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Chapter

Key Components in the Redox-Flow Battery: Bipolar Plates and Gaskets – Different Materials and Processing Methods for Their Usage

Thorsten Hickmann, Toni Adamek, Oliver Zielinski and Thorsten Derieth

Abstract

Graphite filled thermoplastic based composites are an adequate material for bipolar plates in redox flow battery applications. Unlike metals, composite plates can provide excellent resistance to the highly aggressive chemical environment at elevated temperatures in combination with an electrochemical potential in battery operation. The chapter therefore gives an overview of the most important requirements for the graphite-plastic composite material and thus also for the bipolar plates, as well as the different characterization methods of the bipolar plates. In the following, both the modern composite materials based on polypropylene (PP) and polyvinylidene fluoride (PVDF) and their general properties are described with a focus on improved long-term stability. Furthermore, recycling is also considered. One section is dedicated to seals, which - as so often - are an underestimated component of redox flow batteries. In this gasket part of the chapter, the most common materials and interactions between gaskets and other stack components are presented, as well as the material properties, characterization and processing methods of the gaskets.

Keywords: bipolar plate (BPP), gasket, graphite compound, composite, graphite plate, polypropylene (PP), polyvinylidene fluoride (PVDF), ethylene-propylene-dien-monomer (EPDM), fluoroelastomer (FKM)

1. Introduction

Redox flow batteries (RFB) are electrochemical reactors suitable for storing electrical energy by chemical reactions [1]. Depending on the technology used, this reaction can take place at elevated temperatures and/or in aggressive media, with an electrochemical potential superimposed. In recent years, the technical requirements on materials and components of the reactor of the Redox flow battery have therefore become more and more demanding. The battery unit consists of many stacked cells which are connected in series to a Flow battery stack. Each cell in turn consists of various components such as the proton exchange membrane, seals, frames and
the conductive bipolar plate which provides the connection from cell to cell up to the end of the stack where the generated current is collected.

RFBs, in particular vanadium redox flow batteries (VRFBs), have now reached a considerable degree of technical maturity and the systems are available on the market through many suppliers. However, due to a high remaining cost structure - partly due to a lack of economies of scale - the profitable market introduction of flow batteries still suffers from a high market acceptance.

On the one hand the membrane is considered the heart of a redox flow battery. On the other hand, the bipolar plate is one of the key components of an RFB. However, the Bipolar plate is important, since the plate has an impact on the complete systems, as far as total dimensions, total weight, thermal and electrical properties of the stack and thus of the system is determined by the bipolar plate technology [2].

As already mentioned, the chemical conditions for the materials used in redox flow batteries are challenging [3]. Most systems are operated between 40°C and 60°C in a liquid of dissolved vanadium salts in sulfuric acid. Besides the Vanadium-technology, there also some other technologies (metallobased or organic RFBs), which will not be further considered.

Due to these harsh conditions, superimposed by an electrochemical potential, graphite-based bipolar plates with polymeric binders are used in almost all applications in these battery stacks. The graphite composite plates are an unbeatable material in terms of stability under the above-mentioned corrosive conditions, and the cost-intensive coated metal plates have no chance.

They have been operated very adequately several times over the years. However, due to an intrinsic fragility caused by a high filling load with graphite, graphite composite plates require a greater thickness than metal plates, resulting in more weight and volume of the stack. From a cost point of view, the membrane is certainly considered the dominant part of the redox flow battery stack. However, the bipolar plates tend to be underestimated both in terms of their technical requirements and, in particular, their contribution to the cost structure.

Graphite composite based bipolar plates are manufactured using highly filled compounds [2]. They contain fillers like graphite and/or other electrically conductive carbons incorporated in polymers performing as a gluing binding matrix. The key challenge is the competing interaction between electrical conductivity - achieved by the carbon component - and mechanical stability as well as liquid tightness which is provided by the binding polymer.

The compounding process is the first step to produce highly filled, electrically and thermally conductive pellets for the subsequently following step of forming bipolar plates.

Both compounding and molding processes, which can be injection molding, compression molding or continuously extrusion, are very sensitive to process parameters and need to be carefully controlled. The objective is to manufacture bipolar plates in large volumes and high quality more or less like standard plastic parts. Only by using price cost attractive materials and the consequent focus on process automation by higher volume, the bipolar plate can contribute significantly to a better market acceptance of RFB.

Besides the bipolar plate, the gasket is a very important component of the battery stack and tends to be heavily underestimated. It plays a key role in the mechanical properties of the stack. Inappropriately selected gasket materials may cause cracks in the bipolar plates or may affect the membrane-structure negatively. Despite the fact that the gasket has to seal the stack, the cooperation with other stack components and their cumulative tolerance effects have to be on focus for the stack design and for the operation of its.
The same which is evident for each component is also obviously for the gasket; they have to be cost attractive. Therefore, in some research projects, it is the objective is to suspend gaskets completely and use welding or bonding processes instead.

Technically, the bipolar plate of a RFB stack has to accomplish the following functions [3, 4]:

- conduct electrical current,
- conduct heat and distribute coolant in a eventually incorporated cooling flow field,
- provide mechanical stability of the stack,
- prevent permeation and leakage

However, the functions of the gasket are completely different. The main functions of gaskets in a RFB stack are [5, 6]:

- sealing and leakage prevention of anode and cathode area,
- sealing and leakage prevention of cooling plates,
- compensate tolerances and dimensional changes during stack-assembling caused by interaction with all stack components.

2. Technical requirements of bipolar plates and gaskets

Based on the technical functions described above, a comparison to other technologies is necessary: The Fuel Cells: The US department of energy (DoE) suggested development targets for fuel cell components as shown in the Table 1 for bipolar plates [8]. Although these data are based on communication and data from

<table>
<thead>
<tr>
<th>Technical property</th>
<th>Units</th>
<th>Targeted value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plate weight</td>
<td>kg/kW</td>
<td>&lt; 0.4</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>S/cm</td>
<td>&gt; 100</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>W/m·K</td>
<td>&gt; 10</td>
</tr>
<tr>
<td>Flexural strength</td>
<td>MPa</td>
<td>&gt; 34</td>
</tr>
<tr>
<td>Shore D hardness</td>
<td></td>
<td>&gt; 40</td>
</tr>
<tr>
<td>Temperature resistance</td>
<td>°C</td>
<td>&gt; 70</td>
</tr>
<tr>
<td>Acid uptake</td>
<td></td>
<td>low</td>
</tr>
</tbody>
</table>

Table 1.
Benchmarks for bipolar plates in redox-flow applications defined by DoE [7] and experiences from customer requirements from Eisenhuth GmbH & Co. KG.
conventional low temperature PEM fuel cell developers, most of the targeted values can be directly transferred to Redox-Flow technology.

Additionally, the chemical resistance of the bipolar plate can be characterized by measuring the corrosion current under a potential typical for RFB and using sulfuric acid or something suitable (depending on application as an electrolyte). The detailed parameters and development objectives of this corrosion test are still subject to technical discussions and depend on the anticipated application of the plate. A similar table of functional requirements can be set-up also for gasket materials in RFB.

The gasket material has to be resistant against the selected electrolyte and environment under operating conditions. This is qualified for example by comparison the mechanical properties of recently produced and altered samples. It has to be noted that the values mentioned in Table 2 are for orientation and refer to standard elastomer materials available on the market. Based on these technical requirements, an appropriate feedstock respectively materials for both bipolar plates and gaskets have to be selected.

### 3. General concepts of bipolar plate manufacturing

As mentioned above, composite bipolar plates consist of a binder polymer, which is highly filled with a conductive carbon component. Typical compositions are >80 wt.% conductive filler and < 20 wt.% binder polymer. Compounding, processing and manufacturing is substantially different from conventional polymers due to the high content of filler material in the compound [10]. The function of the carbon filler is to provide electrical and thermal conductivity.

Therefore, a three-dimensional percolating carbon structure is required. Usually, the main carbon component of the plate is synthetic graphite and the second material is carbon black. For producing plates, several options are possible:
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- Compression molding
- Injection molding
- Plate Extrusion
- Foil Extrusion

In all methods, after removal from the process certain after treatment procedures may be necessary. Either to remove the ‘skin’ of the mold release agent from the surface of the plate or as noted in Derieth et al. [9, 10] to remove an accumulation of polymer from the injection. Or compression molding skin.

3.1 Binder polymers

In general, two different concepts of polymer binders can be applied in bipolar plates. First, the binder material can be polymerized or cross-linked in-situ in the composite during molding of the plate (resin method). The used polymer is thermosetting, which provides good mechanical properties at elevated temperatures and often a relatively easy processing [11].

Second, a thermoplastic polymer material can be used in the compounding process (thermoplast method). Since the most materials in RFB are thermoplastic materials, in the following the focus will be also in this consideration. The polymer has to be selected with sufficient chemical, mechanical and thermal stability (e.g. data from [11]). Several material candidates are available on the market in high quality and well-defined configurations for different processing methods and applications due to the usage of additives like waxes, minerals or fibers.

Figure 1 shows the well know pyramidal classification for more than a handful of popular plastics.

3.2 Graphite materials and fillers

While graphite is generally the major filler for bipolar plates to achieve a sufficient conductivity, several other carbon additives can be employed in order to boost conductivity properties of the composite material. Examples for such additives are highly conductive carbon nano tubes (CNT), high surface carbon blacks (CB) or multi-layer graphene nanoplatelets [7].

Due to its crystalline layer structure graphite is inherently anisotropic in its physical properties e.g. electrical conductivity or its mechanical behavior. Electrical conductivity is being provided by the mobility of electrons within the graphite layers of each platelet. Contrary to the conductivity along the layers, graphite is perpendicular to these layers an electrical insulator. Thus, the bipolar plate manufacturing process should ‘promote’ different orientations of the platelets forming isotropic physical properties of the macroscopic plate material. Some additives such as carbon blacks are helpful to increase the number of conductive paths in the carbon-polymer-system. The nano-sized carbon blacks do function as a ‘gap-filler’ in the insulating polymeric matrix between the micro-sized graphite particles and this in consequence increases the overall material conductivity significantly [7].

The overall conductivity in a bipolar plate is generated by a three-dimensional percolating network which consists of conductive particles. The carbon-binder system is always inhomogeneous and can be considered as a two-phase system of conductive carbon paths bonded in a polymer matrix as shown in Figure 2. The structure of the material highly depends on the chemical composition and not less
important on the kind of the chosen processing-approach (compounding, molding, extruding...) and the therefore used parameters. The complete processing chain – from the raw material to the molded plate – has to be carefully controlled to ensure consistency and reproducibility of the bipolar plates.

Carbon blacks can be formed in the gas phase by thermal decomposition of hydrocarbons under different conditions [11] and this results in a broad variety of
materials with differences in surface area, hydrophobicity and conductivity. The different carbon black grades are then available for the adequate application and function.

Keeping this in mind it has to be considered that high surface carbons are more disposed to (undesired) carbon corrosion effects than graphite-based materials, thus their positive conductivity effect has to be balanced against long term stability requirements.

Another important aspect of carbon materials is purity. Since most fuel cell membranes and catalysts are highly sensitive against contamination with iron-ions and other metal residuals, the raw materials for bipolar plates have to be carefully characterized with respect to their contamination level. The carbon or graphite type also mainly determines bipolar plate’s properties like porosity, phosphoric acid uptake or corrosion and hydrophobicity, both regarding the surface and the bulk [11, 12].

3.3 Recycling

At status quo, the amount of waste caused by the production of bipolar plates – an inhomogeneous system consisting of plastic and carbon – is significantly higher when compared to a fully implemented commodity plastic production process [13]. The waste accrues in form of rejects from production, which can be lowered by optimization processes, but also in form of gates, which are necessary for production and dimensioned by material properties. In addition, the systems in which the material is used have a limited lifespan, so the demand of reusage of the parts made of graphite compound or the compound itself is conceivable.

On the other hand, there is the possibility to use secondary materials as feedstock of the graphite compounds to substitute fully or partially the conventional fillers. Conductive fillers like synthetic graphite are valuable resources being produced via different thermal processes, which are similar to other thermal processes e.g. some recycling processes for various other wastes. Some of these processes generate in some degree useful carbon materials [13].
These circumstances and opportunities result in an increasing development of recycling methods with the consequence of a property upgrade of the carbon by combining lower general production costs. In the best case these carbons are suitable for bipolar plates. In Figure 3 the principle of the different recycling opportunities are being described.

4. Characterization data of RFB bipolar plate materials

Certainly, the final criteria of success for any bipolar plate is the in-situ control of performance and stability under real RFB conditions. However, RFB are highly complex systems with numerous sources of inconsistency. Thus, standardized ex-situ bipolar plate characterization is required for material development and quality control. Several test methods are well established for bipolar plates and some are presented below. The list of test methods is not considered to be complete.

4.1 Electrical conductivity measurements (In-plane)

Clearly, electrical conductivity both in-plane and through-plane is one of the most important properties of the bipolar plate. Despite most fuel cell (component) and battery laboratories have access to electrical conductivity testing equipment, by now there is no generally standardized test method for bipolar plates for RFB, and comparing results from different sources can show significant differences, even though the same samples are tested. One of the main reasons may be surface effects and pre-treatment of the sample. As shown in the Figure 4, Eisenhuth has implemented a testing system for this application, which is suited for local in-plane conductivity testing with the option to measure several times at different locations on the plate.

The in-plane conductivity device allows for a conductivity mapping over a sample area of 750x300 mm. Thus, the characterizing of the plates with respect to the degree of homogeneity during production is possible. Conductivity mapping is an important tool both for quality control as well as and furthermore for the material and process development.

For graphite composite plates it is well known that compounding and molding are highly sensitive to process details and may generate inhomogeneous structures on the surface and/or in the inner core of the material. Certainly, the development target is a homogeneous distribution of conductivity with only minimal deviations between different points on the bipolar plate.

For PPG86 and BMA5 or BMA6 plates the compounding and manufacturing process in hot pressing are established and well controlled, and the conductivity mapping shows an even distribution. Irregularities in the conductivity are in some processes unavoidable because of the process-depending-orientation of the particles through different processing influences. For example, in injection molding the filler particles orientate differently from the core to the surface of the produced parts, which results in different conductivities measured In-plane or through-plane. In addition, the regions which will be filled lastly in injection molding show a higher average conductivity compared to the gate region.

A conductivity mapping of a second process example for a PPG86 based plate is shown in Figure 5. This specific plate is produced by plate extrusion. The border area of the plate parallel to the flow direction during the extrusion process seem less conductive.

In terms of hot pressing – a process with a certainly low flow – these described irregularities are more dependent from the overall process stability and experience
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Development in the field of hot pressing by Eisenhuth GmbH & Co. KG in the last years are focused mainly in material research with the aim of reaching higher conductivity, larger plate designs and simultaneously easier production.

In Table 3 technical properties for bipolar plates made by hot pressing are shown. The data is measured with the shown in-plane conductivity measurement.
device and specimen according DIN EN ISO 527 tested on a universal testing device and a microbalance. The comparison between the results shows that the improvement of the standard products from Eisenhuth GmbH & Co. KG has led to an increase of the electrical conductivity from around 75%. But the mechanical behavior seems similar. This is due to optimizing process parameters and periodic testing of new raw materials.

4.2 Qualification of secondary raw materials by thermogravimetric analysis

As described above the material used for the bipolar plates in RFB applications is made out of plastics and conductive fillers like graphite. During RFB operation the bipolar plates are exposed to normal temperatures, such as 40°C. Consequently, all raw materials used for plate manufacturing have to resist approximately 40°C.

Parallel to the shortage of the raw materials, the Vanadium-RFB technology has to compete regarding cost- and technology-aspects to other technologies, in particular with the lithium ion storage technology. Knowing this background, it is more than advisable to look out for alternative materials. Thus, the Eisenhuth GmbH & Co. KG is investigating together with a consortium alternative material sources, in particular from the recycling sector. Two potential processes which produces carbon materials are shown in Figure 6.

Both processes separate carbon in form of agglomerated particles. Tyres consists of rubber filled with carbon pigments to strengthen the material. By the oxygen-less combustion of tyres the carbon will be released and during the pyrolysis process it is being formed to agglomerates.

During methane cracking – a process to produce hydrogen - carbon can agglomerate on particles, which function as. The particles consist of contaminations of the used feed gas or are part of the used catalyst [17].

The samples are called CB-RC for the tyre recycling carbon black and CB-MC for the methane cracking carbon black. Resulting curves of the mass loss over the temperature of TGA from different carbon blacks are shown in Figure 7. Samples of conventional carbon blacks are called CB-C.

The thermogravimetric analysis (TGA) can be used in order to determine the combustion and vaporization temperatures of the materials and allows to quantify the contents of different materials in the compound [19].

During TGA a sample is heated under defined conditions such as gas environment and heating rate. The weight loss as well as the temperature (in correlation to the weight loss) of the sample in the oven is being determined. The TGA is used at Eisenhuth as an instrument of permanent quality control of the process. It also can be used, to get more information about the compound material.

The TGA curves show that the secondary materials contain a high content of ash. The influence of the ash is at that point unknown. At best it does not influence the

<table>
<thead>
<tr>
<th>Technical property values</th>
<th>2018</th>
<th>2020</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PPG86</td>
<td>BMA6</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.8</td>
<td>2.1</td>
</tr>
<tr>
<td>Electrical conductivity (Ω/cm²)</td>
<td>96.2</td>
<td>192.3</td>
</tr>
<tr>
<td>Flexural strength (MPa)</td>
<td>21.1</td>
<td>31.8</td>
</tr>
</tbody>
</table>

Table 3. Technical properties from databases from Eisenhuth GmbH & Co. KG.
Figure 6. Principle of producing carbon black and graphite from used tires (A) and in a hydrogen production in a methane cracking process (B) [13, 16, 18].

Figure 7. TGA data from different carbon blacks. Conventional CB (CB-C) and CB from secondary sources (CB-MC and CB-RC) are compared. The differences in combustion temperatures and contents of ash are significant.

<table>
<thead>
<tr>
<th>Carbon black type</th>
<th>Average combustion temperature / °C</th>
<th>Rest mass (Ash) / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB-C-I</td>
<td>784.4</td>
<td>0.13</td>
</tr>
<tr>
<td>CB-C-II</td>
<td>691.4</td>
<td>0.29</td>
</tr>
<tr>
<td>CB-MC-I</td>
<td>684.7</td>
<td>8.66</td>
</tr>
<tr>
<td>CB-MC-II</td>
<td>666.4</td>
<td>14.86</td>
</tr>
<tr>
<td>CB-MC-III</td>
<td>695.8</td>
<td>10.38</td>
</tr>
<tr>
<td>CB-RC-I</td>
<td>558.4</td>
<td>19.52</td>
</tr>
<tr>
<td>CB-RC-II</td>
<td>541.4</td>
<td>12.45</td>
</tr>
</tbody>
</table>

Table 4. Results of TGA from different CB-types. The CB tested are conventional (CB-C), products from methane cracking (CB-MC) and products from Tyre recycling (CB-RC). The average combustion temperature is at the point of 50% weight loss of the combustible mass.
<table>
<thead>
<tr>
<th>CB used in compound</th>
<th>Filler content / wt. %</th>
<th>Compound conductivity / ( S_{cm} )</th>
<th>Reference conductivity / ( S_{cm} )</th>
<th>CB used in Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB-C-I</td>
<td>78</td>
<td>28.3 ± 2.0</td>
<td>13.2 ± 2.5</td>
<td>None</td>
</tr>
<tr>
<td>CB-C-II</td>
<td>75</td>
<td>12.9 ± 0.9</td>
<td>&lt; 1</td>
<td>CB-C-I</td>
</tr>
<tr>
<td>CB-MC-I</td>
<td>80</td>
<td>11.3 ± 1.2</td>
<td>&lt; 1</td>
<td>None</td>
</tr>
<tr>
<td>CB-MC-II</td>
<td>80</td>
<td>10.6 ± 2.5</td>
<td>&lt; 1</td>
<td>None</td>
</tr>
<tr>
<td>CB-MC-III</td>
<td>80</td>
<td>12.0 ± 1.5</td>
<td>&lt; 1</td>
<td>None</td>
</tr>
<tr>
<td>CB-RC-I</td>
<td>75</td>
<td>8.9 ± 0.7</td>
<td>18.7 ± 0.6</td>
<td>CB-C-I</td>
</tr>
<tr>
<td>CB-RC-II</td>
<td>75</td>
<td>9.0 ± 0.8</td>
<td>18.7 ± 0.6</td>
<td>CB-C-I</td>
</tr>
</tbody>
</table>

Table 5. Results of conductivity measurements from different compounds. Partially consisting of the described CB types from conventional and secondary sources compared to individual references produced parallel the tested compound mixtures.
or at least it has a minor influence on the properties of the compound respectively the plates. In the worst case some critical contaminations are soluble or volatile and will damage the system, in which the material is used. The details are shown in Table 4. The average combustion temperature is extracted from the curves at the point at which 50% of the weight of the combustible mass is lost.

The second that stand out is the difference of the combustion temperatures of the tested CB. A lower combustion temperature under the assumption that the tested materials consists of similar carbon structures is an indication for a higher surface area [20]. It is described that the surface area – normally measured for CB according ASTM D 2414 with dibutyl phthalate (DBP) – has an influence in the percolation threshold and the resulting conductivity of the corresponding compound. The percolation threshold is the small zone in which the compound receives a mayor increase in its electrical conductivity by only adding a very less of filler content [21].

In order to characterize the influence of the different CB types on the conductivity, the secondary CB are integrated and evaluated in various testing and production series to compare the new materials with the current neat carbon black. The Table 5 shows the results of conductivity measurements like described above from different compounds, in which the CB types are used. For comparison individual references from the mentioned testing and production series are listed in the same table. The compounds are made by combining different polymers mostly PP with graphite. Some of the graphite is replaced with the different CB to keep the recorded filler content at the same level for all.

It can be observed that the impact of the secondary CB on the electrical conductivity is noticeable, but far less for CB-MC and CB-RC-types than the qualification by the TGA suggests. The compounds consisting the CB-MC types have a relatively low conductivity compared to standard materials but the reference compound with the same filler content has no measurable conductivity, therefore the CB-MC types seem to reduce the percolation threshold for the filler in the compound. The CB-RC types have compared to conventional CB a smaller impact on the conductivity because half the value of the CB-C-I consisting reference compound with the filler content of 75 wt.% has been measured.

The qualification by the TGA was fitting for the conventional types. Whereas the high differences between the prognosis and the measurement results for the secondary CB types are unexpected and a high level of uncertainty remains. The reason of these differences can be the high content of probably non-conductive contamination or different carbon structures of the particles. Both reasons are possibly responsible for a way lesser combustion temperature during TGA-measurements. The higher the lever of amorphous carbon and impurities so lower the combustion temperature and the achievable level of conductivity.

5. Gaskets application and qualification

Since many years the fuel cell developers invested tremendous efforts in improvement and technological readiness of the core components, such as membranes and electrodes configuration. However, within the last years the gasket material was recognized more and more as an underestimated component. Despite the gasket does not directly contribute to the electrochemical processes, inappropriate gaskets can cause leakages [6].

The increased use and establishment of the systems on the market, primarily among consumers, has resulted in a focus on safety issues during consumption and error sources during mass production.
Common hard gaskets support well defined gaps, however may be compromised in their sealing properties, do not compensate tolerances very well and may put mechanical distortion on the bipolar plates, which can cause cracks or breaking after a long time. On the other hand, with soft gaskets it is more difficult to control the performance of the system cause of limitations in parameters like pressure. These descriptions are analogue to RFB systems.

In general, like the other RFB components the gaskets have to resist temperatures up to 70°C, electrolytes like sulfuric acid or other materials of RFB systems like bromine and contact to electricity. Fluoroelastomers (FKM) and ethylene propylene diene monomer rubber (EPDM) are most likely the materials of choice for several applications.

For certain applications EPDM might be a cost-efficient alternative for systems which can handle the stiffness of this rubbers. The arguments clearly show that gaskets are a highly customized component for each stack manufacturer. For overview, some typical gasket properties for a broad variety of materials are shown in the Table 6.

Along with the rubber materials like silicone (SI), hydrogenated nitrile butadiene rubber (HNBR), EPDM and FKM thermoplastic elastomers (TPE) in form of styrenic block copolymers (TPS), thermoplastic vulcanizates (TPV), thermoplastic polyurethanes (TPU) and thermoplastic polyolefin elastomers (TPO) are listed. These thermoplastic-elastomers have similar properties to rubber but can be processed like “common” thermoplastics and can be softer if required. This has the advantage of easier manufacturing and recycling of the material as well as a broader range for applications.

5.1 Qualification of physical properties affecting gasket production

In order to supply consistent gaskets with appropriate tolerances the viscoelastic properties of the gasket prepolymers and thermoplastics are an important parameter. A low viscosity is beneficial for processing. For plastic materials usually the mold flow rate or mold flow index are specified by the supplier, supporting the manufacturer for plastic parts with processing-relevant- information and –parameters. However, these data are ‘standard data’ and not always compatible with the molding conditions or equipment at the part manufacturer.

In addition, for rubber materials or their pre-polymers and thermoplastic elastomers these data are not available in most cases, because of their impacting

<table>
<thead>
<tr>
<th>Description and Unit</th>
<th>TPS</th>
<th>TPV</th>
<th>TPU</th>
<th>TPO</th>
<th>EPDM</th>
<th>SI</th>
<th>FKM</th>
<th>HNBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness Shore A</td>
<td>2–95</td>
<td>20–95</td>
<td>2–85</td>
<td>65–95</td>
<td>25–85</td>
<td>25–85</td>
<td>50–90</td>
<td>40–90</td>
</tr>
<tr>
<td>Temperature °C</td>
<td>−50 /</td>
<td>−40 /</td>
<td>−40 /</td>
<td>−40 /</td>
<td>−50 /</td>
<td>−70 /</td>
<td>−20 /</td>
<td>−30 /</td>
</tr>
<tr>
<td>Steam resistance</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Oil resistance</td>
<td>++</td>
<td>++</td>
<td>0</td>
<td>++</td>
<td>++</td>
<td>—</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Acid /bases resistance</td>
<td>++</td>
<td>++</td>
<td>0</td>
<td>++</td>
<td>++</td>
<td>—</td>
<td>++</td>
<td>+</td>
</tr>
</tbody>
</table>

Table 6. Gasket material overview with typical physical properties and behavior in system specific conditions used by Eisenhuth GmbH & Co. KG.
viscoelastic behavior. Therefore, Eisenhuth developed a phenomenological test method to characterize polymer materials with respect to processability. In this test, a melt of the used pre-polymer or thermoplastic is pressed into a spiral-shaped mold with a defined pressure under process-relevant temperatures.

The viscous melt flows into the spiral mold and finally stops, when the applied pressure is equal to the ‘back-pressure’ in the mold. The reason therefore is the higher level of the progressing polymerization, vulcanization or solidification of the melt. The length of the helix can be correlated to the viscosity and consequently to the processability. The longer the helix the lower the viscosity. This is helpful to find the processing ranges of materials as far as the viscosity is concerned (Figure 8).

As mentioned, the length of the spiral is a good indicator for the processability. This test has been performed with a variety of potential gasket materials to achieve a data baseline. The values are shown in Figure 9.

The results show that processability depends strongly on the material but different types of the same material have also high differences. Exemplarily shown in the Figure the good processability of some types of thermoplastic elastomer materials cannot be reached by the measured processability of rubber materials.

5.2 Chemical resistance of gasket materials in system specific environments

The processability of the thermoplastic elastomers is convenient but it is necessary to qualify the mechanical and chemical stability of the materials. The called rubbers are commonly used in different applications such as fuel cells and chemical industries, and their long-life behavior is already known.

To ensure the stability of the materials specimen according DIN EN ISO 37 are made and treated in this example in vanadium electrolyte for VRFB applications.

Figure 8.
Spiral mold for characterization processability by injection molding by Eisenhuth GmbH & Co. KG.
The electrolyte is positive charged, so the most aggressive species of vanadium ions is to 1.65 mol/L concentrated in 4 mol/L sulfuric acid. The specimens are treated the same time for around thousand hours and therefore stored in glasses with full surrounding electrolyte. The specimens are tested for tensile strength according DIN EN ISO 37 in a universal testing machine. The resulting Young’s modulus are shown in Figure 10 and are exemplary for the overall changes in mechanical properties of the treated specimens.

It is shown that the stability of the rubbers in the specific environment is good. The modulus is low but there are no major changes measured. In average the thermoplastic elastomers are different to the rubbers. Most of the materials and material types have a higher modulus with low changes. TPU seems not suited for the application, moreover one indication are high changes such as superficial cracks in the surface of the sealing.
6. Conclusions

In this chapter the basics and advantages of graphite bipolar plates could be presented in connection with current research topics at Eisenhuth regarding the reduction of production costs and the related easier market introduction of RFB. Furthermore the suitability of easy to process thermoplastic elastomers as sealing material in RFB was shown.

It was explained that the proposed targets for material properties are not fully achieved, but that progress in materials research is possible. For example, the electrical conductivity of standard materials for RFB could be optimized by about 75% in recent years.

Options to reduce costs through recycling methods and use of secondary resources were discussed. It could be shown that the substitution of commercial carbon types such as synthetic graphite by secondary materials for composite production is possible.

The differences in the processability of rubber types and thermoplastic elastomers were shown by tests in a correspondingly designed injection mold. The chemical stability of some types of thermoplastic elastomers is tested for VRFB.

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Conflict of interest

The authors are part of the company Eisenhuth GmbH & Co. KG, which produces bipolar plates made of graphitic compounds and gaskets for fuel cell, redox-flow battery and heat exchanger purposes.

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