

WHITEPAPER VII

1 cm² M-Cell: Flow Battery Tests

Introduction

Flow battery research and development is largely driven by optimisation of electrodes, electrolytes and flow-cell geometry. In particular for testing of new redox active molecules, only small amounts/volumes are available and for this reason smaller active area are needed. Here the 1 cm² M-cell (<https://redox-flow.com/product/m-cell-full-cell-2/>), is a unique multipurpose electrochemical test cell for advanced electrochemical investigations. Additionally, in a standard laboratory flow-battery setup, only the electrical current and the cell potential are measured. Although these two parameters alone determine the overall performance, it is from an R&D perspective desirable to understand how the individual parts and components contribute to the overall energy losses (anolyte/catholyte redox potentials and overpotentials). This white paper demonstrates how these losses can be mapped out experimentally. The demonstration focuses on battery testing but the M-cell can, however, equally be used for many other purposes, such as half-cell cycling, cyclic voltammetry and studies on low electrolyte volumes. The tests are performed with 2,7-anthraquinone disulfonate (AQDS) and ferrocyanide ([Fe(CN)₆]⁴⁻) as the redox-active molecules. The motivation of this white paper is not so much to demonstrate optimal performance of the chosen chemistry, but rather to demonstrate the capabilities and possibilities of the combined M-cell and OCV-cell setup, which is unique in enabling studies on small electrolyte volumes with full mapping of all relevant potentials.

Definitions of energy levels

Fig. 1 shows a general representation of the energy levels in a flow battery (or any other reversible electrochemical flow system). In the figure, the blue scale represents absolute energy levels with respect to, e.g., the standard hydrogen electrode (SHE). On the absolute scale, the abbreviations are:

- ϵ_{CC-} and ϵ_{CC+} : The potential on the negative and positive side current collectors
- ϵ_- and ϵ_+ : The (redox) potential of the liquid on the negative and positive side – note that it is variable and depends on the state-of-charge and is described by the Nernst equation
- ϵ_{ref} : The potential of (a) reference electrode(s) in the setup

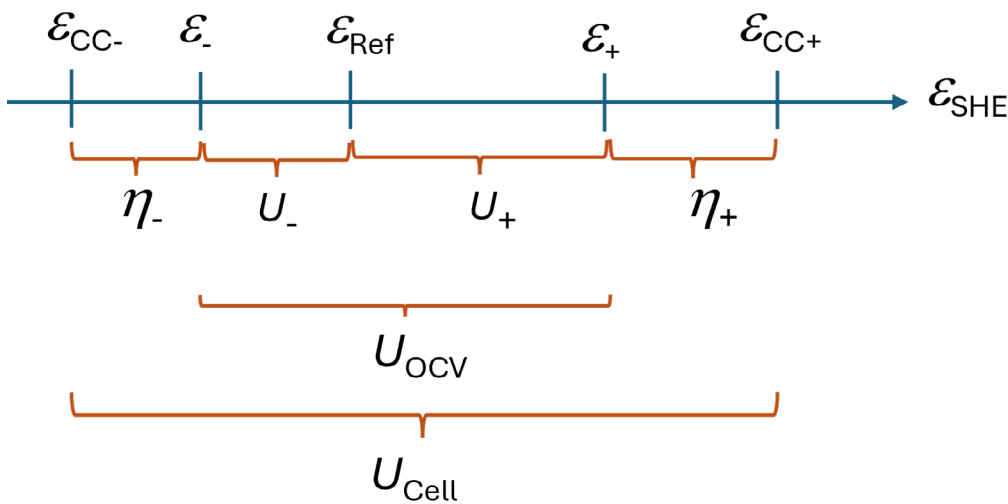


Figure 1 – Energy levels in flow batteries

While the upper (blue) potentials are absolute energy levels, the lower (orange) parts show the measurable voltages. Here

- η_- and η_+ : The overpotentials for charging (discharging) of the negative and positive side liquids
- U_- and U_+ : Measured potentials with respect to a reference electrode to determine the liquid (redox) potentials of the negative (ϵ_-) and positive side (ϵ_+)
- U_{OCV} : Potential measured in an OCV cell
- U_{cell} : The potential measured on the electrochemical cell by battery tester or potentiostat

The overpotentials and the electrolyte redox potentials are the most important parameters for mapping out internal resistive losses. There are multiple experimental approaches¹²³ for a complete mapping of η_- , η_+ , ϵ_- and ϵ_+ .

Experimental setup

All experiments were performed using commercially available electrochemical research equipment from www.redox-flow.com. The electrochemical cell used in this study was the 1 cm² M-cell, a multipurpose electrochemical test cell designed for advanced electrochemical investigations and flexible reference electrode configurations (Fig. 2):

1 Measurement of Overpotentials and Liquid Potentials in Flow Batteries, www.redox-flow.com.
2 Gonzalez, G., & Peljo, P. (2025). Experimental Set-Up for Measurement of Half-Cell and Over-Potentials of Flow Batteries During Operation. *Batteries & Supercaps*, 8(2), e202400394.
3 Langner, J., Melke, J., Ehrenberg, H., & Roth, C. (2014). Determination of overpotentials in all vanadium redox flow batteries. *ECS Transactions*, 58(37), 1.

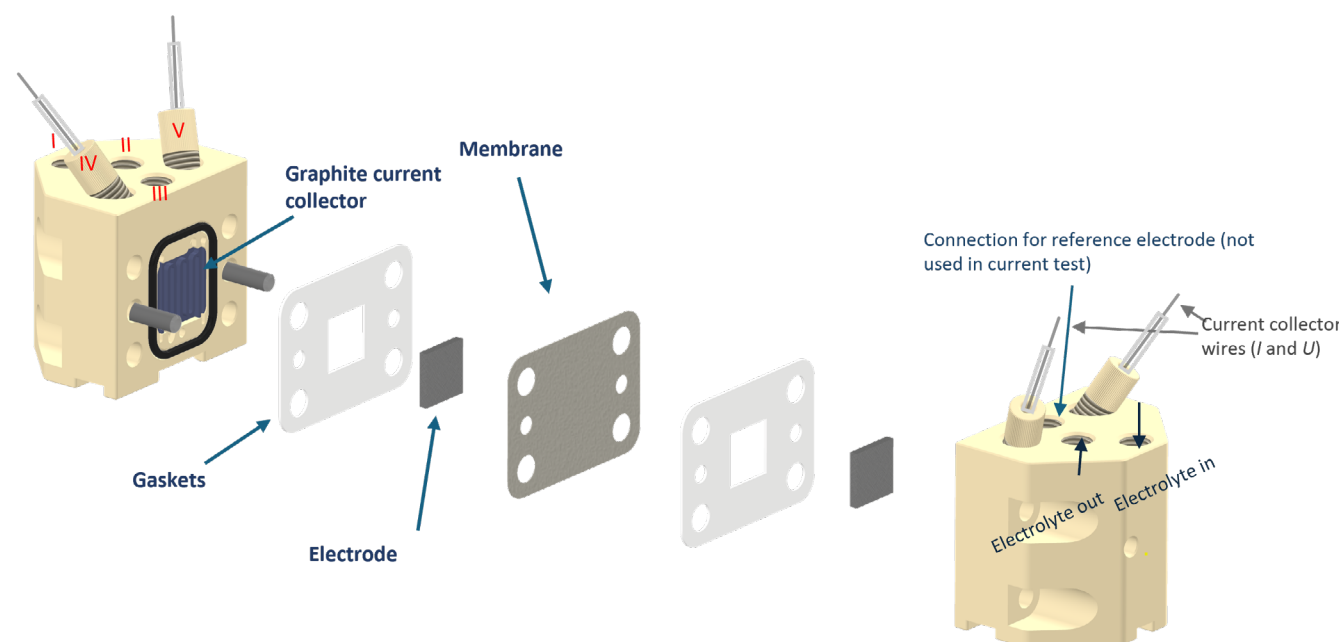


Figure 2 – General configuration of the 1 cm² M-cell operated in closed cell configuration as shown in figure. Several gaskets are stacked to obtain a compressed electrode thickness of 3.3 mm.

- Membrane: 20 µm E620 membrane from Fumatech
- Electrodes: Thermally treated AvCarb carbon felt, 4.7 mm thickness at 30% compression (3.3 mm compressed thickness)
- Current collectors: Graphite based (standard for flow batteries)
- Flow rate: 20 mL/min per side

Additionally, Redox-Flow has developed a unique OCV cell (see the separate white paper *Measurement of Overpotentials and Liquid Potentials in Flow Batteries* for a detailed performance evaluation) that enables an additional chamber to be mounted on the OCV cell. This additional chamber can be used as an ‘internal’ reference electrode in the OCV cell, replacing the external reference electrodes used in conventional setups.

Fig. 3 shows a schematic representation of the setup. Red and blue lines refer to the electric and hydraulic circuits, respectively, while the black parts represent the units in the circuit. The overpotentials (η_- and η_+) are measured directly between the OCV cell and the electrochemical flow cell, while the redox potentials (ε_- and ε_+) are measured with respect to the redox solution in the central chamber through the voltages U_- and U_+ . In the present white paper, the reference solution is a 50%/50% mixture of ferro-/ferricyanide (Zobell’s solution). Since the posolyte is ferrocyanide ($[\text{Fe}(\text{CN})_6]^{4-}$), the reference chamber is placed

on the outside of the positive side of the OCV cell (rather than in the centre, which can also be used) to minimise cross-over of contaminants into the reference solution. Throughout this white paper, all potentials are given with reference to the ferri-/ferrocyanide potential, and for this reason $\varepsilon_- = U_-$ and $\varepsilon_+ = U_+$. The different chambers of the OCV cell are likewise separated by Fumatech E620 membranes.

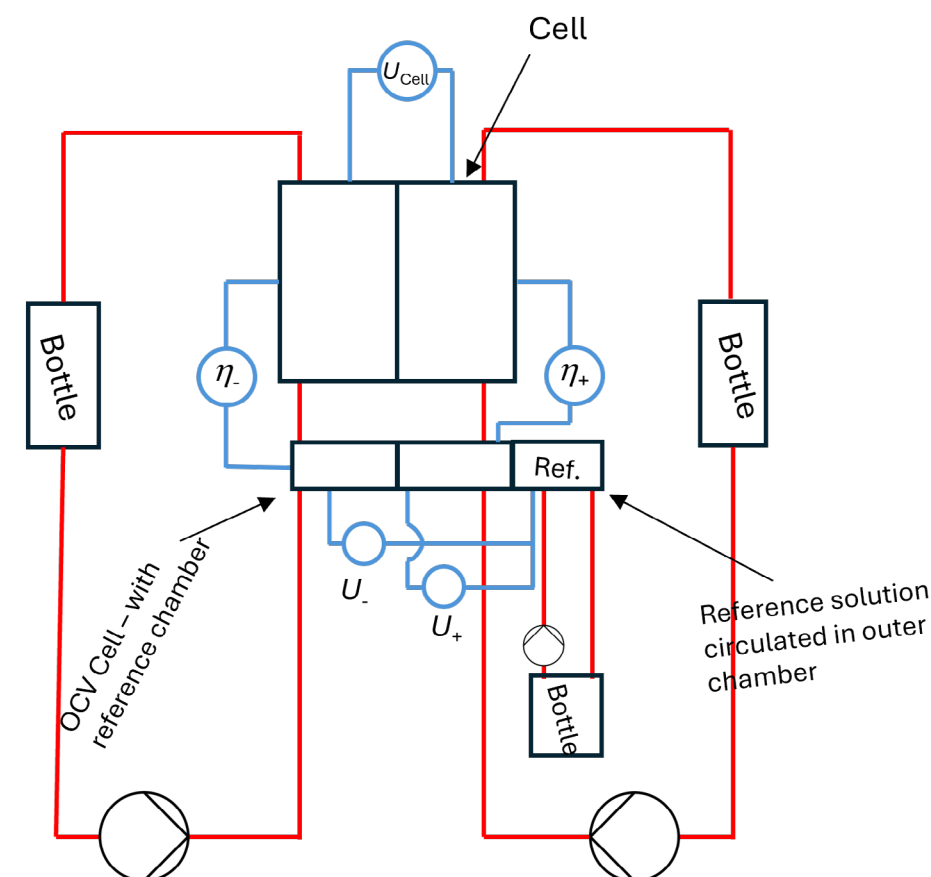


Figure 3 – Schematic representation of a setup with an OCV cell with internal reference.

The reference solution is circulated from an external third reservoir bottle by a peristaltic pump. It is noted that the same peristaltic pump (with three pump heads) is used for both the main cell and the reference chamber of the OCV cell, and that all channels are pumped at 20 mL/min.

In the present test, the electrolyte compositions were:

- Negolyte (120 mAh for 1.5 electron transfer¹): 30 mL – 0.1 M Na₂AQDS (2,7-anthraquinone disulfonate) + 0.25 M Na₂SO₄
- Posolyte (402 mAh): 50 mL – 0.3 M K₄[Fe(CN)₆] + 0.25 M Na₂SO₄
- Reference solution: 40 mL – 0.15 M K₄[Fe(CN)₆] + 0.15 M K₃[Fe(CN)₆] + 0.20 M Na₂SO₄

The posolyte capacity (402 mAh) is thus in clear excess of the negolyte capacity (120 mAh), ensuring that the posolyte is not the capacity-limiting side. Hence, it is the AQDS

negolyte that is being probed in terms of capacity fade.

Additionally, the test setup comprised a 6 V/5 A battery tester equipped with an auxiliary (AUX) measurement unit that records the potentials from the OCV cell (overpotentials and redox potentials). All voltage and current data were recorded with a time resolution of 5 s for the battery cycling and 1 s for the polarisation curves.

Polarisation curve

The polarisation curve was obtained after the battery had been cycled for several days and was recorded at 50% state-of-charge (SOC). It was obtained by applying a constant current and measuring the voltage for 10 s, using the average of the last 3 s as the voltage value in the polarisation curve. Currents were scanned from negative to positive values.

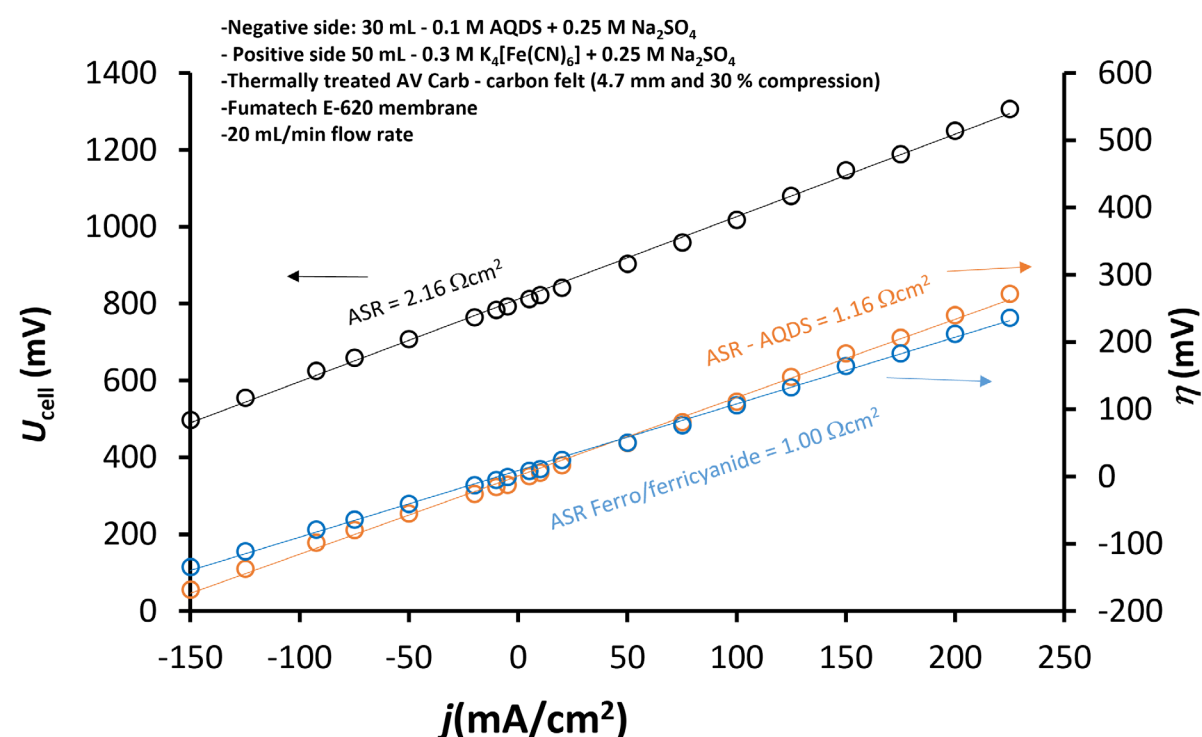


Figure 4 – Polarisation curve and overpotentials for both negative and positive side. Positive current is charging and negative current is discharging

Fig. 4 shows the polarisation curve at 50% SOC, from which a total area-specific resistance (ASR) of $2.16 \Omega \text{ cm}^2$ is found, in agreement with previously reported¹ values of $1.8 \Omega \text{ cm}^2$ to $2.2 \Omega \text{ cm}^2$ for a similar chemistry and electrode configuration but measured on a 25 cm^2 cell. By combining the M-cell with the OCV cell, it is also possible to measure the individual overpotentials, which are likewise shown in Fig. 4, where the ASR related to the

¹ Fenini, F. Et al Impact of pH management on utilization and performance of anthraquinone/ferrocyanide flow batteries, Journal of Power Sources 540 (2022): 231641.

positive side is $1.00 \Omega \text{ cm}^2$ and the ASR related to the negative side is $1.16 \Omega \text{ cm}^2$. The sum of the two ASRs adds up to the total ASR ($2.16 \Omega \text{ cm}^2$) within $0.01 \Omega \text{ cm}^2$, despite the values being obtained from three independent voltage measurements. This not only underlines the robustness of the method, but also demonstrates that the combination of the M-cell and the OCV cell constitutes a powerful setup for the measurement and deconvolution of the individual overpotentials.

Battery cycling

To further demonstrate some of the potential R&D applications, a battery cycling test was conducted on the setup with the OCV cell with internal reference. The cycling protocol consisted of constant-current charging/discharging at 80 mA to voltage limits of 1150 mV and 475 mV, respectively, followed by constant-voltage charging/discharging until the current had decreased to 10 mA.

Fig. 5 shows representative time-series data of all measured parameters between cycle 10 and cycle 20. This includes the battery cell potential and electrical current (top panel), the overpotentials of the negative and positive side (middle panel), and the redox potentials of the negolyte and posolyte (lower panel in Fig. 5). In the following, the overpotential data will not be analysed further as this has already been discussed in the polarisation curve. The primary purpose of Fig. 5 is to illustrate the complete set of parameters that is measured when the OCV cell and the M-cell are combined. Within this interval of early cycles, the curves are stable and reproducible from cycle to cycle, while their evolution over longer time scales is analysed in the following.

Battery cycling data are typically represented through the capacity and the faradaic efficiency, as shown in Fig. 6. The figure shows data from cycle 1 to cycle 180, recorded over a period of approximately 25 days, i.e., a full cycle takes approximately 3.3 hours. The initial capacity (116.2 mAh) is very close to the 120 mAh expected for a 1.5-electron transfer for AQDS.

The capacity is seen to increase slightly with cycle number until approximately cycle 135, after which it decreases rapidly to about 75 mAh at cycle 165. At this cycle, the posolyte was exchanged with a fresh solution of the same volume and composition as the original one, whereby the initial capacity (116.2 mAh) is almost fully restored after the exchange (115.2 mAh). Similarly, the faradaic efficiency is close to 100% in the initial cycles but decreases with cycle number; after the posolyte replacement, it is restored to close to 100%.

The understanding of the capacity-fade behaviour is dramatically improved by measuring the cell potential together with the redox potentials of the electrolytes using the OCV cell with internal reference. Fig. 7 shows the cell potential and the redox potentials of the

posolyte and negolyte for three selected cycles (#15, #160 and #170). Cycle 15 represents the initial behaviour, cycle 160 the behaviour just before the posolyte exchange, and cycle 170 the behaviour after the exchange. For simplicity, only the charging curves are shown. The following observations can be made:

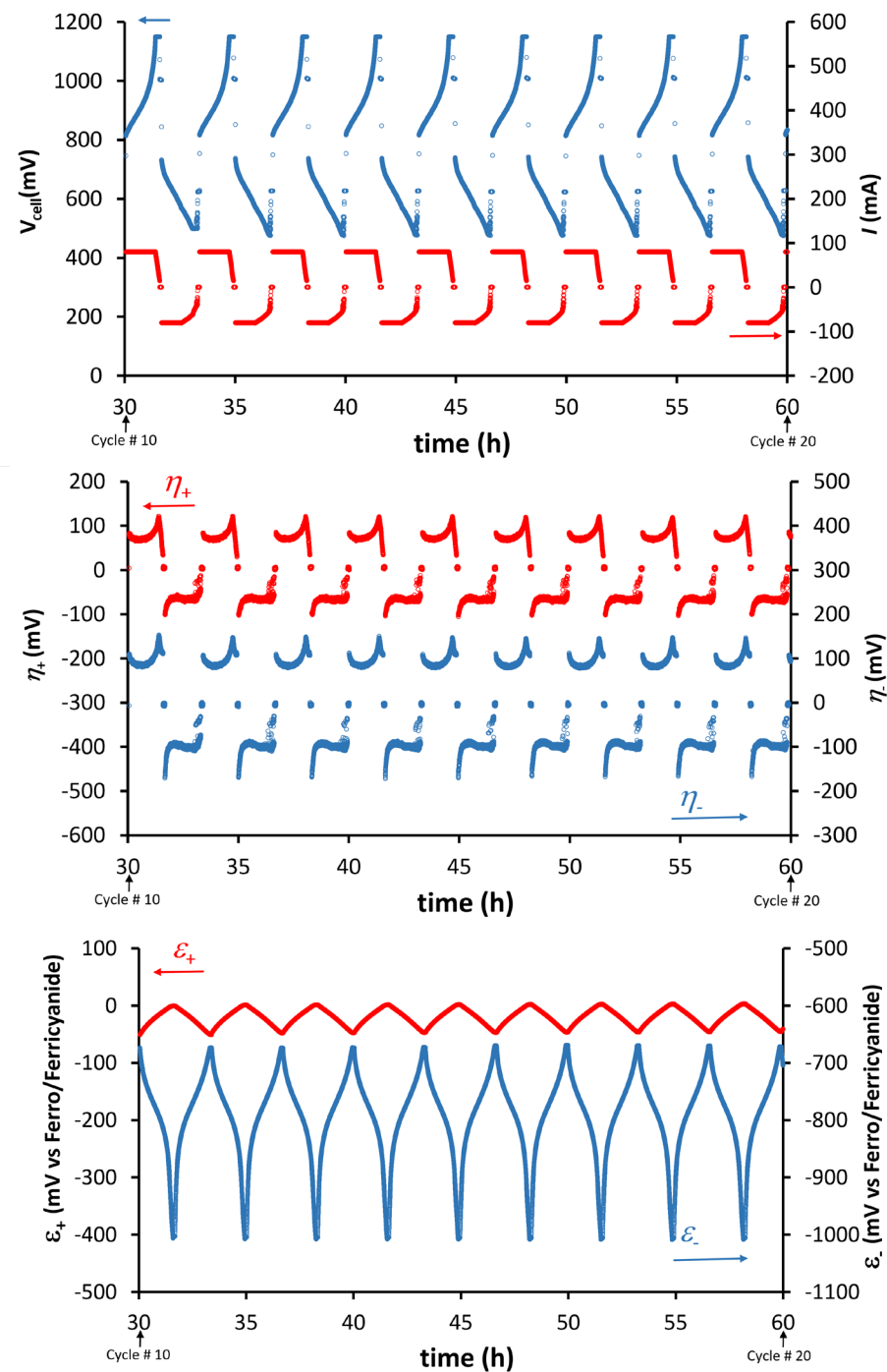


Figure 5 – Time series data of all the measured data between cycle 10 and cycle 20. Cell potential and electrical current (top panel), the overpotential for both the negative and positive side (middle panel) and redox potentials of both the negolyte and posolyte (lower panel).

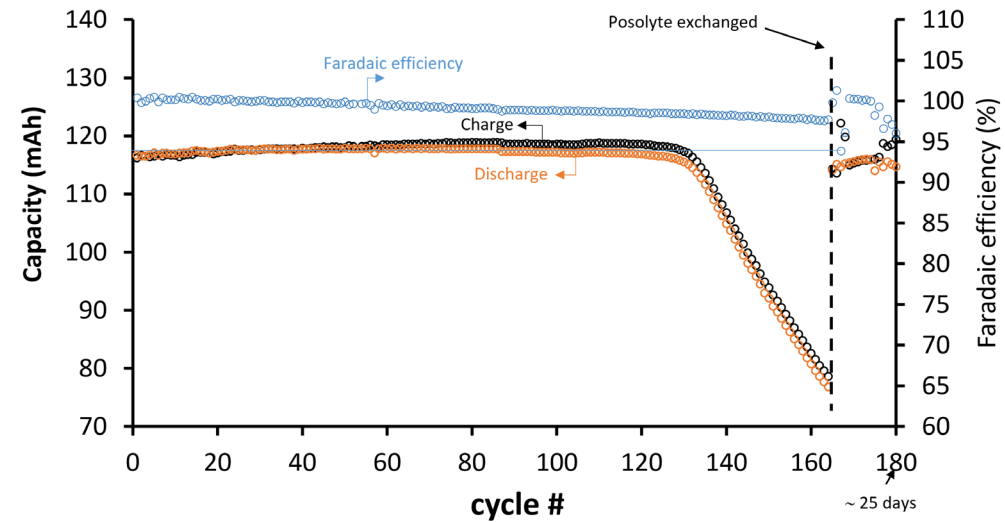


Figure 6 – Charge/discharge capacity and faradaic efficiency vs cycle number. Before cycle 165 the posolyte is exchanged with a new solution of same composition and volume. Duration of full experiment was approximately 25 days

- In the initial cycles (#15), the cell voltage increases monotonically until the voltage limit of 1150 mV is reached, and charging continues until full charge is reached (116.2 mAh). In cycle 160, the voltage is generally higher and full charge is reached already at 80.8 mAh. After the posolyte exchange, the charging curve is almost restored compared to the initial one, with only a slightly smaller capacity.
- (2) The origin of this behaviour can be elucidated from the posolyte and negolyte redox-potential measurements for the same cycles, shown in the lower panel of Fig. 7. For the initial cycles (#15), the posolyte potential (ϵ_+) only increases slightly, from about -50 mV to about 0 mV at full charge, whereas the negolyte potential (ϵ_-) decreases much more, from about -650 mV to about -1000 mV at full charge. This is as expected, since the posolyte (402 mAh) is in excess compared to the AQDS negolyte (120 mAh), whereby the full range of the Nernst potential is observed for the negolyte.
- (3) At cycle 160, the posolyte potential is higher than initially and increases to about 150 mV at full charge (80.8 mAh). Meanwhile, the negolyte potential almost follows the same curve as initially, except that it terminates at the reduced full charge (80.8 mAh).
- (4) In cycle 170, after the posolyte exchange, the posolyte and negolyte potential curves are almost fully restored to those of the initial cycle 15.
- (5) In particular, the increase of the posolyte redox potential indicates that an overall oxidation of the battery takes place. Hereby, the posolyte and negolyte get out of balance, and the posolyte becomes the capacity-limiting factor.

To investigate this further, the evolution of the posolyte and negolyte potentials as a function of cycle number is shown in Fig. 8. The evolution can be represented in several ways; ideally, it should be represented through the posolyte/negolyte SOC, but this would require accurate calibration tables between the SOC and ε_+ and ε_- , which is out of the scope of this white paper. Instead, the proxies $\varepsilon_{\max}$ (the maximum redox potential measured at either full charge or discharge), $\varepsilon_{\min}$ (the minimum redox potential measured at either full charge or discharge) and the time-averaged ε_{avr} have been calculated. The top panel of Fig. 8 shows these parameters for the posolyte. Both $\varepsilon_{\min}$ and ε_{avr} increase monotonically with cycle number. $\varepsilon_{\max}$ follows the same trend, but around cycle 130 it increases rapidly and reaches a value of about 150 mV. After the posolyte exchange, the potentials are restored to values slightly below the initial ones.

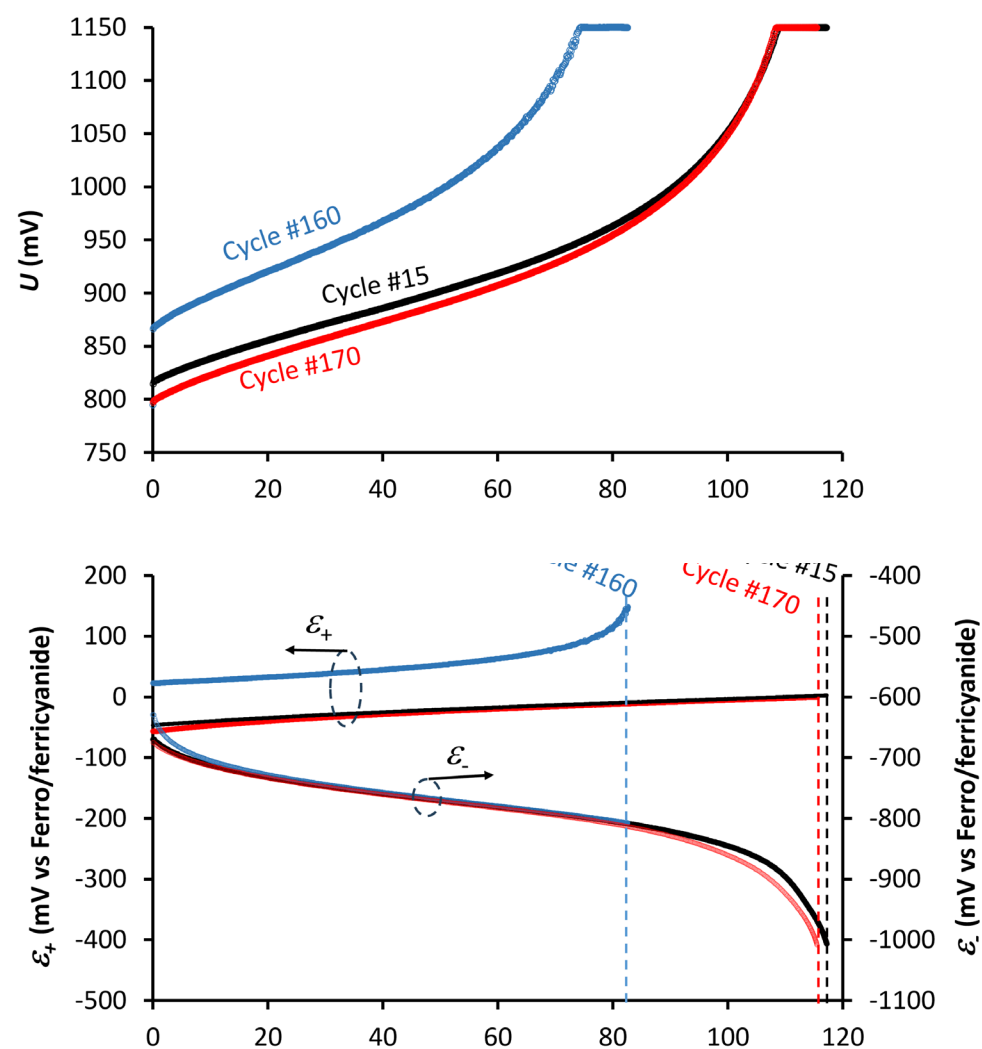


Figure 7 – U_{cell} (top panel), ε_- and ε_+ (bottom panel) for cycle 15, 160 and 170 on charge. Note that relative scale for ε_+ and ε_- are the same. Discharge data are not included in order to make the panels

The lower panel of Fig.8 shows the same parameters for the negolyte. Here, a similar trend is observed: $\varepsilon_{\max}$ increases slowly, while ε_{avr} is almost constant up to cycle 130, after which it increases. $\varepsilon_{\min}$ shows the largest change; initially, it is almost constant at -1000 mV, while just before the posolyte exchange it reaches almost -800 mV. After the posolyte exchange, the redox potentials are almost fully restored to their initial values.

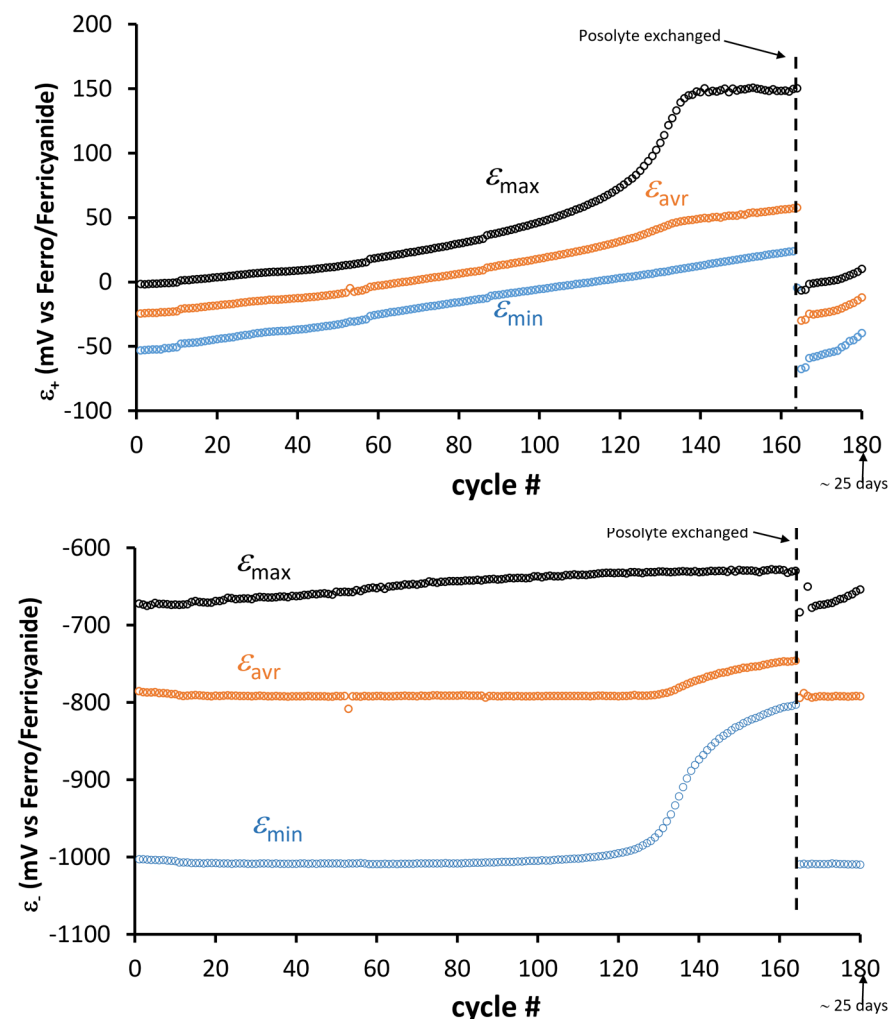


Figure 8 – Maximum, minimum and time-averaged values of the redox potentials for ε_+ (top panel) and ε_- (bottom panel) vs cycle number.

From Figs. 6 and 7, it could only be speculated that an overall oxidation/imbalance of the battery explains the large capacity fade after approximately cycle 130; Fig. 8, however, clearly demonstrates that this is the case. $\varepsilon_{\max}$ for the posolyte reaches a maximum value of about 150 mV at full charge, and since it is measured against the ferro-/ferricyanide reference, this means that the posolyte SOC is above 99 % at this point, whereby the

posolyte becomes the capacity-limiting side. Concurrently, $\epsilon_{\min}$ for the negolyte, i.e. the redox potential at full charge, increases rapidly after cycle 130. This shows that the AQDS can no longer be fully reduced, which corroborates the $\epsilon_{\max}$ data for the posolyte and demonstrates that the posolyte and negolyte have become imbalanced.

Summary

The tests presented in this white paper demonstrate the power of the combined setup of the 1 cm² M-cell and the OCV cell with internal reference, which enables a full mapping of all relevant energy levels in a flow battery. As a demonstration, a long-term durability test with AQDS and ferrocyanide as the redox-active molecules was performed, showing the stability and functionality of the M-cell. The combined measurement of capacity, faradaic efficiency and electrolyte redox potentials made it possible to identify an oxidation-driven imbalance between the posolyte and negolyte as the origin of the observed capacity fade, information that is not accessible from standard cell-voltage measurements alone.

Considerations and recommendations

Choosing the right experimental setup for low volume flow battery cycling, mapping out energy levels and potentials can be done in many ways and how to mitigate effects of O₂ in the air. The table below summarises some considerations for the choice of experimental setup.

When to use the M-cell for flow battery tests?	1. Small volumes and amounts of redox-active molecules – with the Hydraulic Connection Pack for Small Volumes (www.redox-flow.com/product/hydraulic-connection-pack-for-small-volumes/), volumes below 5 mL can be tested. 2. Small active electrode/membrane area – The M-cell has a fixed active area of 1 cm². 3. When combined with the OCV cell with internal reference (www.redox-flow.com/product/ocv-cell/) the M-cell becomes a uniquely powerful setup that enables the measurement of all relevant energy levels in flow battery tests. 4. Versatile cell that can be used for many electrochemical tests
Influence of O ₂ in air	1. Most anolytes (negolytes) for flow batteries can react with O₂ from the air, causing a slow oxidation/imbalance of the flow battery. This manifests itself as a capacity fade that is not related to the ‘true’ intrinsic capacity fade of the battery. 2. Air can enter the battery solutions through (i) bottle caps, (ii) tube feed-throughs into bottles and (iii) gaskets/sealings in the cell. 3. O₂ penetration into flow-battery systems operated in air most often originates from negative (relative) pressure on the suction side of the (peristaltic) pump.
Mitigation of the effects of O ₂ from the air	1. The most efficient mitigation is to place the whole flow battery test setup inside an oxygen-free chamber. However, this may be an expensive and elaborate solution that does not fit all purposes. 2. Bottles/reservoirs can continuously be purged with inert gas (e.g. N₂ or Ar). However, it is important that the gas is humidified before entering the bottle, otherwise water will evaporate rapidly from the redox solutions. 3. It is very important to consider the order of the units in the hydraulic circuit. Redox-Flow always recommends placing the bottles/reservoirs just before the inlet/suction side of the pump; in this case, the effect of the negative pressure is levelled out by the capacitive effect of the head space in the bottles, and less air will be sucked into the bottles (compared to, e.g., a cell placed just before the pump inlet). Additionally, the bottles/reservoirs can be placed inside ventilated, O₂-free surroundings.