The Journal of Open Source Software

RFBzero: A Python package for zero-dimensional simulation of redox flow battery cycling

Eric M. Fell [1], **Jeremy A. Fell** [2], **and Michael J. Aziz** [1]

1 Harvard John A. Paulson School of Engineering and Applied Sciences, 29 Oxford Street, Cambridge, MA, 02138, USA **2** Simon Fraser University, 8888 University Dr W, Burnaby, BC V5A 1S6, Canada

DOI: 10.21105/joss.06537

Software

- Review
- Repository
- Archive

Editor: Jeff Gostick

Reviewers:

- @hjelmj
- @MaximevdHeijden

Submitted: 01 February 2024
Published: 24 June 2024

Overview

`rfbzero.py` is a Python package for zero-dimensional simulation of electrochemical cycling of redox flow batteries. This package currently includes the following modules for initial cell setup and electrolyte description, cycling protocol selection, and optional inputs for various capacity degradation mechanisms and active species crossover:

- *redox flow cell setup*: easy configuration of flow cell and electrolyte parameters.
- *cycling protocol*: quickly define the desired electrochemical cycling protocol.
- *capacity fade mechanisms*: include optional electrolyte degradation mechanisms.
- *crossover*: include optional crossover mechanisms inherent to the electrolytes and cell.

Background

Redox flow batteries (RFBs) are seen as a promising long-duration energy storage technology for grid-scale applications. Zero-dimensional models have previously been developed to understand the electrochemical cycling behaviour of vanadium-based electrolytes in RFBs (König et al., 2018; Lee et al., 2019; Murthy et al., 2018; Pugach et al., 2018), where the dominant capacity fade mechanism involves crossover of active species between negolyte (negative electrolyte) and posolyte (positive electrolyte) reservoirs. The development of next-generation electrolyte chemistries, such as redox-active organic molecules (RAOMs) (Kwabi et al., 2020), in the past decade requires new models that incorporate properties inherent to novel chemistries. It is often the case that RAOMs are sufficiently bulky so as not to experience appreciable membrane crossover in an RFB, yet, unlike vanadium-ion-based electrolytes, they can experience chemical degradation leading to capacity decay. Recent work (Modak & Kwabi, 2021; Neyhouse et al., 2022) has extended VRFB-based zero-dimensional models to now include the effect of simple chemical degradation mechanisms of the redox-active organics in RFBs. At each time step iteration in zero-dimensional models, the concentrations of reduced and oxidized redox-actives are updated via Coulomb counting and the open-circuit voltage (OCV) of the cell is then calculated from the Nernst equation. Species concentrations and cell current are then used to determine the ohmic, activation, and mass transport overpotentials. Summing OCV and overpotentials yields the cell voltage. The cell current for the next time step is then determined by the cell voltage, via the cycling protocol.

However, coupled degradation and/or crossover mechanisms are currently not supported by these existing frameworks and degradation products cannot be tracked internally. Furthermore, the organic RFB literature includes reports of mechanisms of increasing complexity such as self-discharge, dimerization, multi-step degradations, etc. This motivated the development of `rfbzero.py`, and already the inclusion of new degradation mechanisms in the zero-dimensional RFB model has contributed to the understanding of self-discharge mechanisms in aqueous RFBs (Fell et al., 2023).

Statement of need

To date, zero-dimensional RFB models have typically been disseminated in the literature via ad hoc non-generalizable equations/code and often written in proprietary programming languages. With `rfbzero.py` we provide an open-source Python package that proliferates electrochemical engineering learning objectives for RFBs, as well as allows for the expansion of battery diagnostics via understanding of capacity fade mechanisms observed in the RAOM flow battery community.

Current `rfbzero.py` functionality

Cell design

The initial flow cell design can be configured via the `redox_flow_cell.py` module. Examples of adjustable, RFB-specific, parameters include electrode active area, electrode geometric area, cell ohmic resistance, starting concentrations of redox-active species (oxidized and/or reduced), and reservoir volumes of the capacity limiting side (CLS) and non-capacity limiting side (NCLS) electrolytes. The user can also declare the electrolyte configuration of the RFB:

- **Full Cell**: different redox-active species in each reservoir and an OCV > 0 V. Species with the more negative reduction potential in the negolyte and species with the more positive reduction potential in the posolyte.
- **Symmetric Cell**: identical redox-actives in both reservoirs and a 0 V OCV when both reservoirs are at 50% state-of-charge (SOC).

Cycling protocol

Cells can be electrochemically cycled by constant current (CC), constant current followed by constant voltage (CCCV), or constant voltage (CV). CC and CCCV cycling require user input of applied currents, while CCCV and CV cycling require input of current cutoffs for charge and discharge. All techniques require input of voltage limits for charge and discharge. If the desired applied current during CCCV cycling is higher than what the cell can provide, CV cycling takes place.

Degradation mechanisms

Optional capacity fade mechanisms can also be incorporated. These include chemical degradation, chemical redox of active species (e.g. self-discharge), dimerization, or multiple stacked degradation mechanisms. Rate constants and reaction rate orders can be adapted as needed to the electrolyte chemistries in each reservoir.

Crossover mechanisms

Crossover of redox-active species through the ion-exchange membrane, driven by concentration gradients, can also be included in simulations. Permeabilities of oxidized and reduced species, and membrane thickness, can be set by the user.

Simulation outputs

Multiple model outputs can be accessed from the simulation results including: temporal profiles for voltage, current, capacity, SOC, and overpotentials. Half-cycle capacities and duration of cycles can also be accessed.

An Example of the `rfbzero.py` API

The documentation for `rfbzero.py` includes a getting started guide and examples of RFB cells cycled under different protocols. An example for CC cycling at ±100 mA for a symmetric cell with OCV = 0.0 V, charging voltage = 0.2 V, discharging voltage = -0.2 V, and cycled for 500 seconds, is shown below:

```
from redox_flow_cell import ZeroDModel
from experiment import ConstantCurrent


# 1. define symmetric cell and electrolyte parameters
cell = ZeroDModel(
    volume_cls=0.005,   # liters
    volume_ncls=0.050,  # liters
    c_ox_cls=0.01,      # molar
    c_red_cls=0.01,     # molar
    c_ox_ncls=0.01,     # molar
    c_red_ncls=0.01,    # molar
    ocv_50_soc=0.0,     # volts
    resistance=0.5,     # ohms
    k_0_cls=1e-3,       # cm/s
    k_0_ncls=1e-3,      # cm/s
)

# 2. define cycling protocol
protocol = ConstantCurrent(
    voltage_limit_charge=0.2,      # volts
    voltage_limit_discharge=-0.2,  # volts
    current=0.1,                   # amps
)

# 3. simulate the cell, via protocol, for 500 seconds
results = protocol.run(cell_model=cell, duration=500)
```

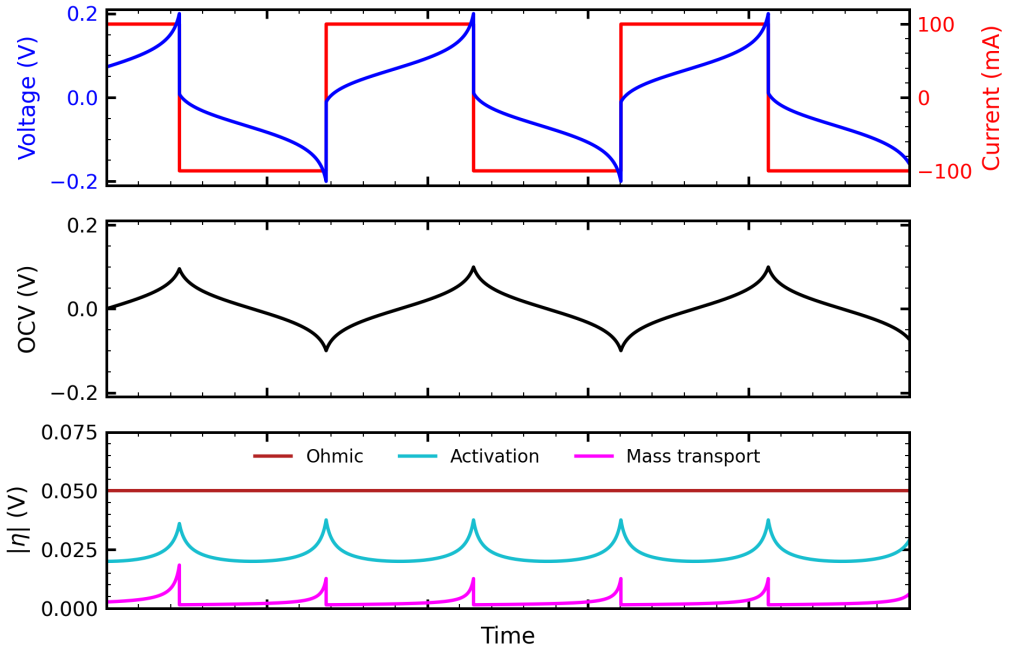

Figure 1: Simulation outputs can be plotted as desired.

A second example of a symmetric cell with CCCV cycling (±50 mA, ±0.2 V, ±5 mA cutoffs), an auto-reduction degradation mechanism, and cycled for 4000 seconds, is shown below:

```
from redox_flow_cell import ZeroDModel
from experiment import ConstantCurrentConstantVoltage
from degradation import AutoReduction


# 1. define symmetric cell and electrolyte parameters
cell = ZeroDModel(
    volume_cls=0.005,   # liters
    volume_ncls=0.010,  # liters
    c_ox_cls=0.01,      # molar
    c_red_cls=0.01,     # molar
    c_ox_ncls=0.01,     # molar
    c_red_ncls=0.01,    # molar
    ocv_50_soc=0.0,     # volts
    resistance=0.5,     # ohms
    k_0_cls=1e-3,       # cm/s
    k_0_ncls=1e-3,      # cm/s
)

# 2. define cycling protocol
protocol = ConstantCurrentConstantVoltage(
    voltage_limit_charge=0.2,         # volts
    voltage_limit_discharge=-0.2,     # volts
    current_cutoff_charge=0.005,      # amps
    current_cutoff_discharge=-0.005,  # amps
    current=0.05,                     # amps
)
```

```
# 3. define chemical degradation
deg = AutoReduction(rate_constant=3e-4)

# 4. simulate the cell with degradation, via protocol, for 4000 seconds
results = protocol.run(cell_model=cell, degradation=deg, duration=4000)
```

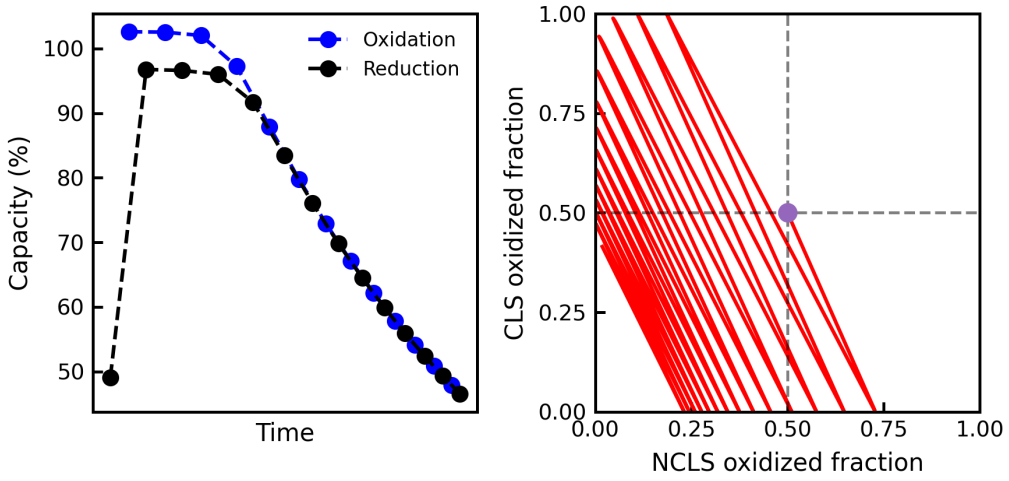

Figure 2: Half-cycle capacities (left) and temporal evolution of reservoir states-of-charge (right) are readily accessed. Symmetric cell starts with both reservoirs at 50% state-of-charge (purple circle).

Acknowledgements

This research was supported by U.S. DOE award DE-AC05-76RL01830 through PNNL subcontract 654799. We thank Prof. David Kwabi, Thomas George, and Jordan Sosa for constructive feedback and testing.

References

Fell, E. M., De Porcellinis, D., Jing, Y., Gutierrez-Venegas, V., George, T. Y., Gordon, R. G., Granados-Focil, S., & Aziz, M. J. (2023). Long-term stability of ferri-/ferrocyanide as an electroactive component for redox flow battery applications: On the origin of apparent capacity fade. *Journal of The Electrochemical Society*, *170*(7), 070525. https://doi.org/10.1149/1945-7111/ace936

König, S., Suriyah, M. R., & Leibfried, T. (2018). Validating and improving a zero-dimensional stack voltage model of the vanadium redox flow battery. *Journal of Power Sources*, *378*, 10–18. https://doi.org/10.1016/j.jpowsour.2017.12.014

Kwabi, D. G., Ji, Y., & Aziz, M. J. (2020). Electrolyte lifetime in aqueous organic redox flow batteries: A critical review. *Chemical Reviews*, *120*(14), 6467–6489. https://doi.org/10.1021/acs.chemrev.9b00599

Lee, S. B., Mitra, K., Pratt, H. D., III, Anderson, T. M., Ramadesigan, V., Chalamala, B. R., & Subramanian, V. R. (2019). Open data, models, and codes for vanadium redox batch cell systems: A systems approach using zero-dimensional models. *Journal of Electrochemical Energy Conversion and Storage*, *17*(011008). https://doi.org/10.1115/1.4044156

Modak, S., & Kwabi, D. G. (2021). A zero-dimensional model for electrochemical behavior and capacity retention in organic flow cells. *Journal of The Electrochemical Society*, *168*(8), 080528. https://doi.org/10.1149/1945-7111/ac1c1f

Murthy, S. K., Sharma, A. K., Choo, C., & Birgersson, E. (2018). Analysis of concentration overpotential in an all-vanadium redox flow battery. *Journal of The Electrochemical Society*, *165*(9), A1746–A1752. https://doi.org/10.1149/2.0681809jes

Neyhouse, B. J., Lee, J., & Brushett, F. R. (2022). Connecting material properties and redox flow cell cycling performance through zero-dimensional models. *Journal of The Electrochemical Society*, *169*(9), 090503. https://doi.org/10.1149/1945-7111/ac86aa

Pugach, M., Kondratenko, M., Briola, S., & Bischi, A. (2018). Zero dimensional dynamic model of vanadium redox flow battery cell incorporating all modes of vanadium ions crossover. *Applied Energy*, *226*, 560–569. https://doi.org/10.1016/j.apenergy.2018.05.124