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Morphology studies on high-temperature polymer electrolyte membrane fuel cell electrodes

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HIGHLIGHTS

- Steady-state cell performance is insensitive to electrode macrostructure variation.
- High surface wettability of the catalyst layer reduces the cell start-up time.
- Electrode microstructure has a major impact on the steady-state cell performance.
- Slow drying process of the catalyst slurry leads to a PTFE-rich electrode surface.

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ABSTRACT

The electrode morphology influences the properties and performance of polymer electrolyte membrane fuel cells (PEMFC). Here we report our studies of two different electrodes for high-temperature PEMFC prepared by spraying and coating and their impact on the fuel cell performance. Differences in 3D microstructure and adhesion between catalyst layer and gas diffusion layer (GDL) of the electrodes were studied with X-ray microtomography. Scanning electrode microscope investigations show hairline cracks between agglomerates on the surface of the sprayed electrode, whereas the coated electrode shows a network of shrinkage cracks in the catalyst layer. The distribution of the electrode binder polytetrafluoroethylene (PTFE) is related to the locally resolved conductivity, which was determined by scanning the electrode surfaces with a conductive atomic force microscopy (AFM) tip. The macrostructures of the sprayed and coated electrodes are different but contain similar pore structures. The coated electrode has a higher PTFE concentration on the top region, which tends to form a nonconductive and less wettable "skin" on the electrode surface and delays the start-up of the fuel cell. In contrast to low-temperature PEMFC, the electrode morphology has only a minor impact on the steady-state cell performance of high-temperature PEMFC.

1. Introduction

In recent years, the high-temperature polymer electrolyte membrane fuel cells (HT-PEMFC) have attracted increasing research interests. The benefits of operating the fuel cell at elevated temperatures (>120 °C) include improved catalyst activity, higher tolerance to impurities such as carbon monoxide in the hydrogen fuel, and much simplified thermal and water management of the system. Generally, the performance of HT-PEMFC is robust under a wide range of operating conditions. All these advantages make the HT-PEMFC ideally suited for applications such as stationary and auxiliary power units [1,2].

A conventional high-temperature membrane electrode assembly (HT-MEA) primarily consists of a polybenzimidazole (PBI) type membrane containing phosphoric acid and two gas diffusion electrodes (GDE), the anode and the cathode, attached to the two surfaces of the membrane. GDEs are usually prepared by spreading a suspension of carbon-supported platinum catalyst, solvent, and binder onto a gas diffusion layer (GDL), followed by drying. Because of the elevated operating temperature of HT-PEMs, polytetrafluoroethylene (PTFE) is often used as the binder material. The commonly used techniques to dispense the catalyst suspension include spraying [3] and coating [4].

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Although a great deal of effort has been devoted to cell performance optimization by altering individual components of the GDE [4–9], there are considerably fewer studies that investigate how these changes might affect the electrode morphology and subsequently impact the cell performance. There are some very limited studies to compare the influences of different catalyst layer deposition methods and electrode morphologies on the performance of GDEs for HT-PEMFC [10] and low-temperature PEMFC [11–15].

In the general field of PEMFCs, there exist a wide range of catalyst deposition methods [16], such as spraying [17], decal transfer [18], painting [10], screen printing [19], rolling [20], sputter deposition [21], coating [4] etc. For our study we selected the two most common methods for HT-PEMFCs, i.e., spraying and coating. With these two different techniques, significant differences in the electrode micro- and macrostructures are expected because the processes and the consistencies of the catalyst suspensions are distinctly different. Spraying is a layer-by-layer process using a relatively dilute catalyst suspension, while coating is a one-step process using a more concentrated and more viscous suspension.

To better understand how these different electrode morphologies affect the electrochemical properties of the GDEs, we conducted extensive studies employing a variety of advanced experimental techniques including X-ray microtomography, conductive atomic force microscopy, and scanning electron microscopy. To characterize the GDEs electrochemically, we fabricated MEAs using these electrodes and evaluated them in single cell tests.

X-ray microtomography is an emerging analytical technique, which is based on the same principle as the well-known X-ray computed tomography (CT) method for medical imaging. It measures variations in X-ray attenuation upon sample rotation to generate cross-sectional images of the samples at various depths into the material with high spatial resolution (0.7–26 μm/pixel) in a non-destructive fashion over large geometric volumes (on the order of 1 mm^3). Furthermore, variations in X-ray absorption also provide information on different phases/elements and their distribution within the sample. In fuel cell research, this technique has been used mainly for visualization of the morphology and water build-up in GDLs [17,22]. Complete MEAs were imaged by Pfrang et al. [23]. Very recently, Jhong et al. [11,12] employed X-ray microtomography to correlate the catalyst layer structures with the fuel cell performance. All these studies were performed for the low-temperature Nafion-based PEM fuel cells.

To investigate the PTFE distribution within the electrode, we performed measurements with atomic force microscopy (AFM). Besides morphology and topography, AFM is also capable of measuring the locally resolved conductivity of the sample. Thereby a Pt-coated AFM tip probes the current between the back and the top of the sample as its moves over its surface. The technique was used before to characterize low-temperature PEM fuel cell membranes and electrodes [24,25], and we find it is specially suited for HT-PEM electrodes due to the distinctive spherical shape of the nonconductive PTFE binder. Furthermore, we took scanning electron microscopy (SEM) images of the catalyst layers to complement our investigations. SEM is a valuable tool for visualization of the surface morphology and porosity of the electrodes.

2. Experimental

2.1. Preparation of GDEs via spraying and coating

Catalyst suspensions containing water (Millipore®), isopropanol, PTFE solution (60%, 3M), and 20% Pt/C (Heraeus) were used for the GDE preparation. The water content was adjusted to optimize the consistency of the suspension for different catalyst deposition processes, resulting in an "ink" for spraying and a "paste" for coating. The weight ratio of the suspension's various compositions (water, isopropanol, PTFE solution, and carbon-supported catalyst) were (15:12:1:1) and (3:12:1:1) for the ink and paste, respectively. To produce a homogenous suspension, a magnetic stirrer was sufficient for mixing the ink, whereas an Ultra-Turrax® dispersing machine (IKA) was used for the paste.

In the next step, the paste was coated onto the microporous layer of a commercially available GDL (10BB, SGL Carbon) with an automated doctor blade technique. The drying process was at room temperature, first in a closed box for 24 h and then in open atmosphere until the weight was constant. The ink, on the other hand, was sprayed in multiple layers directly onto the microporous layer of the same GDL (also 10BB, SGL Carbon) at a substrate temperature of 80 °C. The distance between the spray head and the substrate was about 20 cm, the average drop size was below 0.5 mm, and each layer was dry after about 1 min. For this study, the catalyst loading was kept constant at around 1 mg cm^{-2}, which was calculated from the weight difference between the dried GDE and the GDL. All the GDEs had approximately the same PTFE content of circa 40% by weight.

2.2. Structural characterization of GDEs

2.2.1. Scanning electron microscopy (SEM)

The surface microstructures of the GDEs were studied using a scanning electron microscope (Merlin, Carl Zeiss). Depending on the magnification, the images were taken with an accelerating voltage between 8 and 15 kV. Because of their high intrinsic conductivity, the samples did not require additional conductive coating for SEM.

To image the cross-sections of the GDEs, a Nova Nanolab 200 (FEI) focused ion beam scanning electron microscopy (SEM/FIB) system was employed, which combines an ultra-high resolution field emission SEM with a focused ion beam (FIB) to etch the sample surface. In this microscope, an electron column placed above the sample stage enables imaging at high resolutions down to approximately 1 nm. The gallium-ion source for the FIB is mounted at an angle of 52° relative to the electron column. The SEM accelerating voltage was also between 8 and 15 kV. Due to the high cohesion between the particles and the material density, the sample pores were not filled before sputtering.

2.2.2. X-ray microtomography

Micro-CT 1172 (Skyscan) was used for visualization of the electrode internal structures with a resolution down to a few μm. The X-ray source had a variable accelerating voltage between 20 and 100 kV and a maximum power of 10 W. Lower-energy X-ray is suitable for light and porous materials such as carbon fibers of the GDL, whereas higher-energy is preferred for dense metal materials like platinum in the catalyst layer. The samples were circular specimens with a diameter of 4 mm. They were punched out of the GDEs and mounted onto the rotating sample holder. The 2-D radiographs were recorded on an 11-megapixel camera with a projection angle step of 0.25° per radiograph. As the sample was rotated stepwise over the entire 180° range, 720 projections were taken with a 16-s exposure time for each projection. The accelerating voltage of the X-ray source was set to 40 kV. The radiographs had a resolution of 1 μm per Pixel. The image reconstruction and 3D rendering were conducted using the NRecon reconstruction software (Skyscan), which was part of the Micro-CT system.

2.2.3. Atomic force microscopy (AFM, conductive mode)

The AFM surface conductivity measurements were performed with a commercial AFM system (Multimode 8, Bruker). All images were taken with a combination of the so-called "PeakForce QNM"