

Black-colored Metallic Aluminum Obtained by Electrolytic Etching in a Highly Concentrated LiTf_2N Aqueous Solution

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1. Introduction

Aluminum (Al) surface is electrochemically treated in various ways such as electrochemical etching, anodic oxidation, and color treatment.^{1)–10)} Electrochemical etching of Al is used to enlarge surface area for the application as aluminum electrolytic capacitors. In hydrochloric acid, direct current (DC) etching gives tunnel-like pits while alternative current (AC) etching gives sponge-like pits. Without Cl^- , electrolytic etching of Al is difficult: for example, the use of sulfuric acid gives thick Al oxide layers.

Recently, an amide-containing highly concentrated aqueous (HCA) solution attracts considerable attention as a lithium ion battery electrolyte due to its low free water content and the high stability against water oxidation.^{11)–15)} Thus, the high electrochemical stability would change the anodic oxidation behaviors of aluminum. In this paper, the anodic behavior of Al in the amide-containing HCA solution is studied.

2. Experimental

Lithium bis[(trifluoromethyl) sulfonyl] amide (LiTf_2N ; $\text{Tf} = \text{CF}_3\text{SO}_2$) was purchased from Kishida Chemical and used without further purification. 20–21 mol kg^{-1} LiTf_2N aq., of which water content is 14–15 wt% H_2O , was prepared with ultrapure water and used as electrolyte solution. Al sheets (99% purity) were used as working and counter electrodes. Ag/AgCl immersed in 3.0 mol dm^{-3} NaCl aq. was used as reference electrode (RE), separated from the HCA solution using porous Vycor® glass as liquid junction. Note that conventional KCl aq. is not applicable for Tf_2N^- containing HCA solution because the use of K^+ ion gives the deposition of water-insoluble KTf_2N at around the junction. Cyclic voltammetry was conducted at a scan speed of 2 mV s^{-1} for 15 cycles at room temperature in air without agitation; the 1st scan started at open circuit potential (ca. -0.2 V vs. RE), switched at $+4.0$ V vs. RE — this is because oxygen evolution was observed at around $+4.0$ V —, and ended at $+1.4$ V vs. RE. The 2nd–15th scan were cycled between $+1.4$ V and $+4.0$ V vs. RE (sample #1). Potentiostatic electrolysis at $+2.5$ V vs. RE was conducted for 18 h at the same cell conditions (sample #2): in the first 1 h, the observed anodic currents increased to the order of mA cm^{-2} , and decreased in a few hours to approximately 0.3 mA cm^{-2} , then became almost constant. Both samples showed black appearance at the immersed area (7.5 mm ϕ ; see the inset of Fig. 2 a). It is worth

noting that sample #2 showed the reflectance of about 15% in visible light region, measured using HITACH U-3500.

The microstructure of the anodized Al (sample #1) was observed using scanning electron microscope (SEM, VE-8800; KEYENCE). For transmission electron microscope (TEM, JEM-2100F; JEOL) observation and electron diffraction (ED) measurements, a thin specimen was prepared by sputtering the anodized Al (sample #2) with focused ion beam (FIB, JFIB-2300; JEOL) instruments. The composition was analyzed using energy dispersive X-ray spectroscopy (EDX, JED-2300T; JEOL) attached to the TEM. To visualize local pH change during electrolysis, another run of electrolysis at $+2.5$ V vs. RE was carried out, where bromothymol blue (BTB) solution (Kishida Chemical) was added as a pH indicator. Viscosity was measured at 25 °C using EMS-1000 (Kyoto Electronics Manufacturing).

3. Results and Discussion

Fig. 1 shows the CVs of Al electrode immersed in the HCA solution of LiTf_2N . At every cycle, the back-scan tends to show larger current than the forward-scan, strongly suggesting a pit corrosion. In the previous reports, the potential for anodic stability of Al in the HCA, i.e. the anodic electrochemical window, is approximately $+4.8$ V vs. Li/Li^+ ,^{14),15)} which can be converted to $+1.6$ V vs. Ag/AgCl . In this work, the anodic electrolysis of Al was conducted above the reported electrochemical window, resulting in the enhancement of Al corrosion. Notably, in the previous report, smaller anodic currents were observed as the cycle number

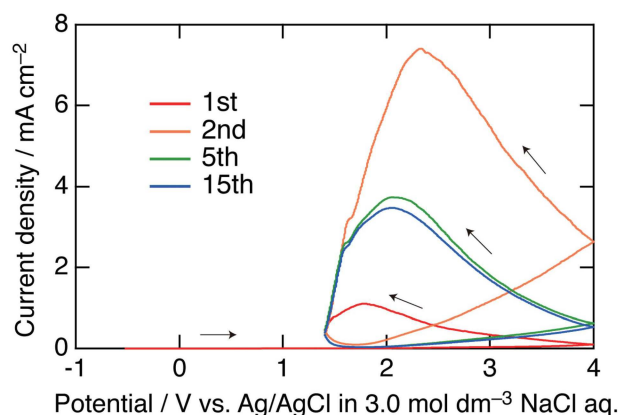


Fig. 1 Cyclic voltammograms of Al electrode immersed in the HCA solution of LiTf_2N . Scan rate: 2 mV s^{-1} .

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increases, suggesting a passivation.^{14),15)} In Fig. 1, by sweeping the potentials to negative direction from +4.0 V vs. Ag/AgCl, broad maxima were observed at around +1.5 V – +2 V, followed by sharp decrease of the anodic currents. Since the potentials for the broad maxima are similar to the reported anodic electrochemical window, passivation of some kind should occur below potentials of the broad maxima.

Fig. 2 displays SEM images of an Al sample (sample #1) anodized in the HCA solution of LiTf_2N . In plan and cross-sectional views, sponge-like pores were found (Figs. 2 a and 2 b). For comparison, the cross-sectional view of a pristine Al sample is shown in Fig. 2 c. The inset of Fig. 2 a displays that the anodized area becomes black, probably due to its highly rough surface and the nanoporous microstructure like in the case of nanoporous gold or silver showing black appearance.¹⁶⁾

The TEM, ED, and TEM-EDX mapping results of the anodized Al (sample #2) are shown in Fig. 3. The bright-field image in Fig. 3 a displays pores (dark area) and skeleton (bright area), and the pore diameter is approximately 100 nm. The ED pattern in Fig. 3 b confirms the porous layer consists of metallic Al with face-centered-cubic structure. The TEM-EDX mapping results of Al in Figs. 3 c-f confirm that Al element is present on entire area of the skeleton while oxygen, fluorine, and sulfur are detected mainly on the edges, which should be derived from Tf_2N^- anions. Thus, a very thin film (few nm) of oxides, fluorides, and sulfides is present on the pore wall surface. Consequently, the porous layer is mainly composed of metallic Al, and it was proved that the anodizing of

Al in the HCA solution does not give thick oxide layers but cause active dissolution of Al.

In contrast to the conventional anodizing treatments, sponge-like pits are formed through DC treatment without using Cl^- ions.^{7)–10)} Instead of Cl^- , it is possible that Tf_2N^- dissolves Al_2O_3 by forming complex ions with Al^{3+} such as $[\text{Al}(\text{Tf}_2\text{N})_x]^{3-x}$.^{17)–20)} However, the obtained pits/pores in the present work is spherical, in contrast to the conventional cube-shaped pits/pores.^{7)–10)} Additionally, sponge-like pit has been obtained only when AC etching is used, by which Cl^- is accumulated to dissolve Al or dissipated to passivate the Al surface. Therefore, another mechanism should exist for the DC etching in the HCA solution.

We speculate that the pH change near the Al electrode causes the unconventional anodizing behavior. Fig. 4 displays the visualized local pH change of the HCA electrolyte before and during electrolysis. Before electrolysis, a glass electrode indicated pH 4 and the color of the HCA solution was yellow and homogeneous (see Fig. 4 a). During the electrolysis, by contrast, the color became inhomogeneous (see Fig. 4 b): the solution near the anode was red, i.e., strongly acidic, and the solution near the cathode was blue, i.e., basic. During electrolysis, bubbles were observed both at anode and cathode. This strongly suggests that O_2 evolves and H^+ is generated at the anode, while H_2 evolved at the cathode. Since the HCA solution is highly viscous (4×10^1 mPa s at 25 °C) and contains few free water, the proton mobility may be greatly lower than those of conventional aqueous solutions. Therefore, the diffusion of the electrochemically generated H^+ and OH^- is anomalously slow to cause the pH difference as shown in Fig. 4. The

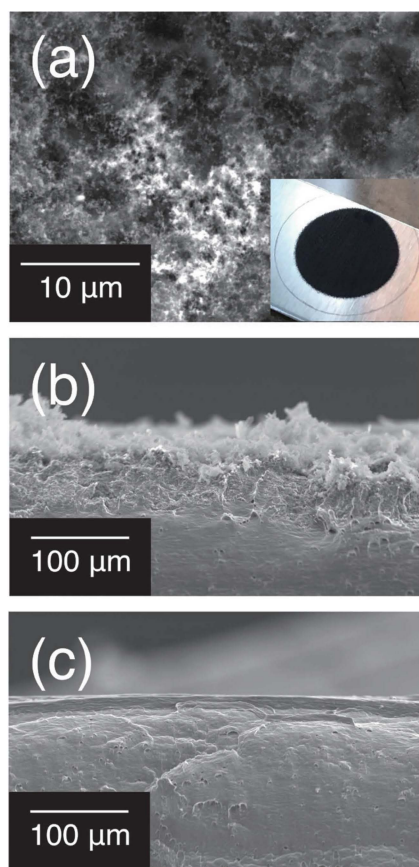


Fig. 2 (a) Plan view and (b) cross sectional view of the anodized Al sample and (c) cross-sectional view of pristine Al sample. Inset of (a) shows photograph.

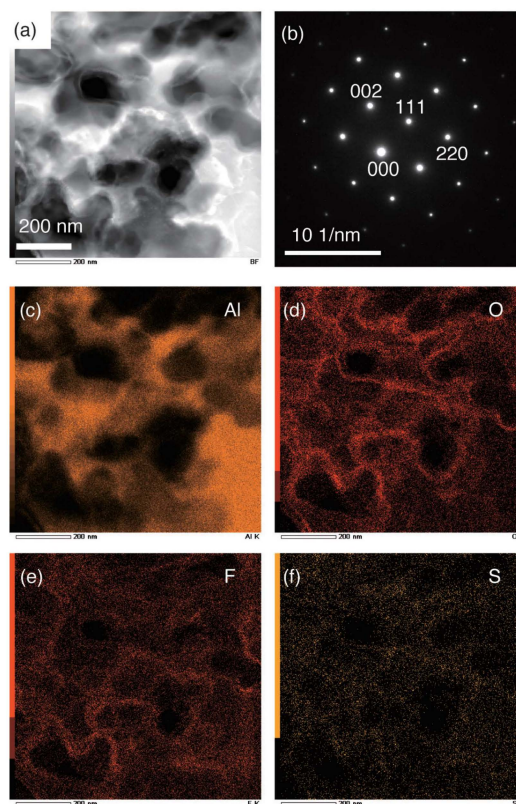


Fig. 3 (a) Bright-field TEM image and (b) electron diffraction pattern toward [110] direction of anodized Al specimen, and (c-f) its EDX mapping results of (c) aluminum, (d) oxygen, (e) fluorine, and (f) sulfur.

results imply that the strongly acidic condition near Al electrode plays an important role in the sponge-like pit/pore formation.

4. Conclusions

Al was anodized in an amide-containing HCA solution. Surprisingly, the anodic polarization resulted in black appearance and spongiform pits. Such “black Al” is very attractive because the blackness derives from structural color, which cannot be degraded by light in contrast to dye-based black alumites. Additionally, its surface is highly conductive, while those of conventional Al materials with black appearance such as black alumites are poorly conductive which easily build up static electricity. The formation mechanism seems to be different from those of conventional anodizing or etching of Al, since (i) a low constant voltage is applied, (ii) LiTf_2N aq. is a weak acid solution and (iii) O_2 gas evolves on working electrode during the anodic polarization. Further researches may include utilization of the black porous Al as battery

current collector, electrolytic capacitor, and optical materials with antistatic properties.

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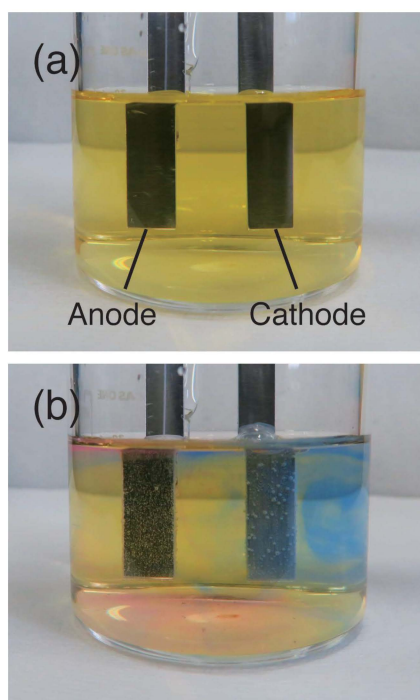


Fig. 4 Local pH change during the potentiostatic electrolysis at +2.5 V vs. RE, visualized using BTB indicator: (a) before electrolysis and (b) during electrolysis.