




Redox-Flow-Batteries

fumasep® membrane types

A member of
BWT – For You and Planet Blue.


fumatech
Functional Membranes for Fuel Cells and Batteries


Energy storage technologies are widely regarded as part of infrastructure for power supply in near future. Electrochemical devices such as redox-flow batteries belong to the most attractive ones when it comes to efficiency.

Redox-flow batteries in general

Redox-Flow Batteries (RFB) represent recently the most advanced electro-chemical energy storage system that is commercialized on level tens of kilowatts to megawatts. A flow battery is charged and discharged via reversible electrochemical reduction-oxidation reactions. These reactions take place typically in two liquid electrolytes separated by an ion-exchange membrane. The RFB is scalable system which can be operated in wide range of conditions. It is supposed to be integrated easily into future smart-grids systems and it is advantageous in connection to wind farms. The batteries are further characterized by high longevity in the range of several years, easy maintenance and high overall energy efficiency exceeding 80 %.

Chemistry of RFB

There are various RFB systems on the market. Among them, the superior position holds vanadium redox flow battery (VRB) that uses vanadium electrolyte on both sides. Such setup gives advantage of avoiding contamination since the electrolytes are of the same nature, made dominantly from vanadium sulfate and sulfuric acid solution. In the charged state, the positive electrode contains V^{5+} ions, while the negative side hosts V^{2+} . During discharging, the V^{5+} is converted into V^{4+} , V^{2+} is converted into V^{3+} plus electric power is yielded (see Fig 1). An eventual migration of ions through separator does not cause any damage of system. There are also other RFB systems, which can be realized within the redox potential window of Hydrogen and Oxygen evolution. All systems strike for either high energy density or lower cost of the electrolyte, such as zinc-bromine, vanadium-bromine, polysulfide bromine, zinc-cerium, iron-chromium or the class of metal air systems such as rechargeable zinc-air batteries.

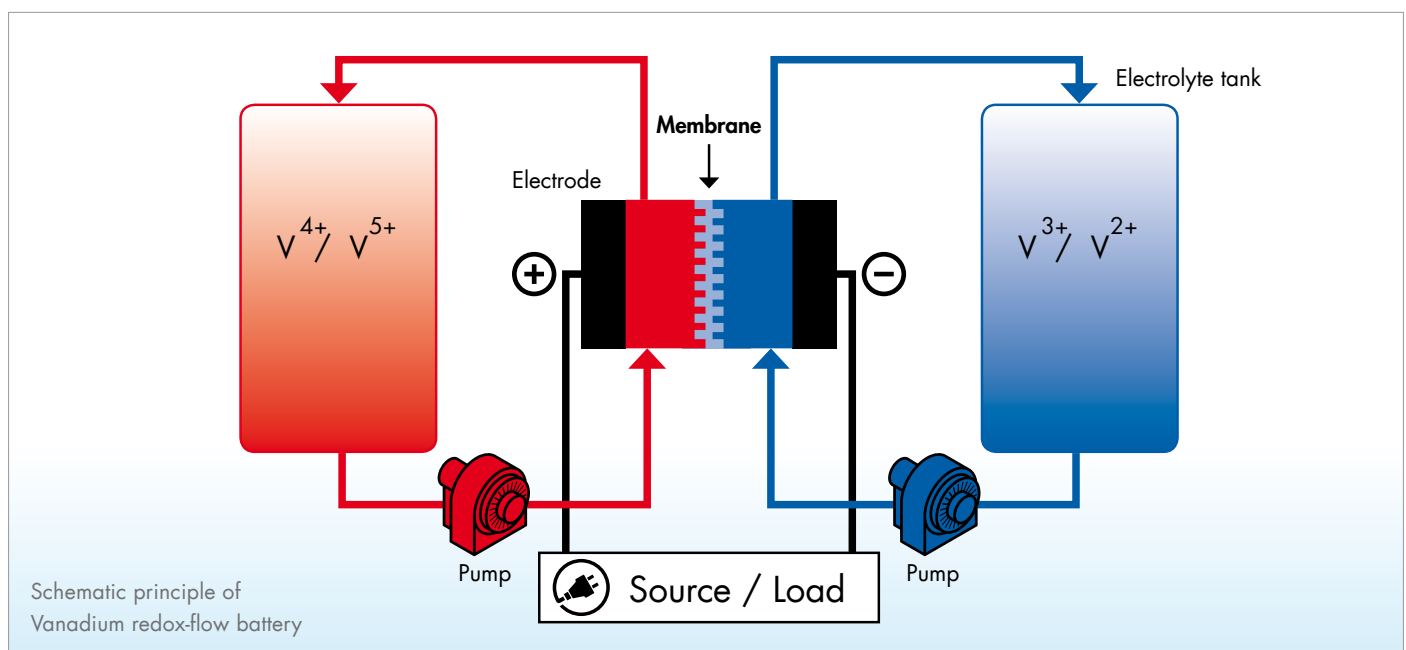
Separators for Redox-Flow Batteries

The fumasep® membrane is the well proven heart of a redox-flow battery. FUMATECH produces non-porous functional anion- and

cation-exchange membranes for various types of batteries. The ion-exchange membranes are superior to porous separators for their high coulombic efficiency and avoidance of significant liquid transfer between both electrolytes. In VRB one can find its right choice, whether aiming on high efficiency or high current density when high speed of charging is required or some compromise between the two modes.

One class of membranes is represented by the anion-exchange ones. Since the energy bearer in redox-flow batteries are Vanadium cations bearing different charges, a selective protonated anion-exchange membrane featuring high rejection of the metallic cations is the optimum choice for maximum efficiency. In this case the Vanadium on the cathode side won't diffuse through the membrane toward anode. On the other hand, the anodic Vanadium species V^{4+} and V^{5+} , which are present as complex anion groups, diffuse slowly through the membrane toward the cathode. This transfer is characterized by osmotic permeability. However, the transfer of the vanadium species is accompanied with other present substances, so no electrolyte concentration changes apply. The capacity can be completely restored by back transfer of catholyte toward anolyte, so the volumes are adjusted to the original level (Fig 2). A superior position among anion exchanged membranes holds the fumasep® FAP-450 having no weak point due to its optimal trade-off between electrolyte management, efficiency, easy maintenance and adaptive behavior to broad range of charging current densities. Among anion-exchange type of material, the right choice for high current density is fumasep® FAP-330-PE. Class of mechanically highly robust membranes is represent by fumasep® FAP-375-PP.

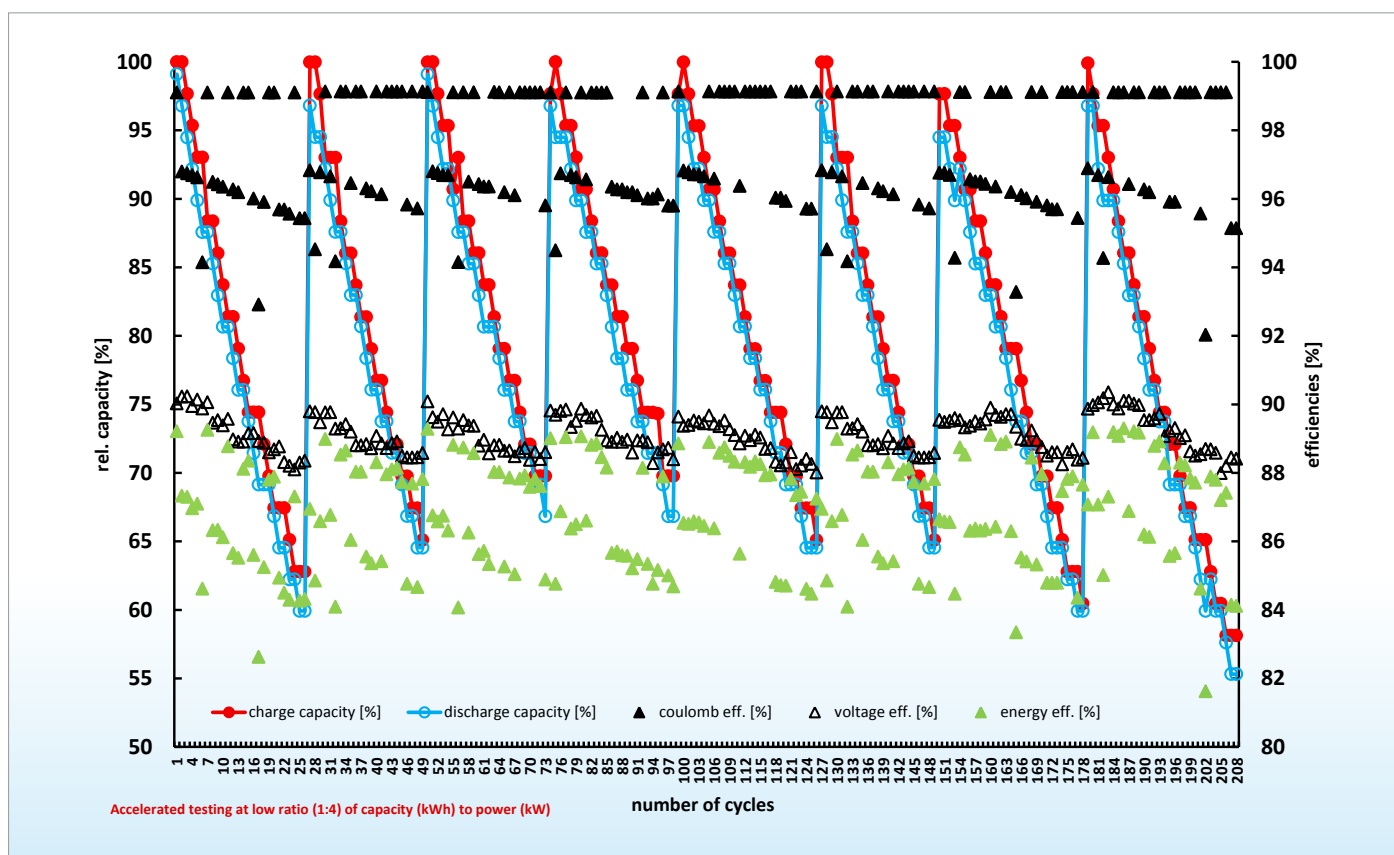
The second class of membranes is represented by cation-exchange membranes, which are primarily a low permeable, proton-conductive barrier to the electrolyte. In this case the anodic species



cannot diffuse toward cathode; on the other hand, Vanadium from cathode in form of V^{2+} and V^{3+} diffuses toward anode. The fumasep® F-930-RFD and FS-930, a low equivalent type PFSA membranes, are the right choices for those preferring low specific area resistance and operation at high current density. The low-cost and high-equivalent-weight PFSA-type cation exchange membrane fumasep® F-1850 is recommended for the modes running at lowest self-discharging and easy maintenance due to negligible electrolyte cross-over. Woven-reinforced membrane fumasep® F-1075-PK is the mechanically robust alternative for non-reinforced PFSA membranes of thickness 100 µm onwards.

The fumasep® membranes have shown proven longevity and chemical durability in range of years under standard conditions. Good to very good performance can be achieved basically with all of the listed membranes. The differences among them are determined mostly by permeability. If required and if suitable, a mechanical reinforcement of the membrane either by ePTFE or PE as well as woven PEEK or PP can be adopted. The membranes are typically available in rolls of 200-1,500 mm width. The membranes can be supplied in sheet form as well. No additional conditioning is necessary and the membranes can be assembled into the cell as delivered.

Profile of charging and discharging of fumasep® FAP-450 anion exchange membrane



Mechanical and physical-chemical properties of membrane for VRB

Membrane	Thickness (µm)	Ion-exchange type	Reinforcement	Mechanical properties			Dimensional swelling (%)
				Young modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	
FAP-330-PE	30	Anion	Yes	> 1000	> 50	> 30	0
FAP-450	50	Anion	No	> 1000	> 25	> 250	< 5
FAP-375-PP	70	Anion	Yes	> 1000	> 35	> 20	< 2
FS-930	30	Cation	No	> 250	> 25	> 100	< 8
F-930-RFD	30	Cation	Yes	> 250	> 25	> 100	< 5
F-1075-PK	80	Cation	Yes	> 1000	> 40	> 20	< 2
F-1850	50	Cation	No	> 620	> 30	> 390	< 2

Electrochemical properties of membrane for VRB

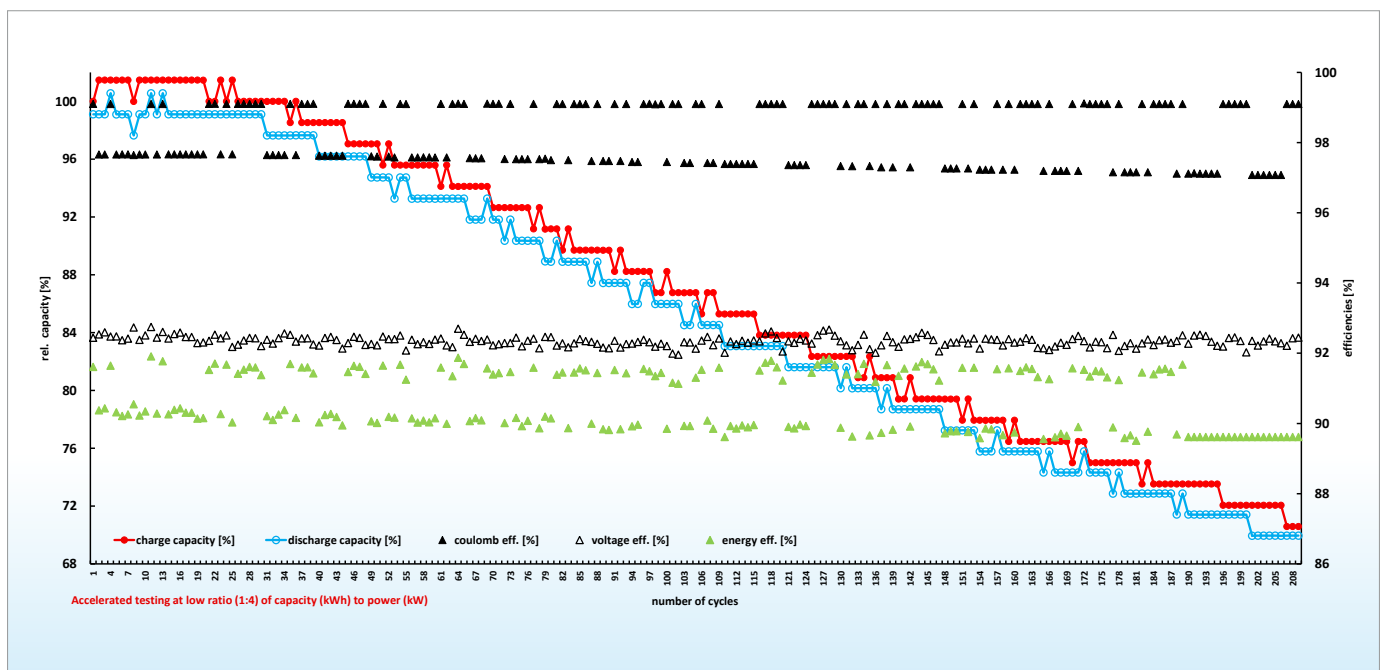
Membrane	Coulomb efficiency (%)	Energy efficiency (%)	Electro-osmotic permeability ($\mu\text{l.cm}^{-2}.\text{hr}^{-1}$)	Osmotic permeability ($\mu\text{l.cm}^{-2}.\text{hr}^{-1}$)	Specific resistance ($\text{m}\Omega.\text{cm}^2$)	Self-discharging ($\text{C.cm}^{-2}.\text{hr}^{-1}$)
FAP-330-PE	95.9	90.5	11.8	9.8	390	4.6
FAP-450	98	89	5.0	3.5	720	3.3
FAP-375-PP	99	89	5.0	3.5	850	3.1
FS-930	96	91	21.8	0.5	290	< 0.35
F-930-RFD	98.5	91	18	0.5	520	< 0.2
F-1075-PK	99.5	90	35	0.5	650	< 0.2
F-1850	99.5	83	30.7	< 0.2	1650	< 0.2

Remarks: The exact number of coulomb efficiency, energy efficiency and permeability is always related to operational conditions. The higher upper limit of SOC, the lower coulomb efficiency is achieved. The higher current density is applied, the lower energy efficiency is yielded. The lower current density is applied, the lower coulomb efficiency is yielded. Permeability follows the changes of coulomb efficiency.

Operating conditions:

- 1.6 M solution of VOSO₄ in mixture with 2 M H₂SO₄
- Single-cell measurement
- Both electrolytes are kept under Nitrogen (purity 2.8 or higher)
- Current density 20-80 mA/cm²
- SOC limit charge 99%
- SOC limit discharge 2%
- Temperature 23 °C +/- 1.5 °C
- Specific resistance is measured by means of electro-impedance spectroscopy in discharging mode when SOC is between 60-50% and current density set to 18 mA/cm². The potential of EIS measurement is read on Pt-wire that is put between membrane and electrode so the measurement is influenced neither by contacting resistance nor by polarisation of electrode.
- Osmotic permeability is calculated as change of electrolyte volumes after completing the charge-discharge cycle.
- Electro-osmotic permeability is calculated as change of volumes of anode and cathode during charging and discharging.
- Self-discharging is measured over period 6-20 hrs from SOC 98% when both electrolyte circulate through cell.

Profile of charging and discharging of fumasep® F-930-RFD cation exchange membrane



The company

Focussing on water as the basis of all forms of life, and energy as the basis for a higher quality of life, FUMATECH “Functional Membranes and Plant Technology” combines the important tasks of providing energy and water. The company is engaged in the field of fuel cell technology and membrane separation technology, particularly for the treatment of aqueous solutions.



FUMATECH draws its particular strengths as a leading producer of ion-exchange membranes from its membership in the BWT Best Water Technology Group.

FUMATECH is committed to develop new products that will accelerate progress in polymer electrolyte fuel cells.

The company is both competent und competitive as a leading supplier of polymers and membranes for manufacturing of membrane electrode assemblies.

The high performance membranes are the heart of a proton exchange membrane (PEM) fuel cell stack.

FUMATECH produces and develops

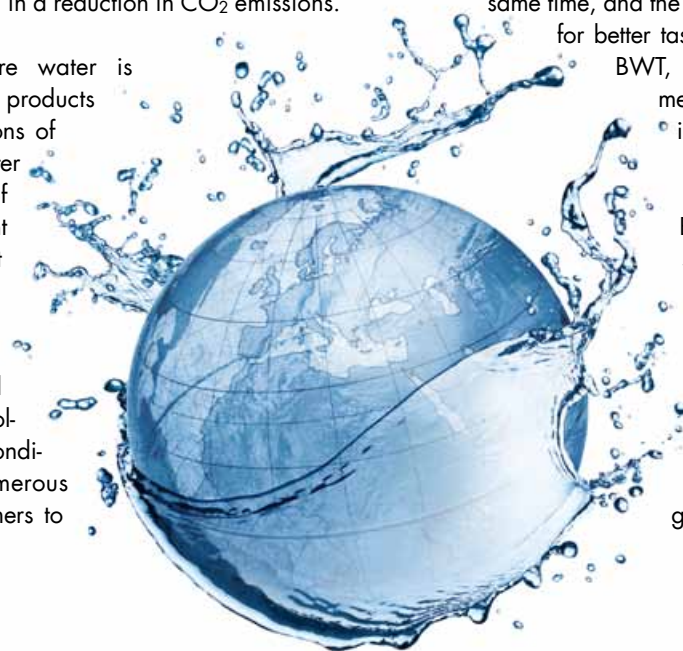
- polyelectrolytes (fumion® ionomers),
 - proton conductive membranes (fumapem® membranes) and
 - separation membranes (fumasep® membranes)
- based on proprietary technology and designed for high precision mass manufacturing.

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|----------------|---|
| ■ fumion® | ionomer resin as granular polymer, in solution form or in dispersion |
| ■ fumion® FF | granular perfluorosulfonyl fluoride resin for extrusion |
| ■ fumapem® F | perfluorosulfonic acid membranes for PEMFC |
| ■ fumapem® AM | polybenzimidazole membranes for high temperature PEMFC |
| ■ fumapem® ST | hydrocarbon membranes for DMFC and PEMFC |
| ■ fumapem® P,E | hydrocarbon membranes for DMFC |
| ■ fumapem® FAA | anion-exchange membrane for alkaline FC |
| ■ fumasep® FAP | anion-exchange membrane for redox flow batteries |
| ■ fumasep® FBM | bipolar membrane |
| ■ fumasep® HF | hollow fibre cartridge for gas humidification |
| ■ fumasep® | ion-exchange membranes for humidifier, electrodialysis and electrolysis |
| ■ fumea® | catalyst coated membranes for water electrolysis |

BWT – The Company

The Best Water Technology Group is Europe's leading water technology company with 3,300 employees and a vast network of partner companies, service staff, installers, planners, architects and hygiene experts. Our R&D teams apply state-of-the-art methods and use the latest processes and materials to create products that are both economical and green. One of the key objectives is to reduce the resource and energy consumption levels of our products, resulting in a reduction in CO₂ emissions.

Practically everywhere where water is involved, BWT's pioneering products have proved their worth millions of times over; where domestic water enters a building ('point of entry') and at its tapping point ('point of use'), for the treatment of seawater, drinking water, mineral water, ultrapure water for pharmaceuticals, water for swimming pools, heating and process water, boiler water, cooling water and water for air-conditioning systems. Our numerous innovations enable our customers to



enjoy the highest levels of safety, hygiene and health in their daily use of water – the precious elixir of life. Among these are: SEPTRON®, the world's first Electrodeionisation module (EDI) with spiral winding, the MDA (manganese oxide activation) method for effective removal of manganese, AQA total bipolar technology for chemical-free limescale protection, SANISAL – the world's first regeneration salt for softening systems that also disinfects at the same time, and the revolutionary new Mg²⁺ technology for better tasting filtered water, coffee and tea.

BWT, with its unique, high-performance membranes for fuel cells and batteries, is setting the 21st century standard for the supply of clean energy.

BWT – For You and Planet Blue signifies our mission to take ecological, economic and social responsibility, and to provide our customers with the best products, systems, technologies and services in all areas of water treatment, while making a valuable contribution to the preservation of our blue planet's global resources.



For You and Planet Blue.

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