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Final report

PEEC-LOSSES – Reduktion der Transportverluste in Polymerelektrolyt-Elektrolyse Zellen

Development of new Porous Transport Layer Structures for Improved Performance



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The author of this report bears the entire responsibility for the content and for the conclusions drawn therefrom.

Summary

The interplay of the structure of Ti porous layers and polymer electrolyte water electrolysis performance overvoltages is investigated. The identification of limiting fundamental processes paves the way for the innovative design of a new class of low cost, highly efficient transport layers.

Zusammenfassung

Der Zusammenhang zwischen der Struktur der porösen Transportschichten basierend auf Titan und der Spannungsverluste in Polymerelektrolyt Wasserelektrolyse-Zellen wird untersucht. Die Identifizierung der limitierenden Prozessen ermöglicht die Entwicklung einer neuen Klasse von porösen Transportschichten, die das Potential aufweist hohe Effizienz mit reduzierten Kosten zu erreichen.

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1 Introduction

The steadily global increase of CO_2 emissions and energy consumption induces the societal demand for environmental-friendly energy carriers. When using renewable energy such as solar or wind power, hydrogen represents a promising energy vector. It unites the advantages of a chemical storable reactant and green-fuel for mobile application e.g. fuel cell run vehicles. Polymer electrolyte water electrolysis represents with its high product purity a promising technology for hydrogen production. Furthermore, the dynamic operation and high energy densities enables the implementation of higher shares of renewable energies in the electrical grid system by improved grid balancing and off-season storage.

The evolution of this technology is hindered by the high investment as well as operational costs. The use of the platinum group metal iridium as anodic catalyst is a major cost driver. Optimization of catalyst utilization and catalyst loading reduction are key parameters to decrease OPEX. Furthermore advanced tailored PEWE materials at low investment costs are essential to improve efficiency and enable the development of next generation materials such as ultra-thin membranes.

2 Context

2.1 Background

Polymer electrolyte water electrolysis (PEWE) cells consist of the following main components: membrane, catalyst layer, porous transport layer and bipolar plate. On the anode side, the reactant water is transported from the integrated flow fields in the electrical conductive bipolar plate through the pore space of the porous transport layers towards the catalyst layer where water is split in oxygen and protons by the oxygen evolution reaction. The product gas is transported in a counter flow through PTL. Protons are conducted through the proton ionomer in the catalyst layer and the membrane to the cathode side where hydrogen is formed by the hydrogen evolution reaction. The gas is then transported in analogy to the anode side.

Porous transport layers play a key role in the overall cell configuration. The electrochemically inert Ti materials facilitate not only the media transport but in particular couple electrical and heat conduction between catalyst layer and bipolar plates as well as dictate the mechanical stress applied on the ductile components catalyst and membrane. Recent studies revealed an impact of PTL microstructural properties on all PEWE loss categories^[1, 2].

2.2 Motivation of the Project

Current state of the art sintered Ti PTLs are employed of different fields such as filter application and consequently don't fit the specific requirements for high efficient PTL materials. High surface roughness causes high membrane deformation and micro-crack formation in the ductile components catalyst layer and promote highly heterogeneous contact pressure distribution^[1, 3]. The use of large particle sizes results in lower interfacial contact area between catalyst layer and PTL surface which is identified to be a scaling factor for catalyst utilization, the key parameter towards higher cell efficiency and lower operational costs for PEWEs.^[2]

2.3 Goals

The objective of the project is the development of a new type of Ti PTL with electrochemically tailored surface properties such as high surface area and low surface roughness of PTL to reduce losses induced by the structure of the Ti PTL materials and obtain high catalyst utilization and superior performance compared to state of the art sinter materials used today.

3 Approach and Methodology

3.1 Transport Layer: Governing Design Parameters

In order to reveal the correlation between the structural parameters of PTLs and their electrochemical performance, a systematic matrix of 6 Titanium PTL fibre materials, provided by co-operation partner Bekaert (Belgium) was characterized in the first part of the project. Two different porosities of 56 % and 76 % in combination with 3 fibre diameters of 11, 16and 30 μ m enabled a controlled variation of bulk properties (pore sizes) and surface properties (contact area, surface roughness). The PTL materials are shown in Figure 1.



Figure 1. 3D-rendering of dry structures obtained with X-ray tomographic microscopy, Figure from ^[1].

The electrochemical characterization and correlation to PTL bulk and surface properties revealed a clear dependence of interfacial contact area (ICA) between PTL surface and catalyst layer affecting catalyst utilization and overvoltage losses induced by mass transport, kinetics as well as ohmic resistances.^[1, 2] To date, mass transport losses were treated as a black box and simply related to PTL bulk properties and neglecting the partial utilization of catalyst layers. Using the methodology developed in references ^[1] and ^[2], we could clearly show that mass transport losses are governed by the catalyst layer resistance rather than by the PTL bulk resistances. These novel insights clearly outlined the direction for a concept



of surface tailored porous transport layers featuring low surface roughness to reduce mechanical stress applied on the ductile components catalyst layer and membrane and provide at the same time high interfacial contact areas.

3.2 Novel Material Design

A novel concept of hierarchically structured porous transport layers is pursued, as shown in Figure 2. A fine top-layer, the so-called microporous layer (MPL), is sintered on top of a coarse support layer, providing the mechanical integrity of the multilayer PTL. Abyssal valleys at the surface of the support layer are filed by the small MPL particles and therefore induce smoother surfaces. At the same time higher surface areas are obtained by use of smaller particles due to increased surface area to volume ratio.



Figure 2: 3D volume rendering of multi-layered PTL composed of a fine structured microporous layer and a coarse support layer obtained by X-ray tomographic microscopy.

Economically viable Ti powders based on irregular particles are used to sustain techno-economical relevance with a potential upscaling of the material technology. The materials are produced by cosintering at temperatures of 1150 °C to 1300 °C in vacuum by a Swiss partner comapny. For electrochemical measurement, commercially available catalyst coated membranes based on Nafion 115 (Greenerity, Germany) are used.

3.3 Electrochemical Characterization

The cell voltage is based on the equilibrium voltage at operation conditions E_{rev} and the three main losses associated to kintec overvoltage η_{kin} , ohmic overlotage η_{ohm} and mass tansport overvoltage η_{mtx} :

$$E_{cell} = E_{rev} + \eta_{kin} + \eta_{ohm} + \eta_{mtx} \tag{1}$$

By correcting the cell voltage for ohmic losses, mainly originated by the membrane resistance, the iR-free cell voltage is obtained according to Equation 2:

$$E_{iR-free} = E_{cell} - \eta_{ohm} \tag{2}$$

Polarization curves of the cells with the different materials were recorded at 50 °C and 1 bar in an inhouse developed differential cell set up with an active area of 4 cm². For obtaining iR-free cell voltage, the ohmic resistance was determined via electrochemical impedance spectroscopy at 25 kHz for every voltage step.

3.4 X-ray Tomography

Microstructural properties were analysed based on X-ray tomographic microscopy using a μ CT-scanner phoenix nanotom m (General Electric, Germany). The ex-situ imaging parameters were chosen to be 180 μ A, 80 kV, 1500 projections and exposure time of 1250 ms.

4 Results

4.1 X-ray Tomographic Microscopy Morphology Analysis

It is of importance to quantify the bulk properties of the PTLs to be able to compare designed materials to state of the art PTL materials in literature and to ensure that no transport limitation are expected to occur. In particular high open porosity is essential for high performance. Dense materials can cause high tortuosity in the pore space^[4] and longer transport pathways limiting the access of reactant to the active sites in the catalyst layers.

PTL type [-]	mean particle size [µm]	Mean pore size [µm]	open porosity [%]
Support Layer	15	11	35
Microporous Layer	33	27	34

Table 1: Morphological properties of PTL obtained by X-ray tomographic microscopy analysis.

The support material show similar bulk properties as compared to state of the art sinter material SIKA T10 (GKN Sinter Metals;Germany)^[1] whereas the MPL possesses 50 % smaller particle sizes and 60 %smaller pore sizes compared to the support layer bulk, shown in Table 1. Both PTLs feature high open porosities of 35 %. Therefore, no increased mass transport limitations are expected due to high void tortuosity.

4.2 Electrochemical Analysis

The polarization curves of cells with MPL and without (only single support layer SL) are shown in Figure 3. Higher cell voltages are observed for single-layer-only cells over the entire current density range up to 4 A/cm² compared to MPL type PTLs.

When focusing on relevant current densities of 2 A/cm², SL cells feature ~110 mV higher losses at identical operation conditions resulting in 5 % higher operation cost for electrical energy supply which is considerable due to 70 % contribution of operational cost to total costs of hydrogen produced by PEWE. At potentiostatic conditions of 2 V, the hydrogen production rate was increased by ~33 % from 1.5 to 2 A/cm^2 .



Figure 3:Polarization curve at 50 °C and 1 bar of support-layer-only PTL and microporous layer added PTL.

The iR-free cell voltage versus current density is plotted in a semi-logarithmic plot in Figure 4. Also in the kinetic governed regime up to 100 mA/cm², significantly lower overvoltages were observed for the MPL type PTL. A difference of 20 to 30 mV was obtained at galvanostatic conditions, as shown in the inset. The differences in losses increased at intermediate and high current densities continuously.



Figure 4: Semi-logarithmic plot up to 1 A/cm² with excerpt of kinetic governed regime.

5 Discussion of results

5.1 Origin of Improved Performance

The question arises why the novel MPL material outperforms single layer PTLs. Recent studies revealed that the catalyst layer is only partially utilized.^[2, 5] The key towards higher performance is given by higher catalyst layer utilization which scales with the higher interfacial contact area between PTL and catalyst layer.

The decrease in kinetic overpotentials is one effect of the higher surface area of microporous layer compared to coarse single layer PTLs. An increase in electrochemically active sites result in higher specific exchange current density which is represented in a shift towards lower overvoltages in the kinetic regime as shown in Figure 3.

Mass transport overpotentials are governed by the catalyst layer resistance which in turn scales inversely with catalyst utilization. The decrease in overvoltages is confined by higher catalyst utilization leading to a decrease in kinetic as well as lower mass transport losses. The tailored electrochemical interface of multilayer PTLs therefore has the capability to improve efficiency and reduce surface roughness.

5.2 Technological Assessment

The performance of the developed multilayer PTLs clearly show improved performance compared to the single-layer only material. Even if the SL PTL has similar bulk properties compared to state of the art sinter materials, it was of interest to put the performance into perspective to PTL sinter materials in literature for a transparent comparison.

Figure 5. exemplifies the performance of the two commercial available sinter materials SIKA T10 based on particle^[6] and Bekaert PTL based on 20 μ m Ti fibres[2] and the two in-house developed PTL types at 2 A/cm2 and 50 °C. All cells were characterized at the same test infrastructure and therefore enable a direct comparison. iR-free cell voltages of the single layer materials feature all comparable values in the range of 1.81 to 1.83 V.

The microporous layer type PTL outperforms the single layer PTLs in average by 115 mV. The results clearly highlights the necessity of a tailored PTL material for PEWE applications. Significantly lower overvoltages are obtained at constant current density and therefore reduce operation costs.



Figure 5: Performance comparison of commercially available single layer PTL types SIKA T10 (GKN, Germany)^[6], fibre based PTL (Bekaert, Belgium)^[2] and Paul Scherrer Institut developed single layer only PTL as well as microporous layer added PTL at constant current density of 2 A/cm2 and 50°C.

6 Conclusions and Outlook

A new type of Ti sintered porous transport layer materials with electrochemically tailored surface properties is introduced for polymer water electrolyte water electrolysis. Multi-layered structures composed of a fine top-layer based on fine irregular shaped Ti particles, the so-called microporous layer (MPL), and a coarse support layer (SL) providing mechanical integrity were fabricated. A Eurpean patent application for the material concept and application was filed.

Electrochemical characterization showed lower losees, i.e.superior performance for MPL based PTLs. The origin of performance increase was identified to be related to improved catalyst utilization resulting in lower kinetic as well as mass transport losses.

The performance comparison to state-of-the-art commercially available sintered PTL proofed the superiority of this novel class of PTLs. The support-layer-only material featured similar performance as commercial single layer PTL types and a cell voltage decrease of more than 100 mV was obtained at constant current density of 2 A/cm² compared to the single layer PTLs.

The project provided new insights in efficiency governing PTL parameters and elucidated fundamental design guidelines of PTL materials. The identification of limiting loss processes enabled the design of tailored PTL materials for PEWE with the capability to improve efficiency based on economically viable materials and a mature production technology for product upscaling. The quintessence of this project not only provides a new class of materials but also paves the way for the development of future materials such as more optimized catalyst layers for PEWE.

6.1 Collaboration

The new Ti-sintered porous transport layer materials were designed in collaboration with kmu.support, 8840 Einsiedeln and manufactured by Angst Präzisionsmechanik, 8635 Dürnten.

6.2 Next Steps After End of Project

A continuation of specifically designed PTL materials with improved surface properties will be conducted. The sintering approach of PTLs provides also a large degree of freedom for microstructure as well as geometric design optimization. Based on the novel insights in the limiting process for high performance PEWE cells, tailored subcomponent materials such as improved catalyst morphology will be investigated.

7 Publications and Presentations

7.1 Publications

T. Schuler, R. De Bruycker, T. J. Schmidt and F. N. Büchi, Journal of The Electrochemical Society, 2019, 166, F270-F281.

T. Schuler, T. J. Schmidt and F. N. Büchi, Journal of The Electrochemical Society, 2019, 166, F555-F565.

European Patent application filed: 2019P00557EP - Patent application on the MPL/NPL multilayer PTL.

7.2 Oral Presentations

T. Schuler, T. J. Schmidt and F. N. Büchi, European Fuel Cell Forum, 2017, Lucerne Switzerland

T. Schuler, T. Kimura, T. J. Schmidt and F. N. Büchi, 234th Meeting of The Electrochemical Society, 2018, Cancun Mexico.

T. Schuler, T. Kimura, T. J. Schmidt and F. N. Büchi, 234th Meeting of The Electrochemical Society, 2018, Cancun Mexico.

T. Schuler, R. De Bruycker, T. J. Schmidt and F. N. Büchi, International Conference on Industrial Electrolysis and Industrial Electrochemical Processes, 2019, Barcelona Spain

T. Schuler, R. De Bruycker, T. J. Schmidt and F. N. Büchi, 2nd International Conference on Electrolysis Loen Norway.

T. Schuler, T. J. Schmidt and F. N. Büchi, European Fuel Cell Forum, 2019, Lucerne Switzerland.

T. Schuler, T. J. Schmidt and F. N. Büchi, 236th ECS Meeting, 2019, Atlanta USA.

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List of abbreviations

- CCM Catalyst Coated Membrane
- CL Catalyst Layer
- MPL Microporous Layer
- MTX Mass Transport Loss
- PEWE Polymer Electrolyte Water Electrolysis
- PTL Swiss Federal Office of Energy
- SL Support Layer
- XTM X-ray Tomographic Microscopy