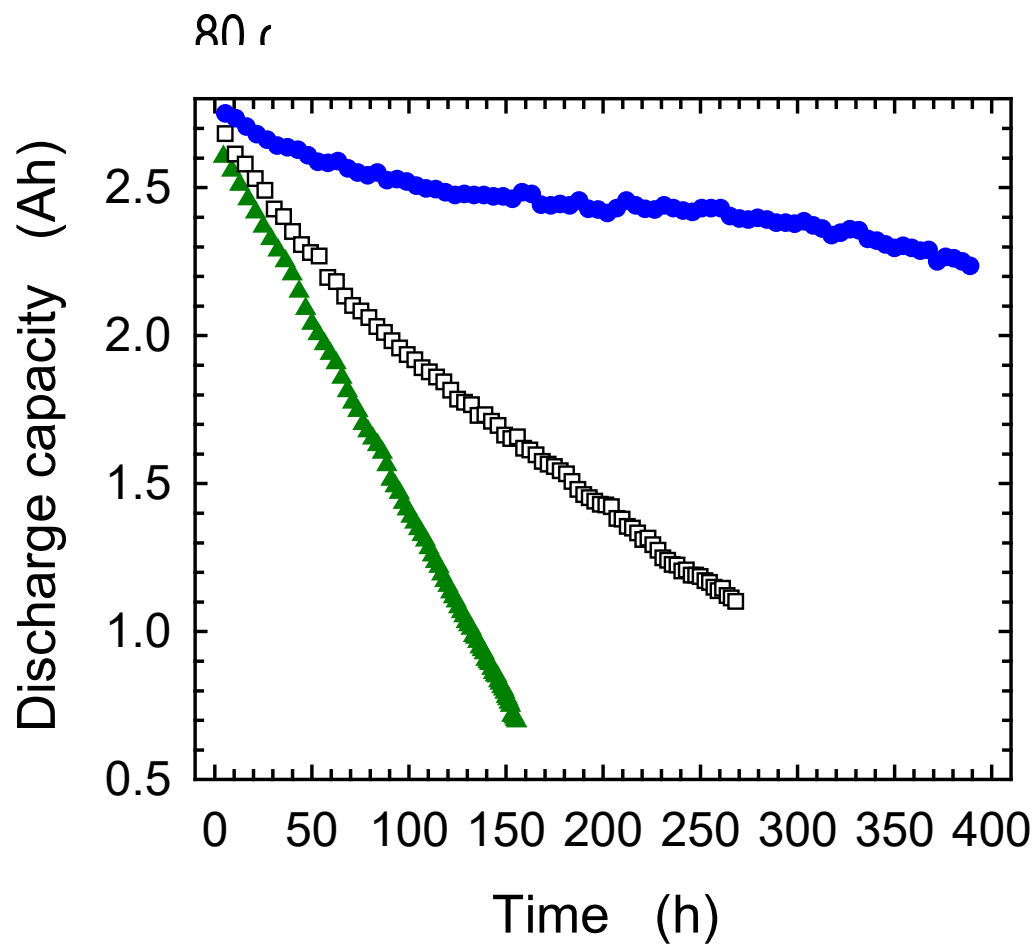




Final report

# RFBmem – Chemistry and Stability of Grafted Membranes for Redox Flow Batteries





**Date:** 10 December 2019

**Place:** Villigen PSI

**Publisher:**

Swiss Federal Office of Energy SFOE  
Research Programme Hydrogen and Fuel Cells  
CH-3003 Bern  
[www.bfe.admin.ch](http://www.bfe.admin.ch)  
[energieforschung@bfe.admin.ch](mailto:energieforschung@bfe.admin.ch)

**Agent:**

Paul Scherrer Institut  
Electrochemistry Laboratory  
5232 Villigen PSI  
[www.psi.ch/lec](http://www.psi.ch/lec)

**Author:**

L. Gubler, Paul Scherrer Institut, [lorenz.gubler@psi.ch](mailto:lorenz.gubler@psi.ch)  
F.J. Oldenburg, Paul Scherrer Institut, [fabio.oldenburg@psi.ch](mailto:fabio.oldenburg@psi.ch)

**SFOE head of domain:** Martin Pulfer, [martin.pulfer@bfe.admin.ch](mailto:martin.pulfer@bfe.admin.ch)  
**SFOE programme manager:** Stefan Oberholzer, [stefan.oberholzer@bfe.admin.ch](mailto:stefan.oberholzer@bfe.admin.ch)  
**SFOE contract number:** SI/501421-01

**The author of this report bears the entire responsibility for the content and for the conclusions drawn therefrom.**

**Swiss Federal Office of Energy SFOE**

Mühlestrasse 4, CH-3063 Ittigen; postal address: CH-3003 Bern  
Phone +41 58 462 56 11 · Fax +41 58 463 25 00 · [contact@bfe.admin.ch](mailto:contact@bfe.admin.ch) · [www.bfe.admin.ch](http://www.bfe.admin.ch)



## Summary

The objective of the research project was the further development of the PSI membrane technology for redox flow batteries with a view to a commercial implementation. The PhD thesis project comprised a continued development of the membrane chemistry by changing the composition of the graft component for improved oxidative stability. A patent application describing this new chemistry has been filed. Furthermore, the vanadium transport properties across different membrane types has been studied in detail. The amphoteric ion-exchange membrane from PSI hereby showed a clear advantage over commercial membranes. A work package on method development was devoted to the study and implementation of an accelerated stress test (AST) to characterize oxidative stability of membranes. By exposing membranes to a solution of cerium(IV) at elevated temperature (up to 80°C), an acceleration factor for degradation of up to 200 could be attained. This method can greatly help to screen membranes and assess their suitability for vanadium redox flow battery applications. In parallel to this project, technology implementation efforts continued, and in March 2019 the PSI spin-off 'Gaia Membranes' was founded. The CTO is Fabio J. Oldenburg, who was the PhD student behind this project. The 'demonstrator' work package of this project supported the scale-up efforts of Gaia Membranes to allow supply of first batches of membranes to customers for evaluation and demonstration purposes. Future work is aimed, on the one hand, at further research in the framework of a follow-up PhD study, and, on the other hand, at continuing the implementation of PSI membrane technology and collaboration with the Gaia Membranes.

## Zusammenfassung

Die Zielsetzung dieses Forschungsprojektes war die Weiterentwicklung der PSI Membrantechnologie für Redox-Flussbatterien im Hinblick auf eine kommerzielle Umsetzung. Die Promotionsarbeit beinhaltete die Optimierung der Membranzusammensetzung durch Anpassung der Pfropfkomponente für eine verbesserte oxidative Stabilität. Die Beschreibung der neuen Membranzusammensetzung wurde zum Patent angemeldet. Weitere Arbeiten beinhalteten die Untersuchung der Vanadium-Transporteigenschaften von verschiedenen Membranen. Dabei zeigte die am PSI entwickelte amphotere Ionentauschermembran deutliche Vorteile gegenüber kommerziellen Membranen. Ein Arbeitspaket zur Methodenentwicklung war beschleunigten Alterungstests von Membranen gewidmet. In Cer(IV) Lösungen bei Temperaturen bis 80°C zeigten Membranen eine um bis einen Faktor 200 beschleunigte oxidative Alterung. Diese Methode ermöglicht es, Membranen effizient zu qualifizieren und ihre Eignung für den Einsatz in Vanadium Redox-Flussbatterien zu prüfen. Gleichzeitig zu diesen Arbeiten wurde die Bemühungen zur kommerziellen Umsetzung vorangetrieben, und im März 2019 wurde 'Gaia Membranes' vom PSI ausgegründet. Der CTO ist Fabio J. Oldenburg, dessen Doktorarbeit durch dieses Projekt finanziert wurde. Im Rahmen des Arbeitspaketes 'Demonstration' wurden die Scale-up Prozessschritte unterstützt und es konnten erste Membranchargen an Kunden zur Evaluation oder Integration in Demonstrationsprojekte geliefert werden. In einem Anschlussprojekt für eine Dissertation wird die Forschung an Membranen für Redox-Flussbatterien fortgeführt. Gleichzeitig wird die Umsetzung der PSI-Membrantechnologie in Zusammenarbeit mit Gaia Membranes weitergeführt.



## Project Overview & Key Results

The requirement for electricity storage increases with the increase in the share of electricity in the grid from inherently intermittent renewable sources, such as wind and solar power. According to the Federal Energy Strategy 2050, future power generation in Switzerland will shift from nuclear power to photovoltaics (11 TWh/a), geothermal power (4.5 TW/a), wind power (4.5 TWh/a), and electricity from waste, biogas and biomass (4.5 TWh/a). Based on simulations, it is estimated that a storage capacity corresponding to 20 % of the energy produced over a year has to be installed in the grid to ensure reliable electricity supply. Taking the projected supply from the non-dispatchable wind and solar power, the required storage capacity is ~3 TWh. Today's pumped hydroelectric storage (PHES) plants can provide a capacity of around 2 TWh. Therefore, new storage capacity needs to be deployed.

Electrochemical energy storage technologies provide a high flexibility in terms of scalability and location-independence. Among the different rechargeable battery types, Li-ion batteries, high-temperature batteries based on sodium, and vanadium redox flow batteries are projected to be key technologies in the future with cumulative global deployed capacities by 2030 on the order of 0.5 TWh. The advantage of flow batteries is the independent scalability of power and energy, because the energy conversion unit (electrochemical cells) and the energy storage unit (electrolyte tanks) are decoupled from one another. This makes it particularly attractive for storage durations of more than 6 h. The vanadium redox flow battery (VRFB) is the flow battery type that is closest to the market. The great advantage is the use of vanadium-ions in both the negative and the positive electrolyte (**Figure 1a**).

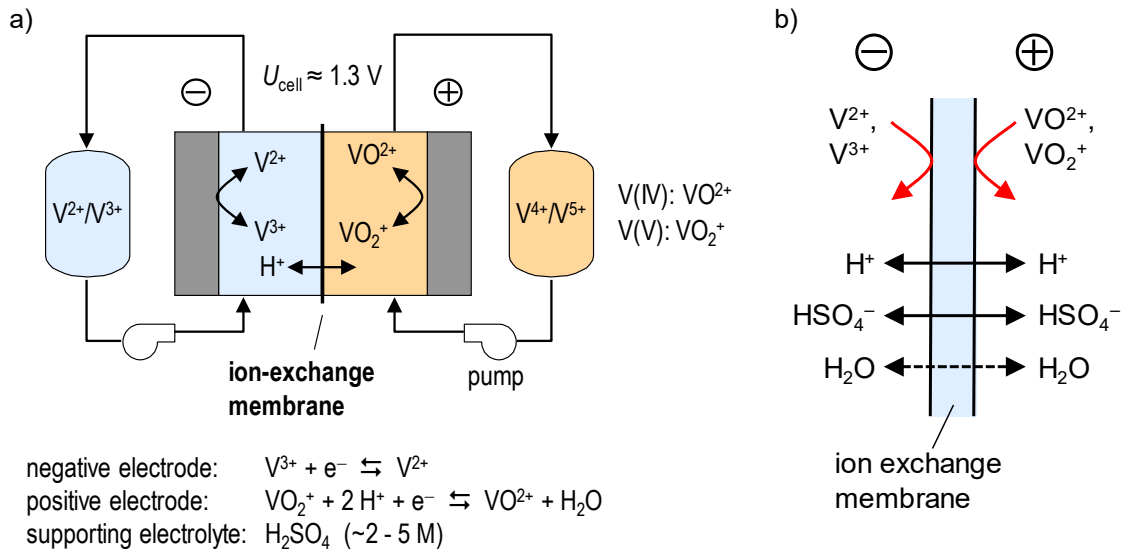


Figure 1. a) Operating principle of an all-vanadium redox flow battery (VRFB). b) Selectivity requirements for an ion-exchange membrane in the VRFB.

The key economic figure of merit of an energy storage technology is the levelized cost of storage (LCOS), i.e., the cost of investment and operation of the facility divided by the electricity output over the lifetime of the installation. Conceptually the LCOS can be represented according to

$$LCOS = \frac{CAPEX + (O \& M)}{\eta \cdot \text{cycles}} \quad (1)$$

where  $CAPEX$  is the investment cost,  $O\&M$  the cost of operation and maintenance (e.g., labor cost),  $\eta$  the charge-discharge round-trip efficiency, and  $\text{cycles}$  the cycle life of the battery. Therefore, the



economical viability of a storage technology can be improved by reducing the cost of the battery components, improving the energy efficiency, increasing the lifetime of the components, or a combination thereof.

This research project was focused on the ion-exchange membrane used as a polymer electrolyte and separator in the VRFB (**Figure 1b**). The role of the membrane is i) to transport ions of the background electrolyte (sulfuric acid), ii) prevent the passage of vanadium ions, and iii) avoid imbalanced species transport to avoid capacity fading due to the net crossover of electrolyte.

The objective of this project was to develop an ion-exchange membrane that is specifically designed for the VRFB based on the radiation grafting technology. Radiation grafted membranes have been in the research focus at PSI for more than two decades, historically mainly with a view to application in fuel cells. The profound expertise in this field was believed to be an important asset to bring the PSI membrane technology forward to a level where industrial implementation is conceivable. In addition to the research topics of this project, a work package focused on scale-up of membrane fabrication was included to allow the preparation of membranes for implementation by industrial partners.

#### *Materials Research & Development*

The objective of the membrane research and development work package was to improve the chemistry of the graft component to improve performance, selectivity and/or the durability of the material. The radiation grafting method used for membrane preparation consists of a sequence of process steps involving electron-beam irradiation, followed by the grafting reaction and post-functionalization of the material (**Figure 2a**). During the grafting reaction, monomers are grown onto the polymer backbone of the base film. At the outset of the project, the monomers used were styrene (S) and acrylonitrile (AN), which both are very common monomers. Initially, the performance of these S-AN based membranes in the cell was extensively studied, in particular the selectivity and transport properties of vanadium, and compared to the commercially available benchmarks Nafion® (= cation exchange membrane) and FAP-450 (= anion exchange membrane). The S-AN grafted membrane is an *amphoteric* ion-exchange membrane (AIEM), meaning that it contains fixed cation as well as anion exchange groups. In the course of this study, a redox titration method was implemented to study the transport of vanadium through the membrane as a function of time to quantify the imbalance of vanadium-ion transport [1]. It was found that in the case of the AIEM, the vanadium-ion transport between charge and discharge is much more balanced than in the case of the pure cation and anion exchange membrane, which leads to a significantly improved capacity retention (cf. **Title Page Figure**).

This was the basis for further development of the membrane. The S-AN membrane was used as a model system and does not have sufficient chemical stability. Therefore, a number of other monomer combinations were explored with a view to improving selectivity and stability. Primarily, the styrene (S) was replaced by  $\alpha$ -methylstyrene (AMS), which has intrinsically improved oxidative stability. Various co-monomers were evaluated, such as glycidylmethacrylate (GMA) and acrylamide (AAM), as precursors for anion exchange groups. Eventually, methyleneglutaronitrile (MGN) was selected as a monomer of choice, owing to its expected high chemical stability and its ability to provide two anion exchange groups per monomer unit. The membrane chemistry based on AMS and MGN was filed for patent at the European patent office [2].

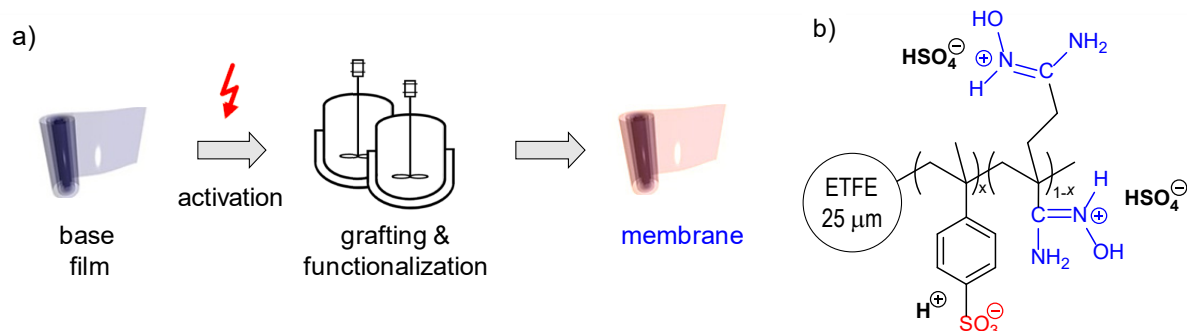


Figure 2. a) Membrane preparation method using electron-beam pre-irradiation grafting and functionalization of a fluoropolymer base film. b) Chemistry of the radiation grafted amphoteric ion-exchange membrane developed in the framework of this project [2].

Amphoteric ion-exchange membranes are characterized by the presence of both cationic and anionic groups fixed on the polymer backbone. We have seen that this leads to some extent to a mutual cancellation of charges in the membrane and an a reduced effective ion exchange capacity. Therefore, we prepared bilayer membranes consisting of a cation exchange polymer (Nafion® 212) laminated to a thin layer of polybenzimidazole (PBI), which when swollen in the sulfuric acid based electrolyte is protonated and assumes anion exchange character. In a bilayer membrane, unlike in the AIEM, interaction of positive and negative fixed charges is restricted to the interface between the two layers. In cell experiments using bilayer membranes with different PBI layer thicknesses (in the range of  $\mu\text{m}$ ), the vanadium transport properties across the membrane was studied also as a function of the current density. As expected, owing to the presence of the anion exchange layer (PBI) vanadium transport was lower and much more balanced. Furthermore, an increase in current density lead to a more pronounced vanadium transport towards the negative side. Hence it was possible to identify a current density with expected zero net vanadium transport, which was shown to yield improved capacity retention during extended charge-discharge cycling tests [3].

In a side-project in collaboration with EMPA, we studied the effect of phosphoric acid on the flow cell performance. Phosphoric acid is used as an additive in commercial vanadium electrolytes containing vanadium sulfates and sulfuric acid to improve its stability and prevent precipitation of vanadium(V) species at elevated temperature. It was found that phosphoric acid improves the kinetics of the negative electrode reaction due to the formation of a complex with vanadium(III). Hence, its presence in the electrolyte also has an advantage on the electrode kinetics [4].

#### *Development of an Accelerated Stress Test Protocol*

The expected calendar lifetime of VRFB components is 15 to 20 years. In the development of new cell components it is impractical to test materials under field-relevant conditions over thousands of hours. To maximize sample throughput and improve statistics of component aging tests, the use of accelerated stress test protocols suggests itself, which should allow an assessment of stability or lifetime of materials within a much shorter period of time, i.e. days or weeks. Such AST methods are of high interest to the flow battery community, as we have learned from flow battery component and system manufacturers. The aim of this work package was therefore to study the degradation kinetics of model membranes exposed to solutions containing different oxidizing agents at temperatures ranging from 30 to 80°C and compare the results to the degradation experienced by the same membranes in the cell over a certain operating time. Vanadium(V) is the vanadium-ion with the highest oxidation number in the VRFB and is known to cause oxidative aging of membrane material. Membrane pieces were therefore immersed in



a solution of 0.1 M V(V) in 2 M sulfuric acid at different temperatures. In addition, a solution of Ce(IV) was used as test solution for membranes, because  $\text{Ce}^{4+}$  is a stronger oxidizing agent than V(V). Thus, it was expected that membrane degradation in Ce(IV) solution will be systematically accelerated. **Figure 3a** shows the state-of-health of a radiation grafted membrane quantified by the content of graft component as a function of time of exposure. It is evident that the rate of degradation increases systematically with temperature. In fact, for both V(V) and Ce(IV) solutions, an apparent activation energy for membrane degradation of  $\sim 50$  kJ/mol is obtained. Taking the rate of membrane degradation in the cell as baseline, an acceleration factor  $\alpha$  can be calculated for the vanadium and cerium solutions at the different temperatures (**Figure 3b**). The highest acceleration factor of  $\sim 200$  is obviously obtained for Ce(IV) solution at  $80^\circ\text{C}$ . This means that for a target lifetime of 10 years, an exposure time in the *ex situ* accelerated stress test of  $\sim 500$  h would be sufficient to characterize membrane stability.

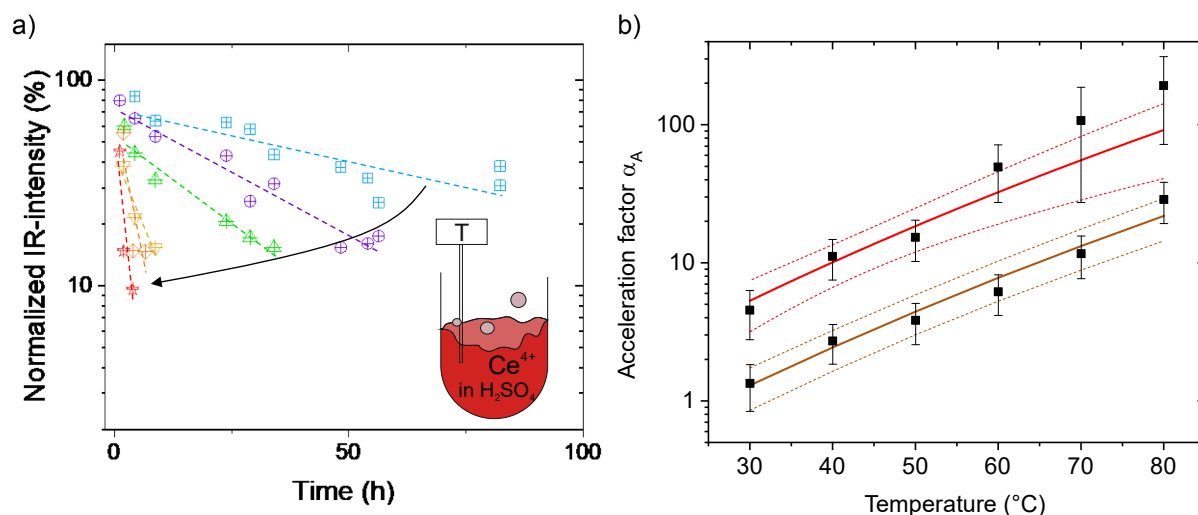


Figure 3. a) Membrane state-of-health based on the content of graft component determined by infrared spectroscopy for different exposure times in 0.1 Ce(IV) solution in 2 M sulfuric acid at different temperatures. b) Acceleration factor of membrane degradation in V(V) and Ce(IV) solutions at different temperature referenced to membrane degradation measured in the single cell.

The AST developed in this work package is not meant to replace *in situ* tests of membranes in the cell. Its target use is that of a screening tool to characterize different candidate membrane materials and down-select them for further testing and qualification in the cell. It therefore helps to increase sample throughput and statistics of membrane stability data. The method has been implemented using radiation grafted model membranes from PSI. For the application of the stress test to other membrane materials and polymer classes, the assumption of a consistent degradation mechanism and transferable composition-property relations to the conditions in the cell needs to be tested and established. When properly implemented, it can provide an “engineering test” or “index test” and can serve as a basis for predictive modeling of the membrane lifetime in VRFBs [5].

### Implementation of Technology

The optimized radiation grafted ion exchange membrane (depicted in Figure 2b) was tested with various OEMs to assess the commercial value for users of the membrane technology. After positive feedback was obtained, a patent application was filed to protect the membrane technology. The next objective was to demonstrate the membrane in a technical stack in a real operation environment. This necessitated the scale-up from lab-sizes of the membrane to technically relevant sizes (Figure 4a). At the same time



quality targets were defined in collaboration with industry partners and their monitoring was implemented into the production process to assess the consistency of quality parameters within one membrane and across different batches. After confirming the achievement of industrial quality targets, a first full-stack test was sold and is currently tested in combination with a PV-plant in Australia (Figure 4b). The test is still ongoing and a detailed feedback of the results pending.

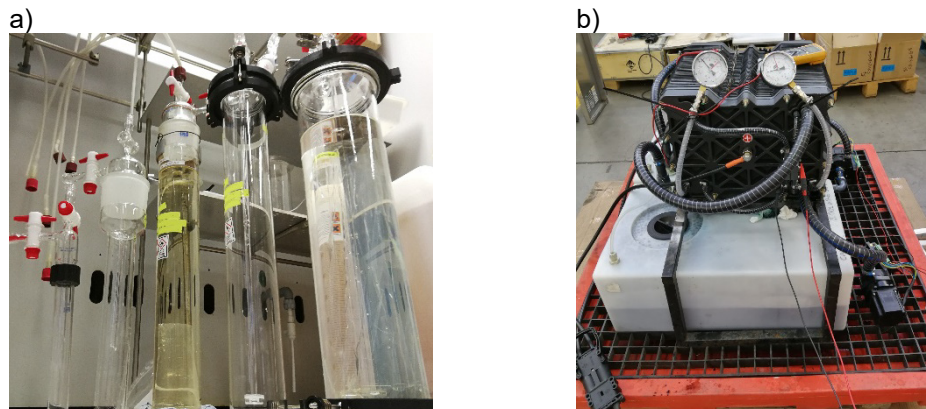


Figure 4. a) Scale-up of the membrane production from 60 mL reactors to 5 L reactors. b) Demonstration of the membrane technology in a 10 kW stack of an industry partner.



## Outlook

The research on flow batteries at PSI started in 2013 with an SNF Sinergia project entitled 'Redox flow electrochemistry for power delivery and cooling (REPCOOL)', a collaboration led by IBM Research in Rüschlikon. In the mean time, we have further developed the membrane technology at PSI and in March 2019, the PSI spin-off company Gaia Membranes (gaiamembranes.com) has been founded. The Bridge Discovery project acquired in 2017 was / is of great importance to develop membrane technology and processes for scale-up. Also, this project contributed significantly to this end. **Figure 5** shows the funding landscape on flow battery membranes at PSI. We have acquired funding for a follow-up research project 'RFBsep' funded by SNF, which is aimed at further developing next generation flow battery composite membranes based on porous battery separator materials. Together with Gaia Membranes, we are furthermore exploring the possibility of a demonstration project supported by BFE.

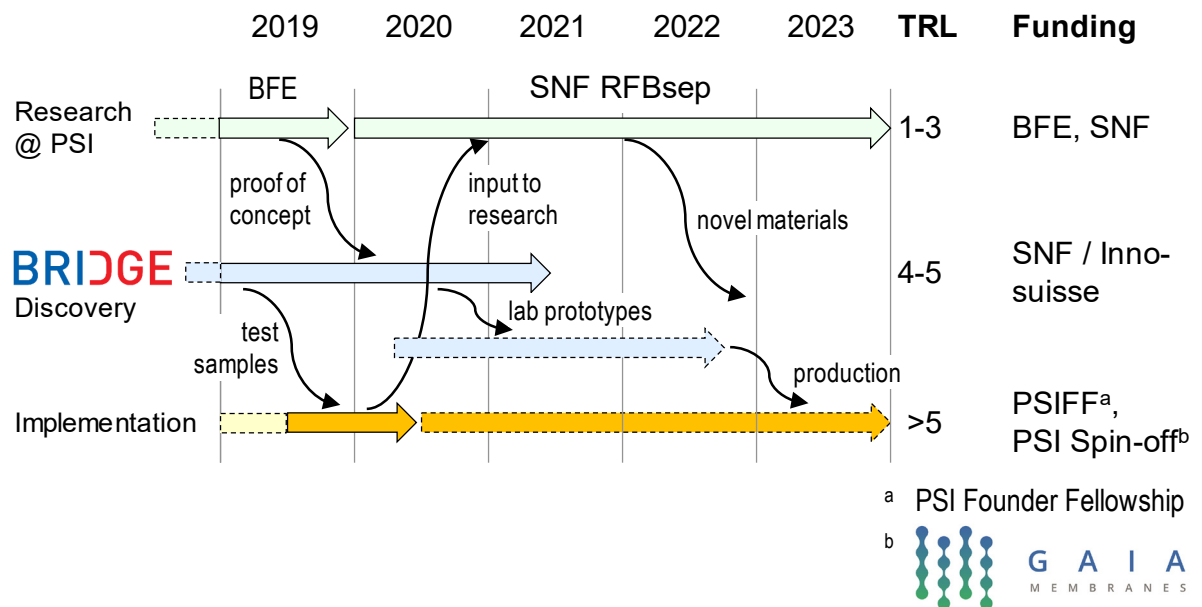


Figure 5. Funding landscape of flow battery membrane research and development at PSI.



## References

1. F.J. Oldenburg, T.J. Schmidt, L. Gubler, "Tackling capacity fading in vanadium flow batteries with amphoteric membranes", *Journal of Power Sources* **368** (2017), 68-72
2. F.J. Oldenburg, A. Albert, L. Gubler, "Amphoteric Electrolyte Membrane and a Redox Flow Battery comprising an Electrolyte Membrane", *European Patent Application, No. 2018P11960EP*, Paul Scherrer Institut, 2018
3. F.J. Oldenburg, E. Nilsson, T.J. Schmidt, L. Gubler, "Tackling Capacity Fading in Vanadium Redox Flow Batteries with Amphoteric Polybenzimidazole/Nafion Bilayer Membranes", *ChemSusChem* **12** (2019), 2920-2627
4. F.J. Oldenburg, M. Bon, D. Perego, D. Polino, T. Laino, L. Gubler, T.J. Schmidt, "Revealing the role of phosphoric acid in all-vanadium redox flow batteries with DFT calculations and in situ analysis", *Phys Chem Chem Phys* **20** (2018), 23664--23673
5. F.J. Oldenburg, A. Ouarga, T.J. Schmidt, L. Gubler, "An Accelerated Stress Test Method for the Assessment of Membrane Lifetime in Vanadium Redox Flow Batteries", *ACS Appl. Mater. Interfaces* (2019), accepted