

“Computational water splitting, where we are now and where to go?”

February 14-15, 2022, on-line event

Transitioning from barrier to porous Al oxides by tuning anodizing parameters

Noémie Ott¹, Claudia Cancellieri¹, Silvano Radeck¹, Pavel Trtik², Patrik Schmutz¹

¹ Empa, Laboratory for Joining Technologies and Corrosion, Dübendorf, Switzerland

² Paul Scherrer Institut, Laboratory for Neutron Scattering and Imaging, Villigen PSI, Switzerland
noemie.ott@empa.ch

Anodizing is a process widely used in the industry as a surface finish for aluminum substrates to provide corrosion protection, wear resistance, insulating properties, and decorative appearance. By varying the anodizing conditions (electrolyte, applied voltage or current), the structure of the formed anodic Al oxide can be tuned and subsequently functionalized, making it highly attractive for various industrial applications, ranging from large lightweight structures down to nanoscale electronics, optoelectronics, catalysts and sensors. With the increase use of aluminum in our societies, understanding the anodic oxide growth mechanisms, especially with regards to the intermediate barrier(-like) oxide layer, is essential.

The first part of this study focuses on the tuning of anodizing parameters (e.g. surface pre-treatment, electrolyte, temperature, galvanostatic vs potentiostatic growth) to transition from true high-field controlled thin barrier to optimal thick barrier-like anodic Al oxides growth. A specific setup with large area electrodes and small electrode distance has been used to characterize, as a function of the current density distribution along the anode, the properties of the barrier-like oxide formation and defects as well the subsequent porous oxide growth rate.

Electrochemical impedance spectroscopy (EIS) supported by Rutherford Backscattering Spectrometry (RBS) show that the barrier-like oxide formed in phosphoric acid is less defective than the one formed in the commonly used sulfuric acid, both still exhibiting pore initiation and growth. Furthermore, different barrier-like oxides are formed by anodizing in phosphonic acids (with different molecular structures) instead of phosphoric acid, demonstrating that anodic oxide properties can be tuned by changing the phosphorus ion chemical environment.

The second part of the study focuses on visualizing and quantifying the water content in porous Al oxides. During the growth of anodic Al oxide layers, water incorporates in the film and influences the intrinsic properties of the oxide formed. We propose a new approach, based on the use of high-resolution neutron imaging, to characterize porous anodic Al oxides [1]. While single crystal Al₂O₃ is almost neutron transparent, porous anodic Al oxides contain, as expected, water incorporated directly in the oxide structure (structural) in addition to the one present in the pores (morphological). Owing to the high sensitivity of neutrons to hydrogen and thus, to small changes in the water content, we furthermore show that the morphological water content in Al oxides formed in sulfuric acid and in phosphoric acid is partially reversible upon heat treatment and immersion. This consequently motivates a proper quantification of the water content when discussing the nature and structure of anodic Al oxides in relation to their intrinsic properties and stability.

[1] Ott N., Cancellieri C., Trtik P., Schmutz P., *Materials Today Advances*, 8 (2020) 100121