Supplementary Information

Fast charging with high capacity for aluminum rechargeable battery using organic additive in ionic liquid electrolyte

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Experimental

Preparation of material and electrolyte

After dissolution of polyvinylidene fluoride (PVDF, pellets, Sigma-Aldrich) in 1-methyl-2-pyrrolidinone (NMP, 99.5%, Sigma-Aldrich) solution, graphite powder (<20 μm, synthetic, Sigma-Aldrich) mixed with the solvent (mixing ratio 9:1) was coated on a nickel current collector and dried at 80°C for 8 h to obtain the cathode. For clean the aluminum metal anode, the irregular oxide passive layer on the aluminum metal (99.99%, Toyo Aluminium K.K., Japan) surface was removed by electrochemical polishing using anhydrous ethanol (99.5%, Samchun) and perchloic acid ($HClO_4$, 60%, Samchun) (3:1) solution. Then, the aluminum metal was washed with anhydrous ethanol. 1-Ethyl-3-methyl imidazolium chloride-aluminum chloride (Sigma-Aldrich) was used as the pristine ionic liquid electrolyte. Electrolytes with the additives were prepared by mixing the pristine ionic liquid with benzene (anhydrous, 99.8%, Sigma-Aldrich), toluene (anhydrous, 99.8%, Sigma-Aldrich), dimethyl carbonate (anhydrous, ≥99%, Sigma-Aldrich), and diethyl carbonate (anhydrous, ≥99%, Sigma-Aldrich). The mixing ratio of additives was based on volume ratio.

Physical measurements

The ionic conductivity for the volume ratio of benzene in the electrolyte was measured using an ionic conductivity meter (CM-25R, TOA-DKK). FT-Raman (Bruker RFS-100/S, Bruker) and NMR (Bruker Advance III, Bruker) analyses were performed to confirm whether benzene influenced the aluminum chloride ($AlCl_4^-$) anions. Using the electrolyte density and the anion ratio obtained from FT-Raman analysis, the concentration of $AlCl_4^-$ participating in the anodic and cathodic electrode reactions can be calculated. The Randles-Sevcik equation was employed to compare the diffusion coefficients of the electrolytes containing various amounts of benzene.

Electrochemical measurements

The electrochemical properties of the cell were analyzed by a custom-made Swagelok-type cell including the electropolished aluminum foil as the anode, graphite powder as the cathode material, and glass fiber (GF/D, Whatman) as the separator. The electrochemical cell was assembled in an Ar-filled glove box (O_2 ppm < 1.0). Cyclic voltammetry (CV) was conducted on an Autolab electrochemical workstation (PGSTAT302N, Metrohm) using various electrolytes with additives. Half-cell CV was performed using Mo metal as the working electrode without the active material and the electropolished aluminum foil as the counter and reference electrodes in potential range of -0.3 to 1.0 V (versus Al/Al^{3+}). Galvanostatic charge/discharge cycling was performed using the battery cell test system (WBCS3000S, WonATech) at various current densities. Electrochemical impedance spectroscopy (EIS) measurements were carried out on an Autolab workstation, at an amplitude of 5 mV over the frequency range of 2 kHz–50 mHz.

Figure S1. Cyclic voltammogram of half-cell with electrolyte containing various additives: (a) pristine electrolyte (b) 10% DMC, (c) 10% DEC, (d) 10% toluene, and (e) 10% benzene.

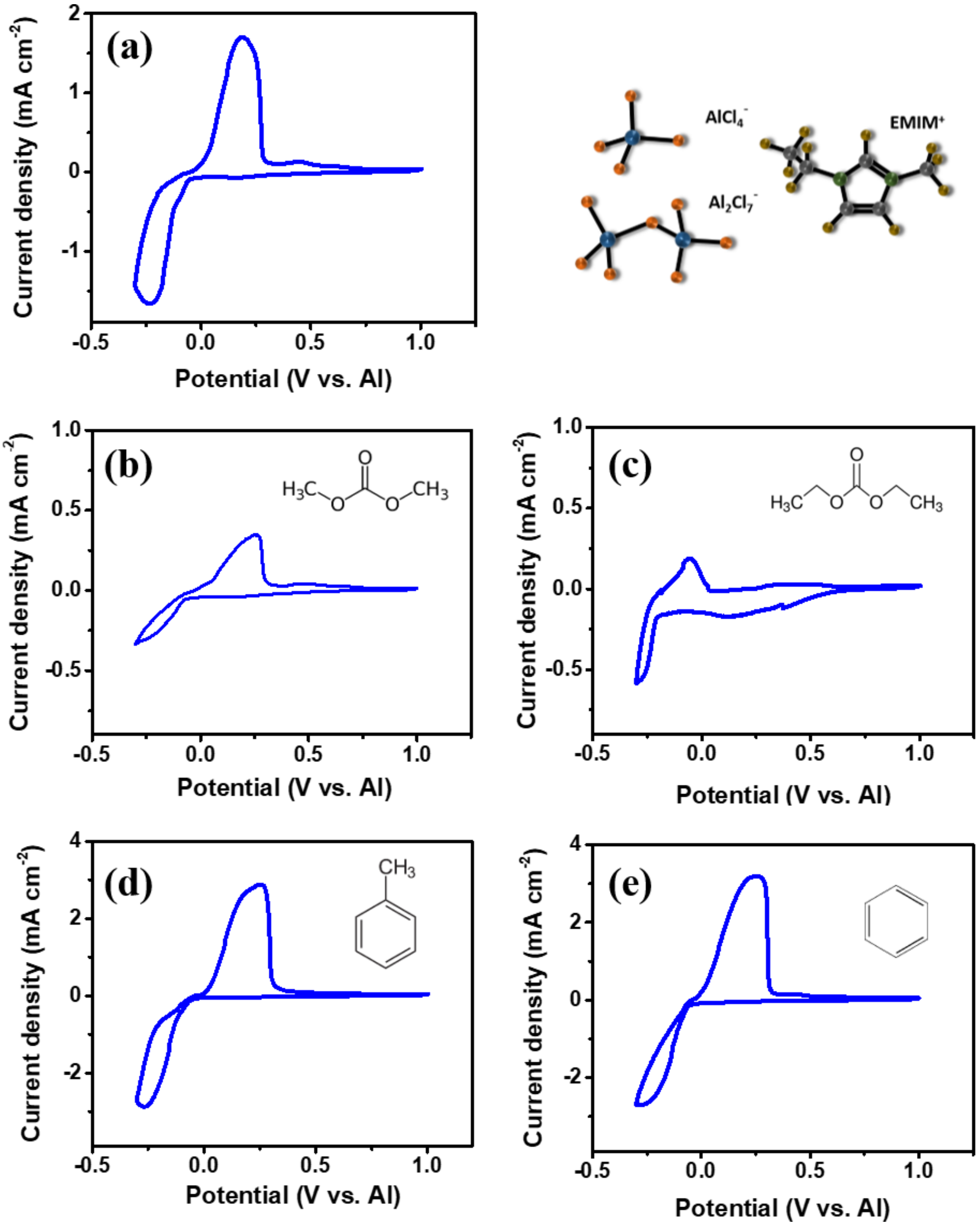

Figure S2. Cyclic voltammogram of half-cell with electrolyte containing (a) toluene and (b) benzene additive (30%, 45%, and 70%).

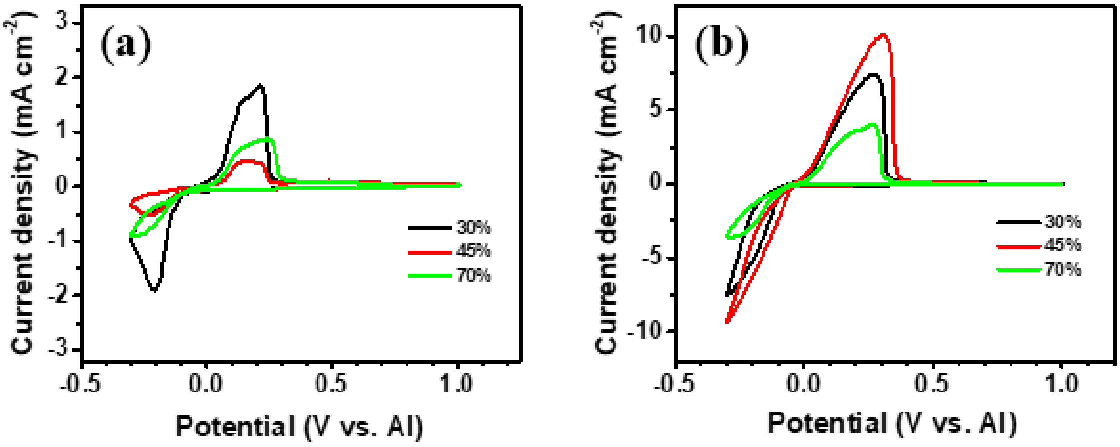

Table S1. Concentration of aluminum chloride anion ($AlCl_4^-$) and ionic conductivity depending on addition ratio of benzene in ionic liquid electrolyte.

Amount of benzene (%)	**Concentration (mol L^{-1})**	**Ionic conductivity (S m^{-1})**
0	5.842	1.59
30	4.089	1.95
40	3.505	2.25
45	3.213	2.43
50	2.921	2.33
70	1.753	1.54

Figure S3. Cyclic voltammogram of half-cell with electrolyte containing (a) 0%, (b) 30%, (c) 45%, and (d) 70% benzene at various scan rates.

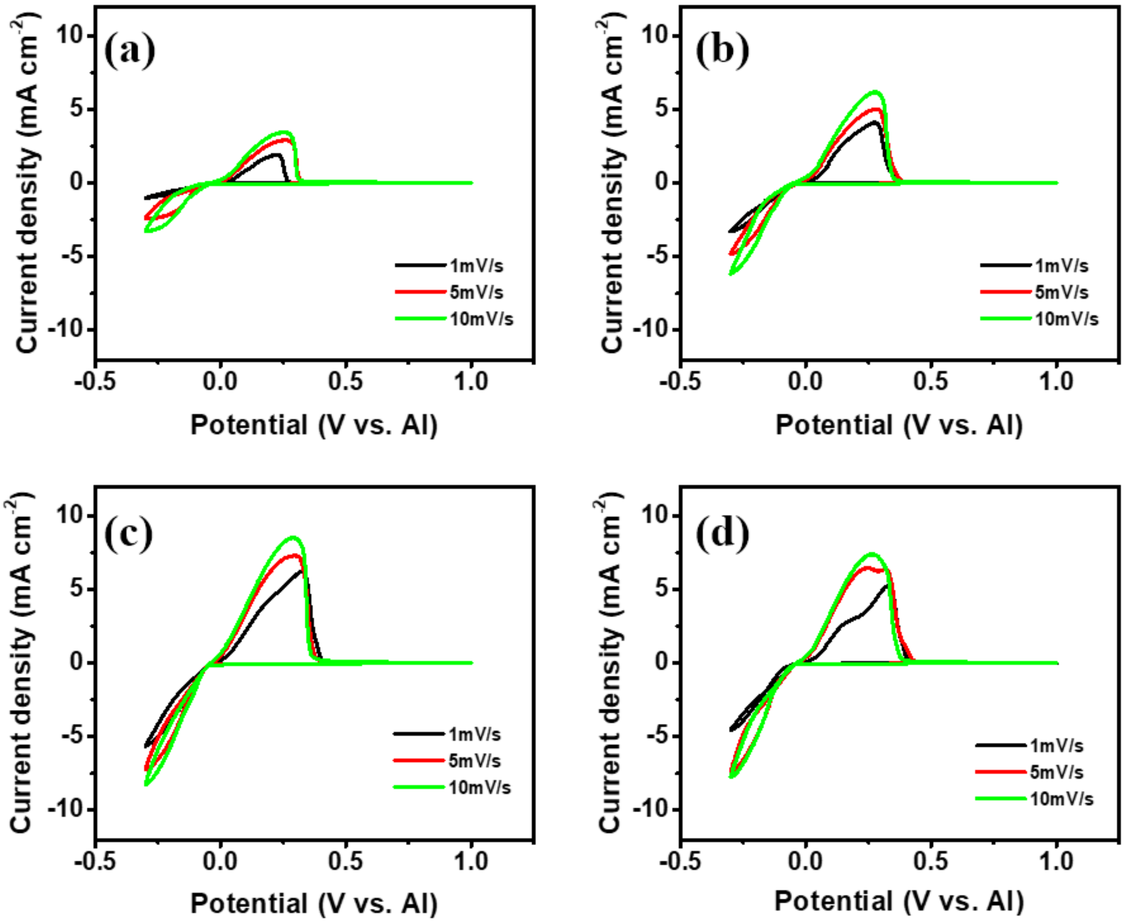

Figure S4. Al NMR of pristine ionic liquid and electrolyte with 45% benzene.

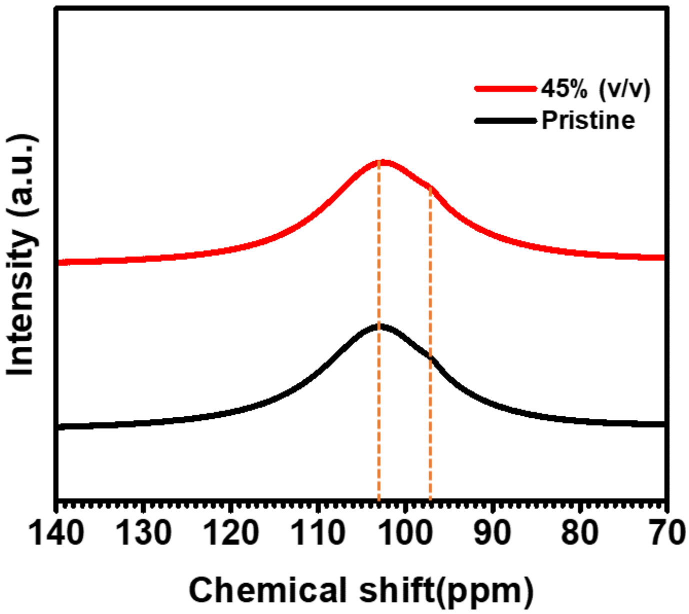

Figure S5. Cyclic voltammogram of (a) half-cell and (b) full-cell using pure benzene as electrolyte. Cyclic voltammogram when using (c) pristine ionic liquid and (d) benzene as electrolyte for a wide range of voltages.

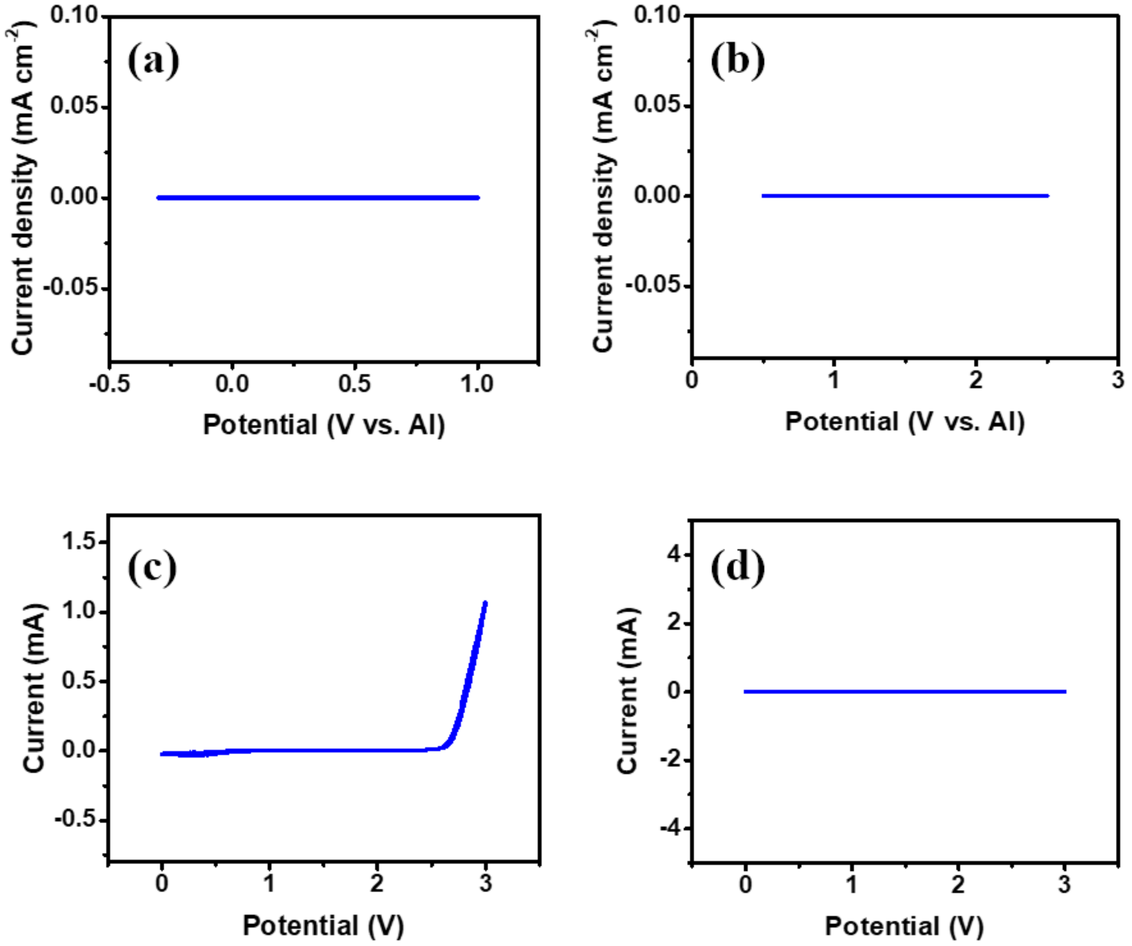

Figure S6. Cycling performance of Al-graphite cell using electrolyte with different volume ratios of benzene at a high current rate of 5,000 mA g^{-1}.

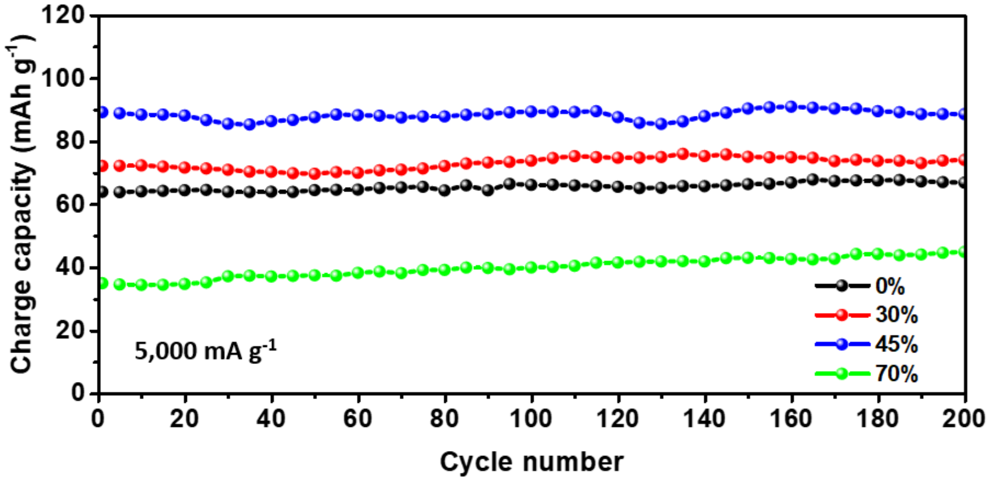

Figure S7. Coulombic efficiency of Al-graphite cell in the ionic liquid electrolyte with 45% benzene at a high current rate of 5 A g^{-1}.