

Karl-Friedrich Berger,
Sandra Kiefer (Hrsg.)

JAHRBUCH 2020

Dichten. Kleben. Polymer.

Sealing in redox flow batteries

Influence of HBr chemical impact

This research project determines what the chemical impact is of HBr-Br₂ electrolyte on elastomer seals in redox flow batteries (RFBs). Proper energy storage is the solution to promote electricity from green energy. Hydrogen bromine redox flow batteries are a new generation of RFBs, which are presently in fast development. Successful application of sealing technology in such designs even benefit other accompanying RFBs. The primary task is to select proper rubber materials, which are chemical and mechanical stable. Fluorinated propylene monomer (FPM) and ethylene propylene diene monomer (EPDM) rubbers deem to be good suitors.

State of art of RFBs

A redox flow battery (RFB) is like any other kind of battery, a way to store energy. In this case electrochemical energy which can be transformed into electrical energy. A noticeable difference with conventional batteries: the electrodes in RFBs do not take part in the redox reaction. The design structure generally exists of the components as shown in **figure 1**. The electrodes have the function of conducting and distributing electrons. The potential energy is stored in the electrolyte, which is separated into external negative and positive containers. A benefit of RFBs is the possibility of decoupling energy and power (by changing sizes). Currently RFBs are more expensive compared to other energy storage batteries due to the need of pumps and expensive materials, but RFBs have the longest life cycle expectancy so over time they can be more economic.

In a hydrogen bromine RFB, one container holds aqueous HBr-Br₂ while the other container holds H₂-gas. In the cell, the gas side is the gas diffusion layer (GDL) where H₂ gas flows through. At the other side of the membrane is the liquid diffusion layer (LDL) where aqueous HBr and Br flows. The ratio HBr-Br depends on the state of charge of the battery. **Figure 2** reveals one way of the battery, charging or discharging depends on the polarity of the battery. The chemical reaction also goes the other way. A proton exchange membrane (PEM) separates the two fluids in the battery cell. A

Von Ing. Detlef Jannes, M. Sc., Akademischer Mitarbeiter, EU Forscher, Dr.-Ing. Frank Bauer, Bereichsleitung Dichtungstechnik & StutCAD, Dipl.-Ing. Lothar Hörl, Oberingenieur Dichtungstechnik I Institut für Maschinenelemente (IMA) Universität Stuttgart | www.ima.uni-stuttgart.de

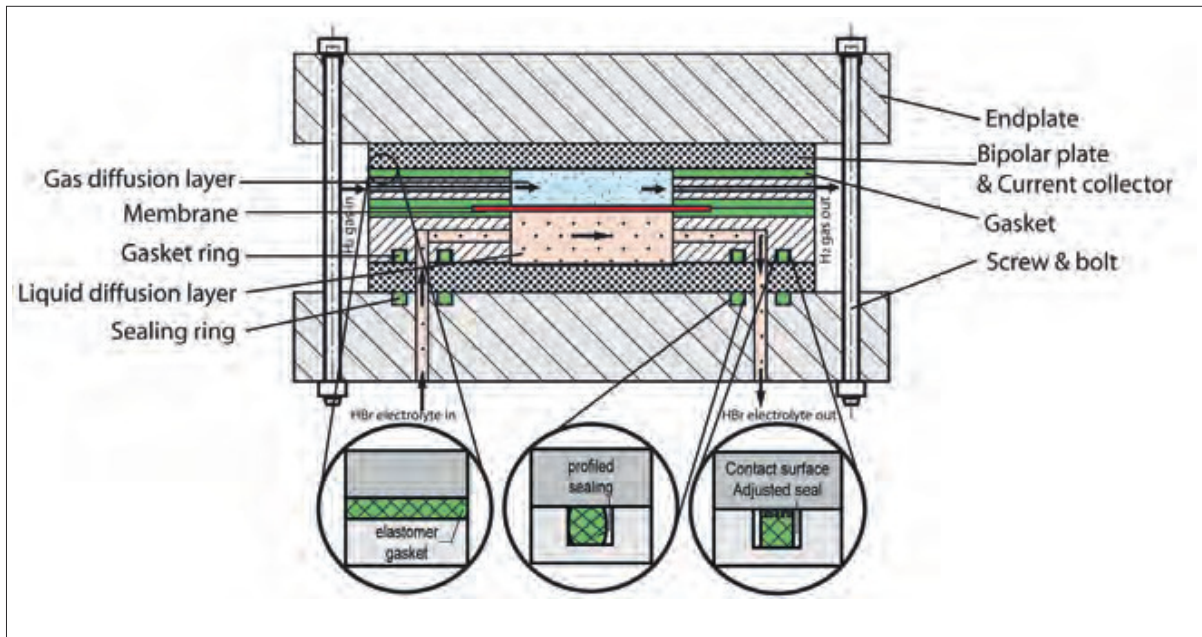


Figure 1: crosssection: breakdown structure of a HBr RFB cell with different sealing concepts (Fig.: IMA)

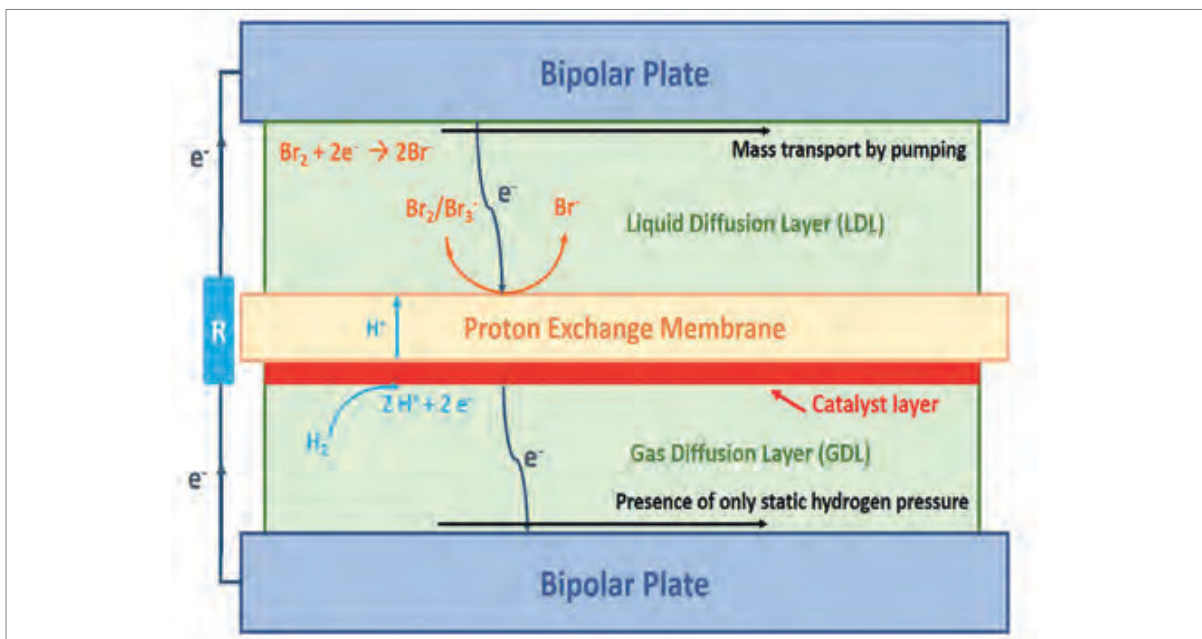


Figure 2: Sketch of the redox reaction inside a HBr RFB cell (Fig.: Elestor b.v.)

common composite material for these RFB membranes exists of woven reinforcing polyether ether ketone (PEEK) covered in a resin of perfluoro sulfonic acid (PFSA). This is a critical component, which needs to be taken into account when leakage occurs. Leakage also happens because of crossover through the membrane, but this phenomenon is not in the scope of this research.

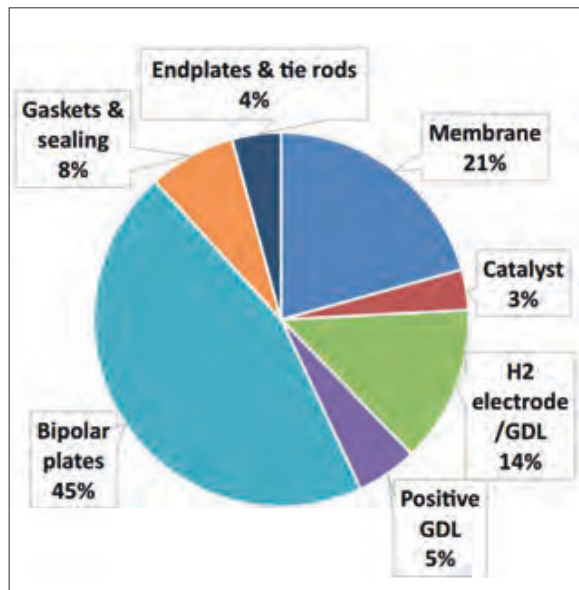


Figure 3: Stack cost breakdown for a HBr design (Source: [1])

The focus lays on elastomer gaskets and seals, which are placed between the membrane and electrodes and between the flow frame and bipolar plate. Sealing rings are mounted at the inlet and outlets of the endplates, flow frames and pumps. It is critical that at all these locations leakage remains minimal. The meaning of compatibility has different answers. Depending on the application, a seal has to withstand all environmental effects. Alternatively, in such a way that it is acceptable for the application to function well for a certain timespan. Realise that zero leakage is not possible, for example there will always be leakage of H₂-gas due to permeability of

materials. The chemical compatibility of the seal is in correlation to the mechanical properties. The electrolyte has influence on the seal, which may be acceptable as long as it does not shorten the lifespan of the redox flow battery. It is of impeccable importance that the seal remains functional in this application. Adequate leakage of H₂-gas near a heat source is flammable. Evaporated bromine and H₂-gas are poisonous. Although bromine has a very distinct salty smell, but H₂-gas is odourless. Leakage of the acid electrolyte creates damage to the whole RFB. Without proper precautions for this possibility, safety cannot be assured. It is even possible that minor leakage rate such as leakage class L_{0,01} (0,01 mg/m·s) has such effect, in time the results can be devastating. Leakage could create short-circuits, corrosion of other components or loss of all electrolyte. Although the elastomer gaskets and sealing rings are minor costs in RFB, failure due to improper design and material selection bring unexpected costs if other components are damaged (**figure 3**). Developers of HBr redox flow battery work mostly with fluorinated elastomers (FPM) because of its universal chemical stability. Although leakage still frequently occurs after some time, especially in thin stacked designs it becomes a dreadful problem.

ISO 1817 submersion tests in electrolyte

Research on the long-term behaviour of these elastomer samples due to chemical attack is required, because trustful seals must withstand the electrolyte for multiple years. We tested the material in harsh environment, it needs to withstand adequately 99,9% Br₂ and 2M HBr – 1M Br. According to the DIN ISO 1817 [2], the submersion must be in multiples of 7 day (± 2 hour's tolerance) for long term. To perform mechanical tension testing after sub-

mersion, the shape is set as dumb-bell according to ISO 37 type 2 [3] with a thickness of 2mm cut out from elastomer sheets.

Critical chemical compatibility submersion testing is best done at higher temperatures for this system. This shows a better long-term behaviour by speeding up the reaction process, if there is any chemical impact. For applications where the seal needs to work for many years this is beneficial instead of testing for many years. The Arrhenius equation states that higher temperature have an exponential effect of the reaction rate. Although be aware that bromine can be very dangerous and difficult to work with, so include safety preparations. Bromine has a boiling point at 58 °C and is very corrosive, so for practical and safety reasons, the submersion test in this research is performed at 50 °C. The maximum working temperature of these hydrogen bromine RFBs should be around 50 °C.



Figure 4: ISO 1817 submersion test of FPM dumb-bells ISO 37 type 2 (Fig.: IMA)

The elastomer plates used, are manufactured longer than 2 months ago. So the samples need to be conditioned. To condition the samples, the ISO 23529 standard applies [3]. It states that the conditioning time for low or elevated temperatures is 10 min. in a relative humidity of 50% for dumb-bell samples. Conditioning is not time-critical, although it is necessary to allow the specimen sufficient time to reach a state of equilibrium. 10 min. is the calculated time needed to reach the specified test temperature with a deviation of not more than 1 K at the centre of the specimen, starting at a temperature of 20 °C. The time required depends on the geometry, material and medium for the heat transfer. For elastomers it is general estimated that the temperature diffusivity is 0.1 mm²/s and the thermal conductivity is 0.2 W/(m·K). The volumetric heat capacity in air is 20 W/(m³·K) [4].

The specimens were completely immersed, so the electrolyte surrounds all surfaces completely and unrestrictedly. The volume of the liquid must be at least 15 times the total volume of the specimens, while the volume of air above the liquid is kept to a minimum. The container should not react with the fluid while at least 5 mm between the container wall and test sample remains. Immediately after submersion, the samples were measured for their dimensions, weight and hardness [2]. FPM samples show enormous swell, they become 2 times bigger and 3 times heavier, but after 7 days the swelling stagnated (**Figure 4**). The hardness changed from 75 ± 5 shore A to 30 shore A in wet condition.

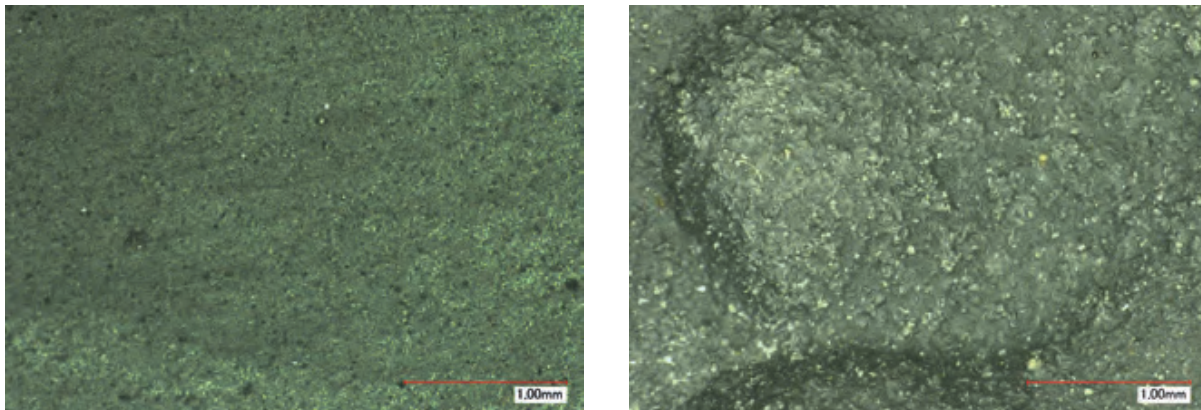


Figure 5: Left: Dry oven at 60°C for 4 hours and rinsed with deionized water. Right: Dry oven 90°C for 1 hours and rinsed with thiosulfate both FPM samples are from the same source, tested according to ISO 1817 in electrolyte, but the right sample underwent wrong after-treatment (Fig.: IMA)

The correct way of drying the samples is to rinse them thoroughly with deionized water and dry in an oven at 60 °C for 4 hours (**Figure 5 left**). The samples should not be cleaned with aqueous thiosulfate. This is a method to neutralise bromine, but unwanted residue forms on the elastomer. Bromine evaporates very fast in the oven due to its low boiling point of 58 °C. Drying on higher temperatures forms vesicles on the FPM samples. Pressure builds up in the elastomer, which leads to plastic deformation on the surface (**Figure 5 right**). The post-submersion mechanical properties of the seal are in such case severely changed; such event would not occur in the battery application.

General composition of FPM and EPDM

Deliberating the theory of the molecular composition and bonding characteristics of FPM and EPDM helps to explain the results of the ISO 1871 submersion test. Chemical crosslinking give elastomer materials high elasticity and crosslinks minimizes viscous flow. In general, hydrocarbon elastomers (**Table 1, line 5**) are cross-linked systems based on sulphur or peroxides. Sulphur is the most common curing agent in the rubber industry. Fluorocarbon elastomers are more complex and demand more curing time to complete successful crosslinks [5]. There are three ways of curing FPM:

- Diamine crosslinking with blocked diamine,
- Ionic cure (Bisphenol AF cross linker) and
- radial cure (peroxide cross linker).

Different curing methods generate different crosslink bonds. Increasing the bond energy also increases the chemical and thermal compatibility. Sulphur cured systems

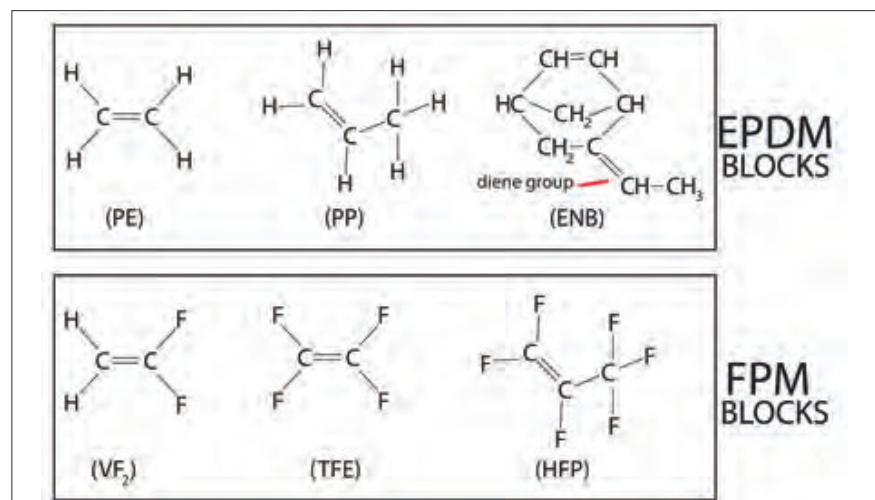
consist of mono (C-S-C), di (C-S-S-C) and polysulfide (C-SX-C) linkages (**Table 1**). With more sulphur in the crosslink, the bonding length becomes longer. Shorter crosslinks result in more tightly cross-linked elastomeric network structure [6]. In the lack of additives, peroxide curing forms (C-C) crosslinks (**Table 1, line 2**). These crosslinks have much higher bonding energy and shorter bonding distance than sulphur curing. Therefore, peroxide curing is according to this theory much more stable; **Table 1** illustrates these different bonding strengths in numbers for these different crosslinks. The values of sulphur and bromine bonded on carbon has almost equal values, this suspects that sulphur curing may not be chemical stable in the HBr electrolyte (**Table 1, line 6**). The reason that fluoro elastomers are so chemical stable is due to the high bonding strength of the fluor atoms on the carbon (**Table 1, line 4**).

1	CH3-O	335 kJ/mol
2	CH3-CH3	368 kJ/mol
3	CH3-S	285 kJ/mol
4	CH3-F	452kJ/mol
5	CH3-H	431 kJ/mol
6	CH3-Br	284 kJ/mol
7	Br-Br	199 kJ/mol

Table 1: Chemical bonding properties of Atoms, Radicals and Bonds related to the elastomers in HBr RFBs [Source: 7]

FPM have two or more blocks consisting mostly of VF₂, HFP and TFE (**Figure 5**). Additional side groups add volume in the structure to prevent the polymer to crystallise. These side groups could exist out of PE, PP and PMVE. The HFP block also helps to increase the amorphous polymer structure; this keeps the chain more rigid and flexible. Bisphenol and peroxide crosslinking are the most common methods for FPM. Biphenol consists of (C-O-C) crosslinks (**Table 1, line 1**). Classic biphenol curing has the presence of Ca(OH)₂, which helps curing, and MgO, which cause scorch problems

Figure 5: EPDM and FPM monomer blocks before polymerisation and crosslinking
(Fig.: IMA)



(premature vulcanisation), but makes better bonding and heat properties compared to diamine curing, although both are ionic reactions [8]. Peroxid crosslinking requires for FPM a cure side monomer (CSM) that holds bromine or iodine. Through the CSM block, the chains can be linked together with free radical reactions [5]. Bisphenol curing happens through the creation of a diene group with dehydrofluorisation [9]. Curing of FPM is not so obvious. FPM is more expensive than EPDM, because manufacturing FPM is more intensive and slower [8].

Ethylene propylene diene monomer (EPDM) elastomers are within the group of hydrocarbon elastomers. EPDM base consists mostly of PE, PP and ENB polymer blocks (**Figure 5**). The ENB block holds a diene group, which creates opportunity for crosslinking. EPDM elastomers are amorphous and nonpolar elastomers [8]. The most common curing methods are sulphur curing and peroxide curing. Sulphur curing requires sulphur, metaloxide (often ZnO) and a vulcanisation accelerator. For Peroxid curing with FPM or EPDM, there is need for activating coagents such as triallyl isocyanurate (TIAC) or triallyl cyanurate (TAC) [9, 10].

Swelling

The samples underwent serious swell during the submersion. After drying the samples, they transformed very close to their initial dimensions. At first sight, it seems no chemical attack occurred. To elaborate swell, assume a model considering elastomers as shaped fluids. Although elastomers seem to be solid after polymerisation, they remain to have some fluid properties. Curing and crosslinking connects the elastomer into a 3D network, a very viscous fluid. Elastomers can easily deform, although it has some shape-memory because of these crosslinks. Issues with compression set and relaxation are due to the slow viscous sliding effect of the polymer chains, these movements create plastic deformation. In the fluid model, elastomers could still thermodynamically mix with other fluids. For example: mineral oil is not soluble in water, but alcohol is soluble in water. This is due to the polarity of the molecules. In the case of RFBs, swelling occurs when the elastomer absorbs the electrolyte; it is mostly reversible by drying the elastomer, evaporation of the liquid. Although it is still possible residue remains within the elastomer, which is not necessarily a sign for chemical attack. Excessive swelling could disrupt the elastomer matrix in such way it loses a lot of strength, even after conditioning. In statical sealing, it can still be acceptable to have swelling rates of up to 50 – 60%, although it still depends on the functionality of the seal in the application [9]. Chemical attack is a more serious concern. In this case, the fluid attacks the molecule structure, first on the surface and through diffusion from the inside. Such chemical attack could be on the structural elastomer, cross-links or on

additional fillers. It is not easy to determine what kind of reaction occurs, especially because the exact composition of the elastomer is unknown. Reverse engineering techniques provides an answer.

In theory, FPM elastomers are polar and are therefore weak against polar solvents like acetone. HBr is by definition a polar acid with an Electronegativity $EN = 0,7$. As a rule of thumb, a molecule is considered polar when the EN value is $0,5$. HBr – Br₂ are considered more polar in aqueous form, ion solvation. Bisphenol curing of FPM holds Ca(OH)₂ and MgO, in this acidic electrolyte, these activators are acidic attractors and increase the swelling rate [9]. Peroxide cured FPM is more stable against such acids due to the lack of such metal oxides, but theoretically also prone to swell in the electrolyte due to their polarity. Mixing FPM with a polar solvent remains the initial elastomer, but with mixed properties. This can have a serious impact on the sealing performance of a redox flow battery, especially in stacked designs with thin layers where mechanical tolerances become the focus point in stack design.

Elastomer Compatibility Index (ECI)

A semi objective way to generate an overview on the mechanical properties of an elastomer after a ISO 1817 submersion is with an ECI (elastomer compatibility index). This creates a baseline for evaluation the effects of the electrolyte on the elastomer. Besides the hardness level, which is in points shore A, the numbers stand in order for following change in % properties compared with the initial elastomer properties: volume, shore A hardness, tensile strength and strain at break.

According to the ISO 37 standard, the tension tests has type 2 samples with a symmetric test length of $20 \pm 0,5\text{mm}$ of the dumb-bell. The samples were cut according to ISO 23529 from initial 2mm elastomer sheets and submerged according ISO 1817. The tensile-testing machine (Instron) follows the ISO 5893 with an operating rate of 200mm/min with a prestress of 0,1 MPa. At least 3 to 4 dumb-bell samples of each material are broken in this specified 20mm test length, incorrect sample breakings were disregarded.

Comparison between line 5 and 6 in **Table 2** show a clear influence of temperature. Some reactions need activation energy so a chemical reaction can commence. Or due to the Arrhenius effect on higher temperature the thermodynamic reactions go much faster. In case of a chemical attack, it is possible it only happens at higher temperature. Because the higher temperature helps the reaction get over the activation energy as long as it is possible through the Gibbs equation, this can also happen with catalysts.

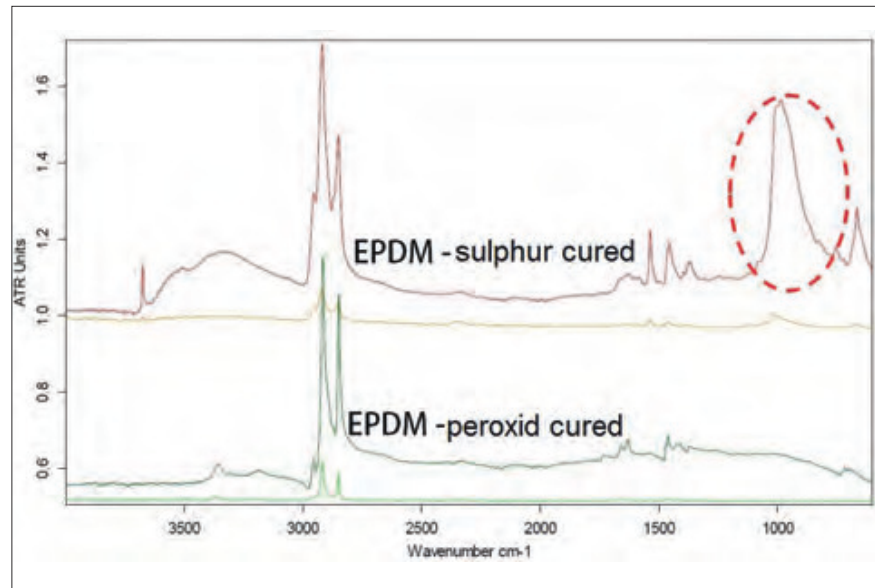
			ΔV	Sh_A	σ_{max}	ϵ_{max}
1	99,9% Br 168h 50 °C	FPM-I	+13	-9	-26	-38
2	2M HBr – 1M Br 672h 50 °C	FPM-I	+33	-10	-42	-64
3	2M HBr – 1M Br 672h 50 °C	FPM-II	+15	-9	-21	-28
4	99,9% Br 168h 50 °C	FPM-III	+9	-5	-28	+59
5	2M HBr – 1M Br 672h 25 °C	FPM-III	+3	+0	+3	-1
6	2M HBr – 1M Br 672h 50 °C	FPM-III	+8	-15	-19	+74
7	2M HBr – 1M Br 672h 50 °C	FPM-IV	+16	-11	-17	+34
8	2M HBr – 1M Br 672h 50 °C	EPDM-P	+4	-3	-6	+2
9	2M HBr – 1M Br 168h 50 °C	EPDM-S	Experiment terminated due to incompatibility			

Table 2: Elastomer compatibility table of FPM and EPDM samples after HBr/Br submersion and drying (Source: IMA)

Comparing results of line 2 and 6 in **Table 2** it is clear there is something different in the composition of the FPM elastomers. The elongation break of the FPM-III elastomers increases while for the FPM-I elastomers decreases. Reason for most FPM samples to increase in elongation break is that the polar electrolyte penetrates deep inside the polymer matrix so the polymer chains loose some of their cohesive force. The elastomer has new mechanical properties, which agrees with the effect of swelling as a two-fluid model. Because even after drying in an oven, some electrolyte molecules remain attached. The strength may remain relatively stable due to the original polymer strength, because crosslinks remain intact.

A chemical reaction that may occur in all the elastomer samples is the brominisation of the unsaturated groups through electrophilic addition, which in a next step to stimulate additional curing [9]. This can also happen with carbon black fillers, a common compound in elastomers. The presence of surface unsaturation in carbon blacks with aqueous bromine promotes crosslinks between the carbon blacks and elastomer [11]. Material analysis of the initial FPM-I elastomers reveals there is significant more carbon black present compared with other FPM elastomers. This may explain the lower

Figure 6: FTIR-ATR measurement of initial EPDM, sulphur and peroxide cured
(Fig.: IMA)



elongation values for the FPM-I and FPM-II elastomers after submersion. An additional effect of high contents of carbon black filler is the unwanted electrical conductivity, which could be a problem in battery applications [12].

EPDM has two common ways of crosslinking mechanisms, peroxide (-P) and sulphur (-S) curing. EPDM-P has stronger crosslinks than EPDM-S, as mentioned before the process is more complex but the crosslinks are chemically more stable (**Figure 6**).

In a first instance, an ISO 1817 submersion test with an unknown EPDM elastomer in 2M HBr – 1M Br₂ revealed incompatibility. These samples were supposed to be peroxide cured EPDM. Within one week of submersion, the samples showed visual results of chemical attack. Additional research with attenuated total reflectance Fourier transform infrared spectroscopy (FTIR-ATR: Bruker) showed that there was a high peak under the 1000 cm⁻¹ frequency [13]. Energy dispersive X-ray spectroscopy (EDX: Phenom) material analysis revealed up to 5, 20% Sulphur. With these observations it is safe to conclude that the elastomer material underwent a sulphur cured method and that, EPDM-S cannot survive in the electrolyte.

Additional tests were performed with peroxide cured EPDM. The results were remarkable good. EPDM-P showed significant less swell compared with all the FPM samples and is chemically stable in the electrolyte. Also the mechanical properties remain very stable (**Table 2**). EPDM is very permeable to gasses [7], compared to FPM this may be a downside for sealing of the GDL.

Conclusion

Various curing systems and elastomers are analysed to conclude what the effects of HBr electrolyte has on EPDM and FPM elastomers. Designers select in general for FPM because of its excellent chemical resistances, but the submersion test revealed that this might not be the best choice of sealing material. Both elastomers seem to be acceptable, but it is wrong to underestimate the effects of additive fillers and coagents for chemical compatibility. Especially the curing system has an impact on the chemical compatibility. Sulphur cured EPDM is not suitable to seal HBr RFBs. Bisphenol cured FPM leaves unwanted metal oxides, which accelerates swell. As a recommendation, it is interesting to use FPM and EPDM-P in the design of an HBr redox flow battery. FPM has much lower gas permeability and is chemically inert; it is a good sealing material on the gas-side. Be wary of crossover of electrolyte liquid through the membrane towards the gas-side, this could still lead to swell of FPM. Such swell may be acceptable, but if this elastomer lays on the bipolar plate, it can create uneven distributed contact pressure. Brittle bipolar plates can crack, which leads to significant costs on the redox flow battery. On the liquid side, it is wise to use EPDM-P. It holds its mechanical properties even when it remains in contact with the electrolyte for a long time. EPDM is in general much cheaper than FPM elastomers. Nevertheless, sustainable sealing performance needs additional research on the mechanical design of the redox flow battery. For all good reasons, it is wise to work close with elastomer manufacturers, consult their experts for tailored advice on a sealing application. Elastomer retailers may be cheaper, but their service may be of unacceptable quality, incorrect and insufficient information.

Grant Agreement



This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie Grant Agreement no. 765289

<https://www.flowcamp-project.eu/>

Project coordinator: Dr. Peter Fischer | peter.fischer@ict.fraunhofer.de | +49 721 4640891

References

- [1] Journal of The electrochemical Society, Volume 163, issue 1, A5049-A5056 (doi: 10.1149/2.0071601jes)
- [2] Elastomer, vulcanized or thermoplastic – Determination of the effect of liquids (ISO 1817:2015)
- [3] Elastomer, vulcanized or thermoplastic — Determination of tensile stress-strain properties (ISO 37:2011)
- [4] Elastomer – General procedures for preparing and conditioning test pieces for physical test methods (ISO 23529:2010)
- [5] Taguet, A.; Ameduri, B.; Boutevin, B. (2005). Crosslinking of Vinylidene Fluoride-Containing Fluoropolymers. Springer-verlag Berlin Heidelberg
- [6] Nah, C.; Kim, S.G.; Jeong, B.; Ahn, J. (2015) Effects of curing systems on the mechanical and chemical ageing resistance properties of gasket compounds based on ethylene-propylene-dienetermonomer rubber in a simulated fuel cell environment. Elsevier
- [7] L. Cottrell, T.L. (1958). The Strengths of Chemical Bonds, Butterworth
- [8] Nagdi, K. (2002) Gummiwerkstoffe ein Ratgeber fuer Anwender. Dr. Gupta Verlag
- [9] Lückmann, M.; Steinhoff, W. (2014) Crosslinking of fluoroelastomers and the influence of final properties, Dupont
- [10] Yoon, J.R., Tsukahara, Y., Kohjiya, S. (1995). Effect of Bromination on EPDM curing behavior and its tensile properties. Departement of Materials Science, Institute of Technology Kyoto
- [11] Puri, B.R.; Bansal, R.C. (1966). Studies in surface chemistry of carbon blacks part III. Interaction of carbon blacks and aqueous bromine. Department of Chemistry, Punjab University
- [12] Hansen, R.S.; Test, R.E (1961), Acid-base properties of carbon black surfaces. Ames Laboratory, Iowa State University
- [13] Coates, J. (2006). Interpretation of infrared spectra, a practical approach. John Wiley and Sons Ltd.