

A Guanidium Salt as a Chaotropic Agent for Aqueous Battery Electrolytes

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Supplementary information

Synthesis Procedure for GdmTFSI: To synthesis the material, 0.0104 mol of LiTFSI (99.9% extra dry, Solvionic) and 0.0052 mol of Guanidium Sulphate (99%, Sigma Aldrich) was dissolved in the minimum volume of water, after which the LiTFSI solution is added dropwise under stirring into the Gdm₂SO₄ forming a cloudy solution. This solution is dried, forming a white precipitate containing a mixture of GdmTFSI and Li₂SO₄. Acetone (10 mL, extra dry, Alfa Aesar) is added to the mixture and stirred for 1 h, after which this mixture is filtered. The filtrate, containing the GdmTFSI, is rotary evaporated under

vacuum to form a cloudy ionic liquid which, once cooled, crystallises to form the desired final product that is dried under vacuum overnight with a yield of 97%.

Single Crystal XRD:

The X-ray diffraction experiment was performed in the XRD platform of the IMPMC (Paris).

A transparent platy crystal (100x50x10 μ m³) was selected and mounted on a MiteGen micro-loop within silicon oil. The data was collected at 293K using a Rigaku *MM007HF* Mo rotating anode diffractometer equipped with a *RAXIS4++* IP detector, Osmic confocal multilayers optics. A 180° omega scan (1 min and 1° width/frame) was carried out and 40087 reflections were collected (20251 independent). Our “homemade” goniometer only allows for omega scans, and this explains the relatively limited completeness (94.6% at the maximum crystallographic resolution). The crystal quality was good however, low thickness limited the diffraction to $d_{\min}=0.9$ Å.

The unit cell parameters determination, refinement and data reduction were carried out with CrysAlisPro RED.¹ The measured reflections were scaled and merged with the same program.

Then, using Olex2 suite, the structure was solved in the P-1 space group with the SHELXT structure solution program (Intrinsic Phasing method) and refined with the SHELXL refinement package using least squares minimisation methods.^{2,3}

The asymmetric unit contains 12 [Gdm]⁺ and 12 [TFSI]⁻ anions. All non-H atoms were refined with anisotropic displacement parameters, RIGU and a few geometrical restraints were applied to some atoms of the 4 disordered [TFSI]⁻ anions.

Crystallographic parameters and data refinement results are given in *Table 1*. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures (**CCDC deposition number # 2284950**).

Identification code	Gua_ (CCDC number 2284950)
Empirical formula	C ₃ H ₆ F ₆ N ₄ O ₄ S ₂
Formula weight	340.24
Temperature/K	293
Crystal system	triclinic
Space group	P-1
a/Å	15.9721(9)
b/Å	18.6173(9)
c/Å	25.1641(5)
α/°	89.960(3)
β/°	85.636(3)
γ/°	87.428(4)
Volume/Å³	7453.5(6)
Z	24
ρ_{calc}/cm³	1.819
μ/mm⁻¹	0.522
F(000)	4080
Crystal size/mm³	0.1 × 0.05 × 0.01
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	3.294 to 46.512
Index ranges	-17 ≤ h ≤ 17, -20 ≤ k ≤ 20, -27 ≤ l ≤ 27
Reflections collected	40087
Independent reflections	20251 [R _{int} = 0.0602, R _{sigma} = 0.0756]
Data/restraints/parameters	20251/306/2452
Goodness-of-fit on F²	1.038
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.1025, wR ₂ = 0.2707
Final R indexes [all data]	R ₁ = 0.1390, wR ₂ = 0.3005
Largest diff. peak/hole / e Å⁻³	1.10/-0.50

Table 1. Crystal data and structure refinement for GdmTFSI.

IR measurements: FTIR spectra were acquired in ATR mode on a NicoletTM iSTM 5 FTIR spectrometer (Thermo Fisher Scientific) in the range of ~500 to 4000 cm⁻¹.

Thermogravimetric Analysis: The thermal stability was analysed by TGA/DSC using a Mettler Toledo TGA/DSC3+LF/1100. Around ~10 mg of the sample was put in an aluminium crucible and heated at a rate of 5°C/min from ambient temperature to 400°C under air.

Inductively Coupled Plasma Mass Spectroscopy: The residual Li content was quantified using inductively coupled plasma mass spectroscopy (ICP-MS, Nexion 2000, Perkin Elmer). Solution used was dilute nitric acid solution (Sigma-Aldrich). To factor in any residual Li content within the stock solution. Five different concentrations of GdmTFSI in this solution were probed and the gradient of these values is used as the Li content of the GdmTFSI powder.

Aqueous solution preparation: GdmTFSI_(aq) solutions were created with ultra-pure water (Millipore® Direct-Q® Purification, 18.2 MΩ·cm at 25°C) in magnet stirred vials at ~ 25°C.

Electrochemical Measurements: ESW measurements was performed using a PTFE embedded glassy carbon disc (3 mm diameter, Pine Research Instrumentation) as working electrode, Pt wire as counter electrode and saturated calomel electrode (SCE) was used as a reference. ~5 mL of electrolyte was used for each measurement. Temperature for 8m GdmTFSI was controlled by flowing water controlled via a chiller into a mantle around the electrochemical glass cell. Cyclic voltammetry experiments were all performed on a VMP3 potentiostat (Bio-Logic) at a 5 mV s⁻¹ scan rate determination with potentials converted Standard Hydrogen Electrode (SHE) from SCE (**+0.248 V**). Separate scans were taken to determine the cathodic and anodic limits. For measurements in acetonitrile, a leak-less Ag/AgCl reference electrode was used and these measurements were carried out in an Ar-filled glovebox (Braun)

Viscosity Measurements: The viscosities of the electrolytes were measured at 25°C using a Lovis 2000 ME rolling ball viscometer, coupled with an Anton Paar DMA 4500 M oscillation U-tube densitometer.

Supplementary Figures

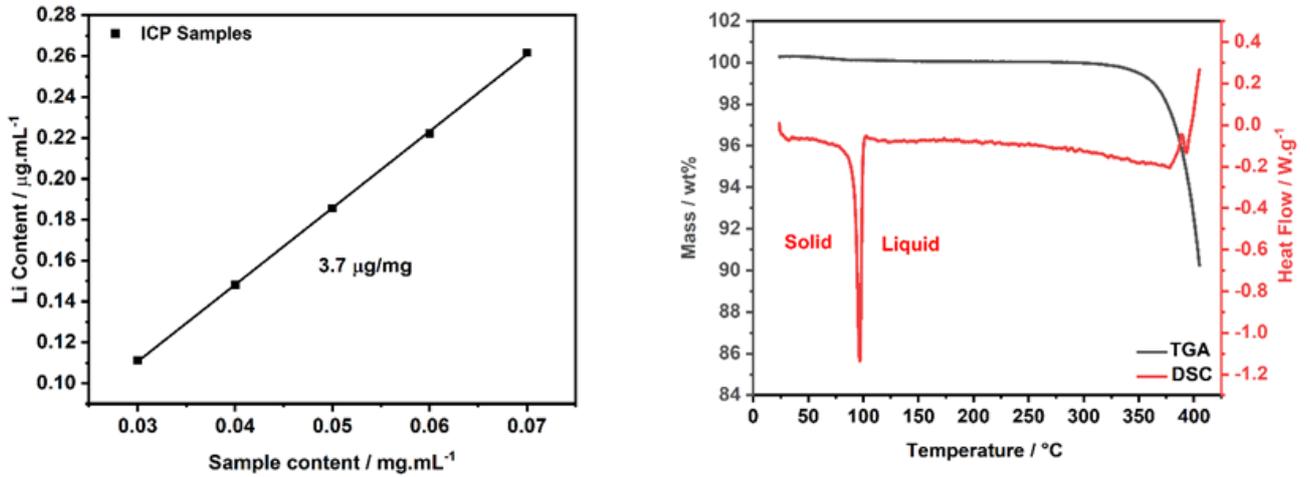


Fig. S1 left - Residual lithium content probed using inductively coupled plasma mass spectrometry (ICP-MS). (right) Thermogravimetric analysis (TGA) in grey and differential scanning calorimetry (DSC) in red.

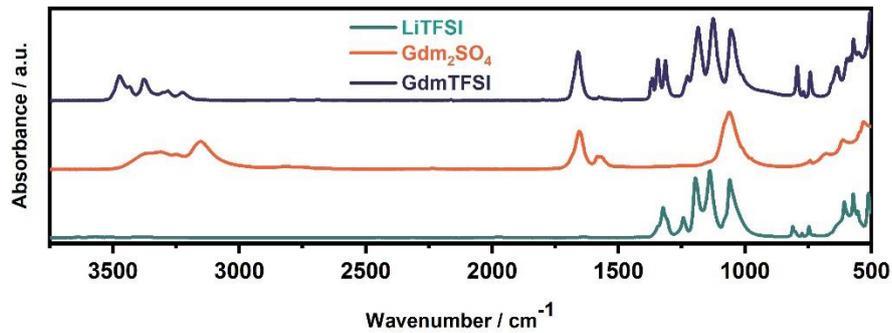


Fig. S2 – Comparison of GdmTFSI vs precursor materials (LiTFSI and Gdm₂SO₄).

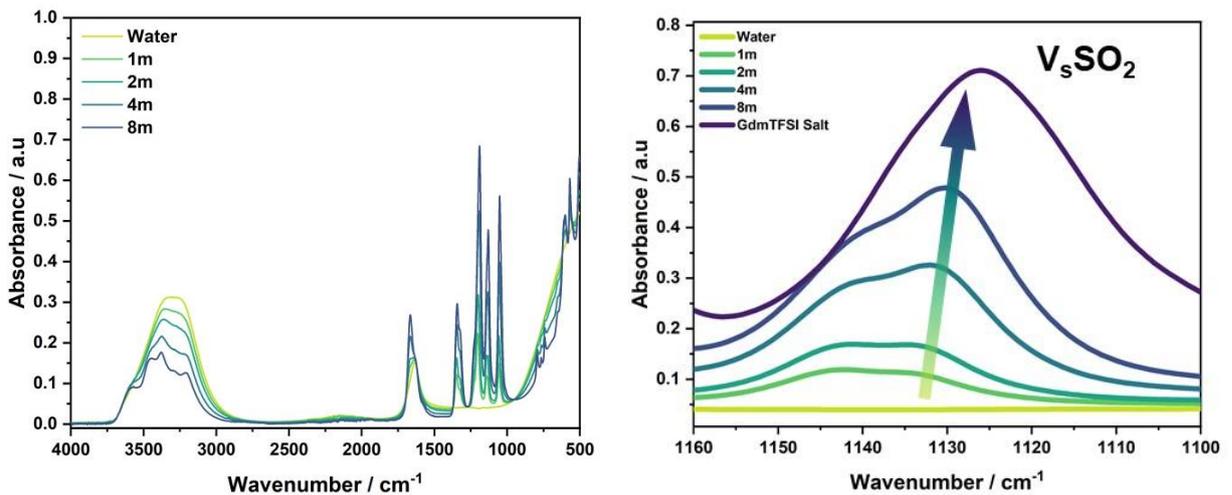


Fig. S3 – Full IR spectra of GdmTFSI_(aq) solutions (left). V_sSO₂ band for pure salt overlaid on GdmTFSI_(aq) solutions (right).

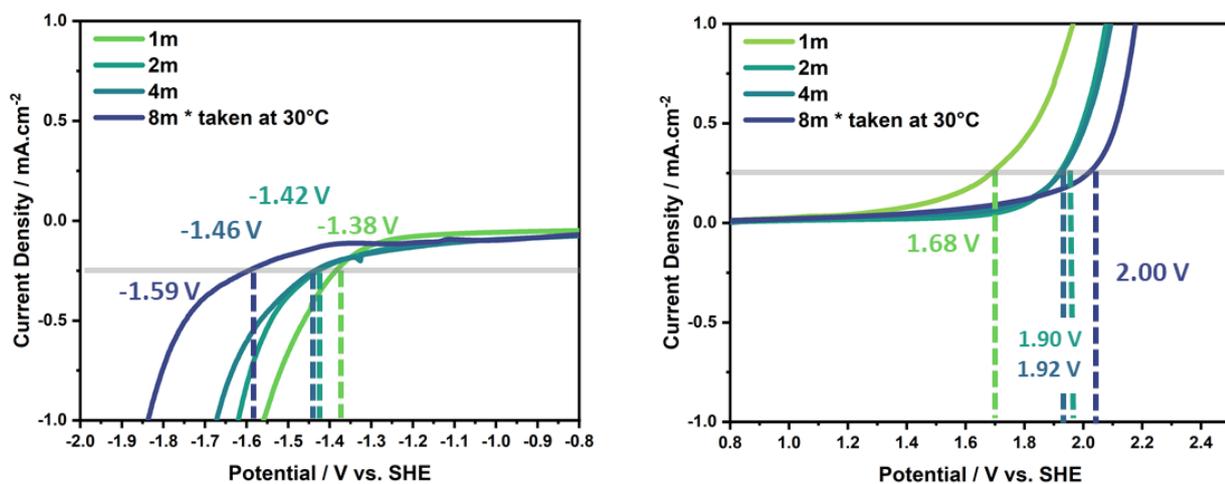


Fig. S4 – (left) reductive limits (right) oxidative limits.

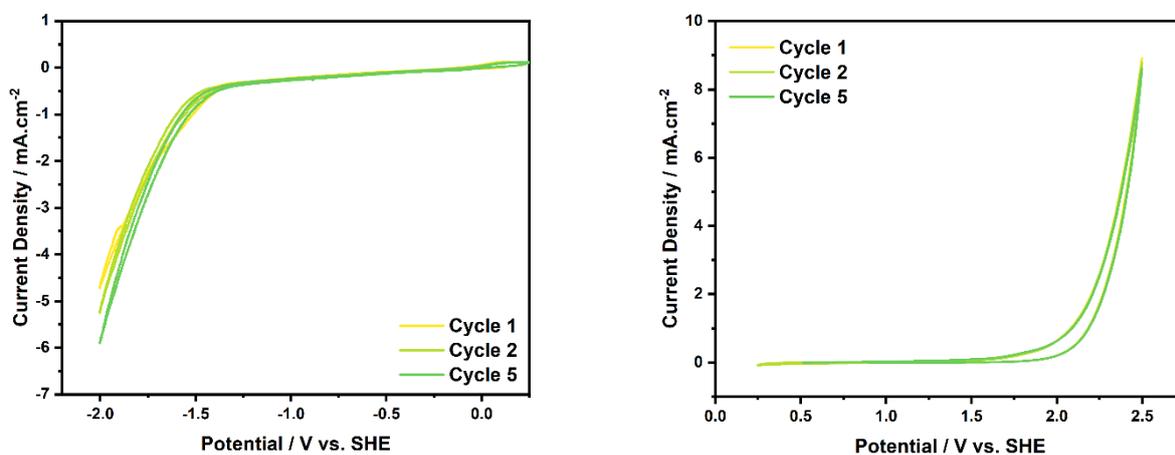


Fig. S5 – Passivation test with 8m GdmTFSI on glassy carbon taken at 5 mV/s (left) in reduction (right) in oxidation. No sign of passivation is noted over 5 cycles.

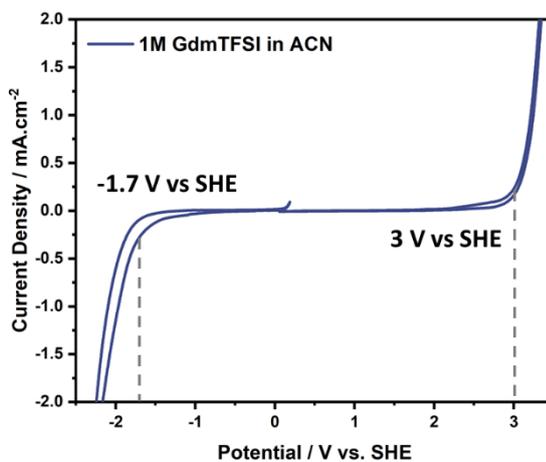


Fig. S6 – Salt decomposition test with 1M GdmTFSI in ACN on glassy carbon taken at 5 mV/s. In line with the expected stability limits with ACN.⁵

Jones-Dole equation

A common way to assess effect of individual ions on water structure is to measure the viscosity of dilute solutions (0.0625 – 1 mol/l) and to determine the B-coefficient from the Jones-Dole equation, calculated through the slope:

$$\left(\frac{\eta}{\eta_{\text{water}}}\right) - 1 = Ac^{\frac{1}{2}} + Bc \quad (\eta = \text{density, A and B = coefficients and c = concentration})$$

Where positive B-coefficient values = kosmotropic and negative values = chaotropic.

A-coefficient	A standard error	B-coefficient	B standard error	R value
-0.068	0.026	0.441	0.035	0.975

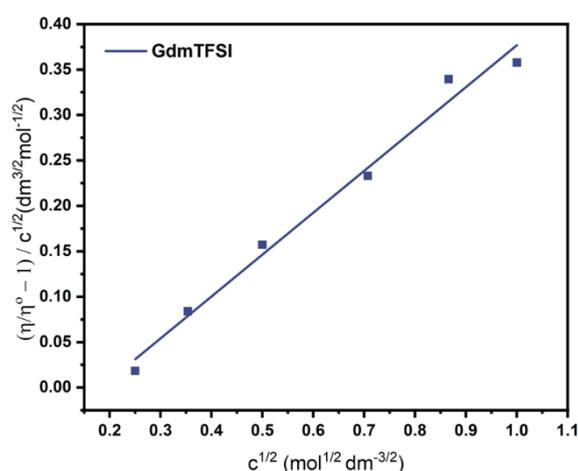


Figure S7. Viscosity measurements for low concentrations (0.0625 to 1 mol L⁻¹) GdmTFSI(aq) where straight line represent a linear fitting with the Jones-Dole equation.

By comparing the results for GdmTFSI with those obtained for LiTFSI from our previous study⁵, we can calculate the effect of the Gdm cation. Gdm is calculated to have a B-coefficient of +0.46, while LiTFSI was revealed to have a B-coefficient of +0.77 where, Li⁺ accounts for +0.18 and TFSI⁻ +0.59. As mentioned in the main text, the positive B-coefficient for TFSI, which is unexpected due to the anion being typically characterized as chaotropic, has been explained by the large size and hydrophobic character of the anions.⁶ Nevertheless, when using these values, we determine that the Gdm cation has a B-coefficient of -0.13, indicating the cation is acting as a chaotrope relative to the Li⁺.

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