Long-term Stable Electrodes Based on Platinum Electrocatalysts Supported on Titanium Sintered Felt for the Use in PEM Fuel Cells

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Abstract. In this work a long-term stable electrode structure, suitable for polymer electrolyte membrane fuel cell (PEMFC) applications is presented. Investigated electrodes are prepared by using sintered titanium felt as porous and current conducting gas diffusion layer, due to its corrosion resistance in acidic environment. Platinum is deposited onto the surface of the titanium fibres by an electrochemical method. This carbon-free electrode structure has been studied regarding stability and performance ex-situ and in-situ by cyclic voltammetry, corrosion tests, i-U polarisation measurements, and accelerated stress tests. Furthermore, the electrode morphology of the catalytic layer on titanium sintered felt has been investigated by means of scanning electron microscopy. Results of this study claim high corrosion stability for the use of these electrodes in PEMFCs. A small-scale laboratory prototype has been realised, which is also presented in this work.

1. Introduction
In autonomously operating sensor systems, batteries are typically used as energy source. Niche applications such as for the determination of environmental conditions in underground deposits (e.g. uranium wastes), often demand low energy and power but require an autonomous operation for decades. Batteries are able to provide sufficient electrical energy at very high efficiency. However, due to degradation mechanisms, these suffer from self-discharge, which consequently inhibits the use of batteries for extended operation periods far beyond ten years without being recharged. As an alternative energy source for a long-term autonomous operation, polymer electrolyte membrane fuel cell (PEMFC) systems with integrated hydrogen and oxygen tanks are proposed as continuous electrical energy generator.

The main principle of a fuel cell is based on the anodic hydrogen oxidation reaction (HOR) and the cathodic oxygen reduction reaction (ORR) resulting in an overall electrochemical reaction expressed by the equation $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{Energy}$ [1].

Typically, relevant components in PEMFCs are based on carbon material or stainless steel with high electrical conductivity. Pole plates made from graphite compound or stainless steel provide necessary gas channels within the cell for the process gases hydrogen and oxygen. These gases are finely distributed to the anodic and cathodic catalysts, respectively, by porous gas diffusion layers
(GDL), which are typically graphitic. As electro catalysts in PEMFCs usually chemically or electrochemically reduced nano-scaled platinum particles supported on graphitic nano-structures are employed. In order to manufacture gas diffusion electrodes (GDE), the catalyst layer is applied onto the GDL. [1]

Although PEMFCs provide high power densities at reasonable efficiencies, carbon corrosion occurs at cell potentials above 0.65 V. This leads to continuous cell degradation mainly due to a loss of catalyst support material which, again, leads to an electrochemical surface area (ECSA) loss and a reduced cell performance.

As electrolyte in PEMFCs functionalized polymer membranes with high proton conductivity such as perfluorinated sulfonic acid (PFSA) based membranes are used. Further relevant degradation in fuel cells arises from poisoning of these membranes due to surface corrosion of metal bipolar plates exposed to the acidic PEMFC environment. Metal cations can enter the polymer by water flow and block the negatively charged sulfuric acid groups within the membrane, which leads to a continuous loss in proton conductivity and, therefore, in decreased cell performance over the operation time. Furthermore, chemical degradation of the membrane provoked by metal cations (radical attack) occurs. For a corrosion resistant protection layer, metal bipolar plates are often coated with noble metals such as gold. Accounting for the costs of noble metal coatings, a deposited gold layer for PEMFC pole plates typically has a thickness of far below 1 micron resulting in a corrosion stability for a few thousand operation hours. [2]

Titanium on the contrary is well known to be nearly completely corrosion stable under acidic environment. E.g. for PEM electrolyzers porous current distributors made from sintered titanium particles or sintered titanium fibers are used as anodic electrode material operating long-term stable at an electrode potential above 1.5 V [3]. In this work we describe an approach for the manufacturing of titanium-based long-term stable GDE for the use in PEMFCs. Two electrodes are hot pressed with proton conductive polymer membrane forming a titanium-based membrane electrode assembly (MEA).

Technical fuel cells have been developed for a subsequent use of prepared long-term stable electrodes. The cell design was engineered according to a sensor application that needs to fit into a bore hole with a diameter of 100 mm. Pole plates made from stainless steel have been plated with an above-average thick anti-corrosive gold coating of about 2 microns. Two pole plates are clamped together having the titanium-based MEA in between to form a single cell. A PEMFC stack has been assembled with 20 single cells that are electrically connected in series being operated with hydrogen and oxygen.

2. Methodology and Experimental Equipment
In order to overcome degradation mechanisms in PEMFCs that result from carbon or stainless-steel corrosion, titanium-based electrodes and pole plates with an anti-corrosive coating have been prepared for a long-term stable PEMFC application. Titanium is well known to be corrosion resistant in acidic environments even at high potentials as e.g. in polymer electrolyte membrane electrolyzers. In this study, titanium substrate made from sintered titanium fibers in micro scale was coated with platinum as electrocatalyst for the hydrogen oxidation reaction as well as for the oxygen reduction reaction.

For this work, prepared electrodes have been investigated regarding their morphology using scanning electron microscope (SEM) as well as their electrochemical activity in sulfuric acid by determining the ECSA. Furthermore, an accelerated stress test has been performed regarding the analysis of the prepared electrodes’ corrosion stability.

The realized technical cells and the manufactured PEMFC stack have been operated in a laboratory test bench under realistic environmental conditions referred to their designated underground application. In-situ tests of the laboratory device are also reported in this work.
2.1. Electrode preparation

Regarding the preparation of long-term stable electrodes, sintered titanium felts have been used as substrate for platinum catalyst deposition. The utilized specimens are circular shaped with a diameter of 30 mm having a thickness of 1 mm and a high porosity above 70%.

In order to remove oxides from the surface for a subsequent platinum deposition, the utilized sintered titanium felts have been pre-treated in two steps. Initially, titanium felts have been cleaned in an electrolytic pickling solution from Wieland Edelmetalle, Germany, based on nitric acid and hydrofluoric acid with a pH-value of 0.5 at room temperature. Voltage has been applied to the felts to provoke anodic dissolution of the titanium/titaniumdioxide surface. A counter electrode based on titanium expanded mesh plated with platinum from Wieland Edelmetalle has been used for this preparation step. The anodic voltage versus the counter electrode was set to 2.5 V.

After rinsing with deionized water, the surface of the titanium work pieces has been plasma treated in argon, in order to remove still remaining contaminations on the titanium surface. A plasma reactor type Pink V 15-G from PINK Thermosysteme GmbH, Germany, was used and the parameters were set to an argon flow rate of 100 ml min⁻¹, at a gas pressure of 60 Pa and a treatment time of 30 min at a microwave power of 400 W.

Consecutively to the plasma physical cleaning process and further rinsing with deionized water, the titanium fibers have been immediately plated with platinum by electrochemical method under argon atmosphere to inhibit the formation of oxides on the titanium surface after the electrode preparation process. A commercially available plating bath type Galvatron Platinbad from Wieland Edelmetalle based on hexachloroplatinic acid has been used. The bath parameters were set to a pH-value of 8 and a temperature of 50 °C. The plating process was performed for 10 min at a constant cathodic voltage of -3.2 V versus the counter electrode (titanium/platinum from Wieland Edelmetalle). During the plating process, the titanium electrode was placed between two counter electrodes that are connected electrically. Subsequently, for an increase in the catalysts electrochemical active surface area by the deposition of micro and nano-scaled platinum particles, the plating mode has been switched to a pulsed plating at a cathodic voltage of -3.0 V versus the counter electrode without interrupting the process. The on-time was set to 10 ms and the off-time was set to 56.7 ms, resulting in a 15% duty cycle. The second part of the plating process was performed for further 10 min.

Regarding the later assembly of polymer membranes with the prepared specimens to form MEAs, electrodes have been impregnated with 0.5 ml proton conductive ionomer solution type Nafion® (5 wt.% in ethanol) subsequently to the platinum plating. The solution has been applied by an air brush coating, while the titanium-based electrode was attached to a heated sample holder. The temperature was set to 60 °C to speed up the evaporation of the ethanol from the electrodes surface.

It was already mentioned that the investigated electrodes consist of two parts, a titanium-based felt with catalyst coating and ionomer impregnation as well as a stainless-steel (type 1.4404/SS 316) pole plate having a labyrinth flow field formed by channels with 1 mm depth and 1 mm width. Regarding the corrosion protection, an ultra-thick gold coating has been applied to these workpieces after preliminary removal of oxides by a plasma physical pre-treatment in argon. The deposition has been performed by an electrochemical method. The commercially available plating solution type Haftgoldbad AC 3 SSF from Wieland Edelmetalle based on potassium dicyanoaurate was utilized at room temperature. A constant cathodic voltage of -3.0 V versus the platinum counter electrode was applied for 10 min. Deposition of the anti-corrosive coating has been performed according to the specification sheet of the electrolyte manufacturer.

2.2. Ex-situ analyses

Surface morphology and cross sections of selected specimens have been investigated using a scanning electron microscope (SEM) type Phillips ESEM XL 30 with an integrated detector for energy dispersive X-ray (EDX) analysis. The focus of this microscopy work has been on the observation of the corrosion protection layers of the titanium-based electrodes (platinum) as well as of the pole plates.
(gold) and the nano/micro structure of the prepared catalyst layer. Furthermore, punctual and area material analyses have been performed by EDX measurements. For understanding the crystalline structure of the deposited platinum catalyst, further material characterization has been performed by means of X-ray diffraction measurements (XRD type Philips X’Pert).

For the electrochemical determination of the ECSA a galvanic cell has been prepared in order to entirely fit prepared electrodes into a sample holder. A platinum foil has been used as a counter electrode, having a circular shape with a diameter of 33 mm. The distance between sample holder and counter electrode was designed to be 30 mm. A saturated calomel electrode has been utilized as a reference. Cyclic voltammetry (CV) has been performed in 0.5 M H$_2$SO$_4$ using a potentiostat/galvanostat type Ivium Technologies Vertex (in three electrodes mode). CV starting potential and vertex potential were set to -0.2 V versus SCE and of 1.2 V versus SCE, respectively, and scan rate was set to 100 mV sec$^{-1}$. ECSA has been calculated after 200 cycles between starting and vertex potential. After determination of the initial ECSA of an investigated sample, an accelerated stress test (AST) that is known for testing automotive PEMFC electrodes has been performed. In analogy to an earlier work [4], samples have been cycled 1,000 times between 0.4 V versus SCE and 1.4 V versus SCE at a scan rate of 1,000 mV sec$^{-1}$. Subsequently to the AST, ECSA has been determined again following the above-mentioned parameters to analyse the change in catalytic activity due to high electrode potentials occurring especially at start-stop operation.

2.3. Cell and stack manufacture

Technical PEMFCs have been assembled using the prepared titanium-based felts with catalytic layer and stainless-steel pole plates with anti-corrosive coating. As a polymer membrane Nafion® type 115 has been used. This rather thick membrane (125 µm) inhibited relevant gas cross-over through the membrane, which was necessary for a long-term PEMFC operation. Regarding the prevention of gas leakage, two gaskets made of polytetrafluoroethylene (PTFE) were located between pole plate and membrane outside the electrochemical active electrode area, which is a typical design for PEMFC applications. Two pole plates, two long-term stable electrodes and a membrane with PTFE gaskets formed a single fuel cell.

![Figure 1. Macrograph of the manufactured lab-scale PEMFC stack operated in its test bench environment.](image)

A fuel cell stack has been manufactured using 20 single cells. To save material and therefore costs, pole plates were designed bipolarly having a flow field on each side of the plate, as it is common for PEMFCs. Each single cell was gas technically connected in parallel and electrically connected in
series. The stack was designed for dead-end operation, meaning gas was fed without having a relevant gas flow through the cells. In order to compress the inner components, especially to decrease contact resistance between the different MEA layers, tie bolts were utilized to clamp the first with the last cell of the PEMFC stack. Furthermore, the stack provided connectors to apply hydrogen and oxygen feed gases as well as a waste water container.

2.4. **Fuel cell testing**

In order to provide the necessary infrastructure for the simulation of the underground environment, a test bench has been constructed, in which the manufactured PEMFC test stack has been operated under relevant testing conditions. The test bench was operated with pure hydrogen and oxygen (quality 5.0) from Linde, Germany. It was equipped with the necessary fuel processing components (pressure regulator, safety valves, mass flow meter etc.) as well as with an oven type Memmert UF55 to simulate the underground temperature. Regarding the determination of electrical specifications of the manufactured PEMFC stack, polarization measurements have been performed by the use of an electronic load type Höcherl & Hackl: DS400 SV20. The fuel cell stack was tested at 80 °C. Gas pressure was adjusted to 1.1 bar absolute. Polarization plots have been determined in constant current mode from open circuit voltage (OCV) to the maximum power point in forward direction.

3. **Results and Discussions**

Presented results indicate high corrosion stability of the prepared titanium-based GDEs as well as of the technical fuel cell that has been manufactured for this study. Microscope images show well distributed platinum nano-particles on the titanium fibers that have been used as a substrate. In cross section analyses dense corrosion protection layers of platinum (on titanium fibers) and gold (on stainless-steel pole plates) have been observed. Furthermore, electrochemical characterization result in high ECSA due to the roughness of the platinum surface of the prepared titanium-based electrodes. From in-situ testing performed by the aid of the assembled fuel cell under simulated underground conditions it can be assumed that the developed components exhibit the required electrochemical performance for the proposed application.

3.1. **Microscopic investigations**

![Figure 2. SEM micrographs of: left) top-view of the gold coating surface, and right) cross-section of the coating/substrate system.](image-url)
Cross-sections of prepared titanium-based electrodes as well as on stainless-steel based pole plates have been investigated by SEM/EDX. Observing the SEM micrographs of the top view and cross-sections of the coated pole plates illustrated in Figure 2 it can be agreed that dense anti-corrosive coatings have been obtained with a thickness of about 2 µm. No oxide layer has been found between coating and stainless-steel substrate resulting in increased adhesion.

The microscopic images of Figure 3 show sintered titanium fibers with platinum coating and particles, respectively. It becomes obvious that only for these fibers situated at the outside of a utilized felt, an entire coating can be claimed. This effect is explained by the electrical field distribution within the galvanic cell (working electrode in between and parallel to two counter electrodes). However, the achieved coating is sufficient for the long-term stable adhesion of the platinum nano particles, which were decorated subsequently. Furthermore, micrographs have been analyzed of platinum particles that have been deposited on the plated titanium fibers by pulsed electro plating process. Nano and micro scaled platinum particles are visible, resulting in a high specific surface area due to a high roughness factor. In addition to that, EDX analysis (see Figure 4) showed only a small amount of oxides having been present on the titanium fibers decorated with platinum.

### 3.2. X-ray analysis

The performed X-ray analysis confirmed the presence of Pt particles with a face-centered cubic crystal structure. Moreover, physical properties such as the average crystallite size were obtained from the X-ray diffraction results. The experiments were conducted in the 2θ range from 20° up to 100° using CuKα radiation. The average crystallite size was determined, employing the Debye-Scherrer equation,
using the full width at half maximum of the Pt (111), Pt (200) and Pt (220) reflection peaks [5]. The X-ray diffractogram presented in Figure 5 shows a typical XRD pattern of the titanium GDL decorated with platinum catalyst particles. The resulting average size of the platinum crystallites was 10 nm underlining the high specific surface area of the prepared catalyst layer.

3.3. CV and ECSA measurements

For a better understanding of the electrochemical processes that take place on the Pt/Ti catalyst, cyclic voltammetry measurements have been performed on selected samples in a manner similar to that of other studies [1, 4]. Figure 6 presents a typical cyclic voltammetry curve obtained from a Pt/Ti electrode with a geometrical surface area of 8.55 cm² immersed in a 0.5 M H₂SO₄ solution in the potential range of -0.2 V to +1.2 V vs. SCE with a constant scan rate of 100 mV s⁻¹ after 200 cycles. Region A characterizes the hydrogen adsorption ($i < 0$) and desorption ($i > 0$) area, region B corresponds to the double layer capacity, and in region C, the platinum oxidation ($i > 0$) and reduction ($i < 0$) processes occur [6] [4].
ECSA has been determined by calculation of charge related to the hydrogen desorption peaks applying a numerical integration algorithm. Taking into account the charge for a polycrystalline platinum surface (210 µC cm\(^{-2}\)) [6], ECSA was obtained by the division of the calculated charge with this value (results shown in Table 1). After the above described AST procedure ECSA has been determined again. Tests revealed a slight increase of the active surface area, which may result from a further cleaning of the catalyst surface from contaminations such as chlorides (arising from the used electrolyte) due to the potentiostatic cycling (Pt oxidation followed by Pt reduction). This result underlines the high stability of prepared samples in contrast to carbon-based electrodes, which typically suffer from ECSA loss after this kind of AST [4].

| Pt-Ti electrode | Geometrical SA [cm\(^2\)] | ECSA [cm\(^2\) cm\(^{-2}\) | ECSA after AST [cm\(^2\) cm\(^{-2}\)] |
|-----------------|--------------------------|-------------------------|----------------------------------|
|                 | 8.55                     | \(\approx 38.60\)      | \(\approx 42.22\)                |

3.4. In-situ tests

From in-situ measurements performed using an electronic load, the PEMFC stack performance at elevated temperatures of 80 °C has been determined by means of recorded polarization curves. The manufactured stack has been operated with hydrogen and oxygen that were supplied to the cells with a slight overpressure of 0.1 bar (dead-end operation). Due to dead-end operation it can be assumed, that the process gases are nearly 100% humidified. From i-U polarization an OCV of 19.5 V and a mean OCV of 0.975 V per cell have been measured (Figure 7). By increasing the stack current, voltage drops rapidly, which may be an effect of high ohmic resistance due to the poor electrical conductivity of titanium components in comparison to typically used graphitic material in combination with the poor ionic conductivity of the rather thick membrane. However, at a stack voltage of about 8.5 V the maximum electrical power has been determined to be in the range of 4 W (0.025 W cm\(^{-2}\)), which is sufficient for the aspired sensor application.

Figure 7. Polarization curves of the manufactured lab-scale PEMFC left) stack and right) single cell.

4. Conclusions and outlook

In this work a preparation route for long-term stable electrodes based on titanium sintered felt has been presented. Material characterization of prepared electrodes revealed high corrosion stability and sufficient electrochemical activity in acidic environment. From these electrodes, a lab-scale PEMFC stack has been manufactured that offered sufficient electrical power for underground sensor applications. However, further in-situ testing is necessary in order to prove long-term stability of the realized technical PEMFC stack as well as to integrate the device into the aspired sensor system.
5. References

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