Application of X-Ray Computed Tomography Imaging in the Evaluation of Aging Effects of Batteries and Fuel Cell Components

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Aims

The increasing amount of electricity from fluctuating renewable energies in the grid requires the implementation of electrochemical energy storage like batteries and conversion devices like fuel cells in order to enable balance between energy supply and demand. There is a variety of systems available which are differing in composition, application and characteristics. An important property is the requested lifetime from applications which are dependent on aging of single necessary components due to harsh environments and operation conditions. In order to optimize the systems and prolong their lifetimes it is necessary to obtain indications about post-operation defects and corrosion within these units. Bearing in mind that many of the single components of these devices are complex porous materials, consisting of various compartments, knowledge not only about the surface topography but also about the bulk morphology is crucial. Therefore, high resolution computed tomography (CT) can be used to image three-dimensional (3D) structures at the micro- and nanoscale, offering also qualitative information on the material's composition and aging effects. The aim of the present paper is to demonstrate the application of CT in the research field of the electrochemical energy storages and conversion devices by investigation and evaluation of three components and giving valuable information regarding their internal alterations and characteristics.

The membrane electrolyte assembly (**MEA**) is the core component of the fuel cell (FC) that converts chemical into electrical energy and heat. In this work the degradation process of a high temperature polymer electrolyte membrane (HT-PEM) FC is demonstrated by analyzing the influence of contact pressure cycling applied to MEAs. The mechanical changes of the MEA due to different operation strategies between beginning of life and end of test can be detected and visualized by means of microCT investigations [1][2].

The bipolar plate (**BPP**) is an important component for vanadium redox flow batteries (VRFB) as it serves as physical separator and electrical conductor of adjacent cells in a stack. These components are usually carbon based composite materials with complex structure. In the VRFB the BPP can be exposed to acidic media and harsh operational conditions [3]. Thus during battery operation the BPP can undergo significant aging. In order to study the aging propagation within the BPP bulk, pristine and aged graphite-polypropylene composite BPP samples were investigated using microCT.

High resolution nanoCT is also a suitable method for characterization of aging phenomena in cathodes for Li-ion batteries. In general the **cathodes** for the Li-ion battery technologies consist of active materials such as $LiCoO_2$, $LiFePO_4$, $LiNi_xMn_yCo_zO_2$, conductive additives and polymer binders [4]. Due to the difference in the X-ray absorption coefficients of the active materials and the binder-conductive additive matrix it is possible to perform separate analysis of both components with the nanoCT.

Method

1. **MEA**: Two studies on contact pressure cycling of HT-PEM MEA consisting of 5 layers with a nominal active area of 25 cm² were carried out. The first test was performed in-situ within a test station under real FC operation conditions (H_2 and air supply, current density of 0.2 A/cm²). The second test was done in a small ex-situ compression unit that was specially developed to fit into the microCT device and that was used without FC operation mode [1][2]. Three repetitive cycles of compression variations using 0.2, 0.5, 1 and 1.5 MPa have been applied in both systems.

2. **BPP**: Overload charging conditions were executed on a BPP with an active surface area of 1 cm² in an ex-situ electrochemical cell using a current density of 100 mA/cm² for 3 h in the positive VRFB electrolyte consisting of 1.6 M vanadium in 2 M sulfric acid and a state of charge of 90%.

3. **Cathode**: Commercially available 2 Ah Li-ion batteries in pouch cell format were continuously charged and discharged in climatic chambers at 25 °C within the voltage range 2.8 to 4.0 V at a C-rate of 1 until reaching different states of health (SOH). After the cell disassembly the different cathodes were characterized using high resolution nanoCT.

CT scanning was performed in order to analyze the inner microstructures of the mentioned single components in energy storage and conversion devices. For the investigations high resolution Skyscan 2011 nanoCT and Skyscan 1172 microCT were applied. 3D reconstruction, image processing, visualization and data analysis were performed by means of included software of the micro and nanoCT equipment (NRecon, DataViewer, CTVox, CTAn, Bruker, Belgium). The scanning parameters are shown in Table 1.

Table 1: Overview of scanning parameters.

Parameter	MEA	BPP	Cathode
Device	microCT	microCT	nanoCT
Source voltage [kV]	78-82	80	80
Optical resolution [µm]	2.50-3.00	1.44	1.00
Rotation step [°]	0.15	0.20	0.18
Averaging frames	4	5	6
Diameter sample size [mm]	6	16	0.75

Results

1. **MEA**: A cross-sectional image of a MEA compressed with 0.2 MPa serves as ante-mortem reference sample (Figure 13a). After completing three compression cycles in the ex-situ compression device, the mechanical changes can be clearly recognized by many defects and gabs within the catalyst layers (Figure 13b). In comparison, the post-mortem imaging analysis of the MEA, which was treated in-situ in the FC test station, is shown in Figure 13c. Apparently, the result is quite similar to that one gained via ex-situ compression tool. However, here the defect catalyst layers are going through the membrane resulting in short-circuit formation. By comparing these in- and ex-situ post-mortem microCT analyses, it is obvious that the influence of compression cycling is immense while the additional effect of FC conditions is only minor to the mechanical degradation of the MEA [1][2].

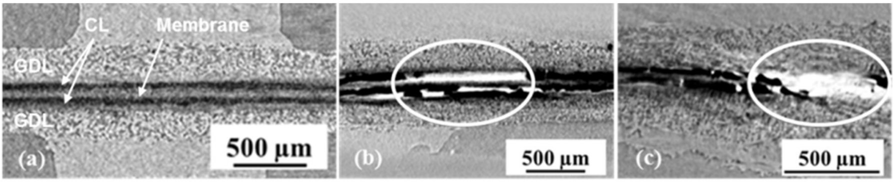

Figure 13: 2D microCT images of MEAs (DataViewer), (a) ex-situ ante-mortem, (b) ex-situ post-mortem and (c) in-situ post-mortem [1]. CL, catalyst layer; GDL, gas diffusion layer.

2. **BPP**: The 3D image of a pristine BPP shows characteristic features of the composite material. It consists of a homogeneously ordered bulk material with integrated segments of local higher density matter and a rough surface texture (Figure 14a). The overload charging conditions led to a damaged surface with increased open porosity, cracks and material loss drawn through the bulk material due to surface oxidation and subsequent CO_2 evolution [5] (Figure 14b). By means of microCT it is possible to visualize the depth of aging effects and the appearance and formation of corrosion events.

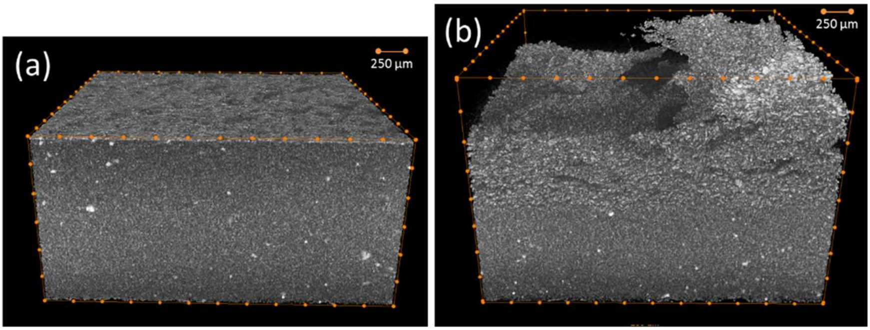

Figure 14: Graphite-polypropylene composite BPP (DataViewer) (a) before and (b) after aging.

3. **Cathode**: The quantitative evaluation of the nanoCT images shows a decrease in the average particle size and an increase in number of particles of $LiCoO_2$ with decreasing SOH of the battery (Figure 15). By means of nanoCT technique the active material particle breaking upon aging was suggested as aging mechanism [6].

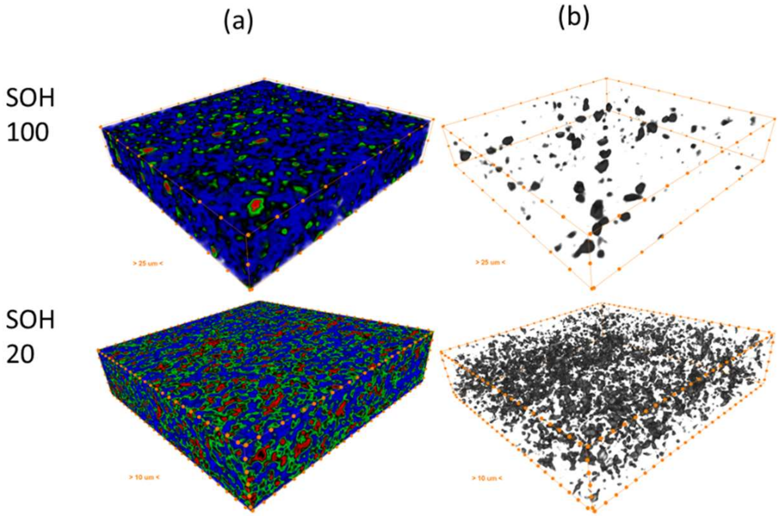

Figure 15: CT images (DataViewer) of (a) $LiCoO_2$ cathodes with different SOH; (b) Objects with highest densities in the $LiCoO_2$ cathodes are pointed out [6].

Conclusion

The lifetime of fuel cells and energy storage systems is determined by alteration and corrosion of single system components. In order to investigate such critical influences on integral components one assessment criteria is the comparison of interior morphological structures between ante- and post-mortem specimens. Therefore X-ray micro and nanoCT are powerful and essential tools to analyze their inner texture, characteristics and aging effects. It was shown that CT is applicable to investigate components such as MEAs, BPPs and electrodes from fuel cells and energy storage systems and to give evidence for their aging mechanisms.

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Acknowledgements
The authors thank the European Commission for supporting this work by the FCH-JU through the project CISTEM (Grant Agreement Number 325262) and the companies Danish Power Systems and Eisenhuth for providing MEAs and BPPs. The main author also kindly acknowledges the Heinrich Böll Stiftung for providing a PhD scholarship.