

Influence of Crossover on Capacity Fade of Symmetric Redox Flow Cells - Supporting Information

Thomas Y. George,^{†,‡} Eric M. Fell,^{†,‡} Kyumin Lee,[†] Michael S. Emanuel,[†] and
Michael J. Aziz^{*,†}

[†]*Harvard John A. Paulson School of Engineering and Applied Sciences, Cambridge,
Massachusetts 02138, USA*

[‡]*Equal contribution*

E-mail: maziz@harvard.edu

Contents

| | |
|---|----|
| Note S1: Fitting <i>operando</i> UV-vis spectra to estimate dimerization kinetics | 11 |
| Note S2: RFBzero code for Figure 4 | 17 |

List of Figures

| | |
|--|----|
| Figure S1 UV-vis calibration of 2,7-AQDS | 1 |
| Figure S2 Symmetric cells with as-received membranes, non-normalized capacity | 1 |
| Figure S3 Permeability measurements, as-received membranes | 2 |
| Figure S4 Permeability measurements, pretreated membranes | 3 |
| Figure S5 Symmetric cells with pretreated membranes, non-normalized capacity | 3 |
| Figure S6 Capacity fade rates and cell ohmic resistances vs. membrane thickness | 4 |
| Figure S7 Capacity contributed by constant current portion of CCCV cycling . | 5 |
| Figure S8 Time spent in CC and CV for CCCV cycling | 6 |
| Figure S9 Simulated cycling of AQDS symmetric cells with as-received membranes | 8 |
| Figure S10 Simulated cycling of AQDS symmetric cells with as-received membranes, only chemical degradation | 8 |
| Figure S11 <i>Operando</i> in-line UV-vis of 0.1 M AQDS cycled in a full cell | 9 |
| Figure S12 Simulated AQDS symmetric cell cycling with varied K_{dimer} and k_f . . | 10 |
| Figure S13 Fitting of forward dimerization rate constant k_f | 12 |
| Figure S14 Calculated vs. observed dimer concentration. | 12 |
| Figure S15 Simulated cycling of symmetric cells with parameters varied | 14 |
| Figure S16 Simulated cycling of symmetric cells with parameters varied, discharge first | 15 |
| Figure S17 Longer simulated cycling of symmetric cells with varied P_{ox} and P_{red} | 16 |

List of Tables

| | | |
|----------|---|----|
| Table S1 | Experimental values and nominal membrane thicknesses for model inputs | 7 |
| Table S2 | Simulated and experimental capacity fade rates | 13 |
| Table S3 | Parameters and simulated fade rates for Figures 5 and S12 | 13 |

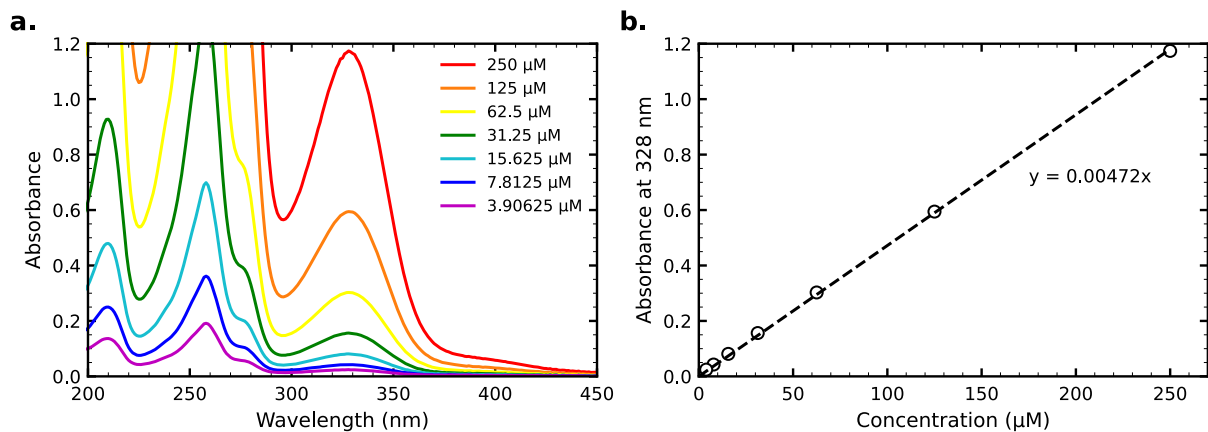


Figure S1: UV-vis calibration of 2,7-AQDS, with a) absorbance spectra of samples prepared by serial dilution in the cuvette and b) calibration curve for absorbance at 328 nm.

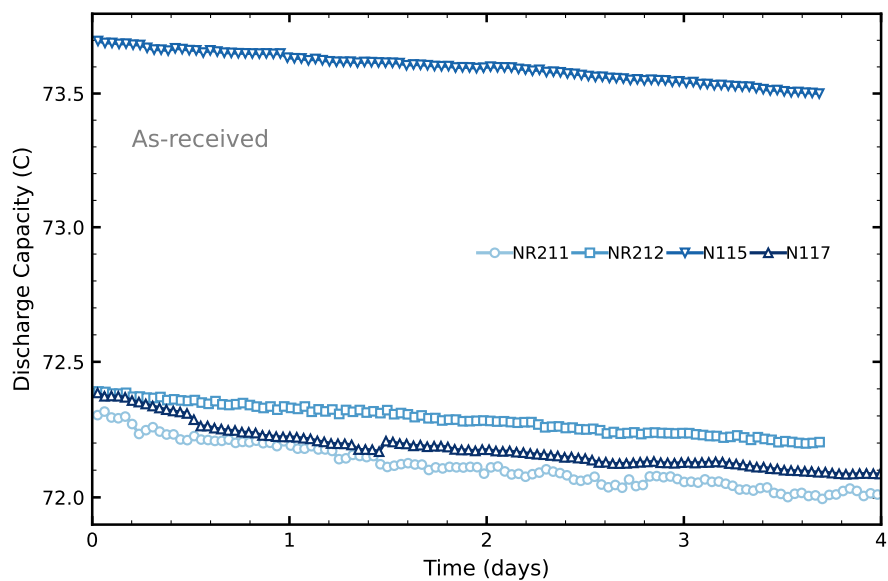


Figure S2: Discharge capacity over time for AQDS symmetric cells with as-received Nafion membranes (see main text Figure 1b for normalized capacity).

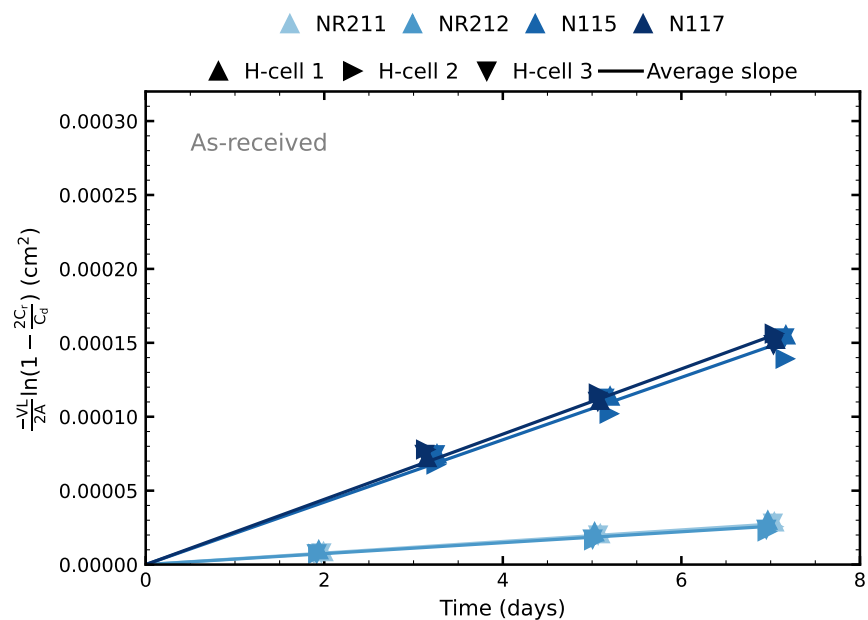


Figure S3: Permeability plot with data from each of three replicate H-cells for each of four different as-received Nafion membranes. The solid lines have the average slope from the three H-cells per condition, where the slope is the permeability. In the expression on the y-axis, V is H-cell chamber volume (10 mL), L is membrane thickness, A is the area of membrane (1.979 cm²), and C_r and C_d are AQDS concentration (where C_d is approximated as constant at 0.1 M and C_r is measured).

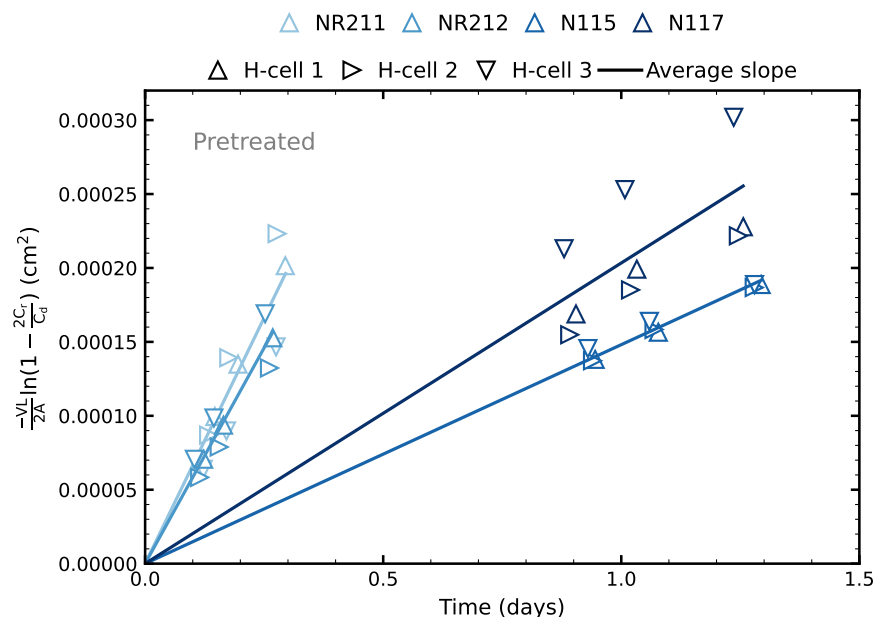


Figure S4: Permeability plot with data from each of three replicate H-cells for each of four different pretreated Nafion membranes. The solid lines have the average slope from the three H-cells per condition, where the slope is the permeability. In the expression on the y-axis, V is H-cell chamber volume (10 mL), L is membrane thickness, A is the area of membrane (1.979 cm^2), and C_r and C_d are AQDS concentration (where C_d is approximated as constant at 0.1 M and C_r is measured).

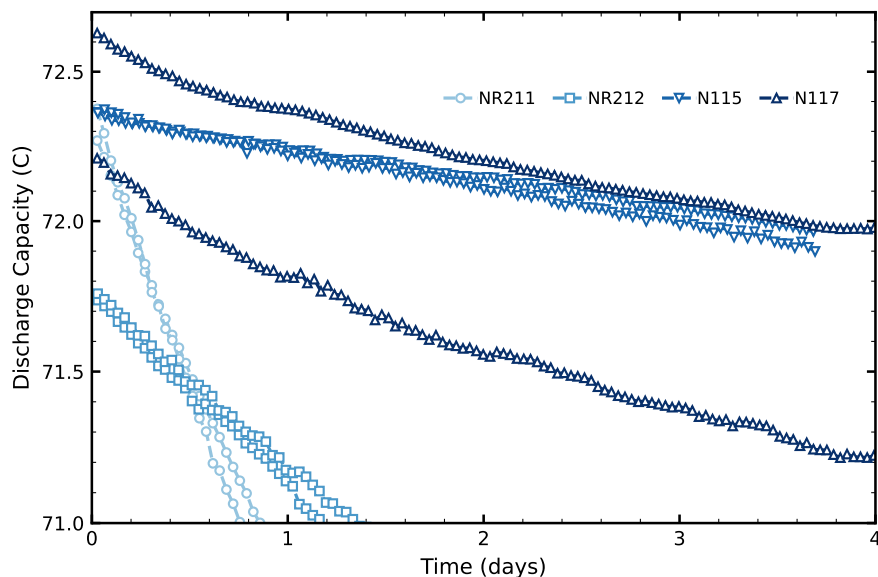


Figure S5: Discharge capacity over time for AQDS symmetric cells with pretreated membranes (duplicate cells shown for each of four membranes, see main text Figure 3a for normalized capacity).

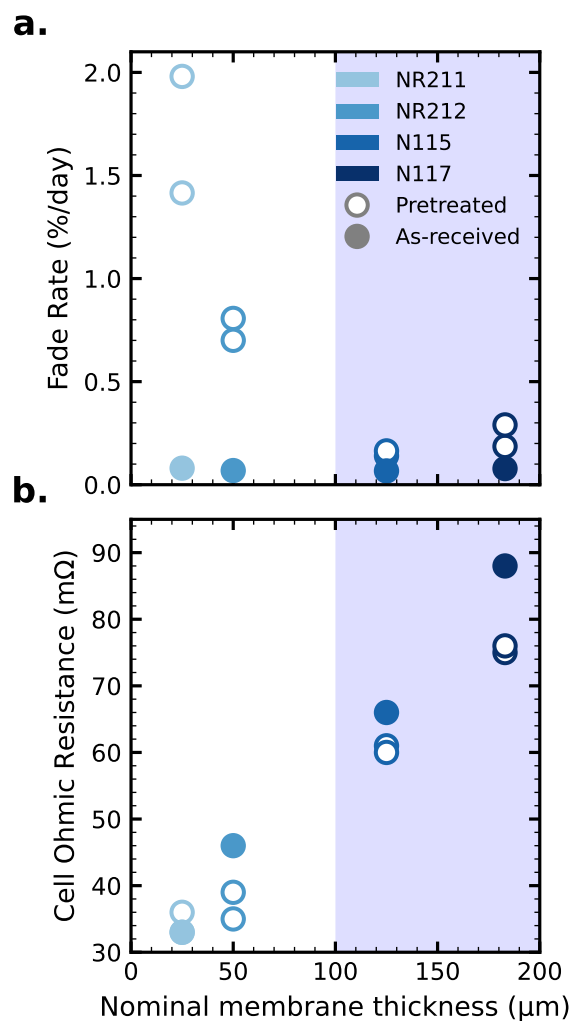


Figure S6: a) Capacity fade rates of AQDS symmetric cells vs. membrane thickness for pretreated and as-received Nafion membranes; and b) Cell ohmic resistance (taken as the high-frequency x-intercept of a Nyquist plot generated with electrochemical impedance spectroscopy) vs. membrane thickness for pretreated and as-received Nafion membranes.

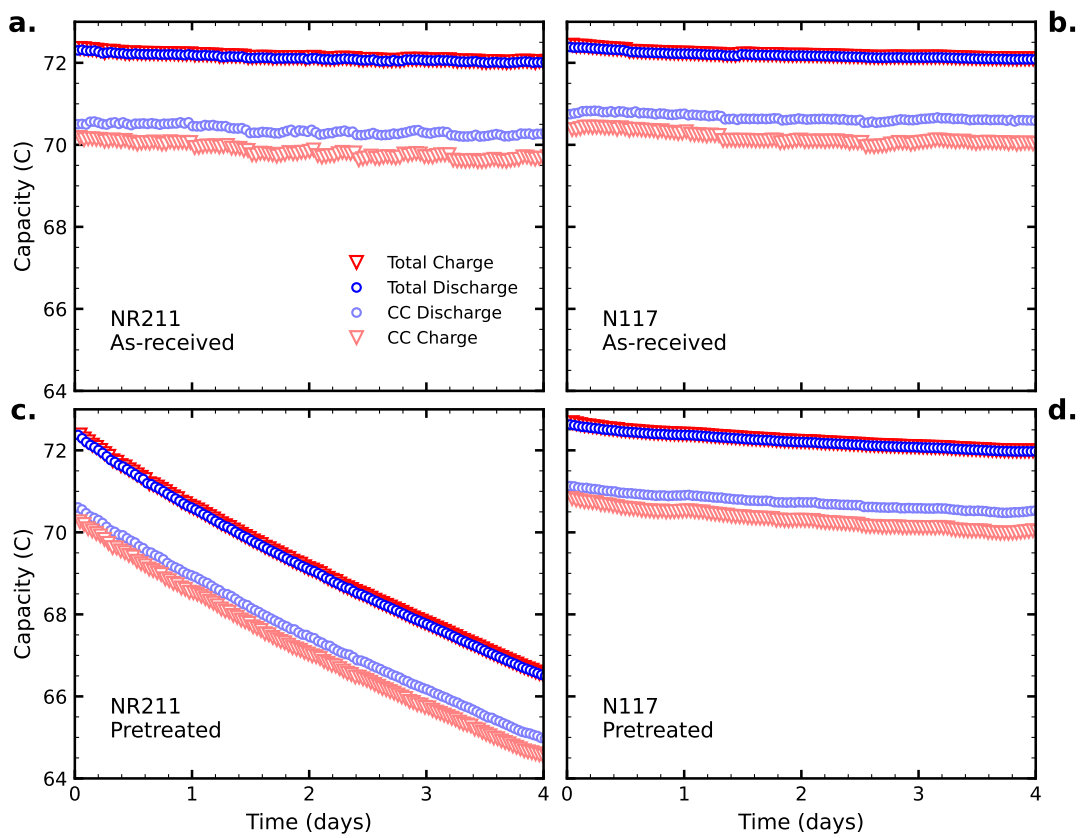


Figure S7: Capacity contribution of constant current (CC) sections of CCCV cycling for select AQDS symmetric cells.

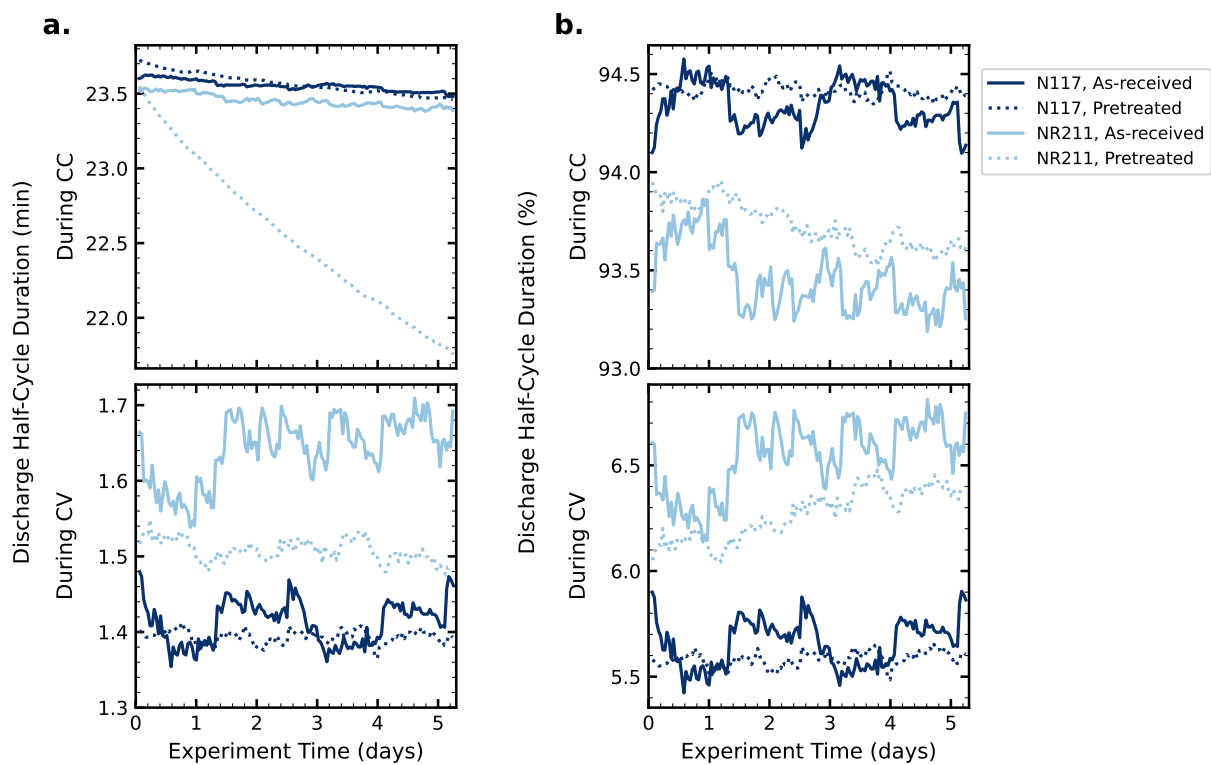


Figure S8: Duration (a) and percent time (b) of discharge half-cycles spent in constant current and constant voltage sections of CCCV cycling protocol for the AQDS symmetric cells shown in Figure S7.

Table S1: Experimental values and nominal membrane thicknesses for model inputs

| Membrane | Condition | Nominal Thickness (μm) | ASR ($\Omega \text{ cm}^2$) | Permeability ($\text{cm}^2 \text{ s}^{-1}$) | Maximum crossover-driven fade rate* (% day $^{-1}$) |
|----------|-------------|--|----------------------------------|--|---|
| NR211 | As-received | 25 | 0.165 | 4.5×10^{-11} | 0.16 |
| | Pretreated | 25 | 0.175 | 8.3×10^{-9} | 29 |
| NR212 | As-received | 50 | 0.230 | 4.0×10^{-11} | 0.069 |
| | Pretreated | 50 | 0.190 | 6.7×10^{-9} | 12 |
| N115 | As-received | 125 | 0.330 | 2.3×10^{-10} | 0.16 |
| | Pretreated | 125 | 0.300 | 1.6×10^{-9} | 1.1 |
| N117 | As-received | 183 | 0.440 | 2.3×10^{-10} | 0.11 |
| | Pretreated | 183 | 0.375 | 2.3×10^{-9} | 1.1 |

*The *maximum crossover-driven fade rate* refers to the rate of loss of active material through a membrane with a given thickness and permeability assuming that crossover is driven by diffusion only and that the receiving side, i.e. the NCLS in this case, has zero concentration of the crossing species. This value is calculated by inputting permeability and solving the equation $\frac{dC}{dt} = -\frac{P\Lambda}{v}C_0$ (which is a simpler version of Equations 2-3 in the main text) in which P is the permeability in Table S1, Λ is the membrane constant ($\Lambda = \frac{A_{geo}}{\text{membrane thickness}}$) with geometric area of 5 cm^2 , v is reservoir volume (5 mL), and C_0 is the initial concentration of 0.1 M (at $t = 0$, $C = C_0$). This value does not represent the actual fade rate of a symmetric cell, in which the driving force for net crossover is much weaker, and instead represents the maximum instantaneous fade rate the permeability could provide, given C_0 , Λ , and v .

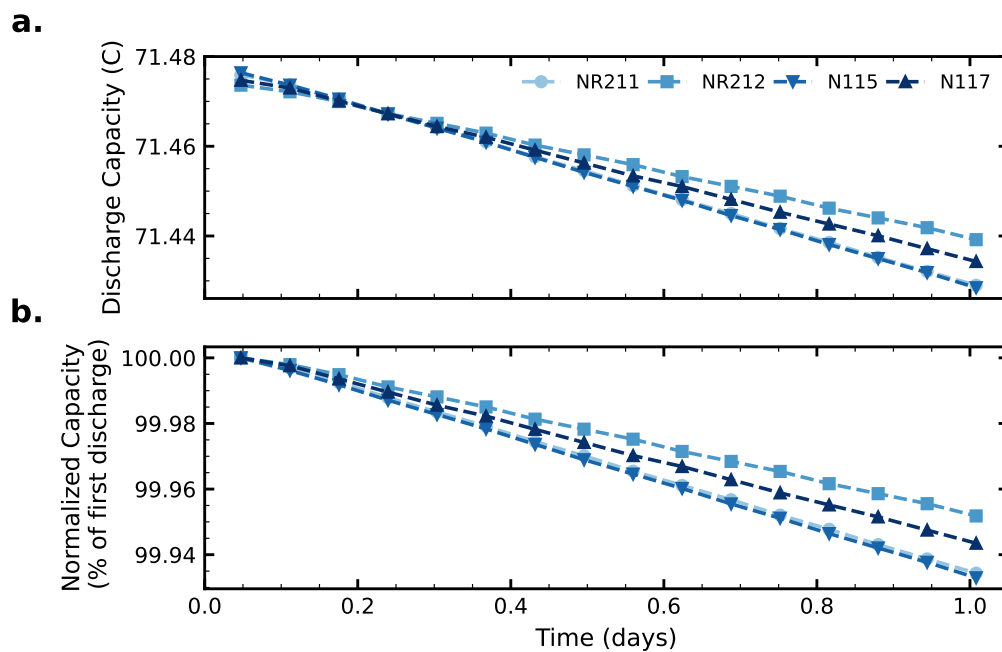


Figure S9: Simulated cycling over time of AQDS symmetric cells with as-received membranes, with $k_{chemdeg} = 1 \times 10^{-8} \text{ s}^{-1}$, $K_{dimer} = 75 \text{ M}^{-1}$, $k_f = 0.030 \text{ M s}^{-1}$.

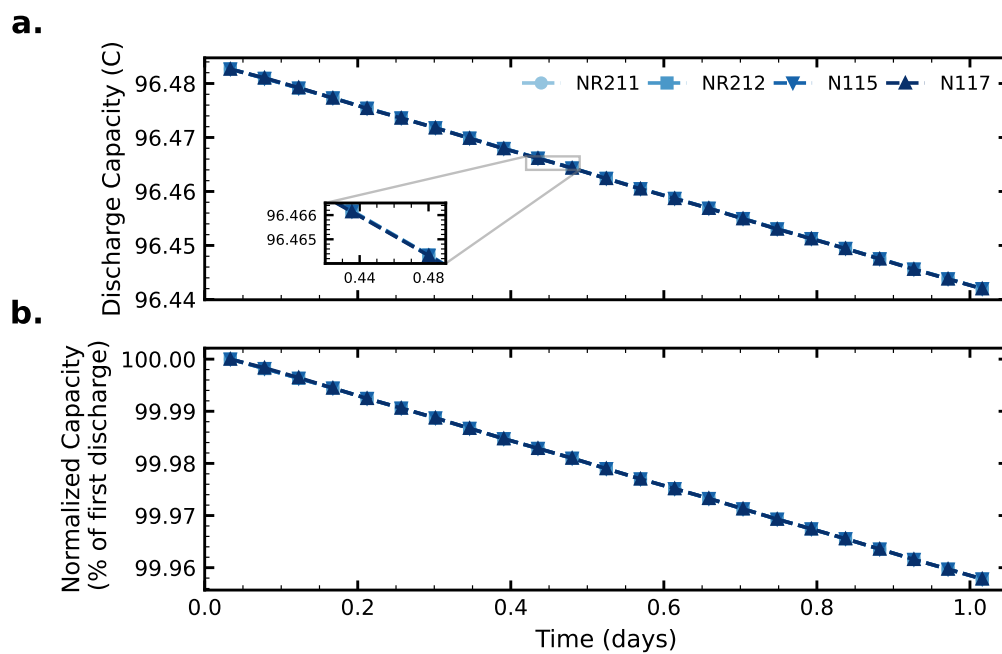


Figure S10: Simulated cycling over time of AQDS symmetric cells with as-received membranes, with $k_{chemdeg} = 1 \times 10^{-8} \text{ s}^{-1}$. Crossover and dimer formation are not included.

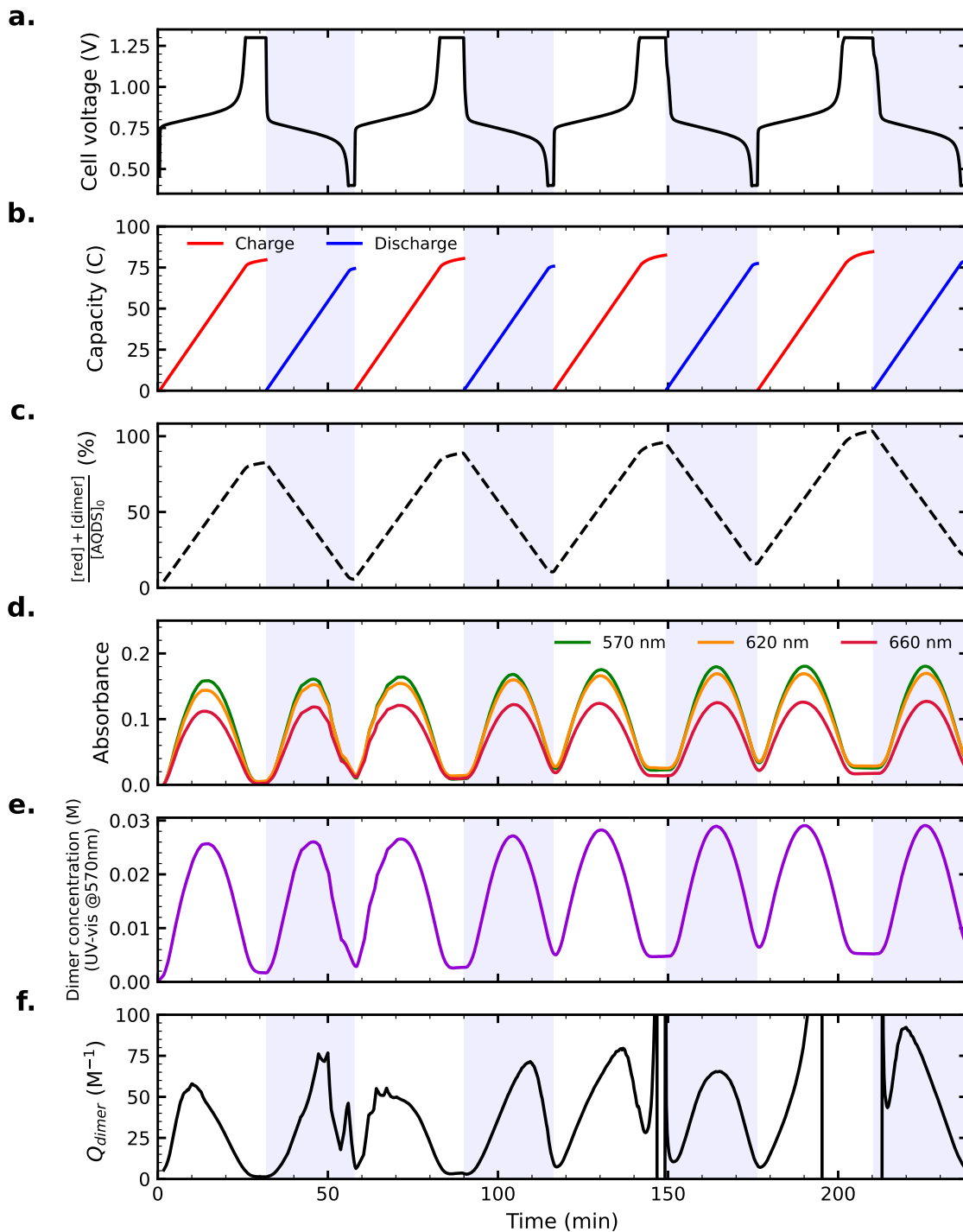


Figure S11: *Operando* in-line UV-vis of 0.1 M AQDS cycled as the CLS in a full cell vs. vanadium. Four cycles are shown with cell voltage and charge/discharge capacity over time shown in panels a) and b) respectively. Percent AQDS in the reduced or dimerized state depicted in c) based on coulometry and UV-vis absorbance measurements (d) used to determine dimer concentration (e). The calculated reaction quotient of dimerization is shown in (f).

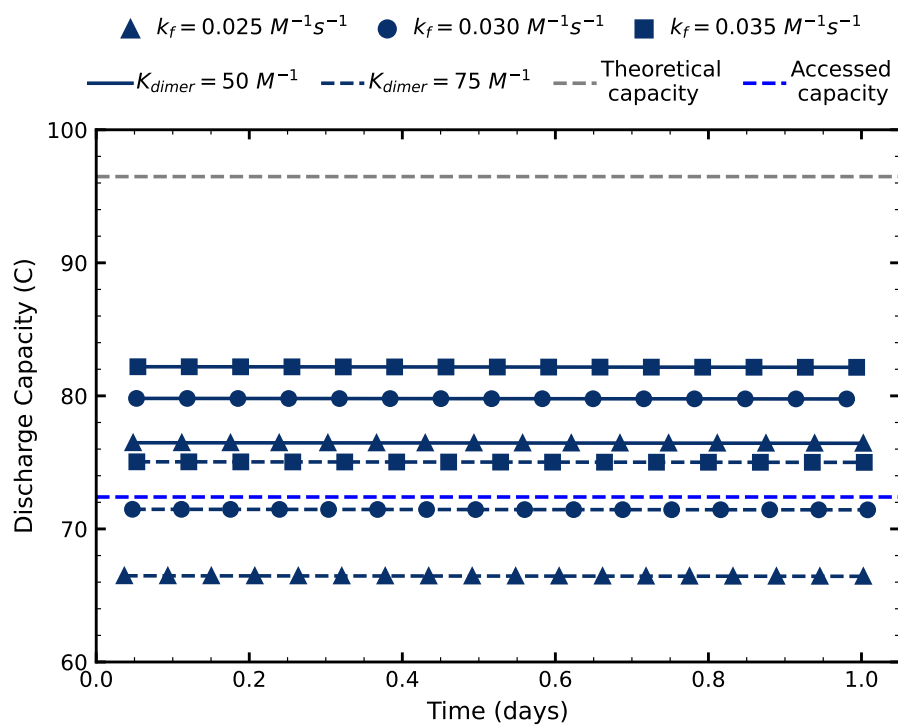


Figure S12: Simulated AQDS symmetric cell cycling with an as-received N117 membrane, with $k_{chemdeg} = 1 \times 10^{-8} \text{ s}^{-1}$ (all cells have 0.06%/day fade rate), with varied K_{dimer} and k_f .

Note S1: Fitting *operando* UV-vis spectra to estimate dimerization kinetics

A direct calculation from the absorbance data at 570, 620 and 660 nm was performed to obtain the dimer concentration (Figure S11). The concentrations of oxidized and reduced AQDS species at the beginning of each charge cycle were calculated from this dimer concentration by setting the concentration of reduced AQDS to zero, which is known to be true at the start of the experiment and a good approximation after a discharge cycle. By similar reasoning, the oxidized AQDS concentration was set to zero at the end of each charge cycle. The concentrations at all intermediate points in each cycle were calculated by linear interpolation between these start and end points, interpolating against the number of coulombs moved during the cycle.

The dimer equilibrium constant K_{eq} was set to 80 M^{-1} to match the previously published figure. Given a candidate value for the forward rate k_f , we directly calculate $k_r = k_f/K_{eq}$. Then we integrate an ODE to simulate the concentration of each species with terms for Faradaic reactions and the net dimer formation rate. A broad range of rate constants was considered. The predicted dimer concentration was compared to the experimental data for each proposed rate constant and the root mean square (RMS) error was calculated. A local minimum for the RMS error was found at $k_f = 0.142 \text{ M}^{-1} \cdot \text{s}^{-1}$. This rate was verified to predict a dimer concentration time series that was a close match for the experimental data. The sweep of candidate forward rates is shown in Figure S13. A comparison of the experimentally observed and calculated dimer concentrations is shown in Figure S14.

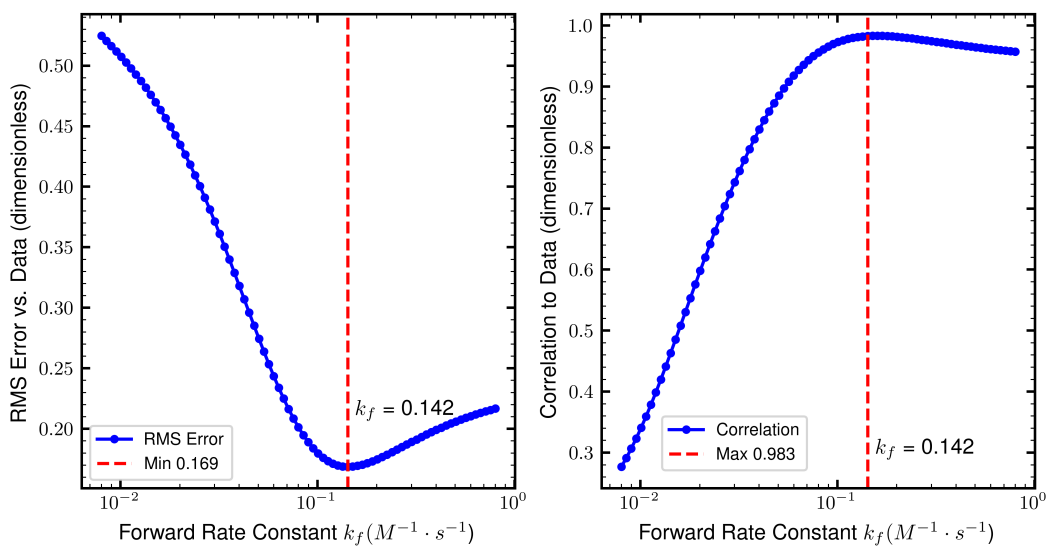


Figure S13: Fitting of forward dimerization rate constant k_f . The dimer equilibrium constant K_{eq} is held at 80 M^{-1} while k_f is varied. An ODE is integrated to predict the dimer concentration over time. The root mean square error and correlation to the experimental concentration data are calculated. The forward rate is estimated at $0.142 \text{ M}^{-1} \cdot \text{s}^{-1}$, which minimizes the RMS error and is close to maximizing the correlation.

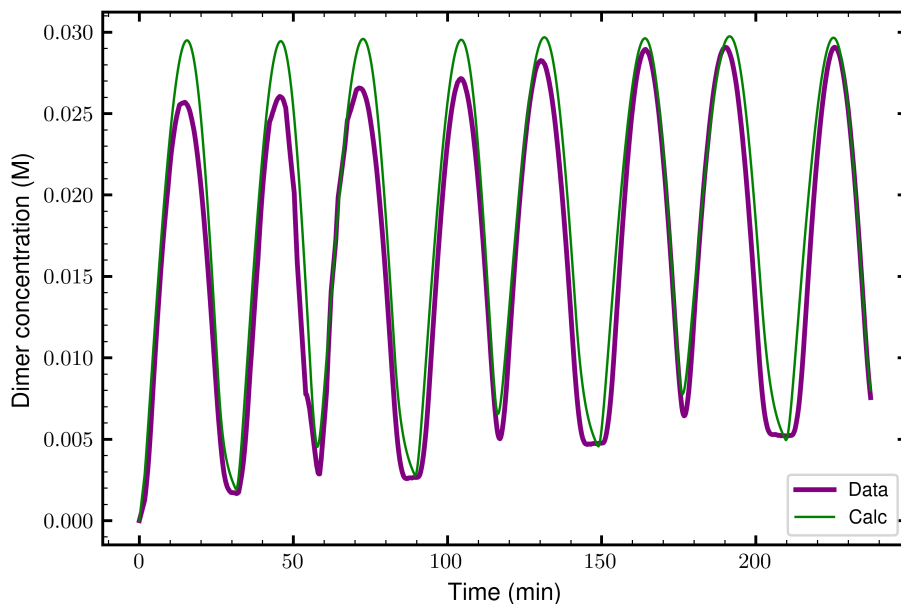


Figure S14: Comparison of calculated dimer concentration (Calc) with observed concentration (Data). The theoretical dimer concentration vs. time was calculated using the fitted $k_f = 0.142 \text{ M}^{-1} \cdot \text{s}^{-1}$.

Table S2: Simulated and experimental capacity fade rates for each membrane condition.
 $k_{chemdeg} = 1 \times 10^{-8} \text{ s}^{-1}$, $K_{dimer} = 75 \text{ M}^{-1}$

| Membrane, condition | Fade rate, sim. (% day ⁻¹) | Shown in | Fade rate, exp. (% day ⁻¹) | Shown in |
|---------------------|---|----------------|---|---------------|
| NR211, As-received | 0.07 | Fig. S9 | 0.08 | Fig. 1 |
| NR212, As-received | 0.05 | | 0.07 | |
| N115, As-received | 0.07 | | 0.07 | |
| N117, As-received | 0.06 | | 0.08 | |
| NR211, Pretreated | 5.95 | Fig. 4 | 1.70 | Fig. 3 |
| NR212, Pretreated | 2.49 | | 0.75 | |
| N115, Pretreated | 0.27 | | 0.15 | |
| N117, Pretreated | 0.27 | | 0.24 | |

Table S3: Model parameters and simulated fade rates (over one day) for scenarios in Figures 5 and S15

| Membrane | K_{dimer} (M ⁻¹) | $k_{chemdeg}$ (s ⁻¹) | P_{ox} (cm ² s ⁻¹) | P_{red} (cm ² s ⁻¹) | Fade rate (% day ⁻¹) | Shown in Fig. 5 subplot |
|----------|-----------------------------------|-------------------------------------|--|---|-------------------------------------|-----------------------------------|
| NR211 | 0 | 1×10^{-8} | 8.3×10^{-9} | 8.3×10^{-9} | 0.04 | a |
| | 75 | | | | 5.95 | |
| | 100 | | | | 6.23 | |
| N117 | 0 | 1×10^{-8} | 2.3×10^{-9} | 2.3×10^{-9} | 0.04 | a |
| | 75 | | | | 0.27 | |
| | 100 | | | | 0.28 | |
| NR211 | 0 | 1×10^{-8} | 8.3×10^{-9} | 8.3×10^{-9} | 0.04 | b |
| | | | 41.5×10^{-9} | 8.3×10^{-9} | 0.35 | |
| | | | 8.3×10^{-9} | 41.5×10^{-9} | -0.27 | |
| N117 | 0 | 1×10^{-8} | 2.3×10^{-9} | 2.3×10^{-9} | 0.04 | b |
| | | | 11.5×10^{-9} | 2.3×10^{-9} | 0.04 | |
| | | | 2.3×10^{-9} | 11.5×10^{-9} | 0.04 | |
| NR211 | 75 | 0 | 8.3×10^{-9} | 8.3×10^{-9} | 5.91 | c |
| | | 1×10^{-8} | | | 5.95 | |
| | | 1×10^{-7} | | | 6.28 | |
| N117 | 75 | 0 | 2.3×10^{-9} | 2.3×10^{-9} | 0.23 | c |
| | | 1×10^{-8} | | | 0.27 | |
| | | 1×10^{-7} | | | 0.60 | |
| NR211 | 0 | 0 | 41.5×10^{-9} | 8.3×10^{-9} | 0.32 | d |
| | | 1×10^{-8} | | | 0.35 | |
| | | 1×10^{-7} | | | 0.62 | |
| N117 | 0 | 0 | 11.5×10^{-9} | 2.3×10^{-9} | 0.00 | d |
| | | 1×10^{-8} | | | 0.04 | |
| | | 1×10^{-7} | | | 0.43 | |

NR211 N117

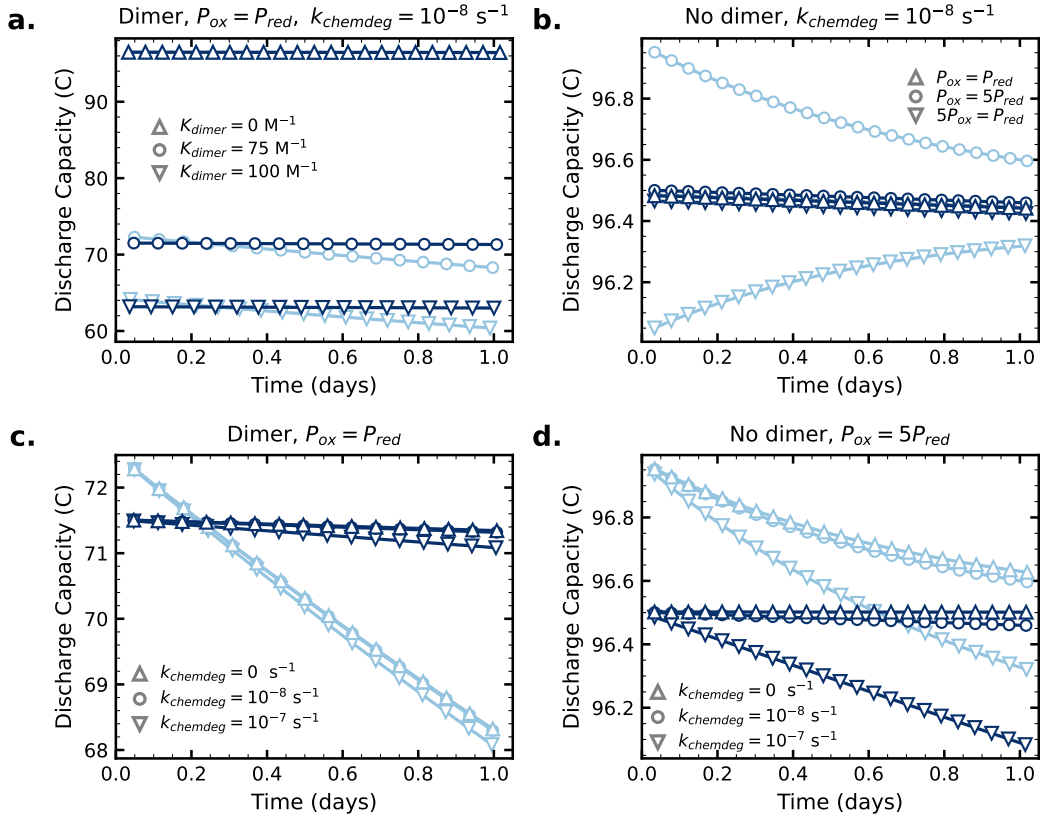


Figure S15: Simulated cycling of symmetric cells with parameters varied to explore other possible modes of net crossover (parameters and resulting capacity fade rates listed in Table S3, normalized capacity in main text Figure 5).

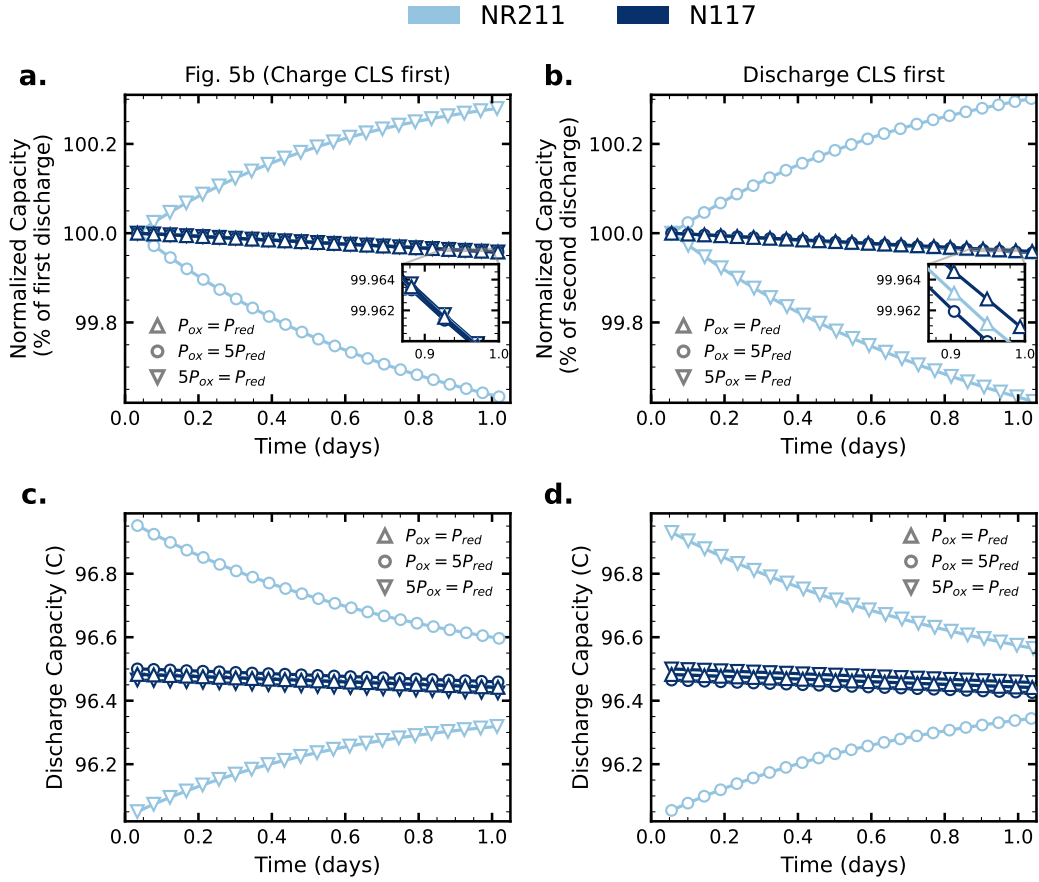


Figure S16: Simulated cycling of symmetric cells with permeability coefficients varied. Normalized discharge capacity: a) is a copy of Fig. 5b where the CLS is charged first; b) identical cell parameters to Fig. 5b except the CLS is discharged first. c) is the temporal discharge capacity of a), and is a copy of Fig.

S15b; d) is the temporal discharge capacity of b). When the CLS is discharged first, the first half-cycle achieves only half capacity (cell starts at 50% SOC) and so the second discharge cycle is used to normalize capacity. This leads to the slight capacity discrepancy between a) and b).

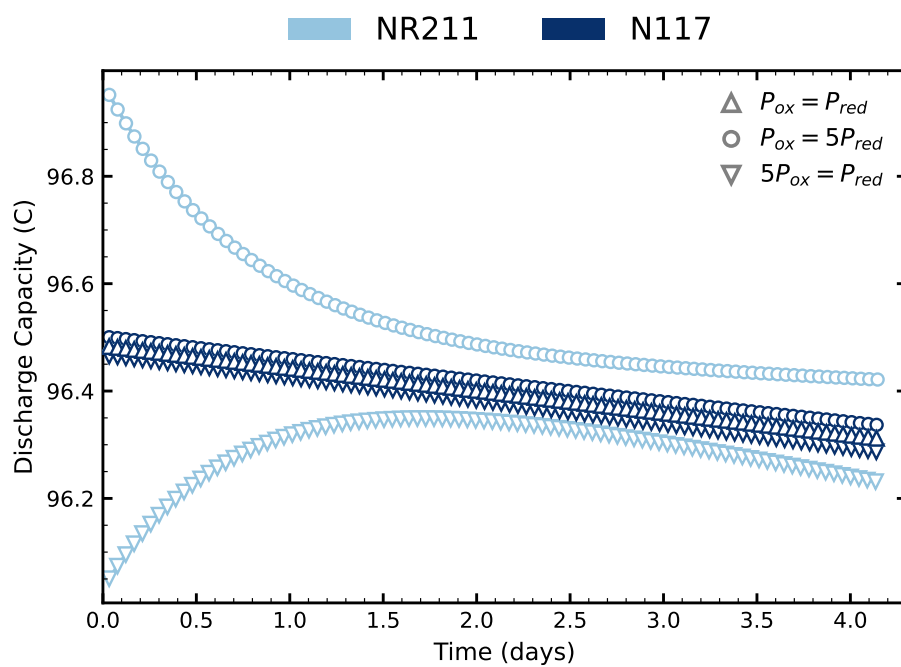


Figure S17: Simulated cycling of symmetric cells over four days with varied P_{ox} and P_{red} (parameters listed in Table S3 corresponding to Figures 5b and S15b).

Note S2: RFBzero code for Figure 4

RFBzero Python code used to generate **Figure 4** is seen below:

```
from rfbzero.redox_flow_cell import ZeroDModel
from rfbzero.experiment import ConstantCurrentConstantVoltage
from rfbzero.crossover import Crossover
from rfbzero.degradation import (ChemicalDegradationReduced,
                                 Dimerization,
                                 MultiDegradationMechanism)

# experimentally determined values for NR211, NR212, N115, N117
thickness = [25, 50, 125, 183] # microns
permeability = [8.3e-9, 6.7e-9, 1.6e-9, 2.3e-9] # cm^2/s
ohmic_resistance = [0.035, 0.038, 0.060, 0.075] # ohms

# initialize first-order chemical degradation
chem_deg = ChemicalDegradationReduced(rate_order=1, rate_constant=1.0e-8)

# set dimer formation rate constants
K_dimer = 75 # 1/M
k_forward = 0.03 # (1/M)/s
k_backward = k_forward / K_dimer # 1/s

for t,p,r in zip(thickness, permeability, ohmic_resistance):
    # define dimerization in CLS and NCLS
    dimer_cls = Dimerization(forward_rate_constant=k_forward,
                             backward_rate_constant=k_backward,
                             )
    dimer_ncls = Dimerization(forward_rate_constant=k_forward,
                              backward_rate_constant=k_backward,
                              )

    # include chemical degradation and dimerization mechanisms in CLS and NCLS
    multi_cls = MultiDegradationMechanism([chem_deg, dimer_cls])
    multi_ncls = MultiDegradationMechanism([chem_deg, dimer_ncls])

# define the symmetric cell setup
cell = ZeroDModel(volume_cls=0.005, # L
                  volume_ncls=0.010, # L
                  c_ox_cls=0.05, # M
                  c_red_cls=0.05, # M
```

```

        c_ox_ncls=0.05,          # M
        c_red_ncls=0.05,        # M
        ocv_50_soc=0.0,         # V
        resistance=r,           # ohms
        k_0_cls=1e-3,           # cm/s
        k_0_ncls=1e-3,          # cm/s
        time_step=0.05,         # sec
        num_electrons_cls=2,     # electrons
        num_electrons_ncls=2,    # electrons
    )

# define the CCCV protocol
protocol = ConstantCurrentConstantVoltage(voltage_limit_charge=0.2,      # V
                                           voltage_limit_discharge=-0.2,  # V
                                           current_cutoff_charge=0.005,    # A
                                           current_cutoff_discharge=-0.005, # A
                                           current=0.05,                    # A
                                           )

# define the crossover mechanism
cross = Crossover(membrane_thickness=t, permeability_ox=p, permeability_red=p)

# putting it all together
all_results = protocol.run(cell_model=cell,
                            duration=90000, # cycle time to simulate (s)
                            cls_degradation=multi_cls,
                            ncls_degradation=multi_ncls,
                            crossover=cross,
                            )

```