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Optimization of printable electrolyte

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Short abstract

Based on previous studies, here the composition of the printable electrolyte of printed batteries was investigated further. In the stack design of a printed battery, the electrolyte layer is located between the anode and cathode and is responsible for ion transport. However, the anode and cathode must not touch each other, so a so-called separator is used. This separator usually is a porous fleece-like material where the pores are filled with electrolyte. If a gel-like electrolyte can be used that is also printable and additionally has the separating function, this would be extremely advantageous for the production process, e.g., in a web press with several printing units. By adding thickener agents such as agar-agar and spacer particles to the classical $ZnCl_2$-electrolyte solution it could be shown that this can be rendered in a paste that works well as a gel-like and printable electrolyte with separator function. The goal of this investigation is to find out the optimum amount of these ingredients.

Keywords: printed batteries, screen printing, printable electrolyte, thickeners, spacers.

1. Introduction and background

According to business analyses e.g., provided by the OE-A organisation (see the OE-A Roadmap, 2023) small, flexible power sources such as printed batteries used to power IoT devices (Internet of Things) will become a promising and well flourishing market in the coming years. Manufacturers such as VARTA have announced at the LOPEC 2023 trade fair that they will set up a production line for printed batteries by the end of 2025.

Whereas printed rechargeable batteries (secondary batteries) are challenging, the non-rechargeable zinc/manganese dioxide chemical system (primary battery) is comparingly simple and has been brought to market earlier by companies such as Enfucell (2019), Blue Spark Technologies (2023), and some more. One recent new player to enter the market of printed batteries in the sector of logistics is the company elmeric (n.d.) which co-operates with VARTA. The printing technique, and mechanical properties of these film batteries have been described earlier (Lanceros-Méndez and Costa, 2018; Hübner, et.al., 2015; 2021).

In this investigation, which is based on previous work (Hübner, et.al., 2022), the so-called stack design of a printed battery is used. Details and layer structure of the design are shown in the explosion drawing in Figure 1.

In printed batteries, the separator mostly is a kind of fleece, a monolayer microporous membrane placed between the electrode layers. One renowned manufacturer of such fleece materials is the company Celgard (2023). In a manufacturing process where several layers are printed subsequently the insertion of such a fleece soaked with electrolyte would be disruptive. Therefore, it would be desirable if the electrolyte could be printed and perform the separator function at the same time. A printable electrolyte fulfilling the separator function by itself would be a great cost saving factor, at least by eliminating the need for the fleece.

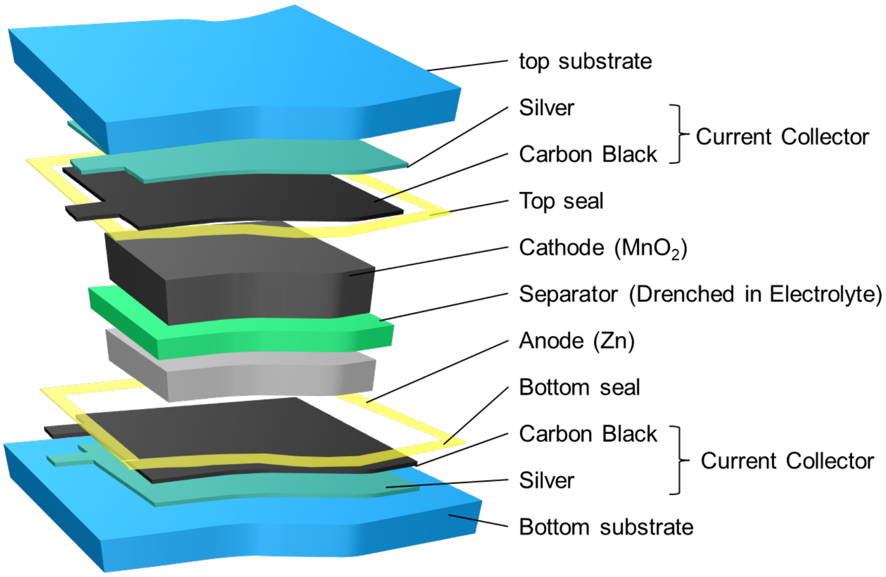

Figure 1: Explosion drawing of a printed battery in stack design

For the zinc/manganese dioxide electrochemical system that is used here, the electrolyte is a salt dissolved in water. According to common experience and previous investigations (Hübner, et al., 2022) the best choice is a 40 % zinc chloride solution.

- Distilled water 60 %.
- Zinc chloride ($ZnCl_2$) 40 %.

However, this solution is almost as liquid as water and therefore cannot be printed using the screen printing process, which produces all other layers, e.g. because of large particles in the electrodes.

The feasibility of making this electrolyte solution printable by adding a gelling agent, in this case agar-agar, and 50 µm PMMA beads as spacers has been shown previously (Hübner, et al., 2022). The idea is illustrated in Figure 2.

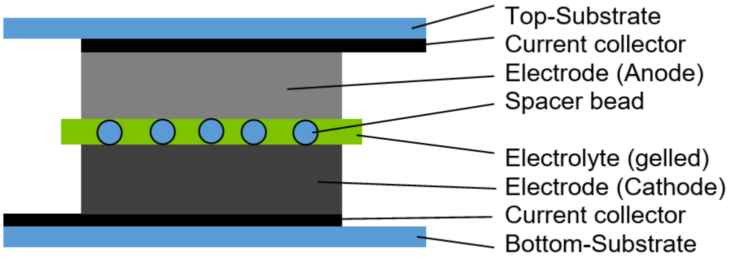

Figure 2: Side view of stack design with added spacers

Agar-agar is a food-safe gelling agent that can be found in many kitchens today. In Asia, the substance has been used for centuries to thicken food. The carbohydrate is made from the cell walls of algae such as red and blue-green algae. Agar-agar is a so-called multiple sugar, which consists of many simple sugars. The chemical structure of agar-agar is very similar to that of native fruits and vegetables. This fibre structure has very good swelling properties. Here, we dissolve agar-agar in the $ZnCl_2$-solution at room temperature and a few percent are sufficient to achieve a screen printable consistency. However, when agar-agar is dissolved in hot water, the liquid becomes even more viscous or even solid.

The aim of the current investigation is to optimise the concentration of agar-agar and PMMA spacers. The addition of these materials should be as low as possible in order not to influence the battery function too much. At the same time, the printability (rheological properties that enable screen printing) must be maintained, and the spacers must ensure sufficient distance between the electrodes to avoid short circuits.

2. Materials and methods

The materials and measurement methods are the same as described detailed earlier in (Hübner, et al., 2022). We measured:

- Rheology of the mixed pastes with a Physica MCR 300 rheometer parallel plate geometry
- Conductivity of the mixed electrolyte pastes using a cup with two immersed nickel strips at a fixed distance and determining the impedance with a Bio-Logic SP-300 potentiostat (Biologic, 2022)
- Electrical characterisation of batteries
    - Capacity (derived from constant current discharge curves)
    - Impedance (inner resistance) with GEIS method Bio-Logic SP-300 potentiostat (Biologic, 2022)

2.1 Printing paste preparation

In comprehensive preliminary experiments it could be found that the interesting range of component additions is for agar-agar from 2 % to 5 % and for the PMMA beads from 3 % to 5 %. Thus, a matrix was set-up for the experiments, which is shown in Table 1. The weight proportion of the four ingredients is given to form 100 g of paste. The ratio 2/3 between ZnCl and H_2O is maintained for all solutions.

Table 1: Matrix of different mixtures, weight proportion in grams to result in total 100 g paste

			PMMA Beads		
			3 %	4 %	5 %
Agar-agar	2 %	ZnCl	38.0 g	37.6 g	37.2 g
		H_2O	57.0 g	56.4 g	55.8 g
	3 %	ZnCl	37.6 g	37.2 g	36.8 g
		H_2O	56.4 g	55.8 g	55.2 g
	4 %	ZnCl	37.2 g	36.8 g	36.4 g
		H_2O	55.8 g	55.2 g	54.6 g
	5 %	ZnCl	36.8 g	36.4 g	36.0 g
		H_2O	55.2 g	54.6 g	54.0 g

For the experiments, the highly pure BioScience agar-agar from vendor CarlRoth (2022) has been used. The poly methyl methacrylate, aka. acrylic glass (PMMA) particles are microspheres with a diameter of 50 µm from the vendor Coating Products OHZ e.K.

For the experiments with these 12 different solutions the following nomenclature is introduced:

- PxAy

where x and y are the percentages of the ingredients. For example, P5A3 means that there is 5 % of PMMA beads and 3 % of agar-agar contained in the paste.

The electrolytes were prepared in laboratory glass jars. The substances were added at room temperature in the following order: first the $ZnCl_2$-salt was stirred into the water, then the thickening agent agar-agar was added in several steps, until it reached the desired percentage. With constant stirring the PMMA beads were added.

2.2 Printing process

All prints were carried out on a semi-automatic laboratory screen-printing machine Ekra E2. The following settings were used:

- squeegee speed 100 mm/s
- squeegee pressure 136 N
- snap-off distance 2 mm.

The screen used was a PET mesh with 21-140 (n-d i.e., mesh count in threads per cm – thread diameter in µm). This is a quite coarse mesh providing a large mesh opening that the PMMA beads can easily pass through.

A two-stroke operation was used, meaning that the flood bar and the squeegee moved two times back and forth.

As in the previous study (Hübner, et al., 2022) pre-printed battery halves (current collectors and electrode materials) were used and only the electrolyte was printed onto both electrodes. For the sealing, a printable, heat and pressure activatable glue was used. Sometimes also a cut out frame of double-sided adhesive tape.

2.3 Conductivity and battery performance

The conductivity of the electrolyte mixtures was measured as described in Hübner, et al. (2022). To determine the battery performance constant current (CC) discharge curves were recorded and a galvanostatic electrochemical impedance spectroscopy (GEIS) performed. A typical discharge curve from which the battery capacity can be derived is shown in Figure 3.

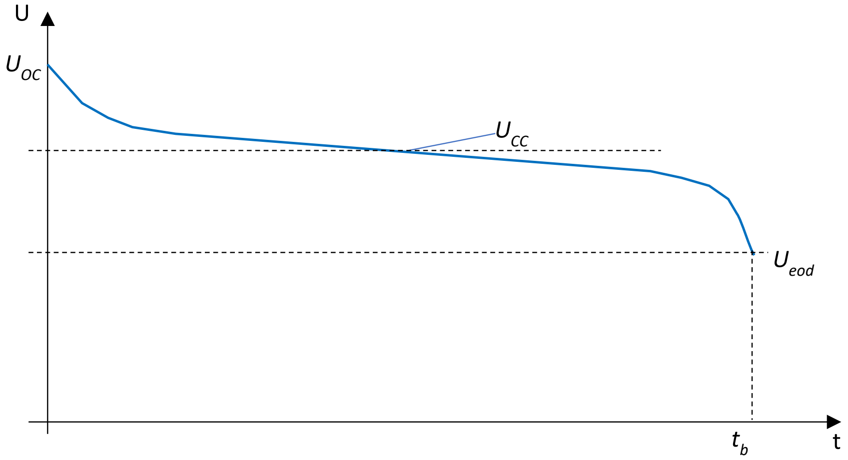

Figure 3: Typical CC-discharge curve of primary battery

For the Zn/MnO_2-system typical values are:

- U_{OC} = 1.6–1.7 V (open circuit voltage)
- U_{CC} = 1.5 V (nominal battery voltage)
- U_{EOD} = 0.9 V (end of duty)

For example, if the battery is discharged with 1 mA and t_b is 20 hours, then the resulting battery capacity is 20 mAh.

The GEIS measurements of the assembled batteries were performed before and after the discharge. The GEIS was conducted with a frequency sweep from 10 kHz to 1 Hz.

There are different possibilities to describe the GEIS behavior of a battery. One of the possible descriptions is an equivalent circuit diagram as shown in Figure 4.

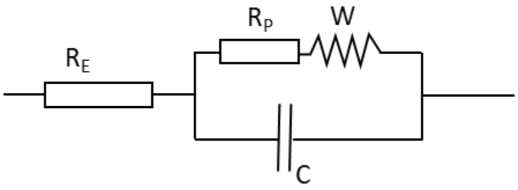

Figure 4: Equivalent circuit diagram

In the diagram, the inner resistances are named *R*. At high frequencies, the capacitor C plays no role and only the inner ohmic resistance R_E matters. At low frequencies C is blocking the current. Then the other resistances start to matter. W is a so-called Warburg impedance representing diffusion processes. The measurement curves of the fully assembled batteries should look like the idealized Nyquist plot depicted in Figure 5.

In the very best case there is no imaginary part at the ends of the half circle, the measurements however show a significant value.

As a measure for the inner resistance of the battery the values R_E and $Im(R_E)$ were considered.

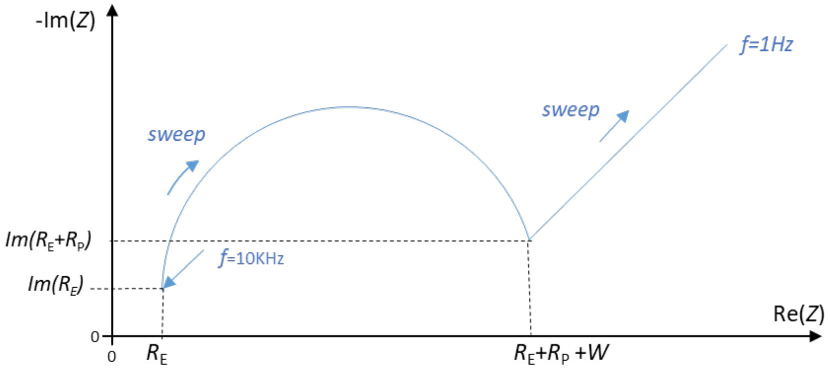

Figure 5: Idealized Nyquist plot of a printed battery

3. Results

3.1 Conductivity

The conductivity of the 12 different pastes have been measured and the result is shown in Table 2 and in a 3D representation in Figure 6.

Table 2: Conductivity of the electrolyte pastes

		PMMA beads		
		3 %	4 %	5 %
Agar-agar	2 %	108 mS·cm^{-1}	117 mS·cm^{-1}	84 mS·cm^{-1}
	3 %	135 mS·cm^{-1}	108 mS·cm^{-1}	123 mS·cm^{-1}
	4 %	124 mS·cm^{-1}	125 mS·cm^{-1}	120 mS·cm^{-1}
	5 %	114 mS·cm^{-1}	116 mS·cm^{-1}	114 mS·cm^{-1}

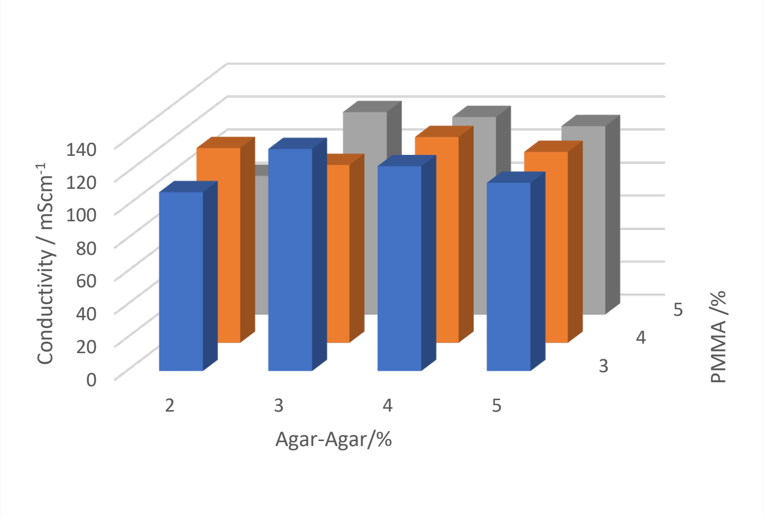

Figure 6: Conductivities of the different pastes

The measured conductivities of the electrolyte pastes are all in the same range between 107 mS·cm^{-1} and 135 mS·cm^{-1}, except for P5A2, which could be an outlier. It should be noted that the measurement method is not very accurate, an error of ±5 mS·cm^{-1} is likely.

For comparison, the pure 40 % $ZnCl_2$-solution has a conductivity of 110 mS·cm^{-1}, which is also in the same range.

It can be assumed that the influence of the agar-agar and PMMA bead content on the battery performance is not very large. In an earlier study (Hübner, et al., 2022), it was shown that the conductivity could even be improved by adding agar-agar. However, no spacer beads were added at that time.

3.2 Printability

The printability of the different pastes was observed during the screen printing process and the results were visually evaluated with regard to the homogeneity of the print and the appearance of bubbles. Some pastes showed very good results, while others had a pronounced tendency to bubble. The P3A2 had such a low viscosity that screen printing was not possible at all. The results are summarised in Table 3.

Table 3: Printability of the electrolyte pastes

		PMMA beads		
		3 %	4 %	5 %
Agar-agar	2 %	printing not possible	very good	very good
	3 %	very good	very good	good
	4 %	good	good	good
	5 %	poor	good	poor

3.3 Rheological behavior

Since the low and high addition levels of agar-agar and PMMA led to non printable mixtures the range of addition was refined. The additions were varied in 3 steps for both agar-agar and PMMA, namely 2.5 %, 3.5 % and 4.5 %. Since the different paste blends showed very similar pronounced shear thinning behavior, shear rate sweeps were performed for comparison and viscosities were recorded at 50 and 100 reciprocal seconds. The resulting values are shown in Figure 7 for the 9 pastes.

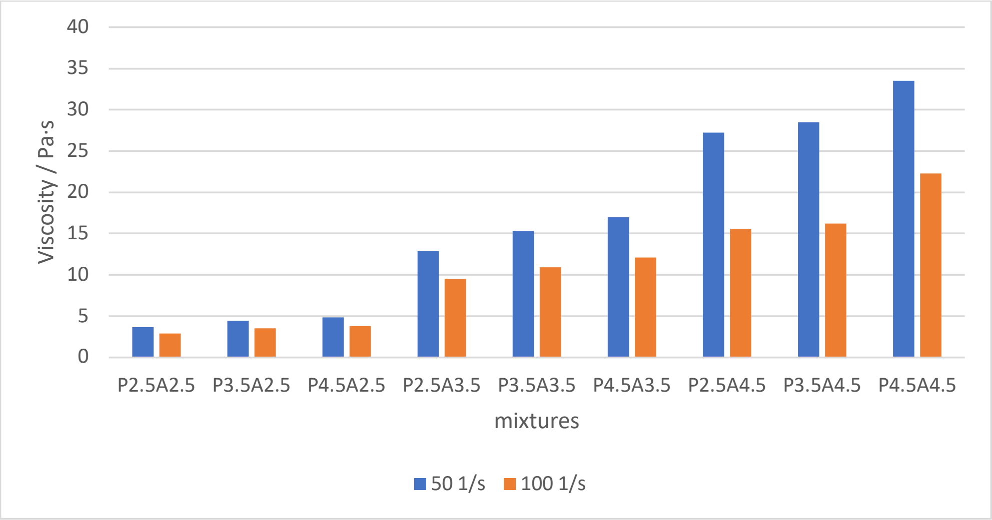

Figure 7: Viscosities of the different pastes

Figure 8 shows the results in a 3D-column chart.

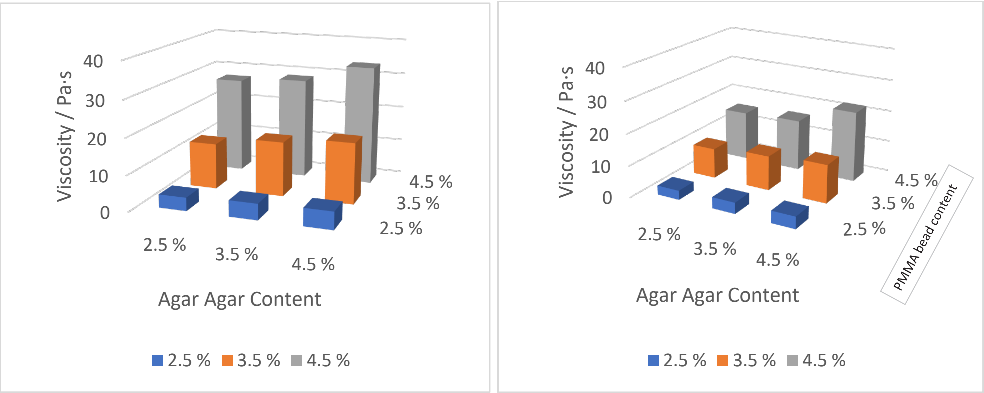

Figure 8: Viscosities of the different pastes left: at a shear rate of 50 s^{-1} and right at 100 s^{-1}

It is obvious and in accordance with the expectations that the viscosity increases with the addition of agar-agar and with the amount of PMMA beads. The optimum value for printability is at about 2.5 % to 3 % for each ingredient. However, printability is not the main focus, the main focus is the function, the battery performance.

3.4 Battery performance

Figure 9 shows the CC-discharge curve of a battery with the P3A5 electrolyte. The overall curve looks good. However, the voltage over the whole curve is too low. The open circuit voltage V_{OC} is only about 1.4 V and should be a little less than 1.7 V. The plateau-voltage V_{CC} is around 1.3 V and should be around 1.5 V. Finally, after reaching V_{EOD} (0.9 V), which is the point at which one can normally assume that the battery is empty and the load of 1 mAh is taken away, the voltage recovers to about 1.32 volts. This means nothing other than that the battery is not flat and still some capacity left over.

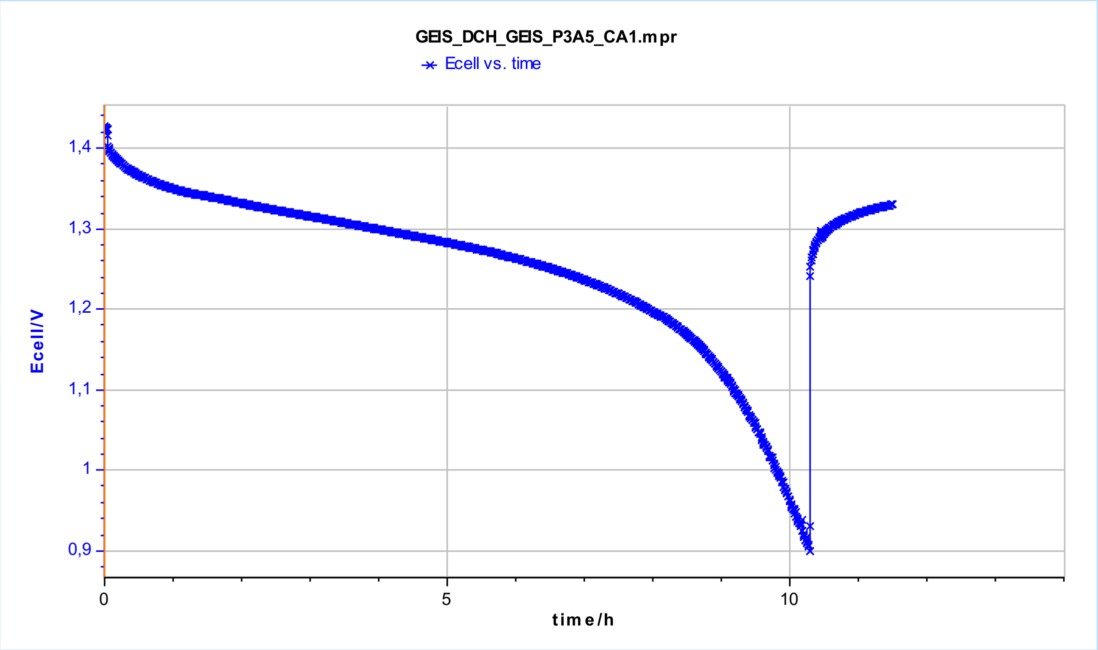

Figure 9: CC discharge curve of a battery with P3A5

Figure 10 shows the results of all assembled batteries. The only battery that achieves satisfactory results is the one with the electrolyte P4A4. As shown in previous reports such as (Hübner, et al., 2022) a capacity of 2 mAh·cm^{-2} is the target minimum value. With an area of 16 cm^2 and a discharge time of 40.3 h the P4A4 shows a quite good capacity of 2.5 mAh·cm^{-2}. As all others show poor or very poor performance. It can be assumed that something went wrong during assembly.

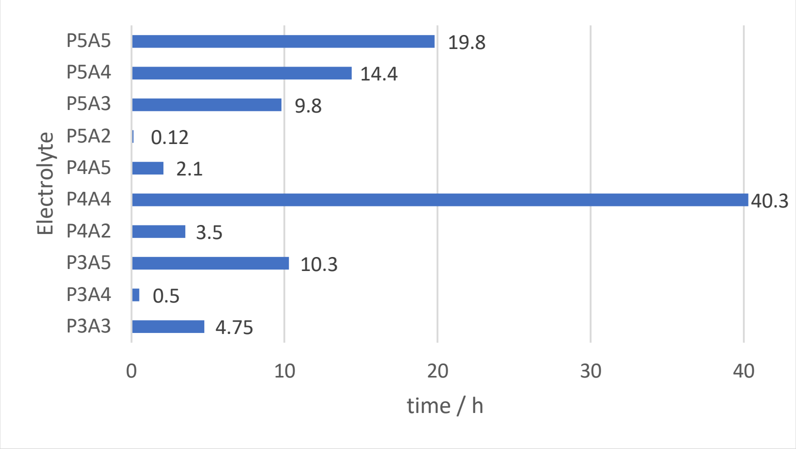

Figure 10: CC discharge results for batteries with different electrolytes

There are several possible reasons for the poor performance:

- Sealing is defective (leakages or even drying out)
- Electrolyte is in touch with the silver (e.g. because beads have punctured the passivation carbon)
- Electrolyte has degraded
- Overall too high inner resistance

The internal resistance (impedance) can serve as an indicator of poor capacitance performance and low voltage level. According to Figure 5 the value of R_E (real and imaginary part) are such indicators. As can be seen in Figure 11 only P4A4 has an acceptable low resistance level.

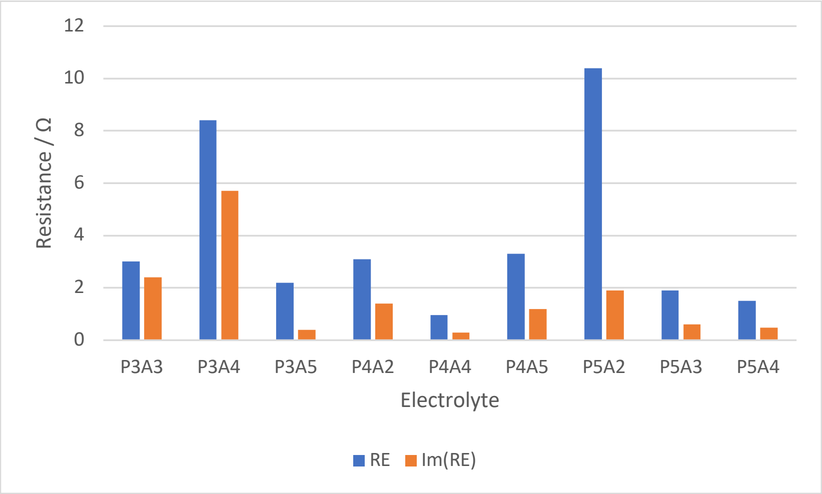

Figure 11: Inner resistances of assembled batteries (real and imaginary part of impedance)

The battery performance of the cells assembled with the intermediate 2.5 % to 4.5 % additions is ongoing and there are hints that one of the electrode layers caused the problem. There will be more investigations until the conference.

4. Conclusion

It could be shown that a printable electrolyte is possible by using a widely available and affordable ingredient agar-agar as thickener agent. By adding PMMA beads with 50 µm diameter the separator function can be realized. Solely printing techniques are the subsequent manufacturing steps avoiding the disruptive process of inserting a fleece soaked with liquid electrolyte.

Some assembled batteries showed very good results in terms of capacity and low inner resistance, however, unexpected results were found with most of the assembled batteries. These results must be verified in repeating the experiments. This is currently ongoing and will be finished with hopefully completely satisfying results until the conference in September.

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OxiFlexIT

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für Bildung
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