

Analyzing transport paths in the air electrode of a zinc air battery using X-ray tomography

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ABSTRACT

X ray tomography was used to investigate the discharge behavior of a zinc air battery in operando. A special battery set up and preparation was used in order to meet both electrochemical and tomographic requirements. The prepared battery was discharged galvanostatically and analyzed with tomographic measurements at a state of charge of 100%, 75% and 65%. End of life of the investigated zinc air battery is reached much earlier than the amount of active zinc particles would allow. This is attributed to an observable blockage of oxygen transport paths in the gas diffusion layer caused by increased flooding with liquid.

Keywords:

Zinc air battery
X-ray tomography
Imaging
Gas diffusion layer
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1. Introduction

Zinc air batteries exhibit a high theoretical energy density as one reactant, namely oxygen, is taken from environmental air, which significantly reduces battery weight. Zinc air batteries electrochemically convert solid Zn particles and OH^- to zincate ions, $\text{Zn}(\text{OH}_4)^{2-}$, which subsequently may react to solid ZnO , H_2O and OH^- . At the air electrode, O_2 and H_2O are electrochemically converted to OH^- . Zinc air batteries can be used with non platinum catalysts and have a low toxicity. In addition the active material Zn is available in sufficient amounts. Currently zinc air batteries are widely used as primary button cells and supply power in the mW range for example for electroacoustic devices. Discharge at high current densities induces strong degradation processes in zinc air battery [1,2]. This reduces the range of possible fields of application, particularly its application for electromobility. The end of life (EOL) for zinc air battery is reached either by complete utilization of zinc, by passivation of active material due to zinc oxide formation on the surface of zinc particles at high current densities, by short circuiting due to dendrite formation causing perforation of the separator or by limitations at the air electrode, such as catalyst poisoning, water loss from the aqueous electrolyte, and blockage of transport paths which cuts off oxygen supply between electrode and environment.

To overcome the latter, better understanding of the underlying reaction and transport processes during zinc air battery operation is

required. Recently, approaches for visualization and quantification of processes within electrochemical systems by magnetic resonance imaging methods [3] and by X ray imaging [4] have been introduced. Imaging methods aim to gain a deeper insight on the electrode level and are used for a wide range of electrochemical systems [5–7]. However, so far no imaging methods are applied to investigate the complex processes in entire zinc air batteries, their air electrodes or zinc electrodes. In this work, we present X ray tomography analysis for an in house built zinc air battery. X ray tomography is a well known technique for in operando and non destructive analysis of dynamic systems such as batteries or fuel cells. With this technique, it is possible to gain detailed information on the underlying processes in the transport paths in the gas diffusion layer (GDL) in zinc air batteries during discharge.

2. Experimental set-up

2.1. Battery design

A special battery set up, as depicted in Fig. 1, was used in order to meet both electrochemical and tomography requirements. Polytetrafluoroethylene (PTFE) was chosen as the specimen holder. PTFE ensures chemical stability for battery operation as well as a high transmittance during tomographic in operando measurements. Furthermore, the dimensions of the specimen holder are chosen sufficiently small to achieve high spatial resolutions.

The zinc electrode current collector consisted of a cylinder shaped 1 mm indentation in a graphite case that was embedded into the PTFE

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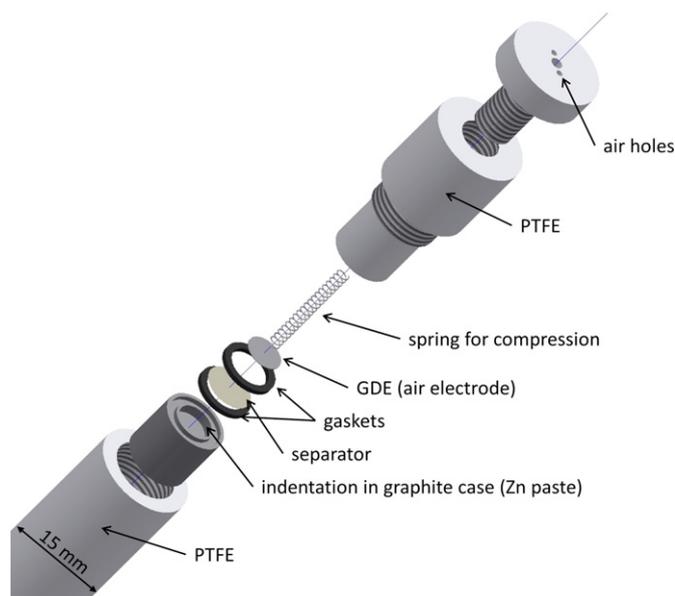


Fig. 1. CAD drawing of the battery set-up.

holder as shown in Fig. 1. Graphite was chosen as a current collector because of its high transmittance during tomographic in operando measurements. A paste, containing i.a. the active material Zn, was filled into the graphite case. A gas diffusion electrode (GDE) consisting of a GDL and a catalyst layer (CL) was used as the air electrode. The zinc and air electrode preparation is given in more detail in Section 3. Additionally, a steel spring ensured electrical contact between the electrochemical measurement device and the GDE, as well as the mechanical compression of separator and GDE.

2.2. Imaging

A conventional X ray tube was used for computer tomographic measurements. The accelerating voltage was tuned to 120 kV while the current at the tungsten anode was adjusted to 83 μ A. A 0.5 mm copper filter was applied in order to avoid beam hardening. 900 radiographic projections were taken for a full tomography. Each angle step was exposed twice for 1.8 s in order to increase the signal to noise ratio. The radiograms were taken using a Hamamatsu flat panel detector with 2316×2316 pixel. Tomographic measurements with an approximate duration of 110 min were taken before battery discharge, after approximately 8 h of operation and after EOL of the battery. To avoid electrochemically induced changes inside the battery during tomographic measurement, no current was drawn from the battery during each tomography.

3. Battery preparation and discharge

The GDE had a diameter of 0.8 cm and was prepared similarly as reported by Müller et al. [8]. A paste with isopropyl alcohol, VulcanXC72R (Cabot) and $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ catalyst (EMPA) was pasted with a loading of 1 mg/cm^2 onto a H2315 series GDL (Freudenberg) and dried at 60 °C.

The active area of the zinc electrode had a diameter of 0.6 cm. The zinc paste was prepared as follows: 207.1 mg Zn (Grillo) was mixed with 12.7 mg CM cellulose (Sigma Aldrich). Subsequently, 87.4 mg of the dry powder mix was filled into the graphite case. Then, 39.3 mg 6 M KOH (Sigma Aldrich) solution containing 4 wt.% ZnO (Grillo) was added. The applied battery separator was Celgard 3401 (Celgard LLC) and was soaked with 6 M KOH solution before assembly. The initial capacity of this battery was approximately 68 mAh. The as prepared zinc air battery was discharged galvanostatically with a

Gamry Reference 3000 Potentiostat/Galvanostat/ZRA at a current of 2 mA until a cut off voltage of 0.70 V, representing the EOL of this battery, was reached. For the tomographic measurement after 8 h of operation, no current was drawn to preserve the battery state of charge (SOC). During discharge, the air electrode was passively operated at ambient atmosphere (20 °C, 40% r.h.).

4. Results

Fig. 2 shows a discharge curve obtained with the as prepared zinc air battery at a discharge current density of 7.1 mA/cm^2 . During discharge, the cell maintains an almost constant potential of 1.05 V. The peak in cell potential at about 8 h of operation is due to zero current condition, which was maintained during the tomographic measurement, and represents battery open circuit potential of about 1.30 V at 75% SOC. After approximately 14.25 h of operation, which corresponds to 65% SOC, cell potential decays drastically and the cut off voltage of 0.70 V is reached.

Fig. 3a), b) and c) visualizes the process of GDL flooding with decreasing SOC from 100% to 65%. The regular pore structure of the GDL is more and more filled with liquid, which results in higher X ray absorption for the tomographic images. This is indicated with increasing light blue areas. Fig. 3d) quantifies the liquid amount in the GDL as a function of SOC in arbitrary units, confirming the liquid accumulation during discharge.

Fig. 4 tracks the change of battery state during operation via X ray tomography with a through plane cross section of the entire battery at 100%, 75% and 65% SOC. To visualize the separator and CL, which are seen on top of the zinc electrode, the shown colors correspond to different gray values than in Fig. 3. With decreasing SOC, a volume change in the zinc electrode is invoked, which lifts separator and CL (orange line). This volume change also leads to flooding of large pores of the GDL with liquid electrolyte, which correlates to increasing X ray attenuation in the GDL with decreasing SOC. An enlarged detail of the GDL from Fig. 4a) is shown in Fig. 4b). The detail is depicted in false colors from blue to red to emphasize the changes in the recorded gray values from the X ray tomography in Fig. 4a).

5. Discussion

It can be deduced from Figs. 3 and 4, that the observed volume change causes a displacement of the electrolyte solution in the zinc

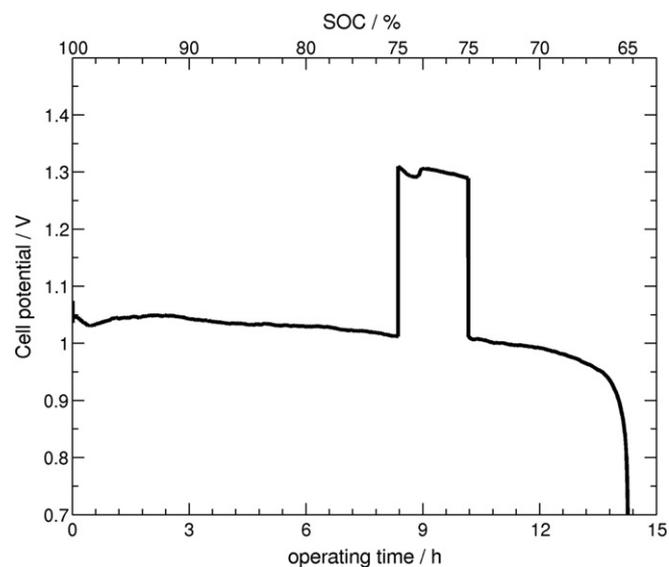


Fig. 2. Discharge curve obtained at 7.1 mA/cm^2 .

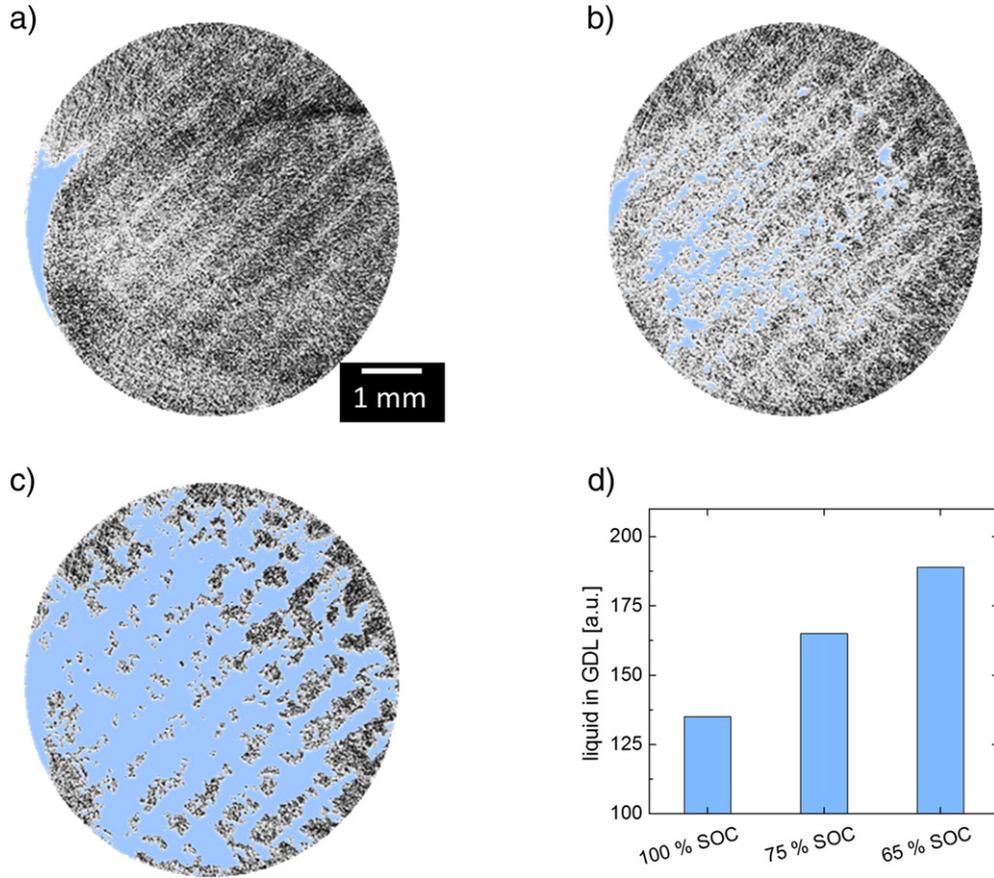


Fig. 3. In-plane cross sections through the GDL at a) 100% SOC, b) 75% SOC and c) 65% SOC. Light blue colored areas indicate higher X-ray attenuation for the tomographic image. d) Quantification of liquid amount in the GDL.

electrode. The electrolyte solution is then transported into the pores of the air electrode GDL, where the amount of flooded pores is increasing with discharge time. The consequence for the obtained cell potential, as shown in Fig. 2, is as follows: due to an increase in the degree of flooding in the GDL pores, the diffusion of oxygen to the reaction zone at the CL is hindered; some transport paths in the GDL might even be blocked completely. Since cell current and as such oxygen consumption in the air electrode are set constant, the oxygen concentration in the CL decreases with advanced operation time. This leads to oxygen starvation in the CL, and finally to a sudden decay in cell potential and

consequently battery EOL. This interpretation is supported by considering the mass transport limited current density i_{limit} [9], which can be calculated with Eq. (1).

$$i_{limit} = \frac{z F D_{O_2} c_{O_2}^{film}}{\delta_{film}} \quad (1)$$

where, z is the number of electrons in the electrochemical reaction at the air electrode, F is the Faraday constant, D_{O_2} is the diffusion coefficient

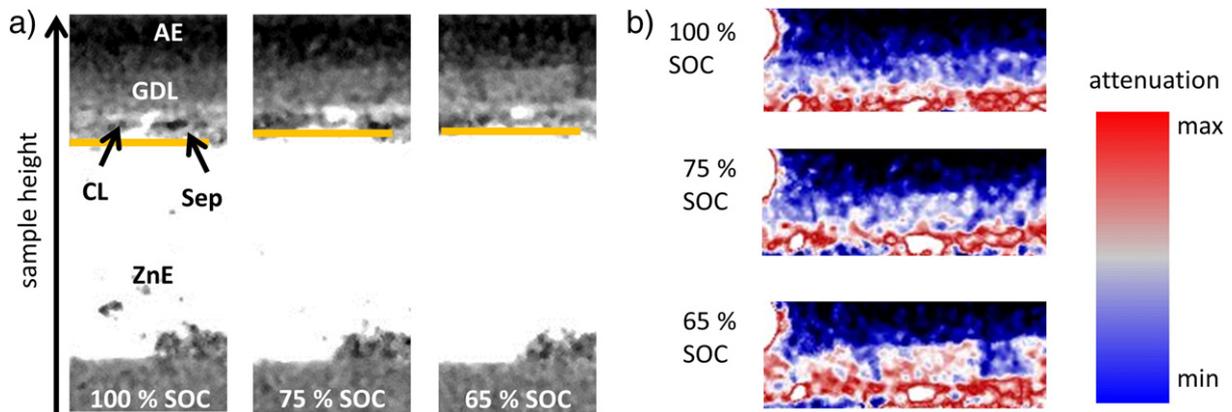


Fig. 4. a) Through-plane cross sections of the zinc air battery for decreasing SOC. Orange lines indicate the volume change of the zinc electrode. The visible gray range is adjusted to better visualize the GDL, where zinc particles are shown in white (GDL – gas diffusion layer, CL – catalyst layer, Sep – separator, ZnE – zinc electrode, AE – air electrode). b) Enlarged detail of the GDL from Fig. 4a) depicted in false color from blue to red. Colors are adjusted to emphasize the change in X-ray attenuation in the GDL pores with decreasing SOC.

of oxygen in the electrolyte, $c_{\text{O}_2}^{\text{film}}$ is the concentration of dissolved oxygen in the electrolyte, and δ_{film} is the film thickness of liquid electrolyte above the CL, i.e. the diffusion layer thickness for oxygen. An increase of δ_{film} above the CL from 2 μm to 200 μm , would diminish the limiting current density by a factor of 100, or would cause drastic decay of cell potential as experimentally observed.

Evidently, EOL is reached for the presented zinc air battery at 65% SOC, i.e. much earlier than the amount of active zinc particles would allow. Our measurements therefore suggest that limitations at the air electrode may cause early EOL at high current densities. This is in contrast to often reported findings [10,11], where zinc passivation is mentioned as the main reason for battery EOL at high current densities.

6. Conclusions

The presented combination of discharge curve measurement and X ray tomography gives an in depth insight into the processes occurring during zinc air battery discharge and adds valuable information about the flooding process in the air electrode GDL. We have shown that during discharge, an increased amount of electrolyte solution in the GDL blocks oxygen transport paths within the GDL, resulting in early EOL. This implies that for further improvement of zinc air batteries, limitations due to diffusion barriers of oxygen need to be considered.

One possible way to overcome such limitations may be active supply of pure oxygen or air.

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