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Membrane Degradation in Vanadium Flow Batteries: Comparison of Artificial and Real Ageing

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Introduction
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- **All-vanadium flow batteries** (VFB) are ideally suitable to store renewable energies
- **Degradation of the components** limits the operational life of the system
- Besides carbon electrodes and the vanadium electrolyte, **ageing of the membrane** separating the half cells is of great interest
- We compare accelerated *ex situ* aged VRFB membranes to membrane samples aged in **commercial battery stacks**

Materials
2

- Four different membranes were tested: two **anion-exchange membranes** (AEM1 and AEM2), a **cation-exchange membrane** (CEM) and a polyvinyl chloride/silicon dioxide based **porous separator** (PS)
- All membranes were tested in pristine state, mechanically aged (pinhole) and chemically aged
- For AEM1, stack-aged membranes from two different installations were provided by CellCube

Membrane	Untreated	Mechanically aged	Chemically aged (time)	Stack-aged
AEM1	pristine	pinhole	aged long (28 d) aged short (1 d)	S1 S2
AEM2	pristine	pinhole	aged long (28 d)	-
CEM	pristine	pinhole	aged long (28 d)	-
PS	pristine	pinhole	aged long (28 d)	-

Methods
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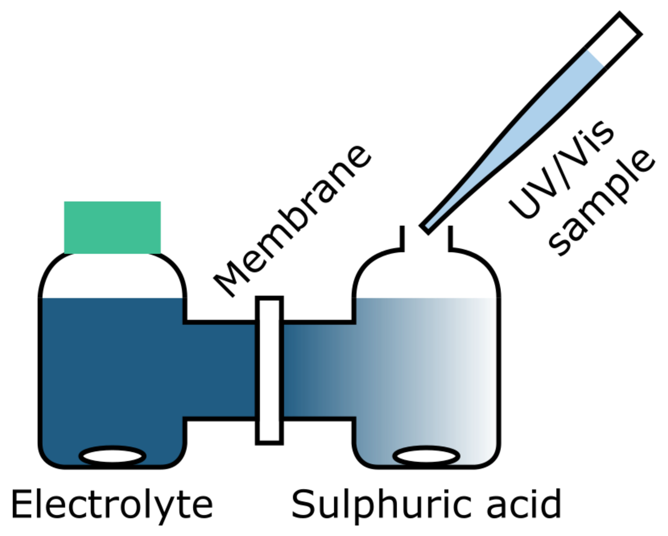
- Immersion of membranes into agressive electrolyte at elevated temperatures for up to four weeks as artificial chemical ageing method[1,2]
- Scanning electron microscopy (SEM)/energy-dispersive X-ray spectroscopy (EDX) on membrane cross-sections
- H-cell vanadium permeability measurements to obtain V(III/IV) permeabilities
- Battery cycling experiments to obtain the coulombic and voltage efficiencies of cells with different membranes



H-cell schematic
Setup for vanadium permeability measurements

SEM images
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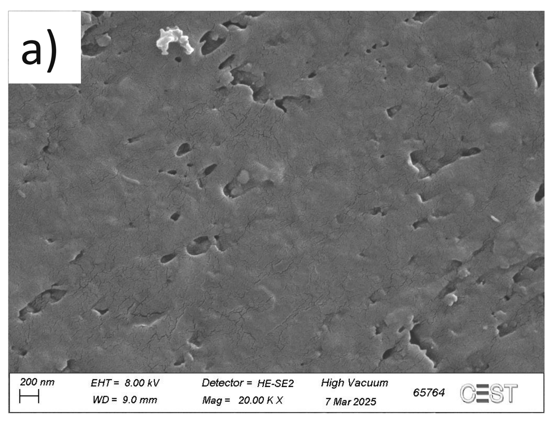
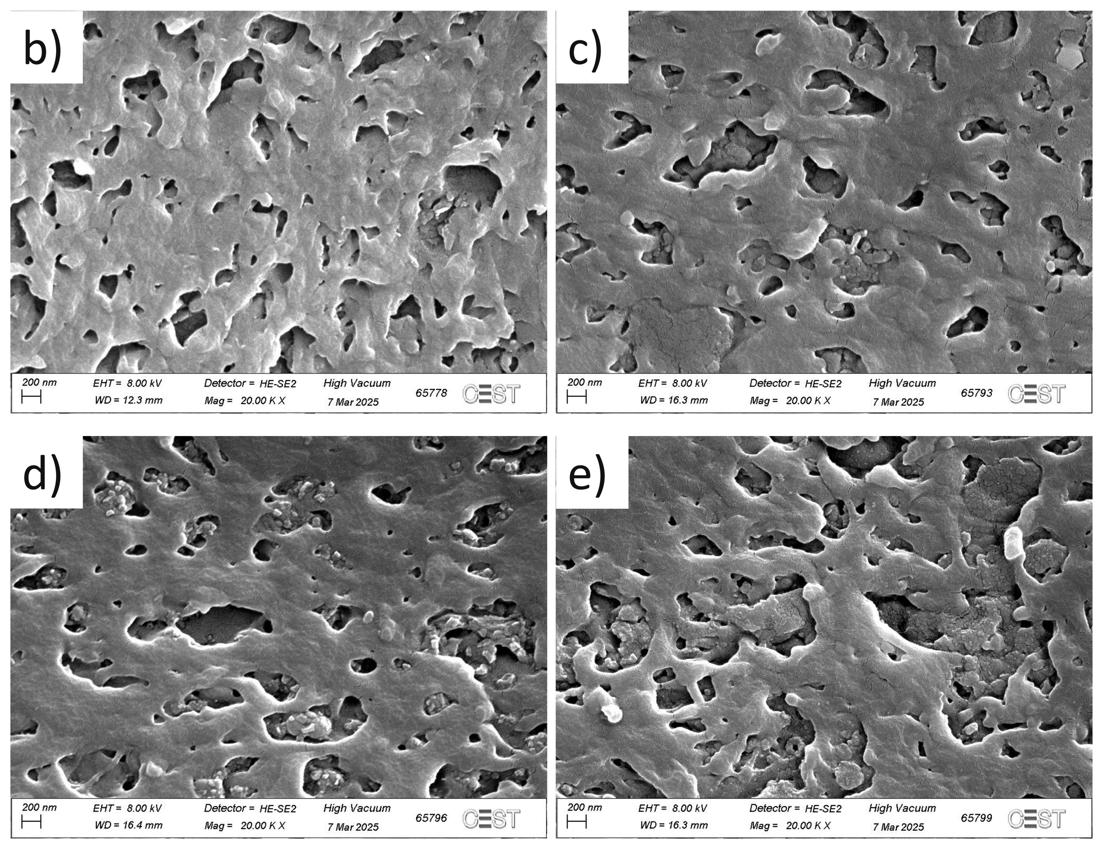
SEM images of AEM1: Membranes become more porous during ageing,
a) pristine, b) aged long, c) aged short, d) S1, e) S2





Results
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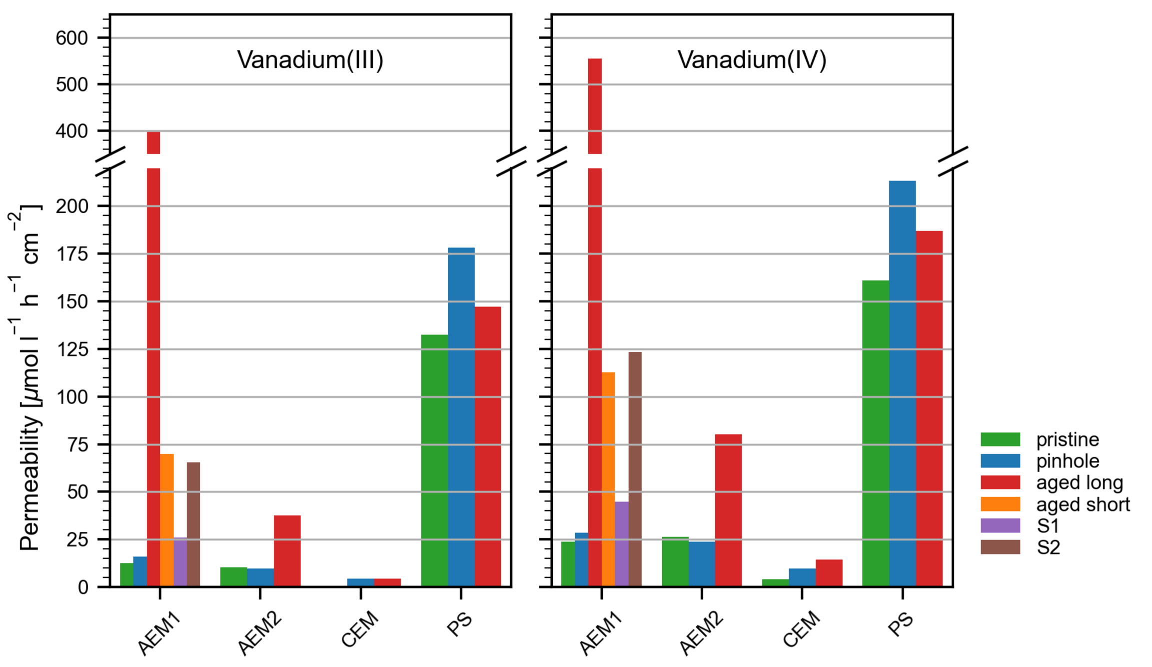
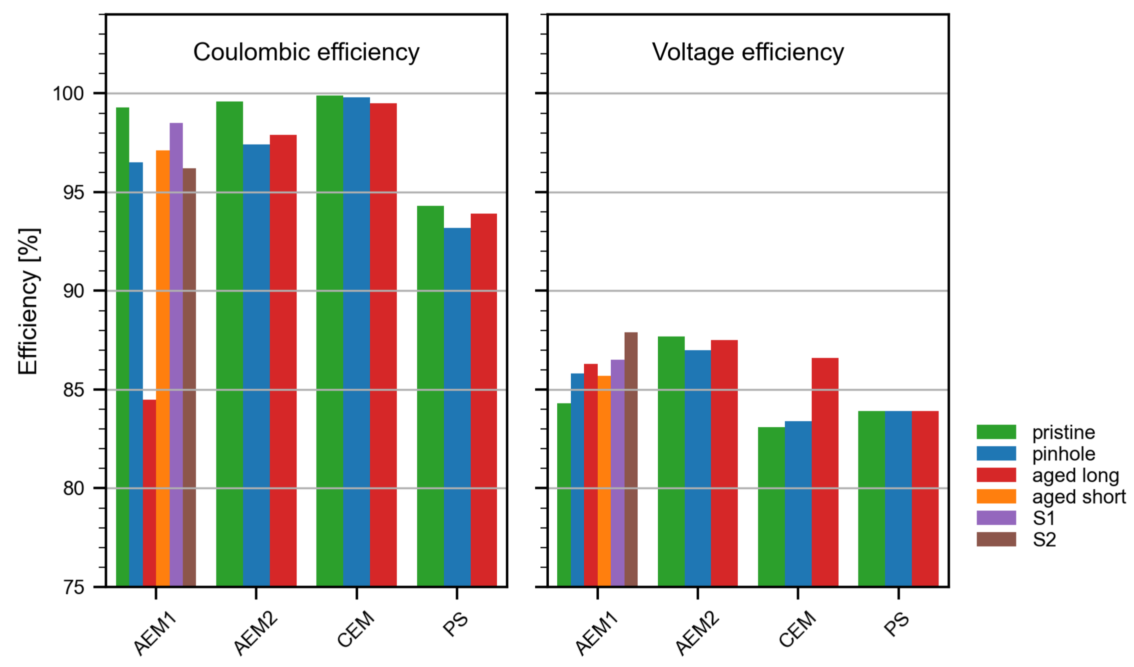
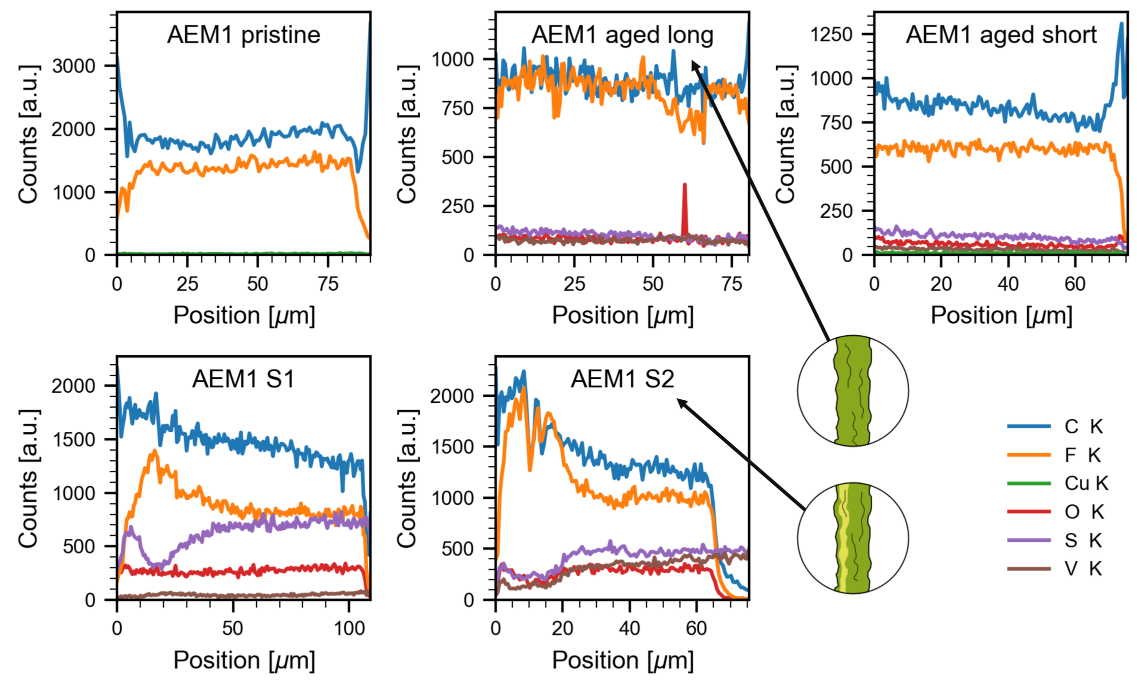


Vanadium permeability (top)
Vanadium(III/IV) permeability increases with ageing duration.



Cell efficiency (top)
Coulombic efficiency of cells with aged membranes is decreased compared to pristine membranes because of increased vanadium crossover and self discharge. The voltage efficiency stagnates or increases with ageing depending on decreasing resistivity of the battery cell respectively the membrane.



EDX analysis of AEM1 (left)
Artificially aged membranes show homogeneous sulphur distribution, indicating a homogeneous ageing process, while S1 and S2 show decreased sulphur content and increased carbon and fluorine abundance on one side, indicating inhomogeneous degradation.

Conclusion
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- Artificial and stack ageing increases porosity and permeability of membranes and decreases the coulombic efficiency
- Physical properties of artificially aged membranes are comparable to stack-aged membranes
- Membranes in stacks degrade mainly on the side in contact to vanadium(IV/V) electrolyte, while artificial ageing leads to homogeneous degradation on both sides of the membrane

Literature
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[1] R. Iwahara, M. Yoshioka, A. Nishimoto, M. Kobayashi, *Toyobo Co Ltd*, **2016**, JP 2016207608.
[2] E. Martin, in *IFBF 2024*, Glasgow, UK, **2024**.

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