Investigation and evaluation of the aging behaviour of technical materials as a selection criterion for use in zinc-air flow batteries

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Abstract

Zinc-air secondary batteries have the potential to act as electrochemical energy storage devices in broad industrial applications. The main arguments for developing marketable systems are the good commercial availability and environmental compatibility of zinc [1]. A consortium of different companies and scientific institutions is engaged in the development of a scalable zinc-air secondary battery. For the establishment of the system, the concept and all components, such as the gas diffusion electrode as well as the zinc electrode, are being investigated and optimised. In order to achieve a certain marketability of the battery after the end of the project, the plastic-based housing, sealing and current-conducting components are also being examined for their long-term stability and suitability. The system concept has high demands on the chemical resistance of the components due to the alkaline electrolyte in use. The plastics in question are typical housing materials with good chemical resistance, soft sealing materials based on thermoplastic elastomers and compounds highly filled with graphite for current conduction within the battery. To evaluate the materials, comparative studies are carried out with regard to the material properties, such as mechanical stability and electrical conductivity, and the combustion behaviour to assess the aging between newly produced and aged parts. In particular, the compounds highly filled with graphite presumably exhibit side reactions in contact with the active materials used in the system due to unavoidable impurities. This behaviour is also integrated in the evaluation of the raw material selection.

1 Introduction

Fluctuating electricity consumption based on times of day, weather conditions and seasonal differences has been relatively well balanced for decades by oil and natural gas-based electricity generation. However, due to the increasing ratio of renewable electricity generation, the fluctuation in the electricity grid is not only dependent on current consumption and peak loads. To compensate for the increased fluctuation, various energy storage systems are used, of which renewable ones are naturally preferred. Basically, a distinction is made between chemical, electrical, electrochemical and mechanical storage. Electrochemical storage units are mostly batteries, which have longer discharge times and storage capacities than electrical storage units but shorter times and capacities than chemical storage units. This makes electrochemical storage interesting for balancing daily and weekly fluctuations directly at the renewable electricity producers or consumers. [2]

A large number of electrochemical storage systems are being developed and are already in use for the purposes described. Rechargeable zinc-air batteries have been known for decades, but no powerful, compact system has been built and tested so far [3]. In the "ZiLsicher" project, such a system is to be designed, built and operated. In addition to the components that define the storage capacity of the battery, all other components required for the production of the battery are to be investigated and characterised with regard to their long-term stability and suitability in order to get as close as possible to a raw material selection that is suitable for series production.

2 Rechargeable zinc air batteries

Currently, lithium-based batteries are among the most developed and widespread energy storage systems, but for various reasons they are demanding in terms of safety on an industrial scale [4]. The vanadium redox-flow battery is a sufficiently marketable system, but establishment is difficult due to high investment costs [5]. Zinc-air batteries are mostly known in the form of primary batteries, but the system is relatively attractive as a large-scale energy storage system due to its high, theoretical energy density and relatively safe and price-stable components. In the battery, potassium hydroxide (KOH) is used as an electrolyte in which zinc hydroxide ions dissolve. When the battery is discharged, zinc dissolves at an anode, and at the same time oxygen from an air stream is consumed at a porous, two-phase separating cathode. During the reverse reaction, i.e. the charging of the battery, oxygen is generated and emitted in the air stream, while zinc deposits. The reactions are shown in equations (1) and (2). [3]

$$Zn + 4OH^- \rightleftharpoons Zn(OH)_4^{2-} + 2e^- \qquad (1)$$

$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \tag{2}$$
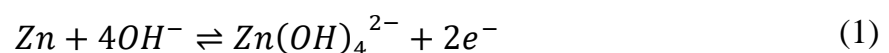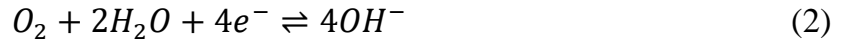
Zinc-air batteries in the form of primary batteries consist of zinc powder in a gel-like structure in combination with the KOH-based electrolyte and an enclosing capsule. At one end of the capsule is the gas-permeable 'gas-diffusion electrode' (GDE). Recharging these batteries is not impossible, but the number of cycles is severely limited. The mechanisms that contribute to passivation of the system and preventing rechargeability, and strategies to weaken this passivation, are sufficiently known [6]. The promising methods to weaken these effects will be brought together in a current project ('ZiL-sicher'-03XP0191E) to design a rechargeable zinc-air battery in the form of a flow-battery stack. A stack describes an assembly of individual flow-battery cells in which the current is conducted through the entire system, which reduces the number of contact points and thus possible weak points for a sealing concept. In flow-battery cells, the electrolyte is not stationary as, for example, in a car battery, but the electrolyte is pumped through the cells, which has various advantages depending on the system.

Construction of stacks requires various components for enclosure and sealing with an optimal mechanical stability for moving fluids, as well as components that enable the conduction of electrons in the stack. All these components should also withstand the electrolyte for as long as possible. A schematic draw of the system is shown in Fig. 1.
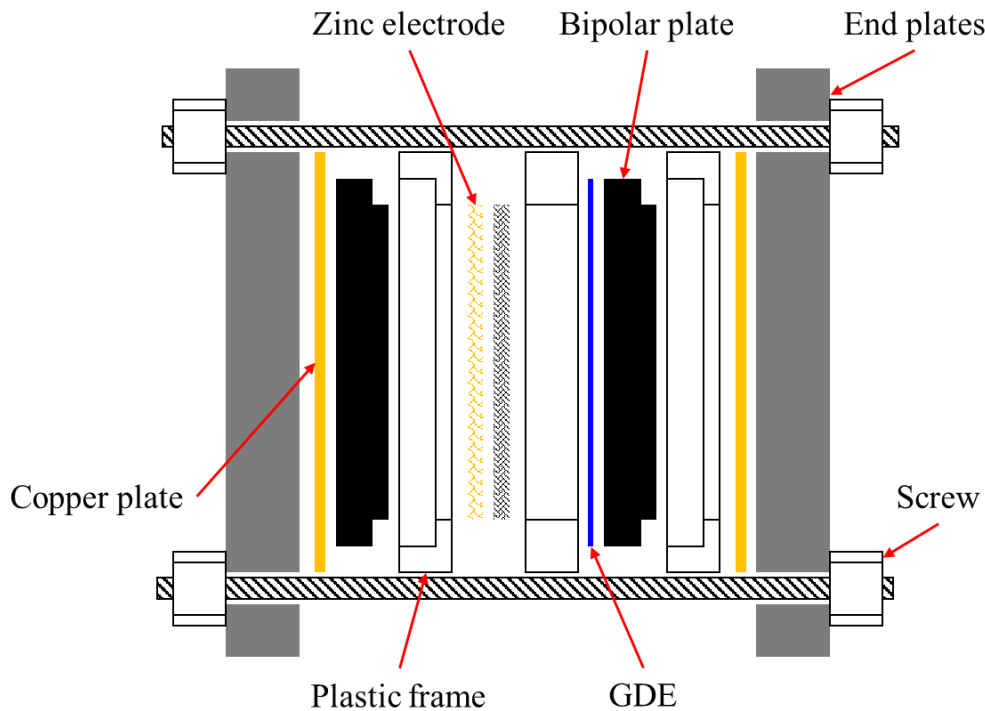

Fig. 1: Schematic structure of a flow stack. Only one cell is shown for simplification.

The stack consists of plastic frames that enclose the electrodes for the electrochemical reactions. The frames have grooves for gaskets in order to maintain a defined thickness during compressing of the assembly. Between pairs of electrodes are the conductive bipolar plates, which are contacted to copper plates at the ends of the stack. The stack is compressed by screwing two opposing end plates made of steel together. On the steel plates are the hose connectors that allow electrolyte and air to be pumped through the stack.

2.1 Bipoplar plates

Bipolar plates act as an electrical link between the individual cells, which enables current conduction within a stack. In this way, the individual cells are automatically connected in series. The aim is to avoid any material transport between the electrically connected half-cells and to keep electrical losses as low as possible. Bipolar plates are used, for example, in fuel cells and vanadium redox-flow batteries. A list of bipolar plate materials is shown in Tab. 1 [7].

Tab. 1: Listing of bipolar plate materials with advantages and disadvantages. [7]

Materials	Advantages	Disadvantages
Pure metals and alloys	-fairly low electrical resistance - high mechanical strength	- low corrosion resistance - high value of contact resistance - high density
Metal-coated metals		- a variable coefficient of thermal expansion - high density
Graphite	- low electrical resistance - high corrosion resistance	- low mechanical strength - high permeability - additional processing for flow-fields
Graphite-polymer-coated metals	- relatively low electrical resistance - high corrosion resistance	- long preparing and processing periods - high temperature production - high cost production
Graphite compounds		

Table 1 shows that metal and graphite materials are used. Depending on the system, the choice is limited due to increased corrosion or lack of mechanical strength at the required thickness of the plates. Since many metals react with potassium hydroxide or will be electrochemically active, graphite bipolar plates are being tested.

2.2   Electrically conductive thermoplastic-compounds

Graphite bipolar plates can be made of pure graphite or, in combination with plastics, of a conductive compound. Graphite has a conductivity of about 1500 S·cm^{-1} [8]. A compound bipolar plate has only a fraction of this conductivity, which is dependent on the degree of filling of conductive particles as well as the shape of these particles. This dependence is called the percolation curve or percolation threshold. The conductivity of the compound increases very slowly with a lower filling grade, since a random as well as homogeneous distribution of a small amount of particles in a plastic matrix creates only a few conductive paths. However, above a certain threshold of the filling level, the probability for the formation of conductive tracks and thus the conductivity increases rapidly. This behaviour is illustrated in Fig. 2. [9]
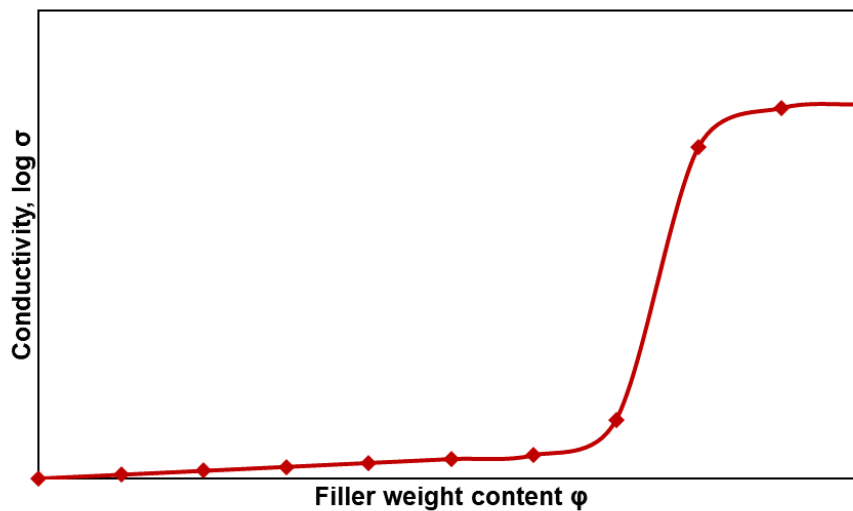

Fig. 2:   *Illustration of the percolation threshold. The principle dependence of the conductivity on the degree of filling of conductive particles in a plastic matrix is shown.*

3   Evaluation methods

The mechanical and electrical properties are used as a basis for evaluating the suitability of the different materials in their respective functions. The results of the property measurements allow a comparison between samples that have been in contact with the electrolyte in stationary aging, freshly produced samples and samples that have been reserved in normalized storage conditions. Further methods, such as thermogravimetric analysis (TGA) and microscopy, are used to interpret possible changes in properties.

3.1   Mechanical stability and electrical properties

A universal testing machine Inspecttable from Hegewald&Peschke is used to evaluate the mechanical and electrical properties of the samples. The strength of the housings and sealing materials is determined by tensile tests based on DIN EN ISO 527 [10] and

DIN EN ISO 37 [11]. The electrical properties are measured with the aid of a specially manufactured attachment for the machine. The set-up is shown in Fig. 3 [12].
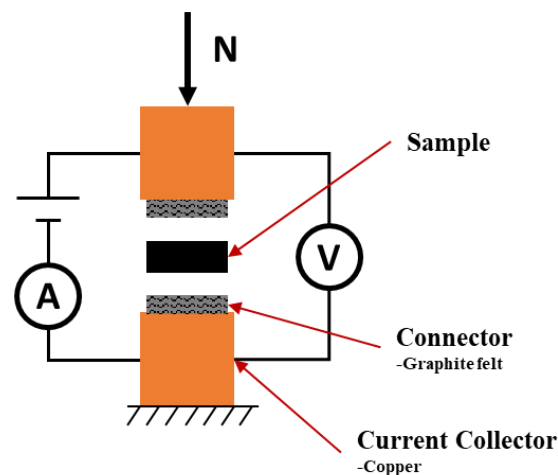

Fig. 3: Schematic representation of the test set-up for measuring the electrical properties of conductive thermoplastic compounds.

The current collectors are connected to resistance meter from Hioki and the resistance is recorded over time. By using the universal testing machine, it is possible to run different pressure-time curves and to regulate the compression of the test specimen. Here, the characteristic value of the electrical property is the specific resistance, which is read at a compression pressure of 10 bar and an instability of the measured value of <5 % with the described testing device.

3.2   Thermogravimetric analysis

For the thermogravimetric analysis, a thermo-microbalance TG 209 F3 from Netzsch is used. This device offers the advantage of providing a qualitative assessment of the melting and combustion temperature via the so-called c-DTA method [13]. The TGA is an analysis method, in which a curve of weight loss of a sample is recorded other time during heating of the sample. The TGA allows to verify the mixing ratio between the plastic and the graphite, because of the high difference of combustion temperature, as well as to approximately identify the sort of polymer and graphite by direct comparison of the combustion behaviour with the TGA results of the presumed material [14, 15]. The progress of combustion at certain times as well as the data output by the c-DTA should be compared in order to draw conclusions from the differences identified during the property measurement. The progress of combustion is shown as the first derivative of the TGA curve (DTG). A visible change in the plastic matrix in the conductive compounds or the specimens of the housing and sealing materials in the TGA can be used to interpret the other test methods.

3.3 Microscopy

An optical method is used to assess the surface structure, primarily for the graphite compounds. When using a Keyence VHX 2000, the surface roughness can be assessed and the distribution of various particles in the plastic matrix can be evaluated by using a polarisation filter. It is believed that the leaching of impurities in the graphite compound as well as the gas evolution occurring at these particles has an influence on the surface structure or quality. [16]

4   Experimental set-up

According to databases of e.g. Bürkle GmbH or Reichelt Chemietechnik GmbH & Co., the polymers PP, PE and PA as well as some types of rubber such as EPDM are generally classified as stable to potassium hydroxide solutions [17]. The behaviour of the engineering plastics based on the polymers can be similar, but different additives and fillers in the plastics also lead to a change in the chemical resistance. Aging tests on finished parts or test specimens are therefore a well-known method used by e.g. manufacturers of plastic parts [18] to ensure the suitability of plastics from certain suppliers.

4.1 Production of specimens

Depending on the type of material to be tested, different manufacturing methods are used for the specimens. The materials for the housings are injection-moulded using a 75 t injection moulding machine from Engel AG in the form of the Specimen A1 described in DIN EN ISO 527. The sample materials are PP, PE and PA brands that are already used in battery applications and are therefore expected to have the highest possible long-term stability in the electrolyte of the zinc-air battery.

The sealing materials are hot-pressed into foils and test specimens of type AB described in DIN EN ISO 37 are cut out of the foils. The materials examined are rubber types that are known to have very good resistance to potassium hydroxide solutions, as well as various thermoplastic elastomers whose resistance to potassium hydroxide solutions is not explicitly described [17].

The conductive graphite compounds are specially produced. Different twin-screw extruders are used for this, depending on the plastic. In the twin-screw extruders, plastics such as PP, PE or PPS are mixed with different graphites. The resulting compound in the form of pellets is shredded and ground to produce plates of about 3 mm thickness in a hot pressing process. The plates are face milled and test specimens are milled out. These are discs of about 13 mm in diameter. The raw materials have already been proven themselves in vanadium redox-flow batteries, which have a high tolerance for impurities, and fuel cells, which have only a low tolerance for impurities in comparison.

4.2   Aging of samples

The samples are aged in closed vessels in 30 wt.-% potassium hydroxide solution. The compound samples are additionally aged in potassium hydroxide solution to which 1 g of zinc per 20 ml of electrolyte is added. The temperature is kept at 22±2 °C. The sealed vessels are kept under a fume cupboard. The reserved samples are stored in PP bags under similar conditions. Several vessels are prepared for one type of material in order to open them at different times. Before removal from storage, the corresponding samples are lightly cleaned and dried before measurements. In addition to the test methods described above, dimensional and weight changes are also recorded.

In the case of the housing plastics, aging is carried out in two stages. After 5 months (5M) and after 10 months (10M), samples of each type of plastic are taken and tested. The compound samples remain in the two solutions for 2 months.

5   Stability of thermoplastics in KOH electrolytes

Visually, the aging samples have not changed. Differences in weight and dimensions are not noticeable with the equipment used. To illustrate the results of the TGA, the melting and combustion temperatures determined via the c-DTA are given in Tab. 2 and exemplary DTG curves are shown in Fig. 4.

Tab. 2:   *Averaged results of the TGA. Values for the melting and combustion temperatures are determined on the basis of the c-DTA curve. Presented are the different samples aging in KOH and the reserved sample stored at air.*

Material	Sample	Melting / °C	Combust / °C
PA	Reserved	244.1	351.1
	5M	246.3	343.0
	10M	247.2	333.9
PE	Reserved	127.6	255.7
	5M	127.7	252.4
	10M	126.6	251.7
PP	Reserved	156.2	233.8
	5M	156.2	230.5
	10M	156.4	234.9

[a] Onset of c-DTA on an identifiable Peak

The c-DTA signal recorded during the TGA is evaluated with an onset plot at the locations of recognisable and identifiable peaks of the melt and combustion. The changes in the values during the two stages of aging are compared with the values of the reserved

samples and the values of the samples tested immediately after manufacturing as reference, like described in chapter 4.2. The comparison to the reserved samples is made to examine the possible changes in properties of the plastic at air. Because of the system, in which the materials should be used, the plastic parts are exposed to different environments. So mayor differences of changes in properties depending on the location can possibly occur, which therefore get additional inner stress in the plastic parts.
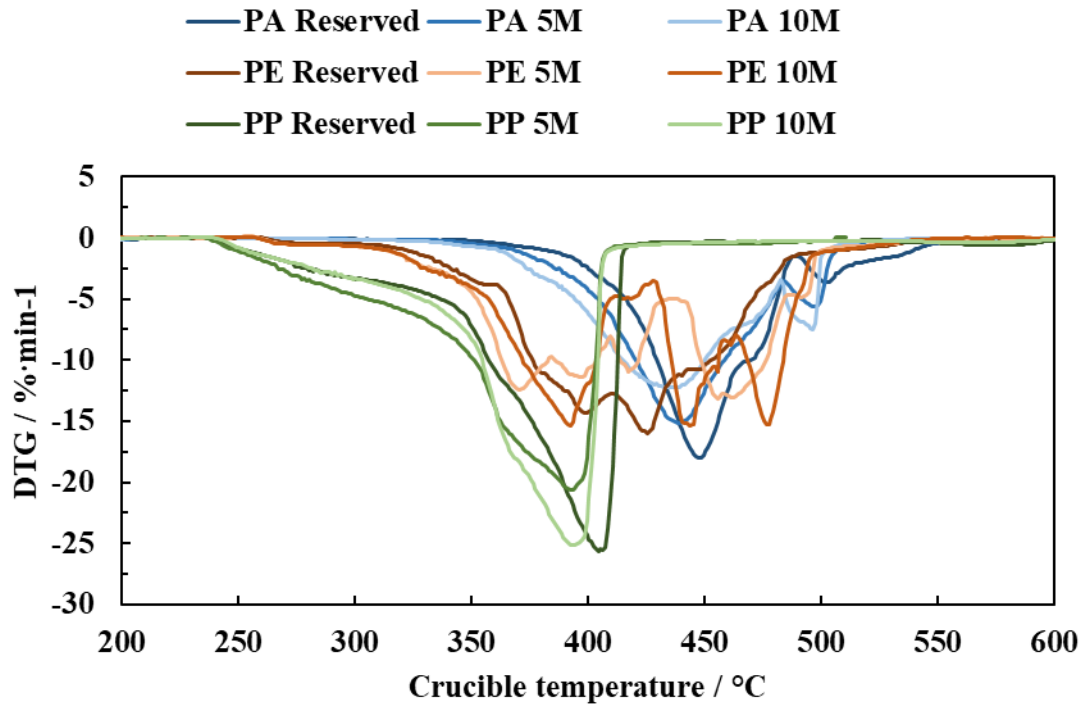

Fig. 4: *Exemplary results of the DTA on housing materials to show the changes in the materials as a function of the aging time. Samples are compared that have been stored for 10 months in air (reserved) and aged for up to 10 months (5M, 10M) in KOH.*

Representative of the mechanical stability of the test specimens, the tensile modulus (E), the tensile strength (σM) and the elongation at yield (εM) are shown for the tested plastics in Fig. 5. The results are compared to the manufacturer's specifications of the different materials.
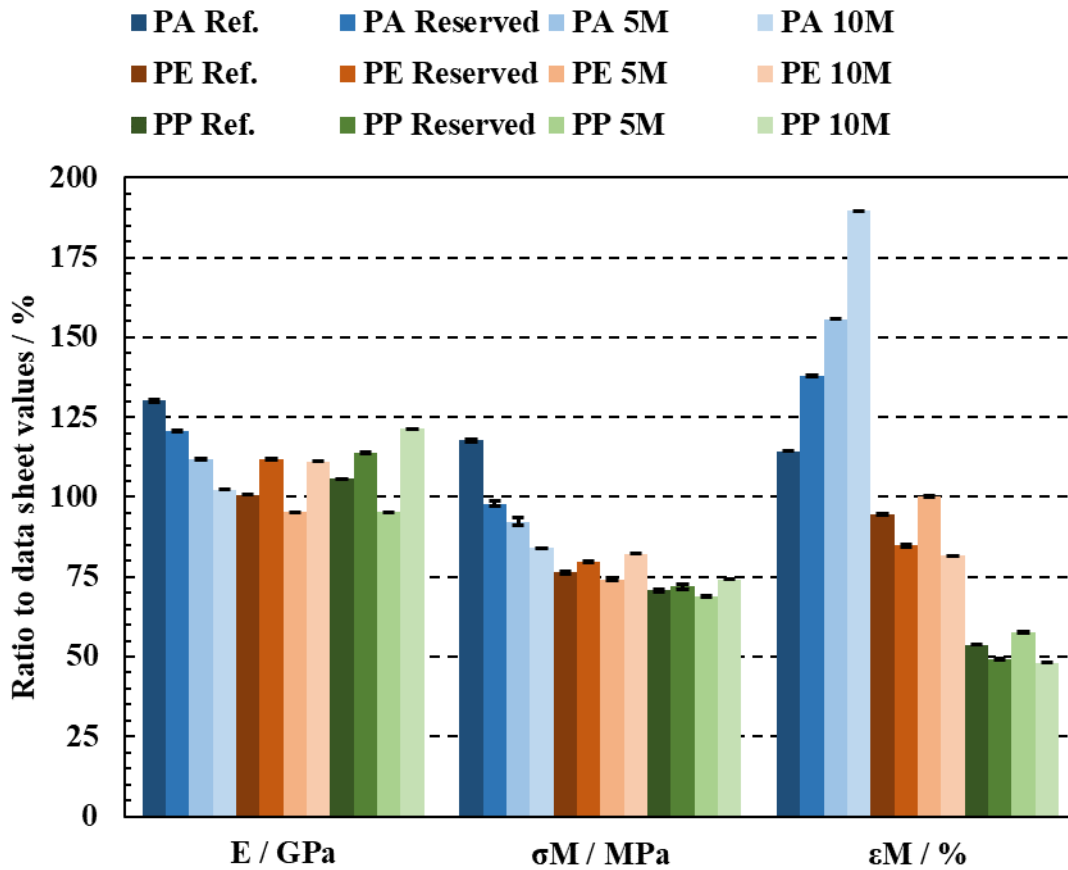
Fig. 5: *Results of tensile tests on casing materials. Samples are compared that have been freshly manufactured, stored for 10 months and aged for up to 10 months.*

Through the qualitative control of the components of the plastics by the TGA, it is assumed to verify and interpret the results of the tensile test. The PA-based plastic shows the highest impairment of strength within the samples, which is clearly reflected in the temperatures shown. The changes are clearly greater when the plastic comes into contact with the electrolyte and when the sample is exposed to it for a longer period of time. Differences in the melting and combustion temperatures of similar plastics may indicate, for example, a different degree of polymerisation or different filler compositions. PP and PE show similar changes in the measured properties. The change in mechanical stability and the melting and combustion temperature is not clearly dependent on the aging time and the lifetime of the specimens. The DTG of PE show an increased separation in the combustion peak for the aged samples. The DTG of PP show a similar behaviour but less distinct. It seems, that the polyolefin plastics show a curing behaviour in KOH, which limits their use as housing material less than the softening of the PA-based plastic.

6 Leaching and gas evolution by electrical conductive compounds

Due to the production methods and origin of the usable raw materials for the conductive compounds, they contain variable proportions of metals and metal combinations as impurities, which are classified as interfering substances depending on the application. Zinc shows dissolution behaviour when in contact with KOH, which results in the emission of hydrogen. This reaction can be accelerated by different substances in contact with the zinc, which not only reduces the efficiency of zinc-based batteries, but is also relevant in terms of safety. [19]

Graphite has a high overpotential compared to hydrogen evolution, so the conductive filler has no expectable influence on the amount of hydrogen evolved. The possibility and quantity of impurities in the filler, on the other hand, is potentially an exclusion criterion for specific raw materials or raw material suppliers. All investigated samples show a strong gassing behaviour at the beginning (a) as shown in Fig. 6.
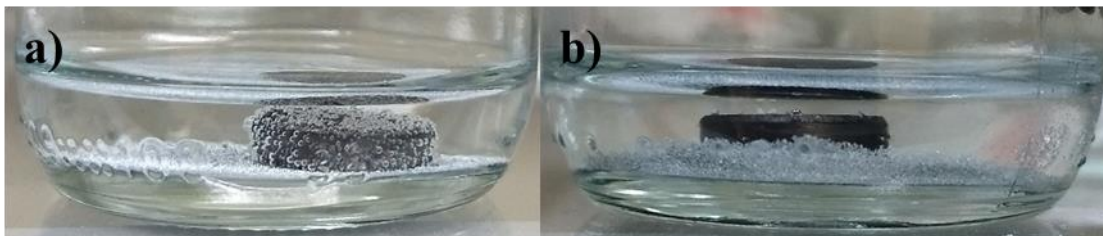
Fig. 6: Exemplary photographs of samples of conductive compounds produced from different plastics but identical graphite mixtures: a) Compound 01 after 2 months; b) Compound 05 after 2 weeks of aging.

However, some of the samples stop doing this over time, as shown in Fig. 6 (b), so it is assumed that most of the impurities on the surface have gone into solution and at the same time the plastic matrix does not undergo any particular changes on the surface. If the plastic matrix swells or decomposes, further impurities are likely to be exposed, which ultimately results in a steady hydrogen evolution. A list of the observations on the samples can be found in Tab. 3, as well as the measured resistances and roughness of the specimens. While the measured resistances indicate only slight changes in the compounds, the samples change relatively strongly on the surface due to contact with the solution. Compound 05 appears to be the most resistant. The arithmetical mean deviation of the assessed profile (Ra) and the average of maximum peak to valley height at several measurement points (Rz) remain stable for this material, whereas other materials show deep holes in the surface that deepen during exposure to KOH, as mainly the Rz values increase significantly. Examples of the surface differences between compound 05 and the others are shown in Fig. 7. Compound 05 is also the only one of the tested compounds to show only slight to no gassing after a short time of exposure.

Tab. 3: Listing of results of electrical conductivity measurement and optical roughness measurement.

Compound	Resistance / mΩ·cm			Roughness / µm						Gassing[a]
	Ref.	KOH	KOH/Zn	Ref.		KOH		KOH/Zn		
				Ra	Rz	Ra	Rz	Ra	Rz	
01	65 ± 2.6	67	60	0.7	4.9	0.9	10.1	1.3	12.3	x
02	43 ± 2.6	50	38	0.6	2.5	0.8	4.3	0.6	4.8	x
03	37 ± 0.8	52	37	1.2	9.5	1.0	11.3	0.9	17.7	x
04	65 ± 3.4	69	54	0.9	4.8	0.7	6.0	0.8	5.5	x
05	55 ± 5.0	49	51	0.4	2.0	0.4	2.3	0.4	2.0	o
06	43 ± 4.8	45	35	0.5	2.2	0.8	6.3	0.7	4.0	x

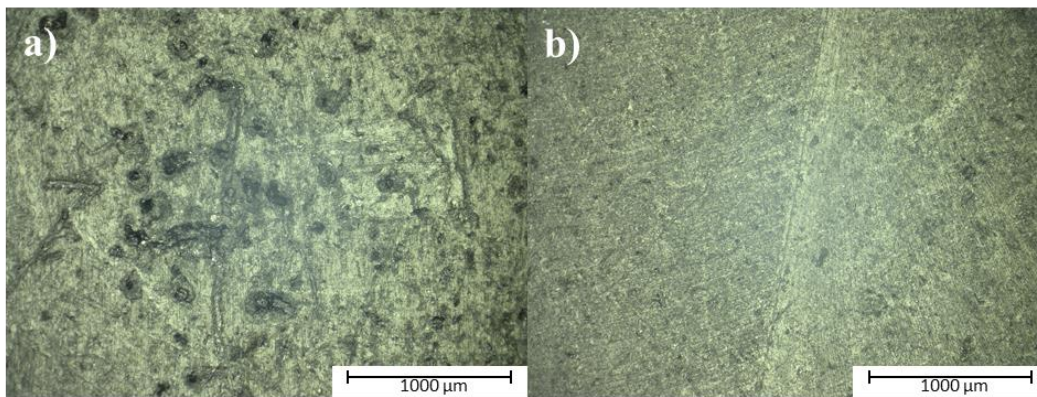[a] Gassing of aged samples in KOH + Zinc solution: x=gassing high, o=gassing low.

Fig. 7: Exemplary microscopy images of the surfaces of compounds 03 (a) and 05 (b) after aging in KOH.

7   Conclusion

The aging of plastic and other materials under certain environmental influences is of particular interest for a newly developed system, if it is to be evaluated with regard to its suitability for series production. With the presented measurement methods and results, a selection for housing and conductor components has been evaluated, so that prototype production of zinc-air battery stacks can be started. For housing of the battery, polypropylene seems a good candidate because of the presumed low reaction to KOH and the low changes in mechanical stability during the 10 months of aging. For the conductive material used as bipolar plate the compound 05 seems promising, although gassing is also noticeable by this material. The stop of gassing and the marginal changes of

the tested properties suggest that the impurities controlled side reactions decrease other time and can therefore probable disposed b pre-treatment of the bipolar plates.

The use of these methods for the evaluation of other plastic-based components is still pending, whereby other characteristics such as electrical properties and strength are also important. For example, in the case of the oxygen electrodes, relevant characteristics would be the activity or efficiency of the electrochemical reaction, which presumably decrease over time [20].

Acknowledgement

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