

A zinc air fuel cell with electrolyte circulation

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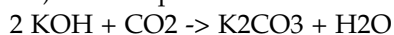
Abstract

Here we introduce a new prototype of the zinc air fuel cell system ZACplus, with electrolyte circulation and a prolonged lifespan of the gas diffusion electrode.

Introduction

Former prototypes of our alkaline zinc-metal-air fuel cell system (called "ZACplus") which we used to demonstrate the generation of electric energy by oxidising zinc metal had closed reaction chambers and were only capable to run for a few hours before the power started to decline. It was observed, that the originally clear electrolyte became more and more enriched with white/grey powder. So one possible reason for this short operating lifespan was probably the enrichment of the reaction product zincate (zinc oxide, ZnO) within the electrolyte, which start to precipitate at a certain concentration and then could be clogging the pores of the gas diffusion electrodes (GDE, also called gas cathodes) [1].

But there are other factors known from the literature, which could be responsible for limiting the GDE lifetime, e.g. the carbonating of the electrolyte (potassium hydroxide, KOH) with carbon dioxide (CO₂) towards potassium carbonate with the reaction



and then the potassium carbonate may clog the GDE-pores.

Another possibility is a drowning of the GDE, also known as premature flooding [2]. It is again the question, how many working hours the GDE could fulfill before. The Literature tells us, that this could be quite different in a range from only a few hours up to several thousands of hours, depending on the cell chemistry [3].

One further reason can be of course a lack of fuel, if the zinc-anode is consumed and done. But in this case its easy to identify it, because then there is a gigantic hole in the zinc plate (which could become easily replaced) and it has nothing to do with any possible degradations of the gas cathode (see figure 1).



Figure 1: Zinc anode which is consumed

To demonstrate the ZnO-clogging on the GDE-pores as possible reason for the decline selectively, a circulation of electrolyte may be sufficient, because the more and more with ZnO enriched electrolyte became transported away and is replaced by fresh one (or by one with at least a lower ZnO-concentration). If ZnO-clogging is really the reason for the decline, then the operational lifetime of the system should become significantly prolonged.

Methods

The components of the system

We use a 5L-Tank as containment (see figure 2) and buffer-reservoir for the fresh electrolyte (see figure 3 and 4) during the circulation. The buffer volume has about 1L and is comparable big (about 14 times) compared to the cell-chambers volume which has 69.5 mL (see figure 6 and 5).

The circulation is driven by a peristaltic pump whose velocity depends on the voltage (that can be between 5V and 12V). At 5V the flow velocity of the electrolyte is 0.43 mL/s or respectively 26.08 mL/min. With an estimated buffer-volume of 1L we need therefore 38.4 minutes for a complete buffer-exchange. With an operating period of e.g. 100 h the

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Received: September 20, 2024, Published: OSEG Germany e.V. Internal Paper



Figure 2: At the right side of the reservoir the 5V pump is mounted



Figure 3: The pump pulls the electrolyte out of the cell's outlet and let it drip from above into the buffer-reservoir

whole buffer volume would pass 156 times through the cell-chamber.

At the top of the cell-chamber are two contacts for the energy flow: One from the gas cathode and the other from the zinc anode. They are connected with a measuring rig, which contains a 1.5 Ohm resistor as load and a volt-meter and an ampere-meter for measuring the power which is consumed by the the load-resistor.

Results

The experiment (and therefore the lifetime of the gas cathode) was running with a duration of 9 Days, or more precisely 211 hours and was way longer than we originally expected.

In the middle of this period the electrolyte was one time completely exchanged, which is recognizable in the graph by the large downward peak in the middle of the timeline.

One can see in the graph, how short before each time the voltage and the current are slightly decreasing, what is correlated to the fact, that the corrosion-whole in the anode becomes bigger and bigger and then they are lying immediately after the exchange again on a higher level.

In the timerange after minute 8000 there is a relativ

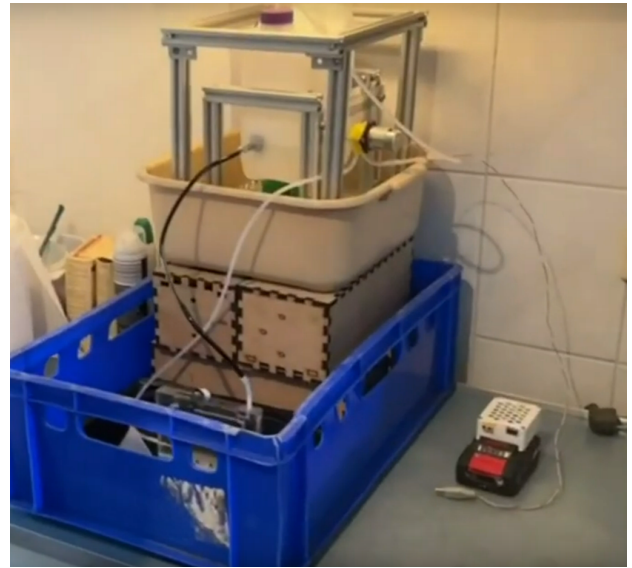


Figure 4: The electrolyte is collected in the lower part of the buffer tank. At a defined height there is a pipe connector mounted into the tank-wall, which acts as an overflow that is connected with a silicone hose to the inlet of the cell-chamber, so that the circulation is closed.

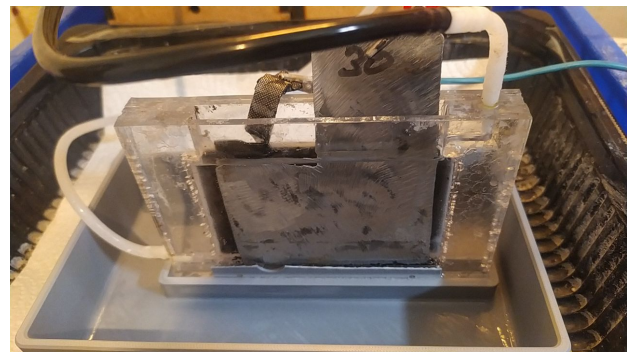


Figure 5: Cell chamber with inlet at the upper right corner and outlet at the lower left corner. The outlet is connected with a silicone hose to the pump.

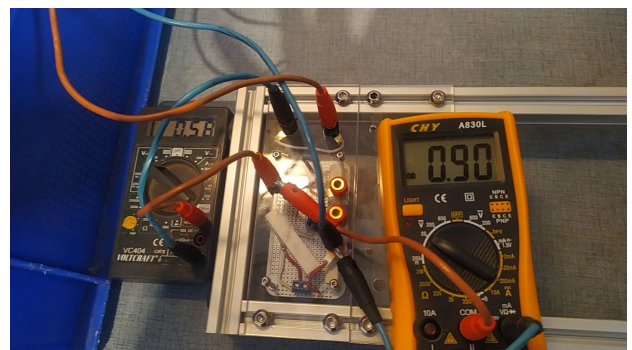


Figure 6: Rig for measuring the voltage and amperage over a 1.5 Ohm load resistor.

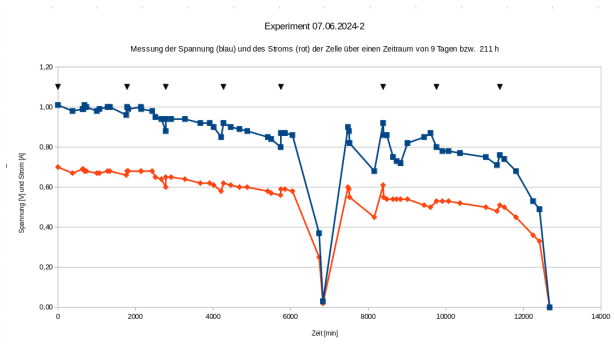


Figure 7: The voltage and current graph showing the whole measuring period

big downward peak. Regarding the black arrows which mark the anode-exchange it becomes obvious, that here was before a longer phase during which the anode wasn't exchanged, so it was probably very strong consumed. This explains the lower voltage- and current-levels, in comparison to the other anode-exchange-peaks, which are usually less distinctive.

After the next exchange there is another downward peak at about min 9000. This is probably an artifact which resulted from the circumstance, that the battery of the voltage-multimeter was low and then had to be exchanged. Furthermore there was an increasing leakage at the upper edge of the gas cathode recognizable which may have influenced this. But the low battery is the more probable explanation, because the peak is only in the voltage-graph, but not in the current-graph, that was measured by another multimeter-device.

Despite all minor peaks there was in total a slight decrease over the whole period, which was declining during the phase with the first electrolyte from about 1.0V to 0.8V and after the total electrolyte exchange again from 0.9V to 0.7V. The second time it was a bit lower despite we had fresh electrolyte. But it could be a first sign of that the pores of the gas cathode were already a little bit clogged from the first electrolyte.

During the whole time there were 8 zinc-plates consumed (like in figure 1, which shows a consumed zinc-anode that consists actually only of a big whole). Each point in time when a zinc anode was exchanged is marked in the diagram by a black arrow.

The total sum of all "burned" (or better oxidized) zinc is 115 g and this was transformed into about 110 Wh Energy, with a 1.5 Ohm load resistor. This results in an energy-density of 956 Wh / Kg (only related to the weight of the zinc, not the electrolyte).

Discussion

What started as a first test of the new prototype developed into a "marathon" measurement series with

Zinkverbrauch			
Anode Nr.	g vorher	g nachher	g Differenz
1	31	12	19
2	20	12	8
3	34	18	16
4	34	20	14
5	26	8	18
6	30	16	14
7	32	14	18
8	32	24	8
gesamt:			115

Figure 8: The summed up zinc consumption of all single anode plates

a duration of 9 Days or 211 h. So the new prototype with electrolyte circulation outperformed our boldest expectations and marked clearly a milestone. It confirmed our hypothesis, that the ZnO-clogging is the most important limiting factor. With the circulation the lifespan of the GDE could become extended from about 20 h up to 211 h, which is 10-times.

And we even didn't rinse with a 100% clean electrolyte. Instead and conditioned by our way lower expectations concerning the experiments duration, the electrolyte of course accumulated during the days more and more zinc oxide, but we didn't want to stop the experiment. So the volume of the buffer tank was flushed in total 343 times through the cell, which explains, why there was over the time a gradual decline of the electric power.

By exchanging at least 1 time the total electrolyte-content of the tank against fresh one we could prolong the lifespan of the GDE significantly but there was a beginning decline caused by already recognizable clogging.

The energy-density of 956 Wh/Kg is an extremely good value, so far we have seen in earlier experiments (without circulation) only a maximum of about 600 Wh/Kg (see [4]), and also in the literature we found so far only a maximum value of about 800 Wh/Kg (acclaimed by the company EOS). To harden this result it should be substantiated by further test series.

Conclusion / Outlooks

This experiment shows further entry points on how to optimize the lifespan of the GDE: One has to care for that the electrolyte is as clean as possible. The easiest way is to simply enlarge the electrolyte volume and we probably will do so. A medium-term solution that we aim at is to clean up and regenerate the electrolyte in a small extra circuit. But for the

moment its important to show, how the purity relates to a long GDE lifespan.

And we have shown here, that there is a clear relation. But beside it is important also to examine, in how far it is really the ZnO what cloggs the GDE-pores, because like its mentioned in the beginning, the carbonization of the potassium by the carbon dioxide in the air could also be a reasonable explanation. Probably it is a mixture of both, ZnO AND potassium carbonate, but we would like to know the relation of both.

A further new insight of this experiment is, that we should use in further longtime-experiments way more thicker zinc anodes, so that we dont have to exchange them each few hours. So far we produced them by recycling old roof gutters (which consists of 99.7% pure zinc), but we are already preparing a new thicker anode type that we can produce by casting.

Another more practical consequence of this experiment: It has been quite exhausting, to write down the sample values by hand over a period of 211 hours or 9 days (sometimes you have to sleep). Therefore we need to develop urgently a new automatic sample-rig within the next workshops, which will be suited for longtime-measurement. Ideally this metering-interface should not only log the data onto itself (and provide a monitoring display), but it also should be able to transmit the sample data over WiFi to a small server (e.g. Raspberry Pi) where they can be collected within a database and graphically processed for visualization by any arbitrary webbrowser frontend on the local network.

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