

Introduction

In situ reference electrodes are valuable in water electrolyzers due to their ability to breakdown the voltage contribution from various processes.¹ We have applied and built on previous work^{1,2,3} in order to deconvolute the anode and cathode potential contributions of a working proton exchange membrane water electrolysis (PEMWE) cell simultaneously. This has allowed:

- Better analysis of testing including performance of different components
- Aid of optimisation of cell design and components
- Evaluation of voltage loss mechanisms
- Understanding of reaction mechanisms, stability and durability issues, and mass and charge transport phenomena
- Standardisation of cell voltage breakdown using *in situ* reference electrodes

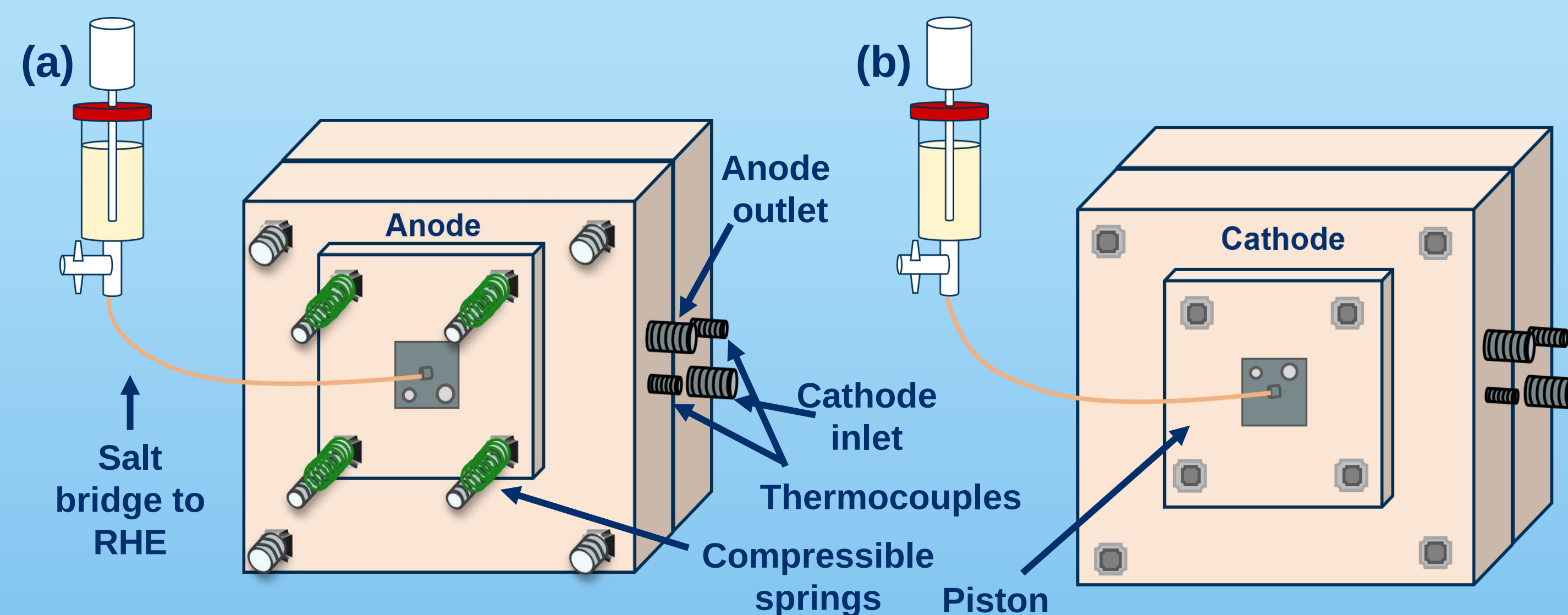


Figure 1 A schematic view of the PEMWE cell designed and manufactured at NPL from (a) anode and (b) cathode side.

Methods

PEMWE Cell Design and Manufacture

- **Figure 1** shows the manufactured cell using polyether ether ketone (PEEK).
- The reference electrodes used were hydrogen reference electrodes.
- The Pt-coated Ti pistons enabled the connections to the potentiostat.
- Cell and components were compressed using springs.

Connection of Catalyst Layers to the Reference Electrode

- PFSA ionomer diluted in EtOH to make a 5 wt% dispersion was dropped onto PTLs to impregnate and create an ionic pathway.³
- Reference electrode salt bridges filled with 0.5 M H₂SO₄ were made using Nafion™ tubing with supporting PTFE tubing. They were hot-pressed on one end to seal and prevent filling solution contaminating the cell.

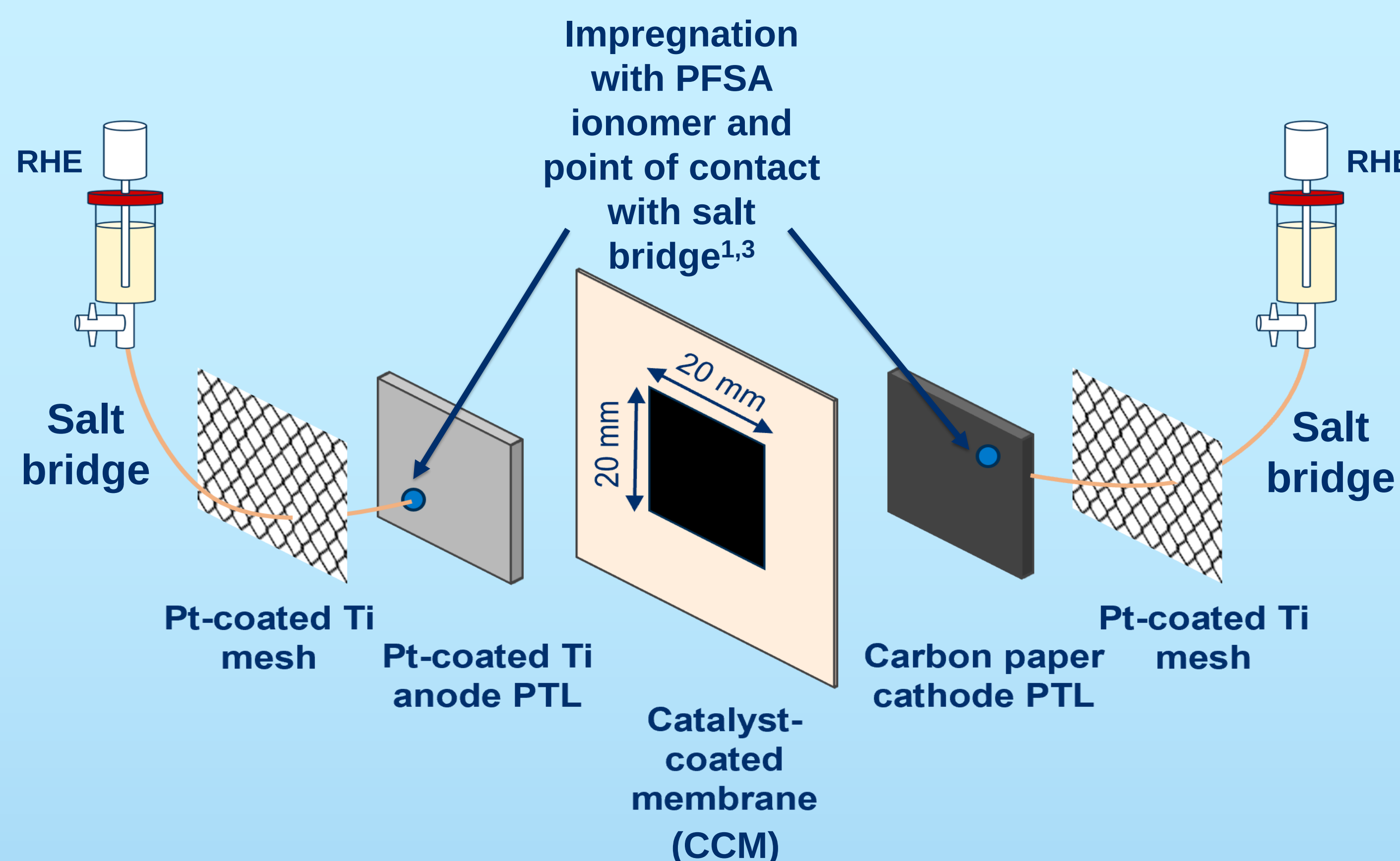


Figure 2 An exploded view of the component assembly for the *in situ* reference electrodes on both the anode and the cathode for simultaneous measurements.

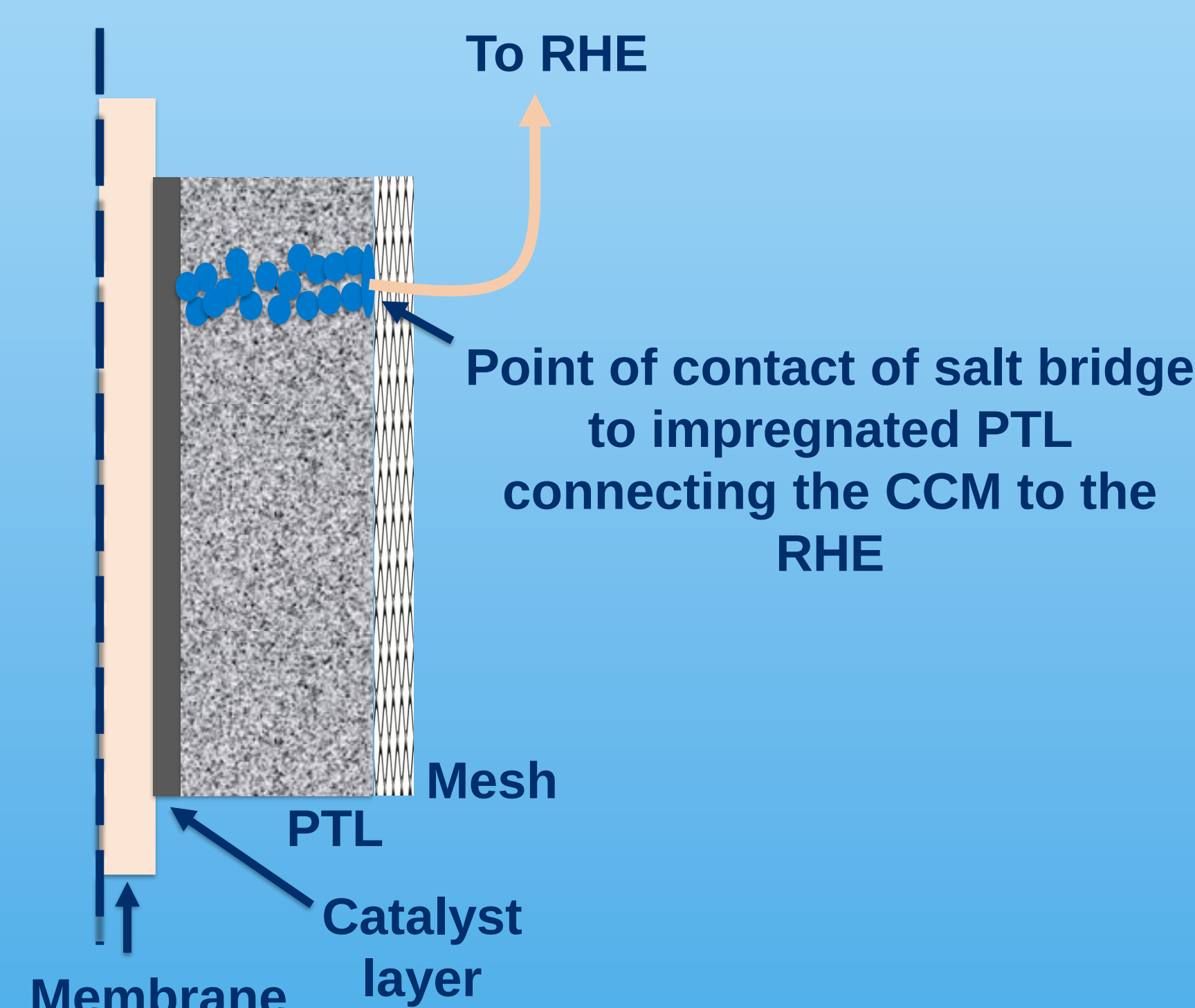


Figure 3 A cross-section of the CCM and PTL.

Results & Discussion

Figure 3 is a visualisation of the ionic conductivity pathway that is created after PFSA ionomer impregnation of the PTL enabling the local potential at the CCM to be connected to the RHE via the salt bridge.

Figure 4 shows an example of a polarisation curve obtained using the cell with *in situ* reference electrodes on both the anode and the cathode.

The polarisation curve demonstrates that the salt bridge reference electrodes with the PFSA ionomer impregnation of the PTLs have been successful as the anode, cathode and overall cell voltages measured were within expected values.

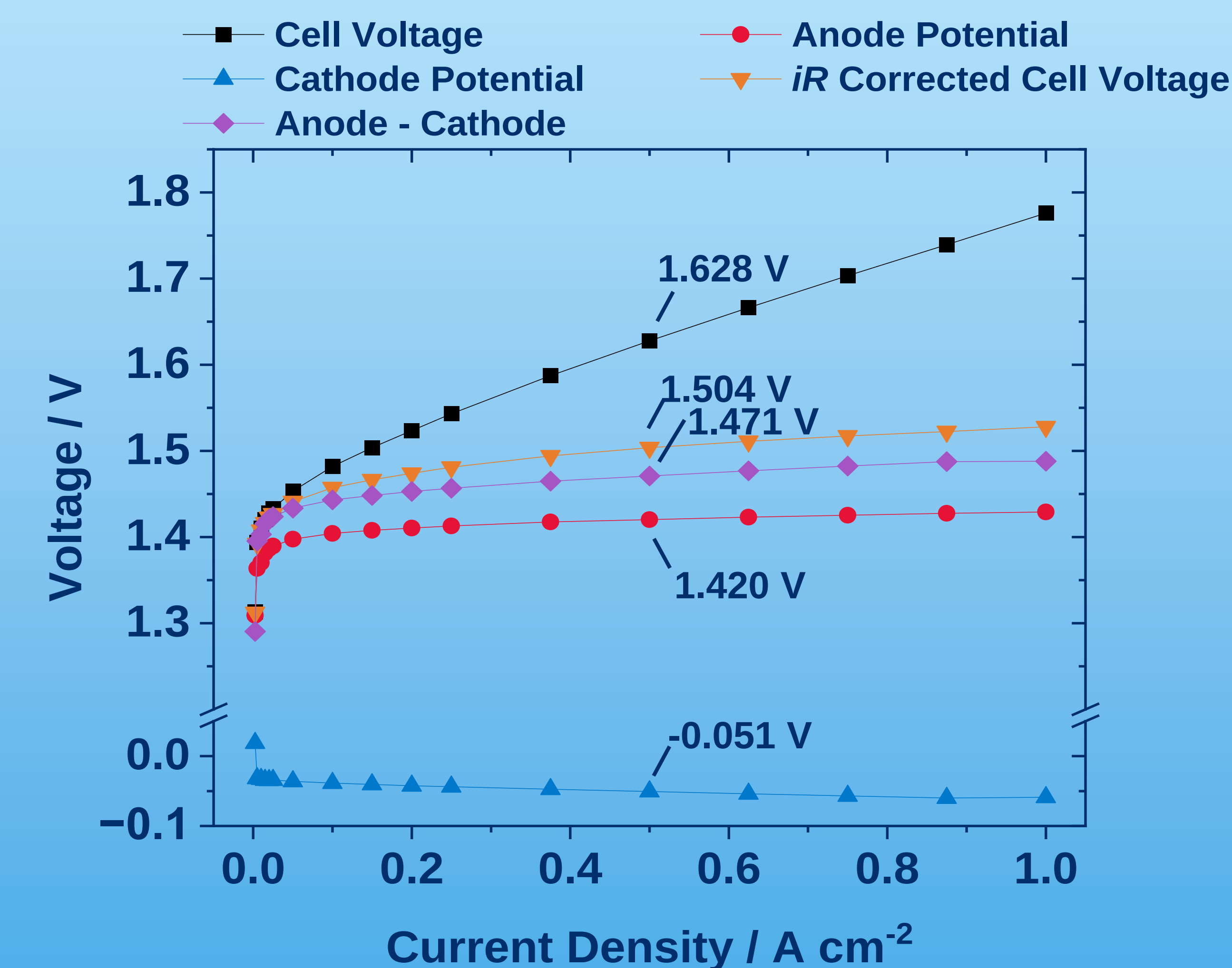


Figure 4 Polarisation curve of the PEMWE cell with deconvoluted anode and cathode contributions at 60 °C with a water flow rate of 100 mL min⁻¹.

Conclusions & Future Work

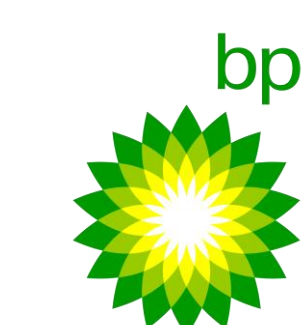
- Successful design and manufacture of PEMWE cell hardware with a capability of using *in situ* reference electrodes.
- Validated measurements via polarization curves showed that the *in situ* reference electrodes were working by simultaneous deconvolution of both the anode and cathode during operation.
- Future work includes the optimization of the PFSA ionomer impregnation as well as other components, such as the PTLs.
- Applicable to more applications such as catalyst screening, component validation, cell performance, and cell/component durability analysis.
- This work will also allow the standardisation of method and procedures.

References

1. 'Application and analysis of a salt bridge reference electrode setup for PEM water electrolysis: towards an extended voltage loss break down'. Böhre, L. V. *et al. J. Electrochem. Soc.*, 2022, **169**, 124513.
2. 'Assessing potential profiles in water electrolyzers to minimise titanium use'. Becker, H. *et al. Energy Environ. Sci.*, 2022, **15**, 2508-2518.
3. 'In situ mapping of potential transients during start-up and shut-down of a polymer electrolyte membrane fuel cell'. Brightman, E., Hinds, G. *J. Power Sources*, 2014, **267**, 160-170.

Acknowledgements

This work was supported by bp plc and the National Measurement System of the UK Department of Science, Innovation and Technology.



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