We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

172,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Protective Coatings for Low-Cost Bipolar Plates and Current Collectors of Proton Exchange Membrane Electrolyzers for Large Scale Energy Storage from Renewables

Philipp Lettenmeier, Aldo S. Gago and
K. Andreas Friedrich

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/intechopen.68528>

Abstract

Hydrogen produced by proton exchange membrane (PEM) electrolysis technology is a promising solution for energy storage, integration of renewables, and power grid stabilization for a cross-sectoral green energy chain. The most expensive components of the PEM electrolyzer stack are the bipolar plates (BPPs) and porous transport layers (PTLs), depending on the design. The high cost is due to the fact that the employed materials need to withstand corrosion at 2 V in acidic environment. Currently, only titanium is the material of choice for the anode side. We use vacuum plasma spraying (VPS) technology to apply highly stable coatings of titanium and niobium to protect stainless steel BPPs from the oxidative conditions on the anode side. The latter is able to decrease the interfacial contact resistance and improves the long-term stability of the electrolyzer. Furthermore, porous transport layers (PTL) can be realized by VPS as well. These coatings can be produced on existing titanium current collectors acting as macro porous layers (MPL). Lastly, free standing multifunctional structures with optimized tortuosity, capillary pressure and gradient porosity are used as current collectors. The coatings and porous structures developed by VPS enable the reduction of the required material and costs without performance losses.

Keywords: coatings, PEM electrolysis, PEM electrolyzers, bipolar plates, cost, current collectors, gas diffusion layer, GDL, hydrogen production

1. Introduction

On November 4, 2016, the Paris Agreement entered into force aiming to limit the global temperature rise to at least 2°C above the pre-industrial level [1, 2]. To achieve this goal, the necessary worldwide net zero carbon emission point is expected to be reached between 2045 and 2060 [3]. The energy sector represents worldwide the biggest greenhouse emitter but thanks to the recent progress in renewable energy technology such as wind, water and solar, the total energy consumption is to be substituted by green energy. However, those energy sources are strongly fluctuating and difficult to control increasing the need of large-scale energy storage. Independently of geological environment, water electrolysis is a promising technology to convert electricity to chemicals such as hydrogen and oxygen by splitting water. Hydrogen is the basis of all relevant energy carriers and enables even the connection of different sectors such as mobility or industry, the two other main greenhouse gas emission sources.

Already in 1800, William Nicholson and Anthony Carlisle established a new field in chemistry by splitting water by using direct current, that is, the electrochemistry [4]. It was Russell and co-workers who published first in 1973 the use of a solid polymer electrolyte (SPE) and anticipate the huge potential for a future energy market [5]. The two main technologies for a sustainable hydrogen production are Alkaline- and polymer exchange membrane (PEM) electrolyzers. Alkaline electrolysis is a well-established and mature technology. However, based on efficiency [6, 7], flexibility [8] and power density [6, 9, 10], the potential of economic hydrogen production by PEM electrolysis is higher, which justifies the increased interest in this technology even if it is more costly. On the other hand, open questions regarding durability and degradation remain. Moreover, the needs of rare and expensive metal, which are required to withstand the harsh acidic conditions, delay the large-scale penetration of PEM electrolyzers in the market. Indeed, potentials up to 2 V, pH values between 2 and 0 in oxygen-saturated environment require outstanding properties of the used materials.

Currently, there is no PEM electrolyzer supplier who does not use iridium as an oxygen evolution reaction (OER) catalyst, which is the rarest metal on earth. However, it is not the electrocatalytic material the one that dominates the production costs of the PEM technology. In fact, the metallic parts such bipolar plates and porous transport layers are the most expensive components of a PEM electrolyzer stack. The main part of a PEM electrolyzer system is the stack consisting of several cells. Each cell consists of an anode (oxygen evolution reaction, OER) and a cathode (hydrogen evolution reaction, HER) separated by an acidic proton conductive membrane. **Figure 1** presents a scheme illustrating the working principle of PEM electrolyzers as well as the internal components. In most cell designs, the electrodes are attached directly to the proton exchange membrane. This membrane electrode assembly (MEA) is the core component of a PEM cell. Current collectors, also called porous transport layers (PTL), on both sides of the MEA are permeable to water and the product gases, allowing electric current to flow to and from the electrodes. The two half-cells are surrounded by bipolar plates (BPP), which have usually flow fields. Their function is to transport the reactant water to the membrane-electrode interface and remove the product gases.

Depending on design, the stack accounts for up to 60% of the overall system cost [11]. The PTL and BPP can be defined as interconnectors and correspond to 50–70% of the stack costs

Figure 1. Scheme of a PEM electrolyzer cell. The anode side is filled with water, which diffuses through the PTL to the iridium electrode. The liquid is subsequently spitted into O₂, 4e⁻ and 4H⁺ by theoretical potentials >1.23 V. The protons are transported to the cathode side by the PEM and combine at the cathode with the electrons from the external circuit forming hydrogen gas.

[7, 11]. These require stable metals mainly on the anode side of the electrolyzer, which is the electrode that splits water into protons, electrons and oxygen. Titanium is the state of the art material for manufacturing BPPs and PTLs. A thin layer of TiO_x passivates the metal protecting it from further degradation and corrosion. However, the material is costly and difficult to manufacture. Furthermore, the semi-conductive behavior of titanium oxides decreases the efficiency requiring often the use of a protective coating to decrease the contact resistance and prevent the oxidation of titanium.

In this chapter, we introduce the reader into the possibility of reducing the predominant asset of the investment cost for PEM electrolyzer by using protective and easily up-scalable coating technologies. Vacuum plasma spraying, a versatile applicable technology to apply various types of coatings to a wide range of surfaces, is used to produce highly stable and multifunctional coatings for cost-effective interconnectors of PEM electrolyzers.

2. Protective and multifunctional coatings for PEM electrolysis

2.1. Vacuum plasma spraying (VPS)

The Swiss engineer Max Ulrich Schoop can be considered as the inventor of the thermal spraying technology which he patented in 1909. Compared to electro/electroless plating, chemical vapor deposition (CVD) or physical vapor deposition (PVD) coating techniques, the “thermal

spray” family enables the production of thick layers of several tens of microns with controlled porosity at scalable production rates. Several metallic and ceramic powders between some nanometers and several hundreds of micrometers can be used as spraying material. Interestingly, the plasma spraying technology is very suitable for the production of low-cost BPPs based on stainless steel substrate and PTLs due to the mechanical stability and relevant thickness of the produced layer [12].

The main part of this technology is the torch, where the gas flows through the annular gap of a finger like cathode and a concentrically surrounding anode. The gas consists of a mixture of Ar, N₂, H₂ and He, and it becomes ionized by electric arcs between the electrodes of several hundred amperes and heats it up to at least 10,000°C. The heat enables the complete or semi melting of the powder and accelerates it in to direction of the substrate [14]. The plasma enthalpy, the powder injection technology and particle size of the material affect this process. A completely melted particle is ideal for producing dense and protective layers. Conversely, partly melted particles can be used for manufacturing porous coatings for multiple purposes. **Figure 2a** and **b** shows a scheme of VPS spraying technology and photo of the plasma torch, respectively.

Aerospace application dominates the use of thermal spray technology, but other industries and especially the automotive sector show an increased interest. An extended overview of all kind of thermal spray technologies and their applications can be found in “Thermal Spray Fundamentals” from Powder to Parts [13]. For PEM electrolyzers, the thermal sprayed coatings need to be highly conductive and thus required the absence of oxygen during the spraying process in order to prevent the formation of semi conductive titanium oxides. In this context, the use of a vacuum chamber is necessary for producing high purity titanium coatings.

2.2. Coated low-cost bipolar plates

In conventional PEM water electrolysis systems, the bipolar plates are often one of the most expensive components accounting for 51% of the stack cost [11, 15–17]. This is due to the high amount of expensive materials such as titanium and the complicated production of this component [18]. The bipolar plates need to meet the following requirements [15, 19–21]:

Figure 2. (a) Scheme of VPS spraying technology and (b) photo of the plasma torch [13].

1. Separation of the gases on the anode and the cathode side
2. Current transfer from the positively charged anode to the negatively charged cathode side
3. Optimal water distribution over the active area toward the anode-side electrode structure
4. Transport of the produced gases

Given these specifications, the materials used for manufacturing conventional bipolar plates must have the following properties [15, 20]:

1. Good electrical and thermal conductivity for very high currents and small contact resistances
2. Optimized flow field for the distribution and inflow of water to the electrochemically active surface of the electrodes and at the same time optimized removal of the produced gases
3. Cathode side: resistance to hydrogen embrittlement and oxidation
4. Anode side: corrosion resistance against oxygen in acidic media and voltages up to 2 V

Rarely, the anode and cathode sides of the bipolar plates are physically two separate plates. That is why the corrosive operating conditions of the anode side and the contact to the acidic membrane determine the material selection [16, 21]. In fact, bipolar plates consist almost exclusively of titanium. The material price of pure titanium (grades 1–2) [6] is comparatively high and the processing is difficult due to its brittleness [18, 22]. Often, a flow field must be chemically etched, resulting in an increase of production cost. Under the aforementioned conditions, the formation of a passive and poorly electrically conductive oxidation layer on titanium is undesirable [23, 24]. Furthermore, the formation of unstable hydroxides at the cathode should be prevented. Both phenomena lead to ohmic losses due to increase of contact resistance and drop in efficiency [25]. These negative effects can be prevented by an additional coating or surface modifications with noble metals [18–28]. Platinum is for this purpose the state of the art material.

In commercial PEM electrolyzers, the anode side requires an anticorrosive layer when using alternative bulk materials such as stainless steel, copper or aluminum to substitute titanium. The corrosion of non-noble metals would release dissolved ions, which poison the MEA, resulting into a strong degradation [28, 29]. On the other hand, these are easy-to-process materials can be coated with corrosion resistant materials through various coating processes. Thin film coatings of Au [30], TiN [31], TiN/C [32], TaN [33] and SnO_2 : F [34] have already been investigated for protecting metallic bipolar plates for PEM fuel cells. All these materials and coatings can hardly withstand the strongly oxidative conditions of the cathode side of the fuel cells and would do so even less under PEM electrolysis conditions. In this regard, a thick film coating is necessary and vacuum plasma spraying technology (VPS, 50 mbar) was chosen to produce protective coatings of Ti for stainless steel (ss, 316 L) BPPs. Titanium particles of 45 μm were completely melted by achieving a plasma enthalpy of 21.3 MJ kg^{-1} and deposited on preheated

stainless steel BPPs. The number of sweeps of the torch over the substrate defines the thickness of the coating. Post-treatment of capillary sealing with an epoxy resin allows for closing possible holes and imperfections and guarantees the complete separation of the stainless steel from the acidic environment of the electrolyzer.

Figure 3a shows a scanning electron microscopy (SEM) image of the Ti coating produced by VPS on a stainless steel BPP (92 E Stack, Hydrogenics). The coating covers the whole surface of the flow field channels as well as the edges and contact area. **Figure 3b** presents a magnified image to the coating where the small holes and imperfections are observable. The rough surface of the coating is polished after the sealing process to provide a conductive and uniform contact area to the porous transport layer. Nevertheless, an additional thin film coating is necessary to prevent the oxidation of the titanium coating and reduce the contact resistance for lower overpotentials, resulting in higher efficiencies.

Platinum is a common material used in the industry as anti-passivation coating for titanium. It has an outstanding conductive behavior but is highly expensive and rare and the substitution of this material by cheaper ones is a pressing challenge. The alternative material for Pt as a surface modification needs to fulfill all the previously mentioned requirements, having better electric properties than TiO_2 but lower cost than Pt. Different valve metals, such as Nb, V, Zr, W, Ti, Ta, Hf, etc. can be considered for this purpose while Nb is the most promising one given its low cost (almost three orders of magnitude lower price) and abundance on the earth crust. Thin films of Pt and Nb were deposited on the thermal sprayed coatings of Ti by magnetron sputtering physical vapor deposition (PVD). The measurement of the interfacial contact resistance (ICR) of Nb/Ti and Pt/Ti coatings on stainless steel (**Figure 4**), Nb/Ti/ss and Pt/Ti/ss, depicts the significantly improved electric behavior of Nb/Ti compared to uncoated Ti, yet not comparable to Pt/Ti. The results suggest that Nb coatings by thermal spraying can be sprayed directly on stainless steel to function as both, corrosion protective layer and surface modification for better conductivity.

Cross-section images of Ti-coated samples with surface modifications of Nb can be seen in **Figure 5a** and **b**. **Figure 5c** presents a stainless steel sample coated Nb coating without the intermediate layer of Ti. The image highlights the marked differences between the two substrates for the Nb film which influence the morphology and the adherence properties. The Nb

Figure 3. (a) SEM image of coated stainless steel BPP (92E Stack, Hydrogenics) with flow field channels and (b) cutaway of the Ti coating.

Figure 4. Interfacial contact resistance (ICR) of Nb-coated titanium, Ti-coated stainless steel without surface modification as well as with surface modification by Pt and Nb respectively [35, 36].

coating has preferred orientated crystals in (110) with the size between 10 and 20 nm. While some peaks for Ti can be observed in the X-ray diffraction (XRD) presented in **Figure 5d**, no reflections of stainless steel components can be detected.

Corrosion tests in simulated PEM electrolysis environment account for the high stability of the coatings. Initially, potentiodynamic measurements were performed at low potential sweep rates to determine the corrosion current (i_{corr}) and potential (E_{corr}) of the pristine samples. Afterwards an accelerated stress test (AST) for 6 h at 2 V vs. Reversible Hydrogen Electrode (RHE) in O_2 -saturated 0.5 M H_2SO_4 was performed, and the resulting current transient represents the stability against corrosion and dissolution of the substrate. Finally, a second potentiodynamic measurement records the material changes. As can be seen in **Figure 6a**, all Ti-coated samples show almost exactly the same behavior than bulk titanium foil (blue curve). However, one can see that the thin coating of Nb by magnetron sputtering PVD is not sufficient to protect the stainless steel against corrosion (inset **Figure 6a**) and the sample experiences pitting corrosions. The current transient for Nb on stainless steel is constantly increasing at a current density level of almost three orders of magnitude higher than the other samples which passivate after approx. 1 h.

The potentiodynamic characterization of the materials is able to provide a detailed overview of the corrosion processes. Before the AST (**Figure 6a**), the E_{corr} for all samples is approx. 0 V in which the cathodic reaction of hydrogen evolution takes place. While all protected samples show a wide passivation region up to 2 V vs. RHE, the Nb/ss specimen displays a trans-passive region at potentials higher than 1.2 V vs. RHE where Fe and Cr oxides dissolve. These oxides as well as molecular O_2 are reduced during the second characterization protocol (**Figure 6c**)

Figure 5. (a) and (b) SEM images of stainless steel samples with Nb/Ti coating. (c) Nb film directly deposited on stainless steel and (d) the XRD spectra of Nb/Ti/ss [35].

Figure 6. Galvanostatic measurements (AST) of the samples Ti/ss, Nb/Ti/ss, Nb/Ti and insert for Nb/ss with adjusted scale in (a) as well as potentiodynamic material characterization before (b) and after (c) the AST [35].

in a cathodic reaction, shifting the corrosion potential of Nb/ss to 0.7 V vs. RHE. From these results, one can conclude that the layer of Ti is able to protect the stainless steel substrates against corrosion, while a much thinner PVD coating is not sufficient for this purpose.

The use of stainless steel as bulk material of BPPs can reduce the material cost. Additional cost reduction can be achieved since stainless steel is easier to machine than titanium. The price of the Ti coatings can be estimated to 30.8 USD m⁻² if industrial production rates can be achieved. This is in sum less than the half for coated stainless steel BPPs than for massive Ti BPPs. The use of Nb instead of Pt as surface modification can additionally reduce the material costs for BPPs. However, the superior electrical properties of Nb vs. Ti observed for the ICR measurements need to be demonstrated in real conditions of PEM electrolyzers. A rainbow stack was assembled to investigate the impact of surface material on anode and cathode side. The coatings were tested and compared to commercially coated-titanium BPPs. The cells are separated in two categories: category 1 corresponds to cells with precious metal surface modification and category 2 to cells with valve metals (Ti or Nb) on the surface on the cathode side, see **Table 1**.

The stainless steel BPPs were coated on both sides with titanium to avoid any possible galvanic corrosion of the cathode surface when in contact with the MEA during standby periods. However, titanium, in contrast to stainless steel, is not susceptible against hydrogen embrittlement. Therefore, a protective coating or surface treatment on the cathode side for the massive titanium BPPs, as well as for Ti-coated stainless steel ones, is required. This assumption is supported with the results presented in **Figure 7**, which correspond to a long-term performance of the rainbow stack. The lower the cell potential (E_{cell}) is, the higher the efficiency of the PEM electrolyzers. Cells 4, 5 and 8, which have either Ti or Nb/Ti coatings on the cathode side, show from the very beginning of the test, significantly worse performance compared with those having Pt. The high E_{cell} can be explained by hydrogen embrittlement of the valve metals. After 500 h, the electrolyzer was switched off for several hours, and oxygen was able to diffuse to the cathode side passivating even further the material. The consequence is a rapid potential increase in the next 500 h of the test. The commercial cells and those coated with Pt

Cell	BPP anode	BPP cathode	Category
1	Commercially coated Ti	Commercially coated Ti	1
2	Commercially coated Ti	Commercially coated Ti	1
3	Ti/ss	Commercially coated Ti	1
4	Ti/ss	Ti/ss	2
5	Pt/Ti/ss	Ti/ss	2
6	Pt/Ti/ss	Pt/Ti/ss	1
7	Nb/Ti/ss	Pt/Ti/ss	1
8	Nb/Ti/ss	Nb/Ti/ss	2

Table 1. Rainbow stack configuration: stainless steel BPPs (92E Stack, Hydrogenics) with the corrosion resistant Ti coating: Ti/ss. BPPs with additional surface modification of Pt and Nb, Pt/Ti/ss and Nb/Ti/ss, respectively. E300 and E400 MEAs (Greenerity) were used [35, 36].

Figure 7. Durability test for 1000 h at constant current density of 1 A cm^{-2} .

on the cathode side show in general a much higher performance. Here, it is also possible to distinguish the positive impact of the Pt and Nb surface modification for the anode side. Cell 3 has higher performance as cell 6 and 7 which have surface modifications. Those cells show also a stable behavior during the entire testing protocol.

The post-mortem analysis of the BPPs proves the protective behavior of the thick film coating of Ti even after 1000 h in real PEM electrolysis conditions. The SEM images of the BPPs show in every case the protective effect of the Ti coating. Differences can be seen for the thin film surface modification. For the anode side, Pt and Nb are still in well adhered to the titanium coating (**Figure 8b**) and **d**), but for the cathode side, only Pt is still in contact to Ti. **Figure 8c** shows clearly that the Nb thin film coating is delaminated allowing for the oxidation of the titanium beneath the Nb.

Summarizing, Ti coating produced by VPS is able to protect the stainless steel BPPs which decrease significantly the material and fabrication cost of these components. In principle, it should be enough to coat the anode side since stainless steel is highly resistant to hydrogen embrittlement. Surface modifications with Nb for reducing the interfacial contact resistance can substitute the expensive Pt without compromising performance and durability. Finally, Nb could be sprayed by VPS directly on the stainless steel substrate thus avoiding the use of PVD techniques, which are expensive and have low deposition rates.

2.3. Production of porous transport layer via VPS

The porous transport layer (PTL), current collector (CC) or gas diffusion layer (GDL) is another key component of commercially available PEM electrolyzers. It assumes the following tasks:

1. Transport of electrons from the catalytic layer to the bipolar plate
2. Transport of the gases produced at the electrode
3. Distributes of the water toward the electrode

Thus, an optimum of the electrical conductivity and the contact resistance as well as the mass transport of the gases and water in the, respectively, opposite direction needs to be met. In addition, the PTL on the anode side requires a large number of additional properties similar to the BPPs:

1. Corrosion resistance for voltages up to 2 V
2. Suitable pore size and porosity [37]
3. Mechanical stability especially against hydrogen embrittlement from cathode crossover
4. Sufficiently low thickness for an optimized removal of the resulting gases
5. Low contact resistance to the adjacent components: Anode catalyst layer and BPP
6. Possibility of up-scaling for industrial production of PEM electrolyzers in the MW to GW range

On the cathode side, the state of the art is carbon paper, which is predominantly used in PEM fuel cell technology. Fine stainless steel fibers, sintered plates and meshes can also be used. Given the moderate conditions on the cathode side, the research concentrates currently to the anode side current collector [38]. On the oxygen side, the environment is more corrosive for these interconnectors because of the pure oxygen atmosphere, low pH and voltages of up to 2 V. For these reasons, corrosion resistant meshes, fibers, foams to sintered structures of titanium or platinum are used [37–44], **Figure 9**.

The electrical resistance of the current collector depends on the porosity and the contact resistance of the bipolar plate with the current collector and electrode. With decreasing pore size and porosity, the electrical resistance of the current collector decreases [37, 40]. Optimum

Figure 8. Post-mortem SEM analysis after 1000 h in use as electrolyzer BPP. (a) overview, (b) Nb/Ti/ss anode, (c) Nb/Ti/ss cathode, (d) Pt/Ti/ss anode, (e) Pt/Ti/ss cathode [35].

Figure 9. Samples of porous transport layers: a) sintered titanium and below carbon GDL; SEM images of b) sintered titanium, c) titanium felt, d) carbon GDL and e) mesh. Images courtesy of Fraunhofer ISE.

porosity of 20–50% and pore sizes between 10 and 13 μm are determined with regard to electrical resistance vs. mass transport issues [37]. With the use of sintered materials, the porosity and pore size can be adjusted by the appropriate choice of the titanium particles, but the possibilities for upscaling are very limited [45]. On the one hand, meshes, fibers and foams are less limited in terms of thickness and shape [46], and they are also cheaper to manufacture [18], but the control of the pore size and porosity is more complex.

The interfacial contact resistance (ICR) from the current collector to the electrode is a decisive factor for the reduction of the ohmic resistance and thus for the efficiency of a PEM cell [40]. The ICR can be greatly reduced by the use of precious metal coatings such as platinum [24, 36, 47, 48]. In PEM fuel cell technology, the problem of water management and contact resistance has been solved by the use of a microporous layer (MPL) [49] which is applied to the gas diffusion layer. The use of micrometer-sized, conductive and hydrophobic particles improves both the contact resistance [49] and the water transport [50]. More than 149 refereed publications have been published since 2002 on this topic in connection with the fuel cell but just one for PEM electrolysis (ISI Web of Knowledge) [45].

Thereby it is possible to produce coatings with similar properties as the MPLs by VPS out of titanium or other stable valve metals such as Nb. The benefit is to have a controlled contact layer to the electrode, optimized contact surface, pore sizes, porosity, etc. The performance of electrolyzer is typically characterized by a polarization curve. The potential is recorded at different current densities. **Figure 10** displays the performance of an electrolysis cell with and without MPL. The inset shows a cross section SEM image of the MPL deposited on the sintered Ti current collector. It can be seen that the polarization curve of the cell with MPL has a lower slope than the one without MPL. The slope of the current potential curve is related to a ohmic drop caused by a decrease of contact resistance. At high current densities and consequently high gas production rates, the cell with MPL shows no mass transport limitation meaning an optimized mass transport behavior, while the cell with standard PTL increases rapidly the potential and a significant loss in efficiency is produced.

The mass transport properties of the MPL can be further improved by VPS coating technology, and it can be applied on Ti meshes and all other mechanical stable structures. Furthermore, by

Figure 10. Polarization curves up to 6 A cm^{-2} of PEM electrolyzer cells with and without MPL. The inset shows an SEM image of the MPL deposited on the sintered Ti current collector [44].

adjusting the spraying parameters, it is possible to produce such porous transport layer without limitation of surface area by reducing the plasma enthalpy one is able to control the state of particle melting and produce highly porous structures. **Figure 11** shows some examples of different porous structures produced with different Ti particle sizes, sweep numbers and plasma enthalpies. **Figure 11a** depicts the production of a free-standing thin, highly porous structure similar to the commercial sintered titanium. By use of smaller particles, a mixture of sintered titanium and MPL can be produced which is mechanically stable and able to stand

Figure 11. SEM cross-section images of (a) free-standing porous layer of $125 \mu\text{m}$ particles, (b) free-standing porous layer of $45 \mu\text{m}$ particles, (c) porous layer of $45 \mu\text{m}$ particles on BPP and (d) multi-functional layer of different particle sizes.

alone as an independent porous transport layer (**Figure 11b**) or can be sprayed directly on the BPP (**Figure 11c**). With VPS technology, thickness, porosity, pore size of the current collectors can be finely tuned to determine important parameters such as capillary pressure, bubble point and tortuosity.

3. Summary

Proton exchange membrane (PEM) electrolysis is a very promising technology for a sustainable hydrogen production and a comprehensive use of renewable energy. PEM electrolyzers are efficient, have high energy densities, and are flexible enough to play an important role for the integration of fluctuating renewables by power grid stabilizing effects. For a large-scale commercialization, the technology needs to become more economically by production cost reduction. Vacuum plasma spraying (VPS) technology is a promising tool to solve pressing question about material substitution. By controlling the spraying parameters, as well highly dense and protective layer can be produced as well porous structures for use as porous transport layers. It handles thereby with the most expensive components and allows the use of stainless steel as basis material for BPPs, which can be protected by VPS coatings. This saves material and fabrication costs. By the use of Nb, it is potentially possible to produce a protective but simultaneously highly conductive coating which may reduce the BPPs cost significantly. By reducing the plasma enthalpy, the powder material can be just partly melted to produce low cost and highly efficient components for use as porous transport layer or any other function such as filter material. The possibilities are endless, and VPS is therefore a promising technology, which can dominate the future PEM electrolysis landscape.

Author details

Philipp Lettenmeier¹, Aldo S. Gago^{1*} and K. Andreas Friedrich^{1,2}

*Address all correspondence to: aldo.gago@dlr.de

1 Institute of Engineering Thermodynamics, German Aerospace Center (DLR), Pfaffenwaldring, Stuttgart, Germany

2 Institute for Energy Storage, University of Stuttgart, Keplerstraße, Stuttgart, Germany

References

- [1] United Nations, Adoption of the Paris Agreement, 2015. <https://unfccc.int/resource/docs/2015/cop21/eng/l09r01.pdf>
- [2] United Nations, Paris Agreement—Entry into Force, 2016. http://unfccc.int/paris_agreement/items/9444.php

- [3] Rogelj J, Luderer G, Pietzcker RC, Kriegler E, Schaeffer M, Krey V, et al. Energy system transformations for limiting end-of-century warming to below 1.5°C. *Nature Climate Change*. 2015;**5**:519-527. DOI: 10.1038/nclimate2572
- [4] Royal Society of Chemistry, Enterprise and Electrolysis. 2003. <http://www.rsc.org/chemistryworld/Issues/2003/August/electrolysis.asp> [Accessed 10-March-2016]
- [5] Russell JH, Nuttall LJ, Fickett AP. Hydrogen generation by solid polymer electrolyte water electrolysis. *American Chemical Society, Division of Fuel Chemistry Preprints of Papers*. 1973;**18**:pp. 24-33
- [6] Carmo M, Fritz DL, Mergel J, Stolten D. A comprehensive review on PEM water electrolysis. *International journal of Hydrogen Energy*. 2013;**38**:4901-4934. DOI: 10.1016/j.ijhydene.2013.01.151
- [7] Friedrich KA. PlanDelyKad: Study on Large Scale Water Electrolysis and Hydrogen Storage (in German). Berlin: German Federal Ministry for Economic Affairs and Energy (BMWi); 2015, (n.d.)
- [8] Eichman J, Harrison KW, Peters M. Novel Electrolyzer Applications: Providing more than just Hydrogen, National Renewable Energy Laboratory, 2014. <https://books.google.com/books?id=X3q3rQEACAAJ&pgis=1> [Accessed 17-December-2015]
- [9] Sutherland E, II. 4 Low-Cost Large-Scale PEM Electrolysis for Renewable Energy Storage, 2013. pp. 22-25. https://www.hydrogen.energy.gov/pdfs/progress13/ii_a_4_ayers_2013.pdf
- [10] Lettenmeier P, Wang R, Abouatallah R, Helmly S, Morawietz T, Hiesgen R, et al. Durable membrane electrode assemblies for proton Exchange membrane electrolyzer systems operating at high current densities, *Electrochimica Acta*. 2016;**210**:502-511 DOI: 10.1016/j.electacta.2016.04.164
- [11] Bertuccioli L, Chan A, Hart D, Lehner F, Madden B, Eleanor Standen: Fuel cells and hydrogen joint undertaking development of water electrolysis in the European Union. 2014. http://www.fch.europa.eu/sites/default/files/study%20electrolyser_0-Logos_0_0.pdf
- [12] Pasumarthi V, Chen Y, Bakshi SR, Agarwal A. Reaction synthesis of Ti₃SiC₂ phase in plasma sprayed coating. *Journal of Alloys and Compounds*. 2009;**484**:113-117. DOI: 10.1016/j.jallcom.2009.04.079
- [13] Fauchais PL, Heberlein JVR, Boulos M. Thermal Spray Fundamentals—From Powder to Part, (n.d.). <http://www.springer.com/de/book/9780387283197> [Accessed 24-October-2016]
- [14] Fauchais P. Understanding plasma spraying. *Journal of Physics D: Applied Physics*. 2004;**37**:R86-R108. DOI: 10.1088/0022-3727/37/9/R02
- [15] Hermann A, Chaudhuri T, Spagnol P. Bipolar plates for PEM fuel cells: A review. *International Journal of Hydrogen Energy*. 2005;**30**:1297-1302. DOI: 10.1016/j.ijhydene.2005.04.016

- [16] Antunes RA, Oliveira MCL, Ett G, Ett V. Corrosion of metal bipolar plates for PEM fuel cells: A review. *International Journal of Hydrogen Energy*. 2010;**35**:3632-3647. DOI: 10.1016/j.ijhydene.2010.01.059
- [17] Ayers KE, Capuano C, Anderson EB. Recent advances in cell cost and efficiency for PEM-based water electrolysis. *ECS Transactions*. 2012;**41**:15-22. DOI: 10.1149/1.3684798
- [18] Kim HG, Kwa LK, Han W, Kwac LK, Han W. The performance and stability of a PEM electrolyzer using 3-D mesh hong. In: *International Conference on Electrical Power and Energy Systems*. Lecture Notes Information Technology; Vol.13, 2012. pp. 373-379
- [19] Wang JT, Wang WW, Wang C, Mao ZQ. Corrosion behavior of three bipolar plate materials in simulated SPE water electrolysis environment. *International Journal of Hydrogen Energy*. 2012;**37**:12069-12073. DOI: 10.1016/j.ijhydene.2012.04.146
- [20] Lee SJ, Huang CH, Chen YP. Investigation of PVD coating on corrosion resistance of metallic bipolar plates in PEM fuel cell. *Journal of Materials Processing Technology*. 2003;**140**:688-693. DOI: 10.1016/S0924-0136(03)00743-X
- [21] André J, Antoni L, Petit JP. Corrosion resistance of stainless steel bipolar plates in a PEFC environment: A comprehensive study. *International Journal of Hydrogen Energy*. 2010;**35**:3684-3697. DOI: 10.1016/j.ijhydene.2010.01.062
- [22] Jin CK, Jeong MG, Kang CG. Fabrication of titanium bipolar plates by rubber forming and performance of single cell using TiN-coated titanium bipolar plates. *International Journal of Hydrogen Energy*. 2014;**39**:21480-21488. DOI: 10.1016/j.ijhydene.2014.03.013
- [23] Jung HY, Huang SY, Ganesan P, Popov BN. Performance of gold-coated titanium bipolar plates in unitized regenerative fuel cell operation. *Journal of Power Sources*. 2009;**194**:972-975. DOI: 10.1016/j.jpowsour.2009.06.030
- [24] Jung HY, Huang SY, Popov BN. High-durability titanium bipolar plate modified by electrochemical deposition of platinum for unitized regenerative fuel cell (URFC). *Journal of Power Sources*. 2010;**195**:1950-1956. DOI: 10.1016/j.jpowsour.2009.10.002
- [25] Wang SH, Peng J, Lui WB. Surface modification and development of titanium bipolar plates for PEM fuel cells. *Journal of Power Sources*. 2006;**160**:485-489. DOI: 10.1016/j.jpowsour.2006.01.020
- [26] Dihrab SS, Sopian K, Alghoul MA, Sulaiman MY. Review of the membrane and bipolar plates materials for conventional and unitized regenerative fuel cells. *Renewable and Sustainable Energy*. 2009;**13**:1663-1668
- [27] Hodgson DR, May B, Adcock PL, Davies DP. New lightweight bipolar plate system for polymer electrolyte membrane fuel cells. *Journal of Power Sources*. 2001;**96**:233-235
- [28] Wang X, Zhang L, Li G, Zhang G, Shao Z, Yi B. The influence of Ferric ion contamination on the solid polymer electrolyte water electrolysis performance. *Electrochimica Acta*. 2015;**158**:253-257

- [29] Sun S, Shao Z, Yu H, Li G, Yi B. Investigations on degradation of the long-term proton exchange membrane water electrolysis stack. *Journal of Power Sources*. 2014;**267**:515-520. DOI: 10.1016/j.jpowsour.2014.05.117
- [30] Kumar A, Ricketts M, Hirano S. Ex situ evaluation of nanometer range gold coating on stainless steel substrate for automotive polymer electrolyte membrane fuel cell bipolar plate. *Journal of Power Sources*. 2010;**195**:1401-1407. DOI: 10.1016/j.jpowsour.2009.09.022
- [31] Wang Y, Northwood DO. Effect of substrate material on the corrosion of TiN-coated stainless steels in simulated anode and cathode environments of proton exchange membrane fuel cells. *Journal of Power Sources*. 2009;**191**:483-488. DOI: 10.1016/j.jpowsour.2009.02.029
- [32] Sun H, Cooke K, Eitzinger G, Hamilton P, Pollet B. Development of PVD coatings for PEMFC metallic bipolar plates. *Thin Solid Films*. 2013;**528**:199-204. DOI: 10.1016/j.tsf.2012.10.094
- [33] Choe C, Choi H, Hong W, Lee JJ. Tantalum nitride coated AISI 316L as bipolar plate for polymer electrolyte membrane fuel cell. *International Journal of Hydrogen Energy*. 2012;**37**:405-411. DOI: 10.1016/j.ijhydene.2011.09.060
- [34] Wang H, Turner JA, SnO₂: F coated ferritic stainless steels for PEM fuel cell bipolar plates. *Journal of Power Sources*. 2007;**170**:387-394. DOI: 10.1016/j.jpowsour.2007.04.028
- [35] Lettenmeier P, Wang R, Abouatallah R, Saruhan B, Freitag O, Gazdzicki P, Gago AS, Friedrich KA. Low-cost and durable bipolar plates for proton exchange membrane electrolyzers. *Scientific Reports*. 2017;**7**:44035; DOI: 10.1038/srep44035. in press
- [36] Lettenmeier P, Wang R, Abouatallah R, Burggraf F, Gago AS, Friedrich KA. Coated stainless steel bipolar plates for proton exchange membrane electrolyzers. *Journal of the Electrochemical Society*. 2016;**163**:F3119-F3124. DOI: 10.1149/2.0141611jes
- [37] Grigoriev SA, Millet P, Volobuev SA, Fateev VN. Optimization of porous current collectors for PEM water electrolyzers. *International Journal of Hydrogen Energy*. 2009;**34**:4968-4973. DOI: 10.1016/j.ijhydene.2008.11.056
- [38] Ito H, Maeda T, Nakano A, Hwang CM, Ishida M, Kato A, et al. Experimental study on porous current collectors of PEM electrolyzers. *International Journal of Hydrogen Energy*. 2012;**37**:7418-7428. DOI: 10.1016/j.ijhydene.2012.01.095
- [39] Selamat OF, Pasaogullari U, Spornjak D, Hussey DS, Jacobson DL, Mat MD. Two-phase flow in a proton exchange membrane electrolyzer visualized in situ by simultaneous neutron radiography and optical imaging. *International Journal of Hydrogen Energy*. 2013;**38**:5823-5835. DOI: 10.1016/j.ijhydene.2013.02.087
- [40] Ito H, Maeda T, Nakano A, Kato A, Yoshida T. Influence of pore structural properties of current collectors on the performance of proton exchange membrane electrolyzer. *Electrochimica Acta*. 2013;**100**:242-248. DOI: 10.1016/j.electacta.2012.05.068

- [41] Arbabi F, Kalantarian A, Abouatallah R, Wang R, Wallace JS, Bazylak A. Feasibility study of using microfluidic platforms for visualizing bubble flows in electrolyzer gas diffusion layers. *Journal of Power Sources*. 2014;**258**:142-149. DOI: 10.1016/j.jpowsour.2014.02.042
- [42] Siracusano S, Di Blasi A, Baglio V, Brunaccini G, Briguglio N, Stassi A, et al. Optimization of components and assembling in a PEM electrolyzer stack, *International journal of Hydrogen Energy*. 2011;**36**:3333-3339. DOI: 10.1016/j.ijhydene.2010.12.044
- [43] Grigoriev SA, Dzhus KA, Bessarabov DG, Millet P. Failure of PEM water electrolysis cells: Case study involving anode dissolution and membrane thinning, *International journal of Hydrogen Energy*. 2014;**39**:20440-20446. DOI: 10.1016/j.ijhydene.2014.05.043
- [44] Lettenmeier P, Kolb S, Burggraf F, Gago AS, Friedrich KA. Towards developing a backing layer for proton exchange membrane electrolyzers, *Journal of Power Sources*. 2016;**311**:153-158. DOI: 10.1016/j.jpowsour.2016.01.100
- [45] Grigoriev SA, Dzhus KA, Bessarabov DG, Millet P. Failure of PEM water electrolysis cells: Case study involving anode dissolution and membrane thinning, *International Journal of Hydrogen Energy*. 2014;**39**:20440-20446. <http://dx.doi.org/10.1016/j.ijhydene.2014.05.043>
- [46] Hwang CM, Ishida M, Ito H, Maeda T, Nakano A, Kato A, et al. Effect of titanium powder loading in gas diffusion layer of a polymer electrolyte unitized reversible fuel cell, *Journal of Power Sources*. 2012;**202**:108-113. DOI: 10.1016/j.jpowsour.2011.11.041
- [47] Gago AS, Ansar SA, Saruhan B, Schulz U, Lettenmeier P, Cañas NA, et al. Protective coatings on stainless steel bipolar plates for proton exchange membrane (PEM) electrolyzers. *Journal of Power Sources*. 2016;**307**:815-825. DOI: 10.1016/j.jpowsour.2015.12.071
- [48] Rakousky C, Reimer U, Wippermann K, Carmo M, Lueke W, Stolten D. An analysis of degradation phenomena in polymer electrolyte membrane water electrolysis. *Journal of Power Sources*. 2016;**326**:120-128. DOI: 10.1016/j.jpowsour.2016.06.082
- [49] Park S, Lee JW, Popov BN. Effect of carbon loading in microporous layer on PEM fuel cell performance. *Journal of Power Sources*. 2006;**163**:357-363. DOI: 10.1016/j.jpowsour.2006.09.020
- [50] Weber AZ, Newman J. Effects of Microporous Layers in Polymer Electrolyte Fuel Cells. *Journal of the Electrochemical Society*. 2005;**152**:A677. DOI: 10.1149/1.1861194