Supporting Information

Sulfone-Based Electrolytes for Aluminium Rechargeable Batteries

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1. Influence of remanent silver in the solution

Since $Al(BF_4)_3$/EiPS = 1/8 was prepared as the supernatant liquid by precipitating the chloride as silver chloride (AgCl) by introducing silver tetrafluoroborate ($AgBF_4$) into $AlCl_3$/EiPS = 1/8(mol), there has to be some silver ion (Ag^+) in the solution as an impurity. As the electrochemical reaction is sensitive to the contaminants, we have investigated the influence of the remaining Ag^+ by changing the concentration in the solution.
Fig. S1 shows the CV curves observed at T = 25°C for a couple of $Al(BF_4)_3$/EiPS = 1/8 with different Ag^+ concentration. When the Ag content is 61% of Al, not only plating but also electroless plating of Ag occurs, resulting in a CV spectrum as if reversible Al deposition and dissolution is observed. We can remove their influence by reducing the remaining Ag content below 8% of Al, by which electrochemical activity is disappeared as shown in the figure.
Based on this experimental result, we used $Al(BF_4)_3$/EiPS = 1/8 with remaining Ag^+ less than 8% of Al whose influence on the electrochemical activities are small enough to be ignored. Actually, even at T = 25°C, $Al(BF_4)_3$/EiPS = 1/8 does not show any electrochemical activities as shown in Fig. 3.

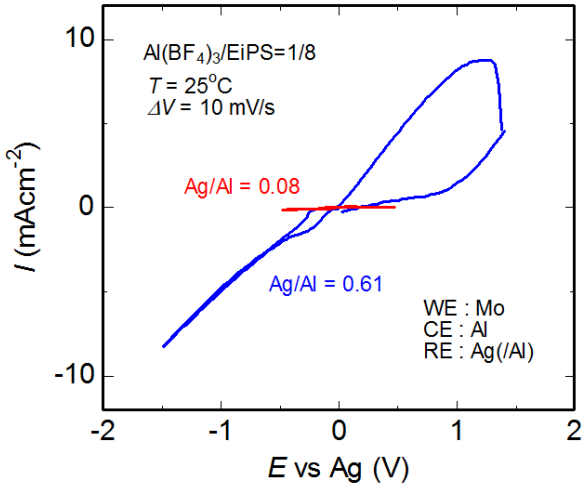

Fig. S1 CV specra for a couple of Al electrolytes whose Ag^+ concentrations are 61% (blue) and 8% (red) of Al, respectively, that was confirmed by the ICP measurements of the solutions. The observed reversible behavior described by blue line is owing to Ag^+, which was confirmed by the experiment without Al content. Potential is plotted with regard to Ag, since in a solution with a plenty of Ag^+, the electroless plating of Ag occurs even even when the Al reference electrode is used.

2. Role of dilutant in sulfone-based Al electrolytes

Al-NMR spectra observed at T = 25°C for for Al electrolytes, $AlCl_3$/EnPS=1/0.7(mol) and $AlCl_3$/EnPS/Toluene=1/0.7/2.9(mol) are plotted in Fig. S2. Here we can see that dilution with toluene does not change the peak position or chemical shift, but make the peak sharper,

indicating that there's no serious interaction between toluene and Al complexes. On the other hand, spectrum at T = 80°C for $AlCl_3$/EnPS = 1/0.7 is also plotted in the same figure, showing the peak sharpening through temperature rising or viscosity decreasing. These results indicate that dilution with toluene has the same effect as the temperature rising, which, we think, is probably due to the viscosity decreasing.

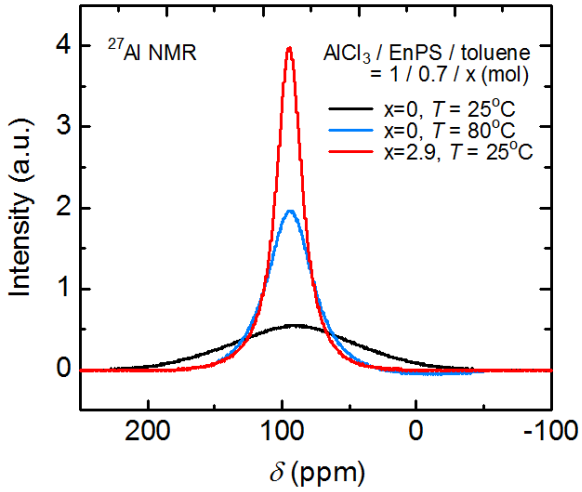

Fig. S2 ^{27}Al NMR spectra for $AlCl_3$/EnPS = 1/0.7(molar ratio) observed at T = 25°C (black) and T = 80°C (blue), and the spectrum for $AlCl_3$/EnPS/toluene = 1/0.7/2.9 at T = 25°C (red).