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Literature review on coating systems for
Aluminium-based bipolar plates.

(Appendix 1 to BALBAS end-report)

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Summary

This literature report on coating systems for Aluminium-based bipolar plates was conducted as a first step of the Balbas project to establish the state-of-the-art and to be used as a base for project decisions going forward in subsequent WPs. Additional to the surface coating technologies reviewed, the report also includes a description of the manufacturing process for Al-based substrate materials used in this project. Possible coatings for metallic bipolar plates includes single element solids (e.g. Ti, C), different carbides, different nitrides (e.g. chromium, titanium, and zirconium nitride), and nickel phosphorous (NiP). Often a multilayer coating is applied, where different layers have different purposes. 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 that a NiP-based sealing layer applied by electroless plating might be advantageous because its higher thickness than coatings applied by other means. However, PVD-based coating from CrN and Ti are interesting options and should be selected for evaluation in the project.

1 Introduction/Background

Bipolar plates (BPP) are fundamental components in modern PEM fuel cell design. The BPP should separate the gases (hydrogen and air) and provide channels/flow patterns for gases, while at the same time conduct electrons from one cell to the other. The bipolar plates also provide channels for the cooling liquid of the fuel cell.

Requirements for a state-of-the-art fuel cell is to operate at a nominal current density of 2 A/cm² with a total voltage decay of 5 μV/h or less (including decay due to membrane and catalyst). The lifetime should be 20000 hours and the total contact resistance of the cell (anode and cathode) should be 15 and 30 mΩ/cm² at beginning and end of life, respectively. During the fuel cell operating life, the BPP will be exposed to electrochemical conditions including oxidizing atmosphere at the cathode and reducing atmosphere at the anode, temperatures between -50 and 95 °C and up to 100% relative humidity.

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

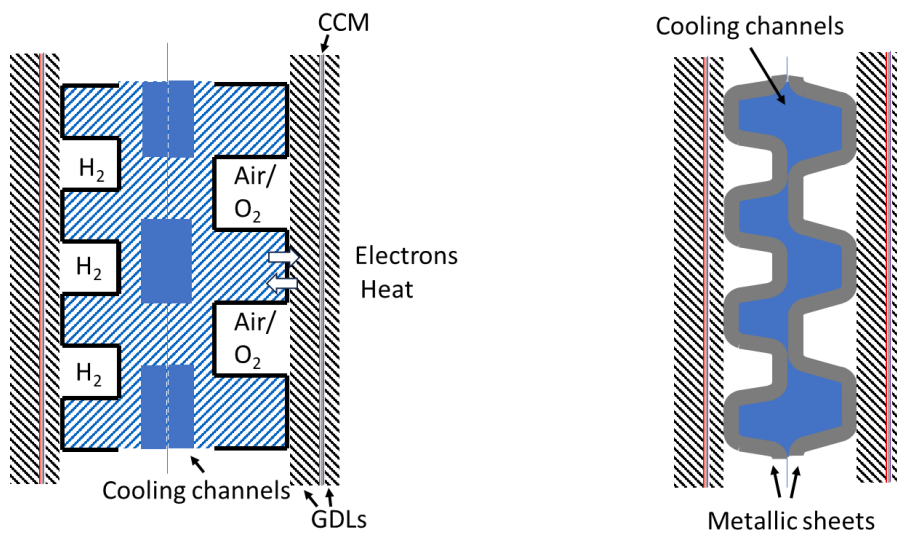


Fig. 1. Schematically illustrated cross sections of graphite based (Fig. 1a, left) and metallic (Fig 1b, right) BPPs, including gas diffusion layers (GDLs) and catalyst coated membranes (CCMs).

BPP can be made of graphite or carbon composites which will give them inherently low contact resistance to the GDL. Furthermore, graphite is chemically stable in the PEMDC environment. Another option is to make the BPP of a metal sheet or foil (0.1 mm) which is less brittle and thus enables thinner BPPs. Thinner BPPs gives higher power density to the fuel cell stack. However, the metallic BPP performance suffer 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 but also provide a small contact resistance to the GDL. Furthermore, it is desirable if the coating adhere well to the substrate and is ductile in order to support the tensile and compressive stresses that appear during forming of the metal sheets.

A surface coating system includes several layers where different layers may serve different purposes as illustrated in Fig. 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 resistance in acidic environments. An interfacial layer between the sealing and surface contact layer may also be needed to ensure good adhesion.

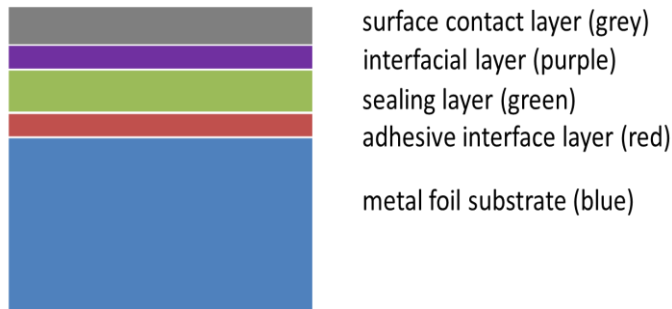


Fig. 2. Illustration of generic coating system for metallic BPP.

Since 2010 there have been several review papers published on BPPs and possible protective surface coatings [1,2,3,4,5,6,7,8,9,10]. The coatings include but are not limited to: Ni-P coatings, nitrides, carbides, carbon coatings, noble metals, and other coatings.

2 Materials manufacturing technologies

Metallic BPPs are today produced from sheet metals that are coated, cut, formed and joined. Coating is either made on the rolled metal surfaces in a coil-to-coil procedure, or on the final formed component plate. The most commonly used metal is stainless steel, primarily of the 316L grade, but also titanium is used.

2.1 Manufacturing of Al-based substrate materials

The production of rolled aluminium can be made in many ways and in this report the process *actually* used for this project is described. The material is made using well known and established industrial full scale metallurgical production processes that are typical for products based on virgin/primary metal. The primary metal is derived from aluminium oxide in a dedicated aluminium smelting facility. There, the virgin metal is then alloyed to reach a predetermined composition and cast using direct chill casting to form a rolling slab. It is then transported to the rolling plant. There, the slab is scalped to remove surface cracks/oxides, near-surface macrosegregation to generally provide a repeatable flat surface suitable for rolling. The size of the slab at this stage is ~4.1 m long, ~1.44 m wide and ~575 mm thick. The slab was placed in a preheating furnace and heated to a temperature in the interval 450-500°C. Upon reaching the set temperature the material was transferred to a reversing hot breakdown rolling mill where it was rolled until it reached a thickness of 18mm, after which it was transferred to a finishing hot rolling machine where it was rolled to a thickness of 3.7 mm and wound to form a coil.

Said coil is then transferred to cold rolling where it is rolled to a thickness of 0.8mm where it is sampled in the full width.

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.

2.2 Plating and electroplating of Ni

Nickel plating is a widely used functional and decorative coating that in most cases give good protection against corrosion. In electronic and electric applications Ni coatings are used on many different types of connectors e.g.

- Pad contacts on printed circuit boards and chip modules for connecting electronic components by soldering or wire bonding. A thin top coating of soft gold is applied to improve the bondability. The Ni layer does also act as a diffusion barrier avoiding copper below the Ni from diffusing to the surface where it would oxidize.
- Mechanical edge contacts on printed circuit boards and high-quality electronic plug-in contacts have a top coating of hard gold to lower the electric contact resistance.
- On power contacts for household equipment, Ni is used without any top coating. The naturally formed passivating oxide film on Ni might need a voltage of about 1 V to break down the oxide (fritting voltage), which is no problem for electric systems applying at least 110 V.
- In a similar way, Ni is used on connectors for batteries.

- Ni is also used in sliding contacts in wind power stations where the application demand combined resistance to corrosion, wear, and arc erosion.

Electrolytic plating of Ni coatings can be done by two different methods, namely electroplating and electroless plating. The two methods will be discussed in the following.

2.2.1 Electroplating of nickel

Electroplating is carried out in an electrolyte containing dissolved nickel ions by connecting the component to be plated as cathode with a nickel anode. Nickel ion will be reduced to metallic nickel at the cathode and form the growing coating. In parallel, nickel will be dissolved as ions from the anode, and thereby maintain the electrolyte composition (see Figure 3).

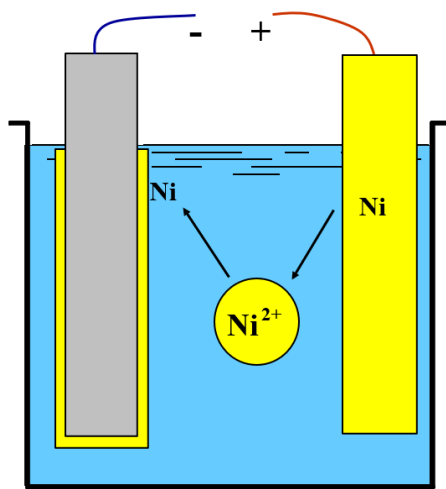


Figure 3: Sketch off an electroplating cell

The material distribution depends on the electric field distribution in the plating tank. Therefore, components with complex shapes will get variation in the coating thickness over the component surface. To partly compensate for this and to manipulate other properties, different organic additives are used in the electrolyte. Additives can have a levelling effect, make the coating bright, or affect mechanical properties like hardness, ductility, and intrinsic stress in the coating.

Watts nickel is the most commonly used family of nickel plating processes. Here the main source of nickel in the electrolyte is from dissolved nickel sulphate. To improve the corrosion protective performance, nickel layers with different low amounts of sulphur can be combined in a duplex coating. A top layer with at least 0.04% S, will offer cathodic protection of a purer intermediate Ni coating (see Figure 4).

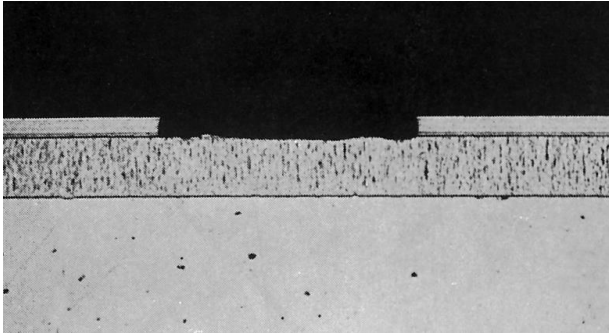


Figure 4: Cross section of a duplex nickel coating. The upper bright Ni layer is less noble than the intermediate semi-bright Ni layer. The latter is galvanic protected by the upper layer, and the risk for corrosion to reach the steel substrate is diminished.

To minimise intrinsic stress in the coating, nickel can be plated from an electrolysed based on sulphamate instead of sulphate. The sulphamate bath deposit coatings with very low intrinsic stress, but the process is more expensive. It is usually used for electroforming where free-standing components are manufactured by plating a thick nickel layer over a mandrel and finally separating the coating from the mandrel.

It is also possible to electroplate nickel alloys. Nickel-tin (approx. 67 wt% tin, equivalent to 50 at%) is used as an extra corrosion resistant coating on electronic connectors. The coating is so stable that nickel allergic people do not react when being in contact with it. The electroplated alloy forms a meta-stable phase that will recrystallize at around 300 °C. So, the application temperature or temperature in subsequent manufacturing steps should be kept below this.

2.2.2 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 5). At the surface the reducing agent oxidize and leaves electrons that are used to 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 the lifetime of the electrolyte, 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).

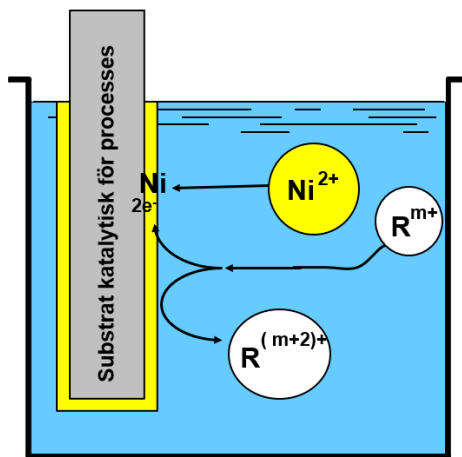


Figure 5: Sketch off an electroless plating reactor

2.2.3 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 ($2\text{Al} + \text{Zn}(\text{OH})_2^{2-} \rightarrow 2\text{Al}(\text{OH})_4^- + \text{Zn}$). 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.

2.3 Physical vapour deposition (PVD)

2.3.1 PVD 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 techniques within magnetron sputtering. Reactive magnetron sputtering and possibly high power impulse magnetron sputtering (HiPIMS) are good techniques to explore.

In reactive sputtering, a metal target is vaporized (sputtered) in a discharge maintained in an atmosphere of $\text{Ar} + \text{N}_2$. The N content in the deposited film is controlled by the N_2 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 is known to have

potential for better adhesion, higher density, as well as better control over intrinsic stresses.

PVD techniques are at the present the most commonly used coating technique for BPP coatings. However, it requires vacuum to perform the deposition, and can therefore be a costly and time-consuming step. 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.

3 Coatings on Al-substrates

3.1 Coating systems on Aluminium substrates

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

- 1) Sealing. Aluminium 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 underlying 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. 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 four groups: metals, phosphides, nitrides, carbides, and carbon coatings.

3.2 Metallic coatings

With the exception of noble metals they do not provide the necessary corrosion resistance. Both Pt and Au have been utilized to coat commercial BPPs. Deposition can be performed both by plating and PVD, since both techniques allow for good thickness control. Coating thicknesses down to the nanometer scale have been utilized to reduce cost¹¹. Even though transition metal coatings cannot serve as a top coat, coatings like Ti, Cr, Sn, etc. can provide good adhesion to the substrate and serve as an interlayer which improves the coverage of the protective coating on the top. There are also several examples in the literature where metals like Ti and Cr have been used as the protective layer [12, 13]. This is especially common when ceramics based on Ti and Cr are used for the top coat, with the advantage that both the metal and ceramic layer can be produced by PVD.

NiP and NiMoP coatings applied by electroless plating and electroplating has been investigated for PEMFC [14]. These are more cost-effective coatings. Results from ex-situ corrosion cell testing indicates that NP provides better protection than NiMoP. However, this result could be related to the surface structure since the NiP coating was “spongy” and the NiMoP coating had cracks. In another work a Ni-P-PTFE coating was applied [15]. In a previous project lead by RISE, NiP on aluminium was studied for the current collector for the PEMFC.

Nitrides are one of the most studied classes of coatings, with TiN and CrN being the most commonly published. Binary coatings are also most feasible for industrial applications, while ternary and quaternary compounds are challenging to deposit. Several authors report that the electrical and corrosion properties of metal nitride single layers are sufficient when applied on stainless steel (SS)[16,17,18,19]. Other authors, on the other hand, conclude that the single-layer coating does not meet the BPP requirements. One suggested reason for not meeting the corrosion resistance criteria is pinhole formation in the coating. To mitigate this, multi-layer coatings are often applied, as it is assumed that the pinholes in the coating layers will not align. The fact the multiple coating layers can be applied in the same coating chamber by switching targets simplifies this strategy for the PVD technique.

SS metals can also be nitrided by thermal and plasma methods [20,21,22,23]. However, these strategies are not as effective as adding a new layer on top of the SS surface.

Nitride coatings on Al substrate have been tested in literature [24,25]. However, the corrosion resistance has not met the DOE requirements. This might be due to defects in the coatings.

3.3 Carbides

Carbide coatings are less commonly studied than nitrides even though electrical and corrosion properties are sufficient. Carbides are attractive for BPP since they contain carbon and can be used to smoothly go from a metal with good adhesion to the substrate to a carbon topcoat [26]. The so-called MAX phase coating, used by the Swedish company Impact Coatings, is among the ternary carbides that has been applied on SS metals [27,28]. However, also for the carbides it is the binary CrC and TiC that are most commonly studied on SS metals [29,30,31]. There are only a few examples in the literature where carbides were coated on Al based substrates for fuel cell applications [32]. Although some studies have successfully proven the feasibility of utilizing carbide coatings such as CrC on aluminium with decreased contact resistance, increased corrosion potential, and long durability tests, the coating parameters have not met the industry standard when it comes to thickness. This is crucial in an industrial application due to the added production time of a thicker coating, as well as a reduction in the power density of the stack.

3.4 Carbon coatings

Amorphous carbons (a-C) are often used as top coatings since they will have a low interfacial contact resistance to the carbon based gas diffusion layer (GDL) [33,34,35,36,37]. A common strategy for a-C coatings is to start with either Cr or Ti as an interfacial layer, continue with the respective binary carbide as a protective layer and finish with a-C as the top coat. In this way, all coating layers can be produced in the same PVD chamber with only two targets for the deposition. A-Cs have, in recent years, been commonly studied as a protective coating for SS metals [38].

Graphene is another type of carbon coating that has been considered promising as a coating for Al based BPPs [39]. Graphene coatings can be applied with a number of

techniques. In one example graphene oxide (GO) was applied by immersing a Al substrate sample in an GO aqueous solution. Graphene was subsequently obtained by drying and heat treatment at 400 °C [40]. Several companies, including Toyota and Alleima, have reported that they use carbon as their top coating.

3.5 Other

In this group we include coating with higher atom numbers, including W and Ta [41,42,43]. These elements form very stable oxides, and can, therefore, significantly improve the corrosion resistance. However, these stable oxides generally show higher contact resistance. Another group of metallic coatings are high entropy alloys. These alloys have several elements in close to equal amounts, as opposed to having one major element with minor additions as is common in more traditional alloys. The high entropy alloys give new opportunities to tailor material properties. Some groups have investigated the suitability of utilizing high entropy alloys for bipolar plates with SS as the substrate [44,45]. The focus has in general been on the corrosion resistance and not the contact resistance.

Other type of coatings may also include conducting polymers or composite/multicomponent coatings [46,47]. These coatings can be applied by non-vacuum techniques and are therefore more affordable than the PVD techniques utilized today. Although, coatings on SS metals are most common there are also examples where they have been coated on Al based substrates [48] and polyaniline coatings with incorporated carbon nanotubes shows promising results.

4 Discussion

In the aluminium manufacturing process impurity inclusions (usually oxides) are formed and during the rolling process some of those impurities will be at or close to the surface, leading to surface defects and cracks. Furthermore, the rolling process gives a somewhat uneven surface with ridges that in some cases can be overfolded. Therefore, the Al-foil surface will have cracks and pits with a size in the order of several micrometers, and these defects must be considered when choosing a coating system.

PVD coatings are versatile and compositions of coatings can be varied in numerous ways. However, it is difficult to provide a uniform PVD coating that is thicker than a few micrometer. Plating of Ni alloys can easily provide coatings that are several tens of micrometers and therefore it might be better than PVD coatings to bridge the surface cracks and pits of the aluminium surface. Thus, the hypothesis is that plating by NiP could provide a better sealing layer with fewer pinholes. However, experimental proof of this hypothesis still remains to be seen and that is one of the objectives of the Balbas project.

Regarding the surface contact layer a carbon based coating is generally considered the best choice because of good interfacial contact to the carbon based gas diffusion layer. For this layer thin PVD coatings are advantageous since they can be applied with an interfacial layer (Ti or Cr) that creates a good electrical and mechanical contact to the sealing layer beneath.

For the Balbas project NiP applied by plating, CrN and Ti applied by PVD have been selected. Special emphasis will be given on testing how coatings with different thicknesses behave in the corrosive environments and tests being applied in the investigations of the preceding work packages.

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