



New Concept of Electronically and Protonic Conductive Polymer Structures for the Proton Exchange Membrane Water Electrolysis Produced by Additive Manufacturing

Annabelle Maletzko, Linda Brösgen, Christian Tchoffo Kaffo, Eduardo Daniel Gomez Villa, Julia Melke, Christof Hübner, and Carl-Christoph Höhne*

The polymer electrolyte membrane (PEM) water electrolysis is a promising technology for the production of hydrogen from water using fluctuating renewable electricity sources. However, the investment cost of the PEM electrolysis technology has to be lowered considerably to achieve a widespread application. Polymer materials can be used as low-cost materials to solve this issue. However, the conditions within the electrolysis cells are challenging for polymeric materials, especially for materials used within the oxygen-evolving electrode. This study reports the new concept of electronically and protonic conductive polymer structures for the PEM water electrolysis produced by additive manufacturing and first results of investigations on compounds suitable for this concept.

1. Introduction

To achieve the demanding goals of international climate protection policy, such as the Paris Agreement of 2015,^[1] a profound change in energy infrastructure is necessary. Hydrogen has the potential to become a crucial part of a more sustainable energy future. Through electrolysis, H₂ can be produced from water and renewable energy. The most promising technology for large-scale generation of H₂ from fluctuating renewable electricity sources is the proton exchange membrane (PEM) water electrolysis. This is due to high achievable current densities, fast response to dynamic load conditions, high H₂ purity, and the possibility of generating H₂ at higher pressures, making storage easier.^[2] However, intense research is needed to develop cost-effective

components and manufacturing processes, enabling widespread application, so that the current approximately 95 % of worldwide H₂ production from fossil fuels^[3,4] can be reduced or replaced by a sustainable H₂ production.

High equipment costs in the PEM water electrolysis come mainly from material restrictions on the oxygen-evolving electrode. For example, due to the high electrical potentials (2 V) required for water splitting, the use of precious metal catalysts is necessary.^[5] The material and shape of the porous transport layer (PTL) are also critical, as it has to provide optimal two-phase mass

transport and simultaneously ensure electron transfer from the electrode to the bipolar plates. Due to the highly oxidative conditions, porous titanium,^[6] sometimes coated with noble metals to increase corrosion stability,^[7] has been used as the base material for PTLs. Both qualities – mass transfer and electron transfer – are affected inversely by PTL porosity.

This paper presents the new concept of a multifunctional PTL for the electrodes in PEM water electrolyzers made from both electronically and protonic conductive polymer structures, which are produced by additive manufacturing (AM). Additionally, first results of investigations on compounds suitable for this concept are reported.

2. Results and Discussion

2.1. Concept Idea of a New PTL for the PEM Water Electrolysis

The oxygen-evolving electrode (anode) is the expensive part of a PEM water electrolyzer. Not only the catalyst, typically IrO₂, but also the PTL are responsible therefore. State-of-the-art PTLs of the anode typically consist of a fleece of thin disordered titanium fibers without any additional functionality beside mass transfer and electron transfer. The Ti fleece is located between a bipolar plate and the catalyst layer on the surface of a protonic conductive polymer membrane (proton exchange membrane). To lower the equipment costs of the anode, more cost-efficient materials and manufacturing processes as well as less material use (more efficient anodes) seem to be desirable. Beside material cost, this new PTL concept is also conceivable for, e.g., the gas diffusion layer of the hydrogen-evolving electrode (cathode).

A. Maletzko, L. Brösgen, C. T. Kaffo, E. D. G. Villa, J. Melke, C. Hübner, C.-C. Höhne
Fraunhofer-Institut für Chemische Technologie ICT
Joseph-von-Fraunhofer Str. 7, 76327 Pfinztal, Germany
E-mail: carl-christoph.hoehne@ict.fraunhofer.de

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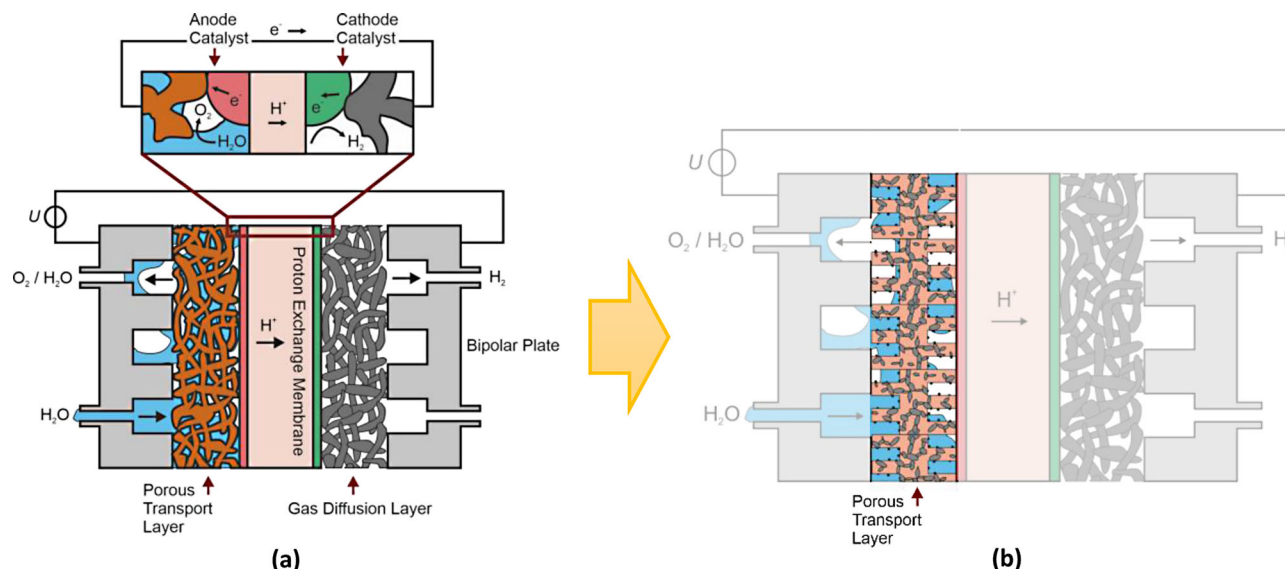


Figure 1. a) State-of-the-art PEM water electrolysis using a titanium based PTL. b) New multifunctional PTL produced by AM using a polymeric compound.

Polymer compounds offer a great potential in terms of cost-efficiency, material properties, which can be easily tailor-made by, e.g., polymer additives, and in terms of individual shaping options during the component production in particular by AM. Therefore, the main idea of the new PTL concept are PTLs produced from polymer compounds by AM. In particular, the option to create specific internal structures, given by the AM process, to guide the material flows inside the PTL seems to be promising. To be able to use polymer compounds as PTL, the polymer compound must be electrically conductive.

Additionally, the expansion of the catalyst layer from the surface of the proton exchange membrane to the surface of the PTL seems to be a method to increase the anode efficiency and lower the overall catalyst amount. It is assumed that for a sufficient catalytic activity of the new catalyst containing PTL, the polymer compound used for the PTL has to be proton conductive.

This new concept idea of a multifunctional polymeric PTL for the oxygen-evolving electrode of a PEM water electrolyzer is shown in **Figure 1**.

2.2. Conductivity of Polymer Compounds

Electrically conductivity of polymer materials can be achieved by adding electrically conductive additives. However, the electrically conductivity of these polymer compounds highly depends on the polymer compound processing.

To evaluate the compounding and additive manufacturing process of electrically conductive compounds, the model material system polylactic acid (PLA) as polymer and carbon nano tubes (CNT) as electrically conductive additives were used. The influence on the electrical through-plane conductivity of the additive amount, compounding method, and test sample preparation were analyzed, see **Figure 2**.

The in-house prepared compounds were produced using two different compounders – a 16 mm compounder and a minicomponenter.

It was found that the compounder type shows a significant impact on the resulting material performance. Pressed foils of compounds produced with the minicomponenter reached a one order of magnitude higher overall electrical conductivity level – an effect, which is assumed as caused by undesired CNT agglomerates.

The CNT content also has a significant influence on the electrical conductivity as can be seen at pressed films containing 2 wt.-% or 5 wt.-% CNTs produced with the minicomponenter or the 16 mm compounder and 3D-printed structures containing 2 wt.-% or 7 wt.-% CNTs.

For PLA/CNT compounds of the minicomponenter containing 2 wt.-% of CNTs, pressed foils show with $5.4 \pm 1.39 \cdot 10^{-3} \text{ S cm}^{-1}$ a higher electrical conductivity than printed sheets (electrical conductivity: $2.27 \pm 4.34 \cdot 10^{-5} \text{ S cm}^{-1}$). This observation supports the assumption that the electrical conductivity of pressed foils is significantly influenced by CNT agglomerates with a size of the foil thickness. These agglomerates can connect the two faces of the foil. Within the 3D-printing process, each layer is printed on top of the previous layer. As each layer is printed completely before the next layer is printed on top of the previous one, agglomerates, even larger agglomerates, within the compound filament are printed into one layer.

For printed grids, the conductivity even decreases in comparison to printed sheets. It is assumed that the weld lines created during the AM process are responsible for this.

Beside the tendencies observed for CNT amount, compounding and test sample production technology, the deviations of the electrical conductivity test results for each test sample set are very high. An inhomogeneous CNT distribution within the PLA matrix is assumed to be responsible for this observation. In addition to the inhomogeneous material structure on nano and micro scale (electrically conductive CNTs and electrically insulating

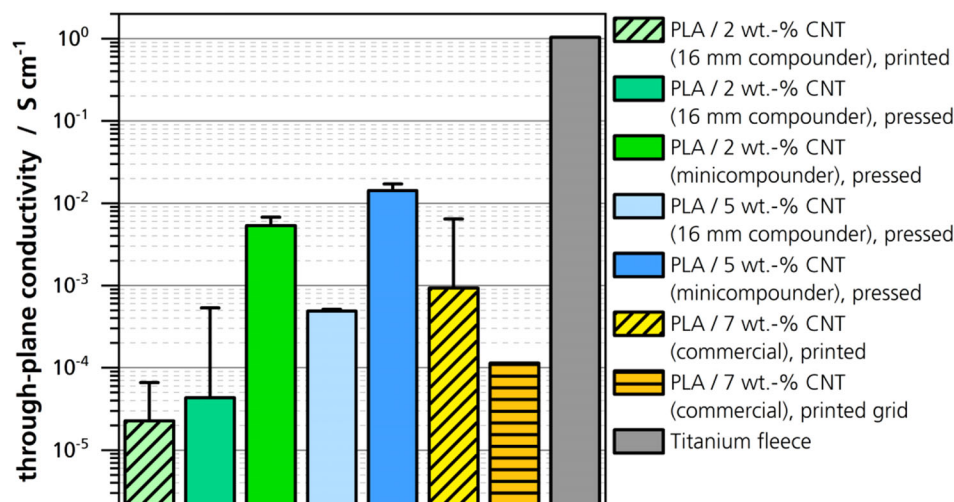


Figure 2. Electrical conductivity (mean value of five samples) of PLA/CNT compounds produced using a minicompounder or 16 mm compounder and commercial compounds. The samples were pressed into foils or printed by fused deposition modeling (FDM).

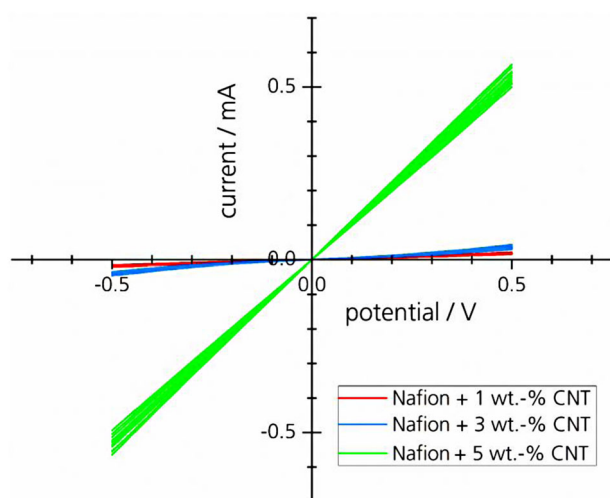


Figure 3. Cyclic voltammetry measurements of Nafion precursor compounds with an amount of 1 wt.-%, 3 wt.-% and 5 wt.-% CNT.

polymer matrix), compounding and processing have influences on the distribution of additives within the polymer compound. To evaluate the electrical conductivity of polymer compounds intended to be used for the produced components by AM, test samples produced by AM and special test methods, which are suitable for electrically conductive compounds, have to be applied.

To include both electrically and protonic conductivity, the ionomer Nafion (in the following indicated as Nafion) is combined with CNTs. As thermoplastic processes like AM cannot process a thermoplastic processable Nafion precursor material (R1100 Chemours) was used. Nafion precursor compounds with an amount of 1 wt.-%, 3 wt.-%, and 5 wt.-% CNT were analyzed by cyclic voltammetry (CV) measurements, see **Figure 3**.

As expected, the pure Nafion precursor shows an insulating behavior, whereas the Nafion precursor samples doped with CNTs show an electrical current. Increasing the degree of CNT filler

content also increases the conductivity. **Figure 3** indicates that the percolation threshold is observed between 3 wt.-% and 5 wt.-% CNT. To further improve the electrical conductivity of Nafion precursor compounds, currently other carbon and metallic material options are under investigation.

As already observed for the electrical conductivity of PLA/CNT compounds, the deviations of the test results for each Nafion/CNT test sample set are relatively high. Therefore, compound production and test sample preparation are currently improved to overcome this issue.

2.3. Additive Manufacturing of Grid-Shaped Scaffold Structures

For the production of porous PTLs, the new approach follows the manufacturing of, e.g., grid-shaped scaffold structures based on two polymer compounds. One compound comprises an ionomer compound, to which carbonaceous filler material is added to ensure electrical conductivity. The other compound consists of a soluble polymer to which the catalyst powder is added. The structure of the novel PTL concept is produced by a two-component AM process. Using this process, porous structures on the scale of several hundred micrometers in thickness and pore size are accessible, making them suitable as PTL for PEM water electrolysis.

As material model system, PLA/CNT compounds are printed to grid-shaped scaffold structures. Printed grid-shaped scaffold structures are known from medical engineering applications.^[8,9] A high degree of grid stability is expected, especially in grid-shaped scaffold structures with a layer offset between layers of the same filament orientation, e.g., a horizontal offset between layer *i* and layer *i*+2, as shown in **Figure 4**. During the AM process, the interspaces of the grid-shaped scaffold structure are filled with a compound based on a soluble polymer. To incorporate catalytic active areas on the surface of the PLA grid, the soluble compound contains metal oxide catalysts. After the removal of the water-soluble polymer, the metal oxide catalyst particles are expected to remain on the surface of the PLA-grid, see **Figure 5**.

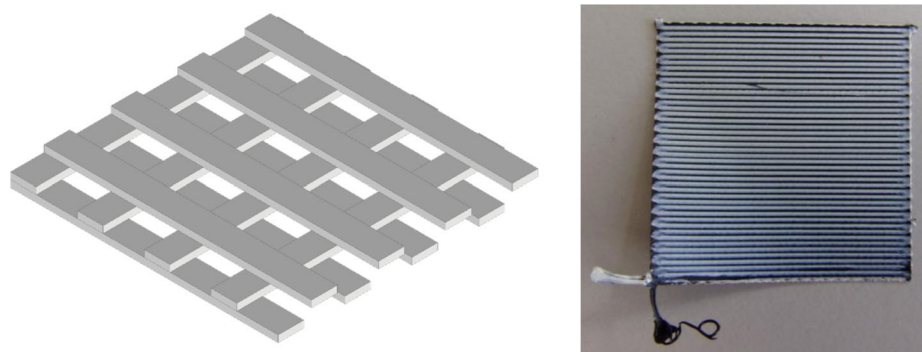


Figure 4. Left: Grid-shaped scaffold structure model. Right: Grid-shaped scaffold structure produced by AM from the two polymer materials, PLA/CNT (5 wt.-%) and PVA-TiO₂ (10 wt.-%) with three layers.

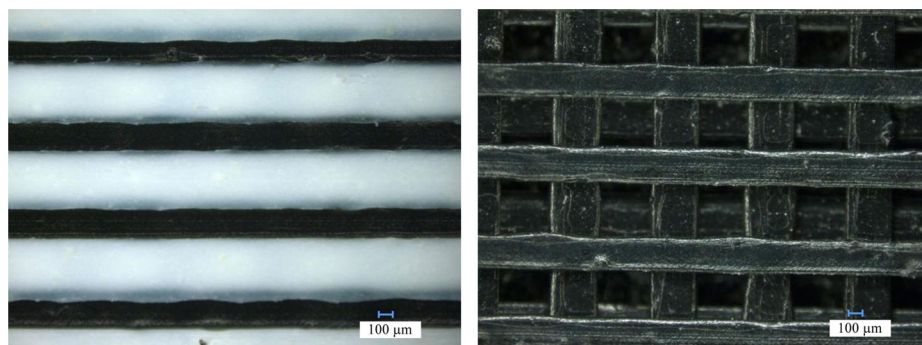


Figure 5. Section of the grid-shaped scaffold structure produced by AM from the two polymer materials, PLA/CNT (5 wt.-%) and PVA-TiO₂ (10 wt.-%) with three layers. Left: Structure before water treatment; Right: Structure after water treatment.

This method is expected to extend the catalytic activity into the PTL structure and is expected to greatly increase the active surface for a given cell size. Due to the high material cost of the noble metal catalyst, TiO₂ was used in combination with Poly(vinyl alcohol) (PVA) as a model system for the AM investigations.

Grid-shaped scaffold structures are able to produce by two-filament AM using PLA/CNT (5 wt.-%) and PVA-TiO₂ (10 wt.-%). On the outer surface of the structure, scattered remaining TiO₂ particles are observed after water treatment of the structure. However, the amount of remaining TiO₂ particles, especially on the inner surface of the structure, as well as about adhesive strength of the particle-polymer is still under investigation.

3. Conclusion

Here we presented a new concept idea of a multifunctional polymeric PTL for PEM water electrolysis. We assume that for a polymeric PTL, polymer compounds are necessary which have as their main features:

- Electrically conductive
- Protonic conductive
- Thermoplastic processing properties
- High corrosion resistance / oxidation resistance

The electrical conductivity of the material model system PLA/CNT as well as of the ionomer compound Nafion/CNT was

investigated. However, due to the observation made for pressed foils and AM structures, the evaluation of the electrical conductivity of a polymeric material intended for AM using pressed foils seems not to be an efficient method. A reproducible method to print electrically conductive polymers by AM methods and to determine the electrical conductivity of these printed structures by a consistent method seems to be necessary. Such methods are currently under development.

Furthermore, grid-shaped scaffold structures were produced by AM from the two-polymer material PLA/CNT and PVA-TiO₂. After the removal of the PVA, TiO₂ particles remain on the structure surface. However, the TiO₂ amount and the adhesive strength of the particle-polymer link are still under evaluation. Additionally, the electrochemical stability of the compounds during water electrolysis operation conditions using electrical potentials of 2 V is essential and under investigation.

4. Experimental Section

Commercial filaments and in house produced filaments were used for the AM. To produce filaments, polymer compounds were prepared by melt-extrusion of grounded polymeric material premixed with powdery polymer additives using a minicompounder HAAKE MiniLab (two counter-rotating cylindrical screws; speed: 80–120 rpm; using material amounts as small as 5 g) from Thermo-Haake or a 27 mm extruder Leistritz 27 HP from Leistritz. Filaments are produced by injection molding of small filament rods using a HAAKE MiniJet II piston injection molding system from ThermoFisher Scientific, by filament extrusion using a 16 mm HAAKE-PolyLab

/ Rheocord by ThermoFisher Scientific or by filament extrusion using a 9 mm extruder ZE 9 HMI from Three-Tec.

For the characterization of the electrical conductivity, the compounds were pressed into foils using a lab press from Collin. For the AM, an FDM printer Ultimaker 3 from Ultimaker BV was used. To operate the small filament rods within the Ultimaker 3, the rods were welded onto commercial filaments to obtain filaments with a usable length. Better control of the individual printing parameters could be achieved by manually programming the G-Code of the print model using the RepetierHost software for visualization. For the PLA/CNT compounds, the printed structures and pressed foils out of granulated compound were analyzed by measuring the through-plane electrical conductivity on a test rig with a Keithley Model 2400 source meter using a 0.17 MPa contact pressure.

For the characterization of the Nafion/CNT compounds, square test samples with a length of 25 mm and a thickness of 0.15–0.35 mm were cut from a pressed foil. For the CV measurements, the potential was cycled between -0.5 and 0.5 V with a rate of 25 mV s⁻¹ for 10 cycles. All measurements were done at room temperature.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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- [1] *The Paris Agreement*, **2015**.
- [2] M. Carmo, D. L. Fritz, J. Mergel, D. Stolten, *Int. J. Hydrogen Energy* **2013**, *38*, 4901.
- [3] L. Bertuccioli, A. Chan, D. Hart, F. Lehner, B. Madden, E. Standen, *Fuel Cells and Hydrogen Joint Undertaking* **2014**.
- [4] M. Balat, *Int. J. Hydrogen Energy* **2008**, *33*, 4013.
- [5] T. Reier, H. N. Nong, D. Teschner, R. Schlögl, P. Strasser, *Adv. Energy Mater.* **2017**, *7*, 1601275.
- [6] P. Lettenmeier, S. Kolb, F. Burggraf, A. S. Gago, K. A. Friedrich, *J. Power Sources* **2016**, *311*, 153.
- [7] C. Rakousky, G. P. Keeley, K. Wippermann, M. Carmo, D. Stolten, *Electrochim. Acta* **2018**, *278*, 324.
- [8] M. H. Too, K. F. Leong, C. K. Chua, Z. H. Du, S. F. Yang, C. M. Cheah, S. L. Ho, *Int. J. Adv. Manuf. Technol.* **2002**, *19*, 217.
- [9] D. Espalin, K. Arcaute, D. Rodriguez, F. Medina, M. Posner, R. Wicker, *Rapid Prototyping J.* **2010**, *16*, 164.