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Designing an Industrially-Situated Virtual Laboratory to Support Electrochemistry Learning in Chemical Engineering

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A PhD student working at Tufts University working with Dr. Milo Koretsky to research engineering epistemic practices in the context of virtual and physical lab activities.

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Abstract

The use of electrochemical processes in industry has grown rapidly over the past decade and is predicted to continue that way. Chemistry and engineering students need access to effective electrochemical education within their programs to address this growing need for electrochemical knowledge. This paper describes a virtual laboratory designed to address a gap in the educational tools currently available for electrochemistry. The laboratory uses a software package based on a mathematical model that simulates both species decay and crossover within a redox flow battery (RFB) cell over multiple charge-discharge cycles. The laboratory positions students as engineers working on a realistic task where they design and troubleshoot an RFB system to power buildings on campus. The problem is intended to be personally relevant for students as well as expose them to environmentally just engineering work. To design their battery system, students need to use scientific concepts to select from different electrolyte chemistries, electrodes, and membranes. Based on data and their own assumptions, students will need to assess the viability of their design and make improvements accordingly. After students have created a battery design that meets the deliverables of the activity, they will need to troubleshoot one of many possible realistic problems that can occur. This activity attempts to engage students in practices typical of real engineering work, including working in teams, designing experiments, learning from failure, and managing uncertainty. Rather than doing measures after students leave the laboratory, we investigate which engineering epistemic practices they engage in while completing the laboratory. This laboratory looks to leverage and develop ideas from research on industrially-situated laboratories in the context of electrochemistry by engaging students in productive engineering practice.

Nomenclature

I, Current the battery is cycled at (A)
V^{+}, Volume of electrolyte in the posolyte tank (m^3)
V^{-}, Volume of electrolyte in the negolyte tank (m^3)
F, Faraday's constant (96,485 C mol^{-1})
b, column vector containing the constant reaction terms (mol m^{-3} s^{-1})
K, matrix containing rate constants for species decay and crossover in the system (mol m^{-3} s^{-1})
C, Column vector containing all bulk concentration (mol m^{-3})
$C_{A}^{\infty,+}$, Bulk concentration of species A in the positive half-cell (mol m^{-3})
$C_{A+}^{\infty,+}$, Bulk concentration of species A^{+} in the positive half-cell (mol m^{-3})
$C_{B}^{\infty,-}$, Bulk concentration of species B in the positive half-cell (mol m^{-3})
$C_{B+}^{\infty,-}$, Bulk concentration of species B+ in the positive half-cell (mol m^{-3})
$k_{d,A+}$, Rate constant for decay of species A^{+} (s^{-1})
$k_{d,B}$, Rate constant for decay of species B (s^{-1})
f_{A}, Fraction of species A^{+} which undergoes reversible self-discharge (-)
f_{B}, Fraction of species B which undergoes reversible self-discharge (-)
$k_{c,A}^{+}$, Rate constant for the crossover of species A in the positive half cell (s^{-1})

$k_{c,A+}^{+}$, Rate constant for the crossover of species A+ in the positive half cell (s^{-1})
$k_{c,B}^{-}$, Rate constant for the crossover of species B in the negative half cell (s^{-1})
$k_{c,B+}^{-}$, Rate constant for the crossover of species B+ in the negative half cell (s^{-1})

Introduction

It is widely expected that the use of electrochemical processes will grow rapidly in the coming decade [1], [2], [3]. A major enabler to climate-change mitigations will be the electrification of transportation, industry, and buildings, which currently rely on fossil fuels as their primary energy input [4]. Stochastic renewable energy sources like solar and wind are expected to dramatically increase the number of batteries that will be needed to store energy [3]. Additionally, it is projected that the global demand for lithium-ion batteries will grow by almost a factor of ten by 2040, primarily driven by growth in electric vehicles [1], [2]. These batteries use electrochemical processes to store electrical energy as chemical energy.

As production scales, there will be a rapidly increasing need for engineers and scientists to meet emerging workforce requirements [5]. However, the United States (US) currently lacks the educational infrastructure to provide a sufficient number of well-educated incoming engineers and scientists. Typically, electrochemistry is only briefly covered in introductory chemistry curricula and offered as graduate engineering courses, if at all. Thus, there are not enough Bachelors-level engineers and scientists with an understanding of electrochemical fundamentals or development of practical systems [5].

This paper details the preliminary design of an industrially-situated virtual laboratory as part of a larger project developing educational tools to assist in teaching electrochemistry to chemical engineering students. The virtual laboratory tasks students with the design and troubleshooting of a redox flow battery (RFB) to address energy storage needs on their university campus. We present here the instructional approach, mathematical model, and student tasks. The aim is to provide others with a basis to design analogous virtual laboratories for other technological systems and to get feedback from the chemical engineering education community on our design choices.

Industrially-Situated Approach

Several virtual laboratories are available that have been designed to teach electrochemistry concepts [6], [7], [8], [9]. These laboratories are similar to each other in design and implementation, simulating highly idealized “textbook” electrochemical cells. Importantly, they lack the scaffolding and simulation depth to allow for students to engage in ways reflective of practicing engineers. In contrast, the virtual laboratory we have developed includes industrially situated problem statements and an interactive interface that positions students as engineers troubleshooting a real battery system. Instructors can customize aspects of the activity to be level-appropriate for their class context, from first-year chemistry to more advanced engineering courses. Being industrially-situated and tunable, this virtual laboratory can engage students in an authentic and skill-appropriate industrial problem, providing learning opportunities not available from other electrochemistry virtual laboratories.

This type of industrially situated laboratory helps prepare engineering students by providing an authentic engineering project that is completed by a group of students taking on the role of engineers in industry [10], [11], [12]. Often, the problems solved by engineers in the university classroom differ substantially from those seen in the workplace [13]. Primarily, students are often not asked to frame problems, consider multiple solution paths, manage uncertainties, or make decisions in the classroom [14], [15]. Laboratories positioning students as engineers working on a realistic task can encourage active and productive engagement with the problem and with peers [16], [17], [18], [19].

Engaging students in disciplinary practice also has potential to fundamentally address issues of broad dissatisfaction with schooling and of inequitable participation and opportunity to learn [20], [21]. Because the wide array of engineering practices offers numerous avenues for legitimate engagement of learners, technologies and learning environments that engage students in engineering practice can provide access to a more diverse set of learners [22]. Through subsequent participation in such activities, learning in engineering and developing engineering identity become linked and inseparable [23], [24], [25]. As classroom practices and expectations align with how learners see themselves as engineers, what is learned is valued more and has more meaning [26], [27]. Learners consequently become more ready to operationalize what they have learned in professional practice [28].

Theoretical Framework

We take a sociocultural view which conceptualizes learning as the active process of participating in the practices and norms of a community as opposed to a cognitive view of learning as the acquisition of discrete knowledge [21], [29], [30], [31]. Thus, to investigate how student groups are participating in disciplinary practices, we identify how they use *engineering epistemic practices* while completing the laboratory. Engineering epistemic practices are the ways that engineers communicate, justify, and validate knowledge claims as they engage in an engineering task [32], [33], [34].

Epistemic practices can be divided into three categories: conceptual, material, and social. Conceptual practices refer to interactions with the use of theory and models to solve engineering problems [35], [36], [37]. Material practices refer to interactions with the material world such as observing phenomena, using laboratory equipment, or creating design artifacts [30], [38]. Social practices refer to social interactions that contribute to performing engineering work, such as coordinating tasks and co-constructing understanding [39], [40], [41]. Importantly, epistemic practices are interconnected throughout time and can, therefore, interlock interdependently [42]. Previously, we have shown that industrially-situated virtual laboratories that allow for iterative cycles of data collection and design tuning elicit diverse and productive sets of interlocking engineering epistemic practices [42], [43], [44]. This forms the basis for the RFB Industrially Situated Virtual Laboratory, described next.

Laboratory Design

RFBs are an emerging grid storage technology with a number of benefits, including decoupling power and energy, safety, and recyclability [45], [46]. In this system, positive and negative electrolytes are stored in external tanks and pumped through a power-converting electrochemical stack where they are oxidized and reduced to charge and discharge the battery as shown in **Figure 1**. The energy that an RFB stores is determined by the mass of electrolyte stored, while its power is determined by the size and number of cells in the stack(s), allowing each to be scaled separately.

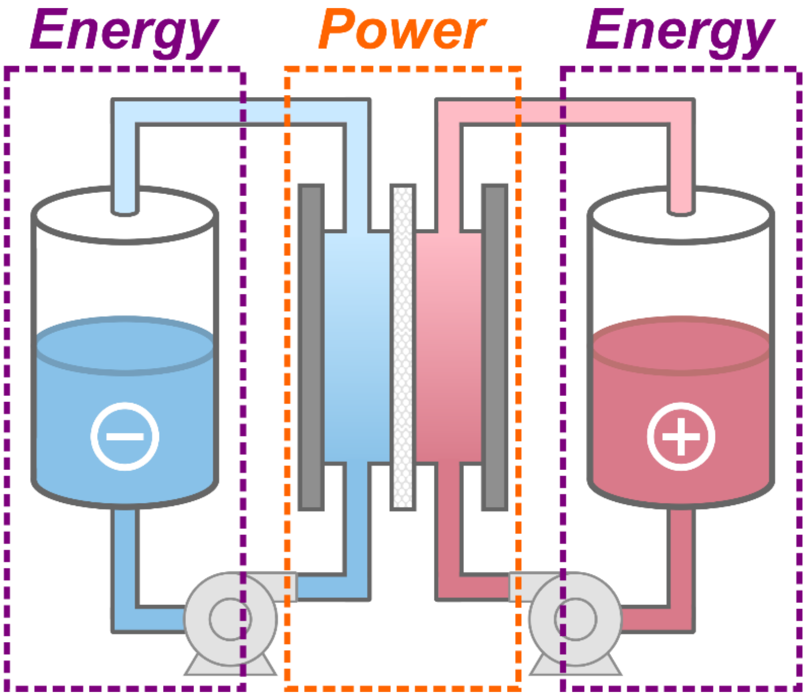

Figure 1: A schematic depicting an RFB cell. The posolyte (+) and negolyte (–) are colored red and blue, respectively, and a membrane separates the two electrolytes at the center of the cell. The electrolyte tank size determines the battery's energy, while the size and number of cells determine the battery's power.

The RFB Industrially Situated Virtual Laboratory is hosted on an online platform called the Concept Warehouse [47], and features a mathematical model housed in an interactive html interface. First, we describe the two main parasitic processes that occur in the battery (species decay and membrane crossover) and, briefly, how they are represented in the mathematical model. Then we describe the two stages in the virtual laboratory: design and troubleshooting.

Parasitic Processes

Throughout the laboratory, students need to make trade-offs between the performance of their battery and budgetary constraints. Here, students need to consider the parasitic processes that occur during RFB operation; these processes are more prevalent with certain active species and membrane configurations. This section briefly describes two crucial parasitic processes: species decay and membrane crossover.

Certain active species will be unstable in their charged states; that is, they can react in ways other than the intended redox reaction, thereby reducing the battery's efficiency. This virtual laboratory assumes two possible mechanisms for these side reactions: irreversible species decay and self-discharge. In the case of decay, active species decompose irreversibly into a non-redox active species; these decay species are assumed to be inert. Alternatively, self-discharge results in a charged active species undergoing a redox reaction; while this reaction is reversible, the electron is no longer available, so it does not contribute to the battery's available capacity. Active species will vary in their overall decay rates as well as the fraction of these events that undergo self-discharge. A schematic showing decay to inert species D and self-discharge pathways for the posolyte (A and A^+) and the negolyte (B^+ and B) is shown in **Figure 2**.

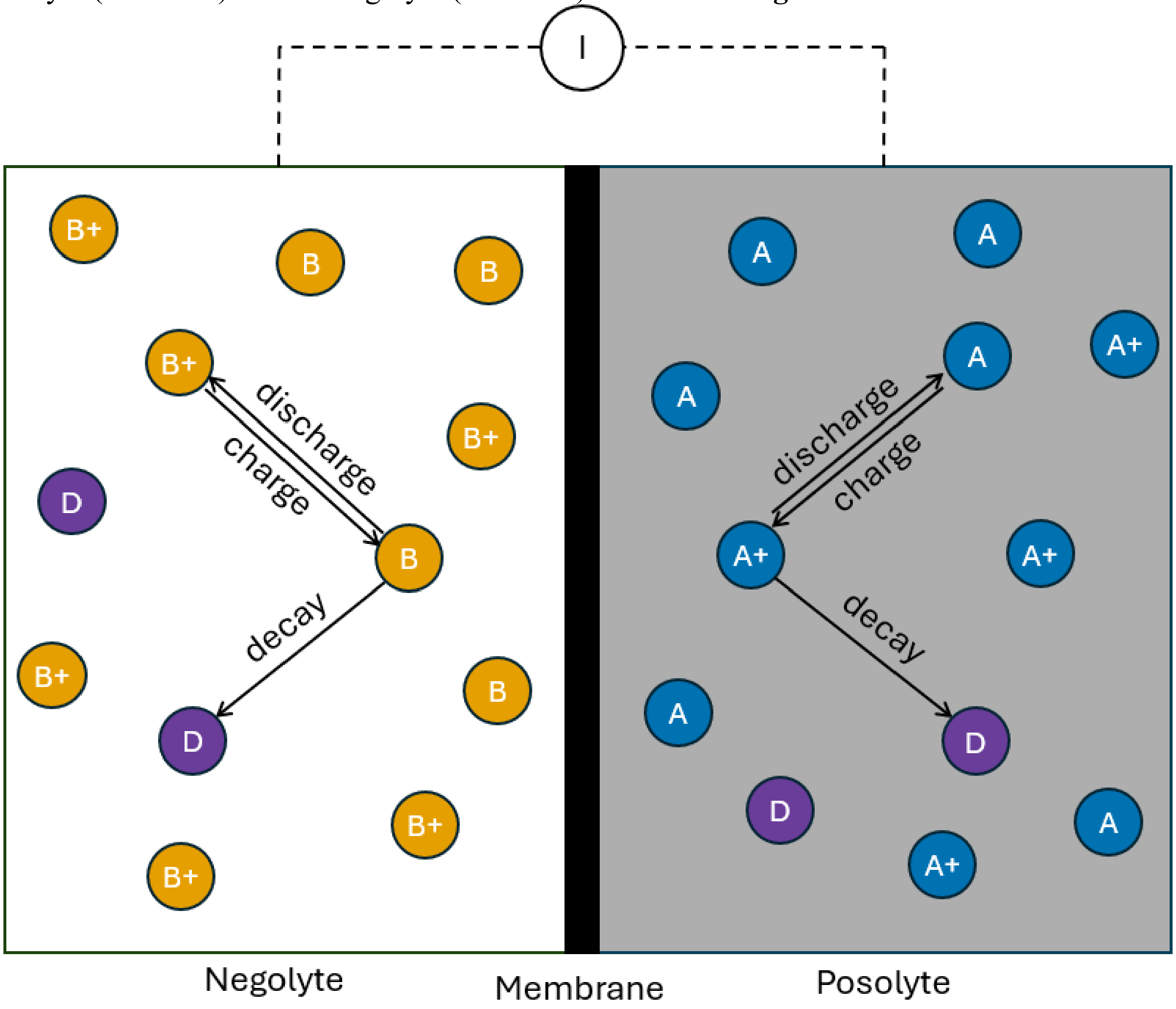

Figure 2: A diagram showing the charge, discharge, and decay pathways undergone by the posolyte (A^+ and A) and negolyte (B and B^+) in a RFB cell. The decay species are represented generally as D; however, in reality this represents a variety of possible decay products.

Membrane crossover occurs when either active species in the posolyte or negolyte cross the membrane into the opposite half-cell. This process reduces the capacity and efficiency of the battery by depleting active species. For the sake of this laboratory, crossed over species are assumed to decay into an inert species, D. Students will need to be mindful of this process, as certain membranes will be more permeable, and certain active species will more readily diffuse through the membrane. A diagram showing crossover for both the posolyte and negolyte are shown in **Figure 3**.

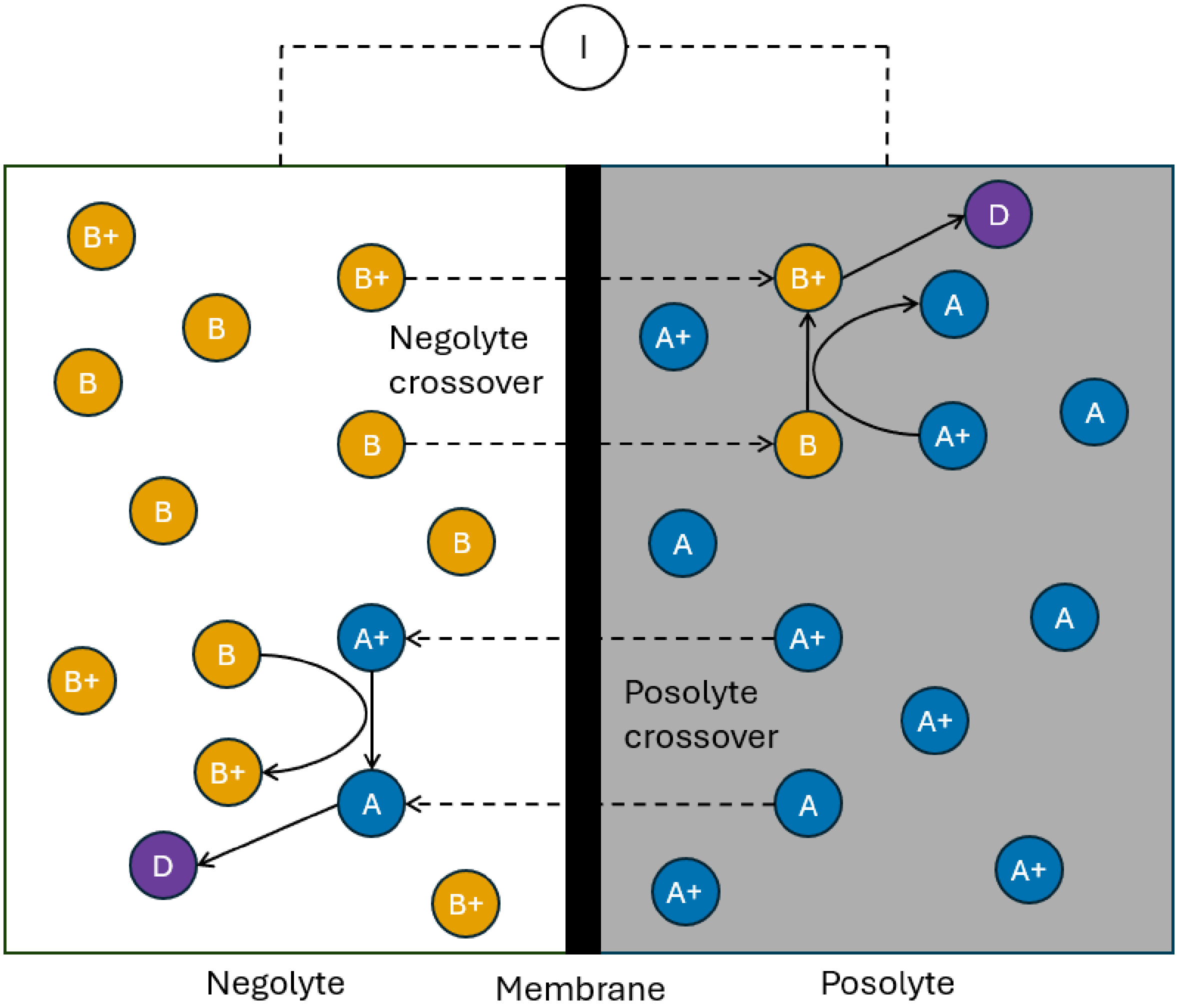

Figure 3: A diagram depicting both posolyte and negolyte crossover in a RFB cell as modeled in the virtual laboratory.

Mathematical Model

While student groups perform charge/discharge experiments as if they are working with a real RFB battery, the quality of the data they work with is critical to their learning. Thus, we incorporate a first-principles mathematical model obscured by added experimental noise as the core to the virtual laboratory design. The mathematical model simulates battery performance based on the material choices made in the student group's battery designs.

The mathematical model adapts the zero-dimensional cycling model for redox flow cells developed by Neyhouse et al. [48]. The following description emphasizes the mathematical representation of species decay and crossover for brevity; for a complete description of the model, we refer the reader to the original paper [48]. The model contains over 30 independent variables for the material properties of battery components (i.e. membrane, electrolytes, electrodes), allowing for flexibility in what design components are available to student groups. Galvanostatic cycling of cells is described through analytically solved mass balances for charged and discharged species, accounting for modes of homogenous active species decay and membrane crossover—two primary RFB failure modes. Active species in the battery are considered generically as A and B^+ and their respective charged states A^+ and B (**Figure 2**). This results in a system of time-dependent differential equations expressed by the matrix Eq. 1.

$$\frac{d}{dt}C = b - KC \tag{1}$$

C (mol m^{-3}) is a column vector containing the concentrations of active species in each half-cell, *b* (mol m^{-3} s^{-1}) is a column vector containing the constant reaction terms (i.e., electrochemical charging / discharging rates), and *K* (mol m^{-3} s^{-1}) is a matrix containing rate constants that describe species decay and crossover in the system. The expanded form of Eq. 1 is shown in two parts, Eq. 2 and Eq. 3, to differentiate species decay and membrane crossover, respectively. However, this is just for illustrative purposes—Eq. 2 and 3 are combined in the actual simulation.

$$\frac{d}{dt}\begin{bmatrix} C_A^{\infty,+} \\ C_{A^+}^{\infty,+} \\ C_B^{\infty,-} \\ C_{B^+}^{\infty,-} \end{bmatrix} = \begin{bmatrix} -\frac{I}{V^+F} \\ \frac{I}{V^+F} \\ \frac{I}{V^-F} \\ -\frac{I}{V^-F} \end{bmatrix} - \begin{bmatrix} 0 & -f_A k_{d,A^+} & 0 & 0 \\ 0 & k_{d,A^+} & 0 & 0 \\ 0 & 0 & k_{d,B} & 0 \\ 0 & 0 & -f_B k_{d,B} & 0 \end{bmatrix} \begin{bmatrix} C_A^{\infty,+} \\ C_{A^+}^{\infty,+} \\ C_B^{\infty,-} \\ C_{B^+}^{\infty,-} \end{bmatrix} \tag{2}$$

Equation 2 shows the expanded forms of *C*, *b*, and *K* when only considering homogenous species decay. The rate constants for the decay of A^+ and B in s^{-1} are represented by $k_{d,A+}$ and $k_{d,B}$. The fractions of A^+ and B that undergo reversible self-discharge are represented by f_A and f_B. The volumes of the posolyte and negolyte tanks are given by V^+ and V^- (m^3), respectively. Finally, *F* (96,485 C mol^{-1}) is Faraday's constant, and *I* (A) is the current the battery is cycled at.

$$\frac{d}{dt}\begin{bmatrix} C_A^{\infty,+} \\ C_{A^+}^{\infty,+} \\ C_B^{\infty,-} \\ C_{B^+}^{\infty,-} \end{bmatrix} = \begin{bmatrix} -\frac{I}{V^+F} \\ \frac{I}{V^+F} \\ \frac{I}{V^-F} \\ -\frac{I}{V^-F} \end{bmatrix} - \begin{bmatrix} k_{c,A}^{+} & 0 & -k_{c,B}^{-} & 0 \\ 0 & k_{c,A^+}^{+} & k_{c,B}^{-} & 0 \\ 0 & k_{c,A^+}^{+}\frac{V^+}{V^-} & k_{c,B}^{-}\frac{V^+}{V^-} & 0 \\ 0 & -k_{c,A^+}^{+}\frac{V^+}{V^-} & 0 & k_{c,B^+}^{-}\frac{V^+}{V^-} \end{bmatrix} \begin{bmatrix} C_A^{\infty,+} \\ C_{A^+}^{\infty,+} \\ C_B^{\infty,-} \\ C_{B^+}^{\infty,-} \end{bmatrix} \tag{3}$$

Equation 3 shows the expanded forms of *C*, *b*, and *K* when only considering membrane crossover. Membrane crossover occurs when active species cross the membrane into the opposite half-cell, decreasing battery performance. The model of crossover used considers mechanisms of diffusion, migration, and electro-osmotic convection [48], [49]. In our application of this model, it is assumed that all crossed-over species decay immediately and cannot cross back over the membrane. The rate constants for the crossover of A, A^+, B, and B^+ are represented in s^{-1} by $k_{c,A}^{+}, k_{c,A+}^{+}, k_{c,B}^{-}, k_{c,B+}^{-}$, respectively.

The model outputs voltage versus time data—calculated from the species concentrations—for galvanostatic cycling of a single RFB cell for the set number of cycles which is then scaled up for a stack of cells. Experimental noise is added to each data point through the addition of a value, randomly selected from a non-standard normal distribution centered around zero. Groups are able to set the number of cycles and time steps in their data but are limited by budget constraints, preventing excessive data collection. With the data generated by the model and their scientific and engineering knowledge, groups need to design and troubleshoot their RFB system.

Design Task

The first stage of the virtual laboratory tasks groups with designing an RFB system that can be used to power a building on their campus to reduce university carbon emissions. Students can typically reference publicly available energy use data from the university to determine the load their battery needs to accommodate. The problem centers engineering practice in environmentally conscious engineering work in a way that is personally relevant to students. A generic data set is available for cases where specific energy use data are not available.

To design their battery system, students use scientific concepts to select from different electrolyte chemistries, and membranes. Currently, the laboratory features four electrolyte chemistries and three membranes, depicted in Table 1. The available components have varying material properties and costs, so students must test multiple configurations and make trade-offs to develop an optimal design. Based on the selected electrolytes, groups may encounter issues with their RFB, such as iR, mass transport, and kinetic limitations, or even a failure to produce any current. Additionally, groups will have to account for budget in their testing, as new battery configurations and larger data sets will accrue extra costs. These constraints are imposed to encourage groups to be intentional in their data collection, making use of first-principles and engineering heuristics rather than a guess and check approach to creating their RFB design. With their experimental design specified, the virtual laboratory automatically provides student groups with voltage versus time data over a number of charge-discharge cycles. Student groups will have the ability to select the number of cycles but will be charged per cycle. Based on data, scientific concepts, instructor support, and their own assumptions, students need to assess the viability of their design and make improvements accordingly. Ultimately, they are responsible for submitting a specific membrane, posolyte, and negolyte system to power the building.

The design task can be curated for more or less complexity based on class level, timeline, and student-teacher goals. Complexity can be tuned in the laboratory in multiple ways, including the available battery components, the number of parameters set by the instructor versus the students, the amount and detail of data that can be collected, and constraints on cost, time, size, and environmental impact.

Table 1: Available electrolyte chemistries and membranes for the design task.

Electrolyte Chemistries	Membranes
[4-OH-TEMPO]Cl / [4-OH-TEMPO]	Nafion® 117
Li_3 / $Li_4[Fe(CN)_6]$	Nafion® NR211
$[BTMAP\text{-}Vi]Cl_4$ / $[BTMAP\text{-}Vi]Cl_3$	BZCY Ceramic
$[(Me)(NPr)V]Cl_3$ / $[(Me)(NPr)V]Cl_2$	-

Troubleshooting Task

In the second task, groups confront engineering troubleshooting by responding to a failure scenario for the RFB design choice they submitted in the first task. Pedagogically useful and industrially relevant failure scenarios have been identified and characterized for this laboratory stage. Each group receives both data and a qualitative description from a uniquely defective RFB, then, using their engineering skills and electrochemical knowledge, diagnose the failure mode, rule out other possibilities, and propose a solution. Potential failure modes with summaries of the descriptions provided are detailed in Table 2.

Table 2: Battery failure modes and their qualitative descriptions which groups may be tasked with troubleshooting

Failure Mode	Description
Membrane fouling	A degraded seal was replaced after the battery's performance decreased; however, this did not improve results.
Malfunctioning mechanicals	A recent power outage led to battery equipment shutting down for an extended period of time. After the outage, battery performance has noticeably decreased.
Oxidation	A pinhole tear was recently identified and fixed in the piping, but battery performance has not improved.
Crossover	Decreasing capacity with no other visual miscues.
Decayed supporting electrolyte	Decreasing battery performance and possible discoloration in the electrolyte tank.

Failure modes are assigned automatically by the laboratory but can also be selected by instructors to give certain groups specific challenges. The troubleshooting task design has several innovative aspects around student learning that we will study. First, the task creates individualized learning, providing each group with a unique troubleshooting component that aligns with both their team goals and progress thus far. Second, this task provides students with the opportunity to engage in interlocking material, conceptual, and social processes reflective of industrial practice (Koretsky et al., 2023). The unique data from the virtual laboratory allows groups to narrow failure scenarios based on scientific theory (e.g., ohmic vs. mass transfer vs. kinetic limitations) while also needing to account for material aspects provided by the system history. Finally, the troubleshooting task allows students to participate in social practices not often available in their schooling. Since each group diagnoses a different issue, instructors can potentially encourage collaboration across the cohort, allowing the sharing of information, knowledge, and ideas without short-circuiting learning.

Summary

The laboratory presented here provides a powerful tool for undergraduate electrochemical engineering education which supports student engagement in interlocking engineering epistemic practices. Student groups will undertake an industrially-situated task by iteratively designing and troubleshooting an RFB system to meet a relevant energy need. This task will encourage students to authentically apply their engineering knowledge and skills while working collaboratively in groups. By providing multiple paths for legitimate participation in engineering practice, this laboratory can resonate with and holistically engage a variety of learners in the field of electrochemical engineering. These types of laboratory tools are essential to address the growing needs of the electrochemical industry and mitigate global climate change. As more electrochemical engineers are needed in the workforce, innovative teaching strategies and tools will be crucial for training these engineers.

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