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Anodic oxidization of Al-Y amorphous alloy ribbons and their capacitive properties

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ABSTRACT

Blackish amorphous aluminium oxide film on AlY₁₀ amorphous alloy ribbons was prepared by anodic polarization process in H₂SO₄ solutions, showing electric storage on uneven surfaces with a convexity of 18 nm in diameter. The longest discharging time was obtained by current ratio (I_2/I_1) of 0.4 at 16 V and 5 mass% H₂SO₄. The discharging time increases and decreases with increasing charging time and charging current, and then saturates after around 100 s and 1 μ A, respectively. The resulting film shows a vertical line after Warburg region in a Nyquist diagram, rapid increases in the imaginary impedance, and a phase angle of -90° at 1 mHz in the Bode diagram, demonstrating evidence for use in an electric distributed constant circuit. The film indicates a switching effect for both positive ($\sim +8.6$ eV) and negative (~ -11.2 eV) potentials.

1. Introduction

The storage of electrical energy is one of the topics currently attracting a great deal of interest in the field of scientific and technological research [1–6]. Efficient, high-energy-density electrical energy storage systems play an important role as a power source for devices such as batteries, fuel cells, and electric double-layer capacitors (EDLCs) [1, 6, 7], and provide effective power supply from a grid.

Following the capacitance studies on Ni-Nb-Zr-H amorphous alloys with femtofarad capacitance tunnels [8] and nanocrystalline de-alloyed Si-Al [9, 10], we found a Ti-Ni-Si amorphous alloy supercapacitor [11], constructed using a distributed constant-circuit with large resistance and small capacitance on an amorphous TiO_{2-x} surface containing many 50–70 nm sized cavities with a higher work function of 5.5 eV [12, 13], that can illuminate a red LED for 37 ms after being charged with 1 mA at 10 V. These materials store AC electricity from 193 - 453 K with a voltage variation between 10 - 150 V and a DC capacitance of ~ 4.8 F (~ 52.8 kF/cm³). A common requirement for electric storage is a surface with nanometer-sized cavities and high electrical resistance. The amorphous materials of interest are completely different from conventional “wet” cells, such as electric double-layer capacitors (EDLCs) and secondary cells, which are controlled through the diffusivity of ions. We termed this device a “dry” electric distributed constant capacitor (EDCC) [9–11].

In this study, we report anodic oxidization conditions for amorphous aluminum oxide ($a\text{-Al}_2\text{O}_{3-y}$, AAO) coated AlY₁₀ alloy supercapacitors, with an aim to obtain further higher capacitances and resistivities. Little research

about anodically oxidized aluminum oxides for supercooled amorphous alloys, however, have been carried out. AAO is of considerable interest for electronic applications such as dielectrics [14, 15], capacitors [16, 17], and photoluminescence [18]. The lower surface energy of AAO compared with those of crystalline coarse polymorphs γ -Al₂O₃ and α -Al₂O₃ provides the most energetically stable phase at a surface area greater than 370 m²/g [19]. Our results showed that insulating blackish AAO with nanometer-sized roughness is an ideal candidate for supercapacitors with various electrical applications. Because anodization of crystalline aluminium in acid electrolytes form the AAO with highly ordered 2D hexagonal cylindrical holes having high aspect ratios [20], AAO layers with nanometer-sized pores having lower aspect ratios are practically unable to be realized through the use of crystalline aluminum. In this study, we report an example realized using amorphous AlY₁₀ alloys.

2. Experimental

Al (99.9 % purity), Y (99.5 % purity) and Fe (99.95 % purity) were melted together by induction heating under 0.09 MPa Ar gas in a carbon crucible. AlY₁₀ and AlY₁₀Fe₅ (nominal compositions) alloys were prepared by melt spinning technique, using a single-wheel melt-quenching apparatus (RQM-T-20, Makabe Giken). A quenching from a melt was done with a tangential velocity of 51.1 m/s in He atmosphere. Ribbon specimens were 50 μ m thick and 1–5 mm wide. The blackish AAO specimens were prepared by using the anodic polarization process in 1, 2, 3, 5 and 10 mass% H₂SO₄ solution at 14-18 V, with AlY₁₀ alloy ribbons under air bubbling of 10 cc/s, using platinum counter electrode. Sample structure was examined by X-ray diffraction (XRD; Rigaku RINT2200) in reflection mode with monochromatic Cu K α radiation. Since the oxidized

surfaces were sandwiched directly by two copper ribbons as electrodes using a clamp [12], we cannot measure directly electron state of the oxide elements by X-ray photoelectron spectroscopy (XPS) method that is characterized by direct irradiation of a beam of X-rays while simultaneously measuring the kinetic energy. Thus we used the noncontact-scanning Kelvin probe-atomic probe-microscopy (NC-AFM, JSPM-5200, JEOL) for direct measurement of absolute electrical potentials between the Pt-coated cantilever tip at 0 and (1 or -100) V and the AAO surface without electrodes.

The charging/discharging behavior of the specimen was analyzed using the galvanostatic charge/discharge on a potentiostat/galvanostat (SP-150, BioLogic Science) with DC of 10 V and current in the range from 1 pA to 1 mA for ~600 s at room temperature, with a complex impedance between 1 mHz and 1 MHz and 10 mV.

3. Results and discussion

3.1 Anodic oxidization of amorphous AlY₁₀ and AlY₁₀Fe₅ alloys and crystalline Al and discharging characteristics

The AAO thin-films are generally prepared by laser deposition [21], plasma electrolytic oxidization [22] and anodic oxidization [18, 23, 24] of crystalline aluminum specimens, and sol-gel method by hydrolysis and polycondensation of an aluminum alkoxides [25]. We selected the anodic oxidization method for formation of the AAO film. With an aim to obtain higher capacitances and resistivity, we carried out anodic oxidization for ribbons of amorphous AlY₁₀ and AlY₁₀Fe₅ alloys and crystalline aluminum at 15 V for 3.6 ks in 10 mass% H₂SO₄ electrolyte. The current-time curves during potentiostatic polarization are shown in Fig. 1(a). All curves show abrupt increase at beginning of oxidization. The amorphous AlY₁₀Fe₅ alloy and the crystalline aluminum

then rapidly decrease up to 10 s, and then the former keeps the decreasing and the latter increases to a steady-stage value, while the amorphous AlY₁₀ alloy shows gradual decrease up to 180 s and then keeps the steady stage. The steady-state curve responds to formation of oxide layers [26]. The maximum values for current density of amorphous AlY₁₀ and AlY₁₀Fe₅ alloys are 36 and 2 times larger than one of crystalline aluminum, respectively. The polarization of the former is characterized by large dissolution of aluminum ions in electrolyte and then slow deposition of amorphous alumina. This would be due to lower formation energy in comparison with that of the latter. On the other hand, the curve of the amorphous AlY₁₀ alloy displays etching due to spark discharging. The surface color reveals light yellowish white for amorphous AlY₁₀Fe₅ alloy and crystalline aluminum, and blackish for amorphous AlY₁₀ one (inset of Fig. 1a). The light yellowish white color comes from cluster structure with a mixture of AlO₄ tetrahedron and AlO₅ hexahedron, while the blackish one is derived from cluster structure of AlO₆ octahedron [27]. Discharging characteristics of anodically oxidized amorphous AlY₁₀ and AlY₁₀Fe₅ alloy and crystalline Al ribbons are investigated, using a potentiostat/galvanostat at room temperature. These results are shown at Fig. 1b. Although the oxidized AlY₁₀ alloy showed superior electric storage up to 420 s, the oxidised AlY₁₀Fe₅ alloy and crystalline Al did not show prolong discharging behaviors over 8 s. Thus we use the anodically oxidized AlY₁₀ alloy in this study.

3.2 Effects of applied voltage, content and oxidization time of H₂SO₄ for discharging time

In order to make clear effects of applied voltage and content of H₂SO₄ for discharging time, we carried out anodic oxidization for 35-340 s at voltages of 14-18 V,

using H₂SO₄ electrolytic solution of 1, 2, 3, 5 and 10 mass%. The discharging times for H₂SO₄ content is shown at Fig. 1c, as a function of applied voltages. Voltages over 16 V make the specimens break down during anodic oxidization. All curves except for 2 mass%H₂SO₄ show maximum discharging times at 16 V. The discharging time at 16 V indicates maximum value at 5 mass%H₂SO₄ (Fig. 1d). A representative X-ray pattern for oxidized specimen obtained at 16 V in 5 mass%H₂SO₄ solution is shown in the inset of Fig. 1d. The XRD pattern of an Al-based amorphous alloy is characterized by a large and broad peak at 38°.

The discharging behaviors under a constant current of 1 nA after charging at DC currents of 1 mA for 50 s are shown in Fig. 2a, as functions of current ratio (I_2/I_1) during anodic oxidisation, where I_1 and I_2 in inset of Fig. 2a are the maximum current corresponding to starting time of oxidization and the minimum current corresponding to final time, respectively. When formation of the oxide film starts from time T_1 of I_1 and continues to time T_2 , Fig. 2a shows the maximum electric storage can be obtained by the ratio of around 0.4, corresponding to formation of quasi-stable oxide film. This suggests an existence of optimum thickness or structure of films for electric storage. Figure 2b shows an AFM image of the surface structure for a specimen oxidized at current ratio of 0.49. The outside porous like appearance of the surface (SEM and AFM image insets of Fig. 2a and Fig. 2b, respectively) bears a close resemblance to that of anodic oxidized amorphous TiO_{2-x} surfaces in previous papers [12, 13]. This figure depicts an uneven surface with a convexity of 18 nm and a concavity of 15 nm in diameter, and 7 nm in depth. The TEM image will be minutely described in the following paper. We use the specimen hereafter.

3.3 Effect of charging current on charging and discharging time

The discharging behavior under a constant current in the range from 1 pA to 100 nA after prompt charging up to 10 V at a DC current of 1 mA is shown in Fig. 3a. The rapid decrease in voltage at the beginning of discharging is analogous to IR drop in EDLCs [28]. The discharging time decreased with increasing charging current. Figure 3b shows discharging behaviors under a constant current of 1 nA after charging for 1, 10 and 50 s. The discharging time increases with increasing charging time and then saturates after around 100 s (inset of Fig. 3b). Fig. 3c shows charging current dependence of charging and discharging time in experiment of Fig. 3b. The charging and discharging times extremely decrease up to 1 μ A and saturate, as charging current increases. Thus we used charging current of 1 mA in this study.

In previous paper [27], we proposed a possible mechanism that electro double layers are formed at the electrically negative convex portion/air and positive concave portion/air interfaces in an uneven surface with nanometer-sized cavities of AAO, when positive voltage is applied to the electrode connecting to the concave portions in charging process, as well as ATO [11]. The charging and discharging procedure is schematically shown in Fig. 4a and b, respectively, using supercapacitors with an electric distributed constant circuit (Fig. 4c). Electrostatic potentials charged at 10 V and discharged down to 5 V are presented at Fig. 4e. These corresponding potentials are indicated by two arrows on the discharging curve (Fig. 4d) characterized by a formula of $E = \exp(-t/1.06)$, where E and t are voltage and discharging time, respectively. Figure f shows an adsorption and desorption reaction formula of electron (coverage θ) at AAO surface for the charging and discharging process, as proposed by Conway *et al.* [29].

Then, we investigate the electricity switching effect of AAO. When the positive 1 V

was applied the specimen (Fig. 5a), we observed an electrostatic potential distribution (inset of Fig. 5c) and the corresponding electrostatic potential profiles down to 8.6 eV in four directions every 90 ° (Fig. 5c). When applying negative 100 V to the specimen (Fig. 5b) for 30s, we observed the potential distribution down to -12.2 eV (see Fig. 3d of Ref. 27). The time dependent potential variation (Fig. 5(d)) shows linear decrease of the potential. This demonstrates the electricity switching effect from positive to negative potentials of the AAO. This behavior was repeated by switching of the electricity, showing the reversible exchange of the electric polarity. This will provide rechargeable dry capacitors in place of practical Li ions, as described at previous paper [27]. The electricity switching on convex and concave portions in connection with charging and discharging is schematically shown at Fig. 5(e), along with cyclic electrostatic potentials. However, we must furthermore make clear changing mechanism of element valence state for sample switched electricity.

3.4 Complex electric evaluation of electric storage

To non-destructively analyze the electrostatic contribution of the specimen, we measured the AC impedance from 1 mHz to 1 MHz in Nyquist and Bode diagrams at room temperature. A complex-plane (Nyquist) plot of the impedance data is shown in Fig. 6a. The specimen's variation in impedance with frequency followed the combined pattern of two semitrue and flat circles. The vertical line of the impedance data (5.0 G Ω) fits a nearly vertical line, as produced by a series RC circuit, as well as a graphene EDLC [31]. There were rapid increases in the imaginary impedance, as compared with the real impedance, in the lower-frequency region of the Bode diagram (Fig. 6b). Moreover, the decrement in phase angle to -90° with decreasing frequency is evidence of DC charging

(Fig. 6c). This means that each capacitor on the AAO specimen is connected with a parallel circuit, *i.e.* with integrate capacitance, $C = \sum_{k=1}^n C_k = nC$. This means that further advances in the development of AAO supercapacitors might be attained by integrating oxide ribbons with a nano-electro mechanical system (NEMS). Thus, AAO offers a nearly ideal electric distributed-constant structure for electric storage. Although the series capacitance was 0.036 μF at 1 mHz (Fig. 6d), the DC capacitance could be increased considerably.

4. Conclusion

Amorphous Al-10 at.%Y and Al-10 at.%Y-5 at.%Fe alloys and crystalline Al prepared by the rotating wheel method were anodically oxidized for 3.6 ks in 1, 2, 3, 5 and 10 mass% H_2SO_4 solution at 14-18 V and 278 K. Because oxidized samples of amorphous Al-10 at.%Y-5 at.%Fe alloy and crystalline Al did not show electric storage, we used blackish ones oxidized at 16 V in 5 mass% H_2SO_4 solution using amorphous Al-10 at.%Y alloys. AFM images showed the uneven alumina surface with a convexity of 18 nm in diameter. The discharging time increases with increasing charging time and then saturates after around 100 s. The charging and discharging times extremely decrease up to 1 μA and saturate with increasing charging current, respectively. The time dependent potential variation showed the electricity switching effect from positive to negative potentials of the AAO. AC impedance measurement showed a vertical line after Warburg region in the Nyquist diagram, rapid increases in the imaginary impedance, as compared with the real impedance, and the phase angle of -90° at 1 mHz in the Bode diagram, demonstrating evidence for series-RC circuit.

References

- [1] B. E. Conway, *Electrochemical Super-capacitors: Scientific Fundamentals and Technology Applications*, Plenum Press, New York, 1999.
- [2] M. Winter, R.J. Brodd, What are batteries, fuel cells, and supercapacitors? *Chem. Rev.* 104 (2004) 4245-4269.
- [3] A. S. Aricò, P. Bruce, B. Scrosati, J.M. Tarascon, W. Schalkwijk, Nanostructured materials for advanced energy conversion and storage devices, *Nat. Mat.* 4 (2005) 366-377.
- [4] M. S. Whittingham, Materials Challenges Facing Electrical Energy Storage, *MRS Bull.* 33 (2008) 411-419.
- [5] P. Simon, Y. Gogotsi, Materials for electrochemical capacitors, *Nat. Mat.* 7 (2008) 845-854.
- [6] M.F. El-Kady, V. Strong, S. Dubin. R.B. Kaner, Laser Scribing of High-Performance and Flexible Graphene-Based Electrochemical Capacitors, *Science* 335 (2012) 1326-1330.
- [7] A. S. Aricó, P. Bruce, B. Scrosati, J. M. Tarascon, W. Van Schalkwijk, Nanostructured materials for advanced energy conversion and storage devices. *Nat. Mat.* 4, 366-377 (2005).
- [8] M. Fukuhara, M. Seto, A. Inoue, AC impedance analysis of a Ni-Nb-Zr-H glassy alloy with femtofarad capacitance tunnels, *Appl. Phys. Lett.* 96 (2010) 043103.
- [9] M. Fukuhara, T. Araki, K. Nagayama, H. Sakuraba, Electric storage in de-alloyed Si-Al alloy ribbons, *Europhys. Lett.* 99 (2012) 47001.
- [10] M. Fukuhara, Electric charging/discharging characteristics of capacitor, using de-alloyed Si-20Al alloy ribbons, *Electric. Electron. Eng.* 3 (2013)

72–76.

- [11] M. Fukuhara, T. Kuroda, F. Hasegawa, Amorphous titanium-oxide supercapacitors, *Sci. Rep.* **6** (2016) 35870.
- [12] M. Fukuhara, H. Yoshida, M. Sato, K. Sugawara, T. Takeuchi, I. Seki, T. Sueyoshi, Superior electric storage in de-alloyed and anodic oxidized Ti-Ni-Si glassy alloy ribbons, *Phys. Stat. Sol. (RRL)*, **7** (2013) 477–480.
- [13] M. Fukuhara, K. Sugawara, Electric charging/discharging characteristics of super capacitor, using de-alloying and anodic oxidized Ti-Ni-Si amorphous alloy ribbons, *Nanoscale Res. Lett.* **9** (2014) 253-1-6.
- [14] G. D. Wilk, R. M. Wallace, J. M. Anthony, High- κ gate dielectrics: Current status and materials properties considerations, *J. Appl. Phys.* **89**, 5243-5275 (2001).
- [15] P. Katiyar, C. Jin, R. J. Narayan, Electrical properties of amorphous aluminium oxide thin films, *Acta Mater.* **53**, 2617-2622 (2005).
- [16] A. I. Mardare, M. Katltenbrunner, N. S. Sariciftci, S. Bauer, A. W. Hassel, Ultra-thin anodic alumina capacitor films for plastic electronics, *Phys. Stat. Sol. A.* **209**, 813-818 (2012).
- [17] R. Kötz, M. Carlen, Principles and applications of electrochemical capacitors, *Electrochim. Acta.* **45**, 2483-2498 (2000).
- [18] G. G. Khan, A. K. Singh, K. Mandal, Structure dependent photoluminescence of nanoporous amorphous anodic aluminium oxide membranes: Role of F^+ center defects, *J. Lumin.* **134**, 772-777 (2013).
- [19] A. H. Tavakoli, P. S. Maram, S. J. Widgeon, J. Rufner, K. van Bethem, S. Ushkov, S. Sen, A. Navrotsky, Amorphous alumina nanoparticles:

- structure, surface energy, and thermodynamic phase stability, *J. Phys. Chem. C* **117**, 17123-17129 (2013).
- [20] H. Masuda, K. Fukuda, Ordered metal nanohole arrays made by a two-step replication of honeycomb structures of anodic alumina, *Science*, **268**, 1466-1468 (1995).
- [21] M. Jiménez de Castro, R. Sera, J. A. Chaos, C. N. Afonso, E. R. Hodgson, Influence of defects on the photoluminescence of pulsed-laser deposited Er-doped amorphous Al₂O₃ films, *Nucl. Instrum. Method Phys. Res.* **B 166–167**, 793–797 (2000).
- [22] X. Nie, I. Meletis, J. C. Jiang, A. Leyland, A. L. Yerokhin, A. Matthews, Abrasive wear/corrosion properties and TEM analysis of Al₂O₃ coatings fabricated using plasm electrolysis, *Surf. Coat. Tech.* **149**, 245–251 (2002).
- [23] A. I. Mardare, M. Katltenbrunner, N. S. Sariciftci, S. Bauer, A. W. Hassel, Ultra-thin anodic alumina capacitor films for plastic electronics, *Phys. Stat. Sol. A* **209**, 813-818 (2012).
- [24] T. Iijima, S. Kato, R. Ikeda, S. Ohki, G. Kido, Structure of duplex oxide layer in porous alumina studied by ²⁷Al MAS and MQMAS NMR, *Chem. Lett.* **34**, 1286-1287 (2005).
- [25] L-J. Yin, G-Z Chen, C. Wang, X. Xu, L-Y. Hao, H. T. Hintzen, Tunable luminescence of CeAl₁₁O₁₈ based phosphors by replacement of (AlO)⁺ by (SiN)⁺ and co-doping with Eu, *J. Sol. Stat. Sci. & Tech.* **3**, R131-138 (2014).
- [26] M. Fukuhara, K Sugawara, Anodic oxidization of Ti-Ni-Si amorphous alloy ribbons and their capacitive and resistive properties, *Thin Solid Films*, **595**, 1–4 (2015), DOI:10.1016/j.tsf.2015.10.041.
- [27] M. Fukuhara, T. Kuroda, F. Hasegawa, T. Hashida, E. Kwon and K. Konno,

- Amorphous aluminium-oxide supercapacitors, *EuroPhys. Lett.*, **123**, 58004 (2018).
- [28] M. Okamura, Characteristics of electric double layer capacitor for ECS usage, *Transistor Technol.* (in Japanese), **4**, (9) 343-351 (2001).
- [29] B. E. Conway, V. Birss and J. Wojtowicz, *J. Power Sources*, **66**, 1-14 (1997).
- [30] M. Itagaki, *Electrochemistry, Impedance Method*, 2nd edition, (Maruzen, Tokyo, 2012).
- [31] J. R. Miller, R. A. Outlaw, and B. C. Holloway, Graphene double-layer capacitor with ac line-filtering performance, *Science* **329**, 1637-1639 (2010).

Figure Legends

Fig. 1 (a) Current-time curves for amorphous AlY_{10} and $AlY_{10}Fe_5$ alloy and crystalline aluminum ribbons during anodic oxidization at 15 V and 278 K for 3.6 ks in 10 mass% H_2SO_4 electrolyte solution. Inset: photographs of crystalline aluminum, amorphous $AlY_{10}Fe_5$ and AlY_{10} alloys after anodic oxidization. (b) Discharging characteristics of anodically oxidized amorphous AlY_{10} and $AlY_{10}Fe_5$ alloy and crystalline Al ribbons. (c) Discharging times for various H_2SO_4 contents, as a function of applied voltages. (d) The effect of H_2SO_4 content for discharging times at 16 V. Inset: XRD pattern.

Fig.2 (a) Effects of current ratio in anodic oxidization on discharging time for AAO. (b) AFM image of the AAO surface. Inset in (a): SEM image, Inset in (b): three-dimensional AFM image.

Fig. 3 (a) Discharging behaviors of the AAO device for voltage at constant currents from 1 pA to 100 nA. (b) Charging time dependence of charging and discharging time after 1 mA-10 V charging. Inset of (b): The charging time dependence of the discharging time. (c) Charging current dependence of charging and discharging time in experiment of Fig. 3(b).

Fig. 4 Charging (a) and discharging (b) procedure for supercapacitor with the electric

distributed constant circuit (c). Electrostatic potential states after charging at 10 V and discharging down to 5 V, indicated by two arrows on the discharging curve (d). (f) Adsorption and desorption reaction formula of an electron for AAO.

Fig. 5 Schematic views of SKPM equipment for application of a positive 1 V (a) and negative 100 V (b). (c) Electrostatic profiles in four directions (L1, L2, L3, and L4) every 90° after the application of positive 1 V for 30 s to the AAO specimen. (d) The time dependent potential variation from 0 to 30s after the application of negative 100 V. (e) Schematic representation of concave and convex dependences of the electron potentials for the concave and convex portions of AAO, respectively. Left and right figures correspond to charging and discharging processes, respectively.

Fig. 6 (a) Nyquist plot as a function of frequency for AAO device. (b) Real and imaginary impedances. (c) Phase angle. (d) Series capacitance.