Doctoral Funding Request

Partnership CEA-Grenoble – SATMA PPC

PhD Thesis Title: Investigation of the tunnel pits densification in an aluminum foil for the realization of electrolytic capacitors.

International context.

Capacitor, one of the most widely used electronics components, has been developed for many electronics such as mobile phone, computer, and digital appliances. Recently, in automotive electronics, the need for high power capacitor has increased largely because of the development of hybrid electronic and fuel cell vehicles. Among the currently existing capacitors, aluminum electrolytic capacitor, which has been used for industrial motor inverter application, is basically composed of an anode foil with a dielectric layer of barrier-type anodic aluminum oxide and a cathode foil with an organic electrolyte-impregnated separator sandwiched in between. The resulting capacitance between the anode and the cathode is $C=C_aC_c/(C_a+C_c)$. For the high voltage use (higher than 100V) and to avoid breakdown voltage, the thickness d_a of the anode must be high compare to the one d_c of the cathode, resulting in a high value of the capacity C_c compare to the one C_a of the anode and finally the resulting capacitance C of the capacitor is $C \cong C_a$. In this context the main point is to investigate the anode. For aluminum capacitor, it is important to maximize the surface area of the electrode because the capacitance C_a is directly proportional to the etched aluminum surface area S_a as well as the permittivity ε_a of the dielectric oxide and inversely proportional to the oxide thickness d_a ($C_a=\varepsilon_r\varepsilon_a S_a/d_a$), where ε_r is vacuum permittivity. The resulting capacitor value is clearly dependent of the area S_a and the structuration of anode is needed (Figure 1). Consequently C_a is around few nF for plane structure and around few µF with structuring the anode with tunnel pits.

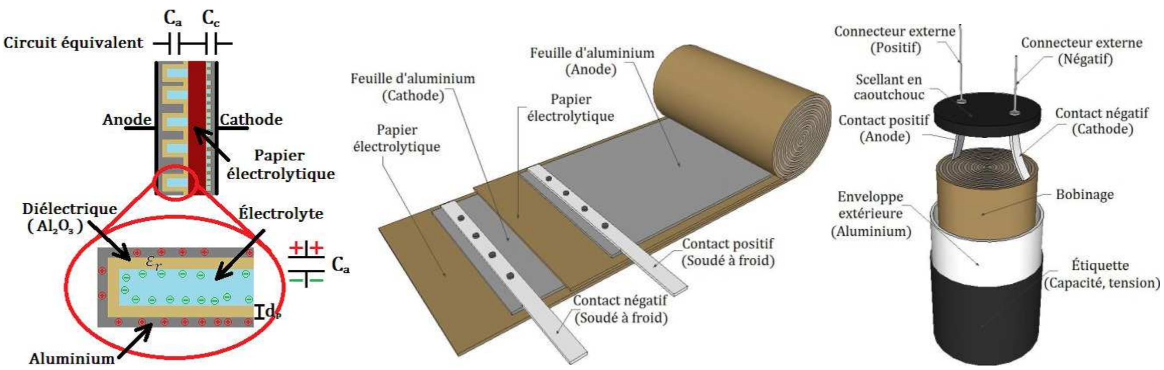

Figure 1 Schematic representation of an electrolytic capacitor.

Objectives

In this work we will fabricate uniform tunnel pits at regular intervals while avoiding an excessive dissolution of the Al surface. The goal of this work is to increase the aluminum surface S_a of the anode through the tunnel pits on an high purity aluminum foil (99.99% (001) oriented), and to inspect the controllability of the etching tunnels. The intended results are to achieved a technological leap relate to the existing results. This investigation will be directly link to the SATMA PPC products. Particular attention will be paid to the publication of patents and articles.

Experimental details

A tunnel pit results from local breakdown of the passive alumina film leading to the metal exposure [1,2]. This corrosion pitting occurs at a weakness of the passive film. The initiation of tunnel pits is generally attributed to the presence of defects in the residual aluminum oxide film. The origin of these defects can be the presence of cracks or inter metallic impurities on which corrosion will mainly occur. Thus, iron is a favorable element for tunnel pits initiation. The electrolyte also plays a role in breaking with Cl^- complex formation. The propagation occurs then with the local oxidation/dissolution of the exposure metal [3,4]. Finally, the tunnel pits stabilization will be controlled by the electrochemical reactions and the environment. Thus, the presence of an oxidant (stronger than water) is essential to stabilize the tunnel pits. The pitting propagates while the electrolyte is sufficiently concentrated in chlorides at the tunnel pits bottom and while the anodic current density is high.

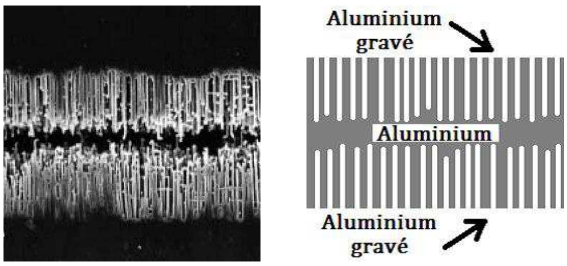

Figure 2: SEM cross section observation of a tunnel pits structure of the anode.

Figure 2 shows a Scanning Electron Microscopy (SEM) cross section and the corresponding scheme. For high voltage capacitors (200-600V) the distance in between tunnels pits is in the order of 1 to 2µm corresponding to a high surface density of few 10^7tunnels/cm². The pitting growth takes place in the (100) direction. Accordingly, the structure of the aluminum foil, (100) oriented, has also a key role.

With all these elements, the different steps of formation and propagation will be investigated for the densification tunnel pits. Several HCl electrolytes will be used (from few 0.1 M up to few 1M), in direct link with the temperature (T from 60°C to 80°C) and also in link with the current density of few 100mA/cm².

Expected work and progress of the PhD thesis

During this work, we will investigate the influence of several parameters for the tunnel pits densification, with the understanding of the tunnel pits formation and propagation. In parallel with the elaboration, the characterization investigations will be essential to understand the formation mechanisms of the achieved material. The characterizations will be first electrochemical and chemical, but also structural with the regular use of electron microscopy (scanning and transmission). Besides, structural observations with x ray diffraction will be conducted at our laboratory. Finally, more detailed investigations will be conducted under x ray beam using a synchrotron radiation source (ESRF or SOLEIL) where we usually perform experiments. *In-situ* measurements of tunnel pits formation under x ray beam will be also performed.

In a first part of the PhD thesis (1 or 1.5 year), the experiments will mainly take place at the CEA-Grenoble INAC (in regular link with the SATMA PPC company). In a second part, the experiments would take place in a more industrial context at the SATMA PPC area.

Qualifications and workplace: Physics and electrochemistry of Materials

The SATMA PPC Company is one of the world's leading manufacturers of aluminum electrolytic capacitors. This industrial partnership is part of the activity "nanoporous alumina for Energy" in existing INAC/CEA-Grenoble past ten years. This team has already made many functional devices for energy-based nanoporous alumina: solar cells, fuel cells, batteries, non-electrolytic capacitors. Industrial partnerships are already underway for fuel cells and non-electrolytic capacitors. Opening up electrolytic capacitors is an opportunity for INAC to access high voltage devices. The partnership will be in both directions since the company SATMA PPC application INAC's scientific expertise to improve these products. By this union of different skills it seems very likely to achieve a technological breakthrough quickly.

The candidate should have a taste for the experience and various technologies which are available in the laboratory. He/She will work at the area of CEA-Minatec and at the SATMA PPC Company. He/She will use the technological platforms. He/She needs to have sound knowledge in electrochemistry and to be interested in industrial middle size company. He/She will need to have a critical mindset, to be curious and autonomous and to keep in mind that all results must match technically and economically with company's specifications. The candidate needs good communication skills and to be a part of this learning organization.

References

[1] N. Osawa, K. Fukuoka, *Corrosion Science* **42**, 585-597 (2000).

[2] D.G.W. Goad, H. Uchi, *J. Appl. Electrochemistry* **30** 285-291(2000).

[3] D. Goad, "Tunnel morphology in anodic etching of aluminum," *Journal of The Electrochemical Society*, vol. 144, no. 6, pp. 1965-1971, 1997.

[4]A. P. Li, F. Muller, A. Birner, K. Nielsch, et U. Gosele, *Journal of Applied Physics*, vol. 84, no. 11, pp. 6023-6026, 1998.