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In-situ two-phase flow investigation of different porous transport layer for a polymer electrolyte membrane (PEM) electrolyzer with neutron spectroscopy

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HIGHLIGHTS

- Gas-water distribution in an electrolysis cell visualized in-situ.
- Gas-water distribution during mass transport limitation visualized.
- Mass transports with different stoichiometry values visualized.

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ABSTRACT

Electrolysis with polymer electrolyte membranes (PEMs) plays an increasingly important role in the development of inconsistent renewable energy technologies and seasonal storage. An effect that reduces the efficiency of PEM electrolysis is the mass transport limitation (MTL), which occurs at higher current densities and leads to a sudden increase in cell potentials. The oxygen generated on the anode side prevents the water from being supplied to the catalyst. Neutron-based imaging (neutron visualization techniques) make it possible to visualize mass transfer processes in the porous transport layer (PTL). When PTL materials are varied and operating modes used, it is possible to investigate the critical point at which the MTL is generated. This paper presents the results of neutron radiography measurements. In the course of the measurements, we have observed PEM electrolysis cells in operation, using different materials as anode PTL. The PTLs are metal plates made of sintered titanium particles, as well as titanium fiber. During the measurements, it was possible to visualize the water-gas distribution in the cell during operation in order to understand the mechanisms of mass transport.

1. Introduction

For the storage of energy in the form of hydrogen, polymer electrolyte membrane (PEM) electrolysis has many advantages as a medium of conversion, because of its quick response to system requirements and compact construction space across a wide range of operation.

In the context of electrolysis, not only do the membrane and flow distributors play an essential role, but also the PTL. On the one hand, a high cost reduction potential exists because the flow distribution and separators currently account for 48% of the cost of an electrolyzer stack [1]. On the other hand, well designed PTL will improve the electrolyzer's efficiency [2]. The primary requirements for PTL have been described in detail by Carmo et al. [3]. PTL for PEM electrolysis should be corrosion-stable, have good electrical conductivity and be mechanically-stable for operation at differential pressures. In addition, they should distribute water so that the reaction can take place evenly, with emerging gas removed efficiently so that the water supply of any range of cells is not blocked. An anode PTL for PEM electrolysis must have the capacity to remove the emerging oxygen quickly and efficiently, so that the water supply to the membrane electrode assembly

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(MEA) is not hindered. Above a certain current density, mass transport limitation (MTL) occurs, depending on the anode PTL used. This is observed on the I-U curve; as the current density increases, the curve will begin to buckle at a certain point. Therefore, it is important to investigate the MTL and find the critical point at which this occurs.

The present literature documents the effort that has been applied in recent years to investigating and optimizing the two-phase flow in the porous PTL. A good overview of the current research topics can be found in the literature [3–6]. Titanium fiber has often been used as a PTL for electrolysis and the influence of the porosity, pores and mesh size on the MTL have been examined [7–10]. In addition, sintered PTL from titanium powder has been manufactured and tested. One detailed study examined PTLs from different sinter particles in electrochemical cells [2]. They determined the optimal properties of the sintered body, which led to better performance in the cell in terms of porosity (30%–50%), pore size (12 µm - 13 µm) and sintered particle size (50 µm - 75 µm). Suermann at al. describe how the PTL morphology and operating conditions affect the mass transport loss [11]. Mo et al. present the production of new porous materials that can be used as PTL in electrolysis cell [12–14].

Observations with optical microscopy and the imaging of gas bubbles arising during water electrolysis allow the correlation between bubble diameter and operating point [15]. Bazylak et al. used 2D mockups of a PTL to investigate the two-phase flow [16], while a microfluidic platform is described in Arbabi's work [16,17], simulating the different PTLs for PEM electrolysis in the lab. Two-dimensional porous networks of metal fiber, sintered PTL and metal foam could thereby be simulated. Meanwhile, information about the pore shape and structure have been extracted from CT images. It was found that capillary forces dominate during bubble transport, even with larger volume flows. In addition, a program was developed to calculate the pressure variation in a bubble during propagation in the PTL. A further study [18] shows how the flow regimes depend on the flow rate. Moreover, ex-situ bubble growth and movement in a channel have been described [19].

Neutron radiography is often used for the visualization of the gas-water distribution in an electrolysis cell *in operando*. Selamet at al [20]. observed gas bubble formation and water distribution in a test electrolysis cell with neutron radiography, where a multilayered, expanded metal was used for the anode PTL. The authors observed the rapid growth, tearing and re-growth of blisters in some zones of PTL. In other zones, the process was similar, but slower or even completely stopped. Hoeh at al. observed and quantified the water-gas distribution in the through-plane of a PEM electrolysis cell with a meander flow field [21]. The in-plane measurement of de Beer at al. show the water-gas distribution in channels of an electrolysis cell in a horizontal and vertical cell orientation [22]. Using neutron radiography, Seweryn at al. observed the in-plane gas-water distribution in a PEM electrolysis cell [23].

Investigations using synchrotron radiography represent a further possibility to visualize the processes in operated cells. Selamet at al [24]. used soft X-ray radiography to visualize the behavior of gas bubbles. The *in-plane* measurement shows how, in different operating modes, the gas bubbles first develop in the PTL, then grow up to the PTL surface and finally become discharged. In another study, synchrotron radiography was used and bubble formation observed between the land and channel of an electrolysis cell [25]. Here, the bubble size and growth cycle were examined as a function of the operating points.

Over the past decade, neutrons and synchrotron radiography and tomography have established themselves as helpful and indispensable methods for the in operando visualization of two-phase phenomena in both PEMFCs and DMFCs. A number of authors have investigated gas bubble formation and movement in the channel of a DMFC [26–28]. Other studies are devoted to two-phase flow in a PEM fuel cell [29–42]. In one of these, a meandering channel structure for a PEM fuel cell was investigated [43]. It was observed that water droplets not only move from the poros transport layer into the channel, but also from the channel to the poros transport layer. In another study, a periodic behavior was observed in blister formation [29].

It has been observed [24,44,45] that gas bubbles form at the channel edge or under the mesh. The same is true for the water droplets in a fuel cell [29,33]. The results indicate that the bubbles always form at the same locations on the PTL surface, while the gases form preferential paths within the porous PTL. At the boundary surface of PTL to the flow channel, it was observed that large bubbles are torn off and transported away from the surface. Similar effects for water drop formation and water transport have also been observed in PEM fuel cells [32,43].

The work presented here is devoted to the visualization of mass transfer processes in a PEM electrolysis cell under critical operating conditions: water starvation (i.e., lower stoichiometry). Until now, the critical operating conditions were only determined by the current-voltage curves. Our work also increases our understanding of such process by visualizing of distribution of gas-water mixture in the PTL at critical operating points. With the help of neutron spectroscopy, the water and gas distribution can be visualized in the electrolysis cell. This allows observing *in situ* what leads to MTL. In addition to purely qualitative observations, the quantity of gas in the pores of the PTL can be quantitatively calculated using the Beer-Lambert law, and the critical operating point precisely defined.

2. Methods

2.1. Samples

Two types of PTL were used for the measurement: samples sintered from irregular shaped titanium particles and titanium fiber. Sinter samples were produced at the Forschungszentrum Jülich. The sintered powder itself was prepared by hydrogenation dehydrogenation (HDH) (Shijiazhuang Runlong Filter Materials, Shijiazhuang, China). The sample was sintered at 800 °C and had a thickness of 513 µm and total porosity of 54%. The titanium fiber samples (GKN Sinter Metals Filters GmbH, Radevormwald, Germany) have a thickness of 1 mm and total porosity of 55%.

2.2. Cells

For the measurement, a test cell was designed that satisfies the conditions of neutron radiography, as well as meets the electrochemical and fluidic requirements (Fig. 1). For the *in-plane* measurement, there should be less beam-attenuating material in the beam path. Therefore a small cell was constructed. The active area is 1.5 cm^2 (10 × 15 mm) and the beam path length through the PTL is 10 mm. Two channel types were tested, namely: continuous parallel channels and channels that interrupted a forced flow in the porous layer (interdigitated channels). However, the water flow does not proceed along the channels, but under the land of the porous medium between the channels. Since there is no direct connection between the inlet and outlet channel (Fig. 1 (5B)) for this flow field structure, the water flow is forced to flow through the PTL. For the thin sintered PTLs, the water was supplied to the anode side with two parallel channels 8 mm long and 2 mm wide. The land on the anode side is 6 mm wide. The thicker titanium fiber sample has interdigitate channels. On the anode side, with the two channels being 8 mm and 3 mm wide, the land width is 9 mm.

A hose pump was used for the water supply on the anode side. The cathode side, meanwhile, was dry and without a water supply. Humidification of cathodes would be possible through cell operation. The land was designed fairly broad compared to commonly used cells. This allowed for a better inside on the water-gas exchange management under the land. The cell was constantly heated to 80 °C using thermocouples and thermal sensors to control the temperature. For the membrane electrode assembly (MEA), a Nafion membrane coated with a catalyst was used. This was the Nafion N117 membrane from DuPont,