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4D *in situ* visualization of electrode morphology changes during accelerated degradation in fuel cells by X-ray computed tomography

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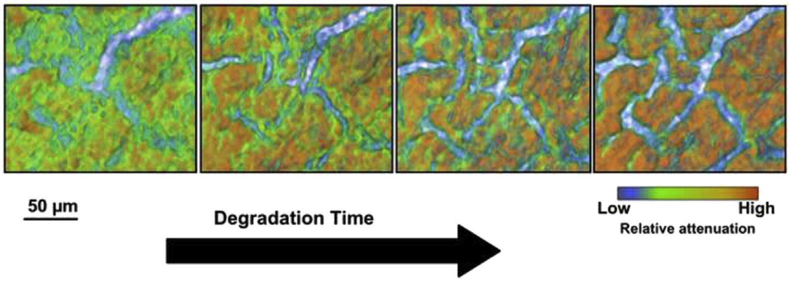
HIGHLIGHTS

- A methodology is developed for 4D *in situ* visualization of electrode degradation.
- Periodic electrochemical diagnostics and XCT images are measured during degradation.
- Electrode degradation differences between land and channel regions are observed.
- Same location tracking reveals cathode catalyst layer crack propagation over time.
- Temporal variations in X-ray attenuation indicate local compositional changes.

GRAPHICAL ABSTRACT



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ABSTRACT

A four-dimensional visualization approach, featuring three dimensions in space and one dimension in time, is proposed to study local electrode degradation effects during voltage cycling in fuel cells. Non-invasive *in situ* micro X-ray computed tomography (XCT) with a custom fuel cell fixture is utilized to track the same cathode catalyst layer domain throughout various degradation times from beginning-of-life (BOL) to end-of-life (EOL). With this unique approach, new information regarding damage features and trends are revealed, including crack propagation and catalyst layer thinning being quantified by means of image processing and analysis methods. Degradation heterogeneities as a result of local environmental variations under land and channel are also explored, with a higher structural degradation rate under channels being observed. Density and compositional changes resulting from carbon corrosion and catalyst layer collapse and thinning are observed by changes in relative X-ray attenuation from BOL to EOL, which also indicate possible vulnerable regions where crack initiation and propagation may occur. Electrochemical diagnostics and morphological features observed by micro-XCT are correlated by additionally collecting effective catalyst surface area, double layer capacitance, and polarization curves prior to imaging at various stages of degradation.

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1. Introduction

Increasing evidence and severity of climate change due to greenhouse gas emissions has pushed the need for government regulations to introduce stricter limits on fossil fuel combustion in new passenger cars, as well as in other light-to heavy-duty vehicles [1]. The need to produce electrical power from renewable energy sources and utilize zero-emission engines has now become the forefront of today's technological evolution, in which electrochemical energy conversion has a central role. Polymer electrolyte fuel cells (PEFCs) are beginning to demonstrate their ability to produce reliable zero-emission power in a variety of commercial applications including automotive and stationary power systems. Further cost and performance degradation improvements present significant opportunities as the technology continues to be refined [2,3].

The lifecycle performance of automotive fuel cells can be affected by degradation of the membrane electrode assembly (MEA) due to a number of chemical and mechanical stresses associated with operational cycles in automotive systems. This performance degradation is a result of various processes which may occur to varying extents, such as corrosion of the catalyst support, membrane thinning, catalyst particle agglomeration and oxidation, loss of hydrophobicity, as well as interfacial effects such as delamination [4–7]. The detailed understanding of these degradation mechanisms is imperative to mitigating their effects and has motivated the need for new methods of investigation to study the state of components at various stages of their lifetime.

Currently, a wide variety of visualization techniques are being used to study PEFC degradation. These include: electron microscopy, neutron imaging, magnetic resonance imaging, X-ray imaging, optical visualization, and thermal mapping [6,8–10]. Among these, only X-ray computed tomography (XCT) has shown to have the ability to obtain sufficient resolution to observe electrode related degradation effects while being non-invasive [4,10–13]. Typically, research regarding XCT has been performed through the use of synchrotron beamlines, which are very costly and of limited availability. It has also been shown that great care must be taken when exposing fuel cell components to the high intensity incident X-ray beam which can compromise fuel cell components, with significant radiation damage occurring after merely 200 s of exposure [15]. This makes repeated scans of the same fuel cell impractical. The use of a laboratory scale micro-XCT, with incident beam intensity orders of magnitude lower than the synchrotron beam, has recently been shown to overcome such radiation damage effects during the exposure time of multiple imaging events while still yielding adequate and relevant radiograms and tomography data sets [16].

Micro-XCT investigations related to fuel cell degradation have so far been primarily limited to *ex situ* studies where the sample has been removed from the fuel cell hardware and cut to size for optimal imaging [12,17,18]. This methodology poses a number of unforeseen problems that may affect the interpretation of the images acquired, including: compression changes, additional mechanical stresses from handling, and changes in relative humidity (RH). Also, previously there have been no visualizations of progressive morphological changes, primarily due to the limitations of the experimental procedure. In order to overcome these effects and limitations, the fuel cell can be visualized *in situ*, where the cell is situated in X-ray transmissive test hardware that also provides necessary operating conditions such as temperature, supply of reactant gases, and monitoring of the cell voltage and current. A unique hardware design would need to be employed which embodies all these elements. Consideration that the X-ray beam attenuates with material thickness, density, and atomic number would imply that no metal components or other non-essential materials should be within the field of view of the imaging area [11,19,20].

In this work, we propose the use of four-dimensional *in situ* visualization of electrode degradation processes in fuel cells. This unique approach is facilitated by a custom-designed, X-ray transparent small-scale fuel cell fixture integrated with a commercial, micro-XCT scanner for non-invasive, repetitive viewing of the same fuel cell domain at various points in time. This effectively provides 4D data across space and time. The proposed approach is demonstrated in this work by visualization of morphological changes in the cathode catalyst layer during various stages of degradation due to voltage cycling.

2. Experimental

2.1. Materials

All fuel cell materials used in this study consisted of catalyst-coated membranes (CCMs) and gas diffusion layers (GDLs). The CCM was composed of a Dupont Nafion® NR211 membrane core with anode and cathode catalyst layers each with a 50:50 Pt/C ratio at 0.1/0.4 mg cm^{-2} Pt loadings, respectively. The anode and cathode GDLs consisted of teflonated Avcarb® non-woven carbon paper coated with a micro-porous layer (MPL). Due to the interest in cathode catalyst layer corrosion in this study, a high crack density CCM was employed. The membrane electrode assembly (MEA) forged from these parts was framed by Kapton® adhesive sheets with a thickness of 80 μm. Kapton® adhesive sheets were also used as gaskets to aid sealing and limit the compression of the GDLs to 20± 5%.

2.2. Fixture design and fabrication

The design of the small-scale fuel cell fixture used in this work has been developed to allow for full operation, at temperature, while applying voltage cycling during accelerated stress testing as well as for *in situ* imaging using a lab-based, commercial XCT system. The fixture design, shown in Fig. 1, was fabricated from compressed carbon/graphite with cured resin (SGL Group), which allows for sufficient transmission of the incident X-ray beam, good electrical and heat transport, and sealing of hydrogen and air gases under pressure. The design was machined by Computer Numeric Control (CNC) to precisely cut the graphite plates into an hourglass shape. As discussed previously, the design is limited in size due to the conditions required for obtaining high signal-to-noise ratio projections to be used in reconstruction of the 3D volume of the sample area [11,19]. The active area was thus limited to 8×3 mm^2, predominantly situated in the central, thin section of the fixture design, as shown in Fig. 1, which was placed in the field of view during imaging. The flow-field was cut to meet similar design requirements of a technical cell consisting of parallel channels [21,22]. Other components necessary for full functionality were positioned in the wide section of the fixture (Fig. 1), including current collectors and voltage measurement leads connected by conductive silver epoxy (8330S, M.G. Chemicals Ltd.), inlet and outlet ports for reactant gases, thermocouple, and miniature cartridge heater (Omega Engineering Inc.). The thermocouple and cartridge heater extended down to approximately 1 mm away from the thin viewing section of the fixture, thereby minimizing temperature gradients within the active area. Housing and compression plate parts were printed from high temperature 3D print material (Object RGD525, Objet Ltd.) which was subjected to a thermal treatment process to increase its heat deflection temperature beyond the PEFC operating temperature.