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Mechanical characterization and durability of sintered porous transport layers for polymer electrolyte membrane electrolysis

Elena Borgardt[a,*], Olha Panchenko[a], Franz Josef Hackemüller[b], Jürgen Giffin[a], Martin Bram[b], Martin Müller[a], Werner Lehnert[a,c], Detlef Stolten[a,c]

[a] Institute of Energy and Climate Research, Electrochemical Process Engineering (IEK-3), Forschungszentrum Jülich GmbH, Germany
[b] Institute of Energy and Climate Research, Materials Synthesis and Processing (IEK-1), Forschungszentrum Jülich GmbH, Germany
[c] Faculty of Mechanical Engineering, RWTH Aachen University, Aachen, Germany

HIGHLIGHTS

- Thin titanium PTLs from tape casting were mechanically characterized.
- For 500 µm PTLs with porosities above 25%, flow field width should be max. 3 mm.
- Contamination with oxygen and carbon lead to the component's early failure.

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ABSTRACT

Differential pressure electrolysis offers the potential for more efficient hydrogen compression. Due to the differential pressures acting within the electrolytic cell, the porous transport layer (PTL) is subjected to high stress. For safety reasons, the PTL's mechanical stability must be ensured. However, the requirements for high porosity and low thickness stand in contrast to that for mechanical stability. Porous transport layers for polymer electrolyte membrane (PEM) electrolysis are typically prepared by means of the thermal sintering of titanium powder. Thus far, the factors that influence the mechanical strength of the sintered bodies and how all requirements can be simultaneously fulfilled have not been investigated. Here, the static and dynamic mechanical properties of thin sintered titanium sheets are investigated ex-situ via tensile tests and periodic loading in a test cell, respectively. In order for a sintered PTL with a thickness of 500 µm and porosities above 25% to be able to withstand 50 bar differential pressure in the cell, the maximum flow field width should be limited to 3 mm. Thus, a method was developed to test the suitability of PTL materials for use in electrolysis for various differential pressures and flow field widths.

1. Introduction

The major expansion of renewable energy technologies in Germany has led to increased surplus energy, especially that generated from sunlight and wind. One viable means of storing this is to convert it into another form [1]. Conversion from electrical energy to chemically-bound energy provides the possibility of storing it in large amounts. Hydrogen can be generated without emitting CO_2 by means of water electrolysis that makes use of renewably-produced electricity. Because of its dynamic operating behavior and the high purity of the gas produced, polymer electrolyte membrane electrolysis has attracted increasing interest [2].

Still, this technology must be improved and its costs reduced to enable electrolysis to be economical in the MW ranges [2]. One possibility for the further development of PEM electrolysis is the transition from pressure-less operation to a differential pressure mode. In a standard electrolysis cell, hydrogen is generated at ambient or low pressure. Hydrogen must, however, be compressed for storage to pressure levels of up to several hundred bar [3]. The hydrogen generated by electrolysis is therefore compressed with a mechanical compressor, which is both cost- and maintenance-intensive though [4]. Alternatively, compressed hydrogen can also be generated directly in the electrolysis cell. When the gas is only compressed on one side of the electrolysis cell, this is referred to as differential pressure. In practice, a high pressure vessel is placed where the hydrogen is extracted. The pressure inside the vessel continuously rises as long as current is

* Corresponding author.
E-mail address: e.borgardt@fz-juelich.de (E. Borgardt).

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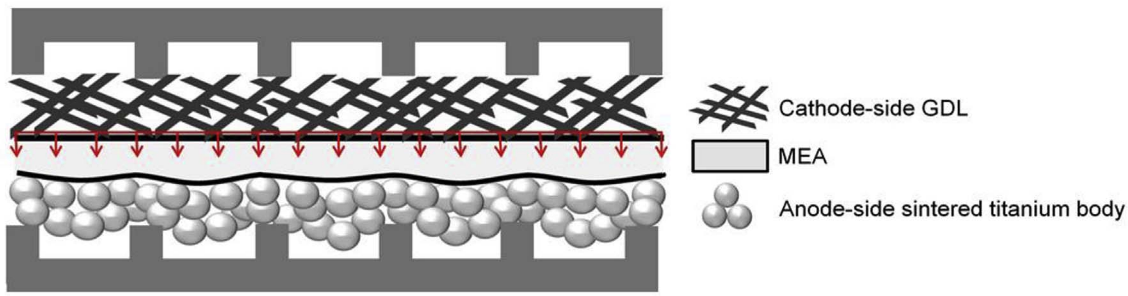

Fig. 1. Two-dimensional PEM electrolysis cell model and effect of differential pressure in the cell.

applied to the cell so that the desired gas pressure can be generated. The minimum voltage required by the electrochemical reaction is, according to the Nernst equation, dependent on hydrogen pressure. It was found that the extra energy the cell needs in order to operate at higher pressures is less than that required for multi-stage compression [5]. The aim of differential pressure electrolysis is thus a more efficient compression of hydrogen. Since hydrogen permeation to the anode increases with increasing hydrogen pressure on the cathode side [6], a critical pressure exists whereby the efficient compression is mitigated by less efficient hydrogen generation. Bensmann et al. [7]. found that hydrogen production from differential pressure operation has the lowest energy demand compared to equal pressure and atmospheric pressure electrolysis until the differential pressure of 40 bar is reached. Thus, electrolysis should only be operated with a small pressure differential.

In differential pressure electrolysis, the hydrogen on the cathode side acts as a force on the MEA. The membrane and catalyst layer are pressed onto the anode-side porous transport layer, which is then pressed against the bipolar plate (Fig. 1). The anode-side PTLs for PEM electrolysis are typically produced from sintered titanium (Ti) powder [1]. In order to keep the electrical and diffusion resistances within the electrolytic cell low and reduce the costs, the sintered PTL should be as thin as possible [8]. In addition, the sintered body must have a high porosity in order to ensure optimum mass flow. Grigoriev et al. [9] found that an optimal porosity for PTLs is in the range of 30–50 vol%. The requirement for high porosity and thin layer structure of the sintered body lowers its mechanical stability. However, mechanical stability must be guaranteed during differential pressure operation. If the mechanical strength of the PTL is not sufficient and the component fails, the membrane is no longer stabilized. Thus, the failure of the sintered body leads to a failure of the CCM and, finally, to the failure of the entire cell.

The mechanical properties of sintered titanium are significantly influenced by the sintering parameters (duration, temperature) and density of the powder. These parameters also have a direct influence on the porosity [10]. The pores act as notches on which the stress on the body is concentrated. However, not only does the volume fraction of the pores cause a change in the mechanical properties, but also the pore shape. The pore shape is considered a parameter for the inner notch effect of the pore, as the sharpness of the pore corner more or less concentrates stresses in the sintered body to a single point [11]. With a higher sintering temperature, the pores become rounder. Thus, the notch effect becomes lower with a higher sintering temperature [12]. Fatigue tests on porous materials show that cracks spread from angular pores on the surface of the material and lead to failure [13]. Fatigue is an effect that occurs when a component is subjected to a recurring load. A fatigue failure is established, even at loads below the critical static load.

Besides the porosity, the chemical composition of the Ti powder is another factor that determines the mechanical properties of the sintered body. The purity of Ti powders is divided into grades that differ in the content of the elements C, H, N, O and Fe [14]. A high oxygen, nitrogen and carbon content lead to brittleness in the Ti component. Moreover, the hardness, yield strength and tensile strength increase as the content of O, C, H and N increases. On the other hand, the formability is reduced [15].

Porous titanium is mainly used in the production of orthopedic or dental implants. Accordingly, mechanical characterizations have largely been carried out with respect to the use of sintered titanium as an implant material [16,17]. To the best of our knowledge, no studies on the mechanical properties of sintered titanium sheets have been published in the literature.

The aim of this work is to analyze the mechanical behavior of titanium PTLs made by tape casting at differential pressures of up to 50 bar. In the project from which this work emerged, it was shown that sintered titanium films with a thickness < 1 mm can be produced. These thin components were tested for use in an electrolysis stack that produces hydrogen with a differential pressure of 50 bar. Therefore, the sintered bodies were examined for stability at this pressure. In the present study, porous titanium sheets were manufactured by sintering the titanium powder tapes of two different powders at various temperatures. Tests were performed to determine the tensile strength and course of stress-strain curves of sintered titanium samples. Experiments were carried out that simulate the stress situation on the sintered body in an electrolysis cell. In this ex-situ pressure test, the samples were pressed against a slot to simulate the flow field of the bipolar plate. Fatigue tests were carried out under a load of 50 bar in order to determine which sintered bodies withstand a recurring build-up and reduction of differential pressure. Finally, scanning electron microscope (SEM) images were analyzed in order to be able to explain the observations from previous experiments.

2. Sample preparation and experimental methods

2.1. Sample preparation

The sintered porous transport layers tested in this work were produced from two different titanium powders. The first was from TLS Technik (Bitterfeld, Germany) and has a spherically-shaped particle form with a particle size of up to 45 µm. From this point on, this is referred to as Ti45 (Fig. 2a). The second powder, which was provided by GKN Filters (Radevormwald, Germany), has an irregular form and is referred to as Hydride-Dehydride (HDH). In Fig. 2b, the morphology of this sample type is shown. The chemical compositions of the powders differ significantly from one another. The oxygen, nitrogen and hydrogen content of the HDH powder is at a higher level than in the case of the spherical powder (Table 1). Ti45 is titanium grade 2, while HDH can be graded 4 [14].

As a manufacturing process, tape casting was applied using the doctor blade method. The slurry was prepared by adding a binder and plasticizer to the titanium powder. The finished slurry was then manually introduced to the tape casting machine and films were cast with thicknesses of approximately 250 µm and 500 µm. The binder was removed at 500 °C under Argon. The sintering process was then carried