Atom-efficient synthesis of a benchmark electrolyte for magnesium battery applications

Scott A. Brown,a, Serena A. Cussen,b Rhiannon Kennard,b Sofia Marchesini, c Jethro J. Pryke,b Annabel Rae,a Stuart D. Robertson,a,* Rudra N. Samajdar,a,c and Andrew J. Wainc*

a WestCHEM, Department of Pure & Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, UK, G1 1XL
b Department of Materials Science and Engineering, The University of Sheffield, Sheffield S1 3JD, UK
c Department of Electromagnetic and Electrochemical Technologies, National Physical Laboratory, Hampton Road, Teddington, UK, TW11 0LW
stuart.d.robertson@strath.ac.uk; andy.wain@npl.co.uk; s.cussen@sheffield.ac.uk

Supporting Information
Electrochemical Performance Measurements

Reagents for synthesis of the Chevrel phase were used as received from Alfa Aesar (copper (II) sulfide 99.8%, molybdenum (IV) sulfide 99% and molybdenum powder 99.95 %). The synthesis of Cu$_2$Mo$_6$S$_8$ was performed following a previously published procedure, with the Cu ions leached out by acid treatment. The Mo$_6$S$_8$ material was finally washed with water and dried under vacuum.[1]

Mg-metal symmetric Swagelok cells were assembled using two Whatman fibre glass separators with thickness 200 μm (required to prevent cell short-circuiting) soaked with the as-prepared electrolyte solutions and placed between two Mg metal electrodes (Goodfellow, 1.0mm thick, 99.9%, with carbon layer scratched off with scalpel). Inconel current collectors, sputter coated with gold, were applied. All preparations were carried out in an Ar-filled glovebox (H$_2$O, O$_2$ <0.5 ppm). For CV measurements, a pelletised cathode was prepared of Mo$_6$S$_8$ (75%), carbon black (15%) and PTFE binder (10%). Electrochemical testing was carried out using a Biologic VSP-300 potentiostat. Polarisation tests on symmetrical cells were performed by applying a constant current of ±200 μA/cm$^2$. Cyclic Voltammograms were performed at a scan rate of 0.1 mV/s at 25°C. Electrolyte ionic conductivity was measured by electrochemical impedance spectroscopy (EIS), using a Solartron 1470E with an AC amplitude of 10 mV, a starting frequency of 1 MHz and a final frequency of 0.01 Hz. The experiment was conducted in a BioLogic Conductivity Cell comprising two platinum electrodes and a nominal cell constant of 1 cm$^{-1}$. All electrochemical measurements were performed at 25 °C.

FTIR and Raman Spectroscopy

FTIR and Raman spectra of all samples were recorded using a commercial spectroscopic cell (ECC-Opto-Std, EL-CELL® GmbH). For FTIR measurements, this cell was interfaced with a ZnSe internal reflection element and fitted to a variable angle ATR-FTIR accessory (VeeMAX™ III, Pike Technologies, USA). The incident light was polarised at 90° and an incidence angle of 45° was employed. The ATR accessory was connected to a Thermo Fisher Nicolet iS50 FTIR spectrometer, equipped with a liquid nitrogen cooled MCT (mercury cadmium telluride) detector. Each spectrum was averaged over 495 acquisitions. Raman scattering measurements were performed using a confocal Raman microscope (inVia Qontor, Renishaw) equipped with a CCD detector, using a 830 nm laser at 5% nominal power (0.46 mW at the sample) and a 1200 lines/mm grating. Each spectrum was acquired with 10 s exposure and 10 accumulations. The background was subtracted using WiRE version 5.1 using an intelligent polynomial fitting. FTIR and Raman spectra were collected for electrolyte samples prepared according to equations 1 or 3 (see main text for discussion). THF. Sample preparation and cell assembly were performed in an Ar filled glove box (MBraun LabMaster Pro SP; O$_2$ < 0.1 ppm; H$_2$O < 0.1 ppm) prior to the measurements.

Synthesis of MgPh$_2$·2THF

Dioxane (5 mL) was added to a solution of PhMgCl (10 mL, 20 mmol, 2 M in THF from Sigma-Aldrich) and stirred at room temperature overnight. The resulting white suspension (dioxane-MgCl$_2$) was then filtered and the THF and excess dioxane were removed in vacuo to concentrate the solution; crystals could then be grown from this solution of the product MgPh$_2$·2THF, confirmed by X-Ray diffraction. Isolated crystalline yield 39 % from a maximum of 50 %.

MgPh$_2$·2THF (0.064 g, 0.2 mmol) was added to an NMR tube fitted with a J Youngs tap and dissolved in 0.5 mL of d$_8$-THF. $^1$H and $^{13}$C NMR was then carried out and the data are shown in Figures S1 and S2, below.

$^1$H NMR (400 MHz, 298 K, d$_8$-THF): δ = 7.69 (m, 4H, o-CH, Ar), 6.98 (t, 4H, m-CH, Ar), 6.89 (tt, 2H, p-CH, Ar), 3.63 (t, 8H, O-CH$_2$-CH$_2$), 1.76 (m, 8H, O-CH$_2$-CH$_2$)

$^{13}$C NMR (400 MHz, 298 K, d$_8$-THF): δ = 140.12 (o-CH, Ar), 125.11 (m-CH, Ar), 123.25 (p-CH, Ar), 66.41 (O-CH$_2$-CH$_2$), 24.15 (O-CH$_2$-CH$_2$)
Figure S1 $^1$H NMR spectrum of MgPh$_2$·2THF in d$_8$-THF

Figure S2 $^{13}$C NMR spectrum of MgPh$_2$·2THF in d$_8$-THF
Synthesis of \([\text{Mg}_2\text{Cl}_3 \cdot 6\text{THF}]^+ \cdot \text{[AlPh}_4^-]\)~

\(\text{MgPh}_2\cdot2\text{THF} (0.646 \text{ g}, 2 \text{ mmol})\) and \(\text{AlCl}_3 (0.133 \text{ g}, 1 \text{ mmol})\) were added to the same Schlenk flask in an argon atmosphere glove box. 7 mL of THF was then added slowly at 0°C and the solution slightly heated to dissolve the reactants, the solution was then stirred at room temperature overnight. Colourless crystals were obtained by slowly layering hexane on top of the solution (0.288 g, 31 % crystalline yield). Excess hexane was then added to the filtrate after collection of the crystals resulting in another white precipitate. The precipitate was then collected via filtration and dried \textit{in vacuo} and found to be \([\text{Mg}_2\text{Cl}_3 \cdot 6\text{THF}]^+ \cdot \text{[AlPh}_4^-]\) by NMR spectroscopy (0.631 g, 68 % yield). Total yield 99 %.

\textit{In situ} preparation

In an argon filled glove box \(\text{AlCl}_3 (0.013 \text{ g}, 0.1 \text{ mmol})\) was weighed out in a small vial. The \(\text{MgPh}_2\cdot2\text{THF}\) solution from the NMR tube was then syringed into the vial and stirred until all reactants had dissolved. The solution was then transferred back into the NMR tube and \(^1\text{H}, \, \text{^13C}\) and \(^{27}\text{Al}\) NMR spectroscopic measurements were performed. The data are shown in Figures S3-S8, below.

\(^1\text{H}\) NMR (400 MHz, 298 K, d\(_8\)-THF): \(\delta = 7.67\) (d, 8H, o-C\(_\text{H}\), Ar), 6.94 (t, 8H, m-C\(_\text{H}\), Ar), 6.89 (dt, 4H, p-C\(_\text{H}\), Ar), 3.58 (t, 16H, O-C\(_\text{H}_2\)-CH\(_2\)), 1.71 (m, 16H, O-CH\(_2\)-CH\(_2\))

\(^{13}\text{C}\) NMR (400 MHz, 298 K, d\(_8\)-THF): \(\delta = 138.68\) (o-C\(_\text{H}\), Ar), 124.87 (m-C\(_\text{H}\), Ar), 123.50 (p-C\(_\text{H}\), Ar), 66.44 (O-CH\(_2\)-CH\(_2\)), 24.01 (O-CH\(_2\)-CH\(_2\))

\(^{27}\text{Al}\) NMR (104.2 MHz, 298 K, d\(_8\)-THF) \(\delta = 132.90\) ppm (s)

Microanalysis (crystals): Found (Calcd for \([\text{Mg}_2\text{Cl}_3 \cdot 5\text{THF}]^+ \cdot \text{[AlPh}_4^-]\)) C 61.77 (62.11), H 7.32 (7.11).

Microanalysis (precipitate): Found (Calcd for \([\text{Mg}_2\text{Cl}_3 \cdot 5\text{THF}]^+ \cdot \text{[AlPh}_4^-]\)) C 60.79 (62.11), H 7.16 (7.11).

\[\text{Figure S3} \, ^1\text{H}\, \text{NMR spectrum of Crystalised} \, [\text{Mg}_2\text{Cl}_3 \cdot 6\text{THF}]^+ \cdot \text{[AlPh}_4^-]\, \text{in} \, d_8\text{-THF}\]
Figure S4 $^{13}$C NMR spectrum of Crystalised $[\text{Mg}_2\text{Cl}_3\cdot 6\text{THF}]^+ [\text{AlPh}_4]^-$ in $d_8\text{-THF}$

Figure S5 $^{27}$Al NMR spectrum of Crystalised $[\text{Mg}_2\text{Cl}_3\cdot 6\text{THF}]^+ [\text{AlPh}_4]^-$ in $d_8\text{-THF}$
Figure S6 $^1$H NMR spectrum of in situ mixture of 2MgPh$_2$·2THF and AlCl$_3$ in d$_8$-THF

Figure S7 $^{13}$C NMR spectrum of in situ mixture of 2MgPh$_2$·2THF and AlCl$_3$ in d$_8$-THF
Figure S8 $^{27}$Al NMR spectrum of in situ mixture of 2MgPh$_2$·2THF and AlCl$_3$ in $d_8$-THF
Additional FTIR and Raman Spectra

Figure S9: (a) FTIR and (b) Raman spectra of pure THF with the major vibrational modes marked. Individual deconvoluted peaks in the FTIR spectrum are labelled as (P_i).

Figure S10: Deconvoluted FTIR spectra at the low wavenumber region for (a) electrolyte synthesised with stoichiometric control (b) electrolyte synthesised without stoichiometric control. Major peaks are deconvoluted and labelled as (P_i).
Deconvolution of FTIR spectra

FTIR absorption spectra were deconvoluted into individual component peaks as shown in Figure S9a and Figure S10. A Voigt waveform in Origin was used to fit the absorption peaks, iterating until $R^2 > 0.99$.

For the pure THF solvent (Figure S9a), the following peaks were identified:

| Peak | Position / cm$^{-1}$ (all values include a measurement uncertainty of $\pm 4$ cm$^{-1}$) | Vibration (major contributor marked in bold) |
|------|-----------------------------------------------------------------------------------|---------------------------------------------|
| P1   | 1066                                                                              | **C-O-C asymmetric stretch** + $\alpha C_\beta$ asymmetric stretch + ring bend (type B vibrations) |
| P2   | 1027                                                                              | $\beta$CH$_2$ wag + $\beta$CH$_2$ twist + C-O-C symmetric stretch + $\alpha C_\beta$ symmetric stretch + $C_\alpha C_\beta$ stretch + ring bend (type A vibrations) |
| P3   | 907                                                                               | $\beta$CH$_2$ twist + $\alpha$CH$_2$ rock + $C_\beta C_\beta$ asymmetric stretch (type B vibrations) |
| P4   | 875                                                                               | $\beta$CH$_2$ rock + ring bend + C-O-C asymmetric stretch (type B vibrations) |

Note that the 33 normal modes of THF are classified into A and B modes according to the irreducible representation $[\Gamma(C_2)=17A + 16B]$ of the $C_2$ point group which represents the symmetry of the THF molecule in equilibrium in solution.$^{[2]}$

The ratio of the peak area of the satellite peaks ($P_2$ and $P_4$) compared to the primary peaks ($P_1$ and $P_3$, respectively) was calculated from the fit, and for THF these were determined as:

$$\frac{A(P_2)}{A(P_1)} = 0.05...(i)$$

$$\frac{A(P_4)}{A(P_3)} = 0.06...(ii)$$
For the electrolyte synthesised in this paper (Figure S10a) the major peaks were identified as:

| Peak | Position / cm⁻¹ (all values include a measurement uncertainty of ± 4 cm⁻¹) | Vibration (major contributor marked in bold) |
|------|--------------------------------------------------------------------------|------------------------------------------------|
| P1   | 1066                                                                 | **C-O-C asymmetric stretch** + CαCβ asymmetric stretch + ring bend (type B vibrations) |
| P2   | 1031                                                                 | βCH₂ wag + βCH₂ twist + C-O-C symmetric stretch + CαCβ symmetric stretch + CβCβ stretch + ring bend (type A vibrations) |
| P3   | 909                                                                  | βCH₂ twist + αCH₂ rock + CαCβ asymmetric stretch (type B vibrations) |
| P4   | 886                                                                  | βCH₂ wag + βCH₂ rock + αCH₂ rock + **C-O-C symmetric stretch** (type A vibrations) |
| P5   | 874                                                                  | βCH₂ rock + ring bend + C-O-C asymmetric stretch (type B vibrations) |

The ratio of the peak area of the satellite peaks (P₂ and P₄+P₅) compared to the primary peaks (P₁ and P₃, respectively) was calculated from the fit, and for the electrolyte synthesised in this paper these were determined as:

\[
\frac{A(P₂)}{A(P₁)} = 0.26 \ldots (iii) \\
\frac{A(P₄ + P₅)}{A(P₃)} = 0.43 \ldots (iv)
\]
For electrolyte synthesised without stoichiometric control (Figure S10b), the major peaks were identified as:

| Peak | Position / cm$^{-1}$ (all values include a measurement uncertainty of ± 4 cm$^{-1}$) | Vibration (major contributor marked in bold) |
|------|---------------------------------------------------------------------------------|---------------------------------------------|
| P1   | 1066                                                                            | C-O-C asymmetric stretch + C$_\alpha$C$_\beta$ asymmetric stretch + ring bend (type B vibrations) |
| P2   | 1040                                                                            | C$_\alpha$C$_\beta$ symmetric stretch (in distorted/clustered local coordination) |
| P3   | 1026                                                                            | $\beta$CH$_2$ wag + $\beta$CH$_2$ twist + C-O-C symmetric stretch + C$_\alpha$C$_\beta$ symmetric stretch + C$_\beta$C$_\beta$ stretch + ring bend (type A vibrations) |
| P4   | 906                                                                             | $\beta$CH$_2$ twist + $\alpha$CH$_2$ rock + C$_\alpha$C$_\beta$ asymmetric stretch (type B vibrations) |
| P5   | 874                                                                             | $\beta$CH$_2$ rock + ring bend + C-O-C asymmetric stretch (type B vibrations) |
| P6   | 841                                                                             | $\beta$CH$_2$ rock + $\alpha$CH$_2$ twist + C-O-C symmetric stretch + C$_\alpha$C$_\beta$ symmetric stretch + C$_\beta$C$_\beta$ stretch (type A vibrations) |

The ratio of the peak area of the satellite peaks (P$_2$+P$_3$ and P$_5$+P$_6$) compared to the primary peaks (P$_1$ and P$_4$, respectively) was calculated from the fit, and for the electrolyte synthesised without stoichiometric control these were determined as:

\[
\frac{A(P_2 + P_3)}{A(P_1)} = 0.36 \ldots (v) \\
\frac{A(P_5 + P_6)}{A(P_4)} = 0.59 \ldots (vi)
\]

Comparing ratios (iii) to (vi) with (i) and (ii) indicates that presence of the electrolyte increases the relative absorbance associated with satellite peaks of THF at around 1027 cm$^{-1}$ and between 841 cm$^{-1}$ and 886 cm$^{-1}$. This arises as a consequence of coordination of THF to species present in solution (generally the solvent is known to coordinate to the cationic species, i.e. Mg$^{2+}$, present in solution; the other cation, Al$^{3+}$, that gives rise to the anionic species in solution, is preferentially coordinated by organic ligands i.e. phenyl rings) which distorts the overall symmetry of the molecule in solution, thus affecting the normal modes of vibration. Comparison of (iii) and (iv) with (v) and (vi), respectively, indicates a higher absorbance associated with satellite peaks for the stoichiometrically non-controlled synthesis. We believe that this is due to (a) presence of multiple solvent coordinated species and (b) increase in concentration of solvent coordinated species in the solution obtained from non-stoichiometrically controlled synthesis.
Figure S11 Nyquist plots obtained from electrolyte synthesised by traditional method using Grignard reagent (1A), atom efficient method prepared in situ (1B), and crystallized pure electrolyte re-dissolved in THF (1C). The intercept of each trace at the high frequency regime, where $Z'' = 0$, is used to calculate the conductivity (the cell constant for the set-up is 1 cm$^{-1}$).

References

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