Identifying liquid water and ice in model PEMFCs with high temporal-spatial resolutions using energy-selective neutron imaging

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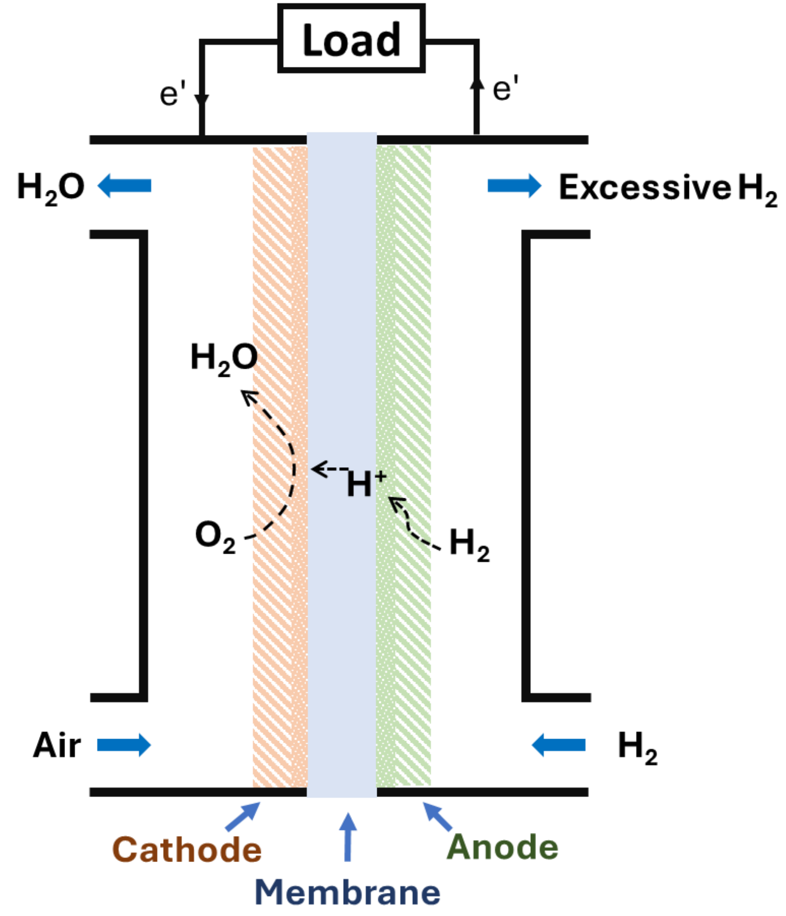
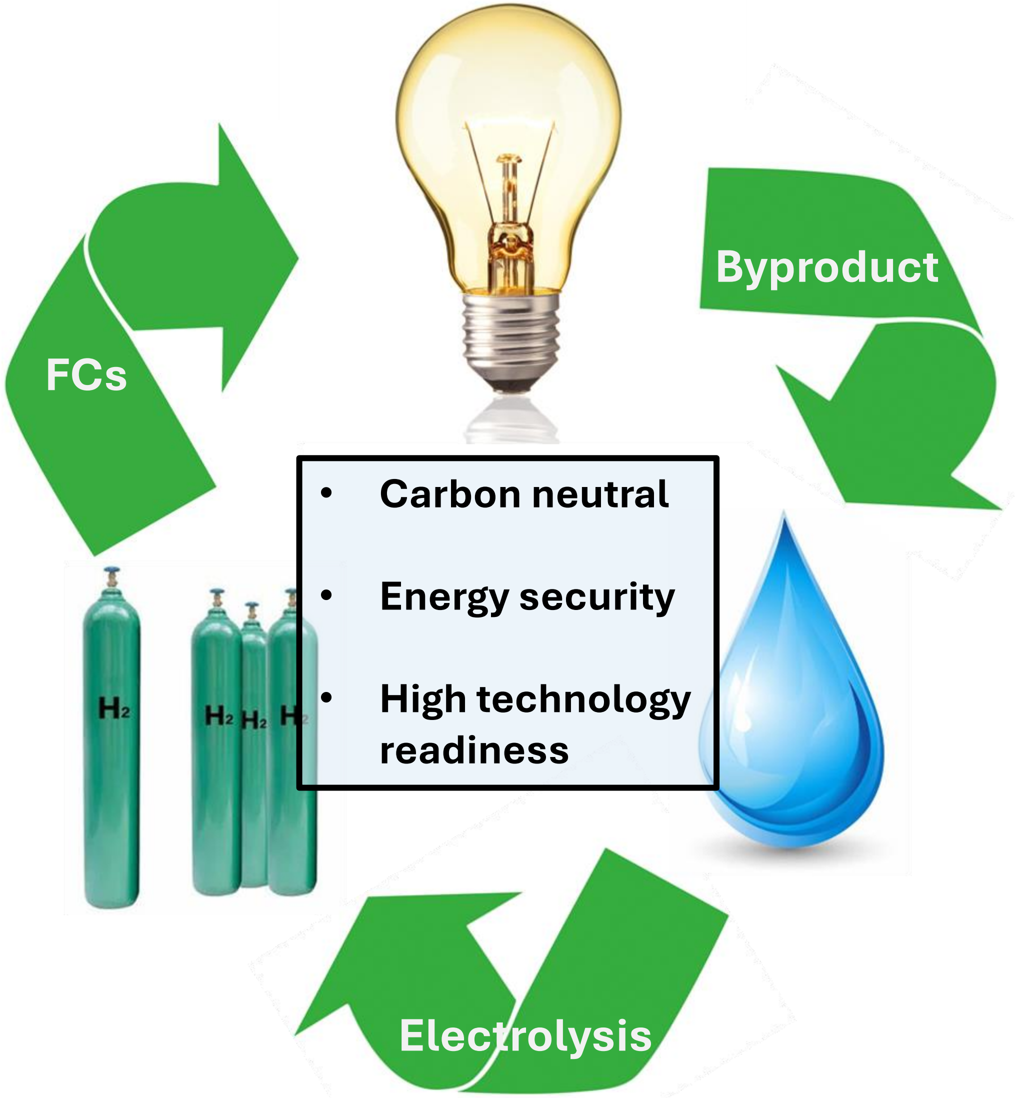
Hydrogen polymer electrolyte membrane fuel cells (PEMFCs)



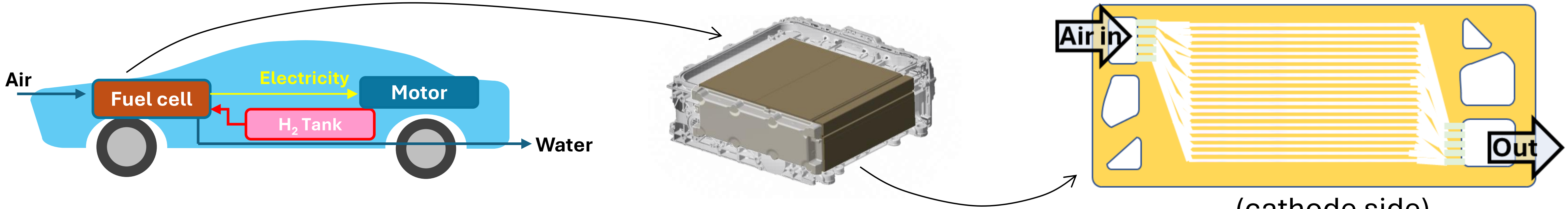
$$H_2 + O_2 = \text{electricity} + H_2O$$



- Carbon neutral
- Energy security
- High technology readiness

PEMFCs for vehicles and their challenges

Fuel cell vehicle | **Fuel cell stack** | **A single cell**



(cathode side)

The 'cold-start' of the PEMFC:

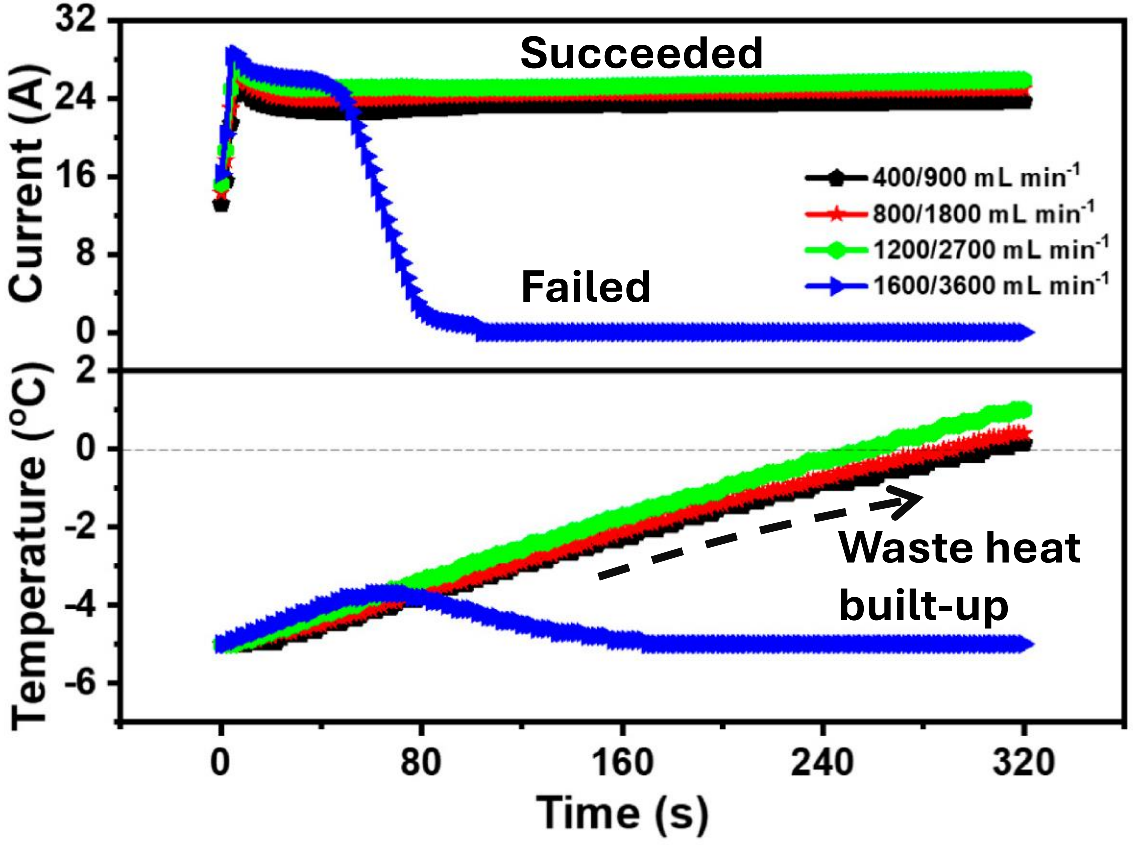
FC starts to generate power at sub-freezing environment

→ Water product frozen to ice, blocking gas supply

→ Electrochemical reaction is suppressed → Reduced power output

PEMFCs for vehicles and their challenges

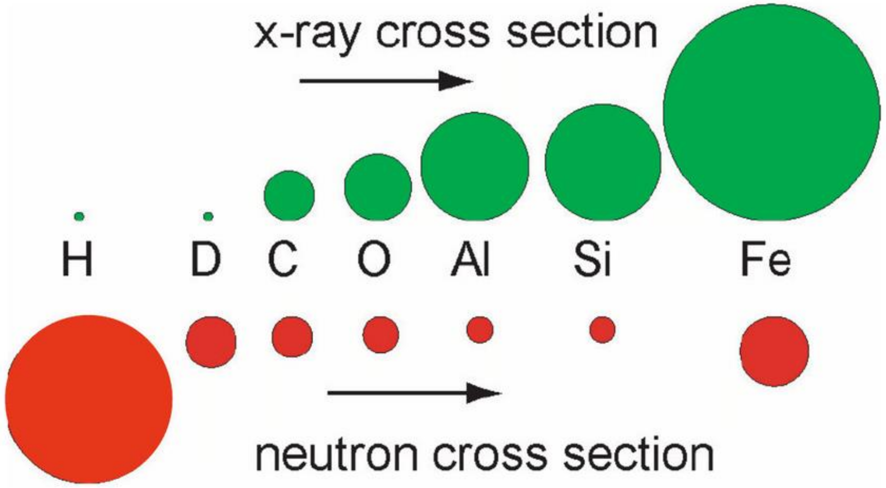
Successful and failed cold-starts*



- For commercialized FC vehicles: post-shutdown purging + self-heating utilizing waste heat from power generation. (enabling start-up at -30°C)
- Start-up strategy, material selection and cell design need to be optimized.
- It is critical to understand the mechanism for the freezing and thawing phenomenon in cell.

*Y. Yang, *et al.*, *Energies*, **14** (2021) 660

Visualizing the water distribution using neutron radiography



Neutron radiography:

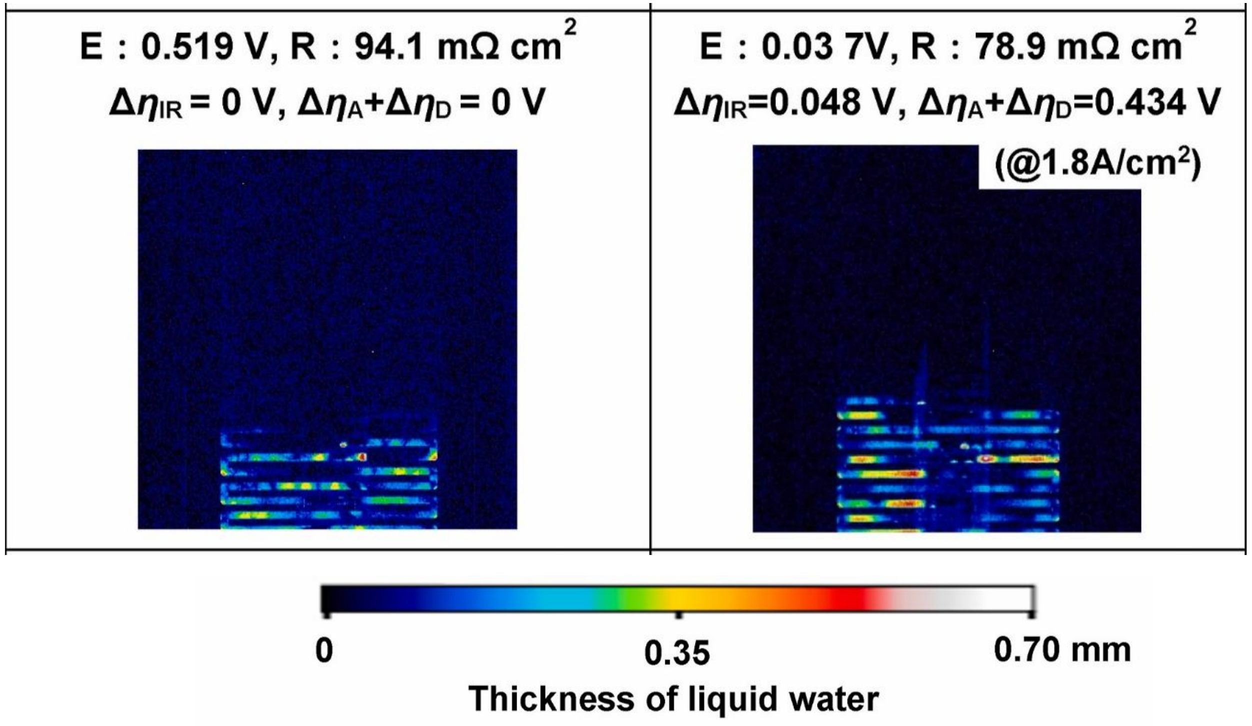
- Sensitive to water
- Non-destructive, non-intrusive
- Allows quantification

Transmission = exp($-\Sigma t$)
Σ: neutron attenuation, t: thickness

Example:

Amount of water at cathode side flow channel as a function of loading condition (i.e., current)*.

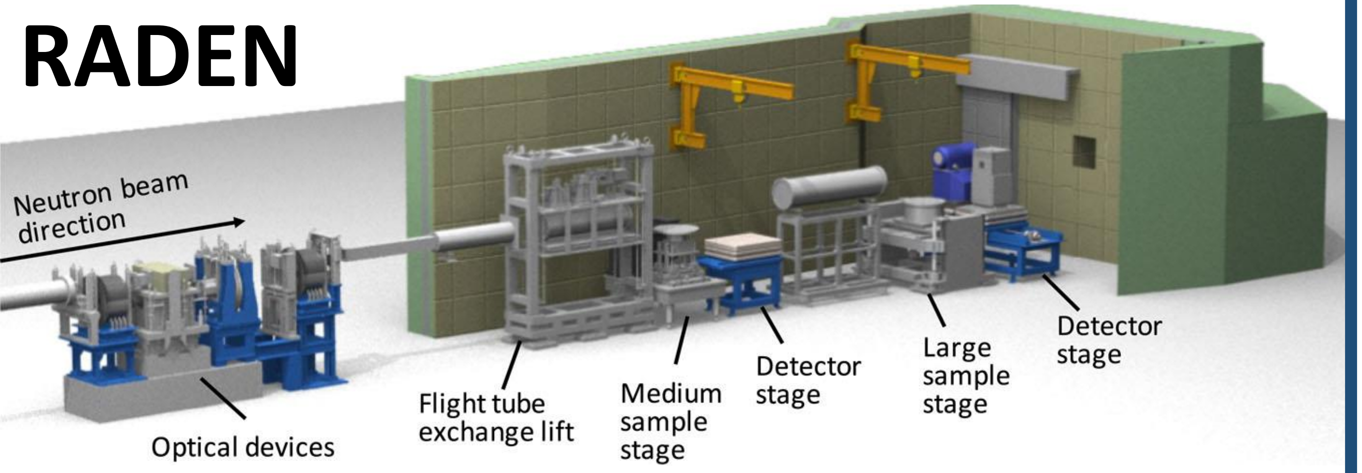
Mid loading, 1A/cm^2 High loading, 1.8A/cm^2



*M. Nasu, *et al.*, *J. Power Sources*, **530** (2022) 231251

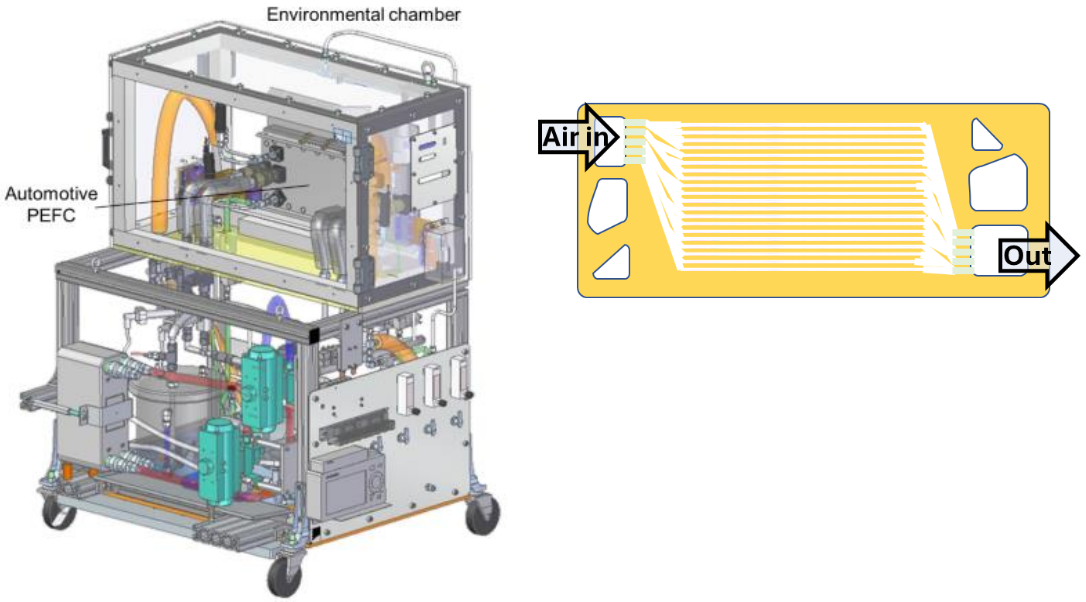
Visualizing the water distribution using neutron radiography

RADEN



- Detector
- Gas supply system
- H_2 dilution unit
- …

TOYOTA CENTRAL R&D LABS



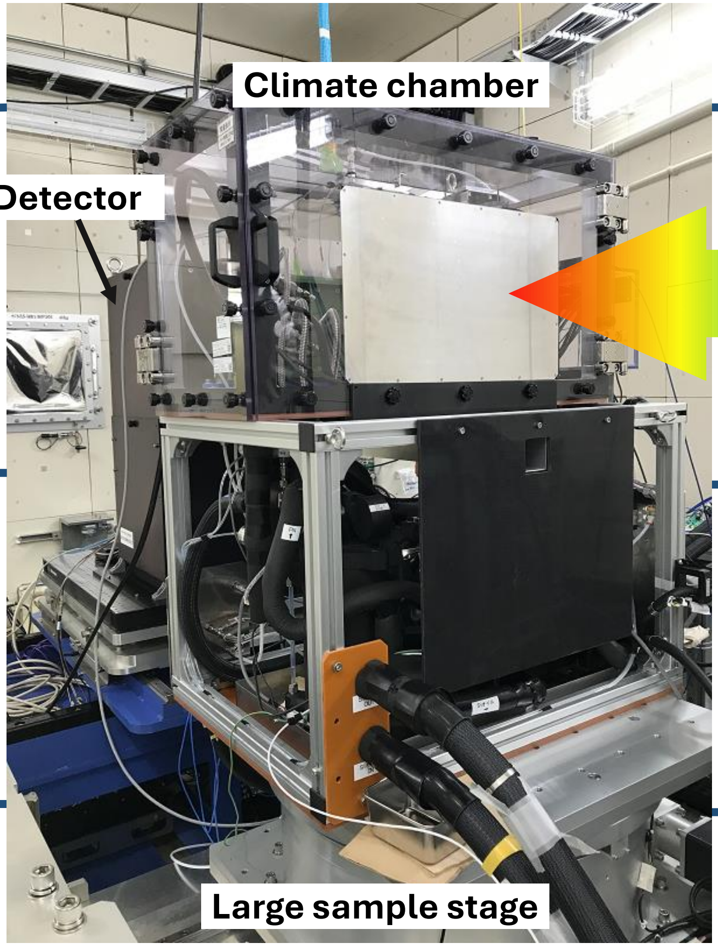
- Cell
- Climate chamber
- Mass flow control
- Workstation
- …

Visualizing the water distribution using neutron radiography

Gas supply control

Electrochem. workstation

Heat exchangers



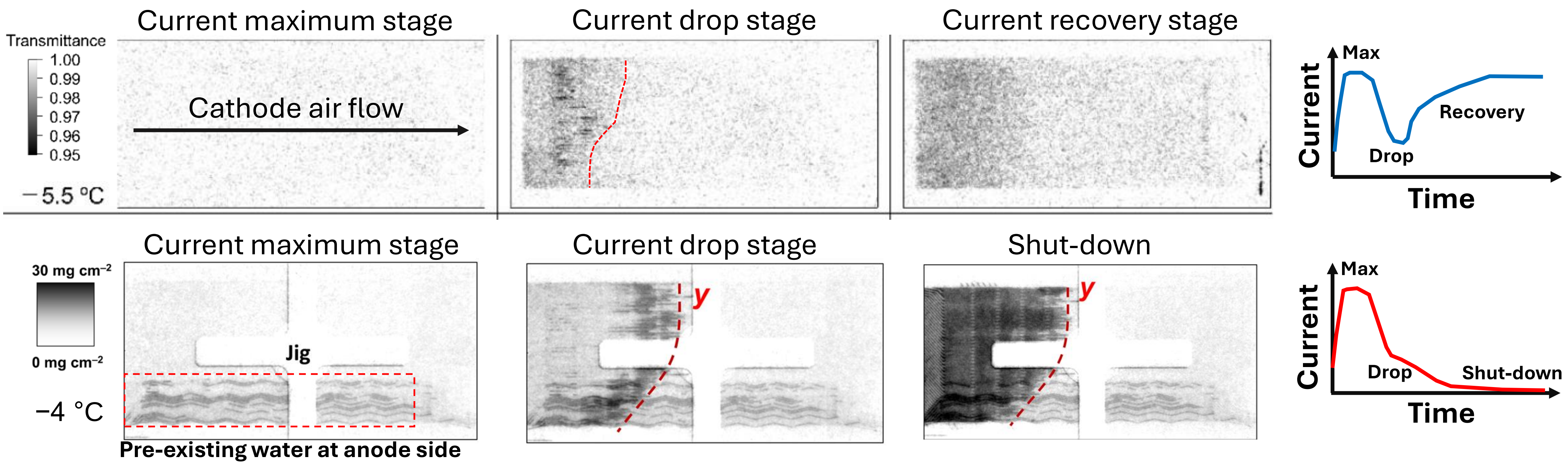
Neutron Beam

Camera control

H_2 dilution unit

Sample stage control

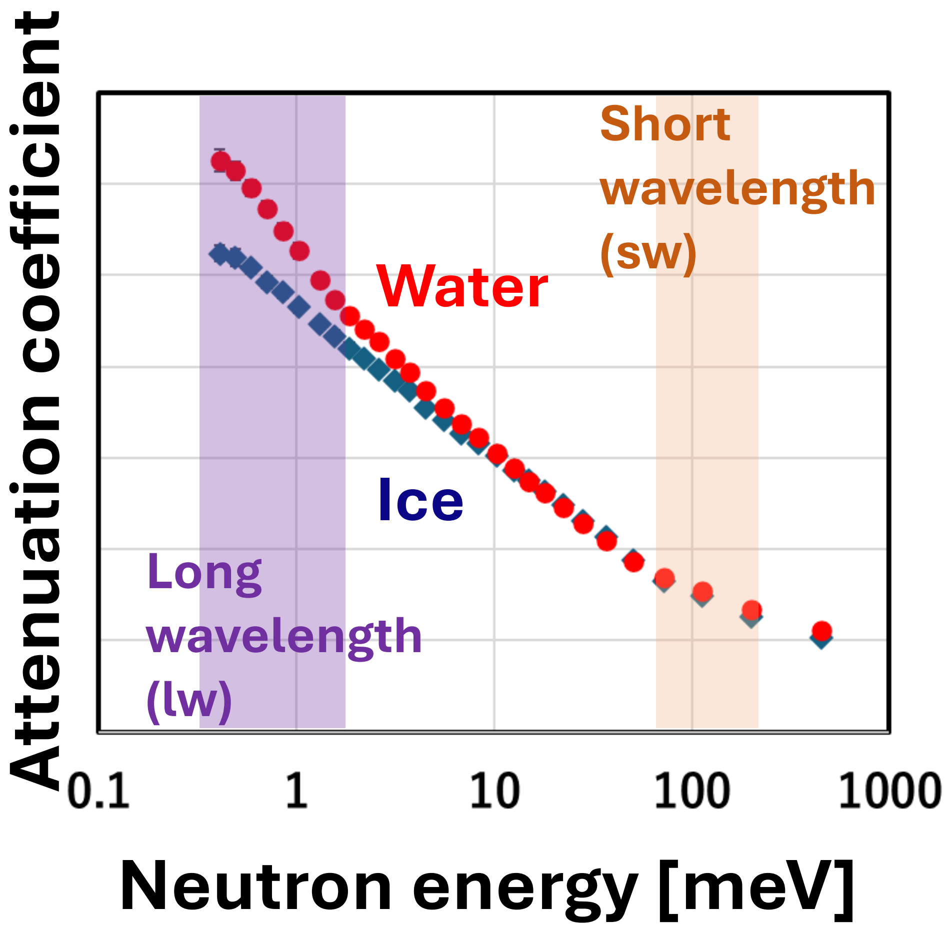
The water behavior during a successful and a failed cold-start



- *T* profiles during a successful and failed cold-start were simulated by the climate chamber.
- Similar water distributions were observed.
- Very different tendency of freezing for upstream and downstream cathode.

W. Yoshimune, *et al.*, *ChemRxiv*, (2024)
Y. Higuchi, *et al.*, *Comms. Eng.*, **3** (2024) 33

Identifying water and ice using energy selective neutron radiography

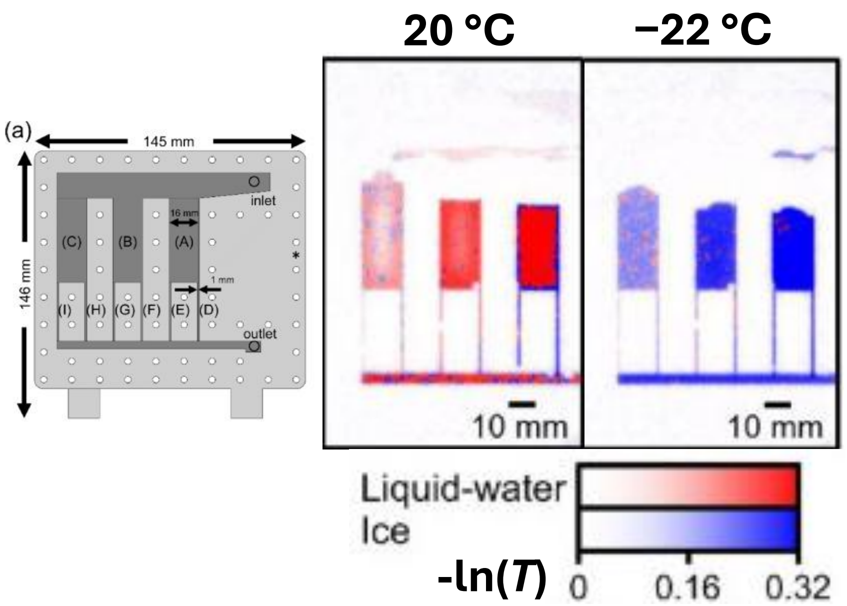


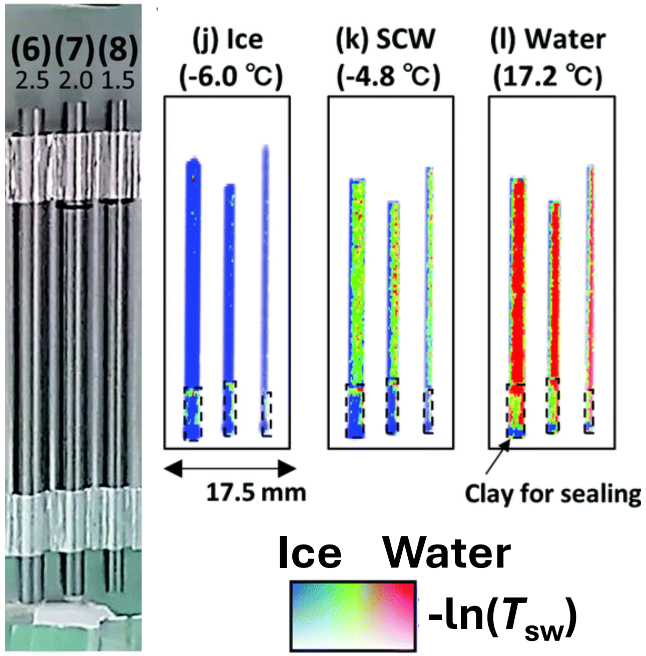
$$\alpha = \frac{\Sigma_{\mathrm{lw}}}{\Sigma_{\mathrm{sw}}} = \frac{-\ln(T_{\mathrm{lw}})}{-\ln(T_{\mathrm{sw}})}$$

T : Neutron transmission

Features of relative attenuation (α):

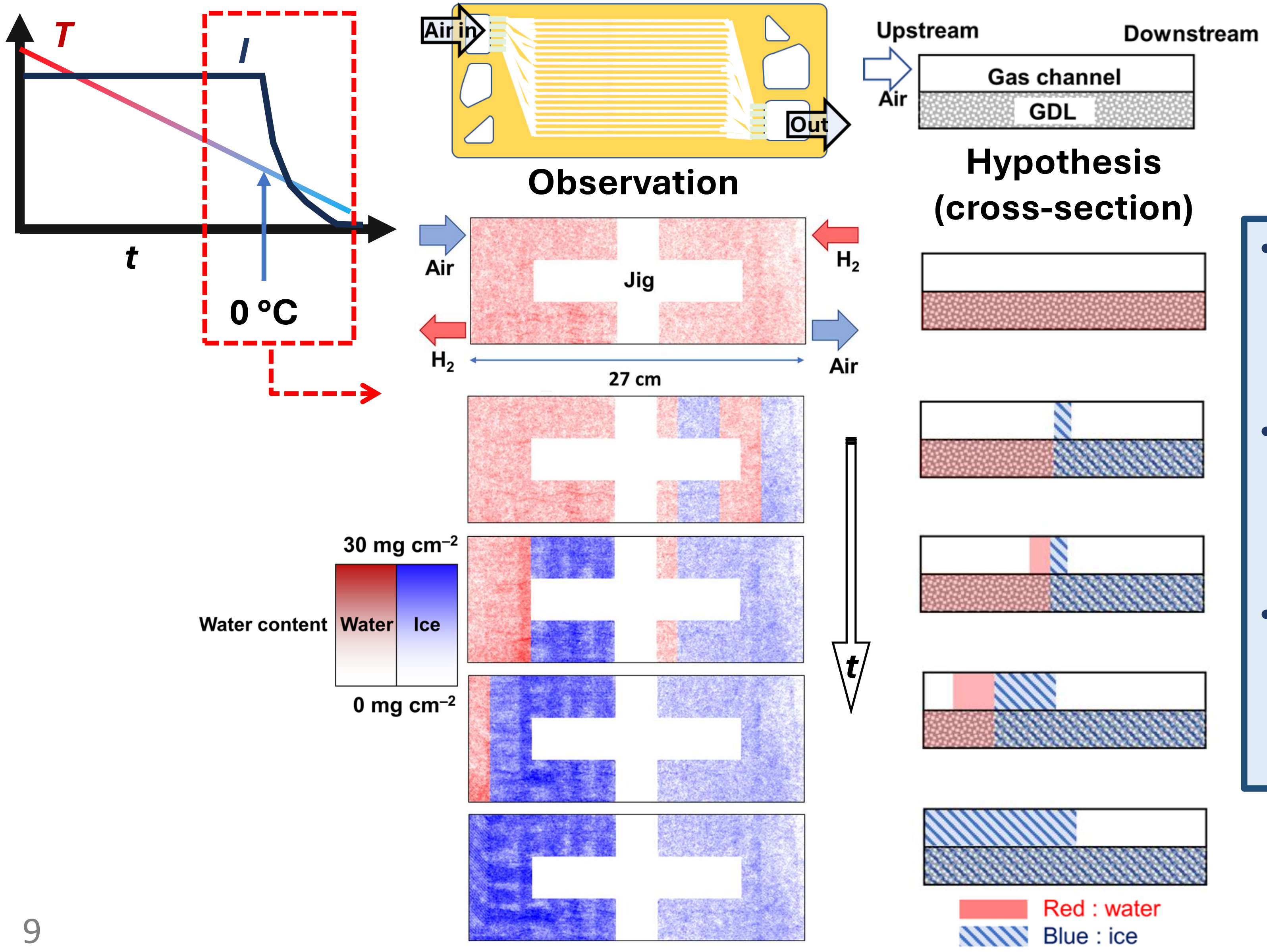
- $\alpha_{\mathrm{water}} > \alpha_{\mathrm{ice}}$
- Independent to water thickness





K. Isegawa, *et al.*, *NIM-A*, **1040** (2022) 167260
Y. Higuchi, *et al.*, *Chem. Phys. Phys. Chem.*, **23** (2021) 1062

Visualization of water and ice in full-sized cell



- Due to the temperature distribution in the large-scale FC, freezing starts from the GDL/CL at cathode downstream.
- ‘Ice front’ propagates from downstream toward upstream, eventually causing a shut-down
- Upstream continues to power before shut-down, the newly generated water accumulates at flow channel and later freezes in-place.

Y. Higuchi, *et al.*, *Comms. Eng.*, **3** (2024) 33

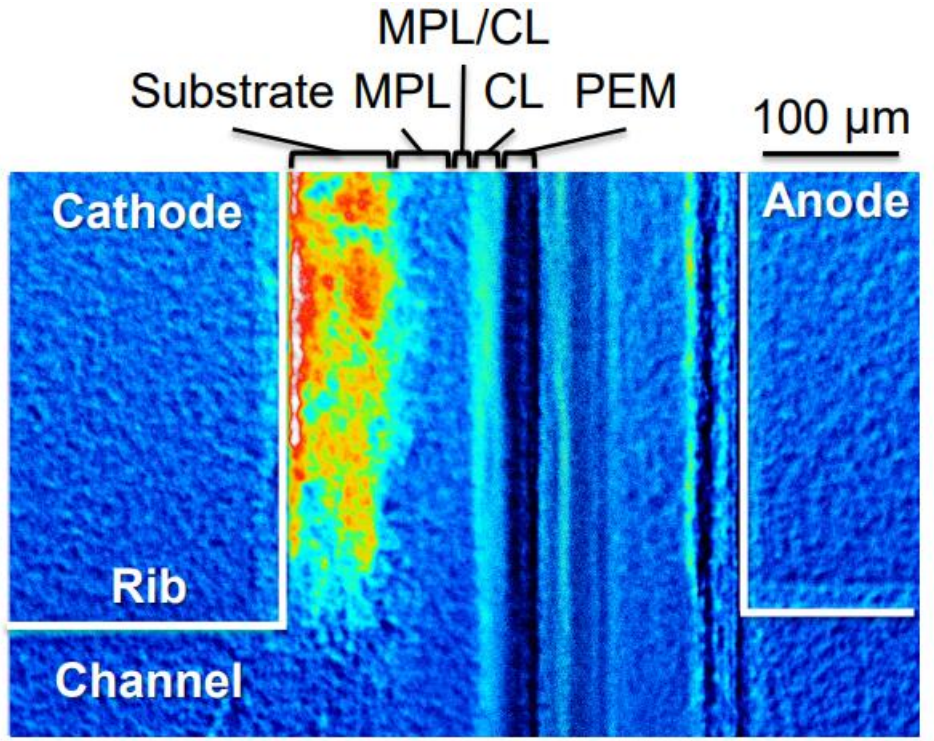
Toward cross-sectional water phase visualization using energy selective neutron radiography

Why cross-section?

- To verify the hypothesis from the full-sized cell observation.
- To understand where on the thickness direction is the freezing most likely to be initiated (CL? GDL? or the interface?).

The low neutron counts during cross-sectional water phase visualization:

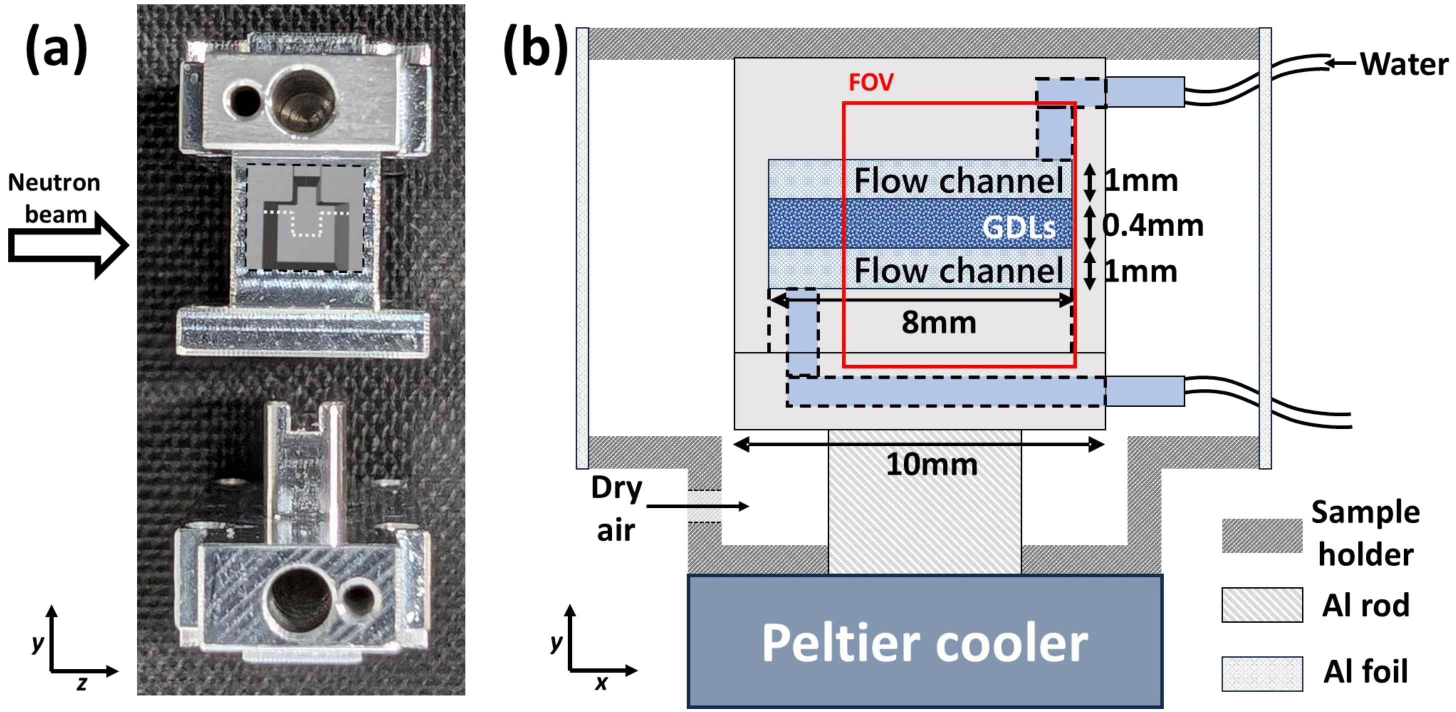
- Area of the cross-section is small → small FoV
- *Operando* imaging → short exposure (integration) time
- Energy selection



Water distribution in the cell cross-section observed by synchrotron X-ray radiography*

*W. Yoshimune, *et al.*, *Adv. Energy Sustainability Res.*, **5** (2024) 2400126

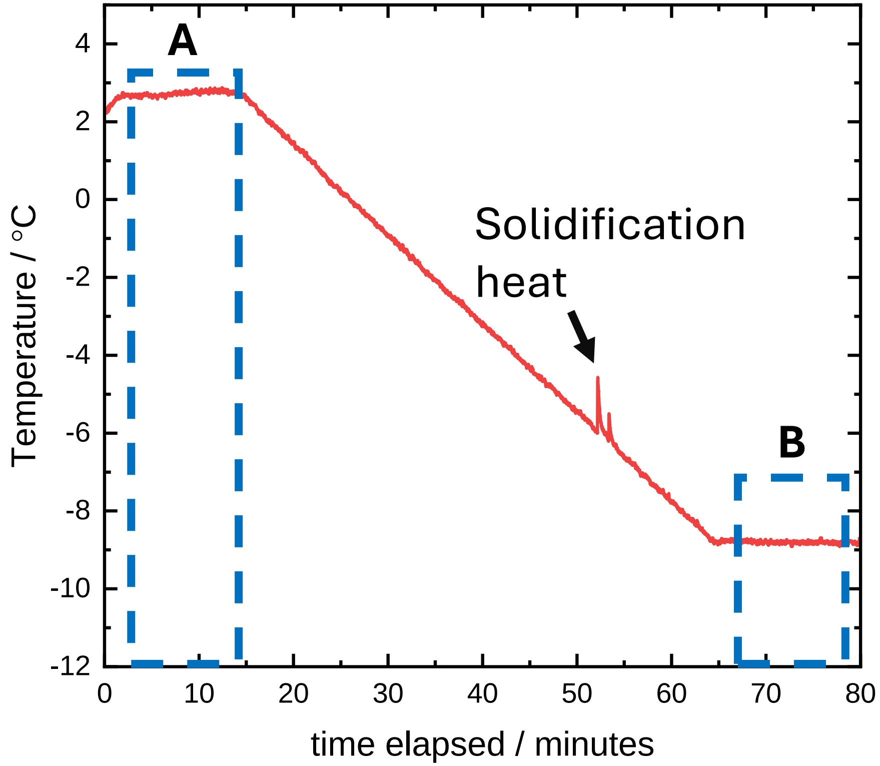
Toward cross-sectional water phase visualization using energy selective neutron radiography

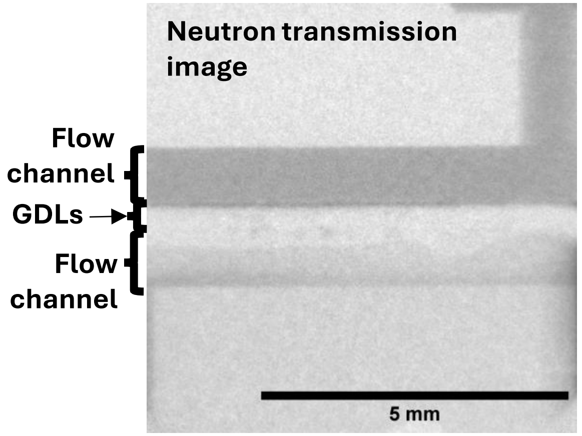


- Non-power-generating model cell
- Conducted at BL15 for higher neutron flux

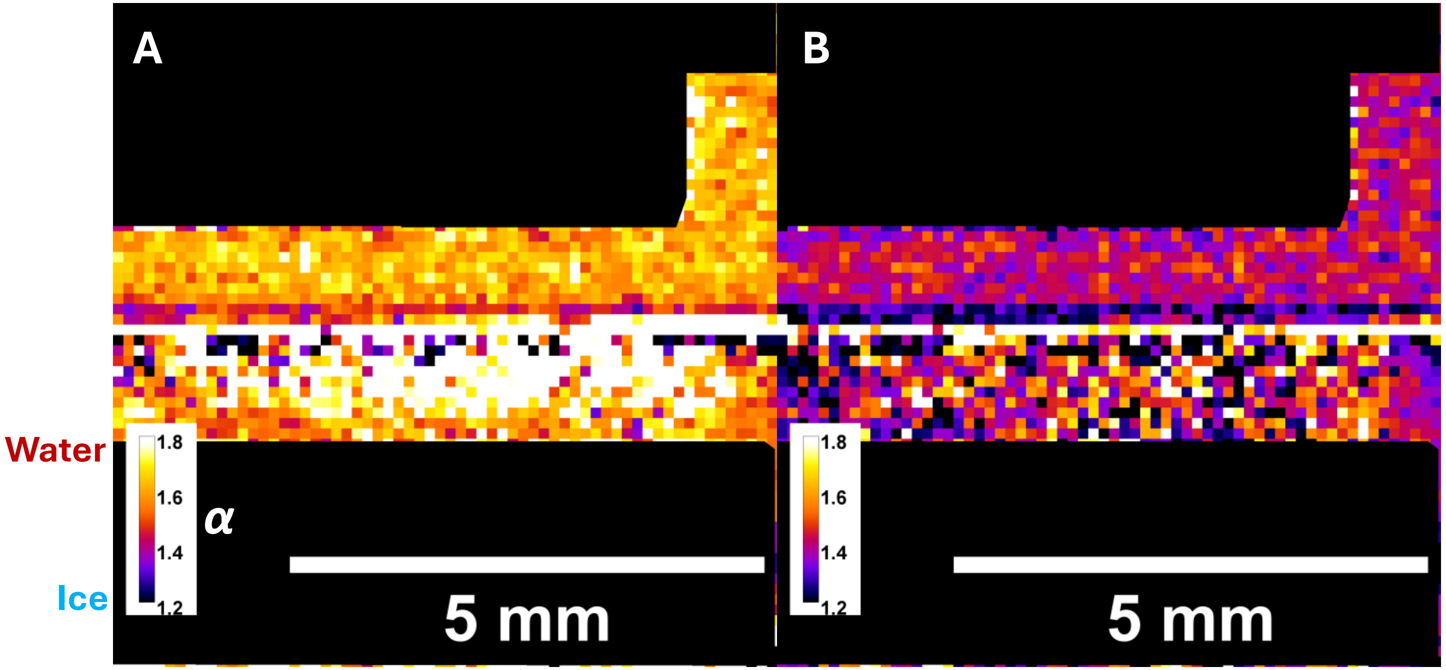
Collimator to detector distance	Sample to detector distance	L/D	FoV	Short wl	Long wl	Exp. time
~7.5 m	14 mm	250	7 × 7 mm^2	2.58 Å	6.92 Å	~5.42s

Cross-sectional observation: steady states





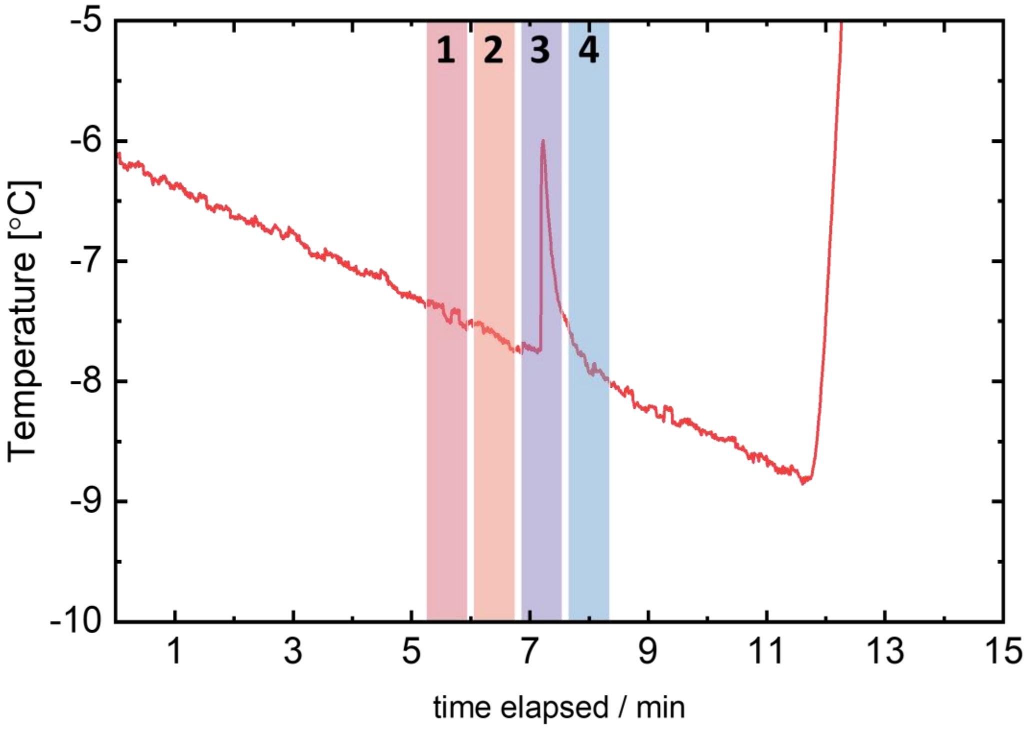
Integration time ~250 s,
Spatial binning size 0.109 mm × 0.109 mm

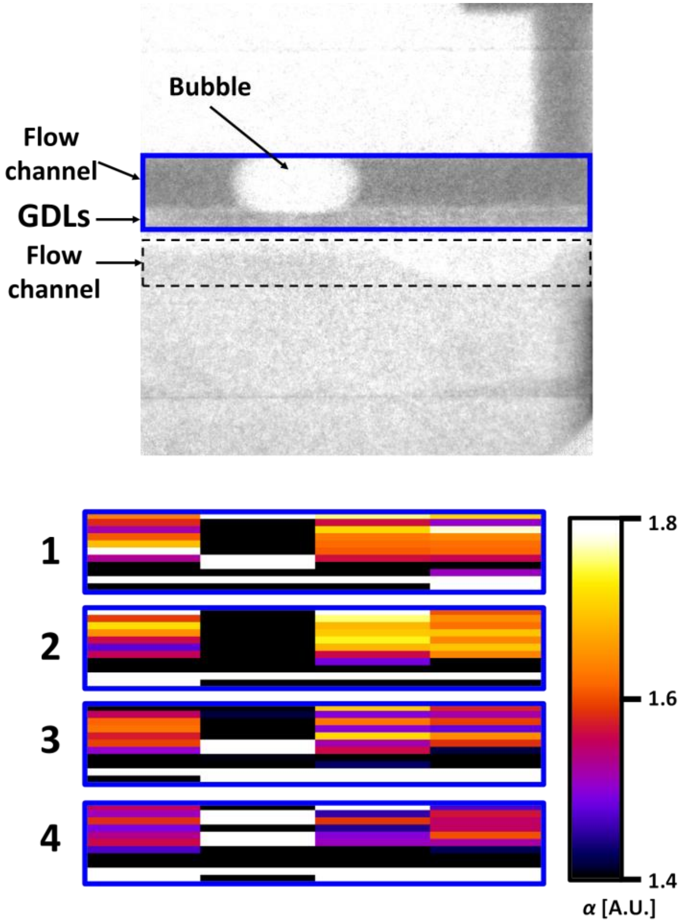


*Areas outside of flow channel and GDL are masked

With sufficient integration time (i.e., neutron counts), relative attenuation image can reliably represent the water phase in small spaces.

Cross-sectional observation: dynamic process





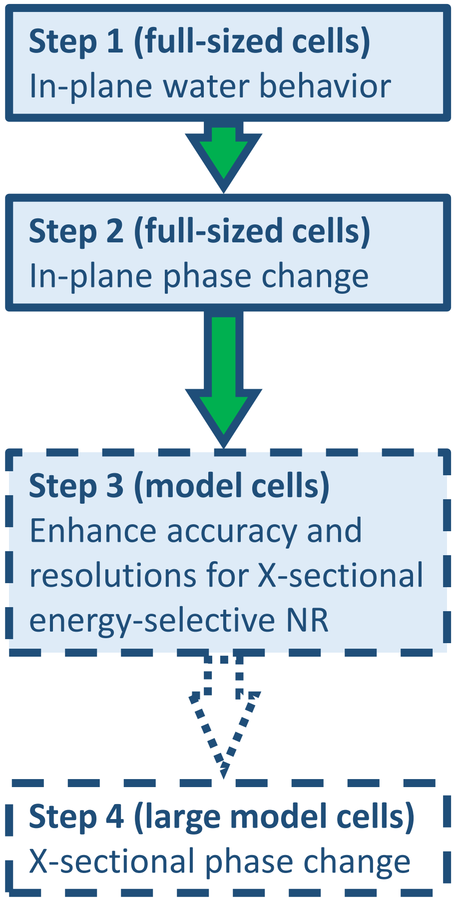
Integration time 22 s
Spatial binning size: 1.75 mm x 0.109 mm

- Trade-off is inevitable due to the low neutron count.
- The integration time and binning size are constraint by the desired resolutions for cross-sectional observation.
- Need to improve experimental techniques to further increase the neutron count

Summary

High-resolution neutron radiography instrument + *operando* techniques (climate chamber) to unravel the cold-start problem for the off-the-shelf vehicle PEMFCs.

- **Ordinary neutron radiography**: effective method of decoding water behavior in cell under realistic scenarios.
- **Energy selective neutron radiography**: directly visualize the distribution of water and ice phases within the sample to pin-point areas that are vulnerable to freezing.
- **Energy selective neutron radiography on cross-sectional direction**: reasonably good resolution for *ex-situ* observations, but challenging to obtain good neutron statistics for *operando* observations.



Acknowledgments

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Thank you!