

Supporting Information for

Rechargeable Aluminum Battery: Effects of Cations in Ionic Liquid Electrolytes

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Experimental Methods

Synthesizing Py13Cl-AlCl₃ and EMIC-AlCl₃ ionic liquids. 1.5g of Py13Cl solid was added to a 20mL glass scintillation vial and was placed in a coffee cooler while the corresponding mass of AlCl₃ was weighing. (1.4 ratio: 1.711g, 1.5 ratio: 1.833g, 1.6 ratio: 1.955g, 1.7 ratio: 2.077g). The AlCl₃ was slowly added with constantly stirring. The mixture was transferred back and forth to the coffee cooler to keep the temperature low at all times. After adding all the AlCl₃, the mixture was left stirring until all the AlCl₃ dissolved. The same method was used to synthesize EMIC-AlCl₃ ionic liquid, just replacing the Py13Cl solid by EMIC solid.

Density, Viscosity, Conductivity measurement. The density of both the Py13Cl-AlCl₃ ionic liquids and EMIC-AlCl₃ ionic liquids was measured using a 2mL pycnometer (Thomas Scientific: 8350B16). The viscosity measurements were done by using NDJ-9S viscometer. The conductivity was measured using a conductivity meter (Mettler Toledo, FiveEasy Plus).

Raman Measurements. Fresh samples of electrolyte were transferred into a small clear plastic pouch inside a glovebox filled with argon gas. A small piece of p-type boron doped silicon wafer was also put into the pouch. The pouch was well sealed inside the glovebox before transferring out. Spectra was acquired using a 532nm Ar⁺ laser. When we acquired the spectrum, we started with a continuous scan with scan frequency of every one second. The focus of the laser was adjusted until the maximum signal of the silicon wafer was reached. Afterwards, the spectrum was acquired. The same procedure was repeated at different silicon wafer locations for at least three times.

Electrodes Preparation. The graphite slurry was made using 87% by weight graphite powder (GP) from Ted Pella, INC. Carbon Powder SP-1 Natural Flake, 3% by weight Poly(vinyl alcohol) from Sigma-Aldrich, average molecular weight 30000-70000, and 10% by weight Poly(acrylic acid) from Polysciences, Inc. 25% aqueous solution with molecular weight ~50000. The solvent for the slurry was D.I. water. The slurry was stirred overnight and coated onto Mitsubishi carbon fiber paper (30 g/m²). The coated electrode was baked in 120 °C vacuum oven for 2 hours, and was kept in 80 °C vacuum oven afterwards. The aluminum foil we used was from Alfa Aesar, 0.25 mm thick, annealed, 99% (metal basis), Si and Fe (combined) typically 1%.

Battery Preparation. The graphite and aluminum electrodes were both pasted onto carbon tape (Ted Pella, 16073) in an aluminum laminated pouch cell case (MTI, EQ-alf-100-210). 3-mm nickel tabs (MTI, EQ-PLiB-NTA3) were used as current collector. Glass fiber filter paper (Whatman GF/A) was used as separator. The cell was put into 80 °C vacuum oven overnight before transferring into an argon filled glovebox, in which electrolyte was put into the cell. The cell was then well sealed inside the glovebox before transferring out for electrochemical measurements.

Electrochemical Measurements. Cyclic voltammetry (CV) was performed on a potentiostat/galvanostat (model CHI 760D, CH Instruments). The graphite slurry used for cyclic voltammetry was usually 1000 times diluted then regular graphite slurry. This was to make the graphite loading very small so the CV peaks could be well discerned. One additional aluminum foil, usually 1-2 mm wide, was pasted onto carbon tape inside the pouch cell to be used as reference electrodes. For aluminum side CV, working, counter, reference electrodes were all aluminum, and the working electrode had size (0.2 cm × 0.2 cm) much smaller than that of the counter electrode (1 cm × 1 cm). The charge-discharge test was performed using device from Neware, BTS80, Version 17.

Rationale for using Si wafer intensity as an external reference to determine the anionic species concentrations

Since there was no cation peak in the Py13Cl-AlCl₃ spectrum, and clear liquid would not form at AlCl₃/Py13Cl ratio equaled to 1, we could only use the silicon wafer signal as the external reference. In addition, we assumed that the laser beam would excite the same volume of electrolyte each time. We believe that such assumptions were reasonable considering the fact that only an estimation on the concentration were needed, and consistent data were produced when Si peak and EMI⁺ peak were used as reference separately. We noticed that once the Si signal was maximized, all the other peaks in the spectrum had intensities that could vary by around 10%. For each AlCl₃/organic chloride ratio IL, a minimum of three spectra were taken at different silicon wafer positions, and background subtraction to each spectrum was performed. The intensities of the silicon wafer were all normalized to 100, and the intensities for AlCl₄⁻ and Al₂Cl₇⁻ were obtained by taking the average intensity over all the spectra we acquired. In this way, the inherent error from the actual experiment could be minimized. The standard deviation obtained from all the spectra were used to determine the errors in the concentration and ion percent calculations.

Density Functional Theory (DFT) and *Ab Initio* Molecular Dynamics (AIMD) Calculations

To find minimum-energy structures we carried out DFT and AIMD calculations using projector-augmented plane-wave code VASP¹ with Perdew-Burke-Ernzerhof (PBE) functional² and D3 correction.^{3,4} The EMI⁺-AlCl₄⁻ and Py13⁺-AlCl₄⁻ systems were modelled by 22Å×22Å×22Å unit cells in which at least 12 Å vacuum exist along x, y, z directions. We used a gamma *k*-point and a cutoff energy of 470 eV. The AIMD simulations were performed for 17 ps and 16 ps in the case of EMI⁺-AlCl₄⁻ and Py13⁺-AlCl₄⁻, respectively, considering the NVT ensemble with a Nosé-Hoover thermostat and *T*=300 K. For both cases, two different configurations were first considered and calculated using DFT, followed by AIMD simulation on the energetically more favourable structure. Afterwards, we carried out DFT calculation on 2 minimum energy structures in the AIMD simulation. By comparing total energies of structures from AIMD and DFT (before AIMD simulation) we determined the minimum energy structures of EMI⁺-AlCl₄⁻ and Py13⁺-AlCl₄⁻.

The interaction energy Δ*E* and the Gibbs free energy change for de-solvation Δ*G* were calculated as described in Ref. 5 using Gaussian and TURBOMOLE with B3LYP/def2-TZVP and B3LYP-D3(BJ)/def2-TZVP.⁶⁻¹⁵ The Gibbs free energy change for de-solvation Δ*G* is determined at 298.15 K by including the temperature dependent rovibrational contributions with the help of statistical thermodynamics. The sizes of the molecules were determined by creating a molecular surface with the COSMO approach based on the unmodified van der Waals radii.^{16,17}

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Error propagation formula for Figure 4

As an example, the error in [AlCl₄⁻] (Figure 4b) was calculated as:

$$\sqrt{\left(\frac{\Delta[\text{AlCl}_4^-]_{1.0}}{[\text{AlCl}_4^-]_{1.0}}\right)^2 + \left(\frac{\Delta I, [\text{AlCl}_4^-]_{1.0}}{I, [\text{AlCl}_4^-]_{1.0}}\right)^2 + \left(\frac{\Delta I, [\text{AlCl}_4^-]_x}{I, [\text{AlCl}_4^-]_x}\right)^2} \times [\text{AlCl}_4^-]_x \quad (\text{S1})$$

In equation S1, Δ[AlCl₄⁻]_{1.0} was 0 (error in AlCl₄⁻ concentration in 1.0 EMIC), Δ*I*, [AlCl₄⁻]_{1.0} and *I*, [AlCl₄⁻]_{1.0} were the error and absolute value of the AlCl₄⁻ Si normalized Raman peak intensity in 1.0 EMIC, respectively. Δ*I*, [AlCl₄⁻]_{*x*} and *I*, [AlCl₄⁻]_{*x*} were the error and absolute value of the AlCl₄⁻ Si normalized Raman peak intensity in *x* EMIC, where *x* = 1.1 – 1.7. [AlCl₄⁻]_{*x*} was the AlCl₄⁻ concentration in *x* EMIC (*x* = 1.1 – 1.7) obtained from equation 2. The errors for other quantities, [Al₂Cl₇⁻], [Al₂Cl₇⁻] / [AlCl₄⁻] and ion percent could be obtained similarly.

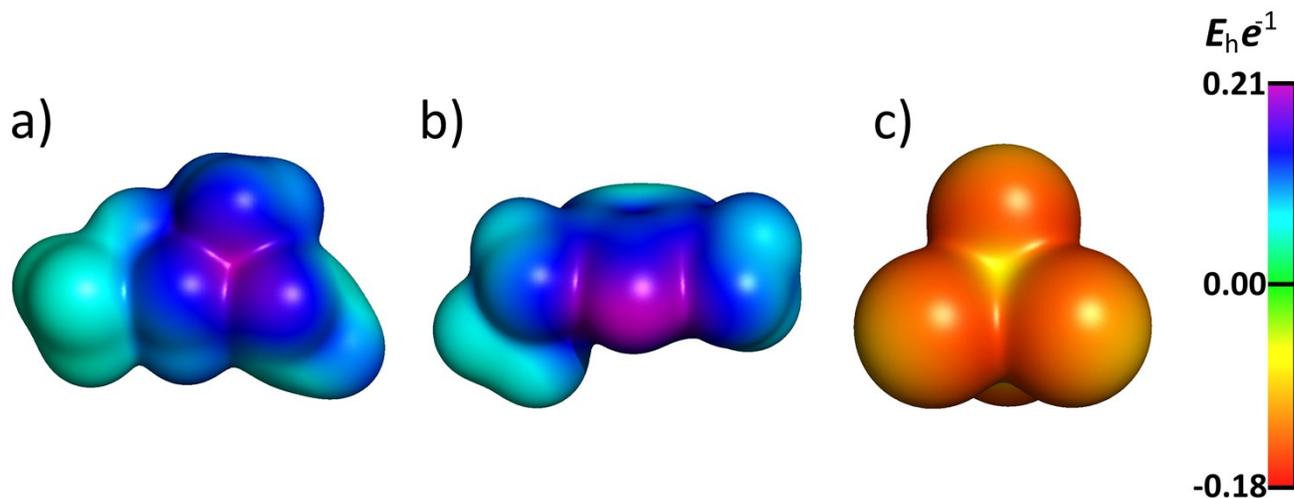


Figure S1 Electrostatic potential maps of a) Py13^+ , b) EMI^+ , and c) AlCl_4^- . Calculations were performed with B3LYP-D3(BJ). Red/orange indicates a negative and blue/purple a positive surface charge. The values in the scale bar are in $E_h e^{-1}$ (Hartree per elementary charge). The sizes of the molecules were determined based on the van der Waals radii to be a) 142 \AA^3 , b) 118 \AA^3 , and c) 105 \AA^3 .

Ionic Liquid	Functional	De-solvation ΔG (kJ/mol)	Interaction Energy ΔE (kJ/mol)
EMIC- AlCl_3	B3LYP/def2-TZVP	249.41	304.25
	B3LYP-D3(BJ)/def2-TZVP	282.90	343.13
Py13- AlCl_3	B3LYP/def2-TZVP	243.93	297.31
	B3LYP-D3(BJ)/def2-TZVP	275.92	334.58

Table S1 De-solvation Gibbs free energy change (at 298.15 K) and interaction energy between EMI^+ and AlCl_4^- as well as Py13^+ and AlCl_4^- in EMIC- AlCl_3 IL and Py13Cl- AlCl_3 IL, respectively, calculated using B3LYP/def2-TZVP or B3LYP-D3(BJ)/def2-TZVP.

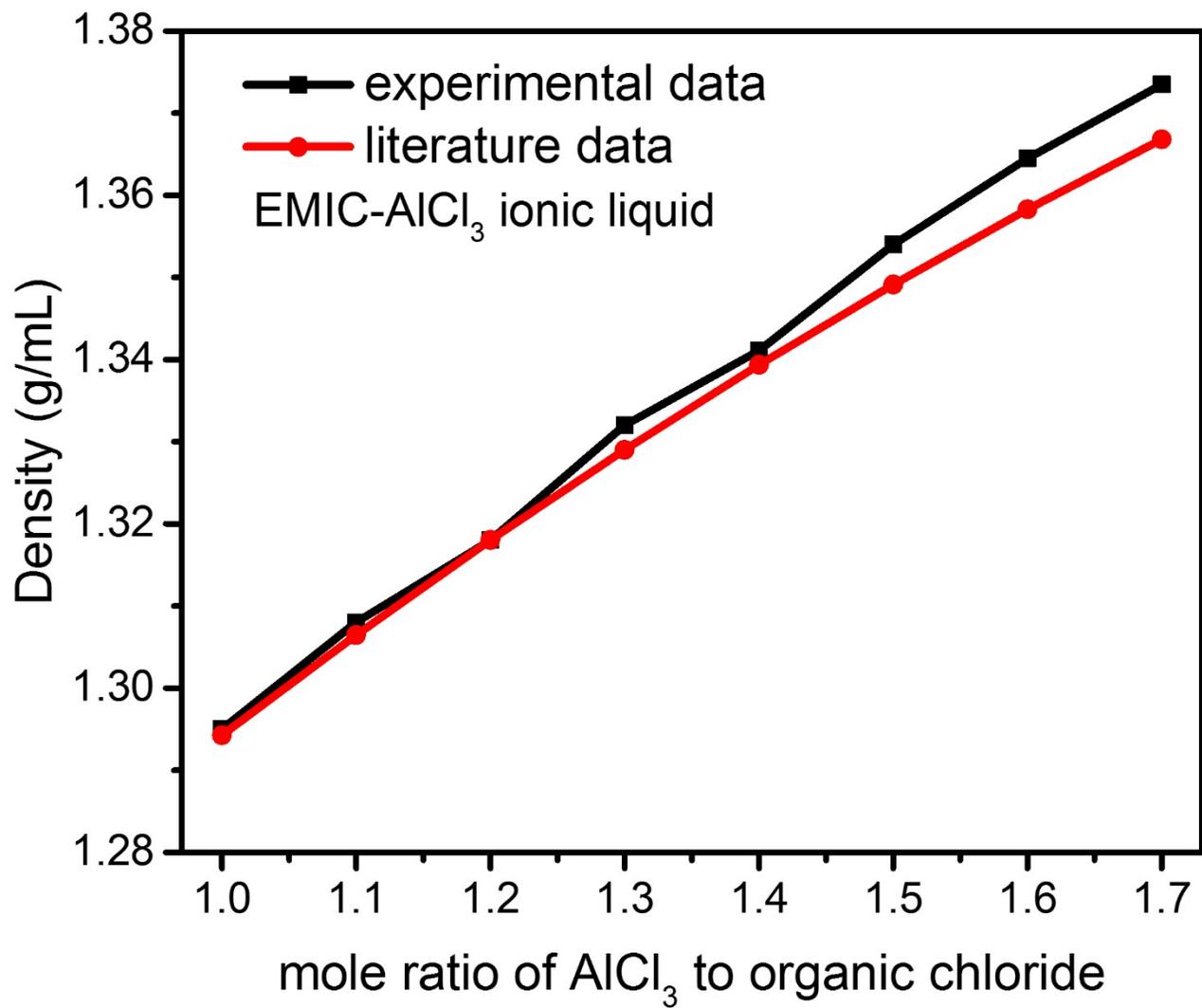


Figure S2 Density comparison between our experimental results and those obtained from literature.²⁰

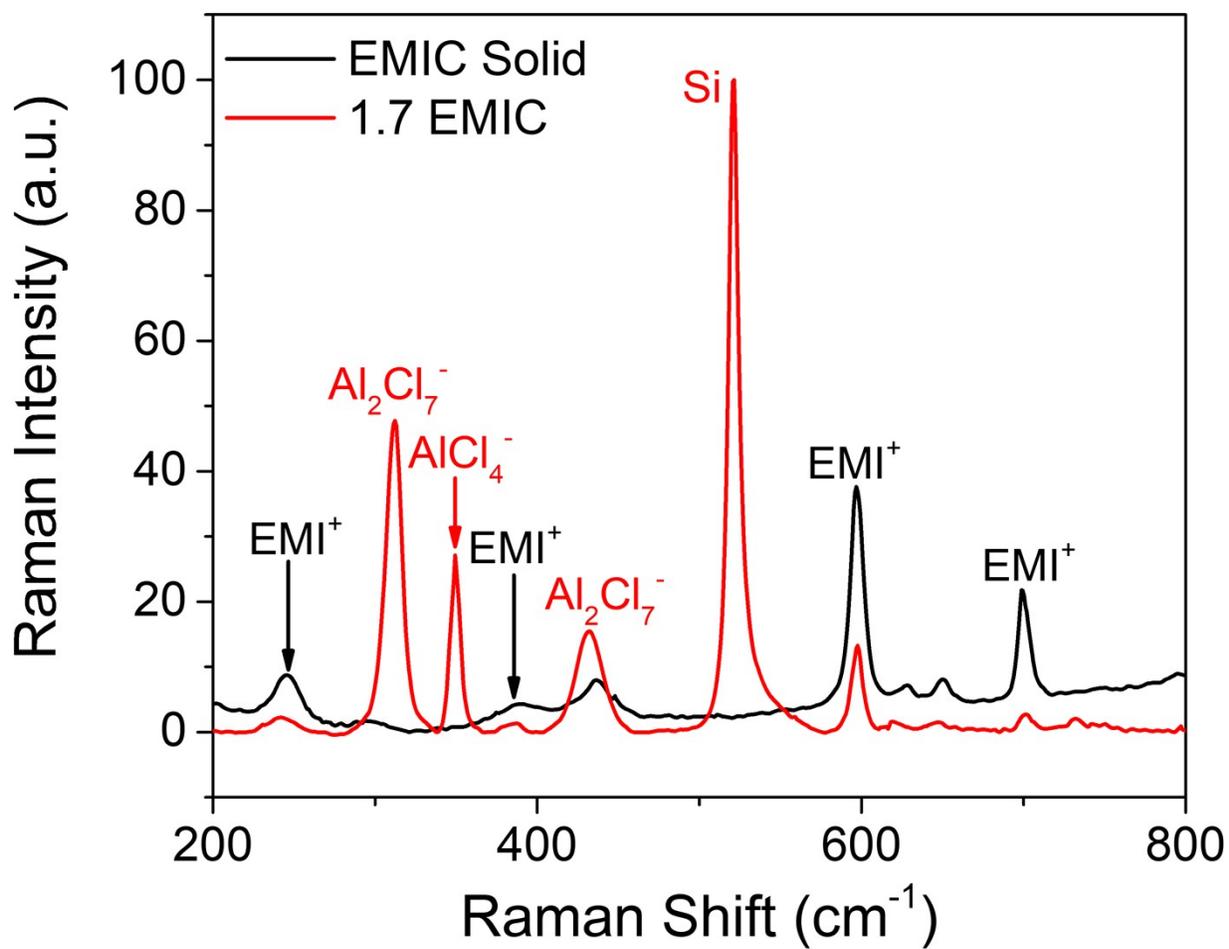


Figure S3 Raman spectrum comparison between EMIC solid and 1.7 EMIC ionic liquid.

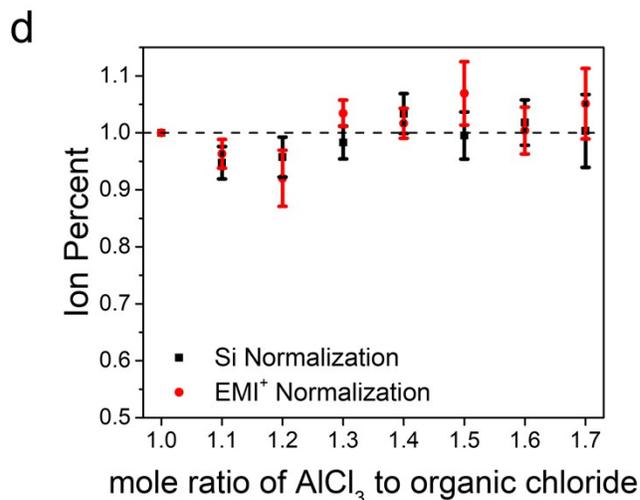
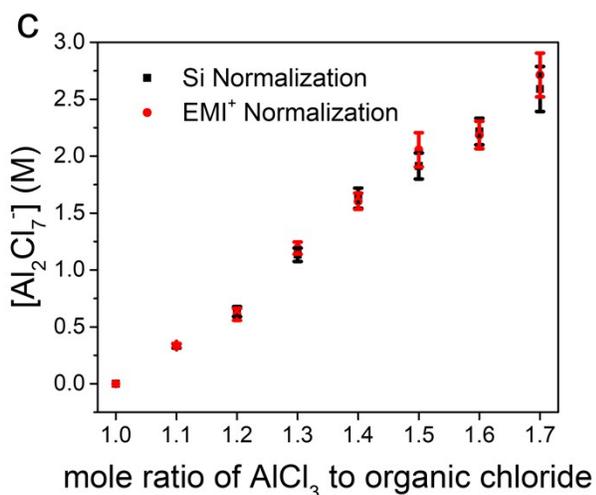
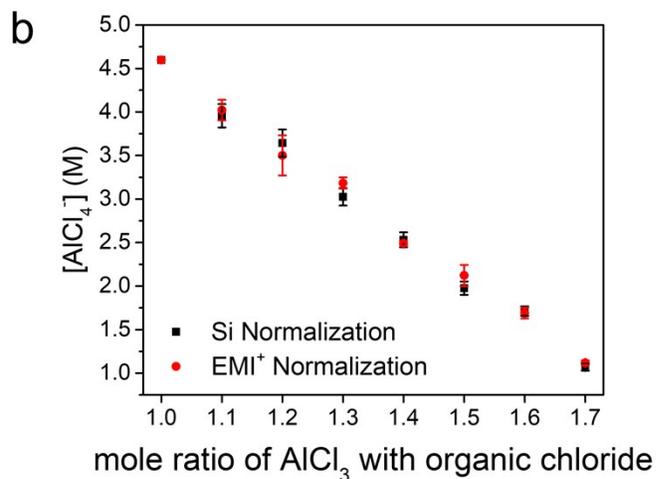
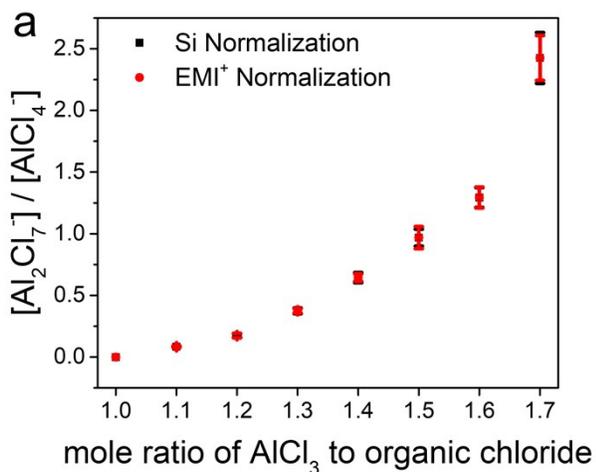


Figure S4 Comparison between EMI⁺ normalization and Si normalization for $AlCl_4^-$, $Al_2Cl_7^-$ concentration and ion percent calculations. a comparison between the ratio of $[Al_2Cl_7^-]$ and $[AlCl_4^-]$ **b** comparison between the $Al_2Cl_7^-$ concentration **c** comparison between the $AlCl_4^-$ concentration **d** comparison between ion percent.