Investigating the Role of Temperature on the Performance of Vanadium Redox Flow Batteries through a Unit-cell Model

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Redox flow batteries for large-scale energy storage

Redox flow batteries (RFBs) are a crucial and mature technology for large-scale energy storage that aims to increase the penetration of renewable energies into fully decarbonized electric grids. However, their competitiveness is hampered by high costs and inefficiencies. In this context, mathematical models can expedite the progress to next-generation RFBs allowing their optimization without the need of expensive prototypes and experimental tests.
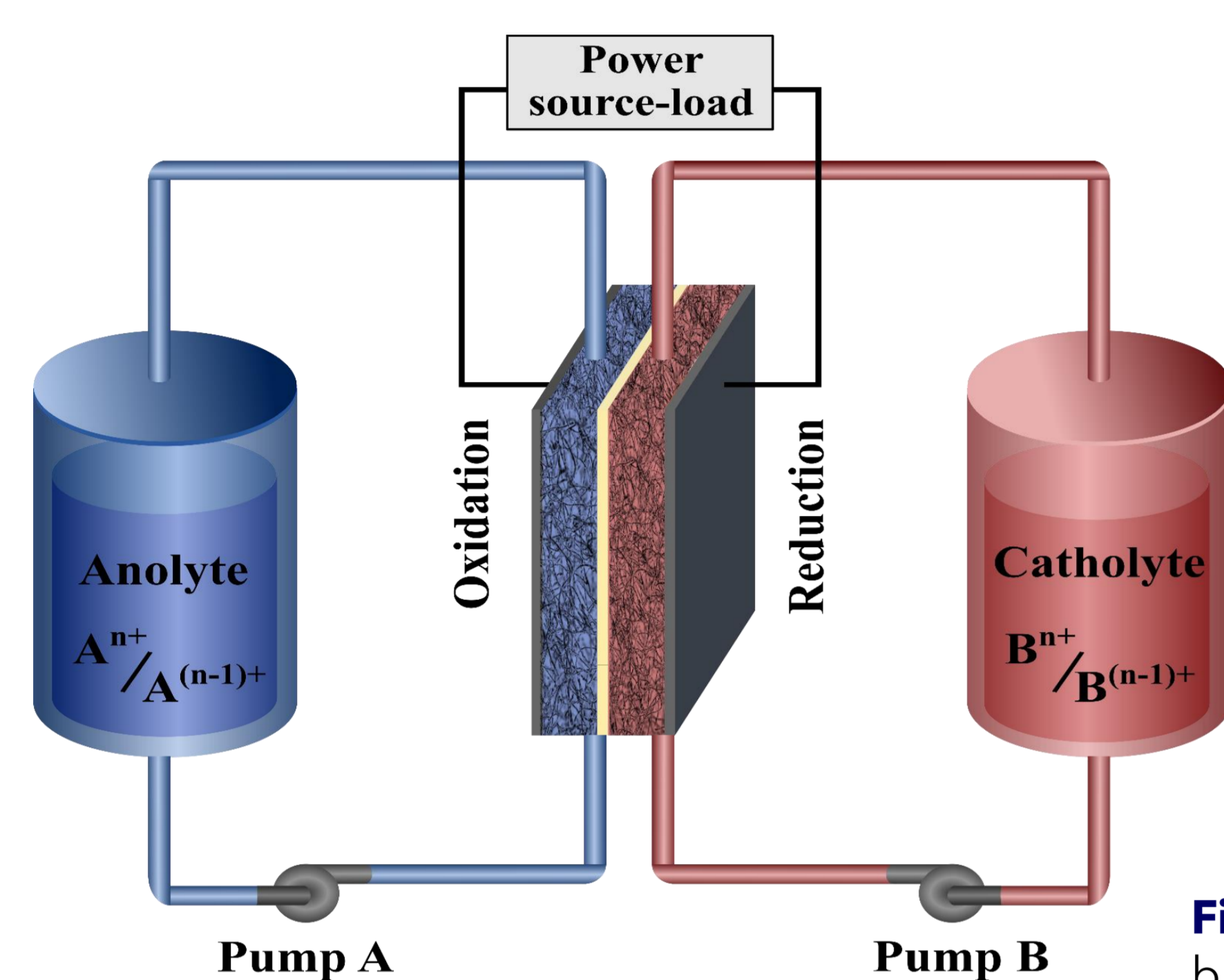

Figure 1: Redox flow battery sketch.
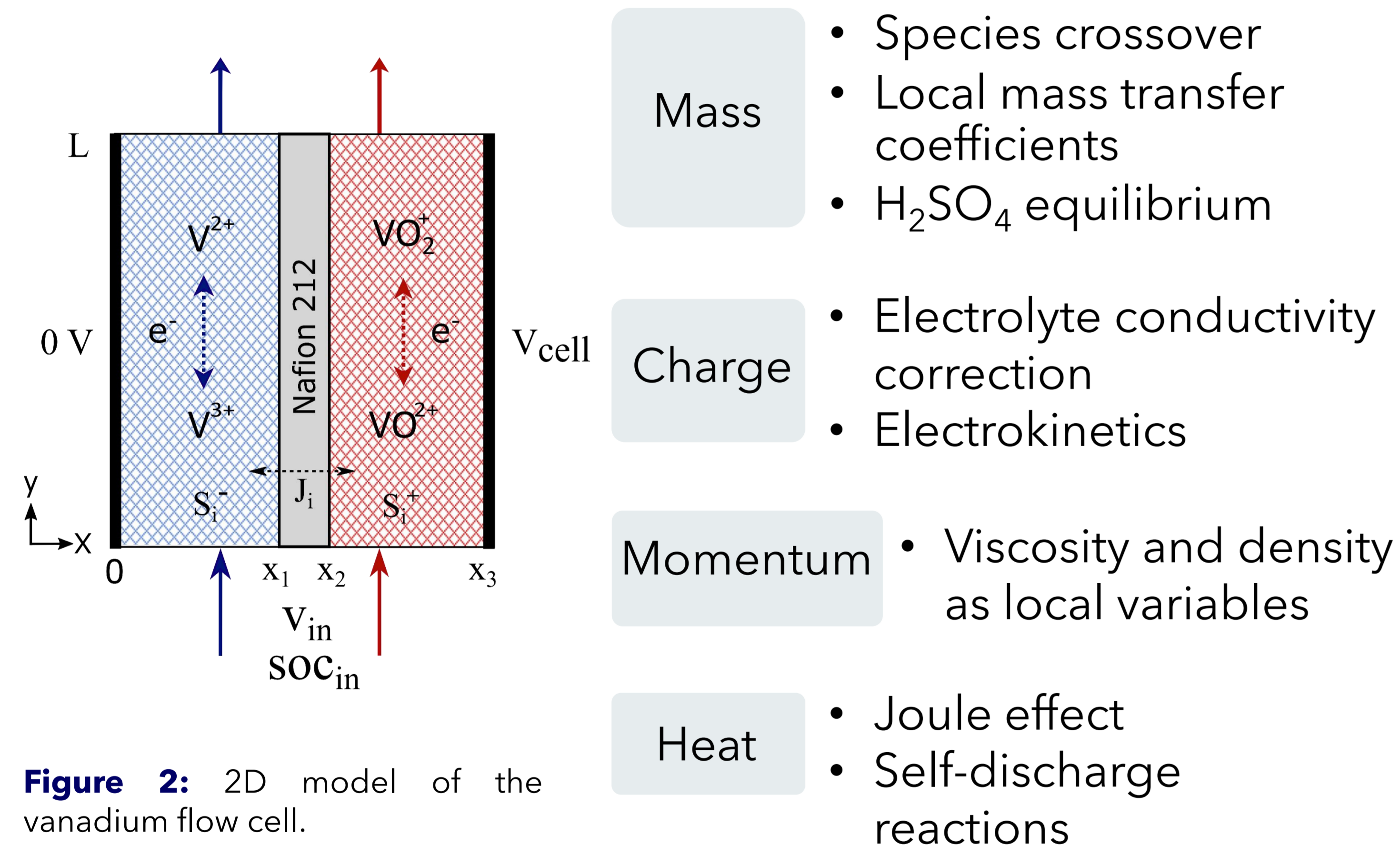
2D continuum model of a vanadium flow cell

Figure 2: 2D model of the vanadium flow cell.

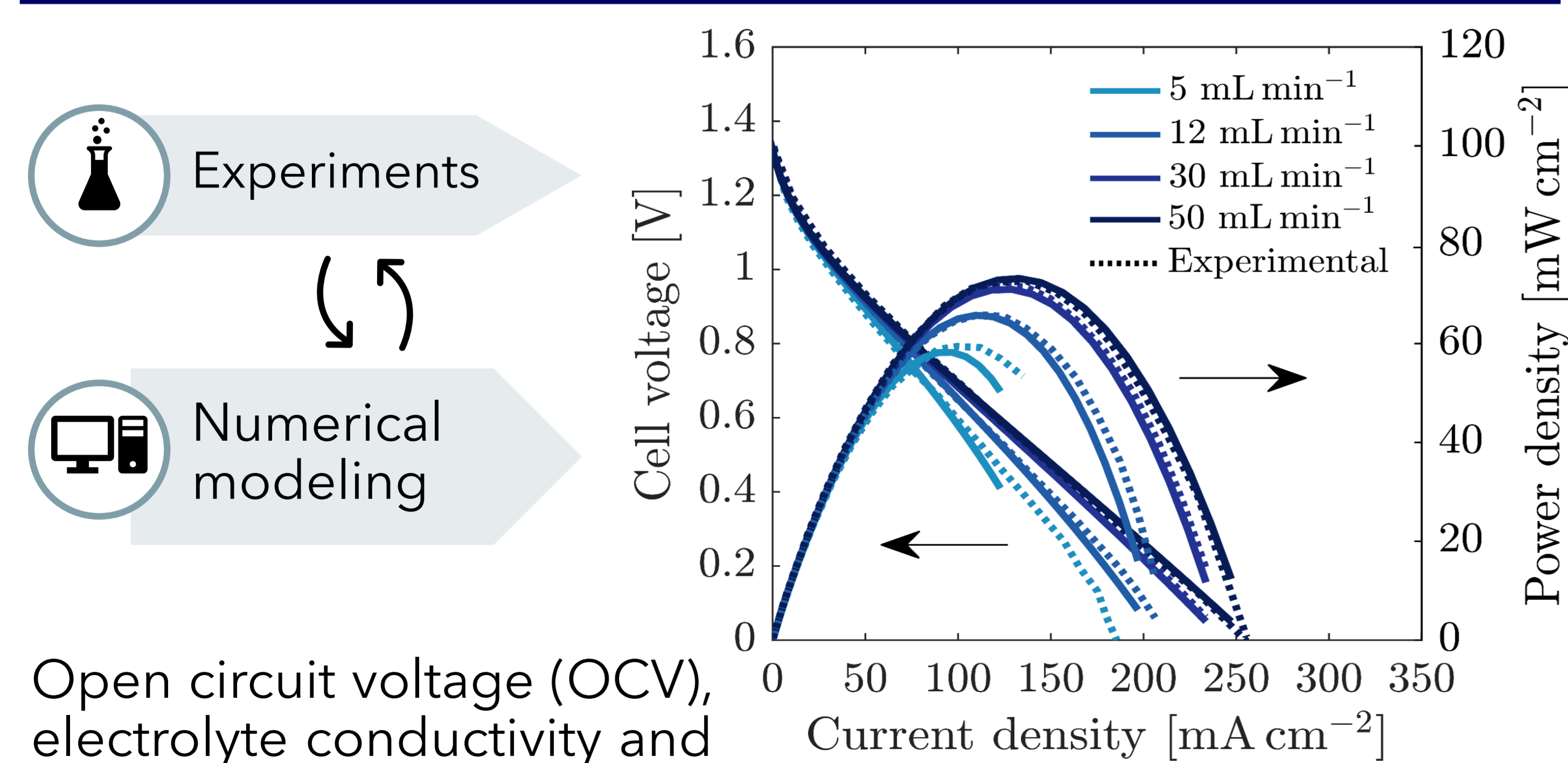| Mass | • Species crossover • Local mass transfer coefficients • H_2SO_4 equilibrium |
Charge	• Electrolyte conductivity correction • Electrokinetics
Momentum	• Viscosity and density as local variables
Heat	• Joule effect • Self-discharge reactions

Isothermal validation

Open circuit voltage (OCV), electrolyte conductivity and polarization were validated at different operating conditions.

Figure 3: Validation at 25°C and 20% SOC for different flow rates.

Capturing the effect of operating conditions

Voltage, SOC, Flow rate, Temperature

Example:

• H_2 and O_2 side reactions
• H_2SO_4 dissociation
• Crossover
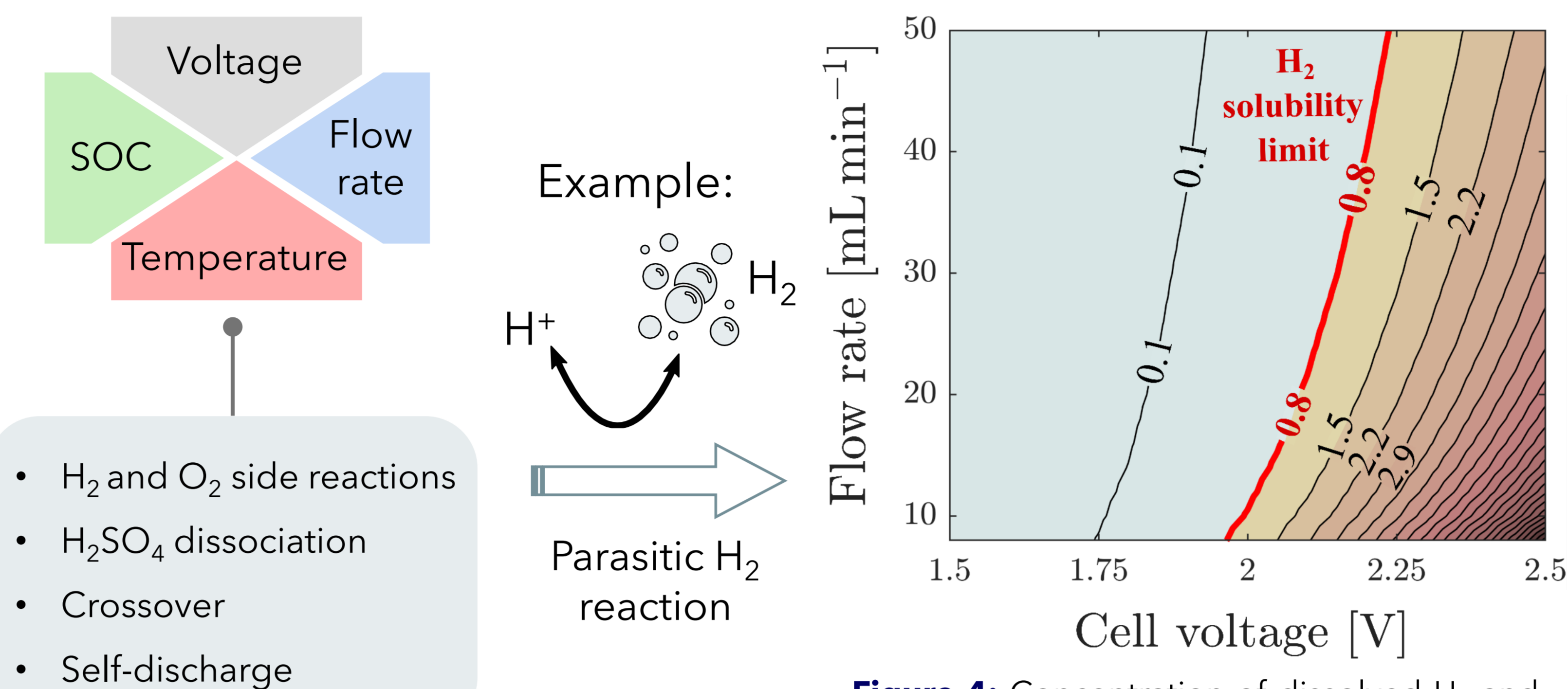• Self-discharge

Parasitic H_2 reaction

Figure 4: Concentration of dissolved H_2 and associated risk of bubble production at different flow rates and cell voltages.

Battery equilibrium potential validation

The equilibrium potential of the battery was validated at different temperatures. Using a reference cell, the open circuit voltage can be monitorized, providing online estimation of SOC from previously obtained experimental data.
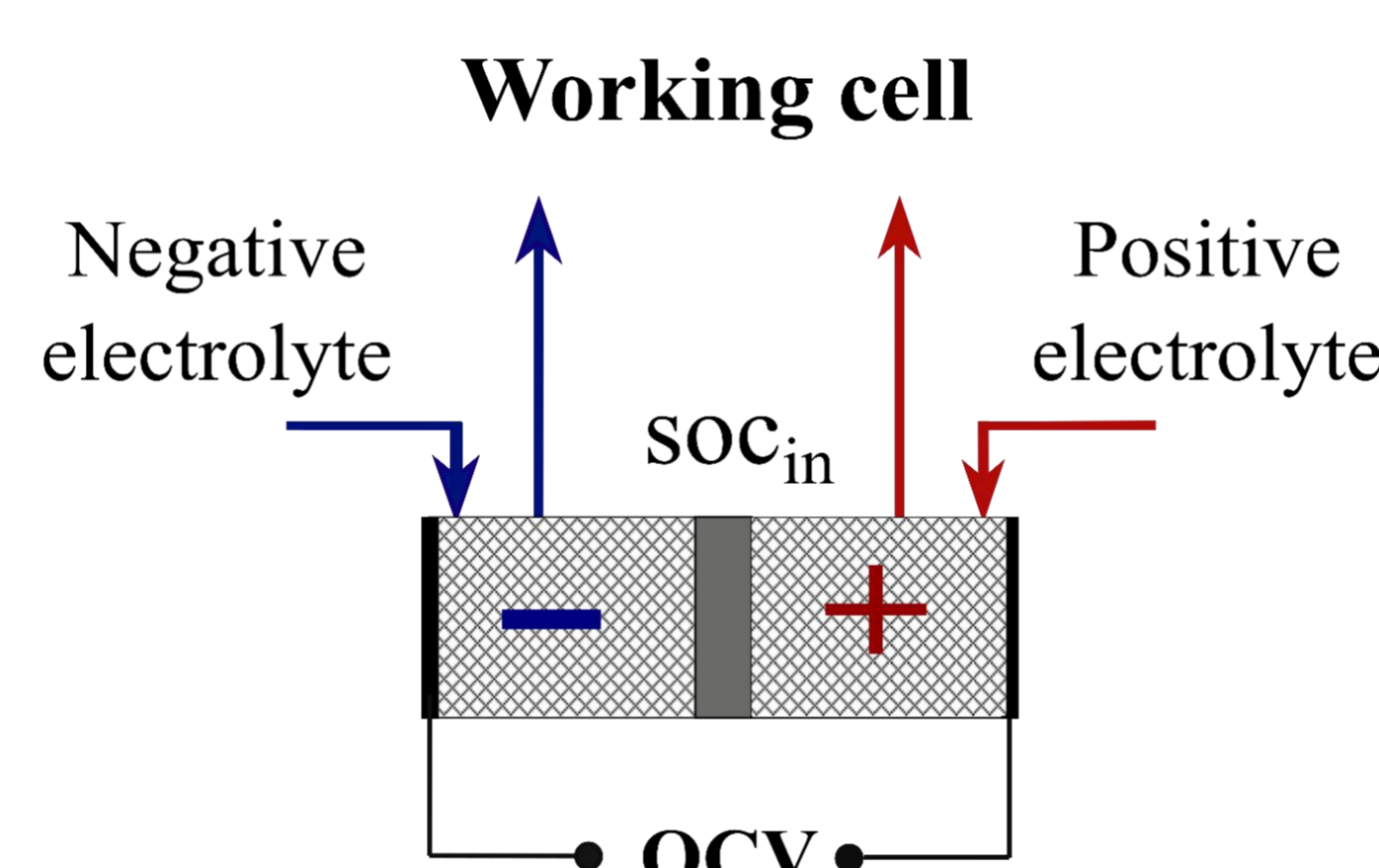

Figure 5: Reference cell connected in series to the working cell for open circuit voltage (OCV) monitorization.
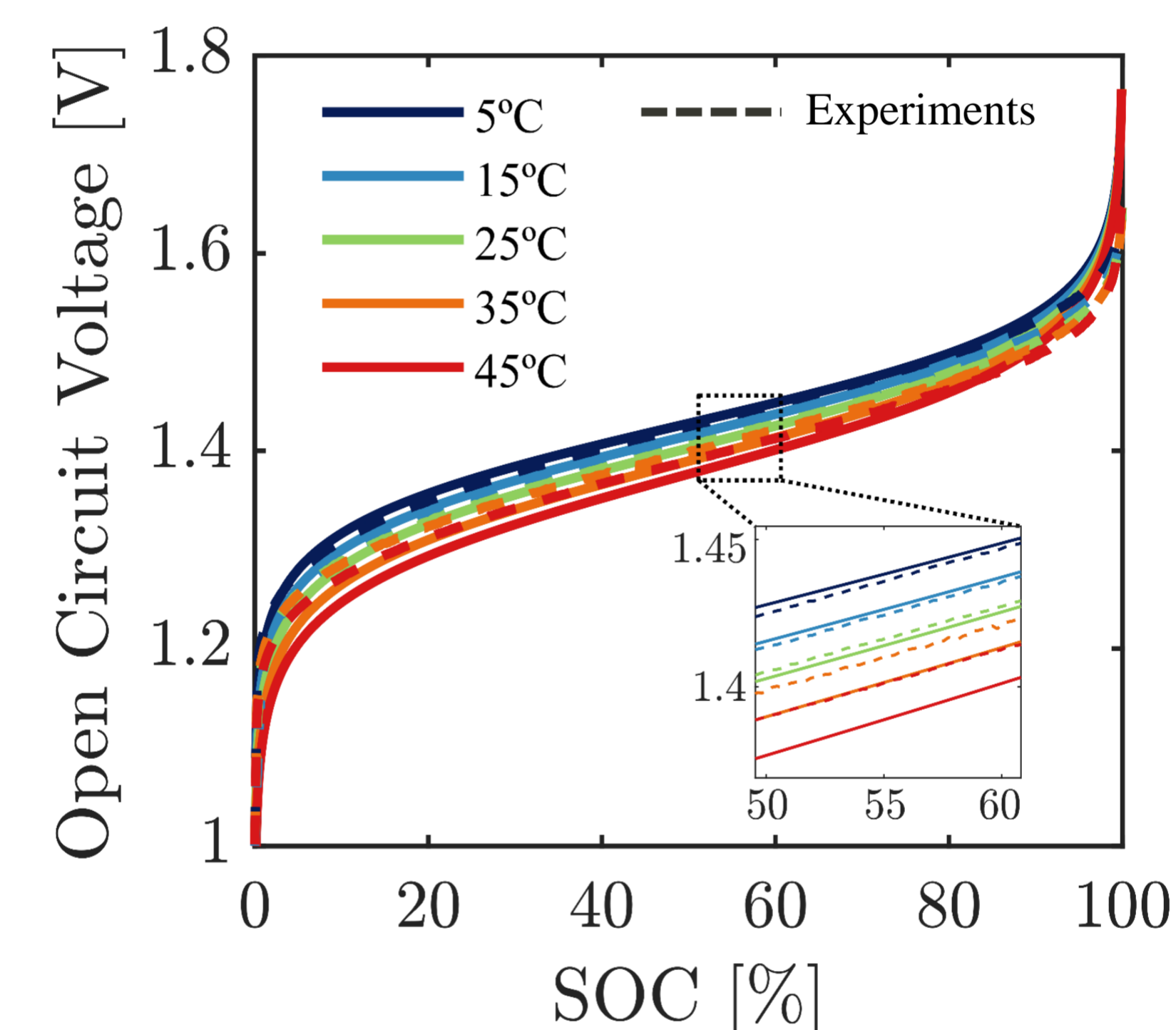

Figure 6: OCV vs. SOC curves measured at different system temperatures.

Temperature improves local mass transfer

Local mass transfer of species depends on temperature and SOC by means of variations in the electrolyte viscosity. Higher values of mass transfer coefficients (k_m) can be achieved by increasing temperature.
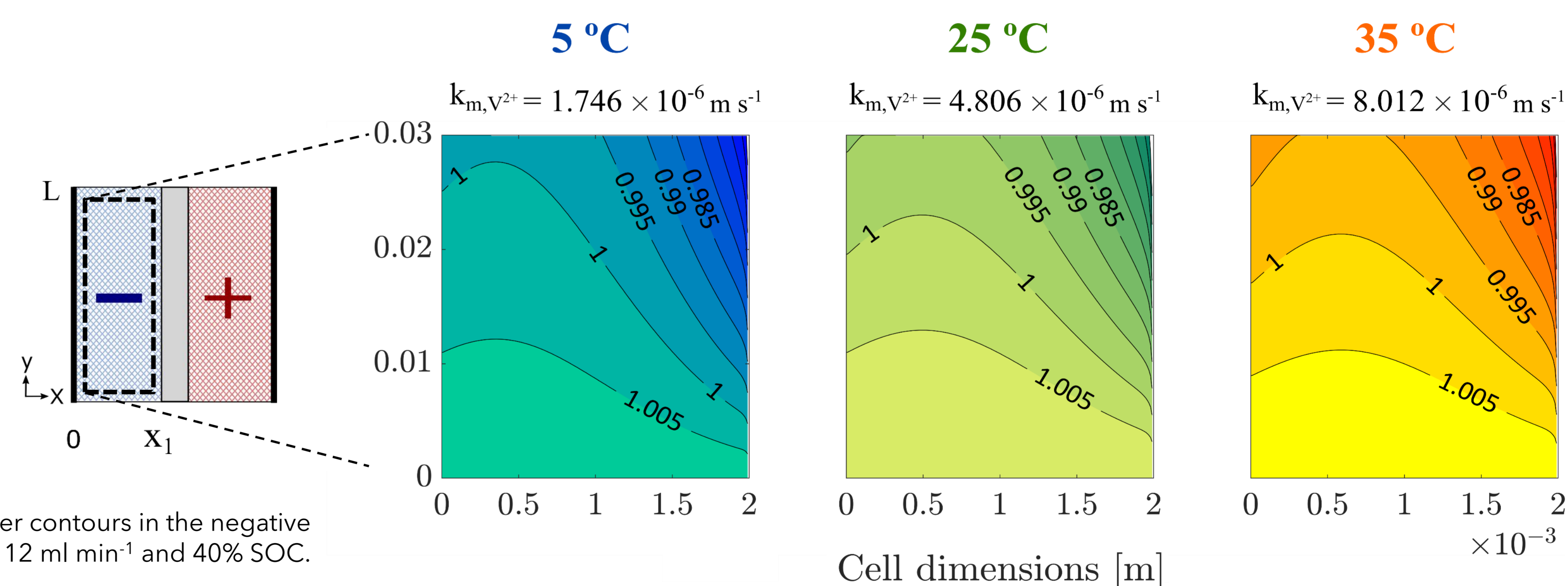

Figure 7: Dimensionless mass transfer contours in the negative half-cell for different temperatures at 12 ml min⁻¹ and 40% SOC.

5 °C $k_{m,V^{2+}} = 1.746 \times 10^{-6}$ m s⁻¹
25 °C $k_{m,V^{2+}} = 4.806 \times 10^{-6}$ m s⁻¹
35 °C $k_{m,V^{2+}} = 8.012 \times 10^{-6}$ m s⁻¹

Overpotential losses

By increasing system temperature the ohmic and mass transfer losses can be alleviated while on the contrary activation overpotential is increased.
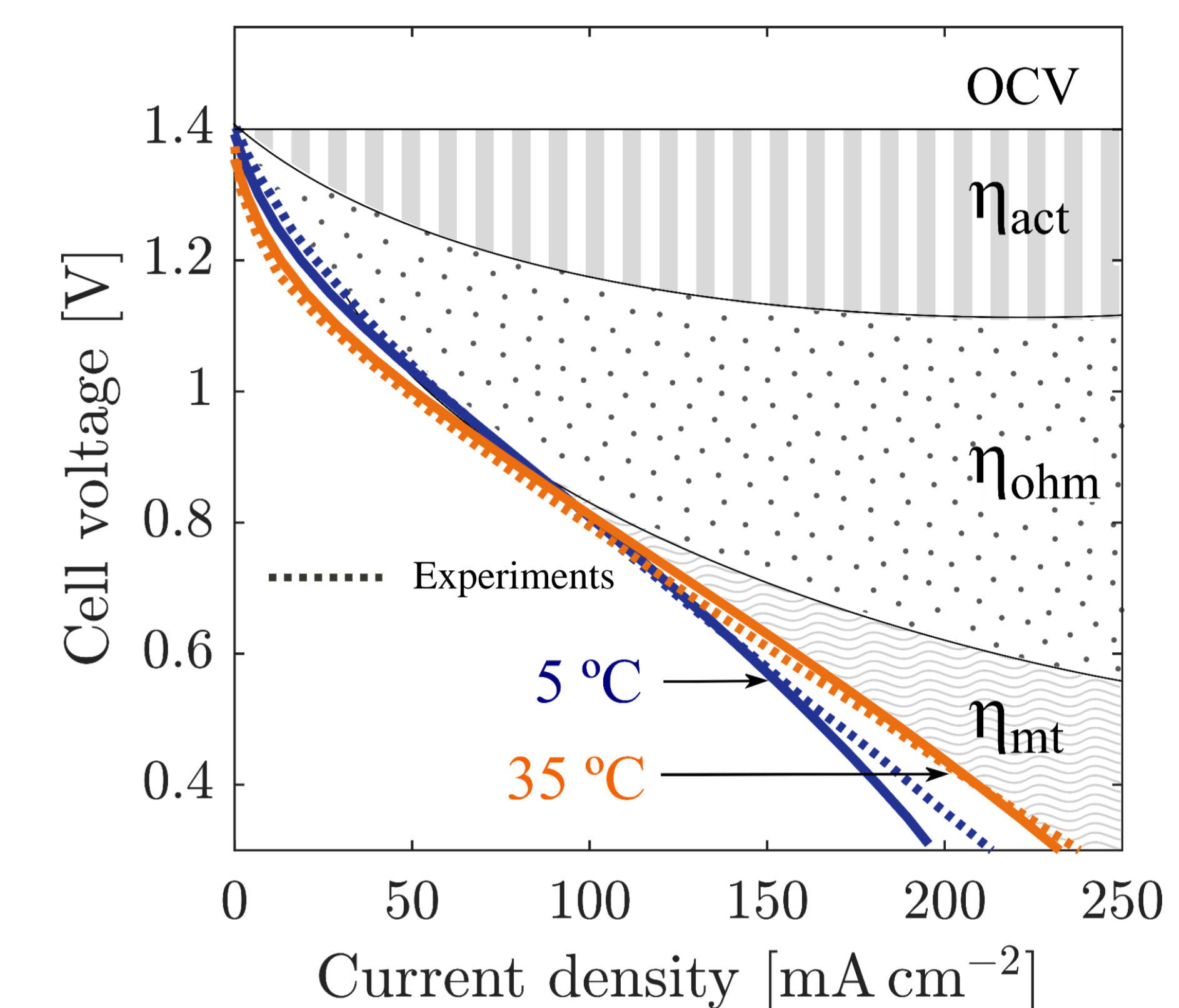

Figure 8: Electrochemical performance under 5°C and 35°C at 12 ml min⁻¹ and 40% SOC.

Temperature	R_{ohm} [Ω cm^2]	η_{act} [V]
5 °C	4.6	0.14
35 °C	3.8	0.17

Table 1: Ohmic resistance and activation overpotential of the battery under 5°C and 35°C at 12 ml min⁻¹ and 40% SOC.

References

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