# Anodization process analysis of the aluminum surfaces in corona discharge

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In this paper, we analyze the role in the anodization process of aluminum surfaces of the charged and neutral species produced in negative corona discharges and of the chemical species present in a polydimethylsiloxane/hydrogen peroxide medium. The morphology and the elemental composition of the porous alumina layer are investigated by X-ray Photoelectron Spectroscopy, Scanning Electron Microscopy and Electron Dispersion Spectroscopy.

## 1. Introduction

Electrochemical oxidation of aluminum surfaces in chemical solutions under direct current conditions is a controlled anodization process usually used for the generation of uniform protective oxide layers [1].

For many applications of aluminum based materials in aerospace, automotive, architectural, and packaging, the corrosion protection is a key issue [2].

As conventional method, it is generally accepted that the alumina ($Al_2O_3$) layers in porous form are generated as follows: first an aluminum oxide layer is grown at the alumina/Al interface due to the counter migration of $Al^{3+}$, $OH^-$ and $O^{2-}$ ions and secondly the dissolution of aluminum oxide at alumina film /solution interface take place [2].

As an alternative method to the classical anodization process, in our previous papers**,** we showed that during the polymerization of a polydimethylsiloxane (PDMS) liquid film lying on the surface of an aluminum substrate in corona discharge, an Al oxide layer is generated at polymer/substrate interface [3, 4]. Running of these kinds of discharges in air at atmospheric pressure has the advantage of simultaneous production of charged (negative or positive ions) and neutral (for example $O_3$) species of oxygen known for their reactive character in the interaction with materials. In the same time, the OH and Si-OH groups generated at polymer/substrate interface determine the formation of Si-O-Al bonds announcing the possibility of counter migration of Si and Al atoms [4].

The negative ions of oxygen, water molecules and consequently the OH radicals present either in liquid or solid film further formed on the substrate due to the PDMS polymerization process [3] are responsible for oxidation of the Al surface in negative corona discharge.

Combing the effect of the corona charged species with the chemical ones respectively by placing a liquid film, formed in a proportion of 33 – 67 % from hydroxyl terminated PDMS liquid precursor and hydrogen peroxide ($H_2O_2$), on the Al surface (anode) in a negative corona discharge produced in air at atmospheric pressure we were able to generate alumina layers with uniform pores distribution [4].

In this paper, we will analyze, in different experimental conditions, the role of the charged and neutral species produced in corona discharge and of the chemical species present in the PDMS/ $H_2O_2$ medium on the pores structure and their distribution into the alumina layer. The morphology and the elemental composition of the porous alumina layer are investigated by X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) and Electron Dispersion Spectroscopy (EDS).

## 2. Experimental set –up and conditions

The negative corona discharge operates in a Trichel pulse regime in air at atmospheric pressure in a point to plane corona discharge electrode configuration, the experimental set-up being presented in [4]. The distance between electrodes is about 10 mm. The cathode (a 20 mm tungsten wire) is placed perpendicular to the centre of the anode (plane electrode) in a glass cage. As anode we used an Al disk electrode with a diameter of 10 mm. A high voltage of 11 kV was applied between electrodes, through a resistor of 5 MΩ, the mean value of the discharge current being of 40 μA.

The negative ions of oxygen $O_2^-$, $O_3^-$, $O_4^-$, $CO_2^-$, $CO_3^-$ produced in the Trichel pulsed regime of the negative corona discharge in the vicinity of the cathode [5] travel to the anode in regular packages. Their transport have a pulsating nature due to the periodical character of positive/negative ions

production respectively destruction processes that take place at the cathode. Thus, the corona discharge current, Figure 1, is formed by regular pulses.

Previously [3], we showed that the uniformity of the current density distribution on the anode surface and the $O_2^-$, $O_3^-$, $O_4^-$, $CO_2^-$, $CO_3^-$ negative ions produced in the Trichel pulse regime of the corona discharge are proper to be used for thin film generation. In a Trichel pulse regime [6], the distribution of the current density on the plane electrode is uniform on a circular surface with a radius given by the relation $r = \sqrt{3}\, d$, where d is the interelectrode gap. In our experimental conditions r = 17.2 mm.

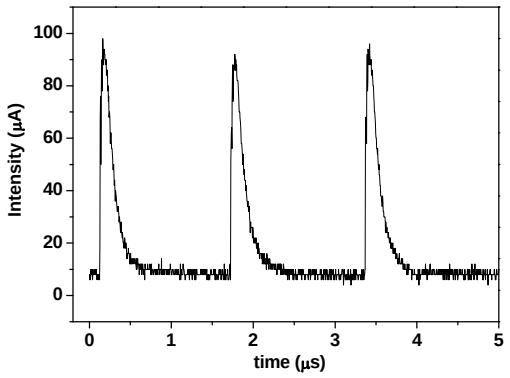



Figure 1: Waveform of the discharge current in the Trichel pulse regime.

A drop of 0.1 μl hydroxyl terminated PDMS liquid precursor stretched on an Al substrate in negative corona discharge is transform into a solid polymer layer after 2 hours [3]. During the polymerization process some the water molecules generated in the PDMS layer can be decomposed under the influence of corona electric fields and associated charges injection generating OH radicals. The Si-OH groups present also in the PDMS layer have proved their utility in the generation of Si-O-Al bonds at polymer/Al substrate interface [3]. In the same time, at polymer/Al substrate interface an anodization process occurs, the main responsible for the alumina layer formation being the negative ions of oxygen produced in corona discharge, the water molecules and the OH groups resulting as byproducts of the polymerization process [3,4].

In experimental conditions described above, we placed a 10 μl of liquid precursor on an optical polished Al substrate (anode). This liquid precursor contains PDMS / $H_2O_2$ in a 33-67 % proportion. The presence of the addition PDMS/$H_2O_2$ medium on the anode does not change the electrical regime of the corona discharge and its optical characteristics. By the stretch of the PDMS liquid under negative corona charges injection the uniform covering of the substrate with the $H_2O_2$ is assured. The further decomposition of $H_2O_2$ in negative corona discharge gives an enhanced infusion of water molecules and OH radicals at the surface of the Al substrate, knowing that hydrogen peroxide can be involved in the following reactions:

$$H_2O_2 \rightarrow H_2O + ½\ O_2 \text{ [7]}$$
$$OH\cdot + H_2O_2 \rightarrow H_2O + HO_2 \text{ [7]}$$
$$HO_2\cdot + H_2O_2 \rightarrow O_2 + H_2O + OH \text{ [7]}$$
$$2O_3 + H_2O \rightarrow OH\cdot + O_2 + HO_2 \text{ [7]}$$

The solid layers, formed after the processing in negative corona discharge of the PDMS/$H_2O_2$ in different experimental conditions, have been chemically removed and the anodized Al substrates were investigated.

## 3. Results and discussions

Chemical elements present in a porous alumina layer are important to be determined for the identification of the mechanisms responsible for the anodization of the Al substrate.

### 3.1 XPS investigations

By X-ray photoelectron spectroscopy (XPS) were investigated the chemical processes induced by the PDMS/$H_2O_2$ medium at the Al substrate surface. In the XPS spectrum of the porous anodic Al oxide layer obtained after 5 hours of corona discharge processing time, Figure 2, can be observed beside the peaks of Al 2p and O 1s one peak characteristic to Si atoms, Si 2p.

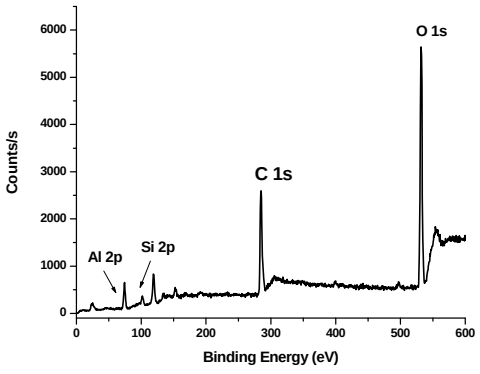


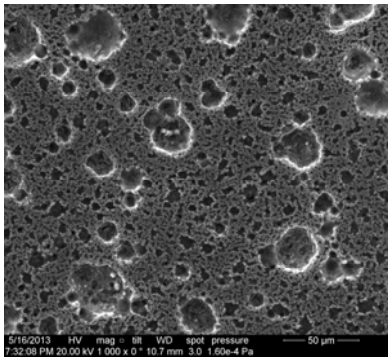

Figure 2: XPS spectrum of the porous alumina layer.

### 3.2 SEM analysis

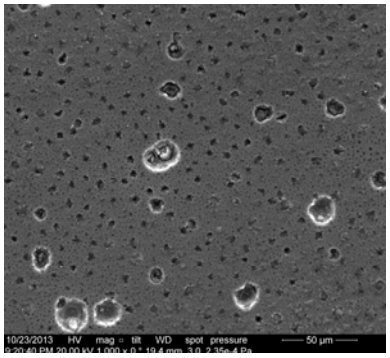
By Scanning Electron Microscopy (SEM) we investigated the morphology of the anodic Al oxide layers. In Figure 4 are presented the images of the porous alumina layers obtained in different

experimental conditions in corona discharges produced in air at atmospheric pressure.

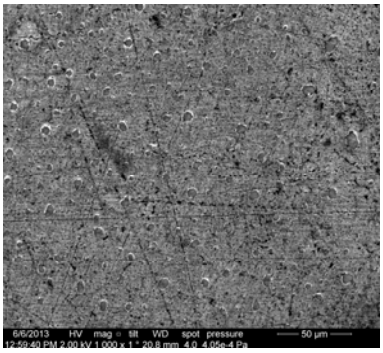
The role of the charged and neutral species produced in corona discharge and those of the chemical species generated in PDMS/ $H_2O_2$ medium on the anodization process of Al surfaces can be analysed from the SEM images presented in Figure 3. Thus, function of the corona discharge processing time and PDMS respectively PDMS/ $H_2O_2$ media presence on the Al surface, the pores shape is changed.



a)



b)



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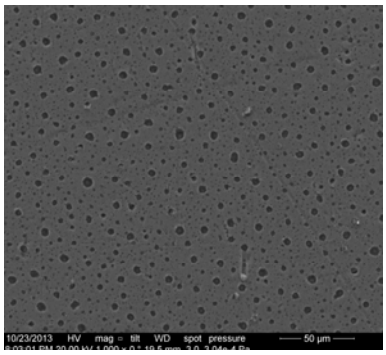

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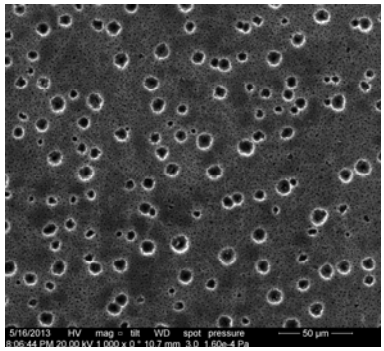

e)

Figure 3: SEM images of porous anodic Al oxide layers obtained in the following experimental conditions: a) ) I = 40 μA, 6 h of corona discharge processing time; b) I = 40 μA, 0.1μl of PDMS, 6 h of corona discharge processing time; c) I = 40 μA, 10 μl of PDMS (33%) - $H_2O_2$ (67%), 3 h of corona discharge processing time; d) I = 40 μA, 10 μl of PDMS (33%) - $H_2O_2$ (67%), 5 h of corona discharge processing time; e) I = 40 μA, 10 μl of PDMS (33%) - $H_2O_2$ (67%), 6 h of corona discharge processing time.

### 3.3 EDS investigations

Elemental compositional analysis was done using energy dispersive X- ray spectroscopy (EDS). All spectra were acquired with an EDAX Inc. SiLi detector attached inside the scanning electron microscope. All the measurements were performed at a voltage of 10 kV.

The EDS spectrum of the porous anodic Al oxide layer is displayed in Figure 4. Beside the peaks of Al and O, a peak characteristic to Si atoms can be observed in this spectrum, its intensity increasing with the processing time. As the SEM images from Figure 3 show no residual pieces of polymer on the surface of porous alumina layer, it result that during the anodization process of the substrate the Si atoms are incorporated into the anodic Al oxide layer.

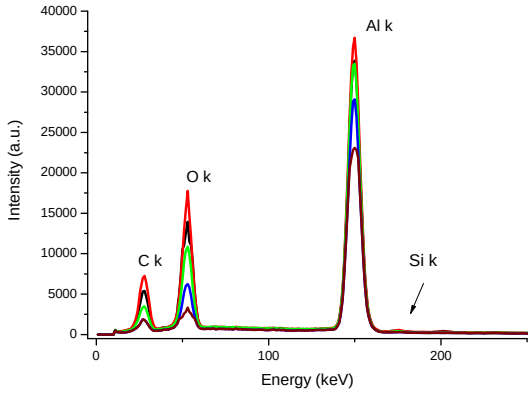


Figure 4: EDS spectrum of the porous alumina layers generated in different experimental conditions: I = 40 µA, 6 h of corona discharge processing time (brown line); I = 40 µA, 0.1 µl of PDMS, 6 h of corona discharge processing time (blue line); I = 40 µA, 10 µl of PDMS (33%)/$H_2O_2$ (67%), 3 h of corona discharge processing time (green line); I = 40 µA, 10 µl of PDMS (33%)/$H_2O_2$ (67%), 5 h of corona discharge processing time (black line); I = 40 µA, 10 µl of PDMS (33%)/$H_2O_2$ (67%), 6 h of corona discharge processing time (red line).

In both XPS and EDS spectra presented above can be observed the Si atoms (coming from PDMS respectively PDMS/$H_2O_2$ medium) incorporation into the porous alumina layer. This result can be explained if we consider that in a classical electrochemical anodization process of Al there are two stages in the pores formation due to the competing oxidation and dissolution processes: a) the growth of aluminum oxide due to the counter migration of $Al^{3+}$, $OH^-$ and $O^{2-}$ ions; b) the dissolution of aluminum oxide at the interface between the alumina film and solution [4].

## 4. Conclusions

In this paper we report the formation of porous anodic Al oxide layers in negative corona discharges both in the absence respectively presence of the PDMS/$H_2O_2$ medium lying on the surface of the Al substrate (anode). We observed that porous alumina layers could be generated only by the negative ions of oxygen and neutral species ($O_3$) produced in negative corona discharge in air at atmospheric pressure. An enhanced infusion of $H_2O$ and OH radicals at the Al substrate surface is assured by the decomposition in the discharge of the $H_2O$ and $H_2O_2$ present in the PDMS respectively PDMS/$H_2O_2$ medium. Even in the negative corona discharges produced in air at atmospheric pressure porous alumina layers are generated, the formation of pores with regular shapes and uniform distributed structures is favorites by the chemical radicals generated in the PDMS respectively PDMS/$H_2O_2$ medium as the SEM images show.
The XPS and EDS measurements indicate that during the pores formation mechanism the Si atoms coming from the PDMS are incorporated into the porous anodic Al oxide layer.

## 5. Acknowledgements

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