

## SUPPORTING INFORMATION

### Novel and versatile room temperature ionic liquids for energy storage

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### ***General Information***

Tris(2-(2-methoxyethoxy)ethyl)amine (95 %) was obtained from Sigma-Aldrich and purified by passing through an alumina column followed by distillation under vacuum (150 °C, 0.18 mbar). CsCB<sub>11</sub>H<sub>12</sub> was obtained from Katchem (Czech Republic) and used as received. [Mg(DME)<sub>3</sub>][CB<sub>11</sub>H<sub>12</sub>]<sub>2</sub> was prepared according to the published literature.<sup>1</sup> Li-N Tf<sub>2</sub> (99.9 %) was purchased from Chem-supply, and silver trifluoromethanesulfonate (AgOTf) and Mg[BH<sub>4</sub>]<sub>2</sub> (95 %) were purchased Sigma-Aldrich; these salts were used as received. Bromoethane (>99 %) and 1-bromobutane (99 %) were purchased from Sigma-Aldrich and purified via extraction from 1M H<sub>2</sub>SO<sub>4</sub> and neutralised with NaHCO<sub>3</sub>, followed by distillation.<sup>2</sup> Tetraglyme was purified according to literature procedure.<sup>1</sup> All other materials were purchased from Sigma-Aldrich and used as received. Nuclear magnetic spectroscopy and mass spectrometry (detection limit: 0.1 %) were used to confirm the purity of the ionic liquids. Proton (<sup>1</sup>H) (See **Figure S1**) and Carbon (<sup>13</sup>C) NMR spectra were conducted in deuterated dimethylsulfoxide (d-DMSO) (Merck) and carried out in a 400 MHz Bruker DPX-400 spectrometer. Low resolution ESI mass spectra (See **Figure S2**) were recorded on a Micromass Platform II QMS with a cone voltage of 35 V, using methanol as the mobile phase. No peaks corresponding to [Cs]<sup>+</sup> at m/z = 132.9 and [Br]<sup>-</sup> at m/z = 79.0, 80.1 (1 : 1) were observed in the ES<sup>+</sup> and ES<sup>-</sup> mass spectra respectively.

### ***Instrument details***

Differential scanning calorimetry (DSC) was performed over three cycles in the temperature range of -100 °C to 100 °C at a scan rate of 10 °C/min. The melting point is reported using the peak maximum while the onset temperature was chosen for the glass transition temperatures. Thermogravimetric analysis (TGA) was undertaken on a Mettler Toledo TGA/DSC 1 STARe System. Samples were heated at 10 °C/min over a temperature range of 25 to 450 °C under nitrogen.

The density and viscosity of both RTILs in the temperature range of 25 °C to 90 °C were measured using an Anton Paar density meter (model DMA 5000) and an Anton Paar microviscometer (model Lovis 2000 M), respectively. The ionic conductivity of both RTILs in the temperatures range of 25 °C to 90 °C was measured using AC impedance spectroscopy with the frequency ranging from 0.1 Hz to 10 MHz, using a 2-electrode Pt wire dip cell. Measurements were performed with a frequency response

analyser, Solatron 1296. A standard reference of 0.01 M KCl was used to calibrate the cell. All measurements were repeated three times. Errors were less than 0.05 standard deviation across the three measurements for each experiment.

### **Synthesis**

#### **Synthesis of *N*-ethyl-2-(2-methoxyethoxy)-*N,N*-bis(2-(2-methoxyethoxy)ethyl)ethan-1-aminium bromide [N<sub>2(20201)(20201)(20201)</sub>][Br] (1)**

Tris(2-(2-methoxyethoxy)ethyl)amine (10 g, 30.9 mmol) and bromoethane (6.74 g, 61.8 mmol) were mixed in anhydrous acetonitrile (50 mL) and stirred for 48 h at 50 °C under N<sub>2</sub> to give a yellow solution. The solvent was evaporated and the crude product was mixed with water and washed with dichloromethane (6 × 30 mL). The aqueous layer was concentrated *in vacuo* and further dried under high vacuum (8h, 30 °C, 0.35 mbar) to give a yellow viscous oil (9.8 g, yield = 73 %) <sup>1</sup>H NMR: δ 3.85 – 3.82 ppm, 6H, t ; δ 3.59 – 3.57 ppm, 6H, t ; δ 3.53-3.52 ppm, 6H, t ; δ 3.40 ppm, 9H, s ; δ 3.28 ppm, 2H, q ; δ 1.20-1.18 ppm, 3H, s. <sup>13</sup>C NMR: δ 73.4 ppm ; δ 71.1 ppm ; δ 69.5 ppm ; δ 62.1 ppm ; δ 60.3 ppm ; δ 55.3 ppm ; δ 10.1 ppm. MS [ES]<sup>+</sup> = 352.4 MS [ES]<sup>-</sup> = 78.9.

#### **Synthesis of *N*-ethyl-2-(2-methoxyethoxy)-*N,N*-bis(2-(2-methoxyethoxy)ethyl)ethan-1-aminium carba-*closo*-dodecaborate [N<sub>2(20201)(20201)(20201)</sub>][CB<sub>11</sub>H<sub>12</sub>] (IL1)**

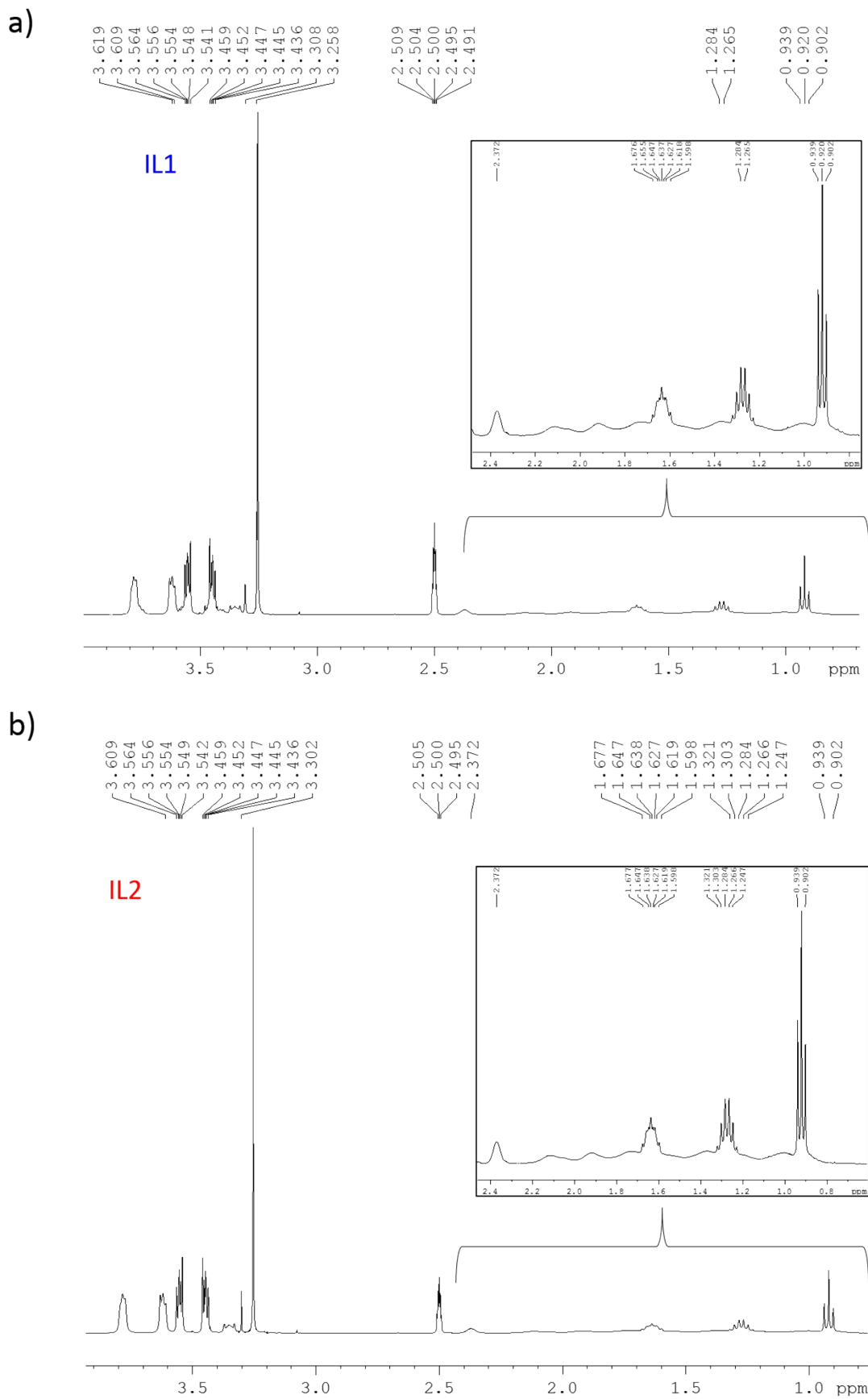
Cesium carba-*closo*-dodecaborate (3.5g, 12.7 mmol) and **1** (5.22 g, 12.1 mmol) were mixed in water (50 mL) and the solution was stirred for 12 h at room temperature. The crude product was extracted with dichloromethane (5 x 30 mL) and the organic layer was concentrated *in vacuo* and dried under high vacuum (48 h, 38 °C, 0.25 mbar) to give a pale yellow oil (water content = 120 ppm). The water content was further reduced by azeotropic distillation (toluene, 50 mL), followed by drying under high vacuum (96 h, 70 °C, 0.30 mbar) (3.7 g, yield = 62 %, water content = 80 ppm). <sup>1</sup>H NMR: δ 3.85 – 3.82 ppm, 6H, t ; δ 3.59 – 3.57 ppm, 6H, t ; δ 3.53-3.52 ppm, 6H, t ; δ 3.40 ppm, 9H, s ; δ 3.28 ppm, 2H, q ; δ 2.4-2.3 ppm, 1H, s (broad) ; δ 2.15 – 1.80 ppm, 10 H, m (broad) ; δ 1.20-1.18 ppm, 3H, s. <sup>13</sup>C NMR : δ 73.4 ppm ; δ 71.1 ppm ; δ 69.5 ppm ; δ 62.1 ppm ; δ 60.3 ppm ; δ 55.3 ppm ; δ 10.1 ppm. MS [ES]<sup>+</sup> = 352.4 MS [ES]<sup>-</sup> = 143.1.

**Synthesis of *N*-butyl-2-(2-methoxyethoxy)-*N,N*-bis(2-(2-methoxyethoxy)ethyl)ethan-1-aminium bromide [N<sub>4(20201)(20201)(20201)</sub>][Br] (2)**

Tris(2-(2-methoxyethoxy)ethyl)amine (10 g, 30.9 mmol) and 1-bromobutane (9.3 g, 67.9 mmol) were mixed in dry acetonitrile (50 mL) and stirred for 60 h at 50 °C under N<sub>2</sub> to give a yellow solution. The solvent was evaporated and the crude product was mixed with water and washed with dichloromethane (6 × 30 mL). The aqueous layer was concentrated *in vacuo* and further dried under high vacuum (8 h, 30 °C, 0.35 mbar) to give a yellow viscous oil (10.5 g, yield = 74 %). <sup>1</sup>H NMR: δ 3.83 – 3.81 ppm, 6H, t ; δ 3.58 – 3.56 ppm, 2H, t ; δ 3.58 – 3.56 ppm, 6H, t ; δ 3.50-3.48 ppm, 6H, t ; δ 3.39 ppm, 9H, s ; δ 3.20 ppm, 2H, t ; δ 1.83-1.80 ppm, 2H, m ; δ 1.33-1.30 ppm, 2H, m ; δ 0.93-0.91 ppm, 3H, s. <sup>13</sup>C NMR : δ 72.2 ppm ; δ 70.1 ppm ; δ 68.9 ppm ; δ 62.1 ppm ; δ 60.1 ppm ; δ 57.9 ppm ; δ 24.0 ppm ; δ 19.3 ppm ; δ 14.0 ppm. MS [ES]<sup>+</sup> = 380.5 MS [ES]<sup>-</sup> = 78.9.

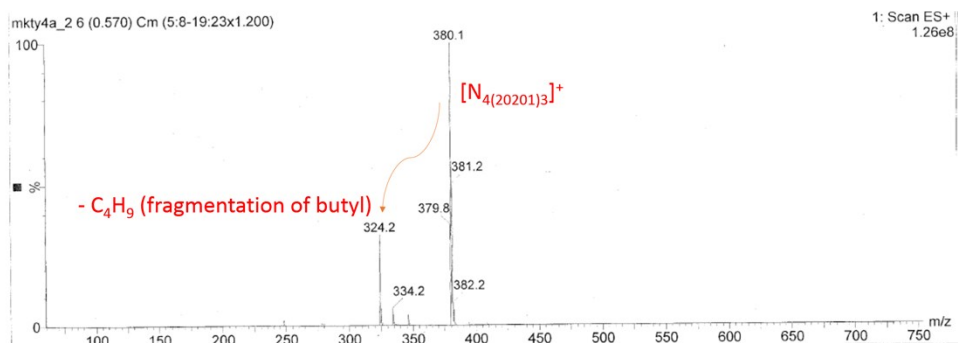
**Synthesis of *N*-butyl-2-(2-methoxyethoxy)-*N,N*-bis(2-(2-methoxyethoxy)ethyl)ethan-1-aminium carba-*closo*-dodecaborate [N<sub>4(20201)(20201)(20201)</sub>][CB<sub>11</sub>H<sub>12</sub>] (IL2)**

Cesium carba-*closo*-dodecaborate (3.5g, 12.7 mmol) and **2** (5.70 g, 12.4 mmol) were mixed in water (50 mL) at room temperature and the resulting suspension was stirred for 12 h at 40 °C to afford a clear solution. The crude product was extracted with dichloromethane (5 x 30 mL) and the organic layer was concentrated *in vacuo* to give a dark yellow oil. The ionic liquid was further purified via a column chromatographic method adapted from literature<sup>3</sup> and further dried under high vacuum (52 h, 42 °C, 0.25 mbar) to produce a pale yellow oil (3.6 g, yield = 55 %, water content = 40 ppm). <sup>1</sup>H NMR: δ 3.83 – 3.81 ppm, 6H, t ; δ 3.58 – 3.56 ppm, 2H, t ; δ 3.58 – 3.56 ppm, 6H, t ; δ 3.50-3.48 ppm, 6H, t ; δ 3.39 ppm, 9H, s ; δ 3.20 ppm, 2H, t ; δ 1.83-1.80 ppm, 2H, m ; ; δ 2.4-2.3 ppm, 1H, s (broad) ; δ 2.15 – 1.80 ppm, 10 H, m (broad) ; δ 1.33-1.30 ppm, 2H, m ; δ 0.93-0.91 ppm, 3H, s. <sup>13</sup>C NMR : δ 72.2 ppm ; δ 70.1 ppm ; δ 68.9 ppm ; δ 62.1 ppm ; δ 60.1 ppm ; δ 57.9 ppm ; δ 24.0 ppm ; δ 19.3 ppm ; δ 14.0 ppm. MS [ES]<sup>+</sup> = 380.5 MS [ES]<sup>-</sup> = 143.1.

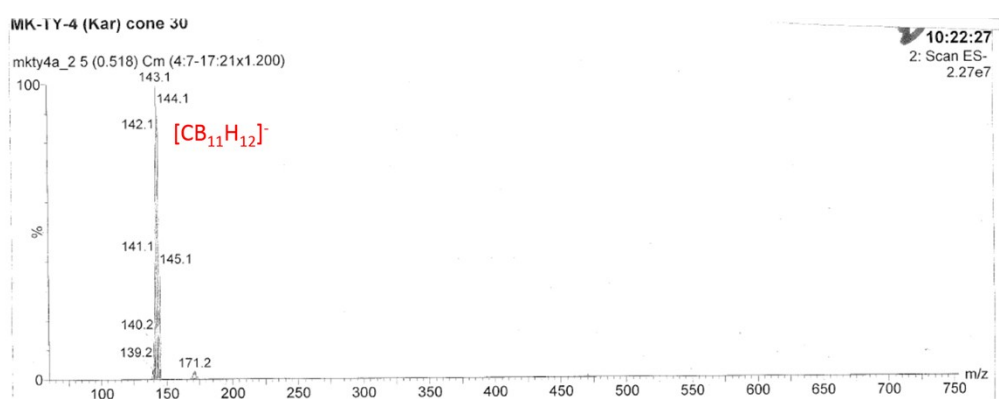


**Figure S1.**  $^1\text{H}$  NMR of a) **IL1** and b) **IL2**. (The  $^1\text{H}$  NMR of both ILs between 0.75 – 2.5 ppm is shown in the inset).

a)



b)

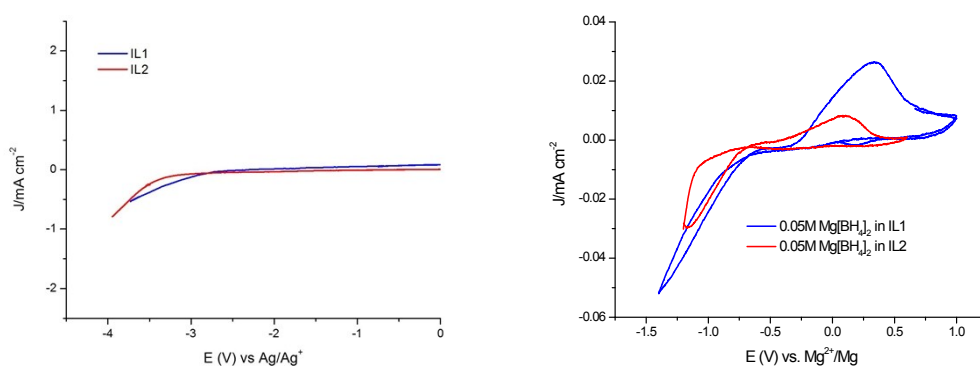


**Figure S2.** a) ES<sup>+</sup> and b) ES<sup>-</sup> of **IL2**

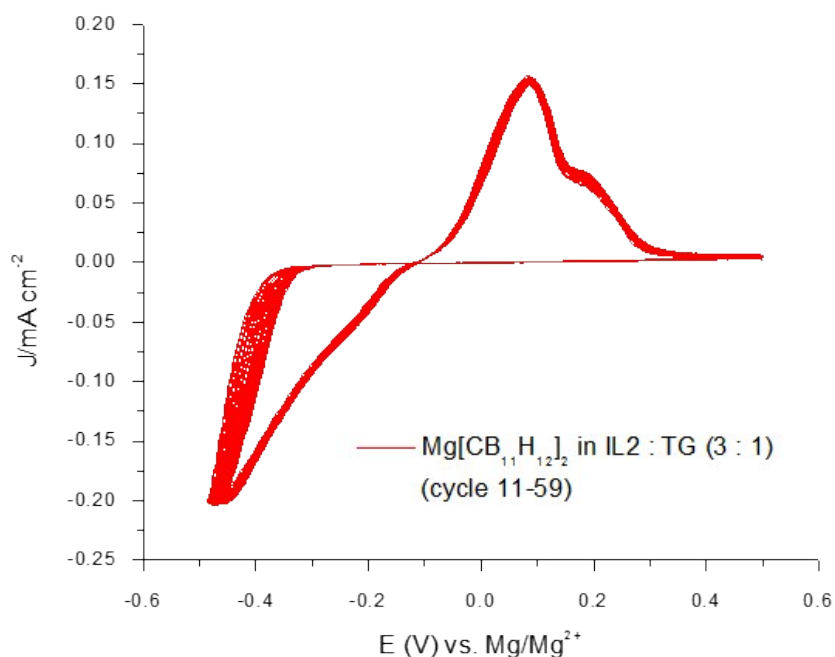
### *Cyclic Voltammetry*

All electrolytes were prepared in an Argon glovebox prior to conducting any experiments. To prepare a saturated Mg[CB<sub>11</sub>H<sub>12</sub>]<sub>2</sub> solution in **IL2** / tetraglyme (3:1), [Mg(DME)<sub>3</sub>][CB<sub>11</sub>H<sub>12</sub>]<sub>2</sub> (25.4 mg) was mixed with **IL2** / tetraglyme (3:1, w/w, 148.4 mg) and stirred under vacuum at 60°C until constant weight (15 mins) to obtain a suspension. To obtain a precise electrochemical window, a non-aqueous Ag/Ag<sup>+</sup> reference electrode was used consisting of a 10 mM AgOTf solution in **IL1**. The LiNTf<sub>2</sub> salt was stirred in **IL2** at 60°C and since the resulting solution was found viscous, the cyclic voltammogram for Li deposition/stripping was run at 60°C. Electrochemical windows were determined using a glassy carbon (GC) working electrode (electrode area = 0.78 mm<sup>2</sup>). The electrolyte was scanned to positive potentials first in small increments to ensure no bromide impurities were present in the electrolyte (which would be detected as the oxidation of bromide E<sub>[Br<sup>-</sup>/Br<sub>2</sub>]</sub> = +0.85 V vs. Ag/Ag<sup>+</sup>). This was followed by scanning a fresh electrolyte to negative potentials

in small increments to ensure no water or metal impurities i.e. cesium ( $E_{[Cs^+/Cs]} = -3.24$  V vs. Ag/Ag<sup>+</sup>) were present in the electrolyte and the absence of these impurities was consistent with the NMR and Mass Spectroscopy results. For all electrochemical cycling of Mg in ionic liquids, a Mg ribbon reference and counter electrodes and platinum disk working electrode (electrode area = 0.78 mm<sup>2</sup>) were used in a 3-electrode system. For all electrochemical cycling of Li in ionic liquids, a Li strip reference electrode, nickel working electrode (electrode area = 1.76 mm<sup>2</sup>) and a platinum counter electrode was used in a 3-electrode system.



**Figure S3.** a) Reductive stability of **IL1** (blue curve) vs. **IL2** (red curve) (Conditions: Ar glove box, WE : GC, RE : Ag(OTf)/**IL1**, CE : Pt; Scan rate : 25 mVs<sup>-1</sup>) ; and b) Cyclic voltammogram of 0.05M Mg[BH<sub>4</sub>]<sub>2</sub> in **IL1** (blue curve) vs. **IL2** (red curve) (Conditions: Ar glove box, WE : Pt, RE : Mg, CE : Mg; Scan rate : 25 mVs<sup>-1</sup>).



**Figure S4.** Cyclic voltammogram with  $-0.2 \text{ mA/cm}^2$  current cut-off of a saturated  $\text{Mg}[\text{CB}_{11}\text{H}_{12}]_2$  solution in **IL2** / tetraglyme (3:1) mixture (cycles 11-59). An approximate coulombic efficiency of 70 % was calculated from the cycling data. (Conditions: Ar glove box, WE : Pt, RE : Mg, CE : Mg; Scan rate :  $25 \text{ mVs}^{-1}$ ).

### ***Symmetric cell cycling***

Cycling was conducted in coin cells at  $25 \text{ }^\circ\text{C}$  where glass fibre was used as a separator. The Mg electrolyte used was prepared as discussed above. Mg disks (15 mm diameter, ESPI Metals) were used as the electrodes. Prior to cell assembly, scrapping of the Mg disks surfaces was conducted to remove the native oxide layer. No cell conditioning procedure was applied and the cells were cycled right after the assembly at  $19 \text{ } \mu\text{A cm}^{-2}$  ( $3 \text{ } \mu\text{Ah}$ ).

### ***Scanning Electron Microscopy***

Following the cycling of a Mg coin cell, the cell was disassembled in dry mbraun glove box ( $\text{H}_2\text{O}$ ,  $\text{O}_2 < 0.1 \text{ ppm}$ ) and the electrodes peeled off from the separator were washed in dry tetraglyme then let to soak in dry monoglyme overnight. The monoglyme was allowed to evaporate from the electrode surface that was then transferred to the electron microscope in air free SEM sample holder. The SEM analysis was conducted in a field emission scanning Jeol microscopy JSH-7800F.



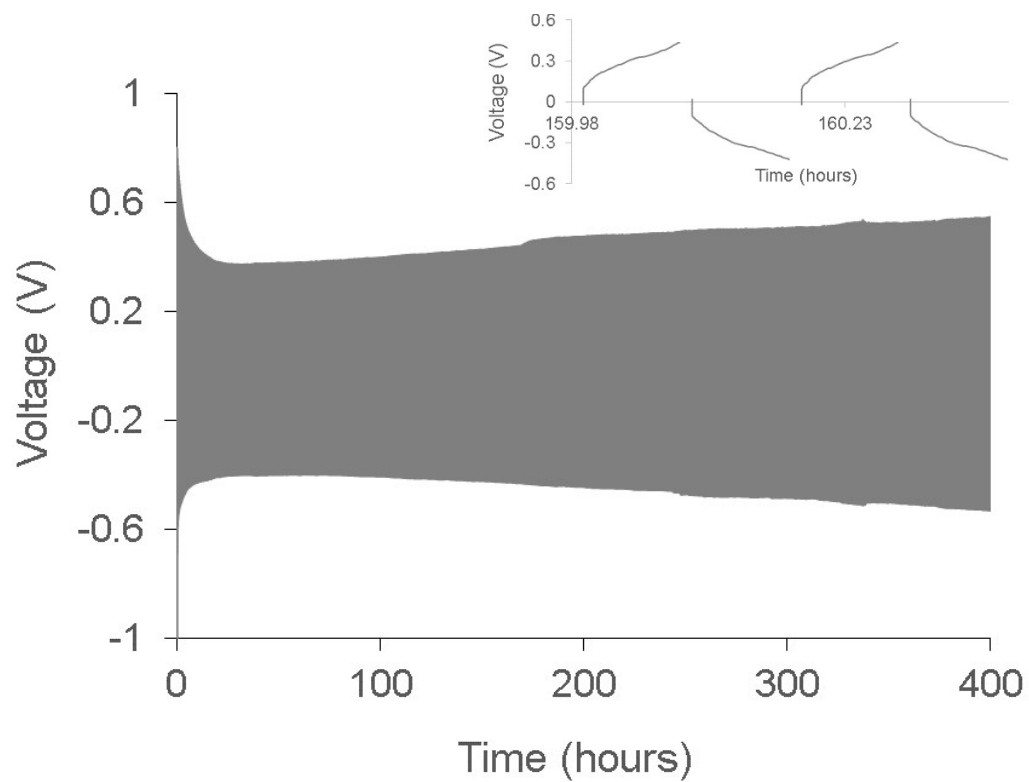


Figure S5: Mg/Mg symmetric coin cell in cycled in  $\text{Mg}[\text{CB}_{11}\text{H}_{12}]_2$  solution in **IL2** / G4 (3:1) at  $19 \mu\text{A cm}^{-2}$  ( $3 \mu\text{Ah}$ ). Glass fiber is used as the separator. Inset shows expanded view of the cycling profile.

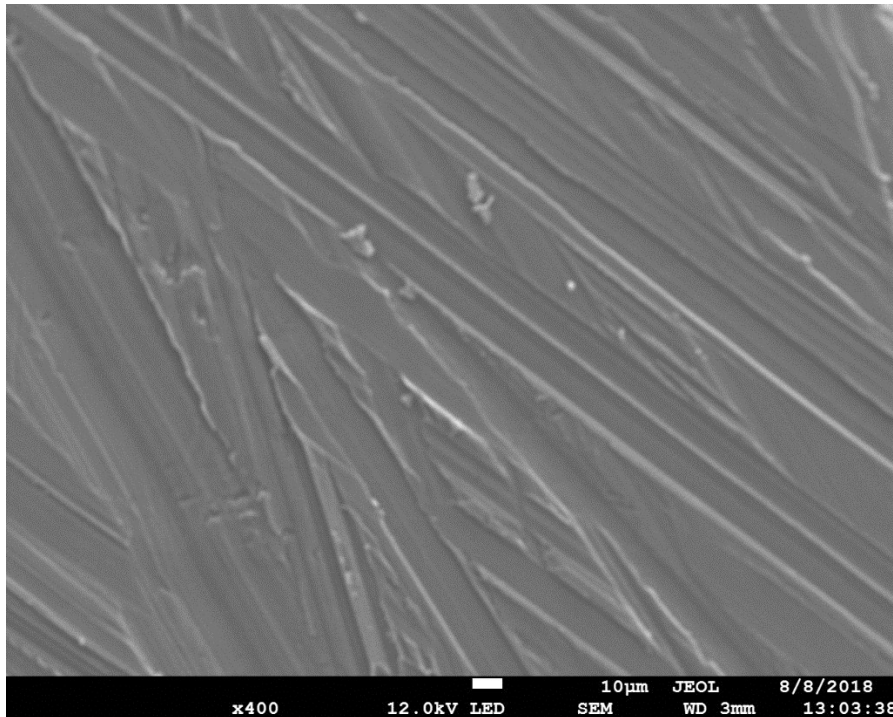


Figure S6: Pristine Mg disk surface prior to Mg cycling. The scrap marks are produced by the glass slide used to remove the native surface oxides.

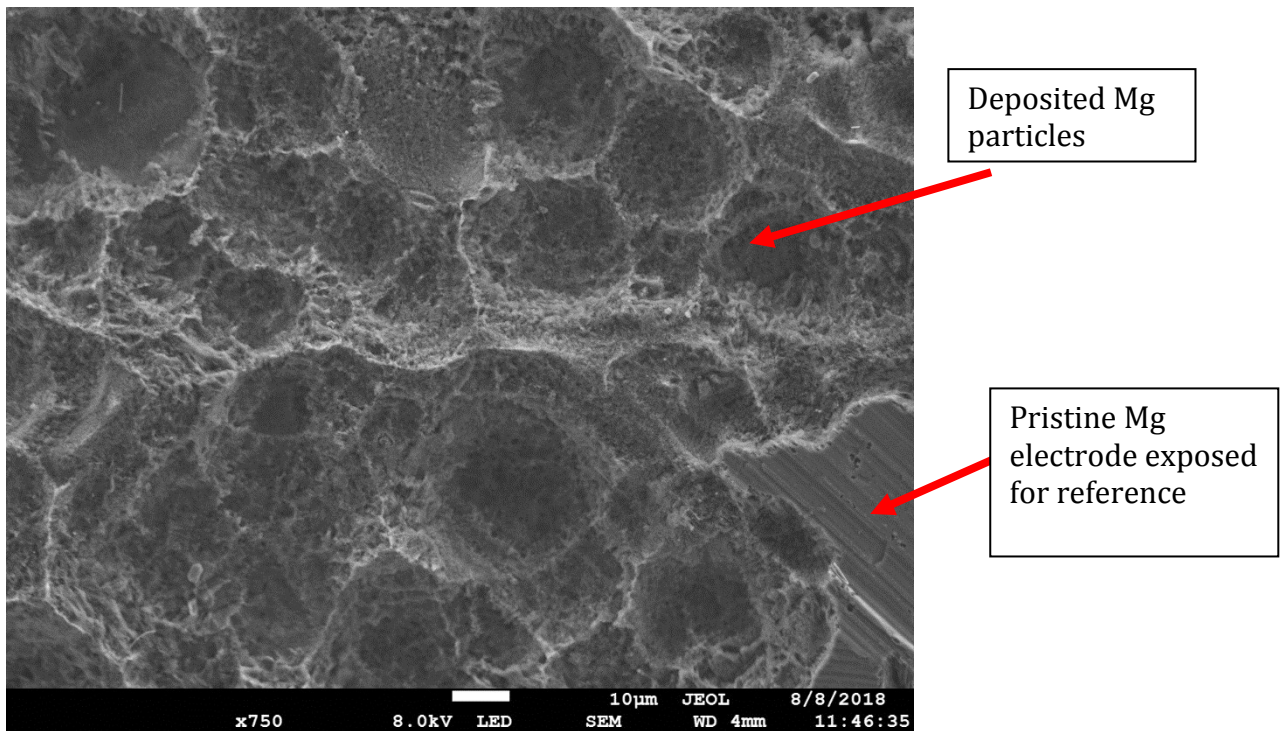


Figure S7: Mg electrode following cell cycling showing deposited Mg with the typical shape of fused spheres. The pristine Mg disk present under the deposits is exposed for reference.

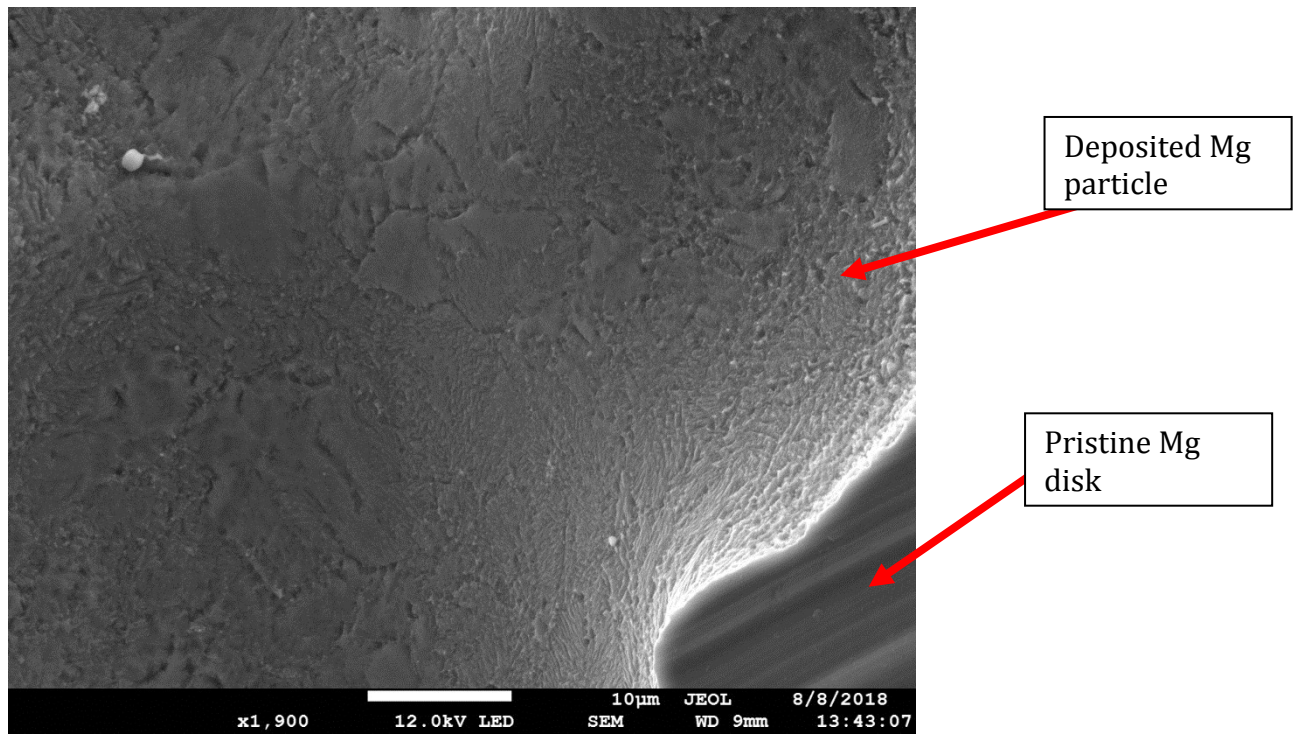


Fig. S8: Expanded view of Mg deposits. For reference pristine Mg is exposed under the Mg deposited particle as evident by the different morphology and scrap marks ( see Fig S6 above).

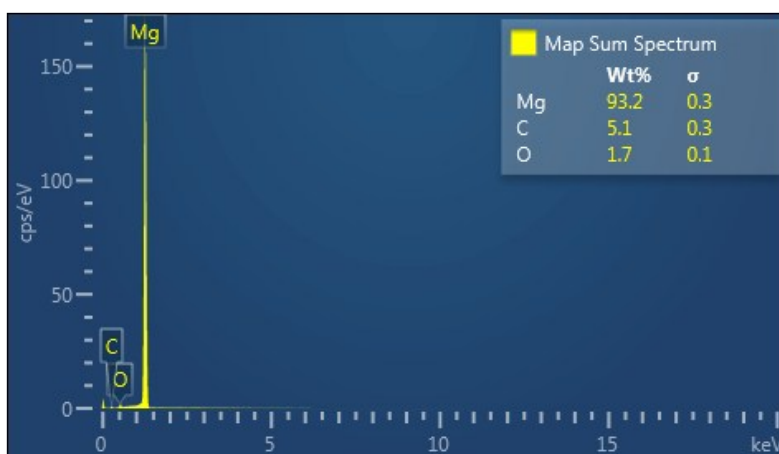
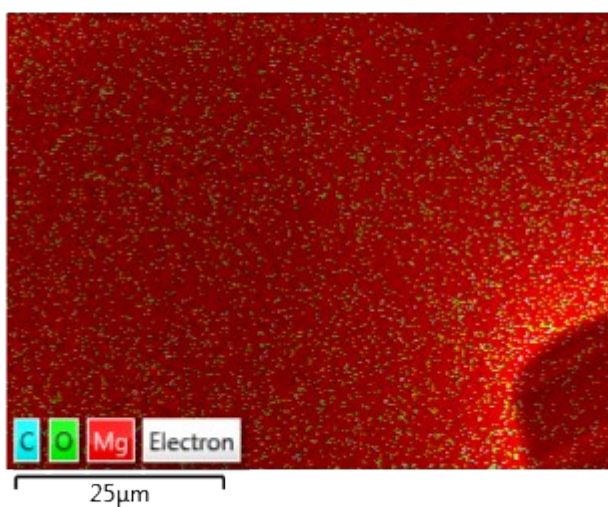
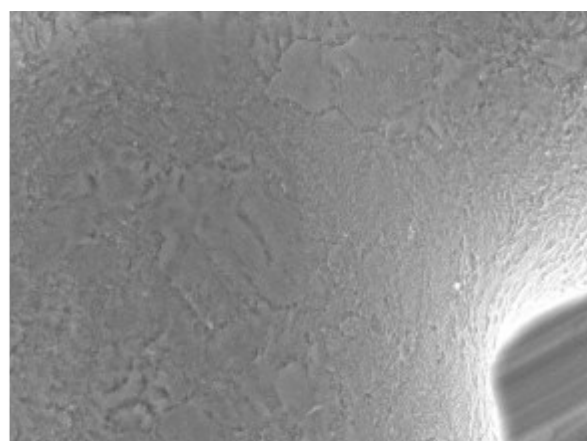
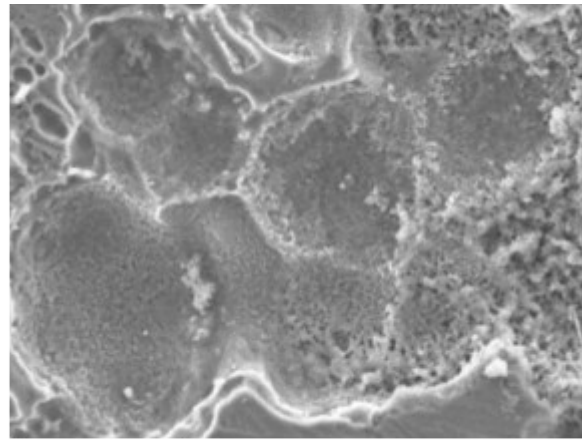
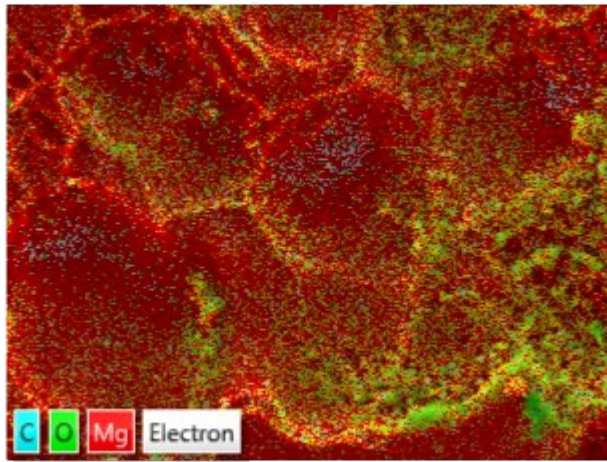


Fig S9: EDX and elemental mapping establishing that the deposits are Mg metal. Oxygen is present due to slight Mg oxidation as expected and C is residual is from the washing process of the ionic liquids.





50 $\mu$ m



50 $\mu$ m

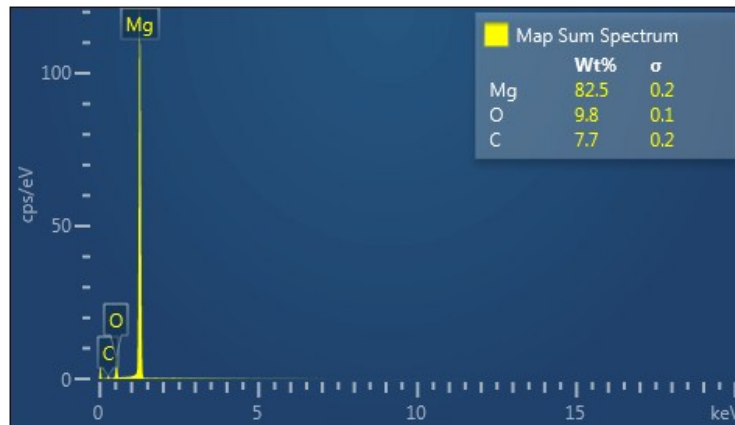


Fig. S10: Elemental mapping and EDX results for deposited Mg particles with the typical shape of fused spheres

1. O. Tutasaus, R. Mohtadi, T. S. Arthur, F. Mizuno, E. G. Nelson and Y. V. Sevryugina, *Angew. Chem. Int. Ed.*, 2015, 54, 7900-7904.
2. M. Gordon Charles, J. Muldoon Mark, M. Wagner, C. Hilgers, H. Davis James and P. Wasserscheid, in *Chapter 2: Synthesis and Purification, Ionic Liquids in Synthesis* eds. P. Wasserscheid and T. Welton, 2008, DOI: doi:10.1002/9783527621194.ch2.
3. M. J. Earle, C. M. Gordon, N. V. Plechkova, K. R. Seddon and T. Welton, *Anal. Chem.*, 2007, 79, 758-764.