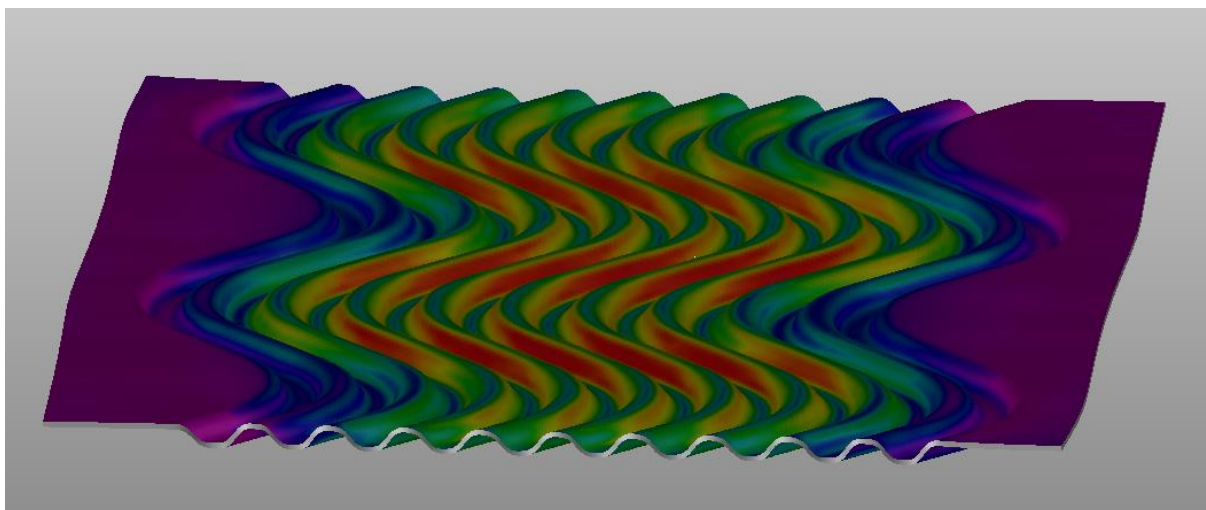




Fuel cell with Aluminum as base material



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Appendix 1: “Literature review on coating systems for Aluminum-based bipolar plates.”

Appendix 2: “Technology for sheet forming and joining of bipolar plates for PEM fuel cell applications.”

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1 Summary

The BALBAS project has covered several aspects of producing Aluminum based bipolar plates (BPP), including thin Aluminum plate manufacturing and preparation for surface coating, coating with different techniques, evaluation by *ex-situ* and *in-situ* methods, and reviewing state-of-the-art for coating technologies, forming technologies and joining technologies. The overall purpose of the BALBAS project was to evaluate the possibility of using Aluminum as a base material for bipolar plates in proton exchange membrane fuel cells (PEMFC). By doing a literature review and by following the recent scientific and commercial publications the increasing interest for Aluminum as a base material for fuel cell bipolar plates has been noticed. However, the application of Aluminum-based BPPs in real PEMFC stacks is still in its infancy and no commercial products are on the market.

In BALBAS coatings of NiP, CrN, Ti, and amorphous carbon (a-C) were fabricated and investigated. The coated samples were evaluated by *ex-situ* corrosion exposure in a corrosion cell and in a climate chamber. They were also examined by several instrumental surface analysis techniques (e.g. SEM-EDS, FTIR, etc). The surface analysis investigation revealed that impurities on the Aluminum substrate surface might have an important impact on the formation of defects and on the performance of the coated samples. Interfacial contact resistance (ICR) measurements were done before and after corrosion exposure. They showed that the coated samples behaved differently to corrosion cell testing and atmospheric corrosion exposure in a climate chamber. Adding a carbon top-layer to NiP and Ti coatings (and even plain Al sample) contributed to a significant improved corrosion resistance in most cases.

NiP|C was selected for *in-situ* fuel cell evaluation, and it behaved surprisingly well. Under the test conditions (70 °C, 60% RH) the coating showed only a small decrease in high frequency resistance during the testing periods of 906 and 473 hours. This result was further confirmed by the *post-test* examination through ICR measurements giving only a small increase. However, there was a difference between the anode and the cathode plates and corroded stains could be observed on the cathode plate surface.

The BALBAS project has shown that, with a proper coating, Aluminum based bipolar plates are feasible for PEMFC and that 1000 h fuel cell operation with acceptable contact resistance performance has been reached. The project work has also improved the methodology for *ex-situ* evaluation of Aluminum based bipolar plates.

2 Sammanfattning på Svenska

BALBAS-projektet har undersökt flera aspekter av att producera aluminiumbaserade bipolära plattor (BPP), inklusive tillverkning av tunn aluminiumplåt och preparering inför ytbeläggning, ytbeläggning med olika tekniker, utvärdering med *ex-situ* och *in-situ* metoder, samt granskning av state-of-the-art för beläggningsteknik, formningsteknik och sammanfogningsteknik. Det övergripande syftet med BALBAS-projektet var att utvärdera möjligheten att använda aluminium som basmaterial för bipolära plattor i polymerbränsleceller (PEMFC). Genom att göra en litteraturstudie och genom att följa de senaste vetenskapliga och kommersiella publikationerna har det ökande intresset för aluminium som basmaterial för

bipolära plattor i bränsleceller observerats. Användningen av aluminiumbaserade BPP:er i verkliga PEMFC-stackar är dock fortfarande i sin linda och inga kommersiella produkter finns på marknaden ännu.

I BALBAS tillverkades och undersöktes beläggningar av NiP, CrN, Ti och amorft kol (a-C). De belagda proverna utvärderades genom korrosionsexponering *ex-situ* i en korrosionscell och i en klimatkammare. De undersöktes också med flera instrumentella ytanalys tekniker (t.ex. SEM-EDS, FTIR, etc.). Ytanalysundersökningen visade att föroreningar på ytan av aluminiumsubstraten kan ha en stor inverkan på bildandet av defekter och på prestandan hos de belagda proverna. Mätningar av gränsytares kontaktresistans (ICR) mellan prov och ett gasdiffusionsskikt (GDL) gjordes före och efter korrosionsexponering. De visade att de belagda proverna betedde sig annorlunda under testning i korrosionscell jämfört med atmosfärisk korrosionsexponering i en klimatkammare. Att lägga till ett kolskikt till NiP- och Ti-beläggningar (även på ren Al-yta) bidrog till en signifikant förbättrad korrosionsbeständighet i de flesta fall.

NiP/C valdes ut för utvärdering *in-situ* i bränslecell, och den uppförde sig förvånansvärt bra. Under testförhållandena (70 °C, 60 % RH) uppvisade beläggningen endast en liten minskning av högfrekvensresistansen under testningstiderna 906 och 473 timmar. Detta resultat bekräftades ytterligare av *post-test* undersökningen genom ICR-mätningar som endast uppvisade en liten ökning. Det fanns dock en skillnad mellan anod- och katod-plattorna och korroderade fläckar kunde observeras på katodplattans yta.

BALBAS-projektet har visat att, med en korrekt beläggning, är aluminiumbaserade bipolära plattor möjliga för PEMFC och att 1000 timmars bränslecellsdrift med acceptabel kontaktresistansprestanda har uppnåtts. Projektarbetet har också förbättrat metodiken för *ex-situ* utvärdering av aluminiumbaserade bipolära plattor.

3 Executive summary in English

Introduction – The BALBAS project has covered several aspects of producing Aluminum based bipolar plates, including thin Aluminum plate manufacturing and preparation for coating, coating with different techniques, evaluation by *ex-situ* and *in-situ* methods, and reviewing state-of-the-art for coating technologies, forming technologies, and joining technologies.

In proton exchange membrane fuel cells (PEMFC) the bipolar plates (BPP) separate the gases (hydrogen and air) and provides channels/flow patterns for gases, while at the same time conduct electrons from one cell to the other. Furthermore, the bipolar plates also provide channels for the cooling liquid of the fuel cell. BPPs are made of graphite/graphite composites or metallic thin sheets. Metallic BPP performance suffers from surface oxidation in the fuel cell environment which leads to poor electrical contact between the GDL and the BPP. For this reason, a protective and electrically conducting surface coating is generally applied on metallic BPPs.

Coatings on aluminum foils/thin sheets for fuel cell applications must provide; sealing, electrical contact, strong adhesion, and ductility; only one layer might not all these requirements. The coating system may thus consist of several layer with different functionality. The coatings most often considered for fuel cells in the literature can be divided in four groups: metals, phosphides, nitrides, carbides, and carbon coatings. Further background information can be obtained from Appendix 1 “Literature review on coating systems for Aluminum-based bipolar plates”.

Purpose, research questions, and methods – The overall purpose of the BALBAS project is to evaluate the possibility of using Aluminum as a base material for bipolar plates in PEMFC. Further, to develop a methodology for evaluating corrosion properties and contact resistance of surface coatings on bipolar plates and to apply the methods to several coating systems on aluminum substrates.

The research questions studied in the project are related to the corrosion protection properties of coatings obtained by plating (e.g. NiP) and physical vapor deposition (PVD, e.g. Ti, C). Finally, *ex-situ* corrosion methods were compared with *in-situ* testing in order to develop relevant screening techniques for the PEM fuel cell application.

The substrate samples were made from an alloy called FA5100 and is one of several bespoke Gränges alloys aimed at applications that require high thermal and electrical conductivity. The substrates were ground and polished on the side to be coated.

In BALBAS coatings of NiP, CrN, Ti, and amorphous carbon (a-C) were explored. The NiP was deposited by electroless plating. A coating thickness of 8-9 μm and a P content of 10-13 wt% was chosen. The CrN was prepared by reactive magnetron sputtering at two thicknesses (0.2 and 0.8 μm). For the Ti (0.2 and 0.8 μm) and a-C (0.1 μm), HiPIMS mode of sputtering was employed. Furthermore, multilayers of either 0.8 μm Ti or 8-9 μm NiP followed by 0.1 μm a-C, deposited as just described, were investigated.

The *ex-situ* evaluation consisted of corrosion exposure in a) corrosion cell according to a DOE standard, by immersing samples in acidic electrolyte at 80°C (0.05 M H₂SO₄ + 0.1 ppm HF, adjusted pH to 3.0 ± 0.1), and b) in a climate chamber giving atmospheric corrosion through an adapted version of the standard IEC 60068-2-38. In brief, the temperature was cycled between -10 and 85 °C for 48 hours, with the humidity varied between 15 and 95 %. This cycle was repeated 10 times for a total duration of 20 days.

The interfacial contact resistance (ICR) to gas diffusion layers (GDLs) was measured on coated samples both before and after corrosion exposure. The samples manufactured in the project has been subject to numerous characterization methods. Additional to the standard techniques e.g. optical and scanning electron microscopy with energy dispersive spectroscopy (OM, SEM-EDS), the coatings have been subjected to advanced instrumental analysis such as micro and nano infrared spectroscopy (micro IR, Nano IR). RISE has supported these activities through internal project financing at RISE (Kunskapsplattformen Avancerad Instrumentell Analys 2023)

One coating system (NiP+C) was selected for *in-situ* evaluation in a PEM fuel cell test rig, a Greenlight Innovation G20 System, equipped with a Gamry 3000 Reference Potentiostat/Galvanostat/ZRA. The fuel cell testing was performed at 70 °C, 60% RH in galvanostatic mode during 473 and 906 hours, and electrochemical impedance spectroscopy (EIS) was carried out several times during the test.

Goals – The overarching goal of the BALBAS-project was to develop an Aluminum-based bipolar plate that fulfil the DOE (Dep. Of Energy, US) requirements regarding contact resistance and lifetime. Specific goals in short: 1) identification of relevant coating systems, 2) further development of methodology for *ex-situ* evaluation of coatings systems, 3) development of a PVD coating process for thin Al sheet substrates, 4) evaluation *ex-situ* of a few candidate coatings and one through *in-situ* fuel cell testing. 5) evaluate the *ex-situ* test methods relevance against the *in-situ* testing in a fuel cell, 6) create a good solid knowledge platform for a follow-up project where also forming and joining can be studied experimentally. Additionally, studies on forming and joining should be presented in a literature review.

Results and discussion – In general, the BALBAS project has been running smoothly with good and flexible collaboration between the partners. The work packages have been executed according to plan and additional resources have come in during the project through an internal RISE funded project (within Kunskapsplattformen Avancerad Instrumentell Analys) which enabled more SEM and FTIR studies and through a new project partner; AP&T that entered the project in the beginning of 2023. AP&T has significantly contributed in AP6 for the forming and joining review and by performing simulations on forming behavior of thin aluminum plates. The review is found in Appendix 2: “Technology for sheet forming and joining of bipolar plates for PEM fuel cell applications.” Results from the project has been disseminated at five conferences/workshops and in two scientific publications.

Figure ES1 below exemplifies the coatings obtained by plating and PVD. All coatings provided a sufficiently low interfacial contact resistance (ICR) prior to corrosion exposure (i.e. $>10 \text{ m}\Omega \text{ cm}^2 @ 150 \text{ N/cm}^2$) and the Ti coating adhered very well to the substrate.

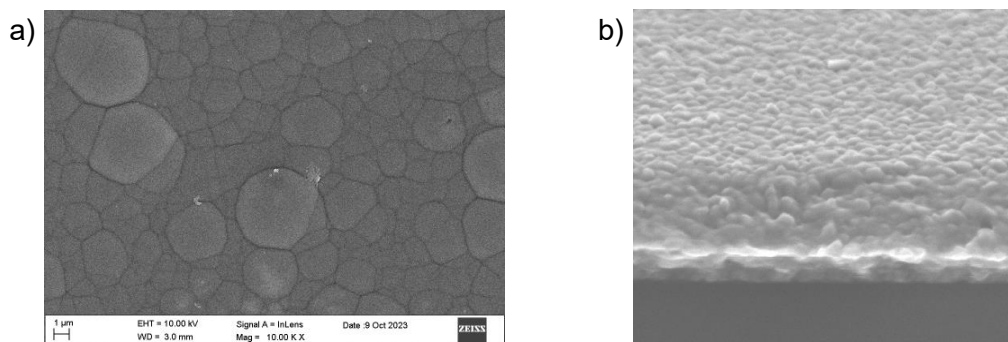


Figure ES1. a) Typical appearance of the NiP coating, b) Ti thin film on Si (HiPIMS with substrate bias of -100V).

Some defects were actually found in the coatings, and it was revealed that the Aluminum substrate contained grains with Si and Fe contamination that might have an important impact on the formation of defects and the performance of the coated samples. Such defects may serve as initiation for pit-hole corrosion. To further improve the quality of the coatings and decrease the number defects, additional surface treatments of the substrate may be required, where one possibility is to apply a thicker interfacial layer which might shield the underlying compositional variations. For the NiP it is possible that thicker coatings and possibly a double coating procedure could shield and seal the underlying surface better. There are also strategies with an additional step to seal the possible defects either using chemical means or atomic layer deposition.

The interfacial contact resistance (ICR) of all pristine coated plates was sufficiently low for fuel cell applications. After corrosion exposure the ICR of all plates increased; however, the increase depended heavily on the coating and corrosion condition as can be seen in Figure ES2. After potentiostatic corrosion exposure, the Al plates coated with Ti had formed a very thick nonconducting oxide layer leading to a ICR over $30\,000\text{ m}\Omega\text{ cm}^2$. In contrast, samples coated with Ti|C showed an increase in ICR from $6.5\text{ m}\Omega\text{ cm}^2$ to 7.2 and $27\text{ m}\Omega\text{ cm}^2$, after corrosion under potentiostatic and atmospheric conditions, respectively. Clearly, the additional top layer of $0.1\text{ }\mu\text{m C}$ contributed to a significant corrosion resistance of these Al plates. Meanwhile, samples with the NiP|C coating exhibited an increase in ICR from 10 to $16\text{ m}\Omega\text{ cm}^2$ after corrosion under potentiostatic conditions, but a very large increase to approximately $600\text{ m}\Omega\text{ cm}^2$ under atmospheric conditions. The large discrepancy raised the question of which method of *ex-situ* ageing is the most appropriate to study the corrosion behaviour of a bipolar plate in a PEM fuel cell. As such, plates coated with NiP|C were used as bipolar plates in a PEM fuel cell. After the fuel cell measurements, both anode and cathode plates exhibited ICRs similar to the plates after potentiostatic corrosion measurements, indicating that this ageing method may be a more suitable *ex-situ* test for at least samples with a NiP|C coating.

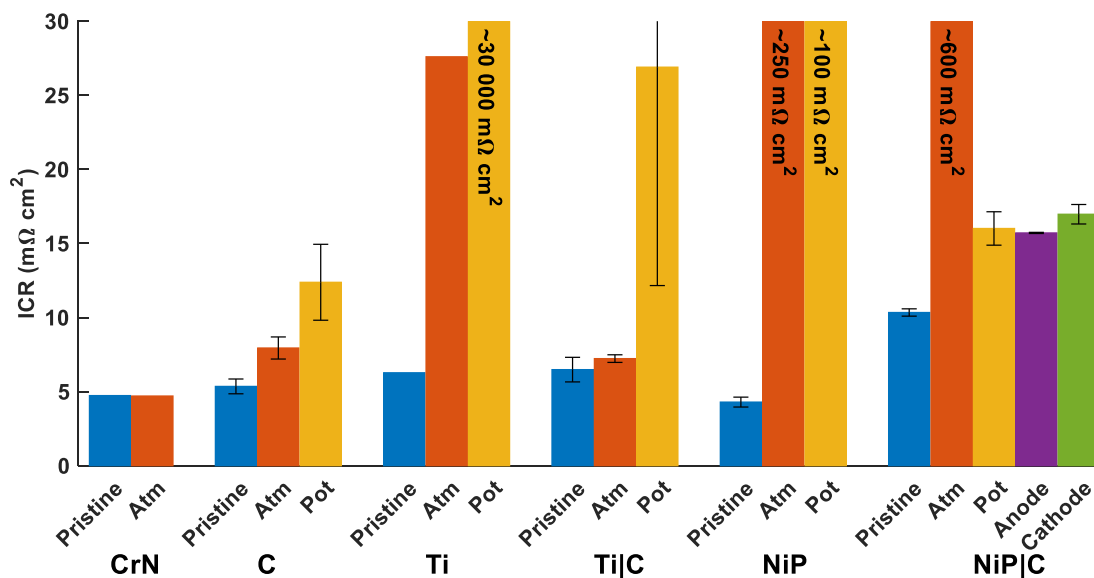


Figure ES2. Interfacial contact resistance (ICR) of aluminium bipolar plates with different coatings at 150 N / cm^2 In pristine conditions as well as aged atmospherically (Atm), potentiostatically (Pot), and *in-situ* fuel cell (as Anode and Cathode bipolar plate). Error bars signify 1 standard deviation based on three repeated measurements for pristine plates and two for corroded. Note that the graphs of Ti|C - Pot, NiP-Atm, and NiP|C are cropped for clarity.

Despite the poor performance during atmospheric exposure, the selected NiP|C behaved surprisingly well under *in-situ* fuel cell tests. Under the test conditions ($70\text{ }^\circ\text{C}$, $60\%\text{ RH}$) the coating

showed only a small decrease in high frequency resistance during the testing periods of 906 and 473 hours. This result was further confirmed by the *post-test* examination through ICR measurements giving only a small increase (see Figure ES2). However, there was a difference between the anode and the cathode plates and corroded stains could be observed on the cathode plate surface. Investigation with FTIR revealed the presence of metal (Al and/or Ni) oxides and hydroxides on the cathode plate surface.

Conclusions and further work – In the BALBAS project we have successfully produced coatings that fulfils the DOE target of contact resistance less than 10 mΩ cm². Both coatings done by electroless plating of NiP and physical vapor deposition coatings of CrN and Ti were successful in this respect.

The ex-situ evaluation methodology was further developed in the BALBAS project and applied to the developed coatings. The investigation revealed that the coatings behaved differently to the corrosion cell and to the atmospheric corrosion exposures. While Ti and Ti|C corroded more heavily in the corrosion cell they were less affected by atmospheric corrosion exposure. For NiP and NiP|C the corrosion cell behavior was acceptable (at least for NiP|C) while the exposure to atmospheric corrosion resulted in more aggressive corrosion. In general, further studies are needed to fully understand the different behaviors of the coatings under ex-situ testing. This will be important to identify an appropriate test methodology for screening of materials for fuel cell applications.

Despite the poor performance during atmospheric exposure, NiP|C behaved surprisingly well under in-situ fuel cell tests. Under the test conditions (70 °C, 60% RH) the coating showed only a small decrease in high frequency resistance during the testing periods of 906 and 473 hours. The BALBAS project has shown that Aluminum based bipolar plates are feasible for PEMFC and that 1000 h fuel cell operation with acceptable contact resistance performance has been reached. However, given the challenging environment in a fuel cell, a duplex coating method for surface treatment of Aluminum is most likely needed and should be investigated in future projects.

The project work has also improved the methodology for ex-situ evaluation of Aluminum based bipolar plates. As in many experimental projects where new evaluation and characterization methods are developed, the insights have led to a better understanding of where the methodology is weak. Looking back at the project we can see that more resources and systematic evaluations are needed before a fuel cell relevant method for atmospheric corrosion tests can be established.

4 Introduction

Bipolar plates (BPPs) are fundamental components in modern proton exchange membrane fuel cell (PEMFC) design. The BPP separates the gases (hydrogen and air) and provides channels/flow patterns for gases, while at the same time conduct electrons from one cell to the other. Furthermore, the bipolar plates also provide channels for the cooling liquid of the fuel cell. Simple sketches of fuel cells with graphite and metallic BPPs may be seen in Figure 1a and b, respectively. Requirements for a state-of-the-art fuel cell is to operate at a nominal current density of 2 A/cm^2 with a total voltage decay of 5 mV/h or less (including decay due to membrane and catalyst). The lifetime is required to be 5000-20000 hours (depending on application) and the contact resistance in the cell (anode and cathode) should be less than $10 \text{ m}\Omega \text{ cm}^2$ at beginning of life.¹ During the fuel cell operating life, the BPP are exposed to electrochemical conditions, including oxidizing atmosphere at the cathode and reducing atmosphere at the anode, temperatures between -50 and $95 \text{ }^\circ\text{C}$ and up to 100% relative humidity. Therefore, the contact resistance may increase, but it should not exceed $30 \text{ m}\Omega \text{ cm}^2$.

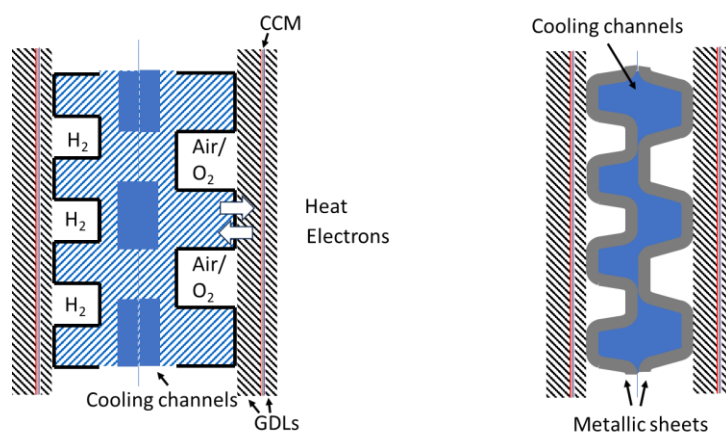


Figure 1. Illustrations of cross-sections of graphite based (a) and metallic (b) BPPs. Note that the direction of current and heat conduction is perpendicular to the BPP surface and gas flowing in the channels.

BPPs made of graphite or carbon composites have inherently low contact resistance to the GDL. Furthermore, graphite is chemically stable in the PEMFC environment. Graphite, however, is bulky and brittle. Therefore, BPP made from a metal sheet or foil is attractive as it can be much thinner ($\sim 0.1 \text{ mm}$) thus enabling lighter fuel cell stacks with higher power density. However, the metallic BPP performance suffers from surface oxidation in the fuel cell environment which leads to poor electrical contact between the GDL and the BPP. For this reason, a surface coating is generally applied on metallic BPPs. The surface coating should protect the metal sheet from corrosion, while minimizing the contact resistance to the GDL. Furthermore, it is desirable that the coating is ductile to support the tensile and compressive stresses that appear during forming of a precoated metal sheet. A surface coating system includes several layers where different layers may serve different purposes as illustrated in Figure 2. The adhesive layer ensures good adhesion between the coating and the metal foil surface. The sealing layer should be as defect-free as possible to protect the metal foil from exposure to the environment. The surface contact layer is optimised for the surface properties wanted. For the BPP coatings, this includes low contact resistance and high corrosion stability in acidic environments. An interfacial layer between the sealing and surface contact layer may also be needed to ensure good adhesion of the surface contact layer on the sealing layer.

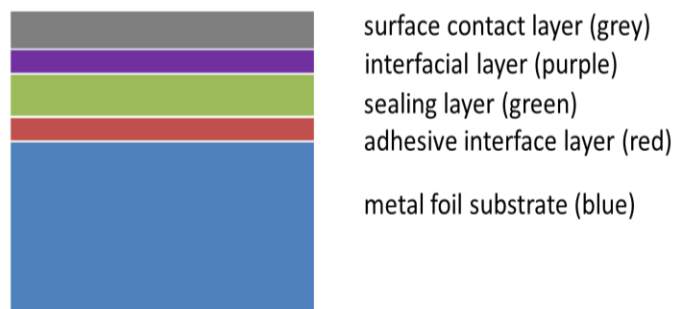


Figure 2. Illustration of generic coating system for metallic BPP.

Coatings on aluminum foils/thin sheets for fuel cell applications must comply to the following aspects:

- 1) Sealing. Aluminum is a non-noble metal susceptible to corrosion and formation of aluminum oxides with poor electrical conductivity. Therefore, the foil surface must be sealed off with a protective coating layer.
- 2) Electrical contact. For fuel cell BPP it is crucial to have good electrical contact between the BPP and the GDL
- 3) Adhesion and ductility. The coating must/should have a good/strong bonding to the surface of the underlaying layer. This is particularly important if the BPP is subjected to forming of the flow pattern after the coating since it will lead to strain and compression of the coating layers. Ductility – the ability to elongate without crack formation – can differ very much, depending on material and layer thickness.

The coating system may thus consist of several layer with different functionality, as discussed above and illustrated in Figure 2. The coatings most often considered for fuel cells in the literature can be divided in four groups: metals, phosphides, nitrides, carbides, and carbon coatings.

Further background information can be obtained from Appendix 1 “Literature review on coating systems for Aluminum-based bipolar plates”.

5 Purpose, research questions and methods

The overall purpose of the BALBAS project is to evaluate the possibility of using Aluminum as a base material for bipolar plates in PEMFC. Further, to develop a methodology for evaluating corrosion properties and contact resistance of surface coatings on bipolar plates and to apply the methods to several coating systems on aluminum substrates.

The main research question investigated in the project was the performance of coated Aluminum alloys bipolar plates in PEM fuel cells (BPP). This required to study the corrosion protection properties of coatings obtained by plating (e.g. NiP) and physical vapor deposition (PVD, e.g. Ti, C). Finally, *ex-situ* corrosion methods were compared with *in-situ* testing in order to develop relevant screening techniques for the PEM fuel cell application.

To begin with a literature search was done and compiled (AP1), see attachment “Literature review on coating systems for Aluminum-based bipolar plates”. Based on the outcome from AP1, several coating materials were selected to be further explored in the project.

5.1 Sample preparations (AP2)

Small samples were produced for basic characterization including *ex-situ* electrochemical testing first. Then, the most promising coating was applied on BPP of a simplified design and investigated in a test PEMFC setup.

Substrate – The material used as substrate in this report has the chemical composition seen in Table 1. The alloy is called FA5100 and is one of several bespoke Gränges alloys aimed at applications that require high thermal and electrical conductivity. It also has a relatively low amount of particle forming alloying ingredients. This is to control/limit the amount and size of particles generated in the casting process and thus provides a more homogeneous surface than is possible for aluminium materials optimised for other properties. It provides a high formability in the soft annealed temper needed for forming, and it is also possible for the material to achieve a relatively high strength after cold deformation.

Table 1. The chemical composition (wt%) of the alloy used as substrate material.

Si	Fe	Cu	Ti	Others, each	Others, total	Al
0.1	0.6	0.1	0.025	<0.05	<0.10	Balance

The sample materials were then cut to the correct length and width. About half the number of samples were then ground and polished on the side to be coated to take away the surface topography imposed on the surface by the rolls. This was made to illustrate the influence of topography on the surface composite in the corrosion testing that follows coating deposition. The grinding was made in the metallurgical laboratory at Gränges, following normal grinding and polishing procedures to provide flat and smooth sample surfaces. After grinding, the samples were cleaned in ultrasonic cleaning with acetone, then ethanol and finally isopropanol to remove as much surface contamination as possible. For the fuel cell tests the plates were not formed with flow channels before coating, because we wanted to have a smooth and constant thickness coating corresponding to the *ex-situ* samples. The flow channels were instead achieved by adding an additional gas diffusion layer with incorporated channels as seen in Figure 6b.

Electroless plating of nickel – Electroless plating does not need external electric current to reduce nickel ion. Instead, the plating solution contains a reducing agent that is able to react on catalytic active surfaces (Figure 3). At the surface, the reducing agent is oxidized and provides electrons, which reduce nickel ions on the surface, thereby forming a coating. The advantage is that the coating becomes very even in thickness since no electric field is applied. The drawback is that the electrolyte changes composition during use, which limits its lifetime, making the process more expensive than electroplating.

The most commonly used reducing agent is hypophosphite. Phosphorous from the hypophosphite will partly co-deposit with the nickel forming a Ni-P alloy with a phosphorous content between 2-13 wt% depending on the specific process used. By more than approx. 9 wt% P, the coating becomes amorphous and more corrosion resistant. Ni-P coating have in general low ductility.

The intrinsic stress in Ni-P coatings decrease with increasing P content and it is possible to obtain compressive stress in high P coatings (>10% P).

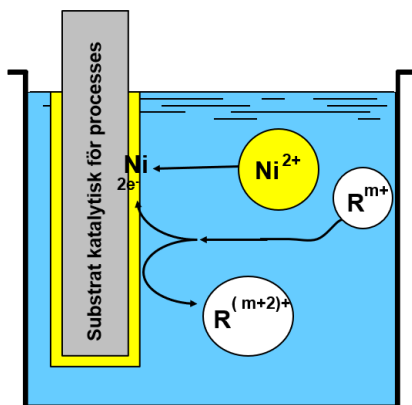


Figure 3. Sketch of an electroless plating reactor

Plating on aluminium substrate – Since aluminium is a very un-noble metal, it will either passivate with a stable oxide film or corrode. In a plating bath both situations will lead to poor adhesion of the coating. To solve this aluminium is pretreated in a so-called zincate process. The zincate process is alkaline and corrosive to the aluminium. It also contains zincate ion that will deposit on the aluminium by ion exchange deposition ($2 \text{ Al (s)} + 3 \text{ Zn(OH)}_4^{2-} \text{ (aq)} \rightarrow 2 \text{ Al(OH)}_4^- \text{ (aq)} + 3 \text{ Zn (s)} + 4 \text{ OH}^- \text{ (aq)}$). Thereby a thin film of adhering zinc will be formed on the surface protecting the aluminium substrate from further corrosion. The surface is now ready to be plated by electroplating or electroless plating from solutions suitable for plating on zinc.

Physical Vapour Deposition techniques – There are several sub-categories of PVD. The choice of technique is based on the substrate material, coating material and desired properties and microstructure. Magnetron sputtering is a technique that has been commercialized, can deposit at high deposition rates and is flexible in that it can deposit both metallic and ceramic coatings. There are several variants of magnetron sputtering. Reactive magnetron sputtering is useful for production of compounds and high power impulse magnetron sputtering (HiPIMS) is useful to achieve strong adhesion and dense films.

Here, reactive magnetron sputtering has been used for the deposition of CrN from a metal target vaporized (sputtered) in a discharge maintained in an atmosphere of Ar+N₂. The N content in the deposited film is controlled by the N₂ supply and the whole range of compositions from e.g. Cr to CrN can be synthesized in the same deposition process. Gradients in the film can also be readily created.

HiPIMS adds additional degree of control to the classical magnetron sputtering. In HiPIMS, the sputtered metal is partially ionized. The ions can be electrically accelerated towards the coated surface. Compared to standard sputtering, HiPIMS gives a better control over the film density, adhesion, as well as intrinsic stresses. The HiPIMS process has been explored for Ti films used in the project.

PVD techniques are at the present the most commonly used coating technique for BPP coatings. However, they require vacuum to perform the deposition and can therefore be costly and time-consuming. To reduce the time and cost of the coating application, the sheet metal can be coated prior to forming and cutting, i.e. in a roll-to-roll process. This does, however, require a coating that is sufficiently ductile to withstand the forming process without the formation of defects penetrating down to the substrate. Also, any scrap falling from the forming process will contain coating material, thereby reducing its value in recycling or making recycling more difficult. Figure 4 is a photo of the deposition system used for PVD depositions of CrN, Ti and C in BALBAS.

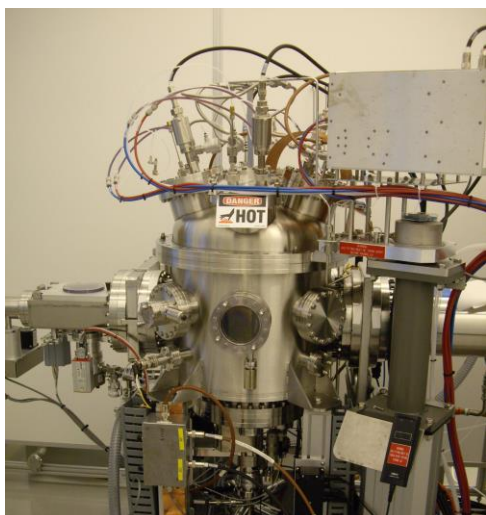


Figure 4. Deposition system used for PVD depositions.

5.2 Corrosion cell testing (AP3)

Corrosion cell testing – The corrosion properties of the films were studied according to DOE standard,¹ by immersing samples in acidic electrolyte (0.05 M H₂SO₄ + 0.1 ppm HF, adjusted pH to 3.0 ± 0.1) at 80°C.

Electrochemical measurements were carried out with a PARSTAT 3000A–DX potentiostat. A three-electrode setup was used where the working electrode was the coated substrate, a Ag/AgCl saturated with KCl ($E = 0.197$ V vs SHE) was used as a reference electrode, and a Pt wire was used as a counter electrode.

The initial corrosion rate under simulated anodic conditions was measured using potentiodynamic polarization (PDP). The electrolyte was deaerated with Ar gas. The open-circuit potential (OCP) was first measured for 30 min, followed by PDP. The potential was swept from – 25 mV vs OCP to 600 mV vs ref, with a scan rate of 0.167 mV/s (10 mV/min). The Tafel module in VersaStudio software was used to calculate the Tafel slopes and determine the corrosion current density j_{corr} . The extrapolation was carried out ±0.1 V away from E_{corr} .

The corrosion rate under simulated cathodic conditions was measured using potentiostatic polarization (PS). The electrolyte was aerated using compressed air. Samples were polarized at 0.6 V vs ref for 24 h initially. Later the polarization time was decreased to 4 h due the fast degradation of the coatings.

5.3 Atmospheric corrosion testing (AP3)

There are several methods to test atmospheric corrosion, taking into account temperature, humidity, gaseous species, rain and salt. To avoid degradation of the membrane and catalyst, the air intake for the fuel cell is filtered, and only temperature and humidity were therefore used as stressors in the atmospheric tests in this project. An adapted version of the IEC 60068-2-38,² as used in the ALUSAP project was chosen. In brief, the temperature was cycled between -10 and 85 °C for 48 hours, with the humidity varied between 15 and 95 %. This cycle was repeated 10 times for a total duration of 20 days or 480 hours, as illustrated in Figure 5.

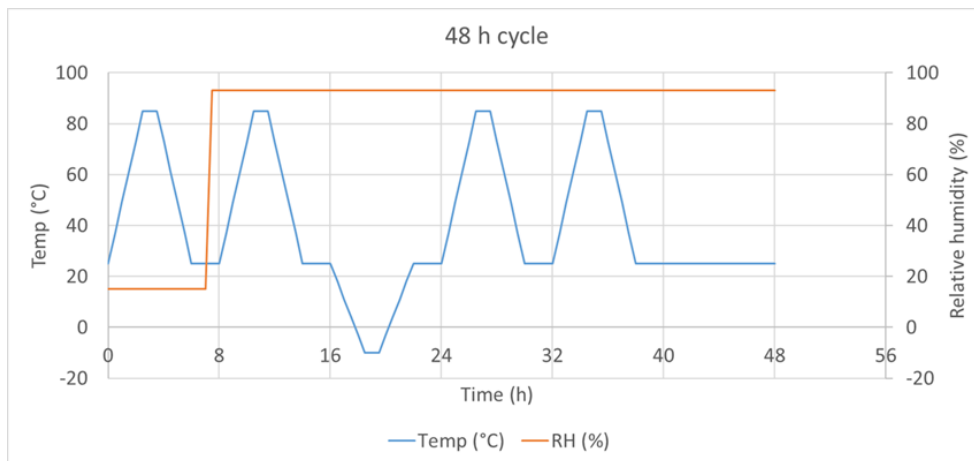


Figure 5. The climate cycle used for the atmospheric corrosion test

5.4 Contact resistance measurements (AP3)

Interfacial contact resistance measurements – To measure the interfacial contact resistance (ICR) two test samples were pressed between two gold-coated brass probes, with a carbon paper in between. For the potentiostatic and fuel cell samples, one sample and a carbon paper were pressed between the probes. The surface area of the probes was $1.7 \times 1.7 \text{ cm}^2$. The bottom probe was placed on a scale, while the top probe was manually lowered to adjust the pressure. An Agilent 34420 A resistance meter was used to measure the resistance by the four-point probe method applying a current of 1 mA between two gold-coated brass probes. A measurement of the carbon paper and probes were subtracted from the measurements for the potentiostatic and fuel cell samples to give the sample to carbon paper ICR. Both the scale and the resistance meter were connected to a logger, and at each applied force, 10 measurement points were averaged.

5.5 Characterisation of coatings and instrumental analysis (AP4)

The samples manufactured in the project has been subject to numerous characterization methods. Additional to the standard techniques e.g. optical and scanning electron microscopy with energy dispersive spectroscopy (OM, SEM-EDS), the coatings have been subjected to advanced instrumental analysis such as micro and nano infrared spectroscopy (micro IR, Nano IR). RISE has supported these activities through internal project financing at RISE (Kunskapsplattformen Avancerad Instrumentell Analys 2023).

The basic structural and chemical characterization of coated surfaces was evaluated by SEM-EDS in Uppsala using a Zeiss Merlin instrument. Cross-sections of selected samples were also prepared by a focused ion beam and investigated in SEM-EDS. RISE in Kista has also performed SEM-EDS studies with their instrument ZEISS GeminiSEM 650

5.6 Fuel cell testing (AP5)

A single-cell fuel cell was assembled as shown in Figure 6a; a detailed description follows. An 0.5 mm thick silicone gasket was placed on the surface of a BPP coated with NiP/C. A Sigracet 39BB GDL, with the same area as the gaskets inner area and handmade flow field patterns (Figure 6b), was placed in the center. Then, a $1.7 \times 1.7 \text{ cm}^2$ gas diffusion electrode (GDE), consisting of a Sigracet 22BB GDL with $0.3 \text{ mg} / \text{cm}^2$ 40% Pt/C, was placed over this GDL. Nafion NR212 was used as membrane, separating the two electrodes.

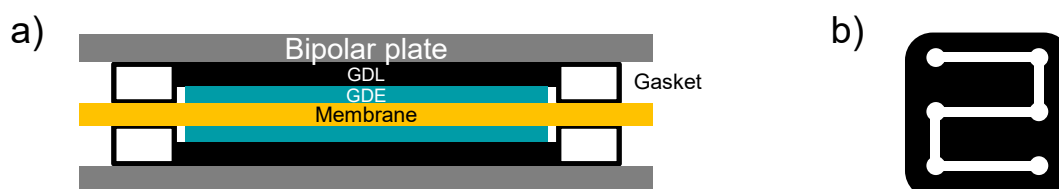


Figure 6. Schematic over the assembly of a single-cell fuel cell (a) and the hand-cut flow fields in a GDL (b)

Fuel cell measurements were conducted on a Greenlight Innovation G20 System, equipped with a Gamry 3000 Reference Potentiostat/Galvanostat/ZRA, and began with purging the cell with a flow on nitrogen, while heating to $40 \text{ }^\circ\text{C}$ and 60% relative humidity (RH). Once this condition and a total purging time of 45 min had been reached, the purging was stopped followed by introducing air and hydrogen to the cathode and anode, respectively. The flow of the gasses was stoichiometrically controlled with a stoichiometry of 10 and 6 of air and hydrogen, respectively, and a minimal stoichiometric current density of $0.24 \text{ A} / \text{cm}^2$. After the introduction of the reactant gasses, an open circuit voltage (OCV) greater than 0.9 V was quickly achieved. Subsequently, a load of $0.10 \text{ A} / \text{cm}^2$ was applied during 15 min and then gradually increased. Meanwhile, the cell was heated to $70 \text{ }^\circ\text{C}$, 60% RH. After this condition had been reached and the voltage was greater than 0.4 V at an applied load of $0.24 \text{ A} / \text{cm}^2$, fuel cell measurements, consisting of polarization curves and electrochemical impedance spectroscopy (EIS) measurements, were performed. In between each measurement series, the cell was cycled between 0.10 and $0.21 \text{ A} / \text{cm}^2$. Galvanostatic polarization curves were recorded from open-circuit to a current density corresponding to a cell voltage just below 0.4 V. The current density was stepwise increased, held for 180 s, after which the voltage and the actual current density was averaged over 60 s. After the voltage had decreased below 0.4 V, the current density was stepwise decreased to open-circuit, while measuring the current and voltage as just described. Galvanostatic EIS measurements were performed at $0.21 \text{ A} / \text{cm}^2$, using an alternating current with a magnitude of $0.02 \text{ A} / \text{cm}^2$, at frequencies between 0.1 and 10^6 Hz .

After a set amount of time, the fuel cell testing ended, and the humidity in the cell was gradually decreased, while purging it with a flow of nitrogen. Subsequently, the cell was quickly disassembled, while still warm to avoid any condensation on the bipolar plates. These were then stored in a silica filled desiccator prior to further characterization.

5.7 Investigation of forming and joining (AP6)

In this work package a literature report is compiled which summarizes technologies for forming and joining of metallic bipolar plates (BPP) for use in Proton exchange membrane fuel cells (PEMFC), with the perspective of using Aluminum as base material. The state-of-the-art technologies are noted, and alternative technologies are presented and discussed.

6 Goals

The overarching goal of the BALBAS-project was to develop an Aluminum-based bipolar plate that fulfil the DOE (Dep. Of Energy, US) requirements regarding contact resistance and lifetime.³

Studies on forming and joining was studied theoretically and should be presented in a literature review.

Specific goals:

Goal 1: Identification of relevant coating systems that can be cost effective in mass production.

Goal 2: A further development of the methodology from the ALUSAP project for *ex-situ* evaluation of materials combinations and coatings systems.

Goal 3: The development and adaption of a PVD coating process for thin Al sheet substrates.

Goal 4: The project shall evaluate a few candidate coatings through *ex-situ* testing and one candidate coating through *in-situ* fuel cell testing.

Goal 5: A comparison is conducted of the *ex-situ* test methods relevance against the *in-situ* testing in a fuel cell.

Goal 6: Based on the other goals and results to create a good solid knowledge platform for a follow-up project where also forming and joining can be studied experimentally.

7 Results and goals fulfillment

In general, this project has been running smoothly with good and flexible collaboration between the partners. The work packages have been executed according to plan and additional resources have come in during the project through an internal RISE funded project (within Kunskapsplattformen Avancerad Instrumentell Analys) which enabled more SEM and FTIR studies and through a new project partner; AP&T that entered the project in the beginning of 2023. AP&T has significantly contributed in AP6 for the forming and joining review and by performing simulations on forming behavior of thin aluminum plates.

In the project all the goals have been achieved and many new insights obtained. In particular the goal of 1000 h fuel cell operation with acceptable contact resistance performance has been reached. Additionally, as in many experimental projects where new evaluation and characterization methods are developed the insights has led to a better understanding of where the methodology is weak. Looking back at the project we can see that more resources and systematic evaluations are needed before a fuel cell relevant method for atmospheric corrosion tests can be established (more in discussion later).

Listing of goals fulfillment:

Goal 1: This goal was fulfilled by conducting the review and identifying techniques suitable for mass production.

Goal 2: The *ex-situ* evaluation methodology was further developed introducing a longer and perhaps more relevant atmospheric climate chamber cycle (than used in ALUSAP) and by introducing additional, more systematic surface characterizations by SEM-EDX, FTIR and ICR.

Goal 3: A PVD coating process for thin Al sheet substrates has been developed and evaluated in several ways, furthermore the PVD process was combined with the electroless NiP-plating method for applying additional surface layers. A scientific paper is being submitted on the matter in the near future.

Goal 4: Several coatings and coating systems were evaluated in the project: CrN, C, Ti, Ti+C, NiP, NiP+C. From this NiP+C was chosen for *in-situ* fuel cell evaluation.

Goal 5: The relevance of the developed *ex-situ* methods to the *in-situ* fuel cell testing has been compared and discussed not only in this report, but also in a scientific publication which is to be submitted soon.

Goal 6: The results and experience gained through this project has led us to submit a follow-up application where the further developed materials and the methodology will be evaluated for high temperature PEMFC for application in aviation.

7.1 Summary of possible coatings systems (AP1)

This section is a summary of the literature review which is enclosed as an appendix to this report (Appendix 1). Additional to the surface coating technologies reviewed, the report also includes a description of the manufacturing process for Aluminum based substrate materials used in this project.

The coating system often consists of several layer with different functionality. A generic four-layer coating system is illustrated in Fig. 2. The coatings mostly considered for fuel cells in the literature can be divided in five groups: metals, phosphides, nitrides, carbides, and carbon coatings. Other than noble metals, which are too expensive for mass production, Ti is known to provide a good corrosion protection and excellent adhesion. Nickel phosphorous (NiP) applied by electroless plating can provide thick and dense coatings and is already today used for current collector plates in PEMFC stacks. Nitrides, carbides and carbon coatings are preferably applied by PVD-methods.

It was concluded from the literature review that a NiP-based sealing layer applied by electroless plating might be advantageous because of its higher thickness than coatings applied by other means. However, PVD-based coatings from CrN and Ti are interesting options and were also selected for evaluation in the project. Coating systems with combined coating methods were also investigated. Both of these coating methods are suitable for mass production and thus Goal 1 of the project is fulfilled.

7.2 Fabrication of coatings (AP2)

Coatings of NiP, CrN, Ti, and amorphous carbon (a-C) were explored. According to Goal 3 of the project a specific of a PVD coating process for thin Al sheet substrates was developed and adapted. The NiP was deposited by electroless deposition described above. A coating thickness of 8-9 μm and a P content of 10-13 wt% was chosen.

The CrN was prepared by reactive magnetron sputtering at two thicknesses, 200 and 800 nm. For the Ti and a-C, HiPIMS mode of sputtering was employed. All the sputter deposited coatings were prepared

in a deposition system CMS-18 shown in Figure 4. The system consists of a cylindrical process chamber with a volume of about 75 L pumped by a cryopump (CTI CryoTorr 8) to a base pressure of about 5×10^{-5} Pa, and a load-lock. The chamber is equipped with four magnetron sputtering sources in a co-sputtering configuration with the target-to-substrate distance of 180 mm. The substrates were placed on a rotating substrate holder. Ti and C sputtering targets with a diameter of 100 mm were operated in HiPIMS mode. Ar mass flow of 60 sccm was used and the deposition pressure was set to 6 mtorr. The depositions started with a glow discharge cleaning using a RF discharge on the substrate holder at a power of 60 W for 120 s. The discharge power for sputtering was provided by a Hipster 1 and a Hipster 6 HiPIMS power supplies for the C and Ti, respectively. A pulse train (10 cycles per discharge pulse) with duty cycle of 20% was set for C target to suppress arcing. The substrate bias was synchronized to the discharge pulses and kept 100 μ s longer to attract all available ions. Ti was deposited using a regular unipolar HiPIMS with a pulse on time of 100 μ s, duty cycle of 5%, and substrate bias as shown in **Fel! Hittar inte referenskälla.**

The deposition conditions for the Ti layer were selected in order to achieve a good adhesion and dense microstructure. The influence of substrate bias is illustrated in Figure , demonstrating that the HiPIMS process with substrate bias produced a fine-grained dense microstructure.

Table 2. Deposition conditions for the PVD of Ti and a-C. “*” indicates the pulse train as described in the text.

Layer	Pulse on time (μ s)	Pulsing frequency (Hz)	Substrate bias (V)	Average power (W)	Thickness (nm)
Ti-adhesion	100	200	-200	400	20
Ti	100	500	-100	500	800
α -C	10 \times 20 μ s*	200	-200	500	100

7.3 Evaluation by corrosion methods (AP3)

7.3.1 Electrochemical corrosion tests

The results of the potentiodynamic polarization (PDP) tests under inert gas bubbling (Ar) are presented in Figure 7 and 8. The values for E_{corr} and I_{corr} are presented in Table 3. The Ti layer had a lower corrosion current than CrN and the thicker coating was more protective than the thinner. The 800 nm thick Ti coating fulfilled the DOE limit of 1 μ A/cm. The variation between samples was high which could be indicate a stochastic corrosion mechanism (e.g. pitting corrosion). When an additional carbon coating was added to the 800 nm Ti coating the corrosion current increased slightly. Noticeably, the thin α -C coating by itself decreased the corrosion current to values similar to the Ti coating.

Table 3. Calculated values for E_{corr} and I_{corr} (1st, 2nd sample).

Coating	E_{corr} [mV vs Ag/AgCl]	I_{corr} uA/cm²
Ti 200 nm	-150, -137	8.4, 1.4
Ti 800 nm	-100, -348	0.5, 0.6
CrN 200 nm	-260, -353	1.0, 9.0
CrN 800 nm	-260, -333	5.7, 2.9
Ti + C	-279, -217	12, 4.7
only C	-275, -266	3.5, 2.8
NiP_unpolished	-272, -315	27, 2.1
NiP_polished	-124, -317	8.7, 59
NiP + C	-14, -65	0.4, 0.9
Bare Al	-878	21

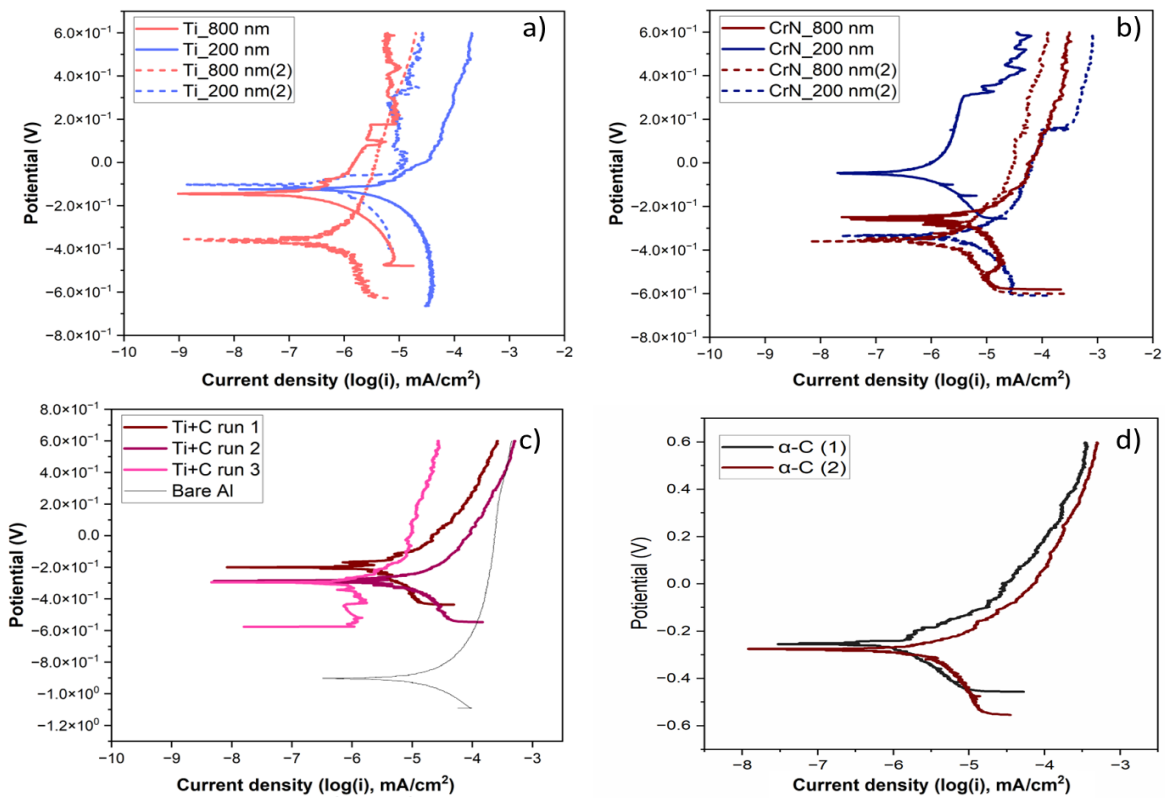


Figure 7. PDP curves of PVD coated Al plates a) Ti coating b) CrN coating c)Ti + C coating d) only α -C

The NiP coating was less protective compared to the PVD coatings, only slightly decreasing the corrosion current. However, when combined with an amorphous carbon coating the corrosion current decreased to below the DOE threshold.

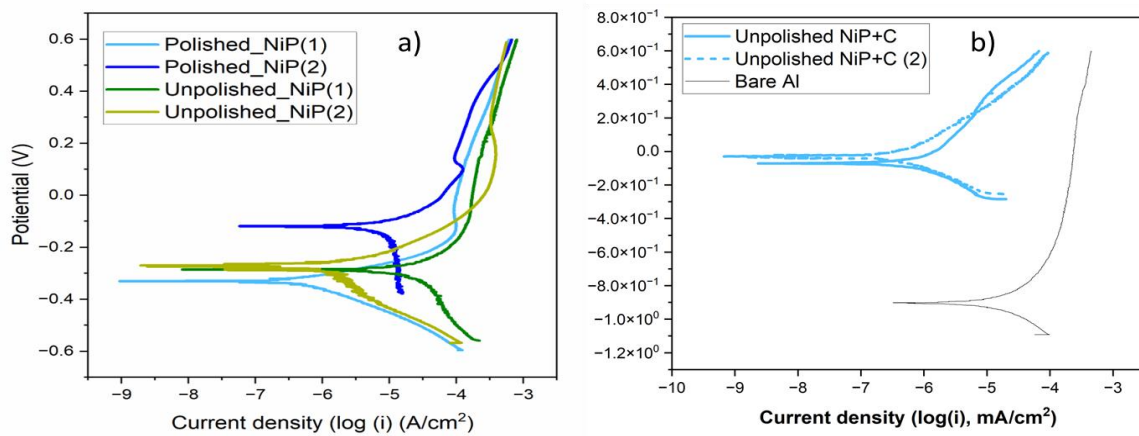


Figure 8. PDP curves of aluminum plates with NiP coating. a) NiP coating on polished and unpolished Al. b) NiP + C coating

The results from potentiostatic polarization (PS) with air bubbling are presented in Figure 9.

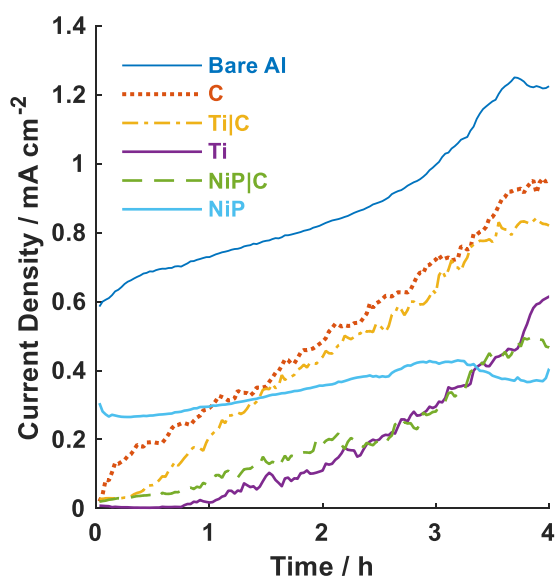


Figure 9. Potentiostatic corrosion measurements at 0.6 V (vs Ag/AgCl and bubbling with air) for neat and coated aluminum.

7.3.2 Atmospheric corrosion testing

After 20 days of climate cycling, some degradation is apparent on all samples, see Figure 10. For the coatings produced by magnetron sputtering, the corrosion is of a localized nature also after climate cycling. For the electroless plated NiP both with and without the C topcoat, more general corrosion attacks are observed after the climate cycling.

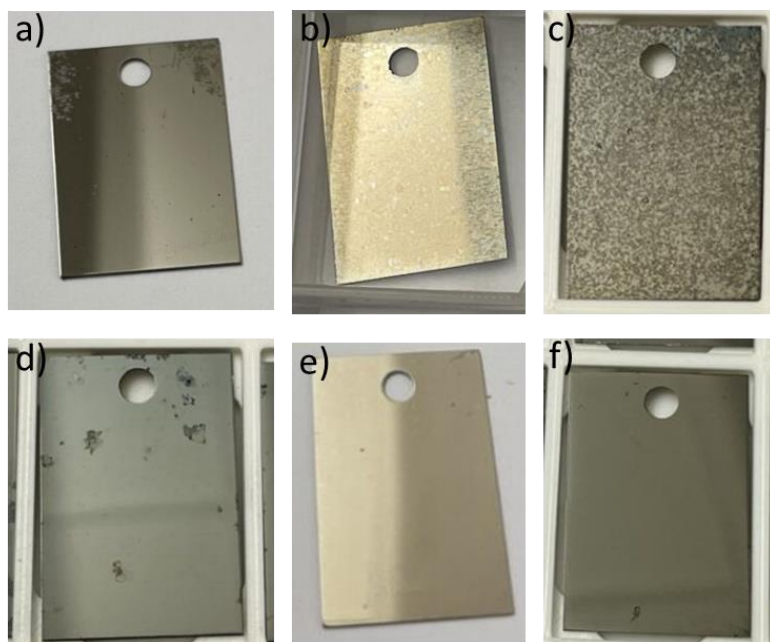


Figure 10. Samples coated with a) CrN 800 nm, b) NiP, c) NiP+C, d) C, e) Ti 800 nm, and f) Ti + C after atmospheric corrosion exposure.

7.4 Materials characterisation of coatings (AP4)

6.4.1 Initial characterization of the coatings and substrates

Initially, all the selected coating materials have been inspected to verify the deposition processes provided reliable results. Figure 11 illustrates the influence of deposition conditions on the Ti films. The optimized process, used further in the project, 11c, resulted in dense thin films with a fine-grained microstructure. This required both ionization of the deposition flux and an application of substrate bias to accelerate the metal ions. Otherwise, a columnar microstructure appeared as in Figure a and b.

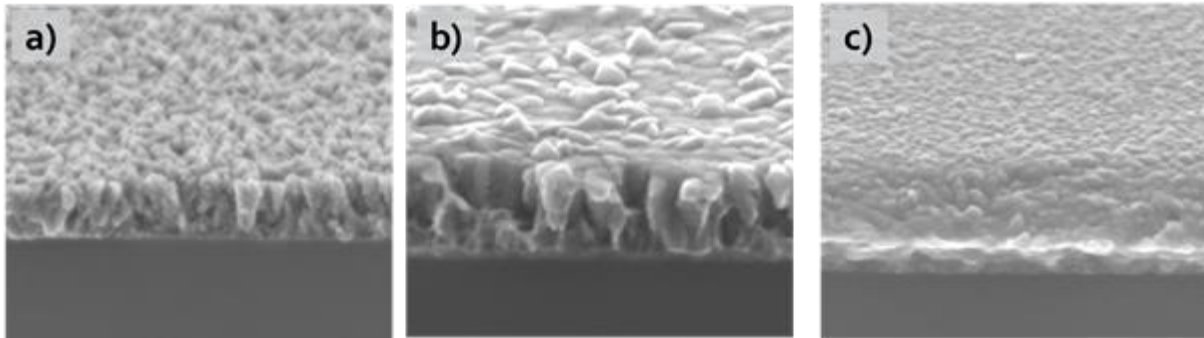


Figure 11. Microstructures of Ti thin films on Si deposited by sputtering: a) columnar film, b) HiPIMS without substrate bias, and c) HiPIMS with substrate bias of -100V (Conditions used in for production of samples in the project).

Corresponding results for the CrN and NiP are shown in Figure 12a and b, respectively. The features visible on the NiP surface don't have any connection with features at the substrate. Rather, they occur during the NiP growth as a result of the high coating thickness. Cross-sectional analysis revealed a rather dense and featureless microstructure of the coating.

In addition to the properties of the thin film itself, conformal coverage of the Al surface and good adhesion are also important. Taking the Ti as an example, Figure shows that a good surface coverage has been achieved. The surface is coating with a scratch in the polished surface. The Ti film has also a good adhesion as demonstrated by a scratch test, Figure b. Here, the Ti film sticks to the surface despite a large plastic deformation at the edge of the scratch track. Although not quantitative, the results indicate that the Ti films are suitable for further testing.

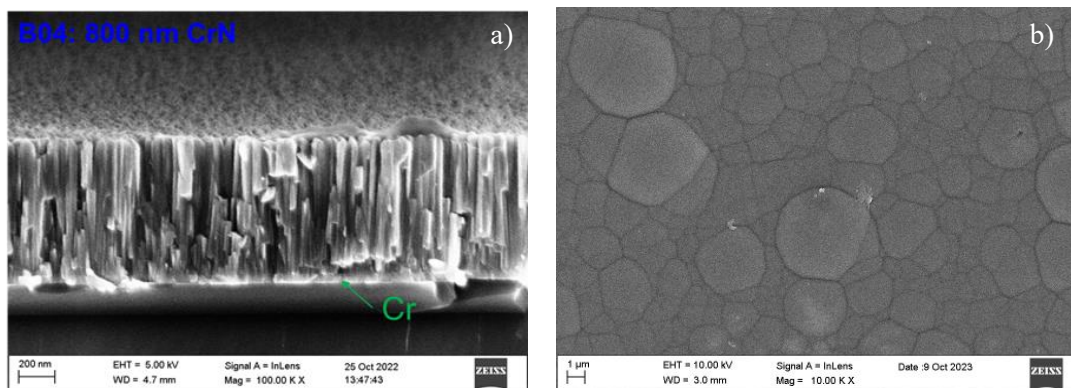


Figure 12a) Microstructure of an CrN film on Al. An interlayer of Cr is highlighted in the image and **b)** Typical appearance of the NiP coating.

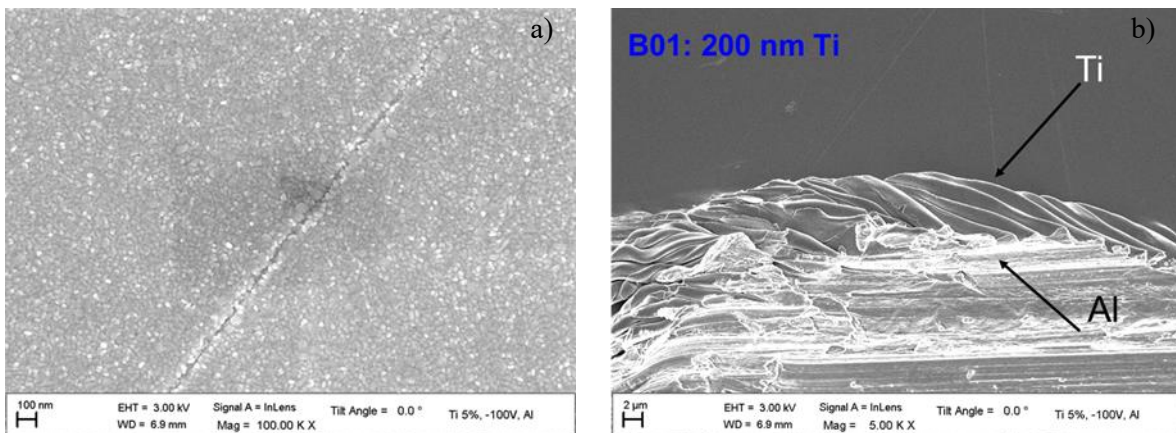


Figure 13 Ti coated Al surface. Top view **a)**, shows a fine microstructure of the Ti layer that coats even imperfections on the substrate surface. Scratched surface, **b)**, indicates good adhesion and ductility of the Ti that accommodates relatively large plastic deformations of the substrate.

Polished substrates have been used in the project to avoid the effect of surface roughness on the coatings. Optical images revealed some scratches on the surface but overall a good looking and smooth surfaces. More detailed analysis by SEM showed a more complex picture with a number of grains on the polished surface. Composition analysis indicates that the brighter grains visible in Figure b contain Fe and Si while the rest of the surface is predominantly Al. Since the used alloy contains both Fe and Si, secondary phases may be present. As discussed later, the grains may have an important impact on the performance of coated systems.

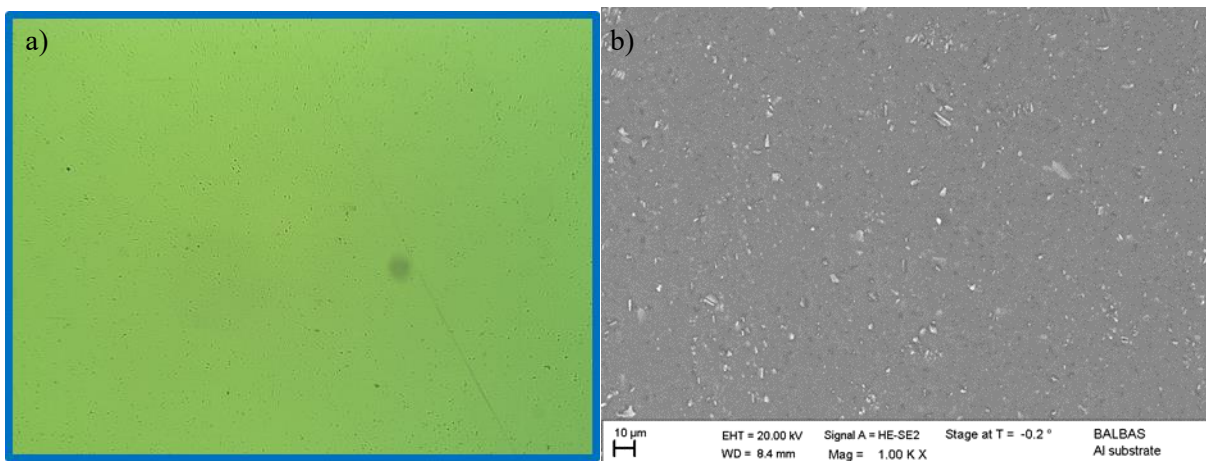


Figure 14. Polished uncoated Al surface in an optical microscope (a) and at a low magnification in SEM (b).

6.4.2 Characterization of corroded surfaces

Surfaces after initial potentiodynamic and potentiostatic tests were evaluated to understand the origin of the limited life-time of the coatings. Figure 7 shows a typical corroded NiP surface, where clear pittings in the coating may be seen as the darker areas in the center of the figure. Furthermore, bright rough particles

may be seen around these holes on the otherwise smooth surface. A similar appearance was observed for Ti coated samples shown in Figure 16 and 17.

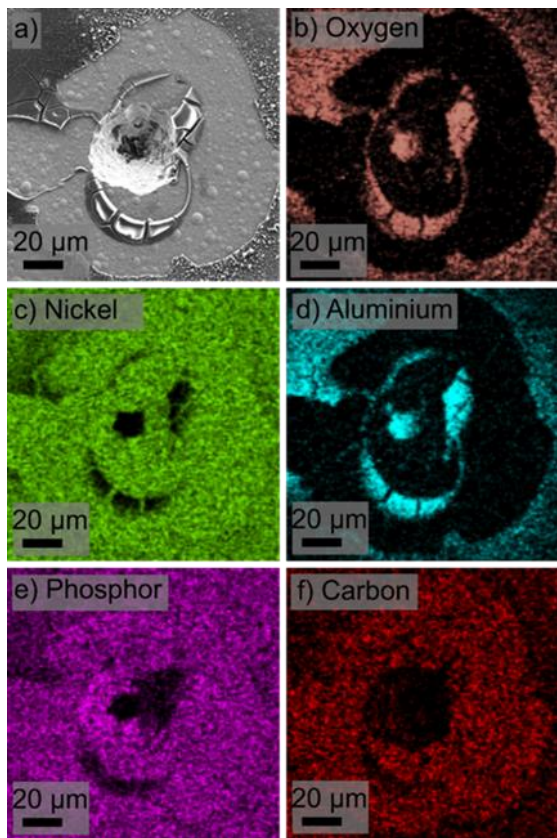


Figure 15. SEM and EDS mapping of a NiP/C coated sample after potentiostatic testing, a) SEM, b) O, c) Ni, d) Al, e) P, f) C.

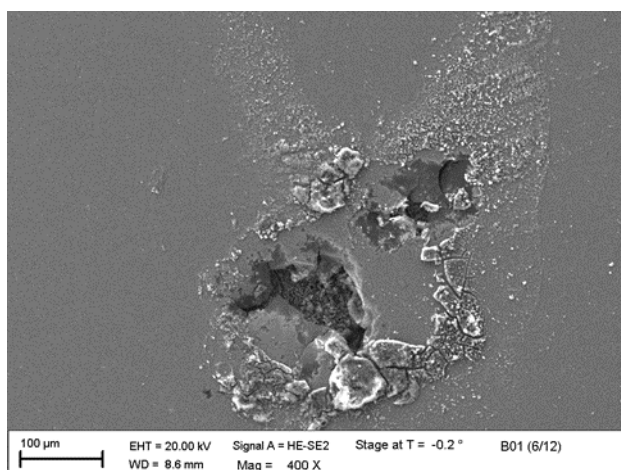


Figure 7. SEM image of a Ti coated sample after potentiostatic testing.

The presence of aluminum on both Ti and NiP coated surfaces (EDS results in Figure 15 and 17) indicates that the pits penetrated all the way through to the substrate. Aluminum, once in contact with the electrolyte, corrodes violently due to galvanic coupling between the coatings and substrate. As a result, the corroded area is quickly growing in size and more Al is exposed. A significant effort has been spent on understanding the initiation of the corrosion.

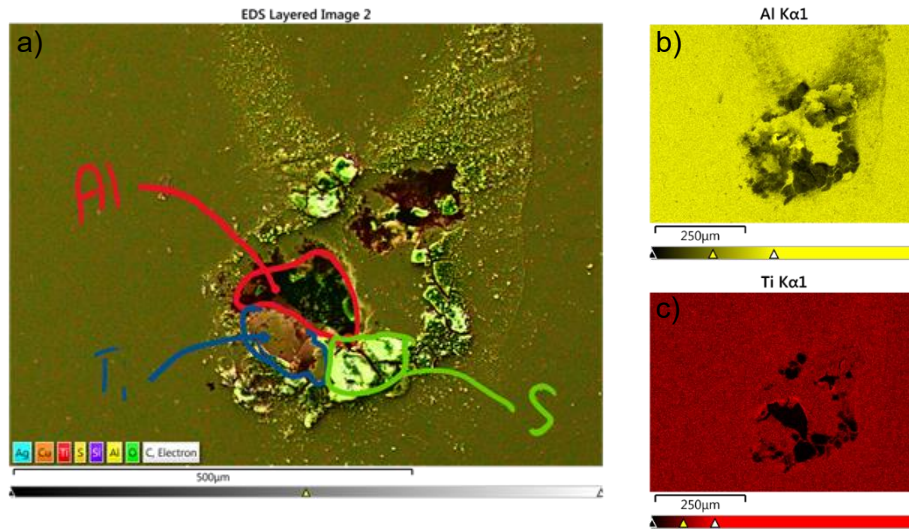


Figure 8a) EDS layered image as well as b) Al and c) Ti compositional maps of the sample area in Figure 7.

In Figure 18 the FTIR spectra of Ti-C and NiP+C coatings exposed to different treatments are given.

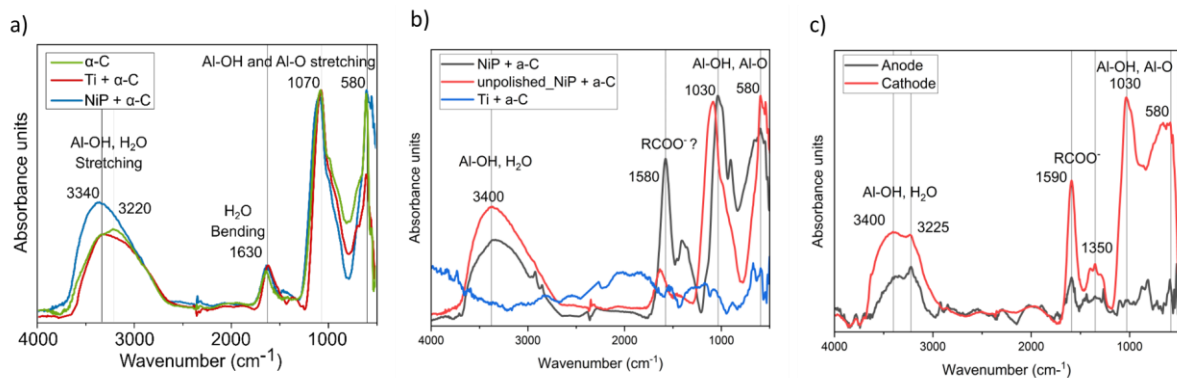


Figure 18. FTIR spectra of samples after a) potentiostatic polarization 4h b) atmospheric corrosion c) fuel cell

The data was obtained to analyze the molecular composition of the corrosion products. All spectra are characterized by broad peaks indicating an unstructured corrosion product. The broad band at 3400 cm^{-1} is assigned to -OH stretching. This can be due to presence of water or metal hydroxides such as Al-OH. The H₂O bending peak at 1630 cm^{-1} present in the spectra of PS samples. This peak could be shifted to 1580 and 1590 cm^{-1} for atmospheric exposure and fuel cell samples. However, due to the relative intensity of the O-H stretch this is not a likely explanation. The $1580-90\text{ cm}^{-1}$ band could then suggest the presence of carboxyl groups from e.g. acetates. For the fuel cell samples this could be from degradation of the organic components of the fuel cell. It might also be due to oxidation of the carbon coating. No FTIR bands were observed for the Ti + α C sample exposed under atmospheric corrosion. The lack of Al-oxide/hydroxide peaks would suggest that under these conditions the corrosion did not penetrate through to the aluminum substrate.

6.4.3 Defect analysis of the PVD thin films

More detailed examination of the Ti coated surface revealed a large number of defects on the Ti surface. Figure 9 shows two representative examples. Figure 9a) displays isolated round particles with a diameter on the order of a μm . An agglomerate of somewhat smaller particles with the size of few 100 nm is visible on Figure 9b). The observed particles resemble macroparticles, droplets ejected during an arc discharge from the sputtering target. Given the relatively high instantaneous current densities in HiPIMS discharges, it is not possible to exclude the possibility of arc events.

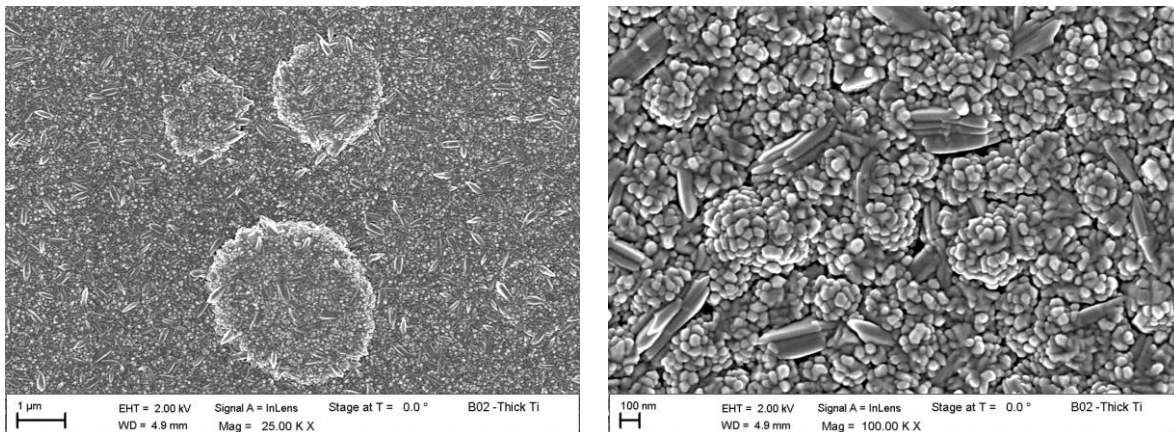


Figure 9. A representative SEM top view of the thick Ti layer with two types of defects observed on the surface.

However, a cross-sectional analysis by FIB (Figure) shows that the defects originate from, or close to, the Al/Ti interface. Interestingly, the defect density on Si reference substrates, deposited simultaneously in the same deposition process, is much lower than on the Al. This points to another origin than arc events on the sputtering target as macroparticles would be expected to form during the whole sputtering process and to be evenly distributed over all the substrates. Furthermore, there is a high density of defects visible even on thinner Ti films. The features act likely as nuclei for the larger particles observed on the thicker films.

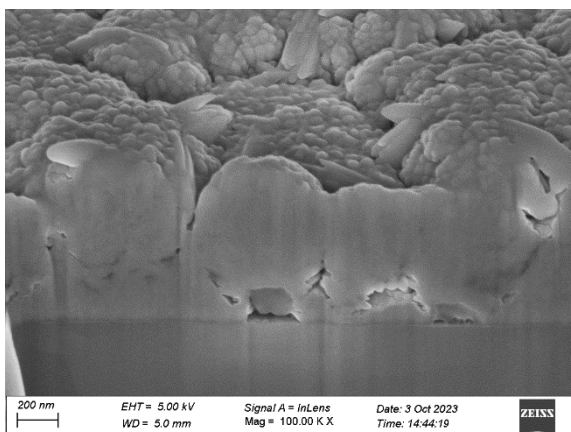


Figure 20. Cross-sectional analysis of a thick Ti layer by FIB.

7.5 Interfacial contact resistance (AP4)

The interfacial contact resistance of all pristine coated plates was sufficiently low for fuel cell applications. In the pristine condition, the plates coated with only NiP exhibited the lowest ICR,

followed by CrN and Ti (Figure). The samples coated with two different types of material (*i.e.*, Ti|C and NiP|C) exhibited the highest ICR. In the case of Ti|C the ICR was only slightly higher than that of the Ti coating (6.3 and 6.5 mΩ cm² for Ti and Ti|C, respectively), while the ICR of NiP|C (10 mΩ cm²) was slightly higher than the sum of the ICR from the NiP and C coatings (4.3 and 5.4 mΩ cm², respectively).

After corrosion exposure the ICR of all plates increased; however, the increase depended heavily on the coating and corrosion condition. After potentiostatic corrosion, the Al plates coated with Ti had formed a very thick nonconducting oxide layer leading to a ICR over 30 000 mΩ cm². In contrast, samples coated with Ti|C showed an increase in ICR from 6.5 mΩ cm² to 7.2 and 27 mΩ cm², after corrosion under potentiostatic and atmospheric conditions, respectively. Clearly, the additional top layer of 0.1 μm C contributed to a significant corrosion resistance of these Al plates. Meanwhile, samples with the NiP|C coating exhibited an increase in ICR from 10 to 16 mΩ cm² after corrosion under potentiostatic conditions but a very large increase to approximately 600 mΩ cm² under atmospheric conditions. The large discrepancy raised the question of which method of *ex-situ* ageing is the most appropriate to study the corrosion behaviour of a bipolar plate in a PEM fuel cell. As such, plates coated with NiP|C were used as bipolar plates in a PEM fuel cell with results shown and discussed in chapter 7.6. After the fuel cell measurements, both anode and cathode plates exhibited ICRs similar to the plates after potentiostatic corrosion measurements, indicating that this ageing method may be a more suitable *ex-situ* test for at least samples with a NiP|C coating.

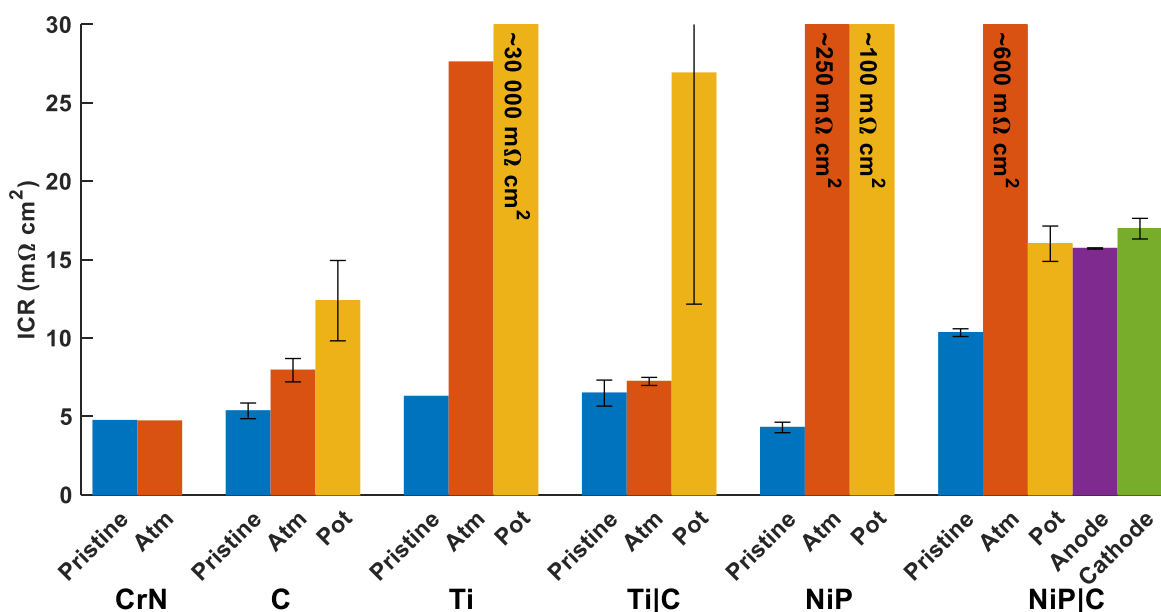


Figure 21. Interfacial contact resistance (ICR) of aluminium bipolar plates with different coatings at 150 N / cm² in pristine conditions as well as aged atmospherically (Atm), potentiostatically (Pot), and *in-situ* fuel cell (as Anode and Cathode bipolar plate). Error bars signify 1 standard deviation based on three repeated measurements for pristine plates and two for corroded. Note that the graphs of Ti|C - Pot, NiP-Atm, and NiP|C are cropped for clarity.

7.6 Fuel cell testing (AP5)

A single cell fuel cell, assembled using aluminium BPPs coated with NiP|C and commercial cell components, was successfully assembled and tested at 70 °C with 60% relative humidity of the inlet gasses; the resulting polarization curves shown in and voltage as function of test time are shown in Figure a and b, respectively. A first trial was conducted for 906 h (38 days), with some initial performance loss after 66 h (~3 days) followed by no further decrease in performance. This may indicate that either only minor corrosion of the bipolar plate occurred or that whatever oxide layer that was

formed only lead to a minor increase in the contact resistance between bipolar plate and membrane electrode assembly. This was further corroborated by measuring the high-frequency resistance (HFR) with electrochemical impedance spectroscopy at 0.21 A / cm^2 after specified days (Figure). No significant changes in the HFR could be observed during the test time, further illustrating either that only a small amount of oxide layer was formed at the surface of the BPP or that the resulting oxide layer does not contribute to a significant increase in resistance.

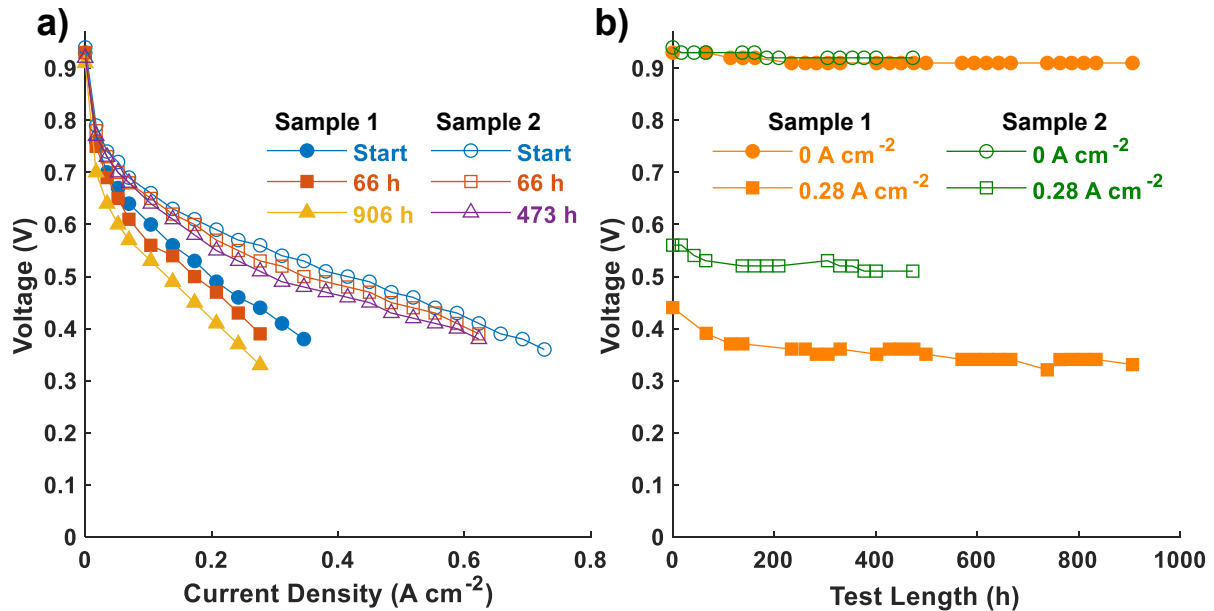


Figure 22. a) Polarization curves after selected test durations b) voltage at open-circuit (0 A cm^{-2}) and 0.28 A cm^{-2} over the entire test durations.

An additional measurement was performed after optimizing the assembly, which lead to a drastic increase in performance. Also here, a minor, initial decrease in performance after 66 h, followed by near constant behavior. After 473 h, this measurement was stopped. While the overall performance was much greater in the latter measurement, both samples showed the same decrease in performance as a function of time. Initially the performance decreased slightly, but then the voltage quickly stabilized with no significant further decrease in voltage as a function of test time.

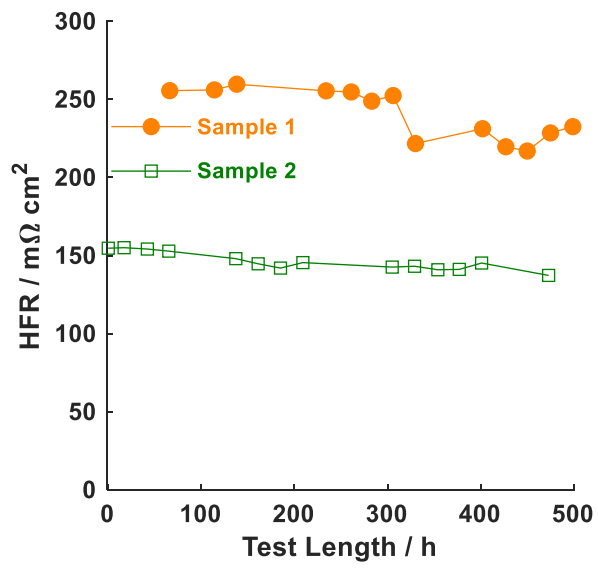


Figure 23. High frequency resistance (HFR) at 0.21 A cm⁻² over the test duration.

7.7 Forming and joining of bipolar plates (AP6)

In a separate report attached (Appendix 2) technologies for sheet forming and joining of bipolar plates for PEMFC applications are reviewed. It summarizes technologies for forming and joining of metallic bipolar plates (BPP), with the perspective of using Aluminum as base material. The state-of-the-art technologies are noted, and alternative technologies are presented and discussed. It is noted that within forming there are many technologies that are used, and no single forming method has obtained a de-facto monopoly, and they compete for their future on the market. Different variants of mechanical stamping processes and hydroforming are used in practice today, and there are alternatives that could be used after further development and/or adaptation.

The study includes a finite element simulation to compare how formability of Aluminum sheet are affected by elevated temperature (i.e. 200°C), see Figure 24.

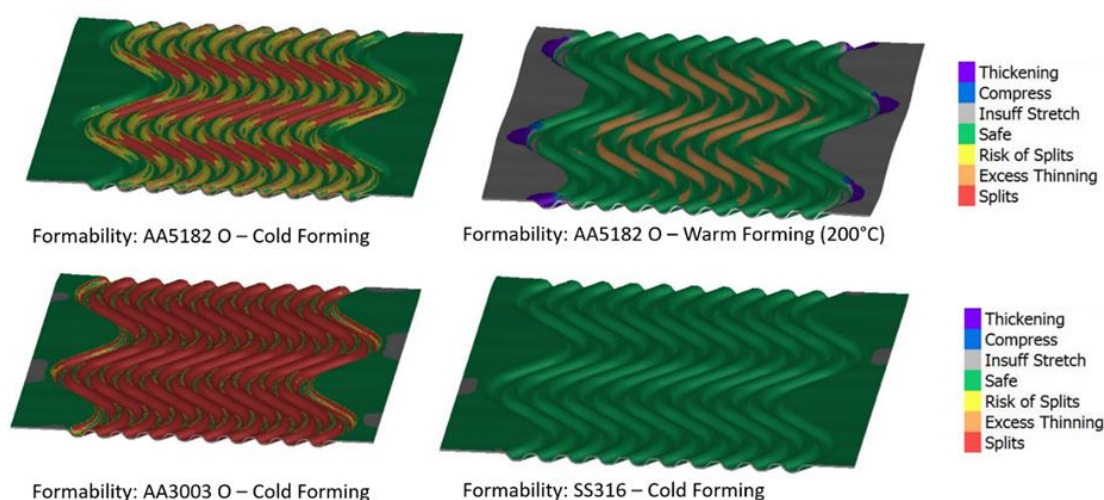


Figure 24. Simulation results regarding formability.

Upon evaluating the forming limit diagrams (FLD), it can be observed that the cold-formed AA3003 alloy in the O temper exceeds the FLC the most. When comparing the AA5182 in the O temper, both cold-formed and at 200 °C, it can be seen that the higher FLC (for 200°C) indicates a possibility of a feasible component. Not only is the FLC shifted to a higher level, but also the major and minor strain distribution deviate between the cold and warm formed components. Higher plane strain values are achieved with warm forming, while on the other hand, stretch forming decreases.

Within the field of BPP joining, there seems to be a clear go-to method that has reached at least a near-monopoly on the market and it is laser welding. Here, this technology is to some extent compared with alternative technologies that potentially could be employed after varying degrees of development and adaptation.

7.8 Discussion of results

The review of different coatings and coating methods for Aluminum based BPPs have shown that there are a number of different coatings techniques that can be used, however, for best results a multilayer coating system should be employed, which may include an interface contact layer, a sealing layer, an additional interface layer, and a surface contact layer. In this project electroless plating of NiP and physical vapour deposition (PVD) of Ti have been the main coatings and techniques employed for creating the sealing layer. The NiP was considerably thicker (~10 μm) than the Ti coatings (200 and 800 nm).

Initial potentiodynamic corrosion tests of the sealing layers revealed a very good performance of the 800 nm Ti layer. Both the NiP and CrN showed much higher corrosion currents. The lifetime of all coated surfaces, however, was relatively short. The best life-time exhibited the NiP coatings.

After addition of the C top coat, the performance dramatically changed. While the corrosion current of NiP was reduced, the corrosion current of Ti coated surfaces increased substantially. Understanding this behaviour required significant effort.

Investigations of the coatings with SEM-EDS have revealed that defects and compositional surface variations have a big effect on the formation of defects in the coatings. Initially, the defects were attributed to imperfections of the Aluminum substrate with various features identified on the uncoated polished surface. Such defects may serve as initiation for pit-hole corrosion. Subsequent analysis, however, highlighted the presence of defect even in coating layers on seemingly nice Al surface. Interestingly, at the same Ti layer on reference Si surfaces were defect free. The tentative explanation is that small imperfections of the substrate can be enhanced during the subsequent PVD deposition and lead to larger defects in the coating. Such defects are especially sensitive to galvanic corrosion when the surface is coated with a layer of C.

To further improve the quality of the coatings and decrease the number defects additional surface treatments of the substrate one possibility is to apply a thicker interfacial layer which might shield the underlying compositional variations. For the NiP it is possible that thicker coatings and possibly a double coating procedure could seal the underlying surface better.⁴ There are also strategies with an additional step to seal the possible defects either using chemical means or atomic layer deposition.

All coatings provided a sufficiently low interfacial contact resistance (ICR) prior to corrosion exposure (i.e. $>10 \text{ m}\Omega\text{cm}^2@150 \text{ N/cm}^2$) and the Ti coating adhered very well to the substrate.

The *ex-situ* evaluation of the coatings by corrosion cell testing indicated that NiP and even more NiP+C (PVD-deposited carbon as a contact layer) provided a better protection to corrosion than Ti. This could be explained by a lower difference in the chemical potential between Al and the NiP as compared to Ti. Furthermore, *post-test* evaluation of interfacial contact resistance did not show a dramatic increase of contact resistance, although the data is somewhat scattered. This could be explained by the localized nature of the pitting corrosion mechanism which means that a large area of the coating remains intact.

Ex-situ evaluation by atmospheric exposure in the climate chamber gave a different result where the Ti coatings were more or less unaffected, but the NiP and specifically NiP+C coatings were severely oxidized. Analysis by FTIR reveal formation of metal (Ni and/or Al) oxides and hydroxides on the NiP samples. These species were not seen for the Ti coating after atmospheric exposure. The results were further confirmed by the ICR measurements where the NiP and NiP+C gave ICR values more than 10 times higher than Ti. These result remains to be fully understood but could be explained by the thicker

NiP coating being more sensitive high humidity and to rapid temperature gradients in the climate chamber. A general observation is that the carbon coating applied with PVD resulted in improved protection for all substrates (plain Al, Ti and NiP) except NiP+C in atmospheric exposure. Further studies are needed to understand this behavior better.

Despite the poor performance during atmospheric exposure, NiP+C behaved surprisingly well under *in-situ* fuel cell tests. Under the test conditions (70 °C, 60% RH) the coating showed only a small decrease in high frequency resistance during the testing periods of 906 and 473 hours (Fig. 22). This result was further confirmed by the *post-test* examination through ICR measurements giving only a small increase. However, there was a difference between the anode and the cathode plates and corroded stains could be observed on the cathode plate surface. Investigation with FTIR revealed the presence of metal (Al and/or Ni) oxides and hydroxides on the cathode plate surface.

The encouraging fuel cell tests opens for a more speculative discussion around commercialization and production of bipolar plates based on Aluminum. During the course of the project one of the Hydrogen aviation pioneering companies Zero Avia has sent out a press release of their intent to use Aluminum based bipolar plates in their future fuel cell stacks. However, there are of course challenges. The review in AP6 shows that Aluminum thin sheets have less formability than stainless steel but that these difficulties can be overcome by warm forming, for example. Also the joining of Aluminum plates is an area that needs further studying. Laser welding is dominating for BPP-production today, but more cost-efficient soldering or brazing techniques might be applicable for Aluminum. Applying of protective coating before or after forming and joining is another question that needs further investigation.

8 Dissemination and publications

8.1 Kunskaps- och resultatpridning

How has/will the project be used and disseminated?	Mark with X	Comments
To increase the knowledge within the area	X	
Transferred to other advanced technical development projects	X	
Transferred to product development projects	X	
Introduction to the market		
To be used in investigations/ policy documents/ permits/ political decisions		

8.2 Publications

Results from the project has been disseminated at five conferences/workshops and in two scientific publications.

Conference contributions:

Uppsala University conference on Solar fuels, Electro fuels, Green hydrogen and CO2 Valorization, October 24-26, 2023, “Corrosion studies on coated aluminium for bipolar plates”, Yao Yao, Smita G. Rao, Live Mølmen, Richard Westergård, Karin Beaussant Törne, Tomas Kubart, Peter Leisner, Anders Lundblad

ISE 37th Topical Meeting, 2024 June 9-12, Stresa, Italy, “Corrosion resistance of coated Al for bipolar plates in PEM fuel cells”, K. Beaussant Törne, S. G. Rao, T. Kubart, Y. Yao, A. Lundblad, H. Nederstedt, L. Mølmen, R. Westergård

Vätgaskonferensen 2023, December 5-6, Stockholm, Poster presentation, “Corrosion studies on coated aluminium for bipolar plates”, Yao Yao, Smita G. Rao, Live Mølmen, Richard Westergård, Karin Beaussant Törne, Tomas Kubart, Peter Leisner, Anders Lundblad

Decarbonization 2024: Advanced Materials and Technologies for a Sustainable Future, March 21, Stockholm, Oral presentation, “Development, characterization and evaluation of aluminum-based bipolar plates for PEM fuel cells”, Anders Lundblad, RISE

19th International Conference on Plasma Surface Engineering, September 2-5, 2024, "Corrosion resistance of thin films prepared by magnetron sputtering on Al surfaces", Tomas Kubart, Abstract accepted for oral presentation

Scientific publications:

Paper 1” Degradation of protective coatings on aluminium substrates for PEMFC bipolar plates”, Authors: Smita G. Rao, Karin Törne, Yao Yao, Live Mølmen, Richard Westergård, Peter Leisner, Anders Lundblad, Tomas Kubart.

Paper 2: “*Ex-situ* and long-term *in-situ* testing of Aluminum-based bipolar plates for PEMFC”, Authors: Hannes Nederstedt, Live Mølmen, Smita Gangaprasad Rao, Karin Beaussant Törne, Yao Yao, Tomas Kubart, Anders Lundblad.

9 Conclusions and continued research

The BALBAS project has covered several aspects of producing Aluminum based bipolar plates, including thin Aluminum plate manufacturing and preparation for coating, coating with different techniques, evaluation by *ex-situ* and *in-situ* methods, and reviewing state-of-the-art for coating technologies, forming technologies and joining technologies.

By doing a literature review and by following the recent scientific and commercial publications the increasing interest for Aluminum as a base material for fuel cell bipolar plates has been noticed. However, the application of Aluminum-based BPPs in real PEM stacks is still in its infancy and no commercial products are on the market.

In the BALBAS project we have successfully produced coatings that fulfils the DOE target of contact resistance less than 10 mOhm*cm². Both coatings done by electroless plating of NiP and physical vapor deposition coatings of CrN and Ti were successful in this respect.

The *ex-situ* methodology that was further developed in the BALBAS project and applied to the developed coatings. The investigation revealed that the coatings behaved differently to the corrosion cell and to the atmospheric corrosion exposures. While Ti and Ti+C corroded more heavily in the corrosion cell they were less affected by atmospheric corrosion exposure. For NiP and NiP+C the corrosion cell behavior was acceptable (at least for NiP+C) while the exposure to atmospheric corrosion resulted in more aggressive corrosion. In general further studies are needed to fully understand the different behaviors of the coatings under *ex-situ* testing. This will be important to identify an appropriate test methodology for screening of materials for fuel cell applications.

Despite the poor performance during atmospheric exposure, NiP+C behaved surprisingly well under *in-situ* fuel cell tests. Under the test conditions (70 °C, 60% RH) the coating showed only a small decrease in high frequency resistance during the testing periods of 906 and 473 hours. The BALBAS project has shown that Aluminum based bipolar plates are feasible for PEMFC and that 1000 h fuel cell operation with acceptable contact resistance performance has been reached. However, given the challenging environment in a fuel cell, a duplex coating method for surface treatment of Aluminum is most likely needed and should be investigated in future projects.

The project work has also improved the methodology for *ex-situ* evaluation of Aluminum based bipolar plates. As in many experimental projects where new evaluation and characterization methods are developed the insights has led to a better understanding of where the methodology is weak. Looking back at the project we can see that more resources and systematic evaluations are needed before a fuel cell relevant method for atmospheric corrosion tests can be established.

10 Participating partners and contact persons



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