Anodization Behavior of Aluminum in Ionic Liquids with a Small Amount of Water

Kazuyuki TATEISHI, a,*, Hiroyuki OGINO, a Akiko WAKI, a Takahiro OHISHI, a Mutsuaki MURAKAMI, a, b* Hidetaka ASOH, b and Sachiko ONO b

ABSTRACT

We investigated the anodic oxidation of aluminum in ionic liquids (ILs) by the constant-voltage rising rate (C-V) method and constant-current density (C-C) method, with characterization by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The structure of the oxide layer and the reaction efficiency varied with the type of IL, the applied voltage, the forming method, and the water content. A homogeneous Al2O3 film with a superior dielectric property was formed by the C-V method (100 mV/s) in 1-butyl-3-methylimidazolium benzoate (BMIm-BEN, water content 0.81 wt%) at 40 V. Although a homogeneous barrier-type Al2O3 film was also formed in 1-butyl-3-methylimidazolium mandelate (BMIm-MAN, water content 0.34 wt%) at 40 V, some anion species existed in the film, and its jump-voltage characteristics was inferior to that of the film formed in BMIm-BEN. The relative permittivity of the film formed in BMIm-BEN was almost equal to that of the Al2O3 film formed in adipate (1.0 wt%) aqueous solution, but the dielectric constant of the film formed in BMIm-MAN was 1.5 times larger. In contrast, a heterogeneous porous Al2O3 film containing a large amount of anion molecules was formed in 1-ethyl-3-methylimidazolium acetate (EMIm-ACE, water content 0.79 wt%) at 40 V. Since the source of oxygen for anodic oxidation is the small amount of water in the ILs, the water content strongly affected the characteristics of the formed Al2O3 layer.

Keywords : Ionic Liquid, Anodic Oxidation, Aluminum Oxide, Breakdown Voltage

1. Introduction

The anodic oxidation of aluminum is a technique used to form a stable aluminum oxide (Al2O3) film on metal surfaces, and this technique has various industrial applications.4-7 Basically, the anodization of aluminum in an aqueous solution does not induce an electrochemical reaction except for oxide film generation. Therefore, the reaction is simply given by

\[ 2\text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^- \] (1)

During the anodization, both O2- and Al3+ ions move in the oxide film owing to application of voltage, resulting in the formation of a new oxide layer at the oxide film/solution interface and the metal Al/oxide film interface, respectively.

\[ \text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^- \] (2)

At the same time, water dissociates at the film/solution interface and forms O2- and H+.

\[ \text{H}_2\text{O} \rightarrow \text{O}^{2-} + 2\text{H}^+ \] (3)

The Al3+, which moves from the inside of the film towards the solution, and the O2- form an oxide layer at the interface.

\[ \text{Al}^{3+} + \text{O}^{2-} \rightarrow \text{Al}_2\text{O}_3 \] (4)

However, the characteristics of oxide films are greatly affected by the anodizing conditions, such as the type of electrolyte, temperature, current density, and applied voltage. Porous films produced in an acidic or alkaline solution are used for corrosion protection or ornamental purposes. On the other hand, those produced in neutral solutions such as ammonium salt aqueous solutions can serve as stable barrier-type Al2O3 layers for capacitor dielectrics. The relations between the dielectric property of anodic barrier films, the film structure including anion incorporation, and electrolyte conditions such as current density and electrolyte temperature have been reported. Moreover, it is known that the formation of a porous barrier-type Al2O3 film is affected by the concentration of the electrolyte. For example, it has been reported that the surface of aluminum was covered with barrier-type Al2O3 when it was anodized in dilute (1 M) malic acid, but it was covered with a porous film when it was anodized in high-concentration (5 M) high-temperature malic acid.

However, there have been few papers on the behavior of anodic oxidation in most nonaqueous organic electrolytes. The actions of aluminum electrodes in electrolytic capacitors, Li ion batteries, and electric double-layer capacitors (EDLCs) have been the main subjects of research. The thickness, chemical composition, and structure of the resultant Al2O3 films are markedly affected by the water content. Recently, room-temperature ionic liquids (ILs) have been attracting considerable attention owing to their remarkable properties, such as their negligibly low vapor pressure, thermal stability, and high ionic conductivity. The anodic behavior of aluminum in IL-containing electrolytes has also been studied with the intention of developing a current collector for lithium ion batteries. Since the reaction in ILs is thought to be similar to that in nonaqueous highly concentrated organic electrolytes, the anodic oxidation of aluminum in ILs is very important for the further development of various devices.
To remove as much moisture as possible, the ILs were synthesized by the anion-exchange resin method. To avoid the effect of moisture absorption by the IL, all specimens were degreased in 5 wt% NaOH aqueous solution at 70°C for 20 s, neutralized in 30 wt% HNO3 aqueous solution, and washed with methanol. To produce specimens for examination by X-ray photoelectron spectroscopy (XPS), anodic oxidation was carried out by the above C-V method. After the anodic oxidation, the aluminum electrode was washed with methanol to remove the IL, then dried before the XPS analysis. The XPS measurements were recorded using a PHI Quantum 2000 spectroscope (ULVAC-PHI) with Al-Kα radiation. The depth profiles of three elements (Al2p, C1s, and O1s) in the surface layer were measured by Ar+ bombardment of the surface. The morphologies of the anodic films formed by the C-V and C-C methods were evaluated by field-emission scanning electron microscopy (FE-SEM, JEOL, JSM-6701F).

### 3. Results and Discussion

Figure 1 shows the current-voltage characteristics obtained by the C-V method in EMIm-ACE, BMIm-BEN, and BMIm-MAN. Although an increase in current was observed at approximately 20 V in EMIm-ACE, no such rapid increase was observed in BMIm-BEN and BMIm-MAN at voltages of up to 40 V. The currents flowing at 40 V in BMIm-BEN and BMIm-MAN were 0.7 and 1.0 mA/cm², respectively. Thus, the current observed in BMIm-MAN was larger than that in BMIm-BEN.

Figure 2 shows the voltage-time characteristics in EMIm-ACE, BMIm-BEN, and BMIm-MAN obtained by the C-C method. The increase in voltage in EMIm-ACE was observed to be only approximately 18–19 V, but the voltage increased to 80 V in BMIm-MAN as time progressed. In the case of BMIm-BEN, the voltage increased linearly to 100 V, in contrast to the case of BMIm-MAN. The current efficiency under C-C measurement roughly

<table>
<thead>
<tr>
<th>IL</th>
<th>pKa</th>
<th>Viscosity (mPa·s)</th>
<th>Water content (wt%)</th>
<th>Ionic conductivity (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMIm-ACE</td>
<td>4.8</td>
<td>139</td>
<td>0.79 (7900 ppm)</td>
<td>1.30</td>
</tr>
<tr>
<td>BMIm-BEN</td>
<td>4.2</td>
<td>1570</td>
<td>0.81 (8100 ppm)</td>
<td>0.47</td>
</tr>
<tr>
<td>BMIm-MAN</td>
<td>3.4</td>
<td>2950</td>
<td>0.34 (3400 ppm)</td>
<td>0.26</td>
</tr>
</tbody>
</table>

### 2. Experimental

Three ILs, 1-butyl-3-methylimidazolium benzoate (BMIm-BEN), 1-ethyl-3-methylimidazolium acetate (EMIm-ACE), and 1-butyl-3-methylimidazolium mandelate (BMIm-MAN), were chosen as typical electrolytes to investigate the characteristics of Al2O3 films formed in ILs. A 1.0 wt% aqueous solution of adipate was used as an electrolyte solution to produce a standard sample. The ILs used in this study and their abbreviations, pKa values, viscosities, water contents, and ionic conductivities are given in Table 1. The pKa values given here are the acid dissociation constants in an aqueous solution of the anion molecule constituting the IL.34 EMIm-ACE was purchased from Aldrich Chemical Co., and BMIm-BEN and BMIm-MAN were synthesized by the anion-exchange resin method.35 To remove as much moisture as possible, the ILs were heated at 85°C in a vacuum for 24 h. The water contents were measured by a Karl Fischer Moisture Meter (KF-100 Mitsubishi Chemical Corporation) before the polarization experiment.

Aluminum anode electrodes (purity: 99.99%, 10 mm × 10 mm × 0.5 mm) were purchased from Wako Pure Chemical Industries Ltd. The general procedure for anodic polarization was as follows. The IL was added to the rectangular cathode of an aluminum electrode cell with inner dimensions of 14 mm × 12 mm × 4.5 mm. The surface of the aluminum anode was degreased in 5 wt% NaOH aqueous solution at 70°C for 20 s, neutralized in 30 wt% HNO3 aqueous solution, and washed with methanol. To avoid the effect of moisture absorption by the IL, all electrochemical measurements were performed in a glove box (dew point below −70°C).

As a preliminary experiment, constant current (C-C) measurements were carried out in EMIm-ACE under a constant current density of 1.0 mA/cm² by the three-electrode method using beaker cells and by the two-electrode method with the above-mentioned experimental cell. The two experimental results were in good agreement except for the jump in voltage observed immediately after the start of measurement caused by the drop in iR of the electrolyte used. Thereafter, our measurements were carried out by the two-electrode method using the above-described experimental cell. In the voltage characteristics in Fig. 2, the initial jump in voltage is subtracted from the observed voltage values. A constant-voltage (C-V) rise rate measurement was also performed by the two-electrode method with a constant rate of voltage increase of 100 mV/s. After performing C-V experiments at voltages of up to 40 V, NMR measurements of the ILs used in the experiments were performed to determine whether changes due to a chemical reaction had occurred in the ILs.

Figure 1 shows the current-voltage characteristics obtained by the C-V method in EMIm-ACE, BMIm-BEN, and BMIm-MAN. Although an increase in current was observed at approximately 20 V in EMIm-ACE, no such rapid increase was observed in BMIm-BEN and BMIm-MAN at voltages of up to 40 V. The currents flowing at 40 V in BMIm-BEN and BMIm-MAN were 0.7 and 1.0 mA/cm², respectively. Thus, the current observed in BMIm-MAN was larger than that in BMIm-BEN.

Figure 2 shows the voltage-time characteristics in EMIm-ACE, BMIm-BEN, and BMIm-MAN obtained by the C-C method. The increase in voltage in EMIm-ACE was observed to be only approximately 18–19 V, but the voltage increased to 80 V in BMIm-MAN as time progressed. In the case of BMIm-BEN, the voltage increased linearly to 100 V, in contrast to the case of BMIm-MAN. The current efficiency under C-C measurement roughly
Figure 2. Voltage-time characteristics (the initial voltage jump of 3.5 V was deduced) of the aluminum electrode observed under a constant current density (1.0 mA/cm²), in (i) EMIm-ACE, (ii) BMIm-BEN, and (iii) BMIm-MAN. The voltage for (iii) reached at 80 V after 1600 s.

Figure 3. (a) Depth profiles as in text (atomic concentrations) of anodized aluminum formed in EMIm-ACE under a constant rate of voltage increase of 100 mV/s and a maximum applied voltage of 40 V. (b) SEM image of the anodized aluminum layer. The layer has a granular structure and an average thickness of 105 nm.

correspond to slope (dV/dt) of the straight line, and increases in the electric current and the dielectric breakdown voltage (Vd) appear as deviations from the straight line and voltage spikes. Thus, the characteristics differed greatly among the three types of IL.

Figure 3(a) shows XPS depth profiles of aluminum anodized by the C-V method in EMIm-ACE at 40 V. Three atomic elements (Al₂p, O₁s, C₁s) were detected, with the Al₂p and O₁s having a relatively constant atomic ratio of Al₂p/O₁s = 33/58 (= 0.57) up to a sputtering time of 50 min. From the binding energy of the observed Al₂p (74–75 eV) and O₁s (531–532 eV) signals, the film composition was identified as Al₂O₃. The depth profiles of the film anodized in 1.0 wt% aqueous solution of adipate indicated that the atomic ratio of Al₂p/O₁s was 36/63 (= 0.57), however, the film composition was also assumed to be Al₂O₃ including an amount of electrolyte species. The difference between the atomic ratio of Al₂p/O₁s and the result of the binding energy was explained by the measuring the sensitivity of each Al₂p and O₁s elements. In the Al₂O₃ layer, the C₁s intensity decreased with increasing depth. Since it is known that an electrolyte anion species was incorporated into the Al₂O₃ film during anodization, the C₁s is thought to have originated from the anion component of ACE. Thus, when an anion is taken inside of an oxide layer, the resolution reaction of the cation molecule is also promoted on the cathode electrode by the principle of electroneutrality. Actually, a change in the NMR spectrum of EMIm-ACE was observed after the C-V experiments, and the generation of a gas and the deposition of an organic material were also observed on both the cathode and anode electrodes. Therefore, it is thought that a resolution reaction proceeded during the C-V experiment.

When the sputtering time exceeded 50 min, the intensity of the Al₂p peak began to increase and that of the O₁s peak decreased. This meant that the sputtering depth reached the metal aluminum layer. From the increased concentration of the aluminum, the estimated sputtering time corresponding to the film thickness was determined to be 80 min (see the arrow in Fig. 3) by considering the roughness of the aluminum electrode surface and the sputtering radius of Ar⁺ bombardment. A cross-sectional SEM image of the film layer is shown in Fig. 3(b). The layer formed in EMIm-ACE had a granular structure and the average film thickness was 105 nm. Therefore, the sputtering rate of the formed layer was calculated to be 1.3 nm/min.

From the C-V and C-C characteristics of EMIm-ACE, it was thought that the film structure changed from the barrier-type to a porous structure by the dissolution of the formed Al₂O₃ film. Generally, a porous film with hexagonal pillar cells of Al₂O₃ is formed by anodization in an acidic aqueous solution with fine pores passing through the center of each cell. However, it is known that the structure of a barrier and/or porous film formed in an organic electrolyte with a small amount of water differs from the structure formed in an aqueous neutral solution. The film formed in tetramethylammonium hydrogen phthalate/γ-butylolac-tole containing 10 to 1000 ppm of water were found not to be flat and their appearance and thickness were markedly affected by the water content. For example, the film formed at 300 ppm of water had a laminated structure, and the film formed at 700 ppm of water exhibited shallow depressions on the surface and irregular contrast inside the water content. It is interesting that the structure of the anodic oxide changed with the concentration of the electrolyte and/or the water content. The structure of the latter film was similar to that of the film produced in EMIm-ACE [Fig. 3(b)].

Figures 4(a) and 4(b) show the XPS depth profiles and an SEM image of the film formed in BMIm-BEN by the C-V method at 40 V. After the C-V experiment, NMR measurement of the BMIm-BEN was performed. Since the NMR spectrum did not change, we concluded that the resolution reaction of BMIm-BEN did not proceed during the experiment. In this case, only two elements (Al₂p, O₁s) with a constant atomic ratio of Al₂p/O₁s = 36/63 (= 0.57) and no apparent carbon signal were detected up to a sputtering time of approximately 100 min. The sputtering time equivalent to the thickness of the Al₂O₃ film was estimated to be 155 min (see the arrow in Fig. 4). A homogeneous structure with a thickness of 80 nm was observed in the SEM image shown in Fig. 4(b). From the results, the sputtering rate was calculated to be 0.52 nm/min. This was similar to the rate for the barrier-type Al₂O₃ layer obtained in 1.0 wt% adipate aqueous solution (0.43 nm/min).
From the facts that no anion species were contained in the anodic film, and the sputtering rate was lower than that in EMIm-ACE, it can be concluded that the anodic film formed in BMIm-BEN is relatively pure and is barrier-type Al$_2$O$_3$.

Figures 5(a) and 5(b) show the XPS depth profiles and an SEM image of the film formed in BMIm-MAN by the C-V method at 40 V. The NMR spectrum of the BMIm-MAN did not change during the C-V experiment. In this case, anodization was performed on an alkaline degreased Al specimen; thus, the bumpy irregularity of the Al substrate was observed in Fig. 5(b). Two atomic elements (Al$_{2p}$ and O$_{1s}$) with a constant atomic ratio of Al$_{2p}$/O$_{1s}$ = 36/62 (≈ 0.58) were detected up to a sputtering time of approximately 100 min, and a small amount of C$_{1s}$ was also detected in the surface region. The SEM image [Fig. 5(b)] shows a homogeneous film structure with a thickness of 90 nm. The film was thicker than the film formed in BMIm-BEN, and the sputtering rate was computed to be 0.70 nm/min by a similar calculation. This value was larger than that for the anodic alumina layer formed in BMIm-BEN and greatly different from the value for EMIm-ACE. From these results, we concluded that the anodized film formed in BMIm-MAN is also a barrier-type Al$_2$O$_3$ film although its character differs somewhat.

Although the anodization of aluminum in an aqueous (dilute) solution does not induce an electrochemical reaction except for the generation of the oxide film, in some cases it is necessary to considered the a reaction with the solute in the case of a high-concentration solution. Figure 6 shows the reaction mechanism in high-concentration solution such as the ILs. Namely, on the Al$_2$O$_3$/solution interface Al$^{3+}$ is not only combined with an O$^{2-}$ ion but is also combined with the electrolyte anion at the same time, and part of the Al is eluted to the solution as Al$^{3+}$ or an Al$^{3+}$-electrolyte anion complex. Since the deprotonation reaction of H$_2$O or OH$^-$ also occurs when O$^{2-}$ reacts with Al$^{3+}$, the pH of the solution at the interface falls and the film dissolution is promoted. The pH-buffering ability of the electrolyte, the ease of formation of the Al$^{3+}$-electrolyte anion complex, and the ease of dissolution determine
whether or not the formed film dissolves. The electrolyte anion and \( \text{Al}^{3+} \) form a complex with zero electric charge \([\text{Al}_x\text{O}_y\text{R}_z\text{An}^{-}\text{y}/\text{x}]\) (An = anion). This complex is taken into the oxide film or the electrolyte anion dissolves into the solution as a negatively charged anion \([\text{Al}_{3m}^x\text{An}_{3m-x}^{-}\text{y}]/\text{m-xN}\) (3m - xN < 0).

Figures 7(a) and 7(b) show SEM images of the anodized layer in \( \text{BMIm-BEN} \) and \( \text{BMIm-MAN} \) formed at 80 V by the C-V method, respectively. Uniform \( \text{Al}_2\text{O}_3 \) layers were formed in \( \text{BMIm-BEN} \) and \( \text{BMIm-MAN} \) under a constant rate of voltage increase of 100 mV/s and a maximum applied voltage of 80 V. Both structures are homogeneous with average thicknesses of 160 and 140 nm, respectively.

Figure 7. SEM images of the anodized aluminum surfaces formed in (a) \( \text{BMIm-BEN} \) and (b) \( \text{BMIm-MAN} \) under a constant rate of voltage increase of 100 mV/s and a maximum applied voltage of 80 V. Both structures are homogeneous with average thicknesses of 160 and 140 nm, respectively.

\[ \text{Itotal} = I_e + I_{fl} = I_d + I_d + I_d \]  

(5)

On the other hand, \( I_d \) is divided into the anodic oxide layer formation current \( I_d \) and the layer dissolution current \( I_d \), and it is known that an increase in \( I_d \) will eventually lead to the formation of a porous film. Here, it is assumed that \( I_d \) is the current at which the aluminum migrates and elutes directly to the electrolyte as an ion. Therefore, the difference between \( \text{BMIm-BEN} \) and \( \text{BMIm-MAN} \) can be explained by the difference in the rate of dissolution of the \( \text{Al}_2\text{O}_3 \) layer. For this reason, the \( \text{Al}_2\text{O}_3 \) film formed in \( \text{BMIm-MAN} \) at 40 V was thicker than the film formed in \( \text{BMIm-BEN} \) but at 80 V it was thinner.

The jump-voltage characteristics were measured to investigate the barrier nature of the \( \text{Al}_2\text{O}_3 \) films formed in \( \text{BMIm-BEN} \) and \( \text{BMIm-MAN} \). This is a method of observing the behavior of the voltage when a fixed current is applied to a barrier film to evaluate the microstructure and the defects present in the anodic oxide layer.\[12,14,41,42\] The jump-voltage characteristic of the film obtained by anodization in 1.0 wt% adipate aqueous solution under a current density of 1.0 mA/cm\(^2\) is shown in Fig. 8. After a voltage jump in the early stage, the film formed in \( \text{BMIm-BEN} \) exhibited a constant rate of voltage increase over time. However, in the case of the film formed in \( \text{BMIm-MAN} \), the rate of voltage increase was not constant and considerable noise could be observed. The rate of voltage increase was also small, although the withstand voltage of all the films was similar. The noise suggests the existence of defects in the film, and the delay in the current increase is considered to be due to the use of the current for the repair of such defects. The structure of the films formed in \( \text{BMIm-BEN} \) and \( \text{BMIm-MAN} \) is uniform, and no apparent differences between them could be observed by SEM other than their thickness. However, the result in Fig. 8 shows that the dielectric characteristic of the film produced in \( \text{BMIm-BEN} \) is greatly superior to that of the film produced in \( \text{BMIm-MAN} \). In addition, it is noteworthy that the dielectric property of the film produced in \( \text{BMIm-BEN} \) seems to be comparable to that of the film produced in adipate aqueous solution.

To investigate the characteristics of the generated films, the capacitance of the films produced by the C-V method at 40 V was measured in 15 wt% adipate solution at 120 Hz. From the capacitance of each film and the thickness of the film estimated from SEM measurement, we calculated the dielectric constants listed in Table 2. Since the capacitance of the film produced in adipate (1.0 wt%) was 300 nF/cm\(^2\), the dielectric constant was found to be 12.7. This value is slightly larger than the generally accepted relative dielectric constant of an \( \text{Al}_2\text{O}_3 \) film. Although the relative dielectric constant of the film produced in \( \text{BMIm-ACE} \) became unusually large (32.0), this was thought to be caused by the very thin and barrier layer with a high defect in the porous film (Fig. 3). The relative dielectric constants of the films produced in \( \text{BMIm-MAN} \) and \( \text{BMIm-BEN} \) were 1.6 and 0.98 times that of the film produced in adipate, respectively. The former high value obtained in \( \text{BMIm-MAN} \) was attributed to the presence of defects and the unevenness.

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>BMIm-BEN(40V)</th>
<th>BMIm-BEN(80V)</th>
<th>BMIm-MAN(40V)</th>
<th>BMIm-MAN(80V)</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>120</td>
<td>100</td>
<td>80</td>
<td>60</td>
</tr>
<tr>
<td>50</td>
<td>115</td>
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<td>75</td>
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<td>150</td>
<td>105</td>
<td>85</td>
<td>65</td>
<td>45</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>80</td>
<td>60</td>
<td>40</td>
</tr>
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</table>

Figure 8. Jump-voltage characteristics of the \( \text{Al}_2\text{O}_3 \) layers measured in 1 wt% adipate aqueous solution under a current density of 1.0 mA/cm\(^2\). The samples were formed in \( \text{BMIm-BEN} \), \( \text{BMIm-MAN} \) and adipate (1 wt%) under a constant rate of voltage increase of 100 mV/s and maximum applied voltages of 40 and 80 V.
of the film. In addition, the amount of electrolyte incorporated into the film may be an important factor in determining the dielectric constant.\textsuperscript{12}

Figure 9 shows a SEM cross-sectional view of the anodized film surface formed in BMIm-BEN by the C-C method (1.0 mA/cm\textsuperscript{2}). The anodization was ended when voltage reached 80 V. The reaction time in BMIm-BEN is 250 s. The average film thickness is 150 nm. Figure 9. SEM images of the anodized film surface formed in BMIm-BEN by the C-C method (1.0 mA/cm\textsuperscript{2}). The anodization was ended when voltage reached 80 V. The reaction time in BMIm-BEN is 250 s. The average film thickness is 150 nm.

Table 2. Capacity, thickness and relative dielectric constant of the films formed by C-V method at 40 V (100 mV/s).

<table>
<thead>
<tr>
<th></th>
<th>Capacity (nF/cm\textsuperscript{2})</th>
<th>Thickness (nm)</th>
<th>Relative dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMIm-ACE</td>
<td>7640</td>
<td>105</td>
<td>412 (32.0)</td>
</tr>
<tr>
<td>BMIm-BEN</td>
<td>306</td>
<td>80</td>
<td>12.5 (0.98)</td>
</tr>
<tr>
<td>BMIm-MAN</td>
<td>425</td>
<td>92</td>
<td>20.3 (1.6)</td>
</tr>
<tr>
<td>Adipate (1 wt% aqueous sol.)</td>
<td>300</td>
<td>84</td>
<td>12.7 (1.0)</td>
</tr>
</tbody>
</table>

*The capacity was measured in 15 wt\% adipate aqueous solution at 120 Hz.

(4) This process is repeated to produce an electron avalanche. The electrostriction mechanism occurs as follows. When a strong electric field is applied to the dielectric layer, a strong compression stress is applied to the layer. The current becomes concentrated at a crack or a slip owing to the stress, which results in dielectric breakdown. Although the latter mechanism easily occurs in very high concentration solvents such as ILs, it cannot explain the difference in the breakdown voltage for the different the electrolytes. It is thought that the former breakdown mechanism is applicable in very high concentration organic solvents such as ILs. Since the ease of electron pouring by dissociation depend on the electrolyte anion,\textsuperscript{9,44,45} the dielectric breakdown voltage may greatly change with the type of anion molecule in the IL. When an electrolyte anion is inserted in the Al\textsubscript{2}O\textsubscript{3} layer (see Fig. 6), it is known that the mechanical strength and breakdown voltage change, and the layer becomes easily dissolved by the anion in the electrolyte.\textsuperscript{9} It has been described how an oxide film becomes stable by enclosing anions in the Al\textsubscript{2}O\textsubscript{3} layer. However, we consider that when the concentration of the electrolyte is very high, as with the IL, it becomes easy to dissolve the Al\textsubscript{2}O\textsubscript{3} layer. Therefore, an anodic film with a high breakdown voltage cannot be formed in BMIm-ACE; moreover, in BMIm-MAN, the anodic film cannot be formed at a high voltage such as 80 V. Thus, it is concluded that the electron-avalanche mechanism can explain the difference in the breakdown voltage with the type of IL.

The cations of the ILs used in this study are EMIm and BMIm. Although they are not the same, it is thought that their chemical character and structure are similar. Considering the results of anodization in BMIm-TFSA and BMIm-TFA,\textsuperscript{9} it is thought that the type of anion has a strong effect on the anodization. We propose the reason for the difference in anodic oxidation between the three ILs from the viewpoint of their anion structure as follows. Since the anion size of EMIm-ACE is smaller than those of the other two ILs, it more easily penetrates into the Al\textsubscript{2}O\textsubscript{3} layer under an anodic field; the concentration of anions becomes higher than those in the other two ILs, and the Al\textsubscript{2}O\textsubscript{3} layer becomes easier to dissolve. Since the anion of BMIm-MAN has an OH group, the absorption power of its anion,\textsuperscript{9,44,45} the dielectric breakdown voltage may greatly change with the type of anion molecule in the IL. When an electrolyte anion becomes easily dissolved by the anion in the electrolyte.\textsuperscript{9} It has been described how an oxide film becomes stable by enclosing anions in the Al\textsubscript{2}O\textsubscript{3} layer. However, we consider that when the concentration of the electrolyte is very high, as with the IL, it becomes easy to dissolve the Al\textsubscript{2}O\textsubscript{3} layer. Therefore, an anodic film with a high breakdown voltage cannot be formed in BMIm-ACE; moreover, in BMIm-MAN, the anodic film cannot be formed at a high voltage such as 80 V. Thus, it is concluded that the electron-avalanche mechanism can explain the difference in the breakdown voltage with the type of IL.

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anodization was ended after 750 s and the voltage reached 80 V. The water content depends on the solvent, solute, and water content. The water contents of (i) 2.0 wt%, (ii) 10 wt%, (iii) 50 wt%, (iv) 90 wt%. Water content became 10 wt% when the water content changed from 0.34 to 2.0 wt%, the maximum voltage increased from 14 to 26 V, and when the water content became 50 wt%, the voltage fell to 65 V when the water content changed from 0.81 to 2.0 wt%, the maximum voltage fell to 45 V. However, the voltage fell to 65 V when the content became 50 wt%. Figure 10(b) shows an SEM image of the aluminum anodized in BMIm-MAN (the anodization was ended after 750 s when the voltage reached 80 V, and the water content was 2.0 wt%). Under these conditions, a uniform Al2O3 film with an average thickness of 170 nm was formed in BMIm-MAN. That is, when the water content changed from 0.34 to 2.0 wt%, the film thickness and structure changed from 90 nm and porous to 170 nm and barrier-type, respectively. It is surprising that such a small difference in the water content affected the V-T characteristics.

Figure 11 shows the voltage-time characteristics in EMIm-ACE measured by the C-C method at various water contents. The water content in EMIm-ACE measured under a constant current density of 1.0 mA/cm² for water contents of (i) 2.0 wt%, (ii) 10 wt%, (iii) 50 wt%, (iv) 90 wt%. Water content 0.79 wt% (Fig. 2)

V_B values of the anodized layer obtained in an organic solvent are generally low compared with those for an aqueous solution system. However, to form an Al2O3 film with sufficient quality for use as a dielectric oxide with a linear increase in voltage with time and a high V_B value, there is an optimal amount of moisture that depends on the type of IL. Namely, about 1.0 wt% is the optimal amount of moisture in BMIm-BEN, while it is about 10 wt% in BMIm-MAN and EMIm-ACE. Since the oxidation and the dissolution reaction of aluminum occur as competing reactions in an IL, it is thought that the ability of each IL to carry out the anodization reaction depends on how effectively the water is used as a source of oxygen. Further discussion on the effect of the type of IL and water content on the anodization behavior will be given elsewhere.

4. Conclusions

The formation behavior of Al2O3 films by the anodization of aluminum in three types of IL by the C-C and C-V methods was analyzed. An oxide film of porous Al2O3 was formed in EMIm-ACE by the C-V method, while anodization in BMIm-BEN and BMIm-MAN using the same method gave a dense barrier-type Al2O3 film. Differences in the breakdown voltages and the dielectric constants among the two barrier-type Al2O3 films were observed. The formation behavior of the Al2O3 layer varied with the type of IL, the applied voltage, and the water content. Although water is a source of oxygen for the anodization of aluminum, there is an optimal quantity of water, which depends on the type of IL. The anion components of the IL and the water content are the most important factors, and it is thought that the electron avalanche model can explain the breakdown mechanism of aluminum anodization in an IL. The finding that the characteristics of oxide films can be adjusted by the selection of the IL and the water content suggests the potential of ILs as novel electrolytes for the anodization of aluminum.

References