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Vanadium redox flow batteries: from understanding of mass transport phenomena to the engineering of the device and coupling with electrolysis

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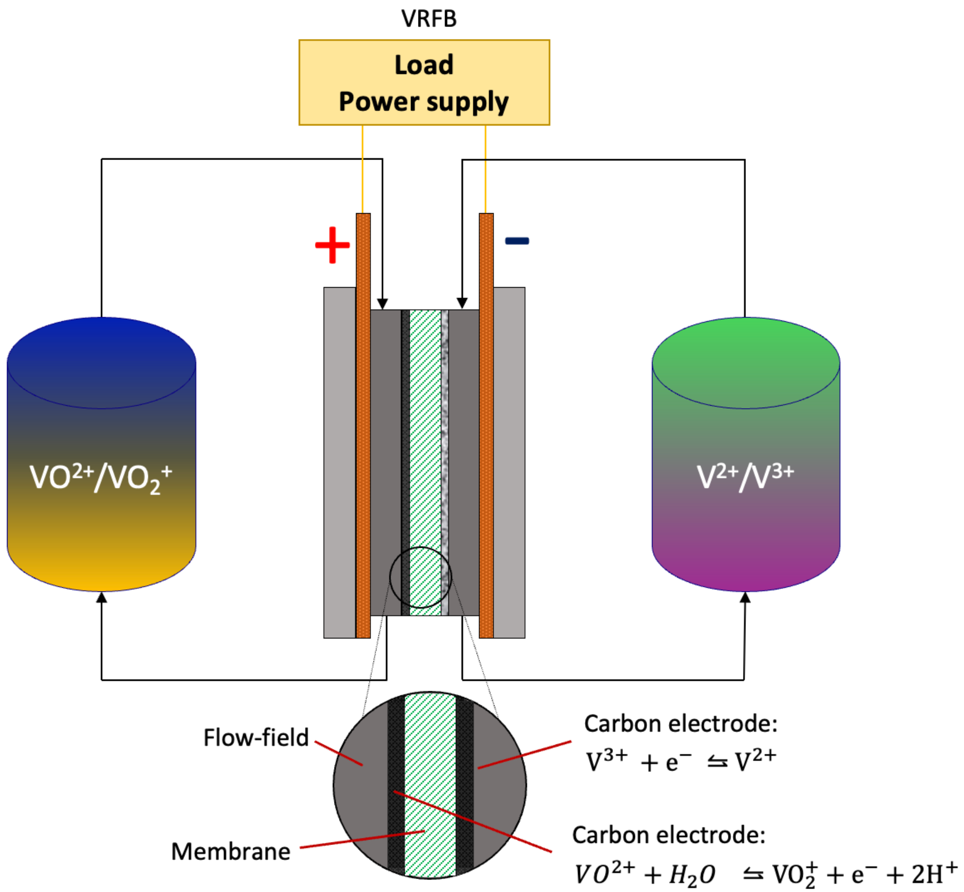
REDHy Webinar - November 25th 2025

Schematic representation of a Vanadium Redox Flow Battery:



Advantages:

- Decoupled power and energy
- Long cycle life
- Safety

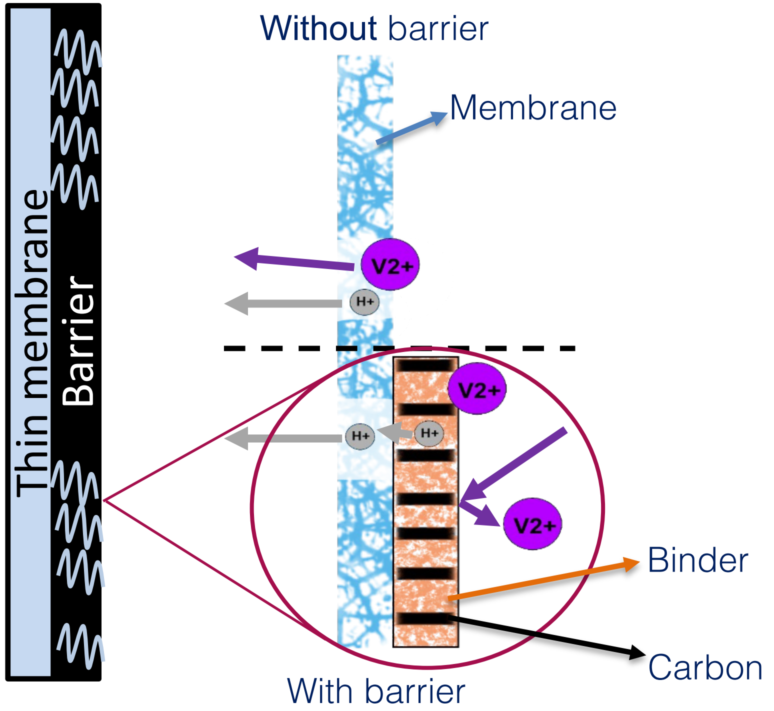
Issues:

- Crossover fluxes through the membrane lead to battery capacity decay: **development of an innovative barrier layer**.
- Effective electrolyte distribution throughout cell active area limits performance in cells characterized by high active area: **engineering of an improved flow-field**.
- For increased storage time electrolyte represents a huge share of investment costs: **development of an innovative dual redox flow battery.**

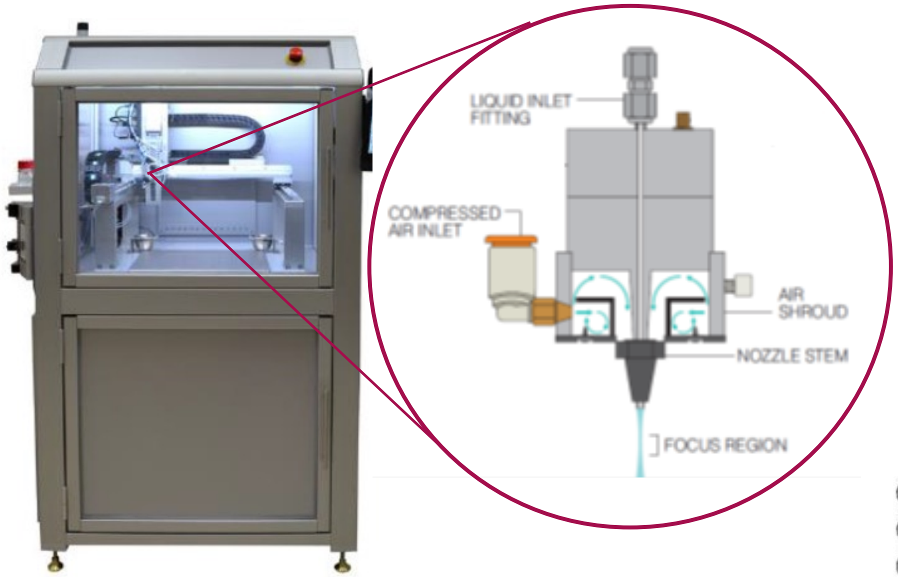
DEVELOPMENT OF INNOVATIVE BARRIER LAYER

Concept: the barrier layer can break the bottleneck of ion/proton selectivity and can be applied to all typologies of RFB.

PATENT WO 2019/197917



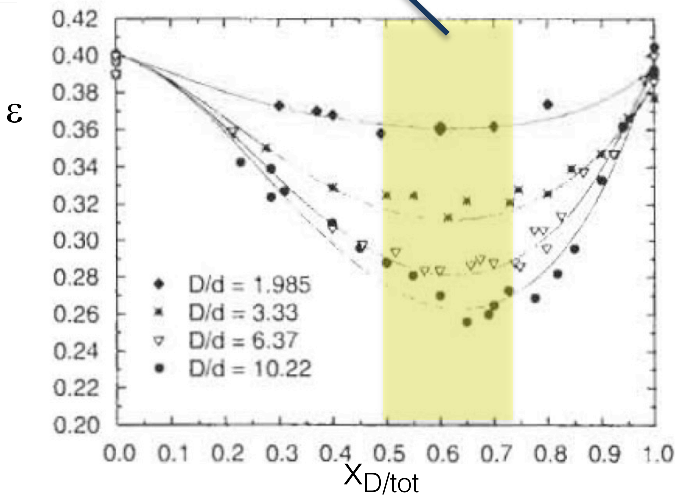
Manufacturing with Sono-Tek ultrasonic spray coating:



Ink composition:

- Vulcan XC-72R (40 nm)
- Silicon dioxide (5-20 nm)
- Nafion® dispersion D2021
- Ethanol as solvent

$$\frac{m_C}{m_{SiO_2}} = 1$$

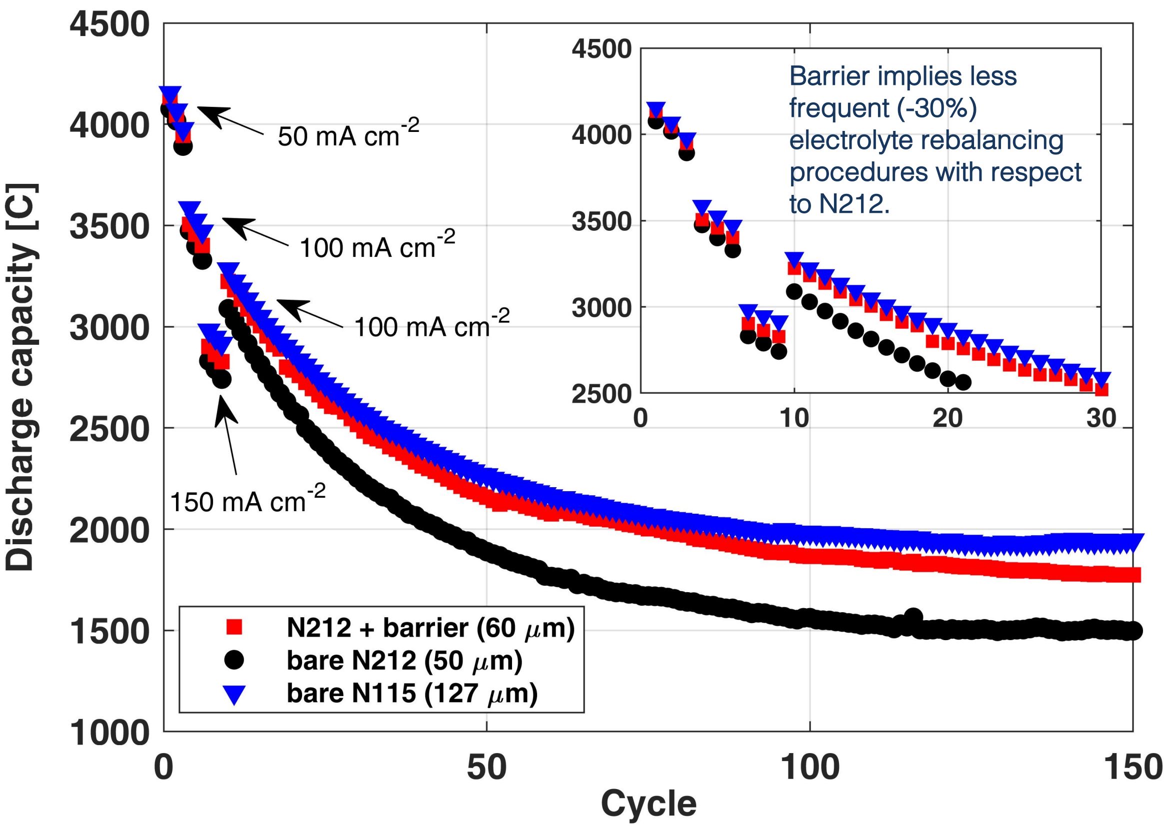


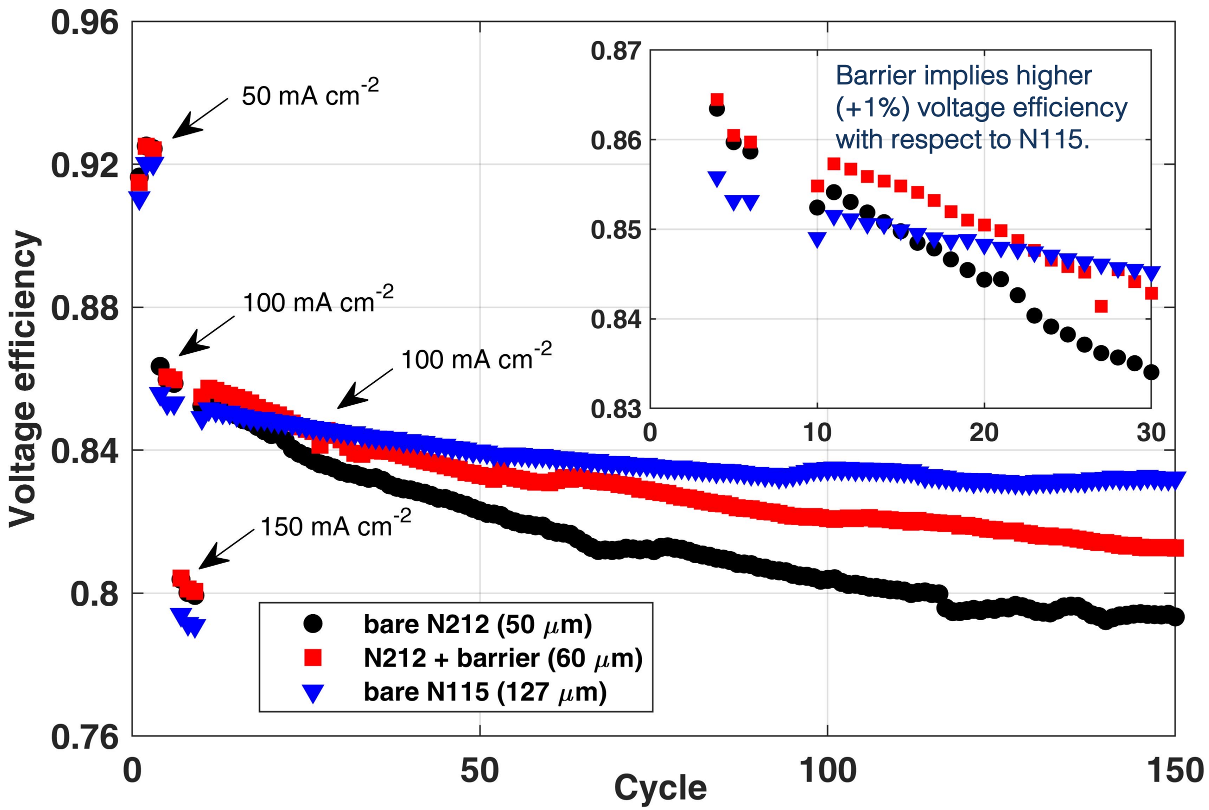
Mota et al., Transactions of The Filtration Society 1 (2001) 101-106.

Deposition parameters:

- plate temperature: 60°C
- ink flow rate: 0.2 ml min^{-1}
- airflow rate: 5 l min^{-1}

Evolution of discharged capacity and voltage efficiency of a VRFB with Nafion® 212 (thickness 50 μm), Nafion® 115 (thickness 127 μm) and Nafion® 212 with a 10 μm barrier, evaluated during cycles at constant current with fixed cut-off voltages in a 25 cm^2 VRFB single cell.





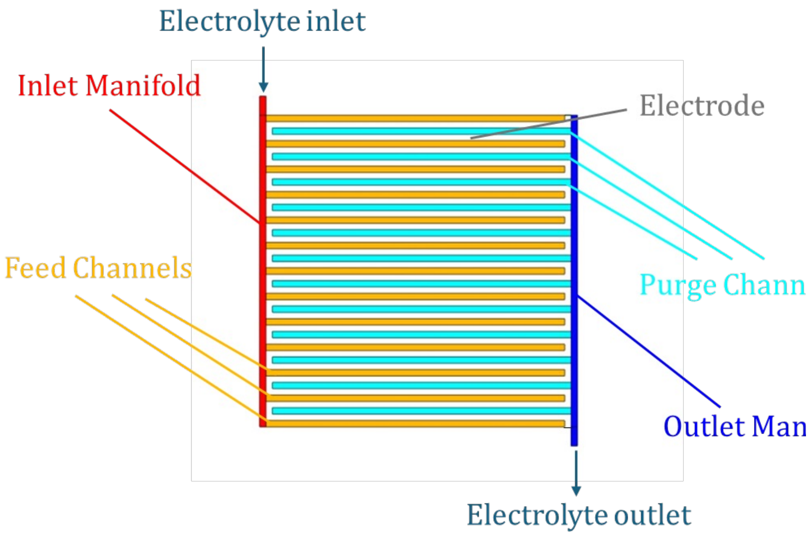
M. Zago et al., Journal of Power Sources 628 (2025) 235908.

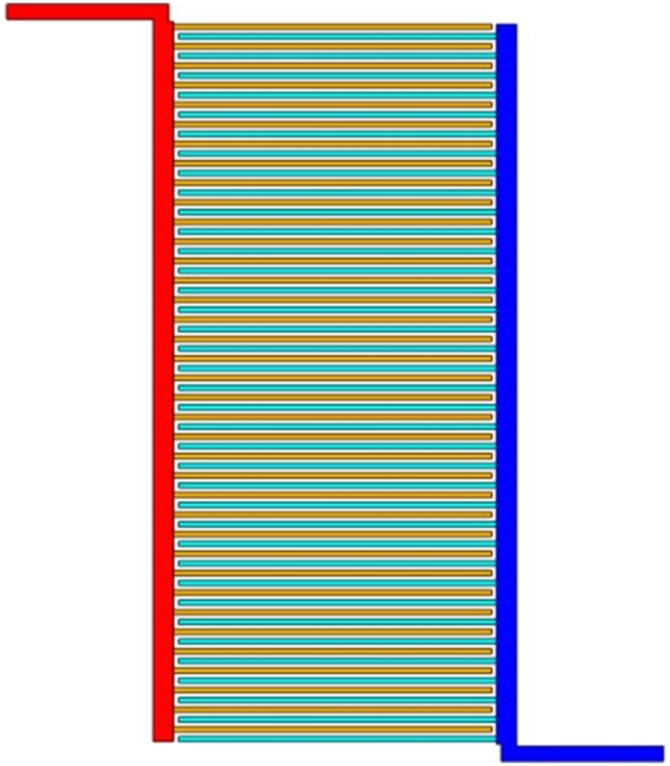
Engineering of an improved flow-field

Performance analysis varying flow-field geometries in order to analyse the effect of electrolyte distribution during active area scale-up . All the flow-fields present 1mm x 1mm square channel section and 1mm rib width.

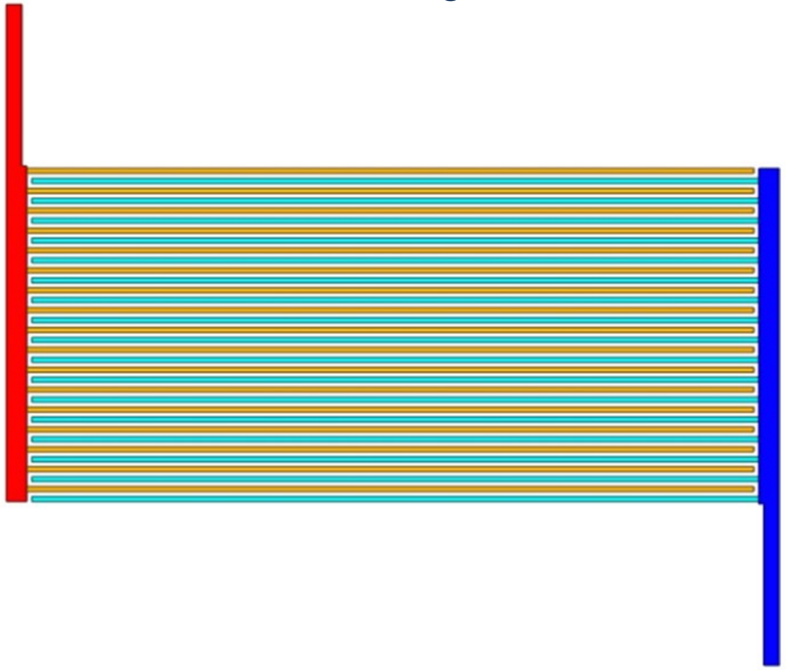
100 cm^2 with short channels

25 cm^2 lab scale

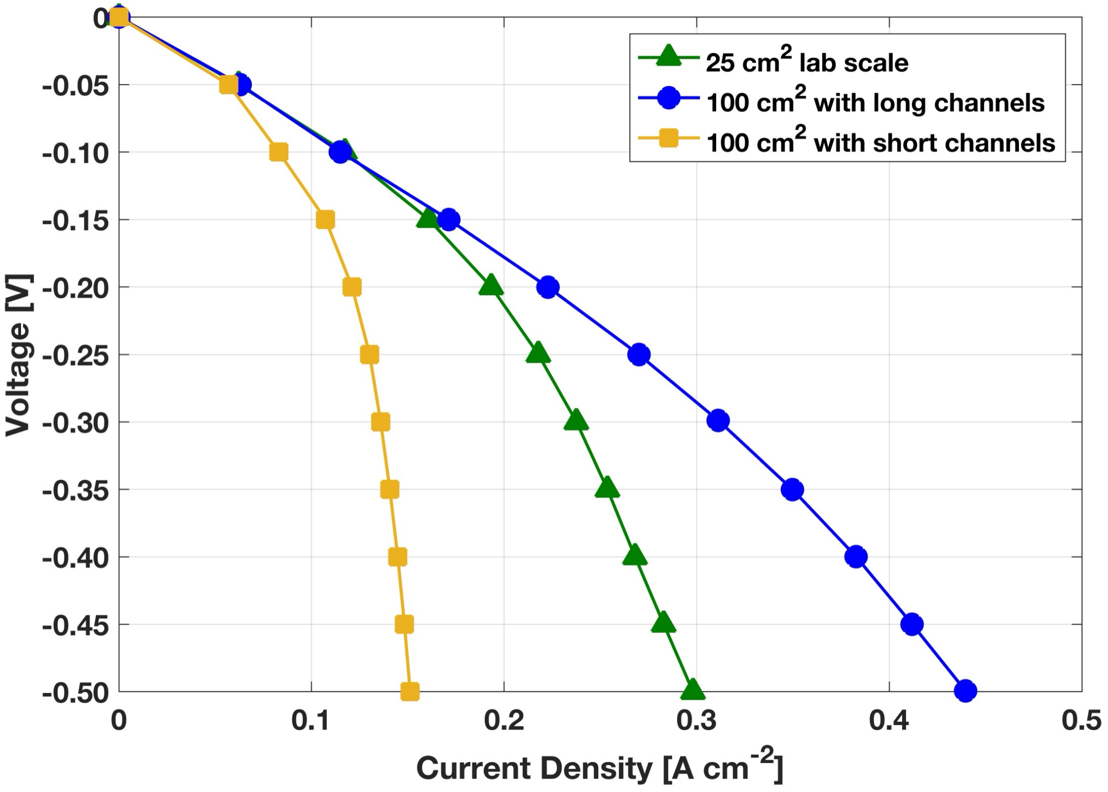




100 cm^2 with long channels



Performance in VRFB symmetric cell with positive electrolyte (1.6M V in 2M H_2SO_4), Nafion® 212 and Sigracet® 39AA:



With the aid of a CFD model, it was possible to prove that all the configurations exhibit an **equal value of mean under-the-rib fluxes** inside the porous electrode, but:

- 25 cm² lab scale → ε = 21.7%
- 100 cm² with short channels → ε = 25.3%
- 100 cm² with long channels → ε = 19.0%

Strong correlation between **performance** and the **heterogeneity of under-the-rib fluxes**

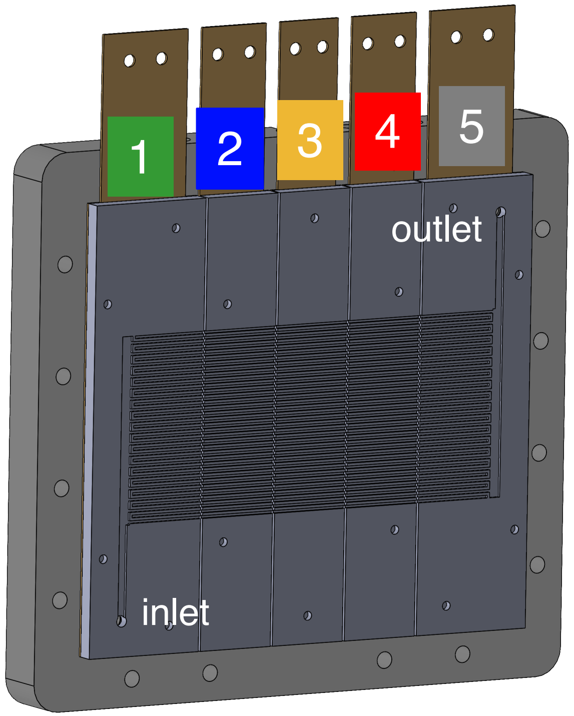
⇩

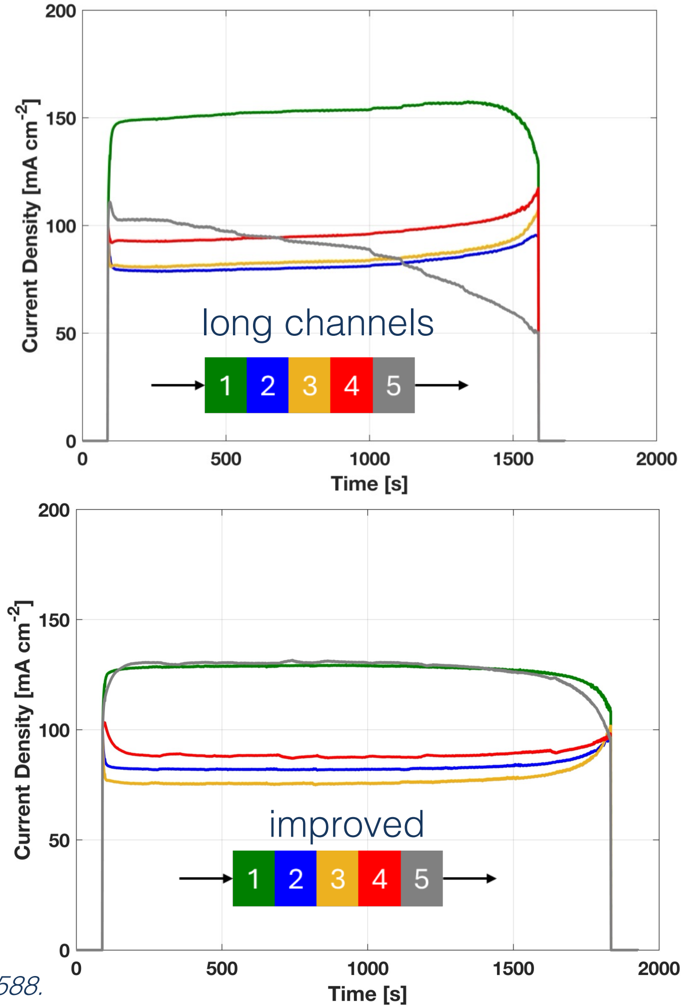
Design of an improved flow field characterized by a reduced heterogeneity of under-the-rib fluxes.

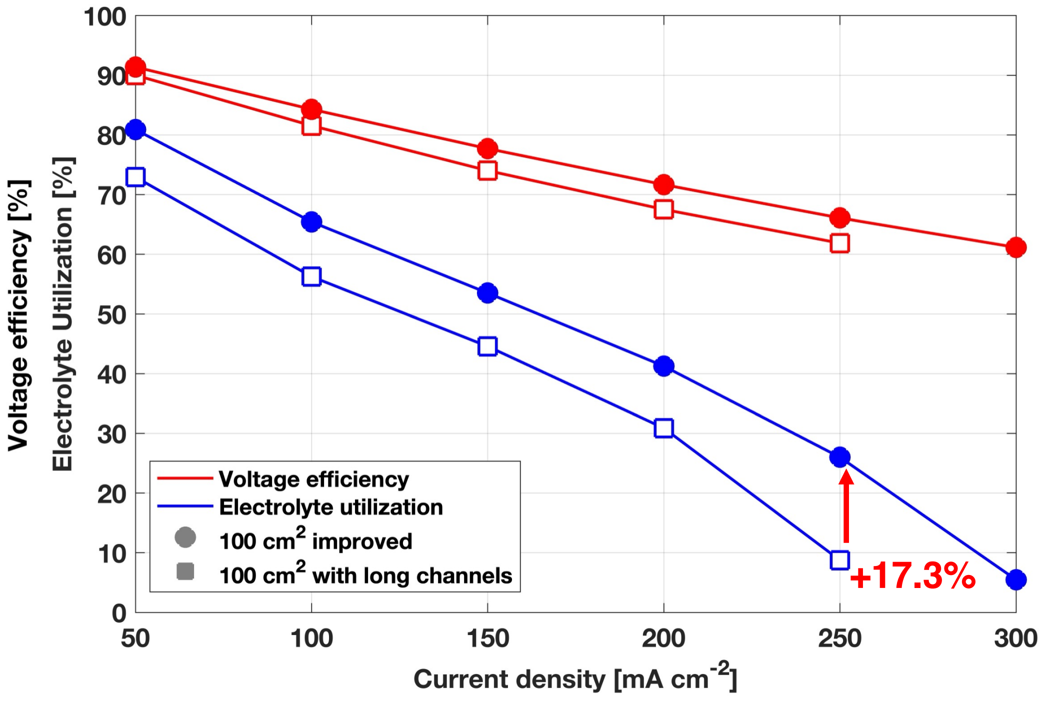
M. Zago et al., Applied Energy 228 (2018) 1057.
M. Zago et al., Journal of Power Sources 526 (2022) 231155.

Engineering of an improved flow-field

The improved distributor is characterized by 8 feed and 8 purge channels with 2.12 mm x 1 mm cross-section, while the rib width is 3.4 mm. From CFD simulations, the obtained heterogeneity index was reduced down to 3.2%.





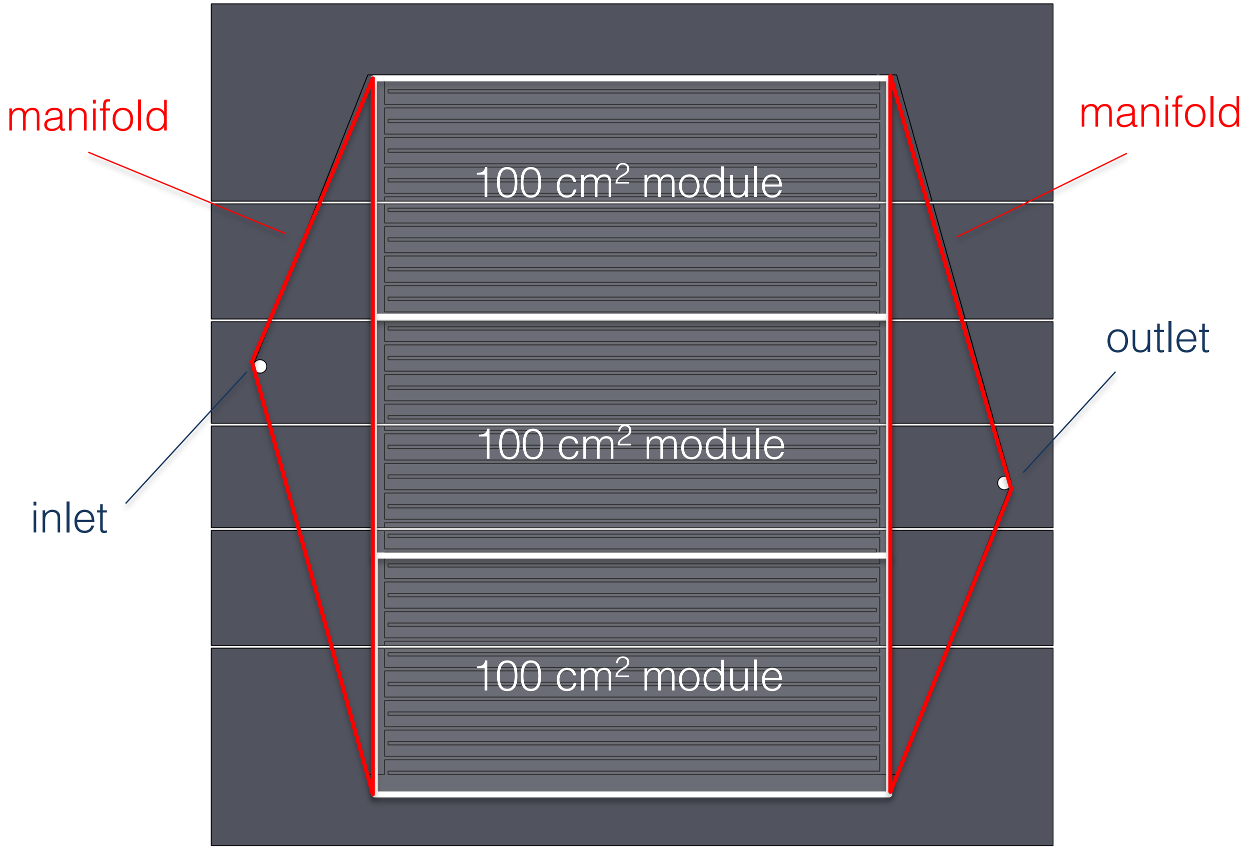


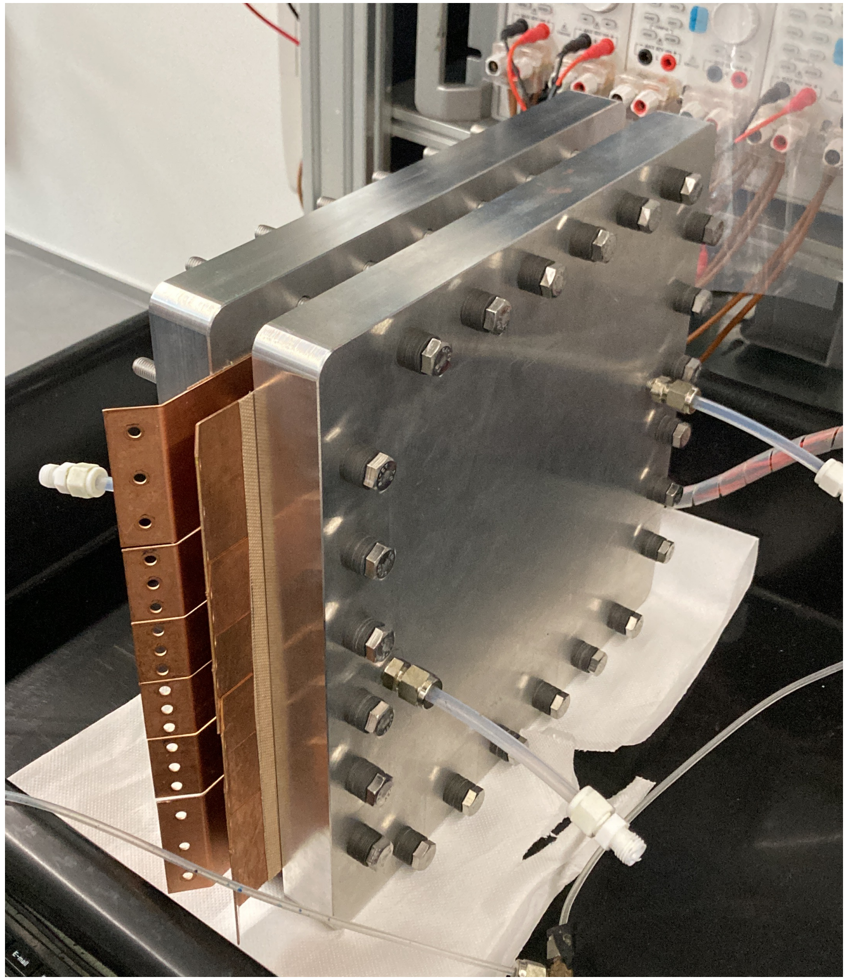
More homogeneous electrolyte distributions leads to **increased battery performance.**

M. Zago et al., Journal of Power Sources 449 (2020) 227588.

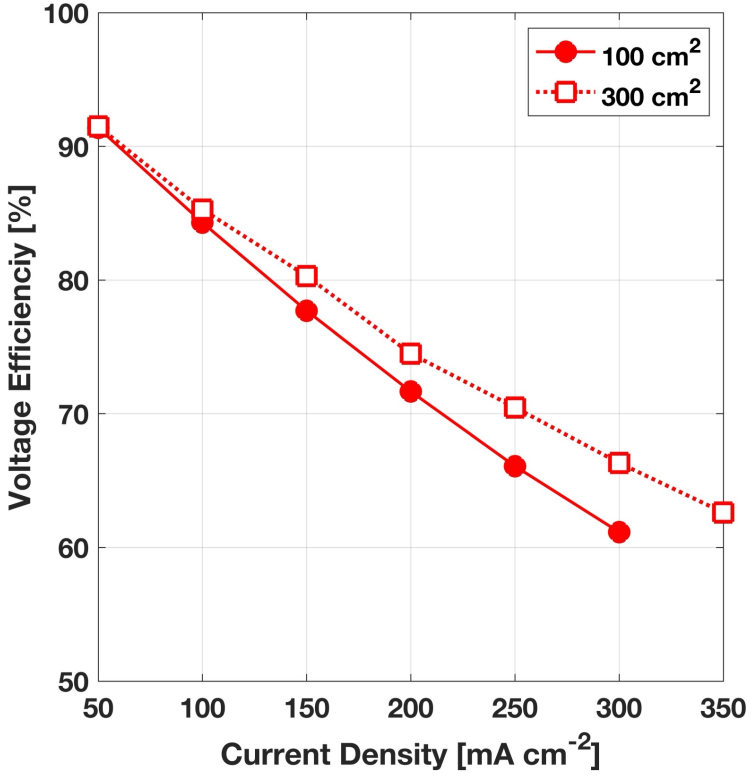
Engineering of an improved flow-field

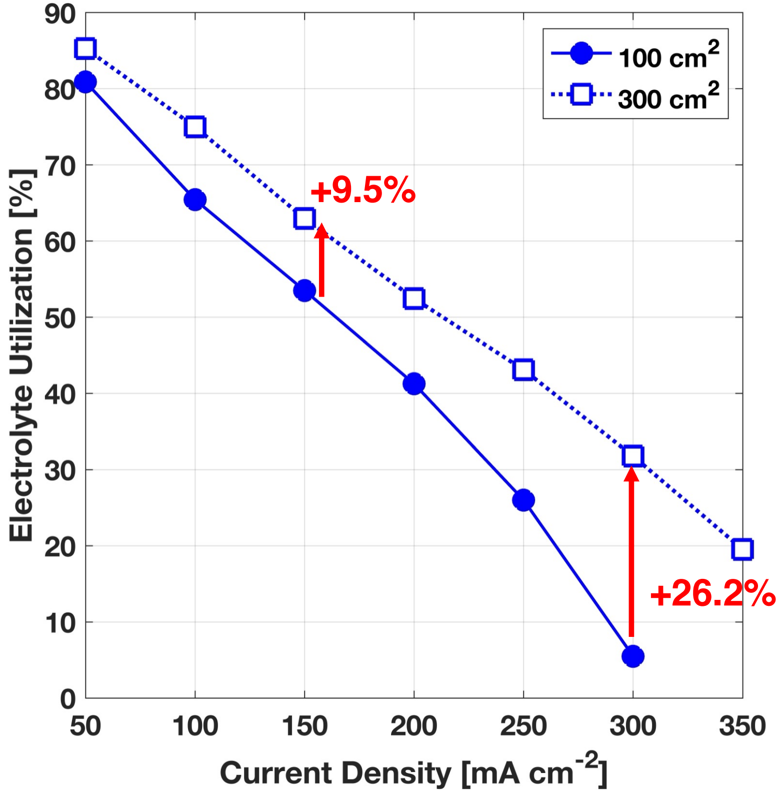
The improved flow field was scaled-up to 300 cm² repeating three times the 100 cm² geometry and introducing a manifold properly designed to favour homogeneous electrolyte distribution in the channels.

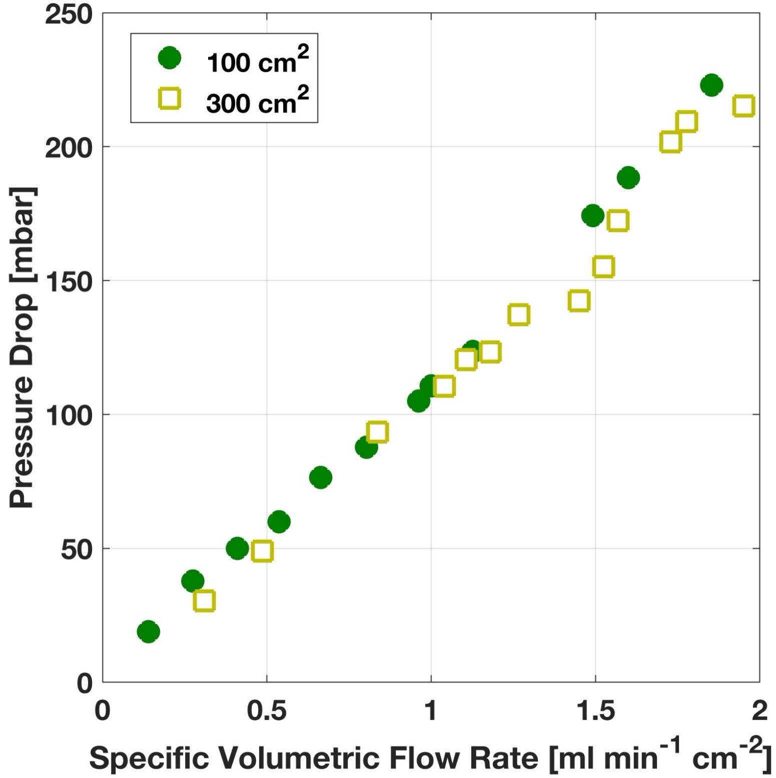




Charge-discharge cycles at constant current between 1V and 1.7 V, cell equipped with Freudenberg H23 and Nafion® 212, 1.6M V in 2M H_2SO_4 at a flow rate of 1.6 ml min^{-1} cm^{-2}:

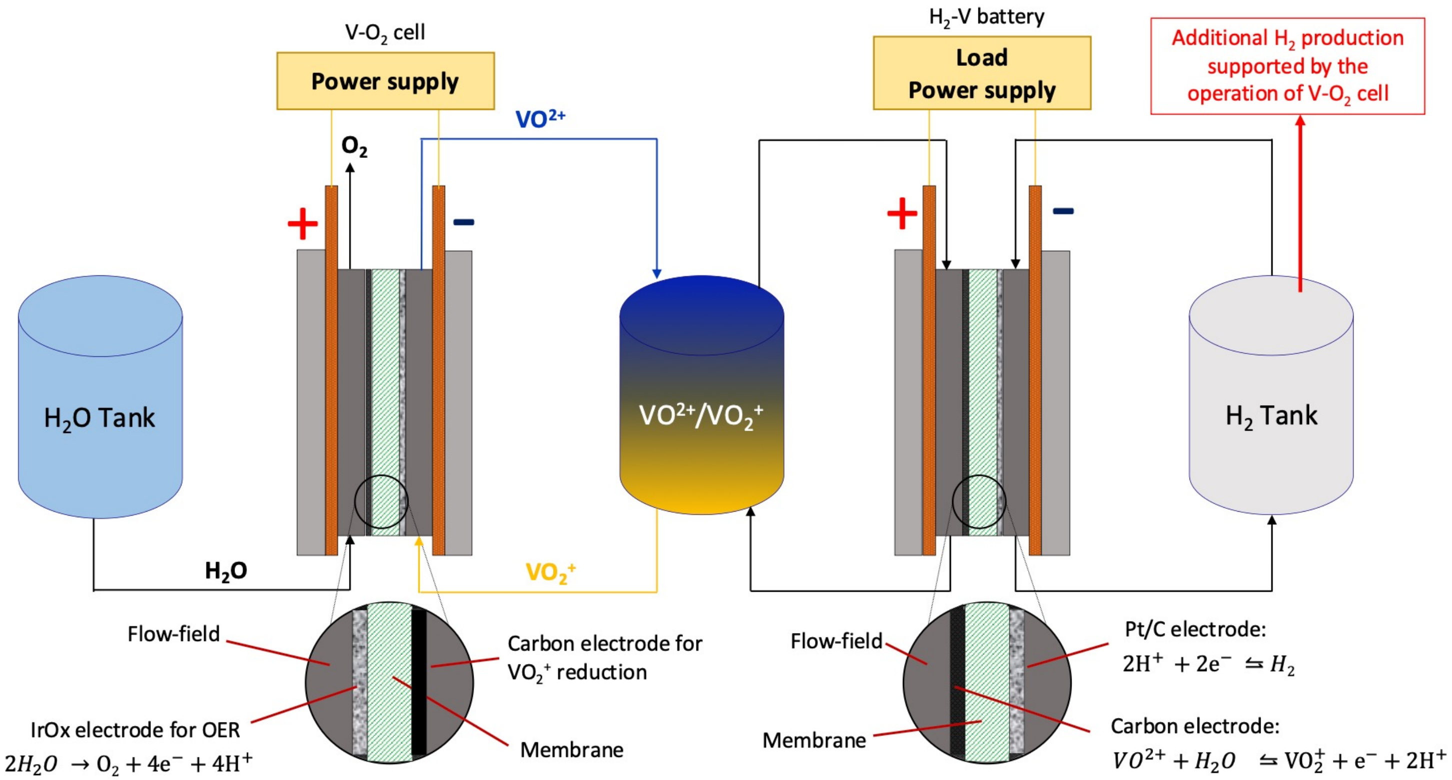






Considerable increase in voltage efficiency and electrolyte utilization due to the more even electrolyte distribution and no variation of pressure drops.

Starting from the work of Piwek et al., a new configuration of dual redox flow battery has been developed:



Advantages of dual redox flow batteries:

- OER and HER are decoupled in space and time, increasing safety of hydrogen production and the flexibility in system design.
- Hydrogen production permits to increase battery storage time with limited volumes of electrolyte.

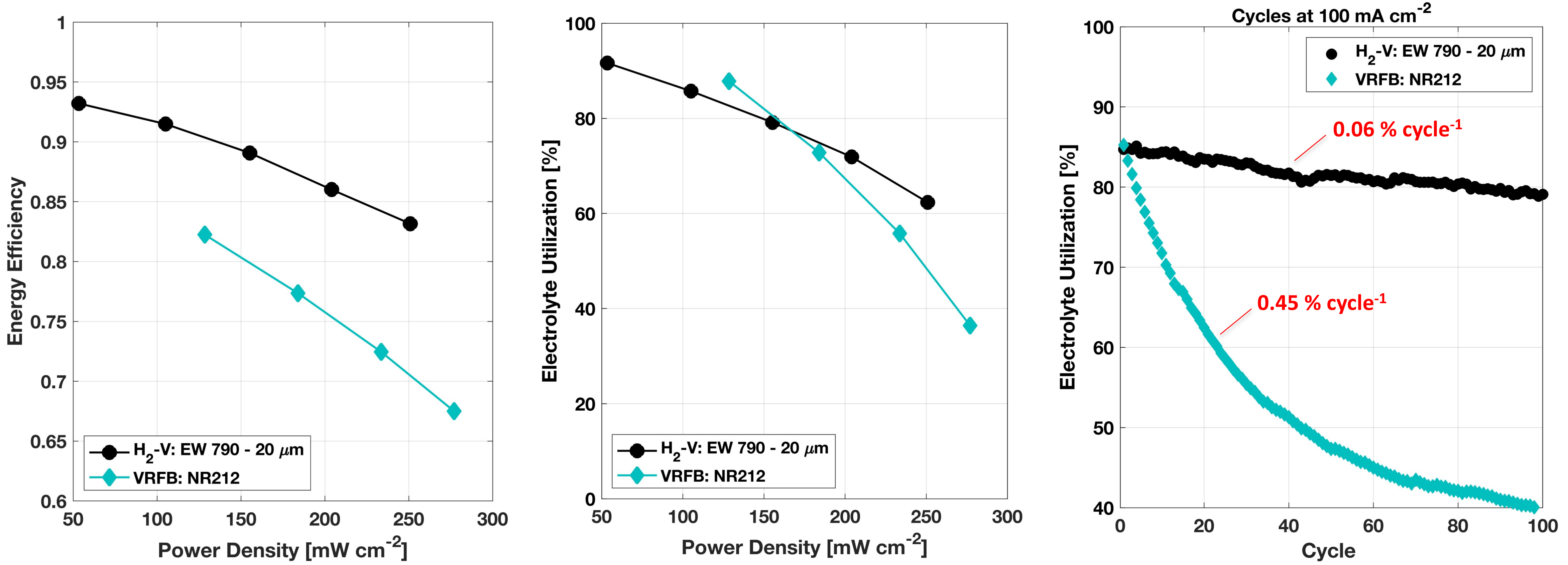
Further advantages of the innovative dual redox flow battery compared to the one developed by Piwek et al.:

- Utilization of one single vanadium electrolyte (VO^{2+}/VO_2^+), limiting the issues related to electrolytes imbalance and electrolyte cost.
- Hydrogen produced in electrochemical device, which permits a better control compared to the chemical reactor.

J. Piwek et al., Journal of Power Sources 439 (2019) 227075.

DEVELOPMENT OF A DUAL REDOX FLOW BATTERY BASED ON H_2-V BATTERY

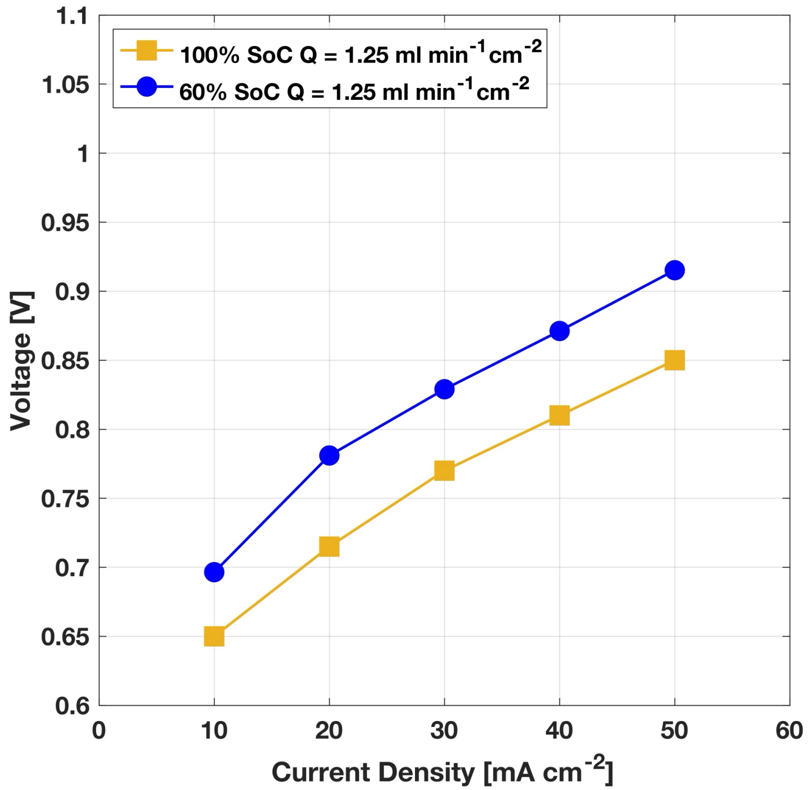
Performance analysis of H_2-V battery employing an Aquivion® based membrane with EW 790 and 20 μm thickness and comparison with VRFB employing Nafion® 212 and GFD 2.5 EA thermically activated carbon felt electrodes.



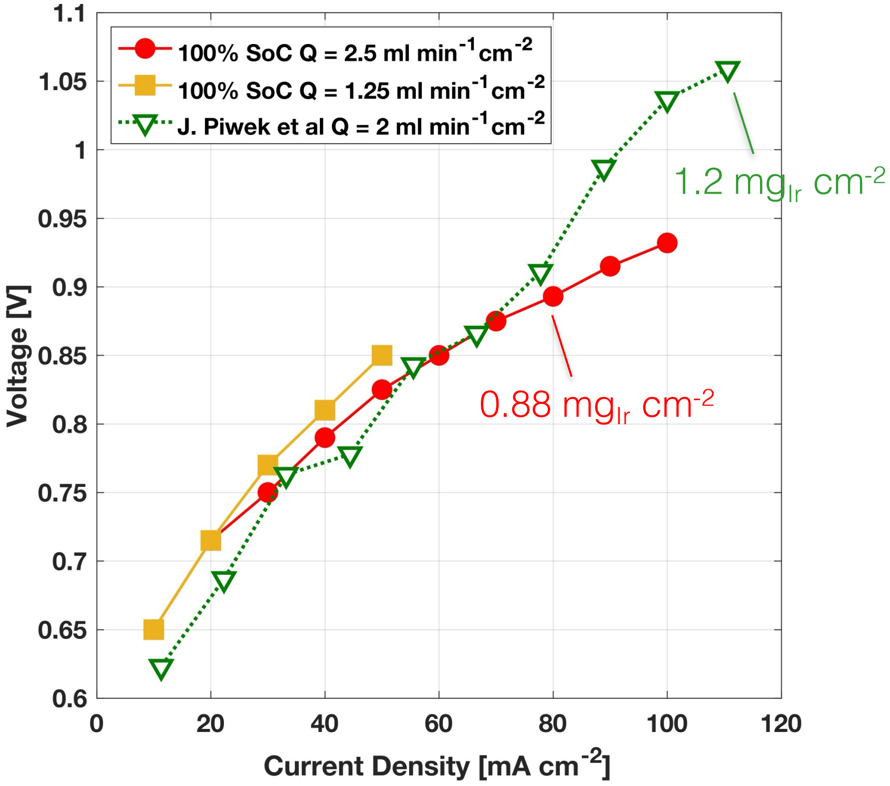
H_2-V battery employing a thin membrane with reduced EW exceeds the performance of a VRFB with SoA components.

Performance analysis of V-O_2 cell employing Freudenberg H23 as negative electrode, 50 μm thick Aquivion® based membrane with EW 720, IrOx 0.88 mg_{Ir} cm^{-2} as positive electrode, coupled with 250 μm thick Bekaert titanium PTL.

Effect of SoC



Effect of flowrate

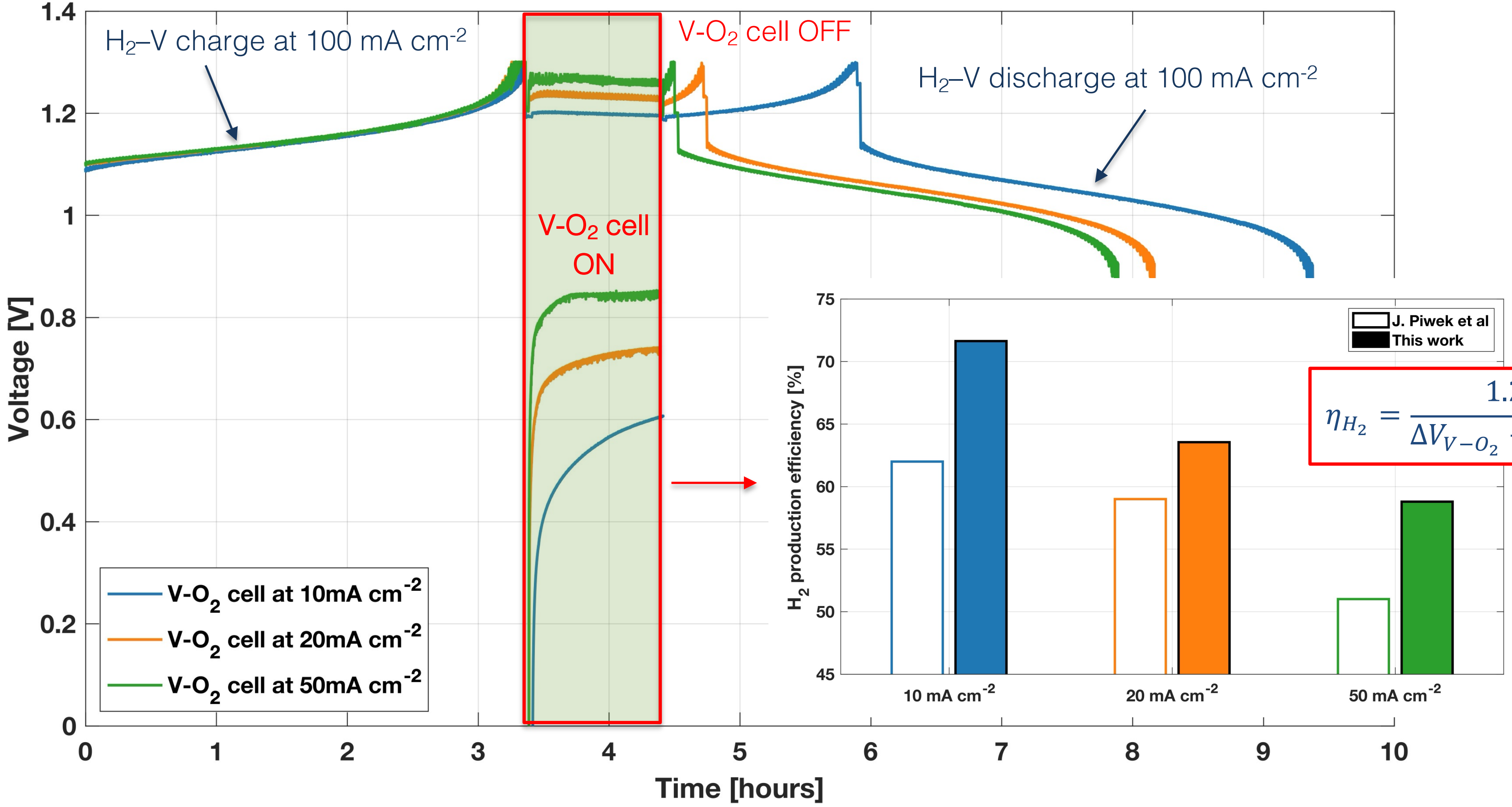


Both SoC and electrolyte flow rate affects V-O_2 performance, even at low operating current. At low operating temperature OER presents sluggish kinetic.

J. Piwek et al., Journal of Power Sources 439 (2019) 227075.

DEVELOPMENT OF A DUAL REDOX FLOW BATTERY BASED ON H_2-V BATTERY

Performance analysis of dual redox flow battery: $V-O_2$ cell operating at the same current density of H_2-V battery.



$$\eta_{H_2} = \frac{1.23}{\Delta V_{V-O_2} + \Delta V_{RFB}}$$

The main highlights regarding flow battery technology are the following:

- Development of an innovative barrier layer: the barrier deposited on N212 limits capacity decay to values comparable with the ones obtained with N115, regardless the considerably different overall thickness of the separators (less than 50%). The presence of the barrier permits also to increase battery voltage efficiency during the first cycles.

- Engineering of an improved flow-field: combining experimental and modelling approach demonstrated that homogeneous electrolyte distribution leads to increased battery performance. The 300 cm^2 improved flow-field further enhances cell performance due to a proper designed of the manifold: compared to the 100 cm^2 geometry the electrolyte utilization increases by 9.5% and 26.2% at 150 mA cm^{-2} and 300 mA cm^{-2}, respectively, with no variation of pressure drops.

- Development of a dual redox flow battery: in H_2-V battery the combination of low membrane thickness and EW led to high battery performance: 83% energy efficiency and 60% electrolyte utilization at 250 mW cm^{-2}. The developed dual redox flow battery permits to increase storage capacity with a reduced amount of vanadium electrolyte: hydrogen production efficiency ranges from 72% to 59% at 10 mA cm^{-2} and 50 mA cm^{-2}, respectively.

Thanks for your attention

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