

Development of Coating to Metallic Surfaces with Capacitive Capabilities for Applications in Electronics

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Abstract. The capacitive properties on aluminum alloy coated by sol-gel are evaluated in this work. The samples were anodized in a H₂SO₄ solution for three different times (15, 20 and 30 min) and subsequently covered by a sol-gel. The capacitance of the samples was evaluated by electrochemical impedance spectroscopy (EIS). Firstly the capacitance of the anodizing samples was evaluated. The second condition was the evaluation of the anodized samples coated by sol-gel. The better capacitance results obtained in the first condition was observed in the blank samples and by the 15 min anodized samples. After the sol-gel deposition, the influence of coating on the overall capacitance was observed. Their stability during the immersion time of the evaluation was observed as well.

Introduction

The development of materials for electrode applications and the diverse types of energy storage are intensively studied [1,2]. The capacitors devices contribute decisively to the development of electronics equipments, since they are key components in all forms of electrical devices and are developed for energy storage [3,4].

The use of aluminum in this type of devices is due to its characteristics such as light weight, thermal and electrical conductivity and corrosion resistance [5,6]. When it is exposed to an oxidant environment form a thin, passive and compact film of aluminum oxide (Al₂O₃) [3,7,8-10]. The surface treatment called anodization is aimed to improve the properties of the oxide [3], since it is controlled by these conditions as electrolyte solution, temperature and pH. The anodizing involves the application of a potential or fixed current density. The growing of the oxide occurs by polarization [5,11]. This technique has been used in the electronics industry for over 50 years, being one of the most utilized processes [3,5,12]. Several studies in this area have been performed aiming to develop and enable the evolution of aluminum applications. In this way, the organic-inorganic hybrid materials, as sol-gel process [12], be an alternative of multifunctional materials, with a combination of features and many types of applications [13]. The combination of those two techniques, anodization and sol-gel, might improve the electrical properties, due to the regular deposition of a sol-gel coating that shifts the overall capacitance (substrate + coating), fundamental property of capacitors [7].

Potentiodynamic polarization is a electrochemical method which assess the corrosion behavior of the aluminum alloy. It measures the corrosion potential of an metallic eletrode according to variation of the current, due to reactions in this surface [14]. This technique might be used to provide data to estimate the most appropriate anodizing conditions

When two components with different chemical compositions are in contact, they establish an electric potential difference between them. This potential difference is accompanied by a separation

of charges. A side is positively charged and the other negatively [15,16]. The double layer capacitance is equivalent to a parallel plate capacitor, and the evaluation of it can be determined by EIS technique. The EIS is an electrochemical technique [17] which evaluates the electrical characteristics of the electrode / solution interface. It is a technique applied to many types of studies, as the electron transport in semiconductor devices and in the study of electrochemical kinetics of different processes [18]. With its utilization it is also possible to determine the capacitance of the coating. The EIS measurements can be compared with an equivalent electrical circuit, and the values of capacitance to each component of the surface then estimated.

Materials and Methods

Materials and Sample Preparation. The aluminum alloy samples were cut into sheets and polished with sandpaper (# 120 to # 600). After that, the sheets were cut again into plates of 4.0 x 3.0cm dimension.

Anodization. The plates were cleaned in two different solutions. Firstly with NaOH 0.5 % wt (CAS 1310-73-2) (Proquímicos), 50 °C for 2 min, after with HNO₃ 2.5 % v (CAS 7697-37-2) (Aldrich) solution, at room temperature for 2 min, followed by the anodizing procedure. Three different times 15, 20 and 30 min, were used to anodizing, in a H₂SO₄ 1.5% v (9664-93-9) (Aldrich) solution doped with 15g/L of aluminum powder, with a current density of 9.7 mA/cm². This process (cleaning+anodizing) was done twice, in order to form a more uniform oxide.

Potentiodynamic Polarization Analysis and EIS. The potentiodynamic polarization technique was used to estimate the most appropriated anodizing conditions. The EIS technique was used to evaluate the double layer capacitance. The analysis were performed at room temperature, in NaCl 3.0 % (CAS 7647-14-5) (Aldrich) at pH 2.7. Essays were performed in Gamry Potentiostat Instruments 3000TM, USA, using a three electrode cell with the electrode of Ag / AgCl (197.2 mV – saturated KCl) as reference. For the Potentiodynamic polarization, the open circuit potential was measured for hundred seconds, and for the EIS technique the initial frequency was 100 kHz and the final frequency was 0.1 Hz, with AC voltage of 10 mV/ms. The tests were performed in triplicate.

Sol-Gel Process. The development of the coating using the sol-gel technique was carried out by two precursors solutions. One precursor solution was 2000 µL Titanium (IV) isopropoxide 97% (CAS 546-68-9) (Aldrich) mixed with 2000µL of ethyl acetoacetate ≤99 % (CAS 141-97-9) (Fluka) by magnetic stirring ultrasound (Sonics Vibra cell, USA) in 60% of the maximum amplitude of the equipment for a period of 90 min.

The second precursor solution of sol-gel was formed by 3422.05 µL GPTMS (3-glicidoxipropiltrimetoxisilano) 98%(CAS 2530-83-8) (Aldrich) mixed with 380 2µL methanol PA (CAS 67-56-1) (FMAIA) and 874.5 µL water acidified with HNO₃ 65% (CAS 7697-37-2) (FMAIA) (pH = 1) by magnetic stirring during 1 h.

Then the solutions 1 and 2 were mixed by ultrasound with 60% amplitude for 1 h. The solution formed remained at rest for one hour, so that the aging of it occurred.

Coating deposition. The deposition was performed by dip coating, using a texturometer (Brazil Extralab TA.XT.plus Texture Analyser, USA). The immersion and emersion rate was 50 mm / min with the immersion time of 1 min. The curing of the coating was carried out in an oven (New Ethics, CA), for 1 h at 120 °C.

Evaluation of Coating. EIS measurements were fitted using an equivalent electrical circuit to evaluate the double layer capacitance.

Results and Discussion

From the results of Potentialdynamic Polarization and EIS the best time for anodization was determined.

Potentiodynamic Polarization. The potentiodynamic polarization results of anodized samples indicate that the 15 min of anodizing has the better conditions. It is shown in Fig. 1 that, the corrosion potential is shifted to more positive values in the 15 min anodization, in relation to blank

sample, as well as other times of anodization. A decrease can be noted for the current density in all times of anodization related to blank.

EIS. The Fig. 2 shows the Nyquist diagram of the firsts 0.5 h of immersion for 15, 20 and 30 min of anodization. The analysis and subsequent modeling of the curves has been performed to obtain the values of double layer capacitance. To do so, it was used the equivalent circuit showed in Fig. 3, what is a characteristic for adsorption systems [19]. The choice of equivalent circuit is due to the characteristics of the curves, showing one depressed capacitive loop at the higher frequency range followed by an inductive loop that is observed in the lower frequency region. This inductive loop might relate to the process of NaCl adsorption on the electrode surface. The impedance response for the electrochemical system reflects a distribution of reactivity that is represented in an equivalent electrical circuit as a constant-phase element (CPE) [20]

The same circuit was applied to fit the measurements for all hours of immersion, once the curves obtained showed the same behavior.

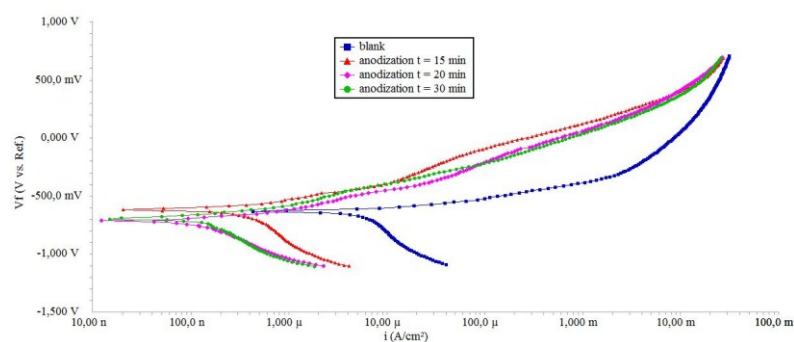


Fig. 1. Polarization curves for de anodization in 3 different times

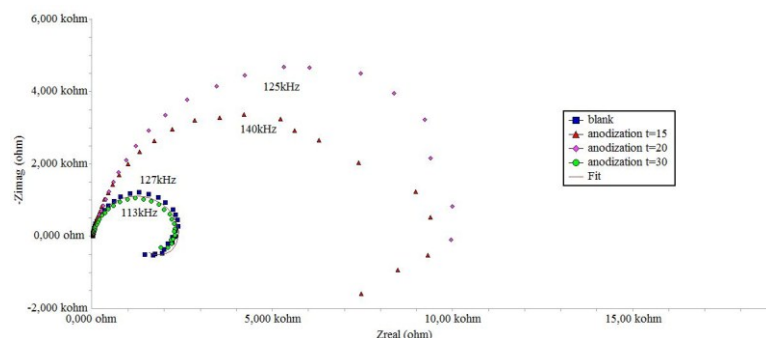


Fig. 2. Nyquist Diagram anodization in 3 different times, at the 0.5 h of analysis.

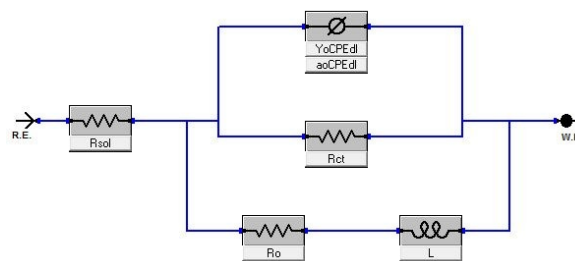


Fig. 3. Model of the equivalent electric circuit used

The values of CPE the double layer capacitance values were determined by the Eq. 1 That considers the maximum frequency ($f_{\text{m\acute{a}x}}$) and the parameters of the CPE (Y_0 and a_0).

$$C = Y_0 (f_{\text{m\acute{a}x}})^{a_0 - 1} \quad (1)$$

Fig. 4 shows the capacitance calculated from a CPE for the anodized samples carried out three times for a period of 120 h. It is possible to observe that higher capacitance is obtained for the native oxide of aluminum (blank samples).

Statistical Analysis. By ANOVA, it was determined that there is no significant variation, with 95% of assurance, for capacitance values in the three times of anodization. Therefore, the time of anodization chosen was the shortest, 15 min. The use of anodization is due to the characteristic of this type of surface treatment, which increases the adhesion of the coating because of the formation of a porous layer [10].

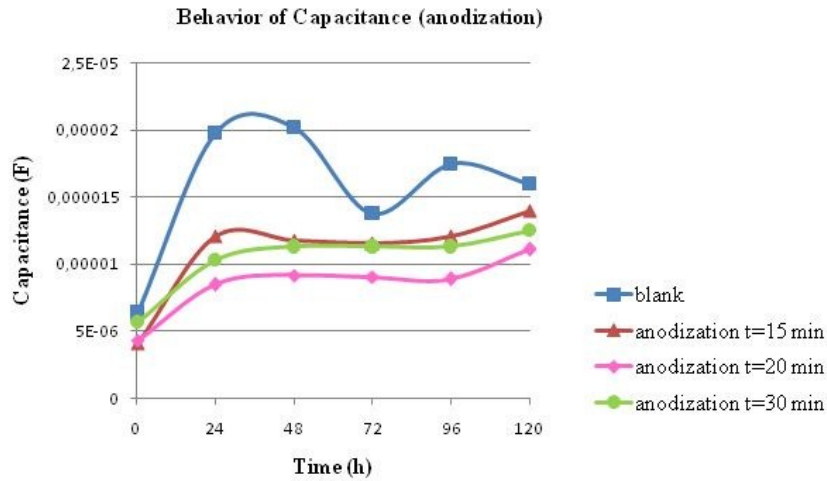


Fig. 4. Behavior of capacitance of anodization in 120h of analysis.

EIS on samples coated by sol-gel. After determining that the 15 min anodizing time was the ideal condition of anodization the coating with TiO_2 by the sol-gel process was done. The values of the capacitance of the aluminum only coated and anodizing plus coating are shown in Fig. 5 for a period of 120 h. The circuit used for modeling the EIS curves is the same above, and the calculation of the capacitance is also the same. It is possible to notice that there is a smaller difference between the capacitance values for several days of analysis, and the difference decreases with the application of the coating, keeping the values of capacitance lower but closer at the same time, indicating a stable capacitance.

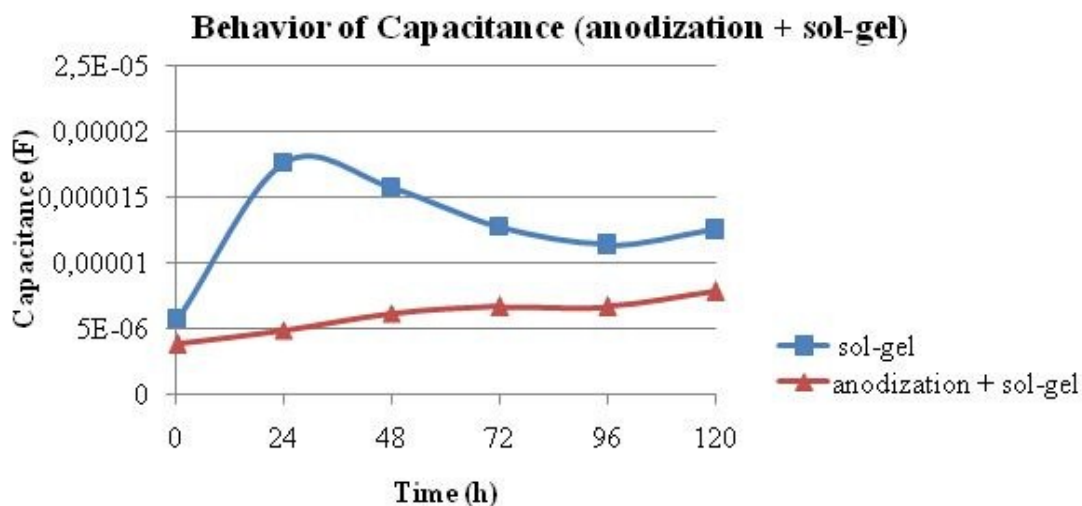


Fig. 5. Behavior of the capacitance with the coating along 120 h.

Conclusions

The graphs show that the coating formed by the sol-gel process provides a lower capacitance than the samples without coating, but with a slight variation between these values over time of analysis, what does not occur when there is an absence of coating. The anodization process aids in the adhesion process of the coating, once the variation of the capacitance of non-anodized aluminum with coating was larger. This might occur due to the dissolution of the sol-gel.

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References

- [1] R. Silva, V. Caliman, and G. G. Silva: Polímeros com Condutividade Iônica: Desafios Fundamentais e Potencial Tecnológico Vol. 15 (2005), p. 249.
- [2] F. Behzadi, M. Moradi, H. R. Karimi-Alavijeh, and A. Gharavi: *Vaccum* Vol. 99 (2014), p. 204.
- [3] F. Trombetta: Elétrolitos à base de líquido iônico tetrafluoroborato de 1-butil-3-metilimidazólio para a aplicação em acapacitores eletrolíticos de alumínio. Mestrado (Dissertação). Porto Alegre, 2010. Universidade Federal do Rio Grande do Sul (UFRGS). (RS).
- [4] K.R. Bray, R.L. C. Wu, S. Fries-carr, and J. Weimer: *Thin Solid Films* Vol. 518 (1) (2009), p. 366.
- [5] C.P. Oliveira: Eletrodeposição de Nanoestruturas de Cobalto em Alumina Anódica Porosa e sua Caracterização Magnética. Doutorado (Tese). São Carlos, 2009. Universidade Federal de São Carlos (UFSCar). SP..
- [6] M.M. Ali and V. Raj: *J. Mater. Sci. Technol.* Vol. 29 (7) (2013), p. 595.
- [7] L.R.B. Holzle: Comportamento eletroquímico do alumínio em misturas etilenoglicol-água. Efeito da adição de agentes quelantes. Doutorado (Tese). Porto Alegre, 2006. Universidade Federal do Rio Grande do Sul (UFRGS). (RS)..
- [8] K.R.L. Castagno: Eletropolimerização de polipirrol sobre a liga de alumínio 1100. Doutorado (Tese). Porto Alegre, 2007. Universidade Federal do Rio Grande do Sul (UFRGS). (RS).
- [9] Tian Lian-peng, Z. Xu-hui, Z. Jing-mao, Z. Xiao-feng, and Z. Yuu: *Trans. Nonferrous Met. Soc. China* 50571006 (2006), p. 1178.
- [10] J.F.T. Júnior: Anodização para obtenção de membranas cerâmicas. Mestrado (Dissertação). Natal, 2007. Universidade Federal do Rio Grande do Norte. (UFRN). (RN)
- [11] F. Bonatto: Síntese e caracterização de nanoestruturas formadas pela anodização de titânio. Mestrado (Dissertação). Porto Alegre, 2009. Universidade Federal do Rio Grande do Sul (UFRGS). (RS).
- [12] R.K. Donato: Líquidos Iônicos como Compatibilizantes para a Preparação de Nanocompósitos Poliméricos de Poliolefinas Apolares e Sílicas. Mestrado (Dissertação). Porto Alegre, 2008. Universidade Federal do Rio Grande do Sul (UFRGS). (RS).
- [13] N.M. José: *Quim. Nov.* Vol. 28 (2) (2005), p. 281.
- [14] V. Gentil: *Corrosão*. (LTC, 4ª ed. 2003).
- [15] G. Castellan: *Fundamentos de Físico-Química*. (LTC Rio de Janeiro, 2007).
- [16] W.J. Moore: *Físico-Química*. (Edgard Blucher 4 ed. Sao Paulo, 1976).
- [17] G.L. Vaz: Eletrodeposição, Caracterização e Estudos de Corrosão de Revestimentos de Ni-Mo e Ni-W. Mestrado (Dissertação). Fortaleza, 2010. Universidade Federal do Ceará (UFC). (CE)
- [18] L.A. Carvalho, P.R. Bueno: *Quimica. Nova* Vol. 29 (4) (2006), p. 796.
- [19] A. Lasia: *Electrochemical Impedance Spectroscopy and its Applications*.
- [20] B. Hirschorn, M.E. Orazem, B. Tribollet, V. Vivier, I. Frateur, and M. Musiani: *Electrochim. Acta* Vol. 55 (21) (2010), p. 6218.