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ADMIST

Advanced Understanding of Micro Structures in Fuel Cells and Batteries through X-ray Imaging

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Project goals

The ADMIST project aims at improving the durability and performance of high (HT) and low (LT) temperature polymer electrolyte fuel cells (PEFC) and Li-ion batteries (LIBs). The lifetime and the performance of these three technologies is largely determined by the microstructure of the constituents, the temporal changes to the microstructure, and the related mass transport properties in the micro-porous domains. X-ray imaging, in particular in-situ X-ray tomographic microscopy (XTM) offers a powerful method to visualize the relevant structures in low and high temperature PEFCs and advanced LiB. In particular X-ray tomography has proven to be an extremely powerful method to reveal the relevant micro-structural details for in- and ex-situ research questions. The aim of ADMIST is to further develop by X-ray imaging for all three applications, leading to a profound understanding and thus the basis of significant improvements for the complex materials.

Status of project

In the second year of the ADMIST project the installation of the laboratory tomographic CT scanner and the verification of it's imaging capabilities provides the basement for the achievement of the scientific goals of the project. The low and high temperature PEFC in-situ/operando setups were adapted to the geometrical requirements of the laboratory CT machine and the expected image quality at could be verified. Structural analysis of ex-situ GDL samples revealed an anisotropy of the pore geometry and explains the preferential direction of liquid-water invasion front in LT-PEFC systems. Additional synchrotron operando XTM measurements with the HT-PEFC setup were used to broaden the understanding of phosphoric acid migration during load cycling for different membrane compositions and it's influence of HT-PEFC performance degradation. The inhomogeneity of different negative electrodes of lithium ion batteries was quantified on different length scales and linked to battery performance by 3D electrochemical simulations. Degradation of LIBs was addressed by exploiting XTM to depict lithium metal dendrite growth and lithium metal plating.

Completed tasks and achieved results

WP 1 CT Scanner Installation

The micro CT scanner “nanotom M” from General Electrics was installed in February 2015 and set into operation until end of March 2015. It features a 7.2 Mpixel flat panel detector and a 180 kV nanofocus X-ray tube with a spot size diameter down to about 800 nm. The imaging capabilities were verified using uing X-ray transmission line chart samples. As specified from the manufacturer, periodic line patterns with line and gap width down to 0.8 um could be identified. **Figure 1** shows, that even finer structures can be detected.

WP 2 HT-PEFC

Movement and redistribution of phosphoric acid within the porous components (catalyst layer, microporous and gas diffusion layers) of a HT-PEFC cell are expected to play a significant role for fuel cell performance and durability. The rearrangement of the phosphoric acid is depicted by operando X-ray micro tomography in a dedicated imaging HT-PEFC. Since the lab CT scanner relies on the principle of geometrical magnification, the positioning of the sample between X-ray source and detector is different than at a synchrotron CT beamline. The sample has to be placed close to the head of the X-ray tube and far from the flat panel detector to achieve high magnification. The present HT-PEFC XTM cell was designed to match with the X-ray microscope at the TOMCAT beamline of the Swiss Light

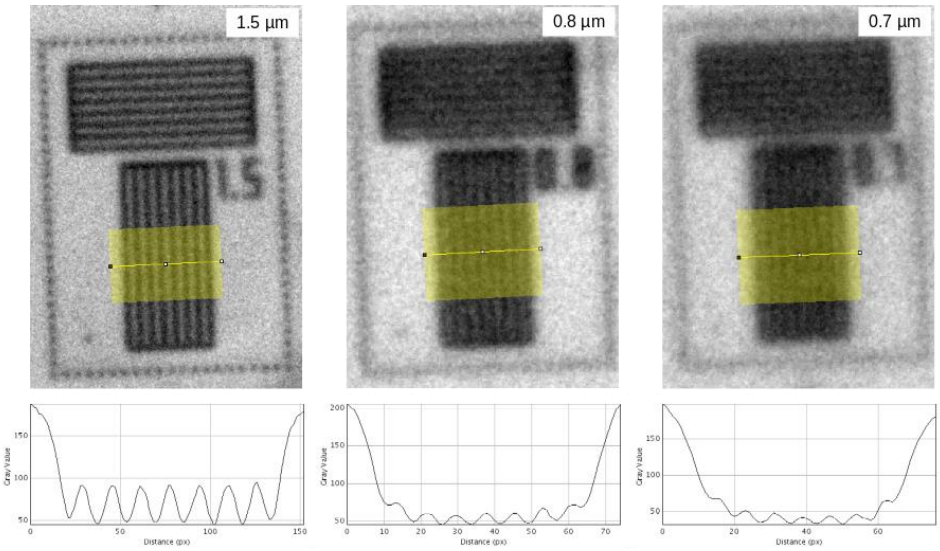

Fig. 1: Line detectability test with a X-ray transmission sample for different feature sizes (1.5 µm (left), 0.8 µm (middle) and 0.7 µm (right)); the averaged transmission profiles (bottom) are evaluated in the yellow domains (top) and reveal the features of the Tungsten structures for all pattern sizes.

Source, but it does not allow to exploit the best possible magnification for the sample diameter of 6 mm, as the sample can not be located close enough at the head of the X-ray tube in the nanotom (see Figure 2a). The cell housing was elongated and fixture of cell components was modified such that the sampling position of the cell can be placed at the required distance to the head of the X-ray tube (see Figure 2b). Thereby, the voxel size reduced from 3.5 µm to 2.2 µm and will allow a precise representation of the GDL fine structures that are based on carbon fibers with diameters of only about 7 µm (see Figure 2c). The Milestone M11 is thus achieved.

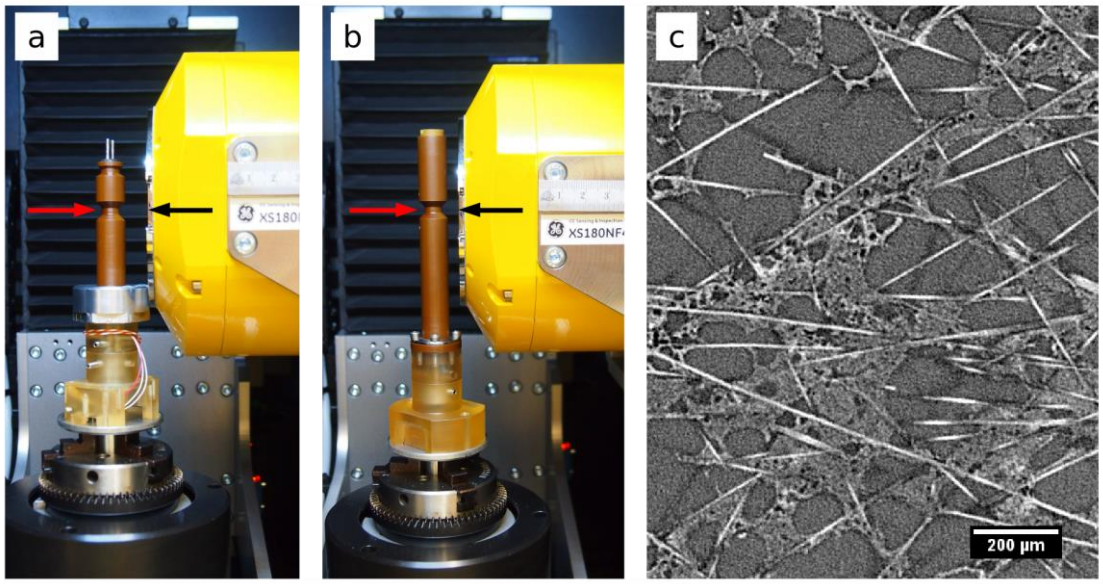

Figure 2: The old (a) and the new (b) HT-PEFC cell design mounted without peripherals in the laboratory scanner and the resulting image (c) of a SGL 24 BA GDL within the new cell housing at 2.2 um per voxel. The black arrow points at the exit point of the X-rays from the yellow head of the X-ray tube; the red arrow points on the measurement position in the cell housing.

Parallel to the modification of the cell design, operando XTM measurements at the TOMCAT beamline were implemented to broaden the understanding of phosphoric acid migration during load cycling for different membrane compositions. It was found that the migration of phosphoric acid towards the anode flow field during high current operation is dependent on the doping level and synthesis process of the membrane. As migration process seems to be dominated by capillary forces on the phosphoric acid in GDL micro-structure, well engineered GDL materials could help to mitigate the process and lower the PA losses at high current density operation (work towards Milestone M26). The results were presented including a conference paper awarded with a student travel award for Sebastian Eberhardt at the 228th ECS conference.

WP 3 LT-PEFC

The accumulation of the liquid water in the void space of the porous materials is a regarded as major limitation for high power density operation of LT-PEFC systems for the use in automotive power trains. Within the ADMIST project an in-situ saturation - capillary pressure XTM imaging setup is used to study the percolation processes during liquid water invasion in the GDL with a setup that is derived from the same design then the HT-PEFC XTM cell. Synergistic effects could be achieved as it redesigned together with the HT-PEFC such that now also this setup can benefit from smallest possible voxel size for 6 mm sample diameter (Milestone M15). It could be shown that the percolation front is stable during the scan times of up to 1 to two hours, but also shorter scan times are in reach. The segmentation procedures are currently adapted to handle CT data with a lower signal to noise ratio (Milestone M18).

Additional, structural analysis of ex-situ GDL samples revealed an anisotropy of the pore geometry and explains the preferential direction of liquid-water invasion front in LT-PEFC systems. The bottlenecks that define breakthrough position of the percolation paths of from the catalyst layer towards the flowfield could be located in the mixed region of the macroporous substrate and the microporous layer coating of the GDL (see Figure 3).

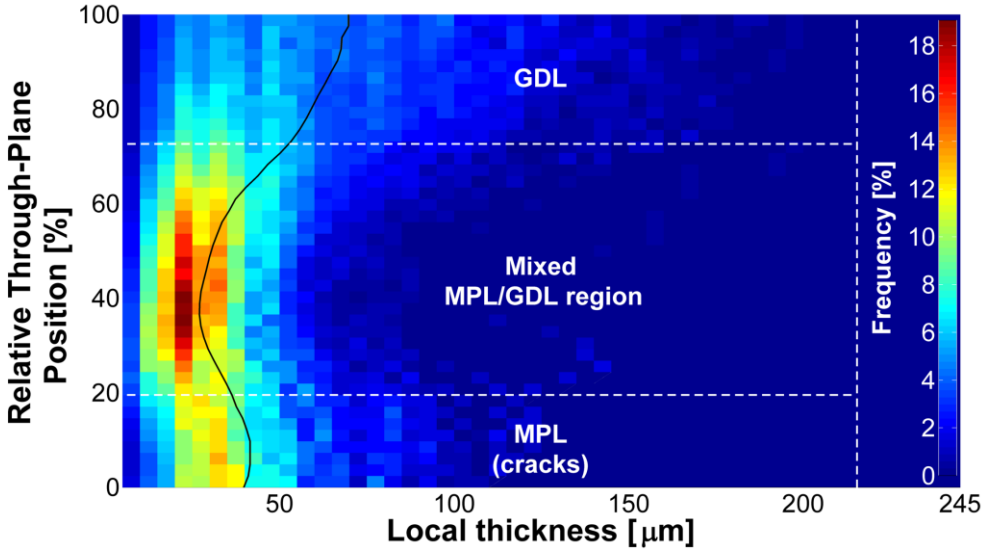

Figure 3: Color-coded in-plane continuous phase size distribution (cPSD) of SGL 24BC as a function of through-plane position in the GDL. The average local thickness over the through-plane direction is depicted as the black line (from Lamibrac et. al. in press, Journal of the Electrochemical Society).

WP 4 LIB

In the first 18 months of the project, we successfully worked to quantify electrode microstructure and inhomogeneity over multiple length scales (Milestone M12). Using x-ray tomographic microscopy, we obtain three-dimensional reconstructions of carbon-based negative electrodes from four different lithium ion battery manufacturers (**Figure 4**). We statistically quantified the inhomogeneity of each electrode over multiple length scales and performed electrochemical simulations on the digitalized microstructures to isolate and understand the influence of inhomogeneity on different microstructural parameters on battery performance. We demonstrated that the extent of heterogeneity can be assessed by examining the spread in particle surface area, particle size, and effective transport values (**Figure 5**), and quantified how inhomogeneity of electrode microstructure plays an important role in limiting battery performance by lowering accessible capacity and increasing the risk of degradation from non-uniform current distributions. Our findings suggest that manufacturers aiming to improve electrode homogeneity should prioritize selection of monodisperse particles, since a heterogeneous particle size distribution not only lowers the accessible capacity but also leads to a non-uniform effective transport parameter, increasing the risk of lithium concentrations in the electrolyte that locally exceed the solubility limit during fast discharge. The mean particle size must be selected based on known side reactions, the solid-state diffusion coefficient, and the desired operating conditions. This work has been written up for publication is currently waiting for approval from the industrial partners, who provided the samples. Simon Muller won the Zuger Wissenschaft Prize for this work. We are now extending this to cathodes.

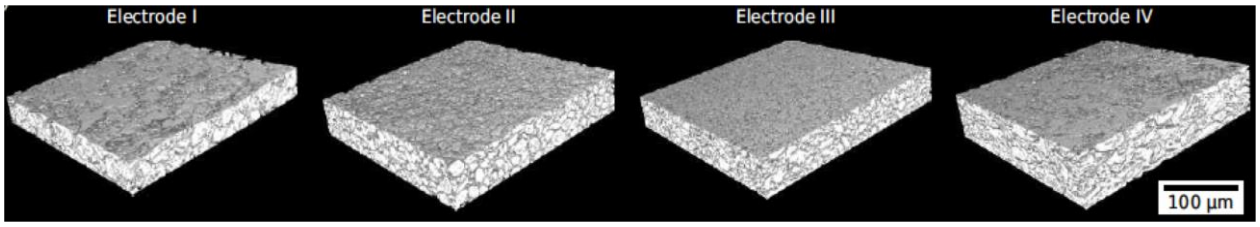

Figure 4: Surface rendering of the different LIB negative electrode types.

Now, to work towards Milestone M24, we are exploring different ways to investigate degradation in lithium ion batteries. Very promising is the use of x-ray tomography to identify lithium plating and lithium metal dendrite growth. The protocol that is being developed is as follows. A battery is cycled and then disassembled under in an Argon-filled glovebox. Lithium metal (in the form of plated or dendritic lithium) can then be stained slowly with OsO_4 at low temperatures (to counteract the exothermic nature of the reaction), which results in LiO_2 and OsO_2 (as well as associated compounds). This results in sample with high-contrast between the Os and the lithium that can be imaged by x-ray tomography. Following identification of places with plating or dendritic growth, finer resolution images can be obtained with FIB-SEM tomography.

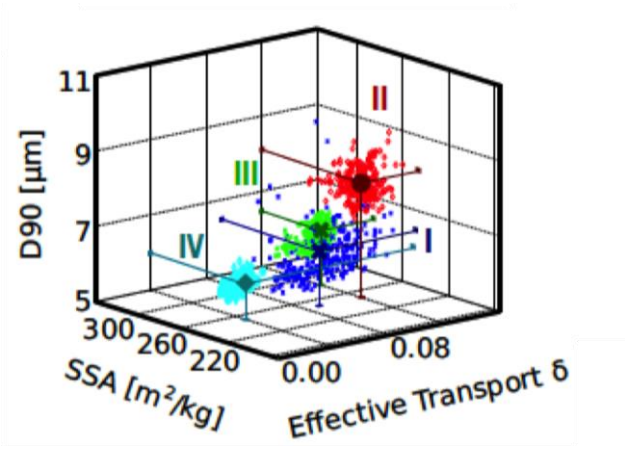

Figure 5: Scatter plot of the particle size (D90-values), particle surface areas (SSA) and effectice transport parameter δ, that describes the limitation of diffusive transport pore space properties.

National Cooperation

ADMIST is a cooperation between PSI and ETHZ. Work is performed in collaboration with different industrial partners.

International Cooperation

BASF being a main financing partner in the ADMIST project

Abbreviations

LIB	Lithium Ion Battery
PEFC	Polymer Electrolyte Fuel Cell
LT	Low Temperature
HT	High Temperature
GDL	Gas Diffusion Layer
XTM	X-ray Tomographic Microscopy