Tomographic Reconstruction and Analysis of a Silver CO$_2$ Reduction Cathode

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Tomographic reconstruction has been well established as a valuable tool in the analysis of polymer electrolyte fuel cell (PEMFC) electrodes. While forays have been made into applying it to polymer electrolyte water electrolyzer (PEMWE) electrodes, CO$_2$ electrolyzer electrodes are still new ground. Here a tomographic analysis of an electrochemical CO$_2$ reduction gas diffusion electrode by means of focused ion beam scanning electron microscope tomography is presented. The reconstruction shows a porosity of 68%. While most of the porosity is on the nanoscale, a broad tail of micropores is observed in the distribution. The spatial distribution of the pores is nonuniform. The large pores are concentrated in the center of the layer in the through-plane direction. From the reconstruction, an effective diffusivity factor of 0.5 for the large pores is calculated. The Knudsen number of 0.19 obtained from the direction. From the reconstruction, an effective diffusivity factor of 0.5 for the catalyst layer is calculated. The Knudsen number of 0.19 obtained from the later shows that the diffusion is mostly in the bulk regime. Flooding of the catalyst layer is likely to decrease the effective diffusivity factor substantially.

1. Introduction

The CO$_2$ reduction reaction (CO$_2$RR) allows for the production of fossil free feedstock and fuels. In particular, the electrochemical CO$_2$RR enables direct power-to-X technology, that is the integration of electricity from (intermittent) renewable sources into the formation process of various valuable products. Technoeconomic analyses of CO$_2$ electrolyzers have identified current density and energy efficiency as the key benchmarks of this technology.[1-5] They further estimate that for adoption of this technology high current densities (hundreds of mA cm$^{-2}$ or more) are required. The current density of the batch cells, which are ubiquitous in CO$_2$RR catalyst research, is intrinsically limited. This points to flow cells with gas diffusion electrodes (GDEs) as a more promising solution. Endrődi et al.[6] and Weeke et al.[7] provide reviews of publications on flow cells using GDEs. Both highlight how flow cells and GDEs enable the aforementioned increase in current density and energy efficiency. Further recent publications demonstrate high current densities using GDEs.[8-10] The morphology of these electrodes is likely instrumental to their outstanding properties.

Polymer electrolyte fuel cells (PEMFCs) and polymer electrolyte water electrolyzers (PEMWEs) serve as models for CO$_2$ electrolyzers, having achieved current densities in excess of amperes per square centimeter using GDE-based electrodes.[11-14] We suggest that if we wish to emulate the high current densities found in PEMWEs or PEMFCs, we need to understand the structure of CO$_2$RR GDEs to subsequently improve it. Especially, we need to understand how the structure–property relations are similar and different from those found in PEMFCs and PEMWEs. This understanding in turn would enable rational design of catalyst layers (CLs), thus guiding the optimization of the manufacturing processes.

To give an example: A point of discussion in some recent publications and perspectives has been the nature of the CO$_2$RR GDEs application for CO$_2$ reduction, Cook et al. proposed a three-phase boundary mechanism according to which CO$_2$ reacts directly from the gas phase.[15] This model has been called into question. Burdyny and Smith[16] posit that for adoption of this technology CO$_2$ reforming is fully flooded during operation; Weng et al.[17] propose that a thin layer of electrolyte covers the catalyst surface, in analogy to ionomer coverages often found in fuel cell models. This again points to the need for an improved understanding of electrode structure, especially its wetting behavior.
Additionally, there is reason to believe that the conditions found in flow cells may differ substantially from those found in batch cells. GDEs may therefore not only be required for scale-up, but also be needed to ensure realistic conditions for catalyst tests. In fact, recent publications show catalyst tests for fundamental catalyst research being performed in a GDE configuration. This implies that understanding of catalyst layer morphology will likely become instrumental, even for fundamental catalyst research.

Lastly, modeling of CO₂RR GDEs would likely profit from improved knowledge of the GDE and especially its catalyst layer. A recent model of GDE operation features many parameters extracted from studies on polymer electrolyte membrane fuel cells (PEMFCs) or approximations (e.g., effective diffusivities via Bruggeman relation). While this represents a valid starting point, there is of course merit in obtaining empirical values which take into consideration the specifics of CO₂RR GDEs.

In order to gain an understanding of the structure of the electrodes, especially highly successful electrodes, a broad array of microscopy techniques is available. Among these, tomographic reconstruction sticks out due to its ability to resolve structures in three dimensions. So far CO₂ reduction gas diffusion electrodes have been reconstructed using X-ray tomography. Kim et al. resolved the structure of a GDE on the microscale. This allowed for the comparison of hand-painted and spray coated electrodes. Additionally, the benefits of a microporous layer (MPL) between CL and carbon fiber gas diffusion layer (GDL) for the morphology of the catalyst layer could be demonstrated. No quantification of tomographic data, however, was given in that work. Also, what is still lacking is a characterization of the catalyst layer on the nanoscale.

One technique capable of achieving nanometer resolution is focused ion beam scanning electron microscopy (FIB-SEM) tomography. The principle of FIB-SEM tomography is illustrated in Figure 1. A serial section of the sample is performed using a focused ion beam. Thus, the sample volume is sequentially milled away. In-between each milling step the section is imaged using a SEM. The resulting stack of images is segmented (physical interpretation of the grey scale values in the tomographic image). The segmented images are then reconstructed into a 3D volume and can be further analyzed.

Since we wish to emulate the improvements achieved for other electrochemical energy conversion technologies for CO₂ electrolysis, it behooves us to consider tomographic achievements in these fields. FIB-SEM tomography entered the field of electrochemical energy conversion with solid oxide fuel cells. The first low temperature application was the reconstruction of a fuel cell cathode catalyst layer. Similarly, water electrolyzer catalyst layers and battery electrodes have been reconstructed. Singh et al. performed a characterization of a solid oxide electrolysis cell’s (SOEC) CO₂ reduction electrode using FIB-SEM tomography. The authors demonstrate the power of the tomographic analysis by comparing two manufacturing routes for the production of electrodes. They were able to explain the superior performance of one electrode over the other by comparing the density of triple phase boundaries encountered in the samples. For low temperature CO₂ reduction, no nanotomographic analysis of electrodes has been performed so far. In this work we present a tomographic reconstruction of a Silver CO₂ reduction reaction gas diffusion cathode using FIB-SEM tomography. We then used the reconstruction to study the geometry of the CL. Furthermore, we ran transport simulations to determine effective diffusivities for the catalyst layer.

2. Results and Discussion

Prior to the tomographic reconstruction we studied the sample by imaging the surface, cross-section and a FIB cross-section. The surface images are shown in Figure 2, cross-section images in Figure 3 and the FIB cross-section in Figure 4. For

Figure 1. Illustration of the workflow of a tomographic reconstruction by means of a serial focused ion beam (FIB) sectioning and scanning electron microscope (SEM) imaging.
the cross-section we also recorded an energy dispersive X-ray spectroscopy (EDX) map to study the composition of the GDE. This map is reproduced in Figure 3.

From these initial images it is already possible to glean valuable information about the sample. The surface shows two distinct kinds of roughness: the large grains shown in Figure 2A, and the porous structure evident in Figure 2C. This is further demonstrated in the cross-sections. Figure 3 shows the overall structure of the CL and indicates a nonuniform thickness and protrusions. Figure 4 shows the porous structure of the electrode. This gives an indication that one scale may be insufficient to fully resolve the whole electrode catalyst layer structure, as this material is clearly hierarchical. The compositional analysis shows a CL of elemental silver deposited on a two-level diffusion medium (DM). The DM’s upper level is a MPL with pores mostly smaller than that of the catalyst layer. It is high in fluorine content indicating that it is likely heavily treated with Polytetrafluoroethylene (PTFE) in order to ensure nonwetting behavior. The DM’s lower level is composed of carbon fibers. Areas of increased fluorine content are found throughout.

The cross-section shown in Figure 4A is suitable for a serial section and subsequent reconstruction. Consequently, the resulting reconstruction is shown in Figure 4B. The reconstruction has a volume of $558 \times 1000 \times 1076$ voxels or $8.2 \times 14.7 \times 15.8 \ \mu m^3$. The $x$ direction is chosen to be the cross-plane direction. Additionally, the $z$ direction is chosen in the direction of image acquisition.

The model geometry immediately allows access to the porosity of the catalyst layer. This is calculated as the fraction of voxels in the pore space. The porosity is thus 68%. This is a larger porosity than was found both for PEMWE anodes catalyst layers (porosity of 50%)[23] and PEMFC cathodes catalyst layers (porosity of 53% and 65%).[26,27] Another parameter readily available from the model geometry is the surface area which is calculated as $1.1 \times 10^{-6} \ m^2$. From this the specific surface area can be estimated as $5.82 \times 10^6 \ m^2 \ m^{-3}$.

The model geometry also allows for the calculation of pore size (PSD) and grain size distributions (GSD). A histogram of the PSD is shown in Figure 5A; a histogram detailing the GSD is shown in Figure 5B. It can be clearly seen that not only are the individual pores on average larger, the distribution is also heavily tailed. The mean and median pore sizes are 613 and 419 nm, respectively. The mean and median grain sizes are in better agreement at 124 and 126 nm, respectively.

The porosity, PSD and GSD can further be spatially resolved in the different main directions of the reconstruction. A trend was found in the porosity as resolved in the through-plane direction. This is recorded in Figure 6 (alongside the mean grain size and pore size). The porosity is highest at the center of the catalyst layer. Lower porosities are found towards the MPL and surface, the porosity being lowest closest to the surface. As can be seen in the spatially resolved mean pore size, the increase in porosity goes hand in hand with an increase in mean pore size.
We further used the model geometry to calculate transport parameters for the catalyst layer. For this we considered two models of diffusive transport: bulk diffusion and Knudsen diffusion. The former is calculated by solving Fick’s law in the pore volume. The latter is calculated by Monte Carlo methods. The effective diffusivity factor is a geometric factor correcting the diffusion coefficient. It is defined as the fraction of porosity and tortuosity

$$D_{eff} = \frac{\epsilon}{\tau}$$  \hspace{1cm} (1)

where \(\epsilon\) is the porosity and \(\tau\) is the tortuosity. Thus, the diffusivity allows the calculation of tortuosity. For the bulk diffusion we obtained an effective diffusivity factor of 0.46 in the through-plane direction. This leads to a tortuosity of 1.47. For the Knudsen diffusion process, we found an effective diffusivity factor of 0.50. This yields a tortuosity of 1.36. The Bruggeman relation on the other hand underestimates the tortuosity \((\epsilon^{-0.5} = 1.21)\) in this case. It would thus overestimate the diffusivity.

The Knudsen Monte Carlo simulation also provides a value for the characteristic length scale in the distance between collisions with solid surfaces. We can thus calculate the Knudsen number as

$$Kn = \frac{\lambda}{l} = \frac{68.6 \text{ nm}}{354.545 \text{ nm}} = 0.19$$  \hspace{1cm} (2)

where \(\lambda\) is the mean free path (assuming ideal gas behavior) and \(l\) is the characteristic length scale as determined by the Monte Carlo simulation. We thus find that the transport within the length scales of the reconstruction is mostly of bulk nature.

While so far there are no comparable studies of \(\text{CO}_2\text{RR GDEs}\) in literature, it is possible to make limited comparisons to Silver structures used for oxygen reduction in alkaline environments. Tomographic reconstructions of Silver-based oxygen depolarized cathodes (ODCs) using FIB-SEM tomography\(^{28}\) and synchrotron X-ray computed tomography\(^{29}\) have been performed. Neumann et al.\(^{28}\) found significantly lower porosity (=0.37) and tortuosity (=1.09) in the ODC GDEs. In both cases the investigated structure differed markedly from the one we studied. First, the silver component of the GDEs was an order of magnitude thicker. Additionally, the structures encountered ( pores and grains) were also larger by on to two orders of magnitude.

Transport parameter investigations on an ODC were carried out by Danner et al.\(^{30}\) based on a FIB-SEM tomography. They found orientation dependent effective diffusivity factors between 0.27 and 0.45 for unflooded electrodes.

Lastly, EDX maps of the catalyst layer and microporous layer indicate signs of electrolyte infiltration. This is in tune with recent publications, which have postulated that the catalyst layer is flooded or partially flooded during operation.\(^{16}\) Figure 7 shows this map. The potassium signal aligns well with the silver signature of the catalyst layer. Potassium was likely deposited in the catalyst layer by the electrolyte (potassium carbonate). Minor potassium signals are also observed in the GDL likely from the flooding at higher current densities. We cannot conclude from this data whether the catalyst layer is flooded during operation or not, as the flooding and deposition could take place prior, during or after operation. In the case of full flooding, diffusive transport must take place at the much lower aqueous rate \((1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})\). This emphasizes the need for designing catalyst layers with a percolating gas transporting phase.

3. Conclusion

Using FIB-SEM tomography we have reconstructed a model of the CL of a \(\text{CO}_2\text{RR GDE}\). We found a highly porous layer with a nonuniform distribution of pore sizes in the through-plane direction. The porosity is highest at the center of the
layer. We derived estimates for the surface area and relative diffusivity from the reconstruction. These parameters should be used to update models of CO$_2$RR GDEs. Further investigation should be made into the flooding behavior of the catalyst layer; it should be investigated how this flooding affects the diffusivity factor.

The structure of the diffusion medium composed of MPL and fibrous GDL have yet to be explored. We posit that FIB-SEM tomography may serve as an adequate tool for the microporous layer. Ideally the interface between MPL and CL should be studied analogously to results from PEMFCs.[26] The structure of the GDL can be reconstructed by means of micro computed tomography, as has been done for PEMFC GDLs. A full reconstruction of all elements of the GDE would enable full resolution of the GDE as has been proposed for PEMFCs.[31] Such a multiscale reconstruction could be leveraged into more powerful models of CO$_2$RR GDEs.

4. Experimental Section

Sample Preparation: A catalyst ink was prepared by dispersing Ag nanoparticles (Iolitec nanomaterials, 50–60 nm 200 mg) in 1-propanol (3 g). Sustainion[32] XA-9 (dioxide materials 800 mg of 5 wt% solution) was added to the suspension and the resulting ink was sonicated for 30 min. The ratio of polymer to silver was 20%. This differs from values suggested in literature,[33,34] in an unsuccessful effort to maximize the visibility of the ionomer in the reconstruction. The GDE being specifically prepared for a tomographic study; it was not optimized for performance. Following preparation, the ink was dropcasted on a GDL (Freudenberg H23C2 50 cm$^2$), which consists of a microporous carbon black layer and a fiber-based PTFE-bounded backbone. After dropcasting, the GDE was left to dry overnight at room temperature. All electrochemical testing was performed in a commercial flow cell (micro flow cell, ElectroCell A/S). The GDE was operated in 1 M K$_2$CO$_3$ at progressively increasing current densities up to 500 mA cm$^{-2}$. Partial flooding of the electrode was observed for current densities in excess of 200 mA. Electrochemical data can be found in Figures S1–S4 (Supporting Information).

Figure 6. A–D) Porosity GSD and PSD as resolved along the three main directions of the tomography. The orientations are indicated in (B).

Figure 7. EDX map of the catalyst layer and microporous layers. A) Overlay of carbon, fluorine, and silver maps; B) potassium map.
The tomographic studies were performed post operation. The sample preparation procedure follows two distinct paths: one for embedded cross-sections and one for surface images, FIB cross-sections, and FIB serial sections.

**Embedded Cross-Section:** The sample was embedded and infiltrated using an epoxy resin. To this end, a piece cutout from the GDE was sandwiched between to pieces of PTFE using a plastic clip. The assembly was placed into a sample cup and the epoxy resin (EpoThin, Buehler Inc.) poured to cover the entire sample. The sample cup was then placed into a desiccator. Vacuum was applied 3 times using a vacuum pump. The vacuum was maintained for at least 10 min. The infiltrated sample was set to cure overnight.

The cross-section was obtained by grinding and polishing the sample. For this purpose, a sanding machine (Struers GmbH, MetaServ 250) was used. 320 grain silicon carbide sanding paper was used until the cross-section was visible under an optical microscope (Zeiss, AX10). Subsequently finer grains where used, up to 4000 grain. Following the grinding step, the sample was polished in a two-step process. A rotary polishing machine (Struers GmbH, RotoPol-3) was used. For the first step MD Dac polishing plate (Struers) was used together with 3 µm polishing agent (ATM GmbH). In a second step a MD Chem polishing plate (Struers) was used together with 0.25 µm polishing agent (ATM GmbH). The sample was then cleaned by sonication (Elma, S30) in deionized water after grinding and each polishing step.

To prevent charging of the sample or embedding agent under SEM imaging, the sample was carbon coated. For this purpose a carbon sputter coater (Balzers Union, MED 010) was used. The carbon coated sample was fixed on an aluminum stub sample holder. This was done using adhesive, conductive carbon tabs (Plano GmbH, G3347). Conductivity between stub and carbon coated top surface was provided by aluminum conductive tape (Plano GmbH).

The chemical composition of the cross-section was evaluated using EDX. The EDX measurement was performed using an accelerating voltage of 20 kV and at a probe current of 2 nA. The spectrum was analyzed using a silicon drift detector (Oxford Instruments, X-Max 150). The software used for the analysis (AZtec) was provided by the same vendor. All maps shown are processed using the AZtec true map function.

**SEM Surface Images:** A section of ≈8 × 5 mm was cut out from the sample. The cutout was then attached to an aluminum SEM stub using conducting adhesive stickers (G3347, Plano GmbH). The conductivity was further assured by contacting the top of the sample with silver conducting paint (G3692, Plano GmbH).

**FIB Section and Serial Section:** The FIB sectioning was performed using a Zeiss Crossbeam 540 FIB-SEM. The sample stage was tilted to an angle of 54° with respect to the horizontal.

In order to shield the cross-section from unintended beam damage, platinum was deposited above the region of interest. For this purpose, an ion beam deposition was performed over an area of 25 µm × 25 µm. A deposition current of 1.5 nA was employed while providing a platinum precursor gas (trimethyl[methylcyclopentadien]platinum(VI)) using a gas injection system (Orsay Physics, MonoGIS). Thus, the applied dosage rate was 2.4 pA µm².

The cross-section was excavated by ion milling. The front face was milled by applying a beam current of 30 nA. Subsequently trenches were milled on the left and right side of the region of interest to fully excavate it. Last, the front was polished with a current of 1.5 nA.

The serial section was performed with the following cutting and imaging parameters. An ion beam with 30 kV accelerating voltage and 1.5 nA current was used to perform the sectioning. The milled area was a rectangle of width 26.36 and 18 µm depth. The nominal thickness of each slice was 24 nm. After each slice the cross-section was imaged using the SEM column with an acceleration voltage of 3 kV, at a current of 750 pA. The images were recorded with a resolution of 2048 × 1536 pixels. The nominal width was 30 µm and hardware tilt compensation was enabled (36° compensation setting).

The surface of the region of interest was imaged using the FIB. Images were taken both before and after the serial section. From these images it is possible to determine the actual length of the cut volume. From the total number of slices the average slice thickness can be estimated as: 24.36 nm. This is only a slight deviation from the nominally set value of 24 nm.

**Registration and Segmentation:** The images obtained above were processed in MATLAB. For this purpose, the images were read in to create a 3D matrix of greyscale values. The images were further processed by registration of a background feature. Thus aligned, the images were shifted in accordance with the acquisition angle of 54° and computed slice thickness of 24.36 nm. The stack now reproduces a series of images normal to the cutting plane. A box shaped volume was obtained by cropping. This was done by trimming such that neither microporous layer nor the platinum protective layer was included in the stack.

The finished stack of 661 images was then segmented to obtain a logical 3D matrix, comprised of the solid volume fraction and the pores pace (inverse image). The segmentation was performed by an in-house developed optical flow algorithm. The connectivity of the pores space and the solid volume fraction were assessed. By this it was ensured that only pores that are physically accessible were counted. Conversely, no solid volume was considered that would be unphysical. Thus, a model geometry for the catalyst layer was obtained. It should be noted that the segmentation does not distinguish between pore space and materials with a strong contrast to silver. Consequently, the ionic binder was not segmented. The model geometry was up-sampled using bilinear interpolation in order to obtain cubic voxels. Thus, voxels with a side length equal to the SEM acquisition resolution of 14.65 nm were obtained.

**Analysis of the Reconstruction:** Pore size and grain size distributions were calculated using the methodology described by Thiele et al.[25] A MATLAB (MathWorks Inc.) implementation of the algorithm was used. Further analysis of the segmented volume was carried out using GeoDict (math2market GmbH). The model geometry was analyzed using the PoroDict toolbox to obtain surface areas. Calculations were carried out on the geometry using the DiffuDict toolbox. Thus, transport parameters were obtained as well.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

CO2 reduction, FIB-SEM, gas diffusion electrodes, power-to-X technology, tomography

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