The development of multi-layered coating and method for the aluminum bipolar plates of a direct methanol fuel cell

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Abstract

Aluminium as bipolar plate material is one of the most attractive metals among all other metallic-based alternatives due to its good machinability and low costs. However, one major drawback can be found in the low corrosion resistance of the material. Therefore a new CrN/aC-based multi-layer coating was fabricated by physical vapour deposition (PVD) and deposited onto aluminium alloy 1050A samples. The potentiodynamic test results show greatly improved corrosion resistance. The corrosion potential increased 0.37 V, whereas corrosion current decreased by two orders of magnitude at -0.13 V vs Ag/AgCl reference electrode.

In contrast to that, the interfacial contact resistances (ICR) increased significantly due to the low electrical conducitivity of amorphous carbon.

Moreover, an approach to modify the surface texture of the aluminium samples using a high precision UV laser system is also presented in this study (Fig.1). As a result, significantly more hydrophilic wetting behaviour and lower contact resistances could be achieved.
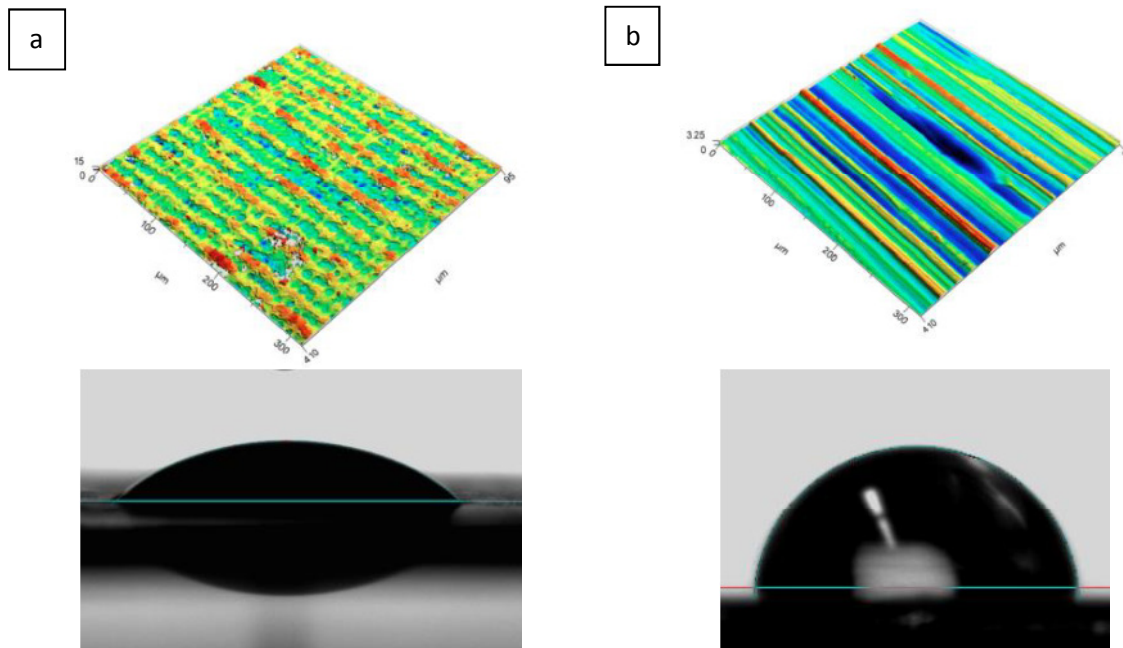
Figure 1: Contact angle and surface texture of the laser-modified uncoated (a) and untreated substrate surfaces (b)

Introduction

Polymer electrolyte membrane fuel cells (PEMFC) are devices, which generate electric power by means of a catalytically electrochemical reaction. The essential benefits of fuel cells are relatively simple technology, silent operation and high efficiency at zero emissions. For small portable applications such as cellular phones or laptops the direct methanol fuel cell (DMFC) has been considered as one of the most promising power source candidates [1, 2]. A DMFC uses liquid methanol as a fuel, which - compared to hydrogen – does not need to be stored in form of metal hydrides or compressed gases since it is liquid. As a consequence larger volumetric and gravimetric energy density of the fuel cell system is reached.

Bipolar plates are one of the most crucial and expensive components in the DMFC [3, 4]. However, they also constitute the main share of the total stack weight, volume and costs. Bipolar plates have a number of functions within the fuel cell stack like separating individual cells, distributing fuel (methanol) and oxidant gas (air) uniformly over the electrode reaction surface, collecting current and maintaining heat and water management. To be able to provide all these operations an ideal bipolar plate material requires sufficient compressive strength, high electrical and thermal conductivity, high electrochemical stability as well as good machinability and relatively low costs [5-7].

Generally, the relevant materials for bipolar plates can be classified as metallic- and carbon-based (graphitic) [8-10]. Due to the excellent electrochemical properties and low bulk resistance, carbon-based compound is the most commonly used material for bipolar plates in PEMFC´s. However, its brittleness limits the thickness of the bipolar plate, resulting in higher volumetric density. On the other hand, light metals could be a proper alternative, because they have several important advantages over carbon-based materials such as high mechanical strength, an excellent thermal and sufficient electrical conductivity as well as a very good machinability. One critical disadvantage of most metallic materials is their susceptibility to corrosion in acid and humid environment as it is found in operating cells, which results in high electrical resistances caused by the passivation of the metallic surface. Furthermore, the corrosion of the metallic bipolar plates leads to contamination of the polymer electrolyte membrane and poisoning of the electrode catalysts [11, 12]. Thus, appropriate coating, which improves corrosion resistance while preserving excellent electrical conductivity is mandatory for metallic-based bipolar plates.

Aluminium as bipolar plate material is one of the most attractive metals among all other metallic-based alternatives, such as stainless steel, nickel, titanium and copper alloy. Due to its light weight, its high mechanic strength as well as its low electric bulk resistance aluminium alloys without a passive film are able to reach all of the DOE bipolar plate targets [13, 14]. However, low corrosion resistance hinders the application as bipolar plate material. In this sense, the surface of the aluminium has to be modified by deposition of corrosion resistant coatings fulfilling high requirements with respect to density [15].

1. Scientific Approach

CrN-layers deposited by physical vapour deposition (PVD) have been identified as promising candidates for corrosion resistive coatings [16]. However, one major drawback can be found in the formation of pitting holes. These defects offer reaction sites, where the substrate metal is exposed to the corrosive media, which results in limited corrosion resistance [17]. One way to overcome this problem is to fabricate

multi-layer coatings where intermediate layers of a different material cover surface defects of the CrN-layer. By alternating CrN-layer and thin intermediate layer a coating with excellent compactness, uniformity and corrosion resistance is realized. Amorphous Carbon (aC) is an interesting candidate for the use as thin intermediate layer because of its high corrosive resistance, the excellent compactness and the good adhesion to CrN. Figure 2 shows a drawing of the coating principle with alternating CrN and aC layers.
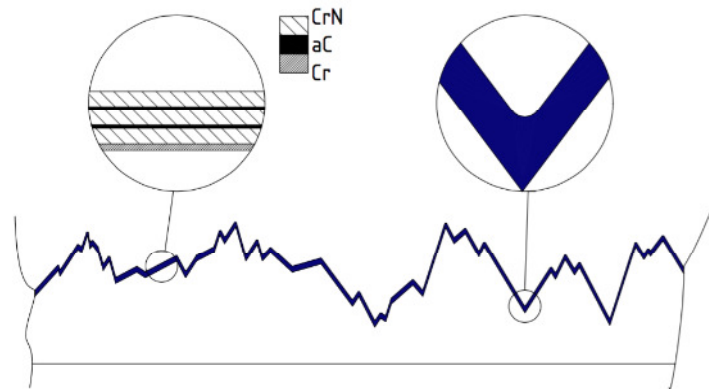

Figure 2: Coating system composition; Effect on the roughness through the coating

This paper presents a study of the influence of the as described multi-layered CrN/aC-based coating deposited on aluminium alloy 1050A samples on the electrical and electrochemical properties.

Moreover, this work presents an approach to combine corrosion resistant coatings with an adjustment of the surface roughness of aluminium bipolar plates using a high precision UV laser system. This way, a greater match to the surface properties of the gas diffusion layer can be achieved which will affect electrical contact resistances and, by that, the performance of the DMFC stack.

Both the performance and the efficiency of the DMFC are significantly influenced by $CO2$ gas bubbles produced at the anode and H_2O droplets occurring at the cathode. These reaction products block the active area of the fuel cell and inhibit mass transfer to the electrode [18, 19]. In order to remove them from the working cell the surface of the flow channels has to be adjusted by means of different contact angles to each side of the bipolar plate separately [20]. These surface modifications can also be realized using high precision UV laser treatment.

2. Experiments/Calculations/Simulations

Sample preparation

In this study, an aluminum alloy 1050A was chosen as a potential material for bipolar plates in DMFC´s as it is of good machinability and low costs. Table 1 shows the nominal compositions of the applied aluminium alloy.

Mg	Si	Cu	Zn	Mn	Fe	Al
0.0 - 0.05	0.0 - 0.25	0.0 - 0.05	0.0 - 0.07	0.0 - 0.05	0.4	Balance

Table 1 – Chemical composition of aluminium alloy (wt.%)

For ICR measurements aluminium sheets with a thickness of 200 µm were cut into 23 mm x 23 mm samples by laser cutting, samples for linear sweep voltammetry measurements were cut into disks with a diameter of 15 mm.

Afterwards, some of the samples were modified by laser ablation to achieve the specific and uniform surface structure using an UV laser system with a wavelength of 365 nm. The applied laser parameters are presented in Table 2.

Frequency	Power	Mark Speed	Repetitions
[kHz]	[W]	[mm/s]	[-]
80	4	800	150

Table 2 – Applied laser parameters

These samples were rinsed in an ultrasonic bath with acetone for approximately 3 min in order to remove particles from the surface. Finally, they were cleaned with de-ionized water and dried at room temperature.

Samples with and without laser-treatment were coated with a 5-fold CrN/aC layer by using PVD deposition technology. The thickness of the intermediate aC-layer was minimized due to its low electric conductivity. The total thickness of the deposited coating was 800 nm.

Characterization

In order to evaluate the effect of the laser-modified surface structure on wetting behaviour static contact angle measurements were carried out using precision contact angle goniometer (Dataphysics OCA 20). For evaluation of the surface roughness, high precision confocal microscopy (Nanofocus µsurf custom) was used.

The surface conductivity for all samples was characterized at room temperature by Interfacial contact resistance (ICR) measurements using an in-house contact resistance measurement apparatus (Fig.3).
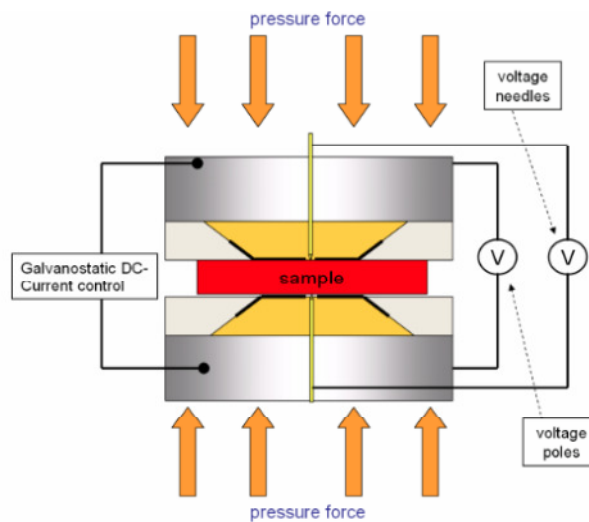

Figure 3: Schematic of in-house contact resistance measurement apparatus

Using this method four different values of electrical current (0.5 A; 1.0 A; 1.5 A; 2.0 A) were applied between sample and gas diffusion layer. The total voltage drop was monitored while the compaction force was gradually increased at each measuring point from 30 to 300 Ncm^{-2}. This total voltage drop is the result of the sum of all the interfacial contact resistances. To calculate the contact resistance of the sample the GDL-resistance and bulk resistance were subtracted from the total resistance.

In order to obtain sufficient data and check the reproducibility the characterization of each sample variation was composed of five single measurements of two nominally identical prepared samples.

Linear sweep voltammetry measurements were performed using a computer-controlled potentiostat/galvanostat (Bank Elektronik PGS 95). A typical three-electrode system, consisting of a thin platinum sheet (auxiliary electrode), the metallic sample (working electrode) and an Ag/AgCl (0.210 V vs. RHE) electrode (reference electrode), was used to measure the corrosion behaviour of the multi-layered CrN/aC-based coating under DMFC anodic operating conditions. In order to simulate typical anodic environment in real DMFC, the electrolyte was composed of 0.5 M H_2SO_4 and 10 vol.-% methanol solution. The samples were stabilized at open circuit potential (OCP) for 30 min. Then the potentiodynamic polarization sweep of the working electrode was performed from -0.7 V to +0.5 V vs. OCP at a scan rate of 1 mV s^{-1}. A constant temperature of 60 °C was realized by an isothermal bath.

3. Results

The contact angles on laser-modified and untreated surfaces as well as on coated and uncoated surfaces are summarized in Table 3. The corresponding contact angle measurements are shown in Figure 4.

Substrate (Al 1050A)		Contact Angle
uncoated	modified	39.3° (a)
coated	modified	56.7° (b)
uncoated	not modified	81.1° (c)
coated	not modified	79.6° (d)

Table 3: Contact angle of the laser-modified and untreated substrate surfaces

As can be observed laser treatment has an enormous impact on the surface properties.

The difference in the contact angle between uncoated modified (a) und uncoated untreated (c) sample surfaces is 41.8°. However, the coating itself has a significantly weaker effect on the surface properties. For both, laser modified and bare aluminium samples the difference of the contact angle before and after coating is less than 20°.
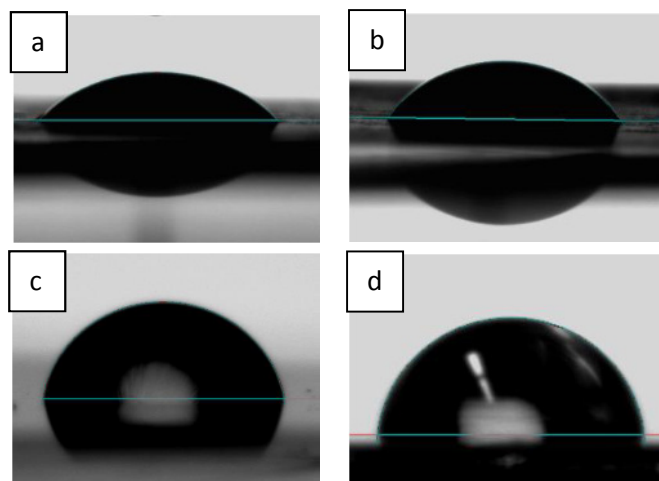

Figure 4: Contact angle of the laser-modified uncoated (a), laser modified coated (b) and untreated uncoated (c) and coated (d) substrate surfaces

The strong effect on wetting behaviour can be attributed to the change in surface roughness after laser treatment. Figure 5 and 6 show uncoated surfaces of bare aluminium alloy and a laser modified sample. As can be observed the surface of the lasermodified
sample exhibits a uniform surface texture with higher roughness amplitudes. This leads to capillary forces that promote wetting.
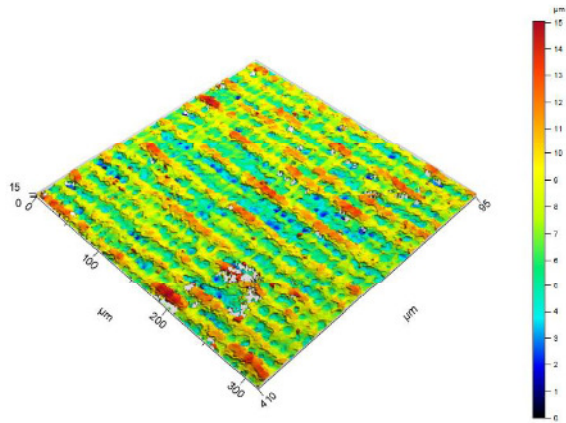

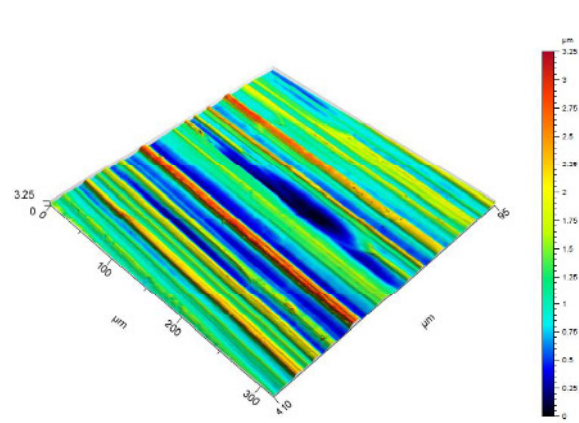Figure 5: Surface texture of the laser-modified 1050A sample

Figure 6: Surface texture of the untreated 1050A sample

ICR measurements

Fig. 7 presents the ICR characterization of the laser-modified samples before and after the coating. It becomes clear, that the coating leads to increased ICR values compared to bare aluminium alloy. This behaviour can be attributed to the intermediate amorphous carbon layers, which exhibit low electrical conductivity.
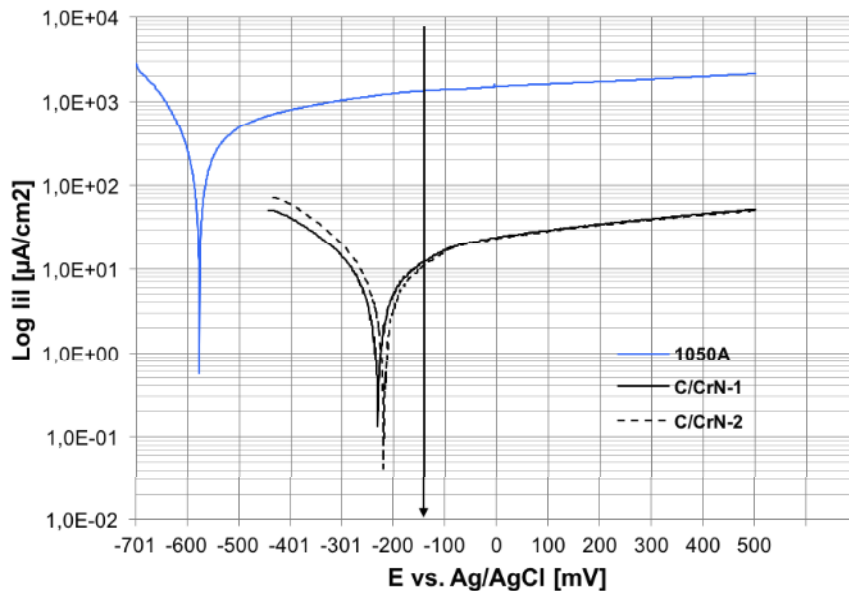

Figure 8: Potentiodynamic curves for bare and coated 1050A in 0.5 M H_2SO_4 + 10 vol.-% CH_3OH solution at 60°C

As can be observed, the corrosion potential (E_{corr}) of the bare 1050A is -0.58 V. However, active-passive transition peak of the coated samples shifts towards more positive values and reaches -0.21 V, which shows that the applied coating has a significantly nobler corrosion behaviour and indicates lower corrosion tendency.

Compared to bare 1050A, the corrosion current density of the coated samples is more than one order of magnitude lower (Tab. 4).

Sample	E_{corr}	I_{corr}	$I_{(-0.13 V)}$
-	$(V_{Ag/AgCl})$	$(\mu A\ cm^{-2})$	$(\mu A\ cm^{-2})$
coated	-247,36	6,91	13,42
uncoated	-608,40	304,10	1356,65

Table 4: Polarisation parameters of 1050A and coated 1050A in 0.5 M H$_2$SO$_4$ + 10 vol.-% CH$_3$OH solution at 60°C

Furthermore, the similar run of the potentiodynamic curves from all coated samples indicates reproducibility of uniformity of the coatings. This is represented through the additional potendiodynamic curve (C/CrN-2), which is also shown in the Figure 6. In all cases, the corrosion current density was within the range between -0.26 and -0.21 V. The corrosion current density (I_{corr}) at -0.13 V vs. Ag/AgCl, which corresponds to the typical anodic operating potential of a DMFC, reaches 13,42 $\mu A\ cm^{-2}$ for coated samples, being two orders of magnitude lower than that of the uncoated 1050A samples.

Conclusions and outlook

A new, corrosion resistive CrN/aC coating for metal bipolar plates in DMFC and a laser ablation method for adjusting wetting behaviour and contact resistances were developed successfully. The corrosion resistance of aluminium alloy 1050A has been improved significantly. The corrosion potential increased 0.37 V, whereas corrosion current decreased by two orders of magnitude at -0.13 V vs Ag/AgCl reference electrode. Laser modification shows great potential for future application in DMFC metal bipolar plates. By using a UV laser system surface texture of aluminium alloy samples was changed via laser ablation. As a result, significantly more hydrophilic wetting behavior and lower contact resistances could be achieved. This gives the opportunity to tune surface texture locally, depending on individual requirement. For example, surface roughness within the flow channels of a bipolar plate may be modified in a different way than on top of the plate where the surface comes into contact with the GDL, requiring a good electrical contact.
Results have also shown that electric conductivity of the coating needs further development. One way to eliminate this problem is to adjust the thickness of the amorphous carbon layers in the coating system or to substitute them with a material that exhibits higher specific electric conductivity.
Moreover, laser modification has to be examined further to obtain a deeper understanding on the influence of different laser parameters on surface texture.

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