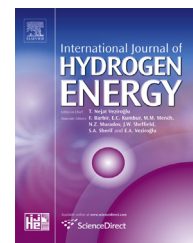


Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Influence of the polytetrafluoroethylene content on the performance of high-temperature polymer electrolyte membrane fuel cell electrodes

Florian Mack^a, Tobias Morawietz^b, Renate Hiesgen^b, Dominik Kramer^a, Viktor Gogel^c, Roswitha Zeis^{a,d,*}

^a Karlsruhe Institute of Technology (KIT), Helmholtz Institute Ulm (HIU), Ulm, Germany

^b University of Applied Sciences Esslingen, Department of Basic Science, Esslingen, Germany

^c Centre for Solar Energy and Hydrogen Research Baden-Wuerttemberg, Division 3, Electrochemical Energy Storage and Conversion, Ulm, Germany

^d Karlsruhe Institute of Technology (KIT), Institute of Physical Chemistry, Karlsruhe, Germany

ARTICLE INFO

Article history:

Received 15 June 2015

Received in revised form

9 February 2016

Accepted 11 February 2016

Available online 7 April 2016

Keywords:

High-temperature polymer electrolyte membrane fuel cell

Polytetrafluoroethylene content

Conductive atomic force microscopy

Membrane electrode assembly

Break-in behavior

Triton X-100

ABSTRACT

In high-temperature polymer electrolyte membrane fuel cells (HT-PEMFCs), the properties of the catalyst layers (catalyst and binder materials) are critical for the performance of membrane electrode assemblies (MEAs). Here we report the optimization of the polytetrafluoroethylene (PTFE) content in the catalyst layers in terms of the fuel cell performance. Investigations with scanning electron microscopy (SEM) showed fewer PTFE filaments in catalyst layers containing a lower amount of PTFE. Spatially resolved conductive atomic force microscopy (AFM) revealed the higher electric conductivity of catalyst layers with reduced PTFE content. Ex-situ measurements indicated optimized phosphoric acid uptake of catalyst layers containing less PTFE. The PTFE content in the catalyst layers was found to have a large effect on the performance of MEAs in single cell experiments. Reduced PTFE content resulted in a decrease of the high frequency and charge-transfer resistance as well as an improved phosphoric acid uptake of the catalyst layers which resulted in enhanced fuel cell performance. The highest performance was obtained with catalyst layers containing 5% PTFE. The break-in behavior of the cells was significantly improved by addition of the non-ionic surfactant Triton X-100 to the catalyst layers.

Copyright © 2016, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

High-temperature polymer electrolyte membrane fuel cells (HT-PEMFCs) operate at temperatures from 140 °C to 200 °C. The HT-PEMFC performance benefits from high working

temperatures due to faster electrode kinetics and a higher tolerance to impurities, e.g. carbon monoxide (CO) [1–3].

Optimization of electrode properties is critical for the stability and performance of fuel cells. A conventional polymer electrolyte membrane fuel cell (PEMFC) electrode primarily

* Corresponding author. Karlsruhe Institute of Technology (KIT), Helmholtz Institute Ulm (HIU), Ulm, Germany.

E-mail address: roswitha.zeis@kit.edu (R. Zeis).

<http://dx.doi.org/10.1016/j.ijhydene.2016.02.156>

0360-3199/Copyright © 2016, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

consists of a gas diffusion layer (GDL) and a catalyst layer made of carbon-supported platinum catalyst and a binder for the mechanical stability. Because of the elevated operating temperature of HT-PEMFCs, Polytetrafluoroethylene (PTFE) is often used as the binder material [4,5]. Nafion is not practical for HT-PEMFCs because under anhydrous conditions it is non-conductive and tends to encapsulate the Pt-nanoparticles [6], resulting in blocking of the catalyst sites for hydrogen oxidation and oxygen reduction reaction.

There have been many studies to investigate the influence of different binders on the performance of HT-PEMFCs [7], e.g. PTFE [8–10], polybenzimidazole (PBI) [11–13], polyurethane [14], polyvinylidene fluoride (PVDF) [15,16] or binderless catalyst layers [17]. The binder is known to have an impact on the mechanical stability of the catalyst layers [18], the phosphoric acid leaching of the membrane electrode assembly (MEA) [19] and the phosphoric acid distribution within the MEA [8,14,20]. Martin et al. demonstrated, that even binderless electrodes had a sufficient durability and MEAs based on these electrodes showed a stable voltage for more than 900 h [17]. However, it is unclear how the binder content affects the microscopic structure and the phosphoric acid uptake of the catalyst layers which are important features for the ionic conductivity, transport properties, and catalyst utilization of the electrodes [21].

To visualize the microscopic structures of HT-PEMFC catalyst layers down to the nanometer scale, we carried out experiments using scanning electron microscopy (SEM) and conductive atomic force microscopy (AFM). Besides morphology and topography, the conductive AFM is also capable of measuring the local conductivity of the sample. These techniques were previously used to characterize low-temperature Nafion-based electrolyte fuel cell membranes [22] and electrodes [23]. However, Nafion is conductive to some extent and usually forms a thin film around the catalyst particles. Therefore it is impossible to distinguish between catalyst particles and Nafion ionomer. The investigated catalyst layers in this work consisted of highly conductive Pt/C catalyst and non-conductive PTFE particles. The conductivity is mainly influenced by the amount of insulating PTFE in the catalyst layer.

In our previous study, it was shown that the PTFE distribution in the catalyst layer, determined by conductive AFM measurements, had a strong influence on the break-in performance of HT-PEMFCs [24]. This is an important aspect not only for commercialization of HT-PEMFCs [25] but also in a research environment, because a long break-in procedure for the fuel cell to reach steady-state performance is often required for the comparability of the results [26]. Therefore, an accelerated break-in procedure is also favorable for fast and reproducible MEA evaluations in research labs. This feature of the high-temperature MEA was rarely investigated in the literature [25–27].

Surfactants as electrolyte additives improve the wetting of the catalyst layers with phosphoric acid and the fuel cell performance of phosphoric acid fuel cells (PAFCs) [28,29]. The surfactant Triton X-100 was previously used as catalyst ink additive for high-temperature direct methanol fuel cells [30] and increased the homogeneity of the catalyst ink and the fuel cell performance.

In this work, the distribution of conductive areas within the catalyst layers was analyzed with conductive AFM, and the microstructure was determined with SEM. The ex-situ phosphoric acid uptake of the catalyst layers with phosphoric acid was determined gravimetrically. Morphology, topography, and phosphoric acid uptake of the catalyst layers with various PTFE contents were compared, and their influence on the high frequency resistance (HFR), charge-transfer resistance (R_{CT}) and performance of the MEAs was investigated through electrochemical characterization of single cells. The influence of the surfactant Triton X-100 as a catalyst ink additive on the break-in behavior was also examined.

Experimental

Phosphoric acid uptake of the catalyst layers

There are different methods to determine the phosphoric acid uptake of the catalyst layers as described in the literature for PAFCs, e.g. the ratio of absorbed phosphoric acid volume to pore volume [31] and the gravimetrically determined phosphoric acid uptake of gas diffusion electrodes (GDEs) [32]. However, measurements of absorbed acid by doping the entire GDE contain systematic errors due to the acid absorbed by the GDL. This is avoided in our experiment by the use of a polyether ether ketone (PEEK) foil as the substrate.

The catalyst ink containing 20% Pt/C (Heraeus) was directly sprayed on the PEEK foil, followed by immersion of the coated PEEK foils in 85% phosphoric acid at room temperature as shown in Fig. 1. Afterward the catalyst layers on the PEEK foils were stored vertically for 5 min to drain excess phosphoric acid, and the acid uptake of the catalyst layers' pores was then determined gravimetrically.

MEA preparation

A catalyst ink was prepared by dispersing 0.5 g 20% Pt/C (Heraeus) in 8 g millipore water and 8 g isopropanol. Subsequently the PTFE dispersion (60%, 3 M) and where appropriate the surfactant Triton X-100 (Sigma Aldrich) were added. The weight percentage of Triton X-100 was similar to the PTFE content in the dry catalyst layer.

Gas diffusion electrodes (GDEs) were prepared by multi-layer deposition of the catalyst ink onto the microporous layer (MPL) of the gas diffusion layer (H2315 C2 from Freudenberg) at a substrate temperature of 80 °C. The ink deposition was done via airbrushing immediately after ink preparation to prevent agglomeration of catalyst and PTFE particles. The catalyst loading was determined by weighing after the GDE was dried. The platinum loadings for all electrodes used in this study were 1.0 mg cm⁻². A more detailed description of the GDE preparation can be found in a recent publication [24].

Membranes were conditioned by immersing AB-PBI membranes (fumapem AM, Fuma-Tech) in 85% phosphoric acid (Carl Roth) at 120 °C for 6 h to achieve a doping level of 5 mol phosphoric acid per repeating unit of AB-PBI. Higher doping levels reduce the mechanical stability and the conductivity of the membrane as shown in a previous study [33].

Download English Version:

<https://daneshyari.com/en/article/1268700>

Download Persian Version:

<https://daneshyari.com/article/1268700>

[Daneshyari.com](https://daneshyari.com)