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Multiscale tomography of nanoporous carbon-supported noble metal catalyst layers

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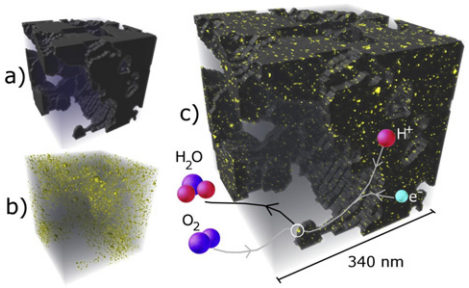
HIGHLIGHTS

- A commercial PEMFC cathode catalyst layer is analyzed by multiscale tomography.
- We propose an approach to combine both tomography information in a single geometry.
- This enables analysis of limiting transport processes based on experimental data.

GRAPHICAL ABSTRACT



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ABSTRACT

Noble metal catalysts are a scarce, non-renewable resource, and yet are required in a wide range of industrial applications, including in polymer electrolyte membrane fuel cells (PEMFCs). The effectiveness of PEMFCs depends not only on the size, active surface area, and distribution of the Pt catalyst nanoparticles, which affects reaction kinetics, but also on the porous structure of the carbon support, which affects mass transport. Unfortunately, the very different size scales – several nm for the Pt catalyst vs. several μm for the porosity features – cannot be characterized by a single method. Here, we present a novel approach for integrating information from both of these size scales to build a single geometrical model. Focused Ion Beam – Scanning Electron Microscope tomography (SEMt) was carried out on a commercial PEMFC cathode catalyst layer to characterize porosity, connectivity as well as pore-size and grain-size distribution. Transmission Electron Microscopy tomography (TEMt) was used to analyze volume and surface area distributions of nanometer sized platinum catalyst particles. Further, we propose an up-scaling approach to translate the information obtained from TEMt to SEMt. Knowledge of catalyst particle locations within the solid support matrix will be critical in enabling the analysis of limiting transport processes in PEMFC CCLs.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are considered to be an important part of the solution to the 21st century global energy challenge [1]. However, after decades of fundamental research, major challenges in the development of electrodes remain unsolved. In particular, the oxygen reduction reaction (ORR) and its

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related transport processes in the Cathode Catalyst Layer (CCL) are generally considered to be one of the major causes of performance loss [2]. Not only are the kinetics of the ORR roughly six orders of magnitude slower than the hydrogen oxidation reaction at the anode [3], the production of H_2O at the cathode can also lead to flooding in the micron to nanometer sized pores in the CCL, thus inhibiting O_2 diffusion. Optimizing the PEMFC CCL is therefore a crucial area of research and requires a thorough understanding of the CCL structure, including the porosity, pore-size-distribution, ionomer distribution, catalyst loading, catalyst distribution and catalyst accessibility for the reactants.

As there is no analysis method which can be used to carry out *in situ* structural investigations at the nm scale, modeling the physical processes occurring at the nanoscale is therefore the only method currently available to improve the fundamental understanding of the CCL. Here electrons, protons and oxygen must come together at the catalytic Pt nanoparticle sites to enable the ORR. Therefore, the quantitative determination of the various transport processes in a CCL relies on detailed knowledge of the morphology of the transport media of the reactants [4]. Pt nanoparticles serve as catalysts for the ORR in a CCL and are a scarce, non-renewable resource, required in a wide range of industrial applications [5]. In PEMFCs, Pt nanoparticles (typically 3–6 nm in diameter) within the catalyst layers at both the anode and cathode are utilized to facilitate the desired redox reactions occurring at both electrodes [6]. Knowledge of the distribution and the precise location of the Pt nanoparticles in the CCL is therefore especially important to allow modeling of the performance of a PEMFC.

To date, there have been two main approaches to obtaining a three-dimensional CCL representation. One is a stochastic approach using assumptions about the material and the second involves a direct approach based on tomographic images. Stochastic reconstructions are three-dimensional structure models produced by utilizing microstructural descriptors [7]. From these, three-dimensional structure models can be produced by a mathematical optimization process [7–9].

The foundation of the direct approach is a three-dimensional image of the CCL. Different tomographic methods exist and each method has advantages and disadvantages as well as covering a specific feature size range [10]. The main advantage of this approach is that no further modeling assumptions must be made, thereby providing a realistic starting point for the CCL morphology. Design assumptions deduced from such a model are therefore more likely to result in improvements in the morphology and microstructure of the CCL.

In the past, Scanning Electron Microscopy (SEM) tomography (SEMt) analysis has been extensively used in material science, including for ceramic systems [11], cement analysis [12], solid oxide fuel cells [13], and very recently, also for PEMFC CCL studies [14]. This imaging method has an anisotropic resolution down to 10 nm in the cutting direction ('*z*-direction') and as low as 1 nm in the remaining directions ('*x*- and *y*-directions') [11]. SEMt is very well suited for the analysis of pore space with pores ranging from a few nm to a few hundred nm in size [15]. A number of publications have focused on PEMFC CCL SEMt within the last year [14–18]. A major drawback of this method, however, is that only pore and solid space can be distinguished [15]. This means that the solid phase cannot be further differentiated into its carbon, ionomer and Pt particle components.

Transmission Electron Microscopy tomography (TEMt) has been used for imaging and analysis of catalyst particles in the past [19,20]. Using this three-dimensional technique, detailed morphological information about the particles is then obtainable [19]. TEM tomography has also been used for the imaging of PEMFC CCLs [21]. Due to the high electron scattering of the noble metal catalyst component, PEMFC samples used for TEM tomography must be very thin (e.g. 100 nm). While TEM, with its sub nm resolution, is excellent for characterizing the Pt nanoparticles in PEMFC CCLs, the typical pore-sizes in the solid support can be up to a few microns [4]. Therefore, a significant portion of the pore space cannot be evaluated by TEMt. While SEMt can differentiate the pore and solid spaces, TEMt provides the very much needed information about the catalyst particles, which is not accessible with SEMt, making these two techniques highly complementary to each another.

In the present work, we present an approach for capturing information from both of these size scales using only one geometric representation. The morphological information obtained from TEMt is combined with the information produced by SEMt and an up-scaling approach to translate the information obtained from TEMt to SEMt is proposed. It is important to note that, while our current work is focused on the application of this method to PEMFC CCLs, it has wider applicability, spanning many disciplines. Specifically, our approach will be of great value in all areas that utilize metal nanoparticles deposited in a porous matrix (e.g. electrodes for electrolysis, battery applications, automobile catalytic converters, etc.).

2. Experimental methods

A commercial Gore PRIMEA A510.1 M710.18 C510.4 PEMFC membrane electrode assembly (MEA) was used to carry out both TEMt and SEMt. The Pt loading (mass of Pt per unit surface area) was 0.1 mg cm^{-2} at the anode and 0.4 mg cm^{-2} at the cathode (Fig. 1). Spatial directions, indicated in the text and in Fig. 1, are maintained in all further discussions. For the SEMt, the surface of a cut is in the *xy* plane.

2.1. TEMt

All TEM work was performed using a Tecnai TF20 G2 FEG-TEM (FEI, Hillsboro, Oregon, USA), located in the Microscopy and Imaging Facility at the University of Calgary, with a Fischione 2040 Dual-Axis Tomography Holder (Fischione Instruments, Export, Pennsylvania, USA). The MEA was embedded in Epon-812 (EMS, Hatfield, Pennsylvania, USA) and approximately 200 nm thick sections were cut using a Leica Ultracut UCT (Leica Microsystems, Wetzlar, Germany).

The sections were placed on one side of a TEM Slot Grid (1 × 2 mm) that was covered with a ~40 nm thin continuous Formvar film (EMS). Colloidal Au particles (10 nm diameter, Cell Microscopy Center, University Medical Center Utrecht, Utrecht, The Netherlands) were

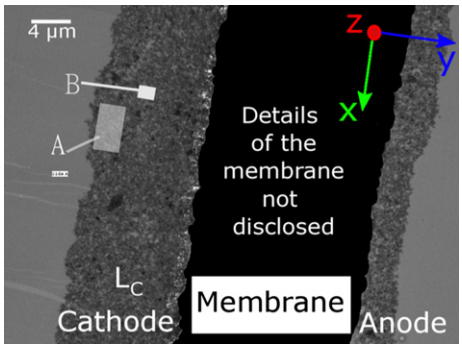

Fig. 1. Schematic of an ultra-microtome cut through the MEA. The cathode, ionomeric membrane separator, and anode are visible, but due to restrictions from the manufacturer, the membrane is blackened. The relative positions of the SEMt sample area (A) and TEMt sample area (B) are schematically indicated. The thickness of the cathode (LC) is 11.4 ± 0.8 µm, as determined from this image. The *x*-, *y*- and *z*-directions are indicated and maintained in all further discussions.