Replacing Titanium Components in Proton Exchange Membrane Electrolysers

A master thesis work by

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DENSYS (2021-2023)

Project:

PROTIS

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Abstract

Titanium-based bipolar plates and Porous Transport Layers (PTLs) currently dominate the cost of Proton Exchange Membrane Water Electrolysis (PEMWE) stacks. Replacing titanium with steel for these components would significantly enhance the cost-efficiency of PEMWE. However, application of stainless-steel components in PEMWE requires functional protective coatings, to avoid dissolution of cations (i.e., iron leaching) and to avoid an increase in contact resistance in the locally acidic aqueous environment. This thesis investigates the replacement of expensive titanium components in PEMWE with cost-effective stainless-steel alternatives and is part of the ANR/FNS Franco-Swiss project PROTIS (Films minces d'oxyde de titane sous-stoechiométrique pour la protection de couches de transport poreuses dans les électrolyseurs PEM). Three key experiments are conducted to assess the impact of different coatings on the conductivity and performance of the PTLs. The interfacial contact resistance of various coatings deposited on titanium PTLs is measured, providing insights into their electrical conductivity and contact resistance. Moreover, a baseline performance of an uncoated stainless-steel PTL in PEMWE conditions is evaluated, highlighting its rapid degradation and the need for protective coatings. And finally, the performance of a Titanium Carbide (TiC) coated Titanium PTL working under anodic conditions in PEMWE is evaluated. The findings underscore the importance of PTL coatings in optimizing electrical performance and highlight the potential of TiC coating as a solution for improving the performance of stainless-steel PTLs. The results provide valuable insights into the selection and evaluation of suitable coatings for stainless-steel components in PEMWE systems, contributing to the advancement of the PROTIS project.

LEMTA

The LEMTA (Laboratoire Énergies et Mécanique Théorique et Appliquée) is a joint research unit of the University of Lorraine and the CNRS. As one of the 5 laboratories of the Jacques Villermaux Research Federation for Mechanics, Energy, and Processes, LEMTA focuses its research activities on Mechanics and Energy, contributing to the creation of new knowledge in the field of engineering sciences. Its distinct research platforms include hydrogen and electrochemical systems, fire science, solid rheology of polymers and composites, and nuclear magnetic resonance imaging and spectroscopy.

With nearly 75 academic staff, 30 administrative and technical staff, and about 60 PhD students and post-doctoral fellows, LEMTA combines multidisciplinary expertise to tackle complex research challenges. The laboratory's extensive experimental resources encompass nine platforms, covering areas such as thermal characterization of materials, radiative transfer, fluid metrology, fires and fires, NMR/MRI, soil mechanics, mechanical characterization, and fuel cells. Advanced non-intrusive commercial techniques and in-house developed methods enhance the research capabilities, including laser-induced fluorescence, rheo-optics, light scattering-based techniques, and thermography.

In summary, LEMTA is a multidisciplinary laboratory dedicated to advancing engineering sciences with a particular focus on Mechanics and Energy. Through its state-of-the-art equipment, collaborative partnerships with industrial and institutional stakeholders, and active engagement in international research initiatives, LEMTA contributes to cutting-edge research, technological advancements, and the energy transition, thus addressing key challenges in sustainable development.

Acknowledgements

I want to express my gratitude and appreciation to the amazing individuals who played pivotal roles in the completion of my master's thesis. First and foremost, I extend my heartfelt appreciation to my incredible supervisor, Giuseppe Sdanghi. His exceptional guidance, unwavering support, and mentorship throughout this research journey have been extraordinary. His motivation kept me going, even on the most challenging days of experimentation, and his willingness to explain complex technical concepts significantly enhanced my understanding.

Next, I owe a debt of thanks to Gaël Maranzana, whose insights, patience, and genuine willingness to share expertise improved the depth and quality of my work. His expert assistance in interpreting results and providing sound advice played a pivotal role in shaping the outcome of the thesis.

Special gratitude goes to Toni Srour for his thorough guidance and support during the experimentation phase. His expertise and commitment to accurate results were truly remarkable and reassuring.

I also want to express my heartfelt appreciation to my colleagues, fellow interns, and the hydrogen team at LEMTA. Their constant support and stimulating discussions enriched my research immensely, shaping my ideas and improving the overall quality of my work.

To everyone mentioned and those not named, your kindness, knowledge, and encouragement during this academic journey are genuinely humbling. This thesis is a product of your wonderful contributions, and for that, I am forever grateful.

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List of Abbreviations

AEL	Alkaline Electrolyser
BOL	Beginning of Life
BPP	Bipolar Plate
CCM	Catalyst Coated Membrane
DC	Direct Current
FC	Fuel Cell
GDL	Gas Diffusion Layer
HER	Hydrogen Evolution Reaction
ICR	Interfacial Contact Resistance
MRI	Magnetic Resonance Imaging
OCV	Open Circuit Voltage
OER	Oxygen Evolution Reaction
PEMFC	Proton Exchange Membrane Fuel Cell
PEMWE	Polymer Electrolyte Membrane Water Electrolyser
PTL	Porous Transport Layer
SOEC	Solid Oxide Membrane Electrolyser
SS	Stainless Steel

Chapter 1. Introduction

1.1 Background

Throughout the last decade, global efforts have been made to reduce the dependence on fossil fuels by devising and maturing green energy technologies. This shift aims to decrease carbon emissions and preserve fossil fuel reserves. While investments have been made in renewable energy generation technologies, energy storage remains a problem due to the intermittent nature of renewable energy. One promising energy storage medium is Hydrogen, which has been gaining attention in recent years. Hydrogen can be efficiently produced using electrolysers powered by renewable energy and can be converted back to electricity through fuel cells.

Various types of electrolysers have been developed based on their electrolyte: (i) Alkaline Electrolysers (AEL), that use a liquid electrolyte such as sodium or potassium hydroxides[1]; (ii) Polymer Exchange Membrane Water Electrolysers (PEMWE), that employ proton conducting membranes; and (iii) Solid Oxide Electrolysis Cells (SOEC) that use solid electrolytes such as ceramic for conducting ions[2].

The SOEC technology is still in the research phase and has not been widely commercialized yet. AEL is the most mature technology as it has been on the market for over a century[3]. However, PEMWE offers certain advantages over AEL in respect to its compact design, higher current densities, shorter startup times, wider load range and faster ramp up and ramp down times. However, one of the major challenges hindering a wider commercial acceptance of PEMWE is its associated high cost.

1.2 Basic Principle of PEMWE

A PEM electrolyser is a device that converts electrical energy into chemical energy by using electricity to break down water into its constituent elements, oxygen and hydrogen. This process involves a series of electrochemical reactions occurring at different parts of the device, which is essentially composed of a polymer membrane sandwiched between two electrodes. Nafion® membranes are the most widely used to date.

At the anode side of the electrolyser, water is oxidized by the electrical current, producing oxygen and protons. The oxygen gas is released from the device, while the protons pass through the proton conducting membrane and the electrons travel through an external circuit. At the cathode side, the electrons combine with the protons that have passed through the membrane, resulting in the production of hydrogen gas. In a PEM fuel cell (FC), the reverse happens. Hydrogen and oxygen are supplied to the cell, and through a series of electrochemical reactions, they produce a DC electric current, water, and heat.

PEM electrolysers follow a standard design illustrated in Figure 1

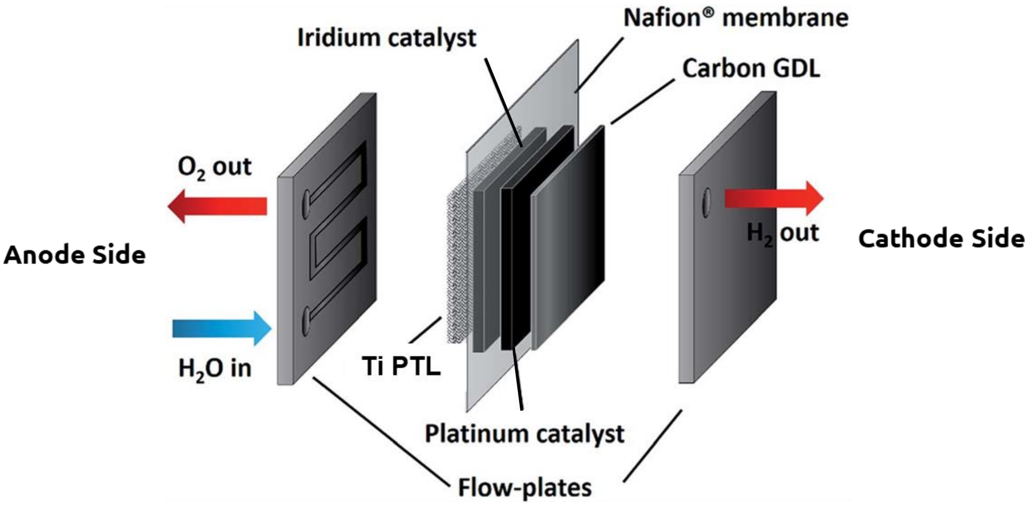

Figure 1 Electrolysis cell components [4]

The electrolyser consists of two half cells, each separated by a thin membrane that conducts protons while insulating electrons. On each side of the membrane, there are porous catalyst layers where the electrochemical reactions take place. These layers, along with the membrane, form the Membrane Electrode Assembly (MEA). Surrounding the MEA, there are current collectors (or porous transport layers) that physically and electrically connect the catalyst layers to the flow plates and ensure efficient fluidic mass transport to and from the membrane. The flow plates provide structural integrity to the cell and serve as a pathway for the movement of reactants and products. In a stack of electrolyser cells, bipolar plates are used to separate one cell from another.

The reactions occurring in a PEM electrolyser can be summarized as follows:

Anodic reaction:

$$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$$

(i)

Cathodic reaction:

$$2H^+ + 2e^- \rightarrow H_2$$

(ii)

Global reaction:

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2$$

(iii)

Equations (i) and (ii) are known as the Oxygen Evolution Reaction (OER) and Hydrogen Evolution Reaction (HER), respectively. Equation (iii) represents the overall reaction resulting from the combination of the two electrochemical half reactions that occur at the electrodes. These reactions take place under acidic conditions and require a DC power source to proceed. The electrolysis process begins when a DC voltage higher than the thermodynamic reversible potential is applied. In reversible conditions where no losses occur, the potential difference between the anode and cathode electrodes is referred to as the reversible cell potential (E_{rev}) and it is referred to as the minimum amount of electrical work needed to split water if the necessary contribution of thermal energy is available. E_{rev} can be calculated using Gibbs free energy of the global water splitting reaction, which is 236.483 kJ/mol at standard conditions of 1atm pressure and 298.15 K temperature, Faraday's constant F, and the number of moles transferred during the reaction.

$$E_{rev} = \frac{\Delta G_R}{nF} = 1.229\,V$$

As mentioned earlier, the biggest hurdle in wider commercialization of PEMWE technology is its high cost and to address this high cost, it is essential to identify critical components. Looking at the cost breakdown of the PEMWE, we can see a rather rough estimate of which components contribute most to the overall cost and it helps in a general identification of components that are most significant in the system. The pie graph below shows the breakdown in three categories namely stack, power supplies and balance of plant [5].

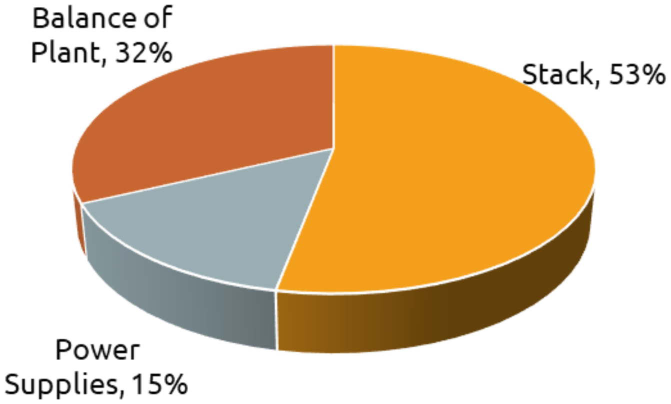

Figure 2 System cost breakdown

Figure 2 shows that the highest cost of a PEMWE system is the cost of the stack itself, indicating that improvements to the cost of the stack can have a huge impact on the overall cost. Balance of plant, although a higher share, is composed of several ancillary components that together make up the whole cost. Therefore, improving the cost of these components might not have a significant impact on the overall system cost.

A breakdown of the stack cost is shown in the following Figure 3

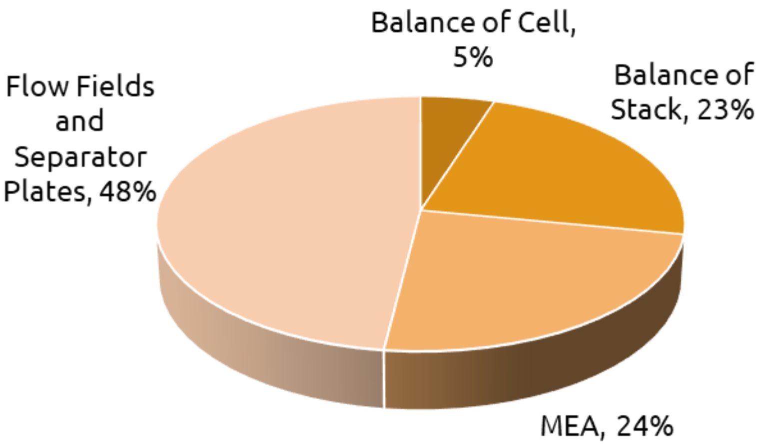

Figure 3 Stack cost breakdown

The cost breakdown analysis reveals that the porous transport layer (PTL) and separator plates or commonly known as bipolar plates (BPP) are major contributors, constituting 48% of the stack cost[5]. Titanium, the prevailing material for PTL and BPP, currently plays a crucial role in this cost structure. Given its inherent expense, exploring alternative materials that fulfill functional and durability criteria becomes a pivotal strategy for substantial cost reduction. Thus, the identification of cost-effective alternatives to titanium could lead to a noteworthy reduction in the overall system cost, rendering PEMWE technology more economically viable for broader commercial use.

1.3 Research Objective

This master thesis is part of the ANR/FNS Franco-Swiss project PROTIS. The objective of this international project is to enhance the economic viability of PEMWE systems by exploring alternative materials for critical components, specifically focusing on the anode side components such as the PTL and BPP. The study aims at identifying and developing cost-effective materials for these components that can maintain or improve performance while significantly reducing the overall system cost. By finding alternative materials that are cheaper yet meet the required functional and durability criteria, the path can be paved for a broader adoption of PEMWE technology in various applications.

The subsequent sections of this report will provide background information on these components of PEMWE systems. This will establish a foundational understanding of their roles and functions. Following the background, a series of experiments will be conducted to assess the performance and characteristics of these components, focusing on parameters such as conductivity, and electrochemical activity. The experimental findings will be analyzed and discussed, contributing to the existing knowledge on component optimization and cost-effectiveness in PEMWE systems. By exploring these avenues, the aim is to actively contribute to the advancement of green energy technologies, thereby facilitating the transition towards a more sustainable and carbon-neutral future.

Chapter 2. Literature Review

2.1 Desired Characteristics

In order to understand the challenges and opportunities in PEMWE systems, it is important to identify the desired characteristics of two critical components: the PTL and BPP.

2.1.1 PTL Characteristics

The design of the PTL in a PEMWE plays a crucial role, due to the high potential, presence of oxygen and acidic environment provided by the Nafion® membrane electrolyte existing in an electrolysis cell. To reach good performances, the PTLs must possess the following properties:

1. Corrosion resistance
2. High electrical conductivity
3. Good mechanical strength
4. High porosity

Harsh PEMWE operation conditions like higher overvoltage of up to 2V at the anode side, corrosive environment (pH < 2), high oxygen and moisture content limit the types of materials that can be employed as the current collectors. Unlike PEM Fuel Cells, carbon cloths/papers cannot be used in PEMWE because of these operating conditions. [6] Additionally, the PTL must provide support to the cell and serve as a conductive path for electrons and heat.

Selecting the right pore size for the PTL can be a challenging task, especially at the anode side. Indeed, the oxygen produced at the catalyst leaves the catalyst site towards the flow plates, while water moves in counter-current through the pores of the PTL to reach the catalyst layer. Larger pores would facilitate this exchange but would hinder the flow of electrons through the non-porous part of the PTL. This is because larger pores would reduce the volume path available for the electrons transport, resulting in reduced efficiency in the form of constriction resistance losses.

2.1.2 BPP Characteristics

Similarly, the bipolar plates in the PEMWE stack serve multiple purposes. They separate the gases, maintain electrical continuity between consecutive cells and provide flow channels to transport reactants and products to and from the PEMWE electrodes. Ideal BPP materials should have following properties [7]:

1. High corrosion resistance
2. Low contact resistance/High electrical conductivity
3. High mechanical strength
4. No permeability to reactant gases
5. Well-designed flow fields

Currently, materials such as titanium, graphite, or gold coated stainless steel are used as BPP materials. However, it's important to note that certain challenges arise due to the interaction of titanium with the operational environment, leading to the formation of a titanium oxide layer at the interface, called a passivation layer, which increases the electrical resistivity of the components.

2.1.3 Interfacial Contact Resistance

Another critical consideration in PEMWE systems is the interfacial contact resistance (ICR) which refers to the electronic resistance at the interface between two different components of

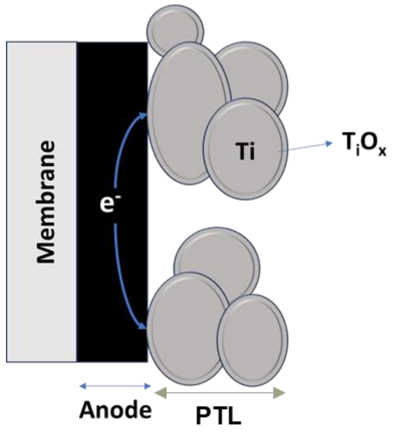

Figure 4 Electron transfer at the interface between the catalyst layer and PTL

the PEMWE system, such as the catalyst layer and PTL, and the PTL and BPP. High contact resistance can significantly impact the overall performance and durability of the system, leading to increased ohmic losses and reduced efficiency. Minimizing the interfacial contact resistance is crucial for optimizing the performance and cost-effectiveness of PEMWE systems.

Poor contact between the components can lead to non-uniform current distribution and the formation of hot spots, which can result in melting of the membrane and defects on its surface[8]. This highlights the importance of achieving good contact between the components to ensure optimal performance and durability of the PEMWE system.

The interfacial contact resistance (R_{int}) can be represented by the equation:

$$R_{int} = \frac{t_{T_iO_x}}{(1 - \varepsilon_c)\sigma_{T_iO_x}}$$

where:

$t_{T_iO_x}$ is the thickness of the titanium oxide layer formed at the interface, ε_c represents the pore surface ratio, which is influenced by the clamping pressure exerted and $\sigma_{T_iO_x}$ denotes the electrical conductivity of the titanium oxide layer.

This equation highlights the relationship between the thickness of the titanium oxide layer, the pore surface ratio, and the electrical conductivity of the titanium oxide layer in determining the interfacial contact resistance. By carefully considering and optimizing these factors, it is possible to minimize the interfacial contact resistance, thereby improving the overall performance and efficiency of the PEMWE system.

Several factors influence the interfacial contact resistance, and understanding these factors is crucial for optimizing the performance of the PEMWE system. The following factors are particularly important[9]:

1. **Surface Morphology**

The surface morphology of the interface plays a role in determining the contact resistance [10]. It is possible to increase the number of contact points between two consecutive components by making the surface as smooth as possible. Hence, the electron transfer can be enhanced.

2. Oxidation Layers at the Interface:

Titanium components are prone to developing a TiO_2 passivation layer at the anode side of the PEMWE cells. This passivation layer at the interface can increase the electrical resistivity and contribute to higher contact resistance. To mitigate this, coating the PTL surface with metals can be a solution to improve conductivity and corrosion resistance at the interface [11].

3. Contact Pressure at the Interface:

The clamping pressure exerted at the interface affects the contact area and, consequently, the number of pathways available for electron transfer. Appropriate clamping pressure is essential to maximize contact and minimize resistance. Bhosale et al. [12] conducted an experiment to examine the relationship between interfacial contact resistance (ICR) and average contact pressure between carbon paper and TiN-coated BPP samples. They observed that increasing the contact pressure resulted in closer contact between surface crests and troughs, leading to a significant decrease in ICR. However, further increases in contact pressure did not reduce ICR as there were no additional pathways for electron flow across the interface. These findings emphasize the importance of optimizing contact pressure to minimize contact resistance between components.

Research efforts have focused on developing materials and coatings giving a reduced interfacial contact resistance. In fuel cells, the contact between BPPs and GDLs is enhanced by coating the metallic BPPs with highly conductive and anti-corrosive coatings [13]–[15]. The gas diffusion layer (GDL) is also coated with microporous layer to have better contact with the BPP[16]. Additionally, the choice of coatings and base materials for the PTL, as well as their surface properties, can also influence the ICR. While research on the effect of clamping pressure on ICR between the bipolar plate and carbon GDL in PEM fuel cells is well-established, there is a lack of studies investigating the impact of clamping pressure on ICR at the interface of Titanium

PTL and catalyst layer in PEM water electrolysers. Therefore, my thesis work aims to fill this gap by focusing on this aspect.

2.2 PTL and BPP Materials

The selection of materials for the anode side of PEMWE systems is of utmost importance due to the harsh and highly corrosive operating conditions, including the presence of oxygen and moisture, high potential, and acidic environment. The choice of materials directly affects the performance and durability of the system. This section highlights the characteristics and limitations of different materials commonly used for anode-side components.

2.2.1 Titanium

Titanium is known for its high initial thermal conductance, low permeability, and excellent mechanical strength, making it an attractive option for PEMWE systems. However, at the anode side of the PEMWE, titanium develops a passivation layer in the oxygen-rich environment. The formation of this passivation layer was experimentally proven by C. Rakousky et al. [17], who demonstrated that Pt-coated titanium exhibits a significantly lower degradation rate (12 μV/h) compared to uncoated titanium (108 μV/h). This passivation layer although to some degree enhances the material's corrosion resistance as it is relatively stable, adherent, and compact but at the same time it increases greatly the contact resistance and the thermal conductivity as the layer itself is semiconducting. G. Lu et al. [19] performed depth profiling of oxidized Ti and found out that the top of passive layer (the metal-oxide interface) is formed by TiO_2, which is a semi-conductor which leads to the increase in the electrical resistance. As a consequence, the electrolysis performance reduces over time. In light of these challenges presented by the titanium oxide passivation layer, researchers have investigated alternative strategies to counter its effects. One promising approach involves the utilization of gold-deposited titanium BPPs, which has shown potential to address the limitations imposed by the passivation layer. H. Y. Jung et al. [18] performed a comparative study and found that the ohmic resistance of fuel cells prepared with bare titanium bipolar plates is approximately 0.40 Ω, while cells incorporating gold-deposited titanium bipolar plates exhibit a significantly reduced ohmic resistance of approximately 0.18 Ω. This observation sheds light on the positive influence of the gold coating on the ohmic resistance of the system.

Graphite is extensively used in fuel cells due to its high conductivity but its application in electrolysers, including PEMWE systems, is problematic due to the harsh operating environment at the anode compartment. Graphite has low mechanical strength, high corrosion rates, is difficult to manufacture and therefore cannot be a good choice of material for PEMWE. The low mechanical strength requires thicker graphite materials, leading to increased ohmic losses. Moreover, the high corrosion rates of graphite result in poor contact with current collectors, further increasing the overall ohmic losses. H.-Y. Jung et al [18] observed these issues when studying carbon-based bipolar plates in electrolysis mode under positive over potentials higher than 2.0 V for 1 hour. They observed that cell performance in the electrolyzer mode significantly decreased with time due to the increased ohmic resistance of the carbon-based bipolar plates. During fuel cell operation, they noticed that the unit cell showed an ohmic resistance of approximately 0.15 Ω, which after operation in electrolyzer mode, increased up to 1.24 Ω

2.2.2 Stainless Steel

One of the alternatives for base materials that has been discussed frequently is stainless steel, but it comes with its own drawbacks. Although it is cheaper, it corrodes easily in PEMWE environment and must therefore be protected by an appropriate coating. A.S. Gago et al. [14] studied the corrosion resistance of coated SS bipolar plates by performing chronoamperometric tests and found out that Pt-Ti-coated SS bipolar plates exhibit similar electrochemical characteristics and properties (e.g. corrosion resistance) as bulk Ti. In the context of the PROTIS project, the aim is to enhance the economic viability of PEMWE systems by exploring alternative materials and coatings for critical components. The project aims to develop cost-effective coating solutions for stainless steel BPPs and PTLs that can mitigate corrosion while maintaining desirable electrochemical characteristics.

2.2.3 Uncoated BPP and PTL

Laedre et al. [20] investigated corrosion on uncoated BPPs made of various metals. Uncoated Titanium BPP and PTL showed generation of a passivation layer of TiO_2 which led to an increase in the interfacial contact resistance. BPPs made of uncoated Molybdenum or alloys containing this metal experienced severe corrosion. Uncoated SS304L, SS316L and tungsten components lead to corrosion as well. Although Niobium and Tantalum remained unchanged in terms of weight demonstrating very low corrosion, but this was attributed to the formation of a passivation layer which leads to increased interfacial contact resistance, which again creates problems.

2.2.4 Poisoning by Foreign Ions

PEMWE membrane electrode assembly is susceptible to poisoning by cationic impurities like Na^+, Ca^{2+}, Cu^{2+}, Ni^{2+} [8], Fe^{3+} [21] etc. The presence of cations can lead to a decline in performance of MEA of PEMWE in different ways. Foreign cations can replace a portion of protons in the Nafion resulting in higher ohmic overpotential since a metallic cation moves much slower than a proton [22]. The overpotential at both electrodes also increases, as the metallic ions get deposited onto the ion exchange sites in the membrane and lead to increase in charge transfer resistance [23]. Platinum metal at the cathode side, where the hydrogen evolution reaction takes place, is very sensitive to poisoning by deposition of foreign ions. Foreign cations can block the platinum active sites in the cathode, leading to an overall decrease in reactivity of the catalyst [24]. The presence of Cu, Mo, Ag, Cd, Sn, Pb resulted in considerable poisoning of the cathode according to the study carried out by Stucki et al. [25] Although the water used in PEMWE is deionized, it might become polluted with metal ions due to corrosion of the stack components. This issue can arise especially when steel piping is used in the water circuit of the balance of plant. Jingke Mo [21] investigated the corrosion effects of SS 316L components on PEMWE. They used SS mesh as PTL for anode side and noticed transport of Fe, Ni oxides through the catalyst coated membrane (CCM) and deposited on carbon cathode. H. Wang and J. A. Turner [26] reported the significant decrease of ionic conductivity of Nafion 112 membranes when soaked in solutions containing higher than 300 ppm of Fe and higher than 200 pm of Cr ions. D.D. Papadias et al. [27] also studied the corrosion behavior of SS316L in simulated PEMFC conditions, and found the main corrosion products to be Fe and Ni. On the other hand, the dissolution rate of Cr was lower, with an increase occurring at potentials higher than 0.8V.

Uncoated Ti PTL leads to corrosion when used at the anode compartment of a PEMWE, and the deposition of Ti oxides on the cathode side was observed. C. Rakousky et al. [28] observed that even Pt coated Ti PTL showed corrosion when the PEMWE cell was operated at high current density (more than 2 A cm^{-2}). After 2000 h of operation, flakes of Pt coating were found deposited on the catalyst layer at the anode side.

2.2.5 Coatings

Due to the high cost related to base metals used for current collectors and bipolar plates and to avoid the issue of foreign ion deposition in PEMWE cells due to corrosion, research is being carried out to find cheaper base metals and enhance their properties by applying coatings to protect them in the harsh PEMWE environment. H. Becker et al.[29] performed experiments on single cell PEMWE and found out that high corrosion potential is achievable at the anode/PTL interface. In addition, they found that the PTL potential becomes completely decoupled from the anode potential far from this interface. Therefore, using a thin Ti layer or suitable coatings can lead to the possibility of using cheaper materials like carbon or stainless steel for PTL.

Moreover, base materials like Ti and SS both need coatings to improve the material's life, to have lower contact resistance and to avoid formation of passivation layers. Characteristics desired in a suitable coating are:

1. Low resistivity
2. High corrosion resistance
3. High thermal conductivity
4. Good durability
5. Good adhesion with base material
6. Very low imperfection density

Chang Liu et al. [30] observed that iridium coated titanium PTLs showed interface resistivity comparable to carbon materials, with ICR reduced by 60 mΩ/cm^2 and significant improvement of PEMWE cell performance. Wang et al. [13] studied the performance of PEMFC stack using an amorphous carbon coated SS 304 bipolar plate. PEMFC with a Cr-C coated SS304 showed a higher efficiency than bare SS304.

Chapter 3. Experimental Methodology

The purpose of the project PROTIS is to replace expensive titanium components in the anode side of PEMWE with cost effective stainless-steel components. This is done by finding suitable coating materials for stainless steel PTL and by assessing their performance and suitability in PEMWE. During my master thesis, I carried out three different experimental campaigns to assess the impact of different coatings on the conductivity and performance of Titanium PTLs.

The first experiment (*ex-situ*) measures the interfacial contact resistance between the catalyst layer and the PTL for different coatings deposited on titanium PTLs, providing insights into their electrical conductivity and contact resistance. The second experiment involves *in-operando* testing of an uncoated stainless-steel PTL, which allowed obtaining important information about its performance and potential challenges related to corrosion. It serves as a baseline reference for comparing coated SS PTLs and assessing the benefits of using protective coatings. These findings will support the objective of developing thin protective coatings for stainless-steel components in PEMWE systems. The third experiment focuses on the *in-operando* testing of a Titanium Carbide (TiC) coated Titanium PTL. The purpose of this experiment is to evaluate the performance of the TiC coating under working anodic conditions in PEMWE. By subjecting the TiC-coated PTL to the operational environment, important data on its electrochemical behavior, corrosion resistance, and overall performance can be obtained. This experiment will help in assessing the suitability and effectiveness of the TiC coating as a potential solution for improving the performance of stainless-steel PTLs.

3.1 Ex-situ Interfacial Contact Resistance Measurements

In this experiment, the interfacial contact resistance was measured between the catalyst layer and the PTL. The goal of these *ex-situ* measurements was to evaluate the effect of the varying clamping force on the contact resistance.

3.1.1 Experimental Setup and Procedure

The catalyst, which was a mixture of 80% IrO2 and 20% ionomer, was spray-coated onto 1.5 cm x 3 cm samples of gold-coated copper to have two different catalyst loadings: 0.6 mg/cm^2 and 2 mg/cm^2. To measure the contact resistance, a current was applied between two gold-coated copper samples, one of which was coated with the catalyst. A hot press was used to adjust the clamping force by moving the lower plate towards the upper plate.

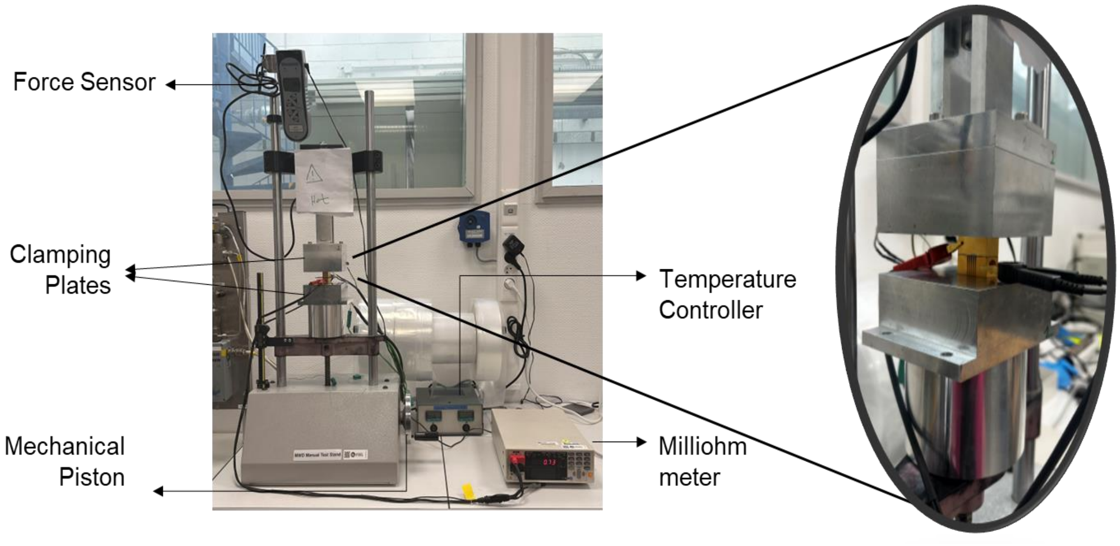

Figure 5 Experimental setup for ICR measurements

For the ICR measurements, the cleaned PTLs with different coatings were placed between the gold-coated copper samples, ensuring that the coated sides faced the catalyst-coated side of the gold sample. The clamping pressure variation was applied, and resistance measurements were taken for both the 0.6 mg/cm^2 and 2 mg/cm^2 catalyst loadings. The following PTLs were tested:

Table 1 Tested PTL Materials

Base Material	Ti	Ti	Ti	Ti	Ti	Ti	SS
Coating	None	TiC	Au	Ir 200 nm	Nb	Pt	None

To ensure accurate ICR measurements, the PTLs were cleaned using a standardized procedure. The uncoated side of the PTLs was polished using sandpaper, followed by immersion in ethanol in a beaker and subsequent ultrasonic bath treatment for 5 minutes. Compressed air was then used to dry the PTLs. This was done to remove any passivation layer that might have formed on the uncoated side of Titanium PTL, in order to ensure correct ICR measurements.

Before proceeding with the ICR measurements, the resistance of the catalyst layer was measured without the presence of the PTL. This measurement served as a baseline to understand the initial resistance characteristics of the catalyst layer for both the 0.6 mg/cm^2 and 2 mg/cm^2 loadings. To evaluate the impact of the clamping force on conductivity, the clamping pressure was gradually increased from 20 to 600 N/cm^2. Resistance measurements were taken at intervals of 20 N/cm^2. The change in resistance with the clamping pressure was monitored for both catalyst loadings. In order to avoid the catalyst sticking to the upper gold coated copper plate, a Teflon sheet was introduced in between both samples while hot pressing.

3.2 Baseline Evaluation of Uncoated Stainless Steel PTL in PEMWE Conditions

This section focuses on the experiment conducted to establish a baseline performance of an uncoated stainless steel PTL under common operating conditions of a PEMWE system. The experiment aimed to provide a comprehensive understanding of its behavior and potential challenges related to corrosion. The outcomes of this experiment would serve as a fundamental reference point for subsequent steps of the PROTIS project with experiments involving coated stainless steel PTLs, enabling a comparative analysis of their corrosion resistance and performance. The experimental setup, including a schematic representation, is described below.

3.2.1 Experimental Setup

The experimental setup for the PEM electrolyser is illustrated in Figure 6. A photo of the original setup is shown in Figure 7.

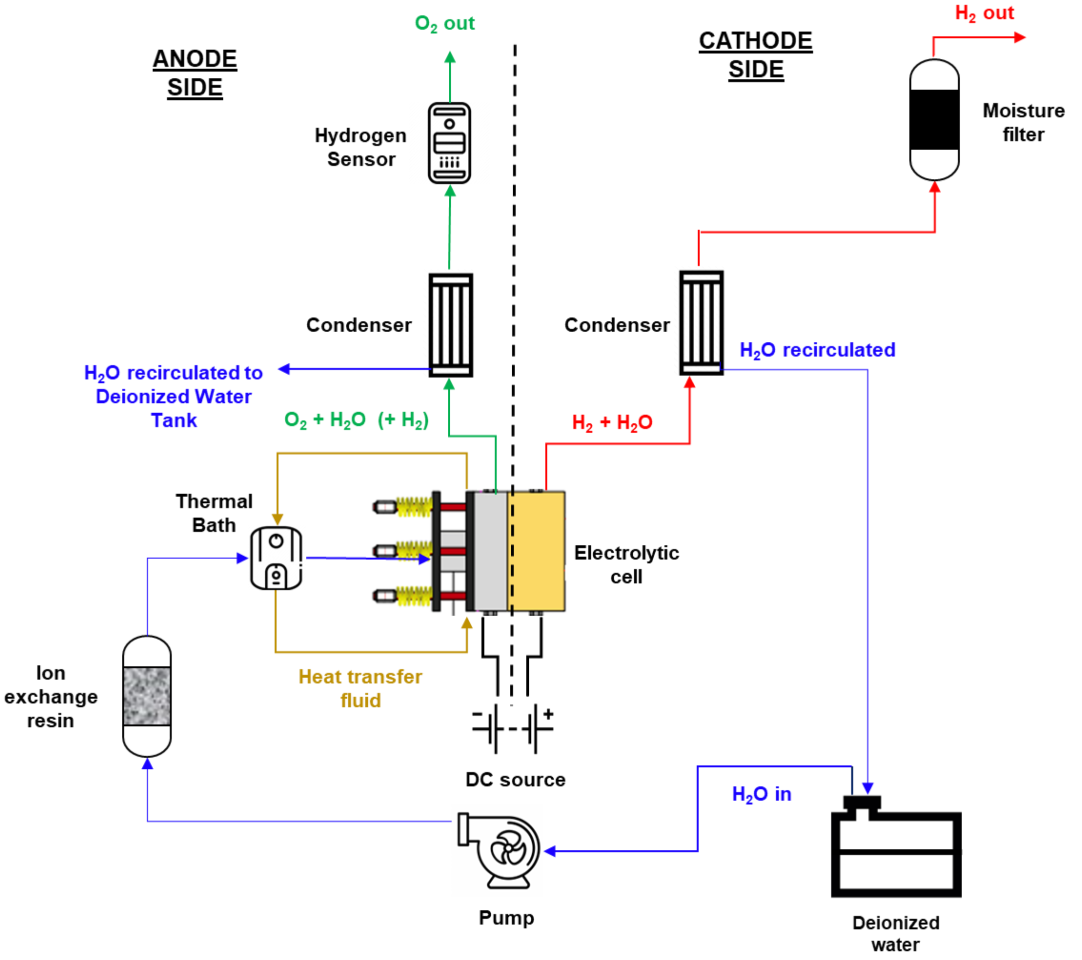

Figure 6 Schematic of the PEMWE experimental setup

The heart of the experimental bench is a single PEM electrolysis cell with a total area of 10x10 cm^2. The active surface area, where the electrochemical reactions occurred, was 5x5 cm^2. A Nafion® 115 proton exchange membrane was used. On the anode side, the catalyst IrO_2 (iridium dioxide) with a loading of 1 mg/cm^2 was used. On the cathode side, platinum catalyst with carbon felt GDL was used. The cathode catalyst loading was also 1 mg/cm^2.

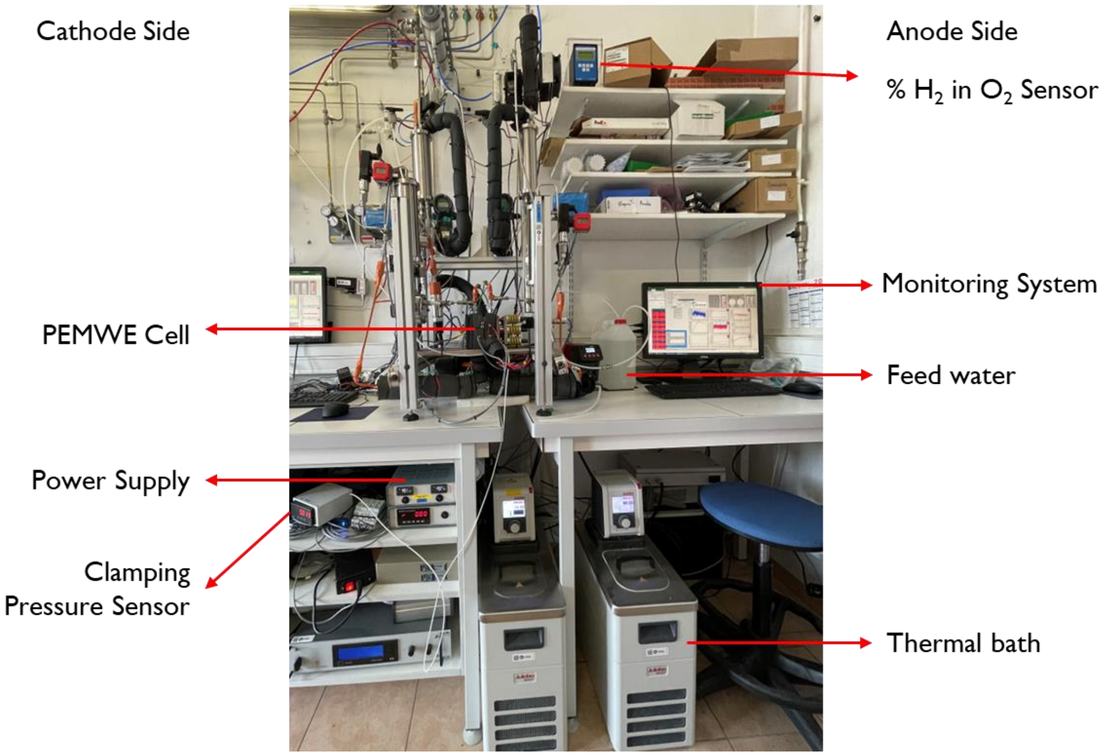

Figure 7 Photo of the original PEMWE setup

A clamping force of 9 N was applied to the cell in order to improve the contact and ensure proper electrical conductivity between the components of the cell. To monitor and measure the applied clamping force, a force sensor was installed within the cell.

The PEM electrolysis cell was operated at a temperature of 60°C and atmospheric pressure at both the anode and cathode compartments. The EHC temperature was set by using a hot water circulating system mechanized in the support plates and driven by a platinum Pt100 probe.

The PEM electrolyser was current controlled, voltage limited, with a voltage limit ranging from 0V to 2.9V. Current and voltage sensors were employed to measure and monitor the electrical parameters during operation.

To ensure water purity and prevent corrosion, the system incorporated diaphragm pumps to supply deionized water to the cell. The water circuit used for temperature regulation was also equipped with a water deionizer to remove any foreign ions that could potentially lead to corrosion, even within the external water circulating system.

The setup included a moisture filter to capture any moisture content present in the outlet of the anode. Additionally, there was a sensor installed to measure the percentage of hydrogen in oxygen, as back permeation of hydrogen could occur through the Nafion® membrane.

3.3 Evaluation of TiC Coated Titanium PTL in PEMWE Conditions

This section presents the experiment conducted to evaluate the performance of a Titanium Carbide (TiC) coated Titanium PTL under operating conditions of a PEMWE system. The purpose of this experiment was to assess the suitability and effectiveness of the TiC coating as a potential solution for improving the performance of stainless-steel PTLs.

3.3.1 Experimental Setup

The experimental setup used for evaluating the TiC coated Titanium PTL was identical to that used for the baseline evaluation of the uncoated stainless-steel PTL. It included a single PEM electrolysis cell with a Nafion® 115 proton exchange membrane, a total area of 10x10 cm^2 and active area of 5x5 cm^2.

On the anode side of the cell, a Titanium Carbide (TiC) coated Titanium PTL was employed instead of an uncoated stainless-steel PTL.

The remaining components and parameters of the experimental setup, such as catalyst loadings, clamping force, temperature, voltage range, and water supply, remained the same as in the baseline evaluation experiment.

Chapter 4. Results and Discussion

4.1 ICR Measurements

4.1.1 Resistance of Catalyst Layers

The resistance measurements of the catalyst layer revealed distinct resistance characteristics for the two catalyst loadings. The 0.6 mg/cm² loading exhibited relatively lower resistance, whereas the 2 mg/cm² loading showed significantly higher resistance.

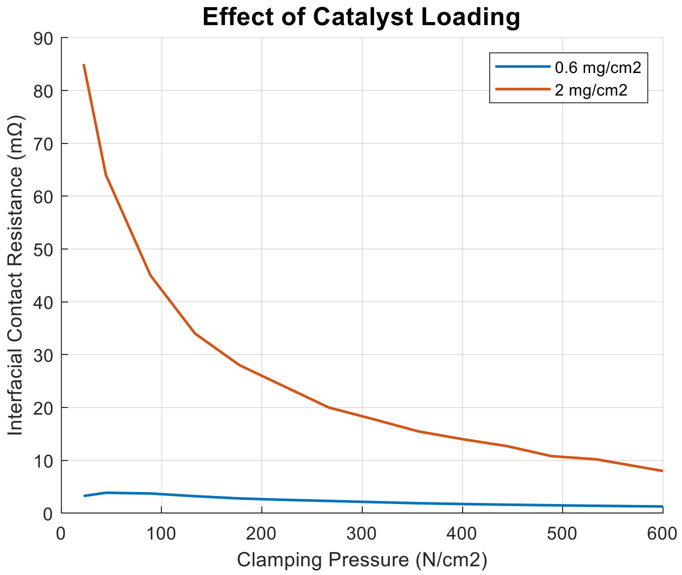

Figure 8 Effect of catalyst loading on ICR

During the ICR measurements, it was observed that, for the 2 mg/cm² loading samples, the resistance was unstable (decreased rapidly as a function of time), particularly at higher clamping pressures. This rapid decrease in resistance suggests potential structural changes occurring in the catalyst coating due to the applied pressure. Further investigation is required to understand the underlying mechanisms responsible for this behavior.

To address the issue of non-uniformity in the catalyst coating, hot pressing was performed on the samples with a 2 mg/cm² catalyst loading. The hot pressing involved subjecting the samples to a temperature of 135°C, which corresponds to the glass transition temperature of Nafion, and a pressure of 1000 N. After cooling down to ambient temperature, the following results were obtained.

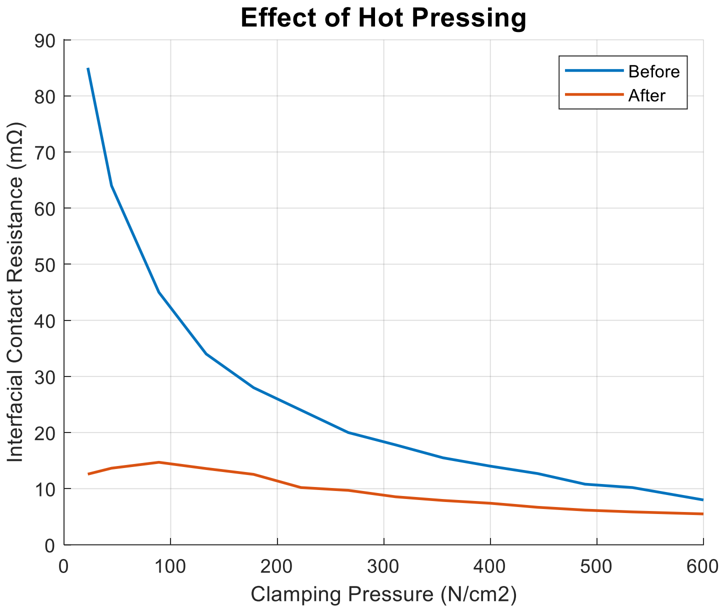

Figure 9 Effect of hot pressing

The hot-pressing process resulted in a decrease in resistance compared to the non-pressed samples and the resistance measurements were also relatively stable as a function of time. This can be explained by the fact that the catalyst coating was a mixture of 80% IrO_2 and 20% ionomer, and the ionomer acted as an electrical insulator by covering the IrO_2 particles which resulted in a higher resistance. On the other hand, the ionomer matrix was compressed after hot pressing, leading to better contact between the IrO_2 particles and the sample surface, resulting in a lower resistance. However, it was observed that the hot-pressing procedure occasionally caused the catalyst layer to stick to the top gold-coated copper sample, even with the use of a Teflon sheet as a barrier. This unintended adhesion of the catalyst layer to the Teflon sheet requires further investigation to develop an improved and optimized coating procedure that ensures a uniform catalyst layer.

4.1.2 Effect of Clamping Pressure on ICR

The effect of varying clamping force on ICR between the catalyst layer and different PTL coatings was investigated. Figure 10 and Figure 11 show the effect of clamping pressure on ICR. The obtained results are represented below.

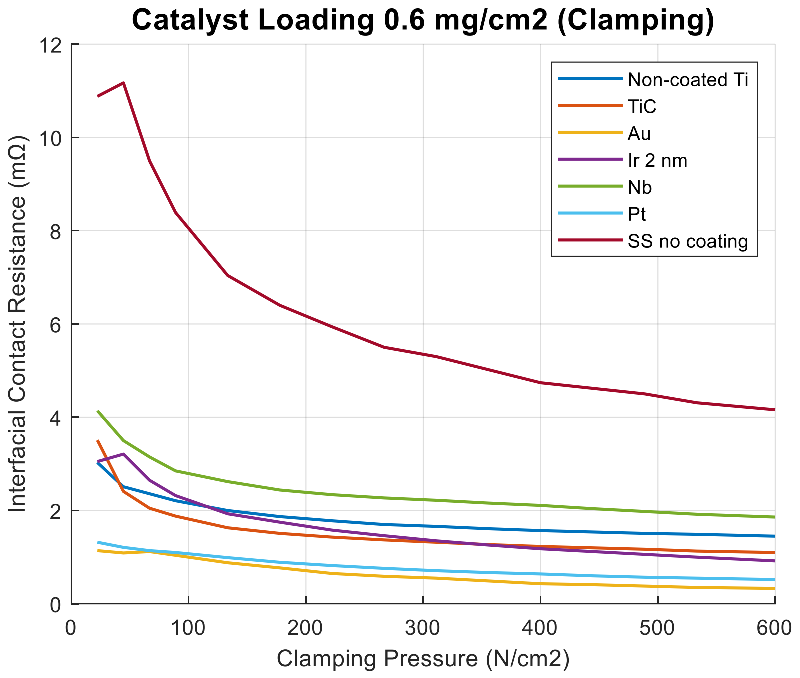

Figure 10 Effect of varying clamping pressure on ICR for 0.6 mg/cm2 catalyst

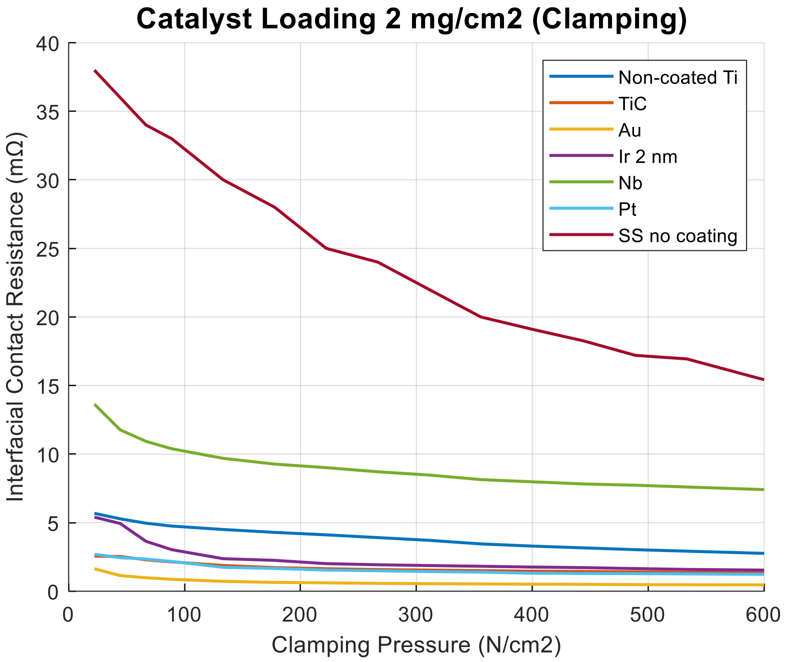

Figure 11 Effect of varying clamping pressure on ICR for 2 mg/cm2 catalyst

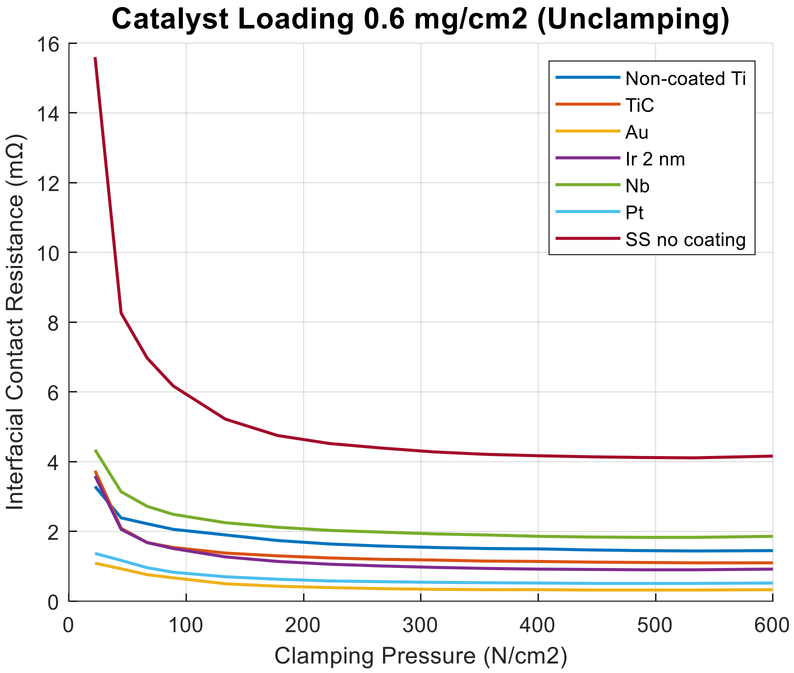

Figure 12 Effect of Unclamping on ICR for 0.6 mg/cm2 catalyst

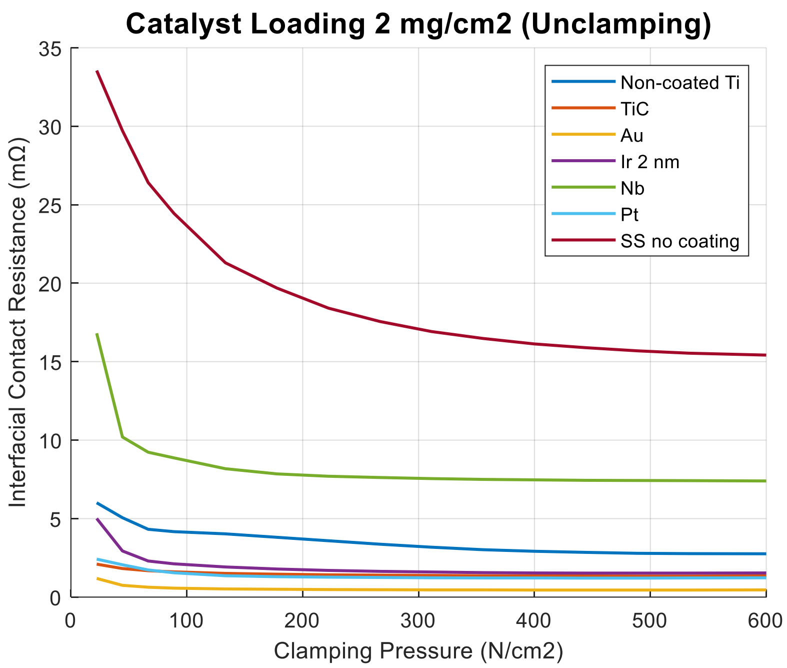

Figure 13 Effect of Unclamping on ICR for 2 mg/cm2 catalyst

The results indicate that gold-coated PTL is the most effective option for improving electrical conductance at the interface, followed by Pt-coated PTL. In contrast, the uncoated stainless steel PTL exhibited the lowest conductance, emphasizing the need for a protective coating to mitigate its poor electrical conductance. Using the 2 mg/cm^2 catalyst loading, at 300 N/cm^2 uncoated Ti PTL showed an ICR of 4.96 mΩ, when the PTL was coated with Pt, the ICR reduced to 2.35 mΩ and was even further reduced to 0.98 mΩ when the Au coated PTL was brought in contact with the catalyst layer. These findings underscore the importance of PTL coatings in optimizing electrical performance.

Furthermore, increasing the clamping pressure led to a reduction in interfacial contact resistance. This decrease in resistance can be attributed to the better physical contact, resulting in improved contact between the PTL and the surface of the sample and enhanced electrical conductivity at the interface.

It is important to note that these measurements were taken *ex situ*, without exposure to corrosive anode conditions in a PEMWE. Therefore, the observed differences in conductance primarily reflect the influence of PTL coatings and clamping pressure on interfacial interactions.

By considering these *ex-situ* resistance measurements, informed decisions can be made regarding the selection of suitable PTL coatings that will provide the desired electrical properties in PEMWE applications.

Additionally, Figure 14 shows a hysteresis that was observed in the resistance during the clamping and unclamping processes. This hysteresis is likely due to irreversible changes in the mechanical properties of the catalyst layer, preventing the generation of similar resistances upon unclamping.Following figure shows the hysteresis observed for TiC coated PTL when in contact with 0.6 mg/cm2 catalyst loading.

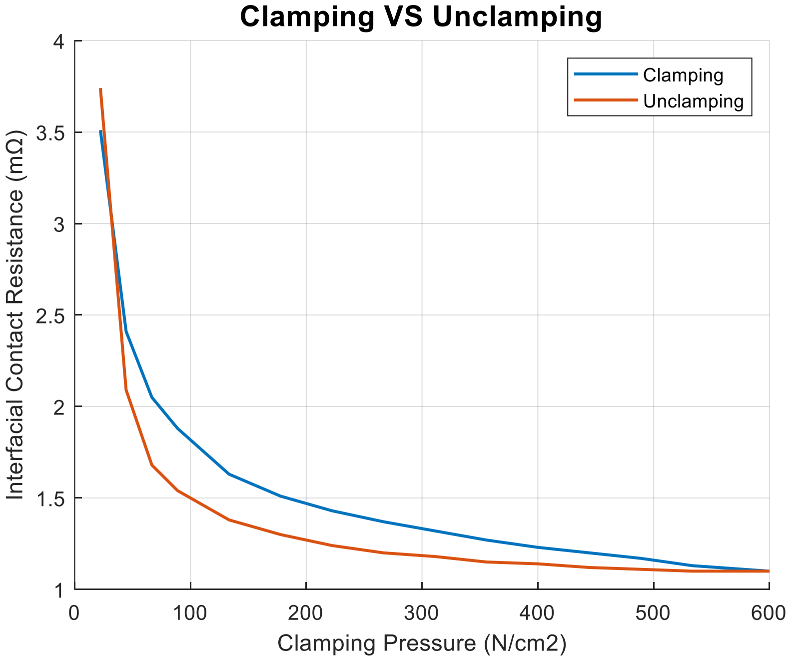

Figure 14 Hysteresis in ICR

4.1.3 Comparison of Ex Situ ICR and In Situ HFR Measurements

A comparison is made between the *ex-situ* ICR measurements conducted in this study and the *in situ* High Frequency Resistance (HFR) measurements performed by Srour et al. [31] during the beginning-of-life (BoL) tests. While there may be differences in testing conditions and methodologies, this comparison provides insights into the electrical behavior of the coatings under varying clamping pressures.

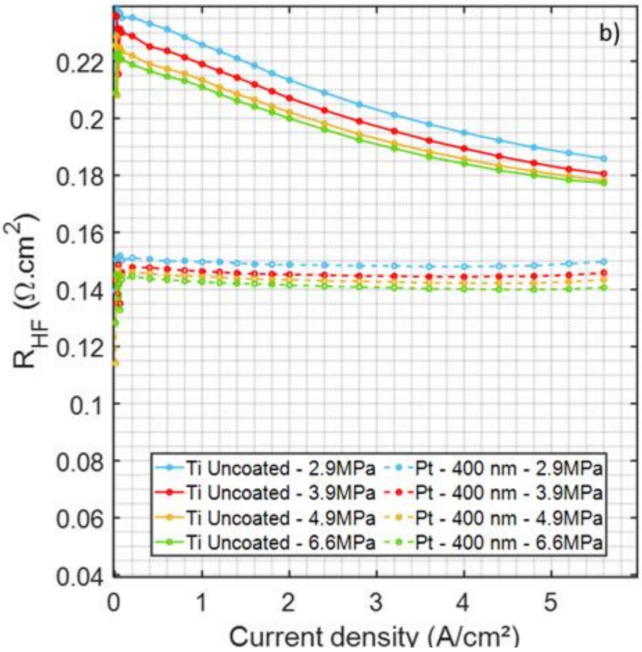

Figure 15 Effect of clamping pressure on HFR (In-situ measurements by Srour et al.)

Both sets of measurements show a consistent trend: an increase in clamping pressure results in a decrease in resistance. This indicates that high clamping pressure improves the contact surface area between the catalyst layer and the PTL, leading to better electrical conductivity. Notably, this trend is observed irrespective of the metal coating used.

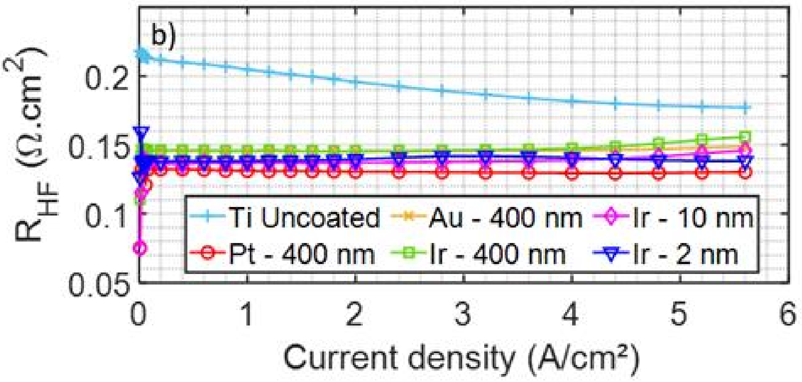

Figure 16 In-situ HFR measurements for different coatings (Srour et al.)

Additionally, the comparison between the *ex-situ* ICR measurements and Srour et al. *in situ* HFR measurements provides valuable insights into the performance of different coatings. *Ex-situ* results demonstrated that the Au coating exhibited lowest ICR. However, Srour et al.'s *in situ* measurements, which were done at a clamping pressure of 660 N/cm^2 showed that the Pt coating displayed the lowest HFR. This is due to the fact that Au coating undergoes continuous dissolution into Au^{3+} ions during electrolysis operations, which can lead to the increase of the HFR and to the redeposition and potential degradation in the PEMWE system. In contrast, our *ex-situ* measurements reflect the Au coating's performance outside the corrosive PEMWE environment, showing it with the lowest resistance.

4.2 Baseline Evaluation of Uncoated Stainless Steel PTL in PEMWE Conditions

The *in-operando* baseline evaluation of the uncoated stainless steel PTL yielded significant results.

The dynamic performance analysis reveals that even the conditioning of the electrolyser system was not possible. **Error! Reference source not found.** shows that the voltage could not stabilize when current was applied

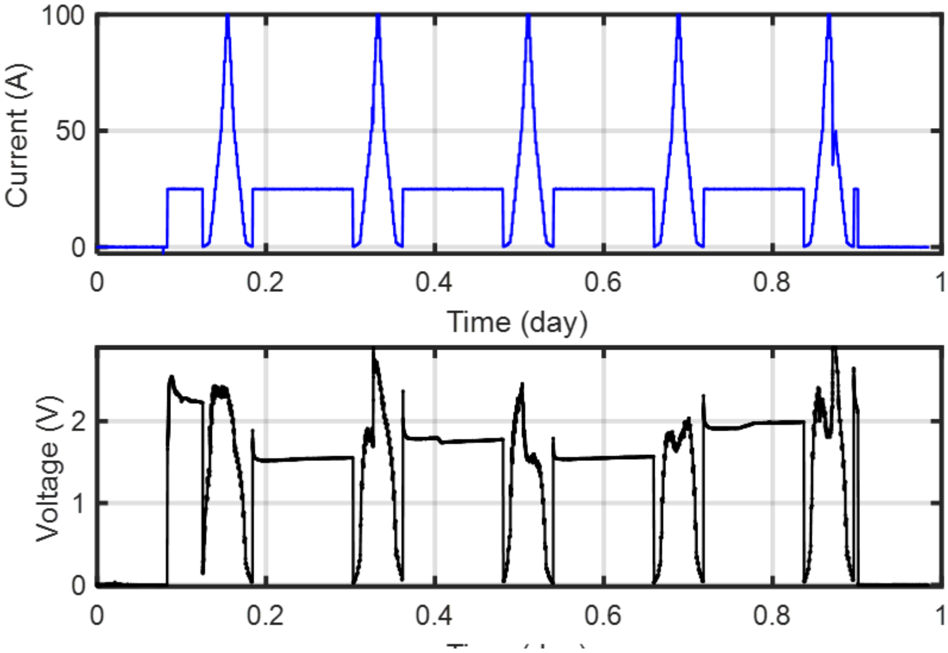

Figure 17 Dynamic performance analysis for Uncoated SS PTL

Additionally, within 10 seconds of applying current, the percentage of hydrogen in oxygen exceeded the allowable limit of 4% by volume, indicating a membrane hole and a short circuit within the cell.

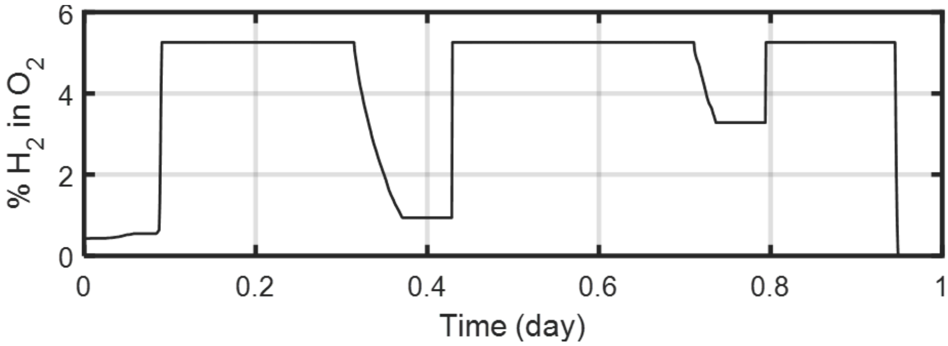

Figure 18 - Percentage of Hydrogen in Oxygen

From this experiment, it can be concluded that using an uncoated stainless steel PTL leads to rapid and severe degradation of PEMWE cell performance. Observation of the Stainless Steel PTL after the experiment showed the presence of Fe^{3+} deposits, indicating corrosion.

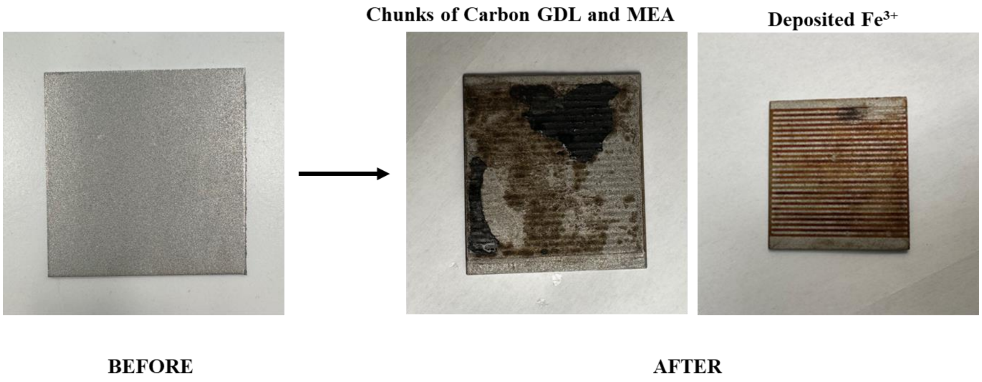

Figure 19 Stainless steel PTL before and after use

Furthermore, the use of an uncoated SS PTL results in the deposition of foreign ions into the membrane, occupying protonic sites and reducing membrane conductivity. Observation of the MEA after the experiment revealed the severe degradation it faced, in terms of losing all its inherent mechanical properties.

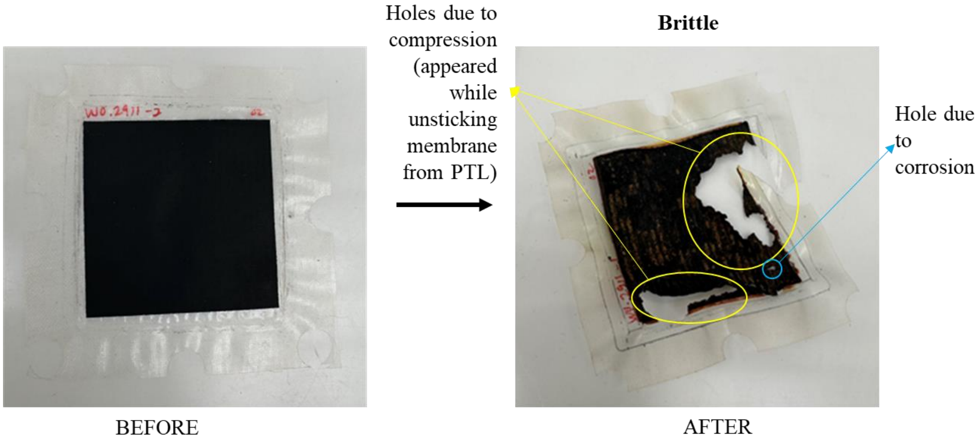

Figure 20 MEA before and after use

These findings highlight the critical importance of employing protective coatings on stainless steel PTLs to mitigate degradation and ensure optimal performance of PEMWE cells.

4.3 Evaluation of TiC-Coated Titanium PTL in PEMWE Conditions

The TiC-coated Titanium PTL showed very promising behavior during the beginning-of-life (BoL) tests. A comparison was made between the polarization curve obtained using TiC-coated PTL and the experimental results of Srour et al., where they tested Au coated Titanium PTL, Pt coated Titanium PTL, Ir coated Titanium PTL, all with a coating thickness of 400 nm, and uncoated Titanium PTL.

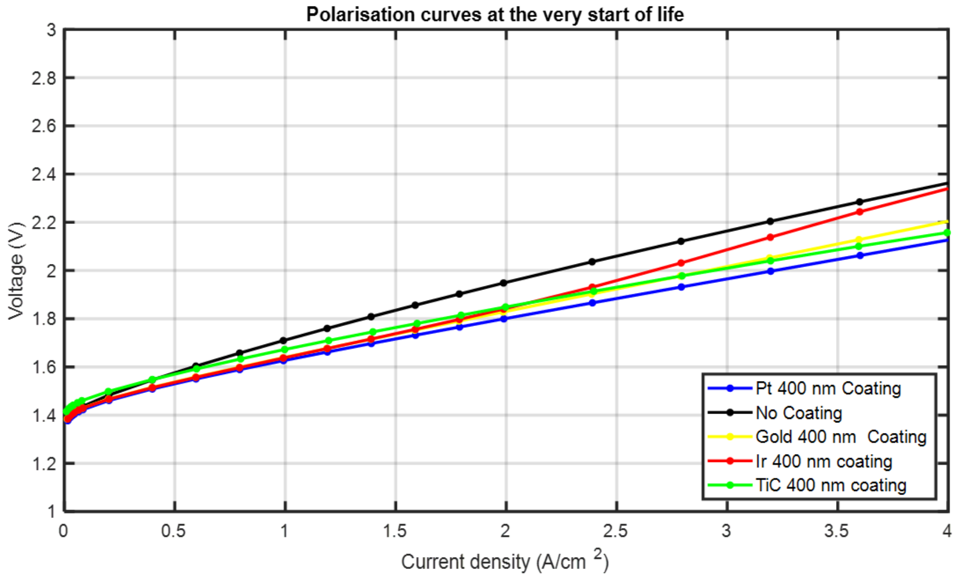

Figure 21 Polarization curves at start of life

The polarization curve obtained at atmospheric pressure and 70°C when using a TiC-coated PTL shows performance comparable with that obtained with Au and Pt coated PTLs. TiC is a much cheaper alternative to gold or platinum coatings and has shown promising results. However, more detailed physicochemical analysis and aging tests are required for a better understanding of its long-term performance and durability.

These initial findings suggest that the TiC coating has the potential to be an effective solution for improving the performance of stainless steel PTLs in PEMWE applications. Further investigations and optimization of the TiC coating process will contribute to the development of cost-effective and high-performance PTL coatings for PEMWE systems.

Chapter 5. Conclusion and Future Work

5.1 Conclusion

In this study, the desired characteristics of the PTL and BPP in PEMWE systems were identified, including corrosion resistance, electrical conductivity, mechanical strength, and porosity. The importance of minimizing interfacial contact resistance (ICR) was emphasized, as high contact resistance can significantly impact system performance and durability. The effects of different factors on ICR, such as surface morphology, oxidation layers, and contact pressure, were identified.

Experimental methodologies were developed to assess the performance and suitability of different coatings for the PTL in PEMWE systems. *Ex-situ* ICR measurements provided insights into the electrical conductivity and contact resistance of various coatings. The results showed that gold-coated PTL exhibited the lowest resistance, followed by Pt-coated PTL, while uncoated stainless steel PTL had the highest resistance. The influence of clamping pressure on ICR was also examined, and it was found that increasing clamping pressure led to a reduction in resistance due to improved contact between the surfaces.

Baseline evaluations were conducted on uncoated stainless steel PTL in PEMWE conditions, revealing rapid degradation and severe performance decline. Corrosion and deposition of foreign ions were observed, highlighting the need for protective coatings to ensure optimal performance and durability.

The evaluation of a TiC-coated titanium PTL showed promising results in terms of performance comparable to gold and platinum-coated PTLs. TiC coating demonstrated potential as a cost-effective solution for improving the performance of stainless steel PTLs in PEMWE applications.

5.2 Future Recommendations

As this study was the foundation for a longer PROTIS project so in the longer scheme of things, further research and comparative studies need be carried out to identify the most suitable coating for stainless steel components in PEMWE systems. This will involve exploring alternative coating materials, optimizing coating thickness and composition, and evaluating their stability, corrosion resistance, electrical conductivity, and cost-effectiveness. The goal would be to find a coating that provides effective protection against corrosion, maintains good electrical conductivity, and ensures long-term durability.

Once suitable coatings for stainless steel components are identified, it is crucial to assess their performance and durability under actual working conditions of a PEMWE system. This will involve subjecting the coated stainless steel PTLs and BPPs to operating conditions, including high overvoltage, acidic environment, and presence of oxygen and moisture, and evaluating their performance, corrosion resistance, and overall system efficiency. Comparative studies with uncoated stainless-steel components will provide valuable insights into the benefits of using protective coatings.

As TiC coating showed promising performance in beginning of life tests, future work will require an in depth physico-chemical characterization of this coating to analyze its properties and its interaction with the underlying titanium substrate. This characterization will provide insights into the coating's stability and electrochemical behavior. Furthermore, performing aging tests on the TiC-coated titanium PTL are required to evaluate its long-term performance, stability, and durability.

The PROTIS project aims to develop innovative coating solutions that will help in replacing titanium components with stainless steel, while enhancing or maintaining the performance and durability of PEMWE systems. The future work outlined in this section is crucial for the advancement of this project and ultimately accelerating a much wider adoption of PEMWE technology commercially.

5.3 Environmental impact of the work

This thesis work aligns with several SDGs established by the United Nations to address global challenges and promote sustainable development. The key SDGs that can be fulfilled through the implementation of the PROTIS project include:

5.3.1 SDG 7: Affordable and Clean Energy

By enhancing the performance and durability of stainless-steel components employing coating materials, in PEMWE, the project contributes to affordable and clean energy production through renewable hydrogen.

5.3.2 SDG 9: Industry, Innovation, and Infrastructure

The development of innovative coatings for stainless steel components represents technological innovation that can advance sustainable industrial practices.

5.3.3 SDG 12: Responsible Consumption and Production

By extending the lifespan of PEMWE components and reducing the need for expensive titanium materials, the project supports responsible resource consumption and production.

5.3.4 SDG 13: Climate Action

The transition to renewable hydrogen production using PEMWE can contribute to climate mitigation efforts by reducing greenhouse gas emissions associated with conventional hydrogen production methods.

5.3.5 SDG 17: Partnerships for the Goals

The collaborative nature of the PROTIS project fosters partnerships between different organizations to achieve sustainable development objectives.

Figure 22 Relevant SDGs

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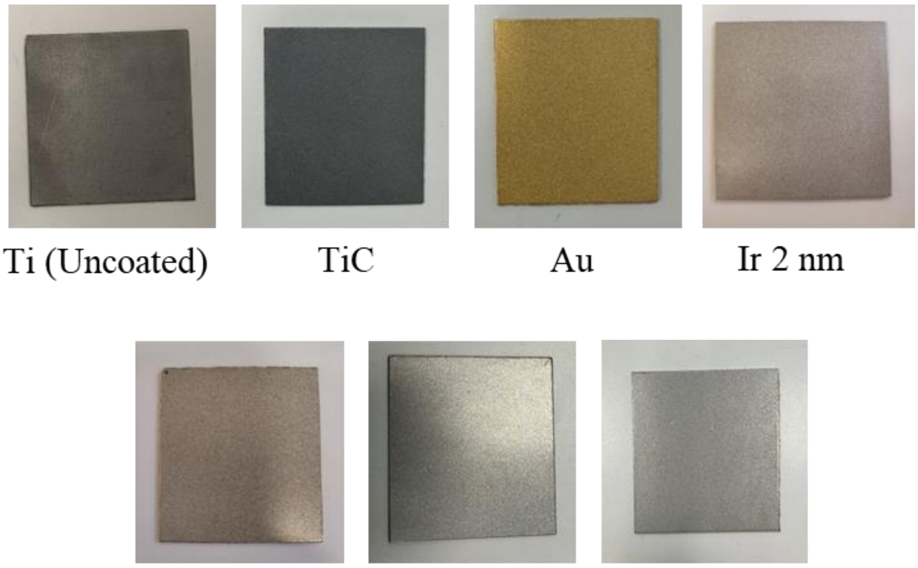
Appendix A

PTL Materials tested for ICR



Ti (Uncoated) TiC Au Ir 2 nm

Nb Pt SS (uncoated)

Figure 23 Tested PTL materials

Catalyst Sample used in ICR measurements

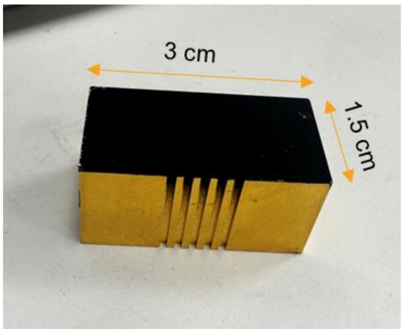


Figure 24 Size of coated catalyst sample

Milliohm meter used for ICR measurements

Figure 25 Milliohm meter used in ICR measurements