we model the transient evolution of species concentration using a two-dimensional version of porous electrode theory with Nernst-Planck fluxes, wherein electrolyte is transported between a reactor and well-mixed tanks. In contrast with previous RFB models we use Marcus-Hush-Chidsey theory to predict redox kinetic rates, instead of the commonly used Butler-Volmer (BV) equation. BV is an empirical model where the rate constants exponentially depend on the overpotential $\eta$ as $k_{\text{ox}}/k_{\text{red}} = k_0 e^{\pm \theta_0 \eta / R T}$, where $k_0$ is the standard rate constant. Although BV is accurate for low overpotentials, at high overpotentials BV predicts extremely large and unrealistic values of rate constants. This effect is particularly important in modeling the capacity fade due to the crossover of redox species where large overpotentials (>$0.5$ V for both AqRFBs and NaqRFBs) are experienced. On the other hand, the Marcus-Hush-Chidsey (MHC) kinetic theory accounts for reorganization energy of solvent $\lambda$ and the finite density of states in the electrode. Further, the MHC theory (both in its original integral form and simplified form) predicts a saturating reaction constant with increasing overpotential as shown in Fig. 1.

In the present work, we present a two-dimensional porous electrode model broadening the scope to any single-electron redox species, and we account for the crossover of all redox species involved in the system. Crossover occurs whenever there exists a gradient in pressure (advection), concentration (diffusion), or electrolyte potential (migration) across the porous separator. Using this model, we study the crossover of redox species by mapping the variation of capacity utilization and capacity fade with two variables: (1) molar-salt ratio ($\gamma = c_{\text{salt}} / c_{\text{redox}}$) and (2) salt-diffusion ratio ($\zeta = D_{\text{salt}} / D_{\text{redox}}$). Further, non-dimensional scaling analysis is conducted based on the Damköhler numbers for redox active and salt species in the electrolyte. Operating regimes for RFBs with non-selective separators are defined using these non-dimensional parameters. In particular, we find that operating RFBs with sufficient supporting electrolyte ($\gamma > 0.6$) and with high redox Damköhler number ensures both high capacity utilization and long cycle life. These findings establish a rational paradigm for the selection and engineering of low-cost, long-life RFB electrolytes.

**Modeling Approach**

**Reactor layout and electrochemistry.**—The RFB simulated here consists of a reactor and two well-mixed tanks storing its electrolytes...
The two porous carbon electrodes in the reactor host the redox reactions and are electrically separated by a non-selective porous separator. This assembly is encased by two current collectors. The reactor uses interdigitated flow fields (IDFFs) that have alternating inlet and outlet channels, a detailed schematic of which is shown in our previous publication.58 The IDFF offers optimal performance with respect to the wetting of electrodes (for conducting electrochemical reactions) and reducing pressure drop.54 Monitoring pressure drops is important in the context of NaAqRFBs as electrolyte viscosity increases rapidly with redox concentration.21,50 Moreover, operating RFBs at higher magnitudes of pressure could force bulk movement of electrolytes through the separator if the respective electrolytes are pumped at different rates or have different viscosities. Such effects could induce electrolyte imbalance and, thus, capacity loss, while potentially affecting membrane life. Also, pumping costs increase, reducing the net effective energy stored/delivered by the battery system. We note that crossover due to bulk electrolyte flow is negligible here since viscosity is assumed to be constant in both electrolytes.

A complete IDFF reactor can be constructed by periodically repeating a 2D ‘unit’ cell as shown in Fig. 2. We therefore conduct our analysis on a representative unit cell of length \( L_e \) (along the direction of the separator), electrode thickness \( H_e \), and porosity \(\epsilon_e\) with flow inlet and outlet channel width of \( L_{in} \). The non-selective separator is modeled as an electrolyte-imbibed, electron-insulating porous medium with thickness \( H_{sep}\), porosity \(\epsilon_{sep}\) and tortuosity \(\tau_{sep}\). The geometrical and transport properties of the reactor and separator are listed in Table 1. The two electrolytes in their pristine condition contain high potential and low potential redox couples, respectively. The primary redox reactions in the high potential electrode and low potential electrode (green dotted boxes in Fig. 2) along with equilibrium potentials at 50% state-of-charge (SOC) are:

\[
R^{1[\pm]} \leftrightarrow O^{1[\pm]} + e^- , E_{1, eq}^0 = 3V \text{ and } \\
O^{2[\pm]} + e^- \leftrightarrow R^{2[\pm]} , E_{2, eq}^0 = 0V
\]

The equilibrium potentials are set to produce a 3 V working voltage RFB. Although a 3 V RFB corresponds to a non-aqueous RFB, the mechanisms explained in this work are applicable in designing both aqueous and non-aqueous RFBs as long as (1) a non-selective separator is used and (2) cell voltage exceeds the overpotential level where Marcus-Hush-Chidsey kinetics become overpotential independent. As the RFB is cycled, crossover of all the four different redox species (\( R^{1[\pm]} , O^{1[\pm]} , R^{2[\pm]} , O^{2[\pm]} \)) from their primary electrode to the counter electrode forces a second set of redox reactions in the counter electrode (pink dotted boxes in Fig. 2). Depending on the charge numbers \( z \) of the redox species, the reactions can be classified either as salt-splitting (SS) or rocking-chair (RC) configuration. In SS configuration one species in each redox couple is neutral requiring the presence of supporting electrolyte for ion transfer across the separator. In RC configuration all redox species have similarly signed non-zero oxidation state,34 and these ions, along with their associated counter ions, can transfer across the separator to maintain electroneutrality. Theoretically RC requires less salt concentration than SS and could therefore be a potential solution toward economical low-salt RFBs.34 In this study, we compare the capacity utilization and capacity fade of RC and SS configurations as a function of salt concentration and the diffusion coefficient of redox species.

### Electrochemical kinetics and governing equations.

A transient, two-dimensional numerical model based on porous-electrode theory55 is developed to model the competitive transport processes that govern RFB performance, particularly transport mechanisms related to crossover. The porous electrode model developed here is a homogenized one, employing a local, volume-averaged formulation for transport processes including electron conduction in electrodes, ion diffusion and migration in electrolytes, and reaction kinetics on the surface of carbon fibers. The electrochemical kinetics of the redox couples are assumed to follow Marcus-Hush-Chidsey (MHC) kinetics. The MHC model is based on microscopic theory of electron transfer and reorganization energy, denoted as \( \lambda \), that relates the interaction between the electrode surface, redox species, and the solvent.52–58 For a general redox reaction given as \( R ↔ O + e^- \), the oxidation \( k_a \) and reduction \( k_{red} \) reaction rate constants for MHC theory are given as:

\[
k_{as/\text{red}} = A \int_{-\infty}^{\infty} \exp\left\{ -\frac{1}{4k_BT} \left( x - \lambda \pm \eta \right)^2 \right\} \frac{dx}{1 + \exp(x/k_BT)} \tag{1}
\]

where \( \eta \) is overpotential, \( A \) is a pre-exponential factor, \( T \) is temperature and \( \lambda \) is the electron energy relative to the Fermi level within the electrode. We use an analytical approximation for \( k_{as/\text{red}} \) (developed previously53) expressed in terms of dimensionless overpotential \( \eta^* = \frac{\eta}{k_BT} \) and re-organization energy \( \lambda^* = \lambda/k_BT \):

\[
k_{as/\text{red}} = \frac{\sqrt{\pi \lambda^*}}{1 + \exp(\pi \eta^*)} \text{erfc} \left[ \frac{1 + \sqrt{\lambda^* + \eta^*}}{2 \sqrt{\lambda^*}} \right]. \tag{2}
\]

The net reaction current density \( i_n \) for the redox reaction \( R ↔ O + e^- \) can therefore be expressed as

\[
i_n = F \left( k_{as}C_R - k_{red}C_O \right), \tag{3}
\]

where \( c_R \) and \( c_O \) are the concentrations of the reduced and oxidized species respectively. A positive overpotential drives the oxidation reaction and a negative overpotential drives the reduction reaction. The overpotential at the electrode/electrolyte interface, given as \( \eta = \phi_i - \phi_e - \phi_{eq} \), is a measure of how high or low the potential of the electrode \( \phi_i \) is with respect to the solution potential \( \phi_e \) and the equilibrium potential \( \phi_{eq} \) of the active compounds. The equilibrium potential at any state of charge / discharge is determined here by the Nernst equation as:

\[
\phi_{eq} = E^0 - \frac{RT}{n_iF} \ln \frac{c_R}{c_O} \tag{4}
\]

where \( E^0 \) is the equilibrium potential at 50% state of charge and \( n_i \) is the number of electrons transferred in the redox reaction (here \( n_i = 1 \)).

The RFB system modeled here consists of 6 different species: the four redox active species (\( R^{1[\pm]} , O^{1[\pm]} , R^{2[\pm]} , O^{2[\pm]} \)) and two supporting electrolyte ions (\( A^+, B^- \)). The local concentrations of these six species are affected by redox reactions and transport processes. The mass conservation equation for each of these species takes the form:

\[
\frac{\partial c_i}{\partial t} + \nabla \cdot ( \mathbf{N}_i ) + S_i = 0 \tag{5}
\]
The superficial velocity \( \bar{u} \) is solved together with the electroneutrality condition throughout the entire domain:

\[
\nabla \cdot (\sigma \nabla \phi) + \sum_{i=1}^{36} a_i \phi_i = 0 \tag{8}
\]

The electrochemical and transport properties of all redox species and supporting electrolytes simulated are listed in Table II. The separator is assumed to be electronically insulating. The RFB is subjected to galvanostatic cycling by applying a constant current density \( i_{\text{app}} = 10 \text{mA/cm}^2 \) on the high potential electrode. The counter electrode current collector is grounded. The left and right sides of the reactor domain are modeled by imposing symmetric (i.e., mirrored) boundary conditions on both potential and concentration fields, so as to mimic a periodically repeating series of IDFF channels. Our previous study \(^{46} \) shows that the flow rate in the reactor should be maintained above twenty times the stoichiometric flow rate in order to minimize mixing losses in the tanks and to achieve capacity utilization of about 85\% of the theoretical maximum. Therefore, in this study we adopt the flow rate entering the reactor to be thirty times the stoichiometric flow rate with a tank-to-electrode volume ratio of twenty. This serves as the boundary condition for Darcy’s equation to establish the 2D superficial velocity field in the electrodes.

The governing equations presented are non-linear and tightly coupled. Therefore, we use numerical methods to discretize the governing equations and to iteratively solve them. In this study, we use the finite-volume technique to discretize the equations on a 2D domain. The discretized equations are solved in MATLAB using a coupled Newton-Raphson iteration algorithm. \(^{61-63} \) Convergence is achieved when the difference in concentration fields is less than \( 10^{-8} \) mol/L and that of potential fields is less than \( 10^{-5} \) V during consecutive iterations.

Verification is an important step in numerical modeling to check the correctness of implementation as computer programming. We verify the present model by choosing appropriate conditions under which analytical solutions exist and by comparing the predictions of the 2D simulation with those analytical solutions. We take inspiration from Wolfram and co-workers \(^{46} \) who studied the redox active shuttling of the catechol-quinone redox couple in a nano gap electrode. The shuttling between the two electrodes is limited by diffusion processes and, under no-flow conditions, the diffusion limited current density in a channel of height \( h \) with \( n \) redox active molecules is given as \( i_{\text{diff}} = \frac{nFzF}{hD_{\text{eff}}} \). Under similar conditions of operation, the diffusion limited current density predicted by our simulation is in 98\% agreement with the analytical expressions over three orders of magnitude variation in redox species concentrations. This comparison verifies our implementation of the species transport equation. Other verification steps related to implementation of mass balance, advection transport, and reaction kinetics (as described in our previous work \(^{48} \)) have been performed, and the results of these tests were well within tolerance limits.

### Results and Discussion

The primary aim of this study is to explain the mechanisms governing the crossover rate of redox active species and their effect on capacity fade. To ensure charge neutrality during the cycling process,
redox active species can transport alongside with supporting electrolyte ions by crossing the separator, leading to material loss. The crossover rate is affected by the concentration, diffusion coefficient, and charge number of redox species relative to the supporting electrolyte. Such processes can lead to interesting phenomenon such as redox active shuttling between the two electrodes. Although zero-dimensional models have been proposed to understand capacity fade due to crossover,23 an in depth understanding of the local processes that produce capacity fade is missing. Here, a 2D model which tracks all dissolved species at all instants in time allows us to quantify the degree of crossover and the spatially resolved reaction currents. With this model we map the performance and capacity fade of RFBs against variations in initial salt concentrations and redox active species diffusion coefficients for both RC and SS configurations. Such analysis can be used to engineer redox active molecules and separator materials.

As there are multiple species and reactions involved, we refer to the redox reactions which are intended for either the high potential electrode (HPE) or the low potential electrode (LPE) as primary reactions. The redox reactions the species experience upon crossing over the separator are referred to as “crossover” reactions (see Figure 2).

Primary reactions: $R_1^{(RX)} \leftrightarrow O_1^{(γO)} + e^- \quad \text{in HPE}$

and $R_2^{(RX)} \leftrightarrow O_2^{(γO)} + e^- \quad \text{in LPE}$

Crossed reactions: $R_2^{(RX)} \leftrightarrow O_2^{(γO)} + e^- \quad \text{in HPE}$

and $R_1^{(RX)} \leftrightarrow O_1^{(γO)} + e^- \quad \text{in LPE}$

We introduce two dimensionless numbers of practical importance to elucidate our results. Molar salt ratio $γ$ is defined as the ratio of the concentration of salt to the concentration of the redox species in the electrolyte $γ = \frac{c_{salt}}{c_{redox}}$. Throughout our analysis, the concentration of redox active species is fixed at 0.5 M and the concentration of salt is varied from 0 M to 1 M ($γ : 0 \rightarrow 2$). The salt-diffusion ratio $ζ$ is the ratio of the diffusion coefficient of salt ions to that of redox active ions $ζ = \frac{D_{salt}}{D_{redox}}$. The value of the diffusion coefficient of salt ions ($A^+, B^-$) is set to that of the PF$_6^-$ anion in EC/PC/DMC20 and $D_{redox}$ is varied systematically by three orders of magnitude ($ζ : 10^{-3} \rightarrow 10^3$). Assuming that Stokesian drag resists diffusional driving forces in solution, the systematic variation of $ζ$ can also be interpreted as scaling redox-molecule Stokes radius relative to that of inert salt ions. This relationship can be expressed in equation form as $ζ = \frac{R_{redox}}{R_{salt}}$, using the Stokes-Einstein equation, where $R_c$ is the Stokes radius of species $i$. Aqueous and non-aqueous RFB electrolytes from the literature also span this range of $ζ$, including these examples:

- DBBB actives and LiPF$_6$ salt in carbonate solvent24 produce $ζ \approx 2$ after estimating $D_{salt}$, from Ref. 66.
- $V^{2+/3+}$ actives and H$_2$SO$_4$ salt in water produce $ζ \approx 5$ and 40, depending on whether $D_{salt}$ for $H^{+}$ or $HSO_4^{-}$ is used, and RAPs and LiPF$_6$ salt in acetonitrile21 produce $ζ \approx 70$ based on measured “rejection ratios.”

A large value of $D_{redox} > 5 \times 10^{-11} m^2/s$ (low $ζ$) implies that the diffusion coefficient of the redox active molecules is on par with salt ions for the assumed value of $D_{salt} = 5 \times 10^{-12} m^2/s$. Although increasing $D_{redox}$ increases the ionic conductivity of electrolyte, redox active molecules actively compete with salt ions for transport across the separator, leading to large capacity fade. Capacity utilization $χ$ is defined as the percentage of theoretical capacity being utilized during a certain charge/discharge cycle. The RFBs here are cycled galvanostatically between 2.5 V to 3.5 V.

Cycling behavior and reaction current distribution.—We first study the cycling performance of an RFB in terms of capacity utilization and coulombic efficiency for ten charge/discharge cycles. For this analysis, a representative RFB with 0.5 M salt concentration ($γ = 1$) and with redox species diffusion coefficient $ζ = 63$ times smaller than that of salt ions, a ratio that is similar magnitude to the “rejection ratio” measured previously21 for RAPs relative to inert salt ions. For the chosen values of $D_{salt}$, current density, and salt concentration this simulation produces a salt Damköhler $Da_{salt}$ equal to 8, which we show later is small enough to facilitate “sufficient supporting electrolyte” behavior where capacity losses are dominated by the diffusive crossover of redox species (rather than by ohmic polarization). Here, we focus on this particular case to illustrate the influence of crossover on reaction current distribution and charge capacity. The cell voltage curve for this case is shown in Figure 3 along with the variation of the capacity utilization during discharge at every cycle. Here, the coulombic efficiency, which was previously correlated to the degree of crossover,31 is 97% indicating that with every cycle there is certain loss of active species due to crossover. Because of this effect the discharge capacity utilization fades by 20% within the first ten cycles.

Reaction current distribution and crossover fluxes.—The dynamics of crossover and redox active species shuttling processes vary significantly within a single charge/discharge cycle step. With variation in state-of-charge, the processes of diffusion and migration can either favor or oppose each other in transferring redox active species across the separator, depending on the direction of current. When the primary redox couple of the HPE ($R_1^{(RX)} / O_1^{(γO)}$) crosses over into the LPE, the large negative overpotential environment in the LPE drives the reduction reaction where almost all $O_1^{(γO)}$ reduces to $R_1^{(RX)}$. This overpotential is negative throughout the charge/discharge cycle. Similarly, when the primary redox couple of the LPE ($R_2^{(RX)} / O_2^{(γO)}$)

![Figure 3](https://example.com/f3.png)
crosses over to the HPE, the large positive overpotential environment drives the oxidation reaction converting all $R^2\text{O}_2$ to $O^2\text{O}$. The total pore-scale reaction current density $i_r(x, y, t)$ is a result of electrode-electrolyte interfacial redox reactions and is different from the galvanostatic applied current density at the current collectors. This reaction current density is calculated from the MHC kinetic model using Equations 2 and 3. Figure 4 shows the development of cell voltage with state-of-charge during the second charge/discharge cycle. Snapshots of the primary and crossed reaction current densities are also shown at two points: near the end of the charge step (A) and early in the discharge step (B). The corresponding cell-voltage is shown as a loop varying with state-of-charge to delineate the capacity utilization during both charge and discharge steps (80% in this case) and the polarization measured by the averaged difference of the voltages during charge and discharge. The cell voltage plot in Fig. 4 also shows that the state-of-charge consumed during the discharge process falls short to complete the loop, indicating coulombic inefficiency due to crossover.

The pore-scale reaction current density is positive during the oxidation process and negative during reduction. While charging the RFB, the redox couple in the HPE undergoes oxidation generating $O^1\text{O}_1$ while the redox couple in the LPE undergoes reduction generating $R^2\text{O}_2$. The oxidation reaction in the HPE is reflected by positive values of $i_{r, \text{primary}}(x, y, t)$ in the HPE and reduction reaction in the LPE are associated with negative values of $i_{r, \text{primary}}(x, y, t)$ in the LPE, as shown in panel A of Fig. 4. Since a large flow rate is chosen, the reaction currents are well distributed within the electrode volume, effectively using the available surface area for conducting reactions. This observation of uniform reaction distribution within the electrodes at high flow rates is consistent with our previous findings and operating the RFB at lower flow rates will bias reactions near the inlets increasing polarization losses. Similarly, during the discharge process (Fig. 4, B1), the primary reaction currents are negative (reduction) in the HPE and positive (oxidation) in the LPE. The primary reaction current distribution $i_{r, \text{primary}}(x, y, t)$ shown at points A and B is representative of the entire charge/discharge step.

The crossed reaction current density $i_{r, \text{cross}}(x, y, t)$ is affected by local overpotential and the availability of redox active species in the counter electrode (degree of crossover). As explained above, the redox couple $R^1\text{O}_2/O^1\text{O}_1$, which is primary to the HPE, undergoes reduction upon crossing over to the LPE. Therefore when $R^1\text{O}_2$ crosses over, it accumulates in the LPE without undergoing any redox reaction. On the contrary when $O^1\text{O}_1$ crosses over into the LPE, it undergoes fast reduction to $R^1\text{O}_2$ due to large negative overpotentials irrespective of the RFB’s state-of-charge. The degree of crossover of each species, characterized by its diffusion and migration rates, varies significantly with state-of-charge. The HPE is rich in the oxidized species $O^1\text{O}_1$ during the end of charging or early in the discharge process, favoring diffusion of $O^1\text{O}_1$ from the HPE to the LPE immediately reducing to $R^1\text{O}_2$ in the LPE. Therefore, as shown in Fig. 4 panels A2 and B2, $i_{r, \text{cross}}(x, y, t)$ of the crossed couple $R^1\text{O}_2/O^1\text{O}_1$ in the LPE becomes negative (reduction) and dominant near the separator region. At the same instant in the charge/discharge cycle, the LPE electrode is plentiful in $R^2\text{O}_2$, which, upon crossing over to the HPE, undergoes oxidation to $O^2\text{O}_2$. Thus, $i_{r, \text{cross}}(x, y, t)$ in both electrodes is significant in magnitude only during the second half of the charging process and during the first half of discharging process. Crossover magnitudes are relatively small otherwise, a mechanistic explanation of which is given later by comparing diffusion and migration contributions. Also, note that the values of $i_{r, \text{cross}}(x, y, t)$ are at least an order of magnitude lower than $i_{r, \text{primary}}(x, y, t)$ and the sign of $i_{r, \text{cross}}(x, y, t)$ is maintained consistently in the HPE and in the LPE (i.e., oxidation and reduction respectively) regardless of charge/discharge cycling phase of the RFB.

To qualitatively estimate the distribution of the crossed reaction current density $i_{r, \text{cross}}(x, y, t)$, the kinetically limited current $I_{\text{kinetic}}^{\text{lim}}$ in the electrode is compared to the species ionic crossover current passing through the separator $I_{\text{cross}}$. At high overpotentials ($|\eta| >> k_B T/\epsilon$) MHC theory predicts a limiting kinetic rate constant:

$$k_{\text{ox/red}}^{\text{lim}} = 4k_0/\text{erfc} \left( \frac{\lambda^* - \sqrt{1 + \sqrt{\lambda^*}}}{2\sqrt{\lambda^*}} \right)$$

For the present simulations we estimate $I_{\text{kinetic}}^{\text{lim}}/I_{\text{cross}}^{\text{lim}} \sim 10^5$, implying that active species should react instantaneously once they have crossed through the separator. This expectation is confirmed by our simulations where reaction hotspots are observed adjacent to the separator, as shown in panels A2 and B2 of Fig. 4.

Diffusion and migration mechanisms govern crossover processes. The relative contribution of these two processes toward crossover varies significantly with active-species charge number, its diffusion coefficient, and the transient concentration fields of all the redox active and salt species involved. Although zero-dimensional, time-independent heuristic models haven been proposed to quantify the

---

Figure 4. Cell voltage variation with state-of-charge during the galvanostatic charge and discharge process of a representative RFB with salt concentration of 0.5 M ($\gamma = 1$) and redox-active species diffusion coefficient of $7.9 \times 10^{-12} \text{m}^2/\text{s}$ ($\zeta = 63$). Snapshots of primary and crossed reaction current density are shown at points A and B along with flow direction indicated by the black arrows (geometry not drawn to scale).
degree and effects of crossover,\textsuperscript{51,68} a comprehensive theory resolving local, time-dependent fields is needed to design RFBs and to engineer their electrolytes. Using the two-dimensional, transient model presented here, we track the time varying diffusion and migration rates of selected redox species, and we further elucidate the findings about crossed reaction current density in Fig. 4. The variation of the concentration of \( O^{1+} \) in the HPE is shown for a single charge/discharge cycle in Fig. 5a along with cell voltage. The diffusion and migration crossover fluxes are shown in Fig. 5b in terms of crossover current fraction along with thumbnails indicating the direction of crossover during charge/discharge. The crossover current fraction is defined as the ratio of the ionic current due to a particular species passing through the separator and the total applied galvanostatic current. The crossover current fraction is positive when species crossover from HPE to LPE and is negative otherwise. The ionic current of \( O^{1+} \) is calculated by multiplying each component of the molar flux (Eq. 7) through the porous separator with solution potential and cell voltage. Therefore, during the charging process, the concentration of \( O^{1+} \) increases in the HPE along with solution potential and cell voltage. Therefore, during the charging process, the gradient of \( O^{1+} \) concentration and solution potential across the separator continuously increases, leading to increased diffusion and migration fluxes with time. The migration fluxes have a squared dependence on the oxidation state of the species involved. As can be seen from Fig. 5b, migration dominates diffusive crossover fluxes for a high oxidation state redox molecule \((z_{\text{red}} = +3)\) during the charging process. During the discharge process, the polarity of electrolyte potential difference across the separator reverses, and the electric field induced migration is thereafter directed from the LPE to the HPE, opposing the direction of diffusive fluxes. Therefore, the net crossover of \( O^{1+} \) is insignificant and is reflected by the decreasing magnitude of the crossed reaction current density during discharge in the LPE (compare LPE in panels A2 and B2 of Fig. 4). On the contrary, the crossover of the redox molecule \( R^{2+} (z_{\text{red}} = +1) \) from the LPE to the HPE is sizable during the discharge process. Figure 5c shows the variation of \( R^{2+} \) concentration in the LPE, and Fig. 5d shows the transient variation of the crossover flux components. During the charge process, the diffusive and migration fluxes oppose each other, resulting in net crossover that is practically insignificant. With the change in polarization of electrolyte potential during discharge, the diffusion and migration mechanisms ensure a net crossover of \( R^{2+} \) from the LPE to the HPE. Therefore, we observe small crossed reaction current density in the HPE during charge (Fig. 4, panel A2), and it is more significant during discharge (Fig. 4, panel B2). In summary, the redox species with the largest charge number in the HPE experiences the maximum degree of crossover, and this process is dominated by migration. Therefore, it is crucial to engineer such high oxidation state redox active molecules to have low diffusion coefficients.

Effects of supporting electrolyte and diffusion coefficient.—In this section we analyze the effects of salt concentration and redox active species diffusion coefficient on rocking-chair (RC) and salt-splitting (SS) RFB configurations. Discharge capacity utilization and

![Figure 5](https://example.com/methodology-figure.png)
The other hand designing redox molecules with high electronic and possess lowest ohmic polarization. Despite this advantage, the RC configuration allows operating RFBs at low salt concentration levels, the capacity utilization at such extremes is very low and is impractical. Both RC and SS configurations require a certain minimum amount of salt to minimize electric field and thereby obtain sufficient discharge capacity utilization. In both these configurations the performance of RFBs is mapped using two non-dimensional variables: (1) the molar-salt ratio defined as the ratio of salt concentration to redox-active species concentration in electrolyte ($\gamma = c_{\text{salt}}/c_{\text{redox}}$) and (2) the salt-diffusion ratio which is the ratio of the diffusion coefficient of salt ions to redox-active species ($\zeta = D_{\text{salt}}/D_{\text{redox}}$). The concentration of redox active molecules is fixed to $c_{\text{redox}} = 0.5 \text{M}$. Larger values of $\gamma$ means that more salt is dissolved in the electrolyte. In addition, the diffusion coefficient of salt ions is set to be representative of fluoride salt derivatives $D_{\text{salt}} = 5 \times 10^{-10} \text{m}^2/\text{s}$ and $D_{\text{redox}}$ is varied to parameterize redox active molecule design. A fast diffusing redox active molecule (small value of $\zeta$) has a diffusion coefficient comparable to that of salt ions and therefore has more crossover. The variation of ionic conductivity in this electrolyte design space of concentration ($\gamma$) and diffusion coefficient ($\zeta$) is given as $k_0 = \sum z_i^2 D_i F^2/RT$ with contributions coming from the four redox-active species and the two salt ions. Electrolytes with large $\gamma$ and low $\zeta$ are most conductive and possess lowest ohmic polarization. Despite this advantage such electrolytes necessarily experience high crossover rates. On the other hand designing redox molecules with high $\zeta$ can reduce the total amount of forty-two and forty-eight cases spanning the design space of $\gamma$ (0 → 2) and $\zeta$ (10 → 1000) were simulated for both RC and SS configurations, respectively. A contour map of discharge utilization capacity fade after ten cycles (%-theory) for the rocking-chair (RC) configuration as a function of dimensionless molar salt ratio $\gamma$ and salt diffusion ratio $\zeta$. The forty-eight dots on the plot show the simulation cases interpolated to populate the figure.

Figure 6. Contour map of discharge utilization during the first cycle along with capacity fade after ten cycles (% theoretical) for the rocking-chair (RC) configuration as a function of dimensionless molar salt ratio $\gamma$ and salt diffusion ratio $\zeta$. The forty-two dots on the plot show the simulation cases interpolated to populate the figure.

Figure 7. Contour map of discharge capacity utilization during the first cycle, along with capacity fade after ten cycles (% theoretical) for salt-splitting (SS) configuration as a function of the dimensionless molar salt ratio $\gamma$ and the salt diffusion ratio $\zeta$. The forty-eight dots on the plot show the simulation cases interpolated to populate the figure.
of SS configured RFBs as a function of molar salt ratio \( \gamma \) and salt diffusion ratio \( \xi \). An appreciable discharge utilization of 80% can be achieved when \( \gamma > 0.5 \). Also, capacity fade rate becomes independent of concentration for \( \gamma > 0.6 \), consistent with excess supporting electrolyte behavior. Compared with the RC configuration (Fig. 6), the SS configuration (Fig. 7) has better capacity retention. The use of smaller charge number redox materials in the SS configuration decreases migration crossover fluxes, benefitting capacity retention. Contrary to the hypothesis that the RC configuration could be the potential pathway for developing low salt RFBs, Figs. 6 and 7 show that the SS configuration has similar performance to the RC configuration. Both configurations require minimum salt concentration levels (\( \gamma > 0.5 \)) for profitable capacity utilization and the SS configuration has an advantage over RC in capacity retention by smaller migration crossover fluxes. Also, the SS configuration achieves the excess supporting electrolyte regime sooner than the RC configuration, reducing its sensitivity of performance to changes in initial salt concentration. That said, the results and conclusions presented thus far are for RFBs using a porous non-selective separator. Crossover and transport mechanisms will change with the use of selective membranes.

Non-dimensional analysis using Damköhler numbers.---The results presented thus far are for a single value of applied current density and for a certain redox species concentration. To extend the scope of application of the present simulations to an RFB with generic materials, design, and operating conditions, we now introduce Damköhler numbers for redox species \( D_{\text{salt}} \) and salt ions \( D_{\text{salt}} \). Here, the Damköhler number of a particular species quantifies the characteristic rate of the net reaction relative to the rate of species transport across the separator. For a redox reaction where \( n_e \) electrons are transferred for every \( e \) formula units of redox active species \( i \), the Damköhler number is \( D_{\text{salt}} = i_{\text{app}} H / (F D_{\text{sep}}^i n_e c_i) \). The rate of capacity fade due to crossover is expected to scale with the transport rate of redox active species across the separator relative to the transport rate of salt ions. This ratio of rates can be estimated by the ratio of salt and redox-active species Damköhler numbers multiplied by the charge number of the particular redox-active species, i.e., \( z_i D_{\text{salt}} / D_{\text{redox}} \). This non-dimensional quantity can also be expressed in terms of molar salt ratio and salt-to-redox diffusion ratio as \( z_i D_{\text{salt}} / D_{\text{redox}} = z_i D_{\text{salt}} / D_{\text{redox}} \). Therefore, the dimensionless number \( z_i D_{\text{salt}} / D_{\text{redox}} \) is independent of applied current density. Figure 8a maps the variation of discharge capacity utilization in the first cycle and of capacity fade after the first ten cycles using \( z_i D_{\text{salt}} / D_{\text{redox}} \). Here, \( z_i \) is the arithmetic average charge number among all redox species involved with \( z_i = 2 \) for the present RC RFB simulations. On this space of \( z_i D_{\text{salt}} / D_{\text{redox}} \) and \( D_{\text{salt}} / D_{\text{redox}} \) three regimes are labeled: (1) redox-shuttle limited, (2) ohmic polarization dominated, and (3) sufficient supporting electrolyte. In the redox shuttle limit regime, the transport rate of redox molecules is comparable to that of salt and therefore the redox molecules shuttle between the two electrodes constantly, leading to poor capacity retention. In the ohmic polarized regime \( (D_{\text{salt}} > 10) \) polarization limits capacity utilization due to its low concentration of supporting electrolyte. The most favorable regime for the efficient and long-term operation of RFBs with non-selective separators is the sufficient supporting electrolyte regime, where discharge capacity utilization exceeds 80%. To achieve such conditions requires that \( z_i D_{\text{salt}} / D_{\text{redox}} < 0.3 \) and \( D_{\text{salt}} < 12 \), such that neither redox shuttling nor ohmic polarization limits cycling. From Figure 8a, operating RFBs in the sufficient supporting electrolyte region and at large values of \( D_{\text{salt}} \) will yield greatest capacity retention. \( D_{\text{redox}} \) can be increased either by increasing applied current density or by engineering redox species to have low diffusion coefficients.

In the sufficient supporting electrolyte regime, the ratio \( z_i D_{\text{salt}} / D_{\text{redox}} \) translates to a monotonous function of the transfer number of redox active species \( t_i \) given as \( z_i D_{\text{salt}} / D_{\text{redox}} = t_i / (1 - t_i) \). In the context of the molecular engineering of RFB electrolytes low redox-species transference number is crucial to maintain high capacity utilization over many cycles. In the sufficient supporting electrolyte region capacity fade is weakly dependent on \( D_{\text{salt}} \) and thus depends primarily on \( D_{\text{redox}} \). We use the six simulated data points in the sufficient supporting electrolyte regime that have smallest \( D_{\text{salt}} \) (marked by ‘*’ in Fig. 8a) to correlate the variation of capacity fade with the Damköhler number of redox species \( D_{\text{redox}} \), as shown in Fig. 8b. The capacity fade decreases with increasing \( D_{\text{redox}} \) as \( \Delta \chi_{10}(\%) = 1.72 \times 10^{-4} \frac{D_{\text{redox}}}{D_{\text{salt}}} \times 10^{-4} \) with a coefficient of determination value \( R^2 \) of 0.9965. For very large values of \( D_{\text{salt}} \), this expression takes the form of a power law dependence where \( \Delta \chi \propto D_{\text{salt}}^{-1} \). This expression can be used in the engineering of redox active molecules and to determine operating conditions for a given RFB electrolyte that are necessary to achieve a target capacity retention level. For example, \( D_{\text{redox}} \) must be greater than \( 1.7 \times 10^2 \) to obtain a capacity retention of 99.9% after ten cycles. Comparing Figs. 6 and 7, the capacity utilization and capacity fade for RC and SS configurations are qualitatively and quantitatively similar. Therefore, the non-dimensional analysis presented through Fig. 8 holds true for both RC and SS configurations.

Conclusions

In the context of engineering cost effective RFBs we develop a mechanistic understanding of the crossover process and the role of supporting electrolyte in RFBs using porous, non-selective separators. To do this we present an RFB model based on porous electrode theory with Marcus-Hush-Chidsey (MHC) kinetics and
Nernst-Planck fluxes. The model predicts the spatial and temporal variation of two sets of redox couples \((R^{1+0}/O^{1−0} & R^{2+2s}/O^{2−02})\), two salt ions \((A^+, B^-)\), solid phase potential, and electrolyte potential. The redox couples could have a rocking-chair (RC) or salt splitting (SS) configuration, the former involving similarly charged ions and neutral species in the latter.

The pore-scale reaction current density distributions simulated here reveal that the reaction current densities resulting from crossover processes are at least an order of magnitude lower than the primary redox reactions and, thus, vary in time significantly during charge/discharge cycling. The diffusion and migration mechanisms that govern crossover (according to Nernst-Planck equation) either enhance or oppose each other in the crossover process depending upon (1) state-of-charge, (2) charge/discharge cycling, and (3) the properties of the redox species. We find that the capacity loss due to crossover is dictated by the highest oxidation state redox species in the high potential electrode and that rate is dominated by migration especially in the second half of the charging process where the cell potential is large. We further extend the study by mapping the discharge utilization and capacity fade of RFBs by varying the amounts of supporting electrolyte and the diffusion coefficient of the redox active molecules. Contrary to expectations of the RC configuration being a possible solution for cost-effective low salt RFBs, we find that both configurations have very low discharge utilization in low salt regimes. The deficiency of positive salt ions in the high potential electrode forces the negative salt ions alone to maintain the electroneutrality by transferring across the separator. Maintaining electroneutrality with negative salt ions alone can only be done when the potential gradient across the membrane is increased, resulting in prematurely reaching cell voltage limits of cycling without actually utilizing active molecules for energy storage. A threshold amount of salt (at least 50% concentration of redox actives in either electrolyte) is needed to obtain 80% of discharge utilization capacity. From the perspective of engineering redox active molecules, the diffusion coefficient of these molecules should be three orders of magnitude lower to secure more than 95% capacity retention for ten cycles at 10 \(\text{mAh} \cdot \text{cm}^{-2}\). In the scope of designing and operating RFBs, the variation of the discharge capacity utilization and the capacity fade of RFBs is presented on a 2D space containing the non-dimensional Damköhler numbers of the salt and the redox active species. Three different regimes dominated by ohmic-polarization, redox active shuffling and sufficient supporting electrolyte are identified in this 2D space. A correlation is established between capacity fade and redox Damköhler number in the sufficient supporting electrolyte regime where capacity fade becomes independent of salt Damköhler number. Designing and operating RFBs in the sufficient supporting electrolyte regime where capacity fade becomes independent of salt Damköhler number. Designing and operating RFBs in the sufficient supporting electrolyte regime with large redox Damköhler numbers ensures high capacity utilization and capacity retention.

The transient porous electrode model with Marcus-Hush-Chidsey kinetics and the simultaneous tracking of six different ions is the first kinetic theory which is based on microscopic properties of the redox active molecules and their interaction with the electrolyte. Representative properties of the redox species and supporting electrolyte ions are chosen to delineate mechanistic understanding of crossover processes and the role of supporting electrolyte. Although specific properties of the species involved may vary from a practical standpoint, the physics that govern crossover presented here are still applicable in designing RFBs. However, the model in its current state neglects hydrodynamic dispersion and pore-scale mass transport resistances and assumes that the counter ions of each redox active species have transport properties similar to the supporting electrolyte ions. The present study motivates the optimization of salt concentration levels, non-selective separator properties, and the engineering of redox active molecules for cost-effective RFBs with long operational life.

Acknowledgments
This work was partially supported by the Joint Center for Energy Storage Research, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences. Additional support was provided by the Department of Mechanical Science and Engineering at the University of Illinois at Urbana-Champaign.

List of Symbols

- \(a\) Volumetric surface area of electrode, \(1/m\)
- \(A^+, B^-\) Inert salt ions
- \(c_i\) Concentration of \(i^{th}\) species, \(M\)
- \(D_i\) Diffusion coefficient of \(i^{th}\) species, \(m^2/s\)
- \(e\) Elementary charge, \(C\)
- \(E^0\) Equilibrium potential at 50% state-of-charge, \(V\)
- \(F\) Faraday’s constant, \(C/mol\)
- \(H\) Thickness, \(m\)
- \(I_{app}\) Applied current density, \(A/m^2\)
- \(I_a\) Reaction current density, \(A/m^2\)
- \(I_{a,primary}\) Primary reaction current density, \(A/m^2\)
- \(I_{a,cross}\) Crossed reaction current density, \(A/m^2\)
- \(k_b\) Boltzmann’s constant, \(J/K\)
- \(k_{ox/red}\) Reaction rate constant during oxidation or reduction, \(m/s\)
- \(k_h\) Hydraulic permeability, \(m^2\)
- \(L_e\) Length of unit cell, \(m\)
- \(L_{out}\) Length of inlet/outlet channel in the unit cell, \(m\)
- \(N\) Species flux, \(mol/m^2 \cdot s\)
- \(P_e\) Péclet number
- \(R\) Universal gas constant, \(J/mol \cdot K\)
- \(R_i\) Stokes radius of species \(i, m\)
- \(R^{1+0}/O^{1−0}\) High potential electrolyte redox couple
- \(R^{2+2s}/O^{2−02}\) Low potential electrolyte redox couple
- \(T\) Temperature, \(K\)
- \(\tau\) Superficial velocity field in porous electrode, \(m/s\)

Greek

- \(\varepsilon\) Porosity
- \(\gamma\) Molar salt ratio
- \(\kappa_0\) Bulk ionic conductivity, \(S/m\)
- \(\nu\) Solvent reorganization energy, \(eV\)
- \(\mu\) Electrolyte viscosity, \(Pa \cdot s\)
- \(\nu_s\) Solid volume fraction of electrode
- \(\eta\) Overpotential, \(V\)
- \(\phi_s\) Solution-phase potential, \(V\)
- \(\phi_{eq}\) Equilibrium potential, \(V\)
- \(\phi_{sol}\) Solid-phase potential, \(V\)
- \(\tau\) Tortuosity
- \(\xi\) Salt diffusion coefficient ratio
- \(z_i\) charge number of \(i^{th}\) species

ORCID

Venkat Pavan Nemani @ https://orcid.org/0000-0003-2901-3086
Kyle C. Smith @ https://orcid.org/0000-0002-1141-1679

References

1. What is U.S. electricity generation by energy source? - FAQ - U.S. Energy Information Administration (EIA).
2. BP Statistical Review of World Energy 2017.
3. EIA - Annual Energy Outlook 2018.
4. A. Z. Weber, M. M. Mench, J. P. Meyers, P. N. Ross, J. T. Gostick, and Q. Liu, “Redox flow batteries: a review,” J. Appl. Electrochem., 41, 1137 (2011).
5. M. Skylas-Kazacos, M. H. Chakrabarti, S. A. Hajimolana, F. S. Mjalli, and M. Saleem, “Progress in Flow Battery Research and Development,” J. Electrochem. Soc., 158, R55 (2011).

6. P. K. Leung, X. Li, C. Ponce de Leon, L. Berlouis, C. T. J. Low, and F. C. Walsh, “Progress in redox flow batteries, remaining challenges and their applications in energy storage,” RSC Adv., 2, 10125 (2012).

7. W. Wang, Q. Luo, B. Li, X. Lei, L. Li, and Z. Yang, “Recent Progress in Redox Flow Battery Research and Development,” Adv. Funct. Mater., 23, 970 (2013).

8. P. Alotto, M. Guarierni, and F. Moro, “Redox flow batteries for the storage of renewable energy: A review,” Renew. Sustain. Energy Rev., 29, 325 (2014).

9. R. P. Darling, K. G. Gallagher, J. A. Kowalski, S. Ha, and F. C. Walsh, “Pathways to low-cost electrochemical energy storage: a comparison of aqueous and nonaqueous flow batteries,” Energy Environ. Sci., 7, 3459 (2014).

10. V. Viswanathan, A. Crawford, D. Stephenson, S. Kim, W. Wang, B. Li, G. Coffey, E. Thomsen, G. Graff, P. Balduccchi, M. Kintner-Meyer, and V. Sprengel, “Cost of performance model for redox flow batteries,” J. Power Sources, 247, 1040 (2014).

11. U. S. Department Of Energy, Energy Storage Program Planning Document (2015).

12. R. F. Gahn, N. H. Hagedorn, and J. S. Ling, Single cell performance studies on the Fe/Cr Redox Energy Storage System using mixed reactant solutions at elevated temperature. NASA Report TM-83385 (1983).

13. M. Rychcik and M. Skylas-Kazacos, “Characteristics of a new all-vanadium redox flow battery,” J. Power Sources, 22, 59 (1988).

14. R. J. Remick and P. G. P. Ang, Electrically rechargeable anionically active reduction-oxidation electrical storage-supply system. U.S. Patent No. 4,485,154 (1984).

15. D. J. Eustace, “Bromine Complexation in Zinc-Bromine Circulating Batteries,” Adv. Energy Mater., 218, 174 (2016).

16. R. M. Darling, K. A. Gondomi, A. D. Stroock, T. D. Clark, M. Mayer, and G. M. Whitesides, “Membraneless Vanadium Redox Flow Battery Using Laminar Flow,” J. Electrochem. Soc., 163, A1806 (2016).

17. K. Cdzynska, “Properties of modified electrolyte for zinc-bromine cells,” Electrochim. Acta, 40, 971 (1995).

18. D. Astruc, “Electro-reservoir complexes and other redox-robust reagents: Functions and applications,” New J. Chem., 33, 1191 (2009).

19. Y. Zhao, Y. Ding, J. Song, G. Li, G. Dong, and Y. Zhao, “Alkaline quinone flow electrochemical energy storage through the ferrocene/ferrocenium redox reaction in aprotic electrolyte,” Angew. Chem. Int. Ed., 53, 11036 (2014).

20. X. Wei, W. Xu, M. Vijayakumar, L. Cosimbescu, T. Liu, V. Sprengel, and W. Wang, “TEMPO-Based Catholyte for High-Energy Density Nonaqueous Redox Flow Batteries,” Adv. Mater., 26, 7649 (2014).

21. K. Lin, Q. Chen, M. R. Gerhardt, L. Tong, S. B. Kim, L. Eisenach, A. W. Valle, D. Handley, R. G. Gordon, M. J. Aziz, and M. P. Marshall, “Alkaline quinone flow battery,” Science, 349, 1529 (2015).

22. G. Nagrajana, J. Hui, K. J. Cheng, T. Lichtenstein, M. Shen, J. S. Moore, and J. Rodriguez-Lopez, “Impact of Redox-Active Polymer Molecular Weight on the Electrocatalytic Properties and Transport Across Porous Separators in Nonaqueous Solvents,” J. Am. Chem. Soc., 136, 16304 (2014).

23. A. Ejigu, P. A. Greoreaxes-Davies, and D. A. Walsh, “Room temperature ionic liquid electrolytes for redox flow batteries,” Electrochem. commun., 54, 55 (2015).

24. Y. Wang, P. He, and H. Li Redox Zone, “Flow Batteries Based on Hybrid Electrolytes: At the Cross Road between Li-ion and Redox Flow Batteries,” Adv. Energy Mater., 2, 770 (2012).

25. F. R. Brusheit, J. T. Vaughugh, and A. N. Jansen, “An All-Organic Non-aqueous Lithium-Ion Redox Flow Battery,” Adv. Energy Mater., 2, 1390 (2012).

26. H. Zhang, H. Zhang, X. Li, Z. Mai, and W. Wei, “Silica modified nanofiltration membranes with improved selectivity for redox flow battery application,” Energy Environ. Sci., 4, 3659 (2011).

27. Z. Yuan, Y. Duan, H. Zhang, X. Li, H. Zhang, and I. Venkelecom, “Advanced porous membranes with ultra-high selectivity and stability for vanadium flow batteries,” Energy Environ. Sci., 9, 441 (2016).

28. Y. Yang, N. Q. Luo, B. Li, V. Sprengel, and W. Wang, “Polyvinyl Chloride/Silica Nanoporous Composite Separator for All-Vanadium Redox Flow Battery Applications,” J. Electrochem. Soc., 160, A1215 (2013).
67. John Newman and Karen E Thomas-Alyea, *Electrochemical Systems*. (2004).

68. R. M. Darling, A. Z. Weber, M. C. Tucker, and M. L. Perry, “The influence of electric field on crossover in redox-flow batteries,” *J. Electrochem. Soc.*, 163, A5014 (2016).

69. I. V. Thorat, D. E. Stephenson, N. A. Zacharias, K. Zaghib, J. N. Harb, and D. R. Wheeler, “Quantifying tortuosity in porous Li-ion battery materials,” *J. Power Sources*, 188, 592 (2009).

70. D. A. G. Bruggeman, “Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen. I. Dielektrizitätskonstanten und Leitfähigkeiten der Mischkörper aus isotropen Substanzen,” *Ann. Phys.*, 416, 636 (1935).

71. M. Burgess, K. Hernández-Burgos, B. H. Simpson, T. Lichtenstein, S. Avetian, G. Nagarjuna, K. J. Cheng, J. S. Moore, and J. Rodríguez-López, “Scanning Electrochemical Microscopy and Hydrodynamic Voltammetry Investigation of Charge Transfer Mechanisms on Redox Active Polymers,” *J. Electrochem. Soc.*, 163, H3006 (2016).