

Polymer gel electrolytes for application in aluminum deposition and rechargeable aluminum ion batteries

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Experimental Section

Preparation room temperature ionic liquid: 1-Ethyl-3-methylimidazolium chloride (EMImCl)

was obtained from Aldrich and was purified by recrystallization and vacuum drying before use. Acrylamide was dried at 60 °C under vacuum for overnight before used for polymerization. Anhydrous dichloromethane, acetonitrile, tetrahydrofuran and toluene were obtained from Aldrich. Acetone was purchased from Aldrich and was purified by refluxing over P₂O₅ overnight and distillation. AlCl₃ was purchased from Fluka Company and was purified by sublimation. The AlCl₃ containing mixtures were prepared by slowly adding calculated amount of AlCl₃ to the imidazolium chloride (or the organic solvent) inside an Argon filled glove box. The mixing ratio of AlCl₃ and EMImCl was fixed at 1.5:1.

Preparation of polymer gel electrolyte: To a cooled solution of AlCl₃ in dichloromethane equal molar acrylamide was added slowly under stirring. After addition it was changed into a

clear yellow solution. Under the protection of nitrogen, calculated amount of AlCl_3 -based ionic liquid was added, followed by addition of initiator AIBN (1 wt% of monomer). Finally, the solution was cast into a Teflon coated aluminum petri dish and was heated at 60 °C for overnight to get a self-standing electrolyte.

Electrochemical and physical measurement: Cyclic voltammetry (CV) was performed inside an Argon filled glove box using a CHI instrument at a scan rate of 100 mV/s. For the three electrode system, Pt was used as the working electrode and Al coil and Al wire were used as counter and reference electrode, respectively. For the polymer gel electrolytes, a two electrode system was used, that is, copper (Cu) plate was used as the working electrode while Al plate was used as the counter and reference electrode. Pt electrode was polished with Al_2O_3 , followed by washing with deionized water and drying. Cu electrode was treated by polishing with sand paper, followed by degreasing in acetone under ultrasonic for 15 min and then activated in 5 wt% HCl aqueous solution for a few minutes to remove possible oxide layer, and finally was rinsed with deionized water and degreased in dichloromethane to remove organic impurities. Al electrode was treated by polishing with sand paper, followed by activation in an acidic solution composed of 1 % HNO_3 , 65 % H_3PO_4 , 5 % acetic acid and water for 5 min, and finally was rinsed thoroughly with deionized water and degreased in acetone for 5 min. Al deposition was performed by using a potentiostatic method at 50 °C for a fixed time length, with Cu plate as cathode and Al plate as the counter and reference electrode.

The ^{27}Al NMR spectra were measured on a Bruker Avance 400 spectrometer with 1.0 M $\text{Al}(\text{NO}_3)_3$ aqueous solution as the external chemical shift standard. Scanning electron

microscopic images were obtained on a Hitachi S-4800 FEG scanning electron microscope with energy-dispersive X-ray spectroscopy analysis attachment. FTIR spectra were obtained on a PerkinElmer Frontier spectrometer. X-Ray diffraction pattern was obtained on a PANalytical X-ray diffractometers. Ionic conductivity was measured using Swagelok cell by stamping the sample between two stainless steel electrodes inside an environmental chamber. The cell was equilibrated at each temperature for 30 minutes before measurement.

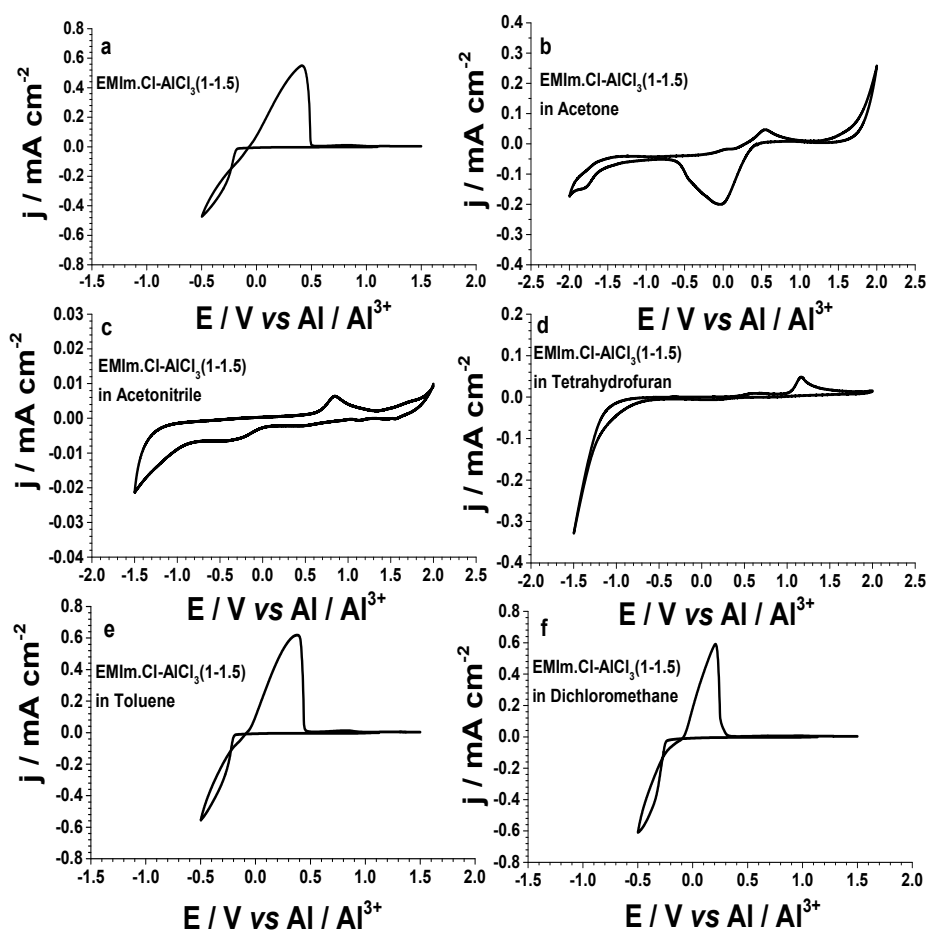


Fig. 1. Cyclic voltammograms of (a) EMImCl-AlCl₃ (1-1.5, in molar ratio) and those of the mixture of equal volume of EMImCl-AlCl₃ (1-1.5) with (b) Acetone, (c) Acetonitrile, (d) Tetrahydrofuran, (e) Toluene, and (f) dichloromethane on a Pt electrode (2 mm in diameter)

under a scan rate of 100 mV/s at room temperature (Al wire was used as the counter and reference electrode).

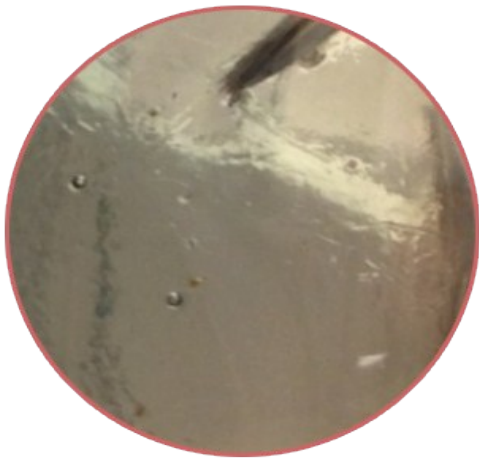
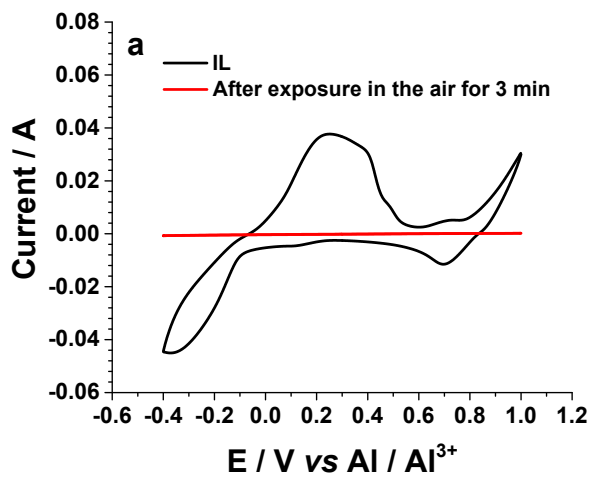


Fig. S2. Picture of a electrolyte containing 60 wt% of EMImCl-AlCl₃ (1-1.5, in molar ratio).



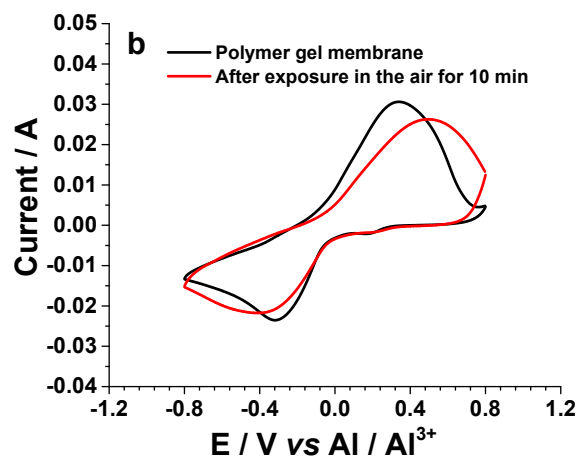


Fig. S3. Comparison of cyclic voltammetry of (a) ionic liquid EMIm.Cl-AlCl₃ (1-1.5) and (b) polymer gel electrolyte before and after exposure to the air at a scan rate of 100 mv/s. Two electrode configuration was used with Cu as working electrode and Al as both counter and reference electrode.