Application of the DIRECTT Algorithm to Sub-Nanometer Electron Tomography

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Abstract. Tomography data obtained from transmission electron microscopes are especially attractive due to their unrivaled spatial resolution in the nanometer range or even less, but they require enormous efforts in sample preparation and suffer from a diverse accumulation of experimental restrictions, which unavoidably result in fundamental reconstruction artifacts. These restrictions refer to: partial opacity, a limited view (limited angle or missing wedge), very few angles (with respect to the detector size), limited to a region of interest (ROI; due to the sample size), variable angular increments as well as sample degradation due the interactions with the electron beam. An advanced version of the DIRECTT (Direct Iterative Reconstruction of Computed Tomography Trajectories) algorithm proves to cope with most of these severe deviations from ideal CT measuring conditions. However, careful data preprocessing is required in order to exploit the capabilities of the algorithm.

Nanometer sized Ruthenium catalyst particles for fuel cell applications are 3D imaged at a few Ångström resolution in order to estimate their partial free surface on carbon black supports, which rule the efficiency of the catalytic activity. Comparisons of DIRECTT reconstructions to the conventional filtered back projection, prove the significant improvements.

Introduction

The first tomographic measurements in transmission electron microscopes were dedicated to questions of molecular biology [1,2]. They have been continuously developed to the direct imaging of functional substructures in biological cells. Since the samples must not exceed volumes of typically some $(100\ \mathrm{nm})^3$, the sample preparation and positioning in the electron beam and the precision of the manipulation system are challenging to the experimenter.

The example presented here is part of research activities focused on renewable energy sources. Fuel cells [3,4], in particular low temperature fuel cells for energy conversion are in the focus of commercial interests. Here, electron tomography is employed for 3D imaging of nanometer sized metallic Ruthenium catalyst particles on carbon black supports in order to estimate their free (reactive) surface. These surfaces essentially rule the efficiency of the catalytist nanoparticles' (e.g Pt or $RuSe_x$) which reduce the activation energy of oxygen reduction (Fig. 1).

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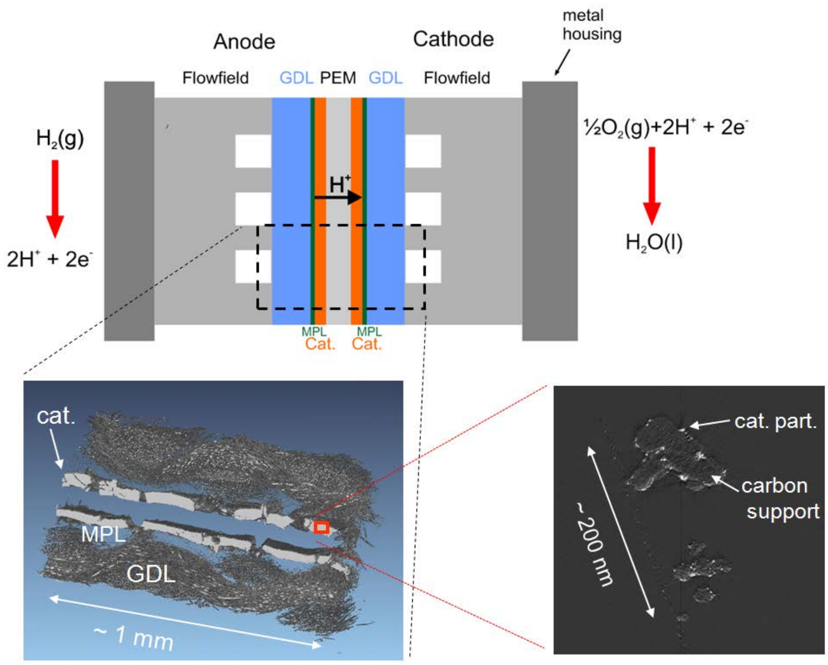

Fig. 1. Schematic set-up and functional principle of a PEM fuel cell (top), magnification of the MEA (Metal Electrode Assembly, bottom left) and components of the catalyst layer (single reconstructed electron CT slice, bottom right); PEM: polymer electrolyte membrane, MPL: Micro porous Layer, GDL: gas diffusion layer.

1. Experimental

Electron microscopic projections (Fig. 2) of catalysts on carbon black support have been performed ex-situ in a Zeiss Libra® Microscope. The bright field images (in zero loss modus) of the samples on copper grids are recorded in parallel beam geometry by 200 keV electrons. The actual detector resolution is 0.14 nm [5, 6]. Due to the sample holder's size (relative to the magnetic pole shoe distance) the rotation regime of the sample holder is limited to ± 70 deg.

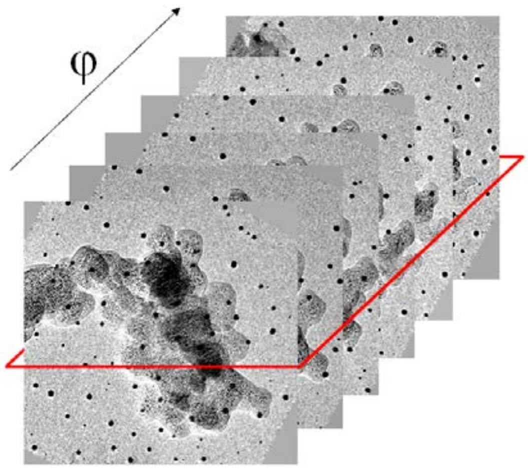

Fig. 2. Series of projections (TEM images) with an indicated plane containing planar sinogram (red). The strongly absorbing gold markers appear black. The small catalyst particles are distributed on (and inside) the cloddish carbon black supports.

Since state-of-the-art manipulators cannot provide nano meter precision of the rotation axes as required for computed tomography the samples are doped by gold markers of about 5 nm size in order to enable repositioning of the sample by their dominant absorption patterns. Tracking of the marker projections reveals the improved orientation (projection angle) and position correction.

2. Restrictions of the measurement

The unique challenge of reconstructing electron tomographic data is to cope with the simultaneous occurrence of multiple restrictions of the inevitable incomplete experimental date sets (Fig. 3).

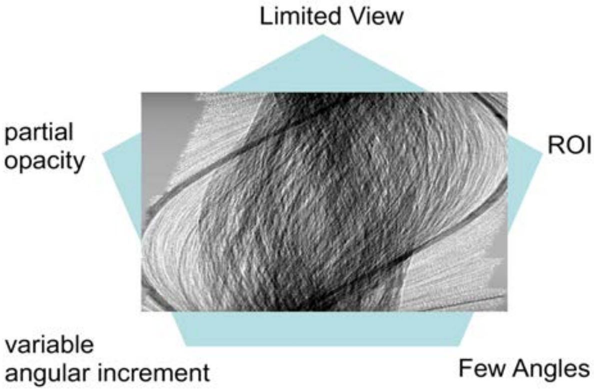

Fig. 3. Simultaneously occurring restrictions of data sets in electron tomography.

Due to the limited rotation of the copper grid and its increasing opacity under inclination an integral Limited View problem arises. The useful angular section is limited to typically 140 deg.

Because of the high electron beam brilliance local material degradations cannot be excluded. Thus, the recording time (about 1 sec per projection) has to be kept as short as possible and the measurements typically comprise merely 140-150 projections. With respect to the detector size (1024 -2048 pixel per line) this marks a tremendously underdetermined Few Angles problem for the reconstructions.

The sample (incl. Au markers) is much larger than the projected cross section, i.e. volume elements near the edge of the reconstructed region are not projected at all rotation angles and the integral mass is not conserved. This corresponds to the well-known region of interest (ROI) problem which hampers the empirical determination of the exact axis position since tracking the center of gravity as a function of phase is pointless. However, the exact knowledge of the rotation axis is highly significant for the achievable reconstruction quality.

High density volume elements (Au markers) are nearly opaque which drives the as-measured intensity out of the valid dynamic range. As a result, the reconstructions by filtered back projection (FBP) suffer from intense streak artifacts, as the chord lengths of the particles do not match meaningful attenuation coefficients. Thus for the concealed partial volume a partial phase dependent Limited View problem results.

From the projected sector and the number of projections a mean angular increment of 1 deg is derived. However, in the electron microscope the sample rotation can only be pre-selected at an accuracy of about 0.2 deg. The resulting sequence of non-equidistant projection angles is created by alignment and rectification of the single projections and needs to be taken into account by the reconstruction procedure [5, 6].

3. Data pre-processing

The reconstruction of the experimental projection data without further refinement results in strong streak artifacts and further suppression of the structural information (Figs. 4 and 5, FBP). In order to reduce these disadvantages data pre-processing is performed with respect to an improved rotation axes. Only after clipping the remaining high densities of the Au markers down to the level of the catalyst particles considerable improvements of the reconstructions can be achieved.

4. Reconstruction by DIRECTT

As our own reconstruction algorithm DIRECTT (Direct Iterative Reconstruction of Computed Tomography Trajectories) [7, 8] has provided good results by model calculations under several restrictions [7, 9] it is applied as well to cope with the challenging reconstruction problems of the present data sets [7,9]. Beyond the earlier achievements of separate model reconstructions for each single type of restrictions (few angles, limited view, ROI) the actual situation reflects a combination of all of them.

All data set restrictions which cannot be treated in advance remain a reconstruction task.

FBP

DIRECTT
(12 iterations)

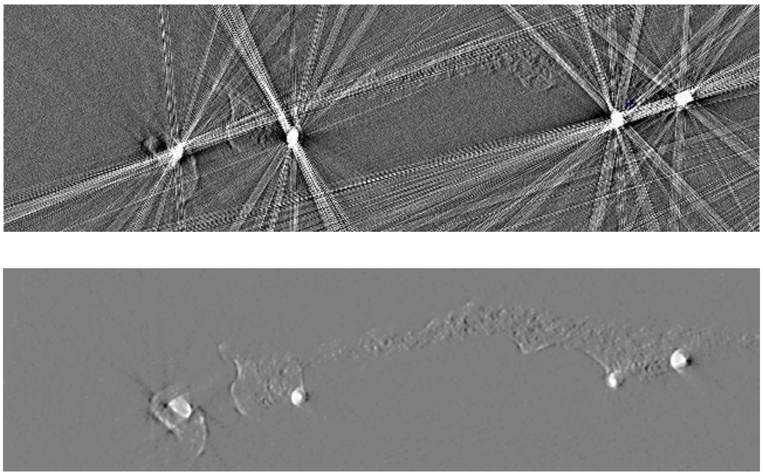

Fig. 4. Comparison of Filtered Backprojection (top, no data pre-processing) to the DIRECTT iteration (bottom).

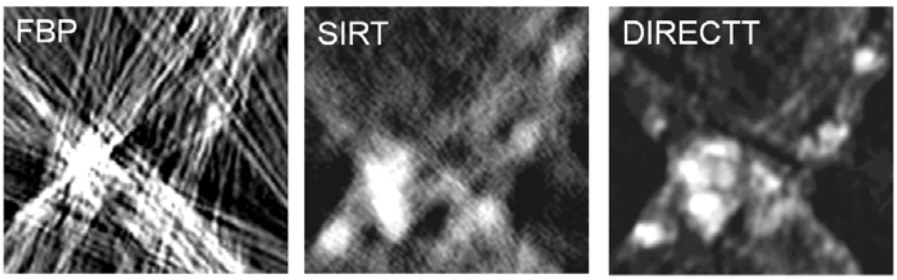

Fig. 5. Quality comparison of different reconstruction algorithms at the example of a catalyst particle agglomerate (reconstruction detail). The dominant streak artifacts appearing in the FBP (left) are purged in the SIRT (Simultaneous Iterative Reconstruction Technique, center) result. However, the central large particle is resolved by application of the DIRECTT algorithm (right) into four separate particles, exclusively.

Because of these difficulties the proper data (intensity, geometry) pre-processing is of high significance for good results. Furthermore it has considerable impact on the iteration properties of the algorithm as it requires repeated treatment of the data including all errors.

The mentioned sequence of non-equidistant projection angles has been implemented to the DIRECTT reconstruction program and results in improved sinusoidal traces of the sinogram as confirmed by tracking of isolated particle projections.

All the other mentioned restrictions are well taken care of by the DIRECTT algorithm. This is possible due to the iteration procedure which for each of the partial reconstructions selects only a small but actually dominant part out of the sinogram traces. The percentage of each selection is determined by both a selection parameter and a weight factor which rule the convergence speed and level of the weight and variance of the residual sonogram [7]. In this way the correct assignment of the different densities is performed.

With respect to the Limited View and ROI restrictions another property of the algorithm is of advantage: the evaluation of the trajectories does not require completeness as the partial trajectory is sufficient for its localization in the reconstruction array.

According to the discussed properties the DIRECTT reconstructions clearly provide better quality in comparison to the other algorithms. The magnified details of the different reconstructions (Figs. 4 and 5) prove the much better spatial resolution and reduced artifacts even versus the SIRT algorithm which is considered to be the most advanced in contemporary electron tomography. Furthermore the reconstruction time needed for SIRT is at least one order of magnitude larger.

5. 3D visualization and advanced analysis

Beyond the discussed 2D details the three-dimensional representation of the reconstruction slices (Fig. 6) demonstrates the size relations and the arrangement of the Ru catalyst particles, the Au marker and the carbon support on the copper grid (masked).

The reconstruction quality permits as well the separation of two carbon modifications and the elliptical fitting of catalyst particles (axes ratio and orientation, Fig. 7). This permits the further separation of the embedded and the freely accessible surface which determines the catalytic activity [6].

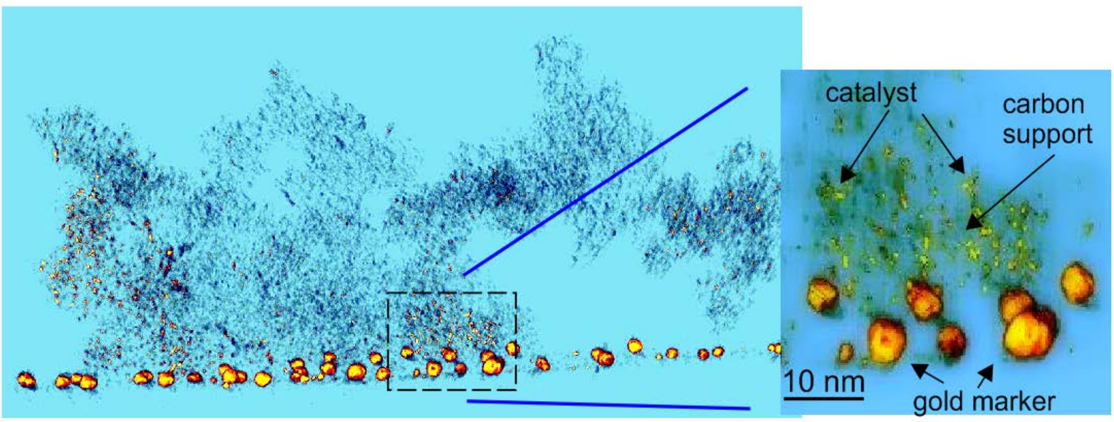

Fig. 6. 3D visualization of Ru catalyst nano particles and magnified detail at about 1 nm spatial resolution; dominant 3–8 nm Au markers on cloddish carbon black supports.

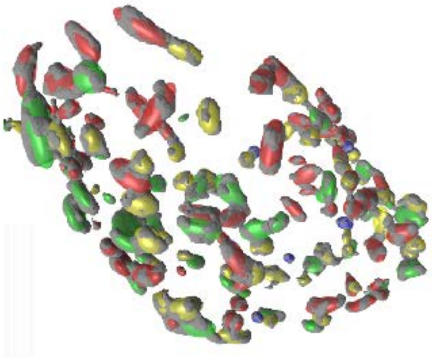 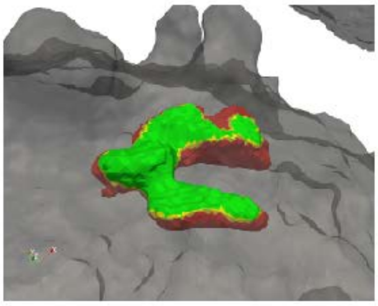

Fig. 7. Examples of analyzing the reconstructed data: left: catalyst particles approximated by ellipsoids (shape, orientation), right: partial embedding of a catalyst particle on carbon black support (reactive surface (green), buried surface (ruby)).

6. Summary

The DIRECTT algorithm together with suited pre-processing proves to handle multiple restrictions which typically occur in experimental electron tomography data, robustly. Advantages with respect to other relevant algorithms are demonstrated by suppression of dominant artifacts and significantly improved spatial resolution of the reconstruction. This is the prerequisite for advanced quantitative analysis of structural details of catalyst materials on the nanometer scale.

Acknowledgement

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