Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Cover page

Title: Exploiting cation aggregation in new magnesium amidohaloaluminate electrolytes for magnesium batteries

Authors: Etienne V. Brouillet,[a] Marco Amores,[b] Serena A. Corr[c, d] and Stuart D. Robertson[a]

[a]*WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, UK*

[b]*Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1, Hongo, Bunkyo-Ku, Tokyo, 113-0033, Japan*

[c]*Department of Chemical and Biological Engineering, University of Sheffield, Sheffield S1 3JD, UK*

[d]*Department of Materials Science and Engineering, University of Sheffield, Sheffield S1 3JD, UK*

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I Experimental details:

Reagents for the Chevrel phase synthesis, copper(II) sulfide, (99.8%, Alfa Aesar), molybdenum(IV) sulfide (99%, Alfa-Aesar) and molybdenum powder (APS 3-7 micron, 99.95%, Alfa-Aesar), were used as received. All reactions and manipulations used for the synthesis of electrolyte complexes, were carried out under a protective dry argon atmosphere using standard Schlenk techniques or an argon-filled glovebox. Diethyl ether and THF were dried by heating to reflux over sodium-benzophenone and distilled under nitrogen or argon prior to use. Electrolyte complexes possessing the mononuclear (MCE), dinuclear (DCE) and trinuclear (TCE) magnesium chloride cation aggregations in conjunction with the common aluminate anion $[(Dipp)(SiMe_3)NAlCl_3]^-$ were synthesised according to the methodology previously developed in our group.[1]

All three electrolytes were isolated by recrystallisation, affording high purity compounds and the electrochemical performance of these magnesium amidohaloaluminate complexes were assessed in Mg metal symmetrical cells and Mg-metal/Mo_6S_8 Chevrel phase battery cells. Electrolyte solutions of the magnesium amidohaloaluminate with a concentration of 0.35 M according to Mg^{2+} were prepared by dissolving the MCE and DCE complexes in THF and the TCE complex in 2-methyltetrahydrofuran (MeTHF).

Mg-metal symmetrical cells in a Swagelok configuration were prepared by inserting two soaked glass fibre separators (Whatman AF/D) with 300 µL of the as-prepared electrolyte solutions between two square pieces (*ca.* 4 mm^2) of Mg-metal (Goodfellow, 1.0 mm thickness, 99.9%, with the surface polished with sand paper prior use). To avoid possible current collector corrosion due to the presence of Cl^- ions in the electrolyte solutions, current collectors made of an Inconel 625 corrosion resistant alloy were employed. Electrolyte solution preparation, cell assembly and Mg-metal polishing were performed in an Argon-filled glovebox with the concentration of oxygen and water below 0.5 ppm.

The synthesis of the $Cu_2Mo_6S_8$ Chevrel phase was carried out following the procedure developed by Kumta *et al.* without modifications.[2] Leaching of Cu ions from $Cu_2Mo_6S_8$ was performed by overnight stirring of the as-synthesised material in 200 mL of a 6 M HCl solution containing 1 mL of HNO_3. After leaching, the Mo_6S_8 material was washed thoroughly with water and dried under vacuum at 80 ^oC.

Powder X-ray diffraction (PXRD) patterns of the as-synthesised Mo_6S_8 Chevrel phase and the electrochemically cycled material were acquired on a PANalytical X'Pert PRO diffractometer (10-60 2θ range, step size of 0.02 degrees and 100 seconds per step).

Swagelok Mg-metal/Mo_6S_8 batteries were prepared in a similar manner as the symmetrical cell by replacing one of the Mg-metal electrodes by a pelletised mixture of Mo_6S_8, carbon black Ketjenblack EC-600JD (AkzoNobel) and PTFE (Sigma Aldrich) in a 75:15:10 weigh ratio. Electrochemical testing of the cells was performed on a Biologic VSP-300 potentiostat equipped with EIS capability.

Potentiostatic EIS measurements were performed on the 10^6 – 0.02 Hz frequency range with 15 points per decade and a voltage perturbation of 100 mV ($V_{rms} \approx 70$ mV). Polarisation tests of symmetrical cells were performed by applying a constant current of ±200 µAh.cm^2 with 2 minutes relaxation steps at OCV between current direction sweeps.

CV analyses were performed at a scan rate of 0.1 mV.s^{-1} over different voltage scan ranges and galvanostatic cycling with potential limitation measurements were carried out at 12.8 mAh.g^{-1} corresponding to a (dis)charge rate of C/10 (considering a theoretical capacity for the Mo_6S_8 Chevrel phase of 128 mAh.g^{-1}).

For *ex-situ* PXRD and SEM analyses, the cycled cells where disassembled in the same Ar-filled glovebox with the Mo_6S_8 Chevrel cathode material washed with dry THF. SEM analyses were performed on a Carl Zeiss Sigma instrument equipped with an Oxford Microanalysis energy dispersive spectrometer for EDX measurements with an electron beam accelerated at 25 kV.

Table 1 Calculated ionic conductivities of MCE, DCE and TCE electrolytes in symmetrical cells from Nyquist plots

Thickness (cm)	0.135		
Area (cm^2)	0.04		
		R_i	Conductivity (S cm^{-1})
	MCE	80	0.084375
	DCE	40	0.16875
	TCE	65	0.103846

Figure S1: Photographs of the separators of a Mg-metal symmetrical cell with TCE electrolyte after the short-circuit in the polarisation test. A clear grey metallic spot can be observed at both sides of the separator.

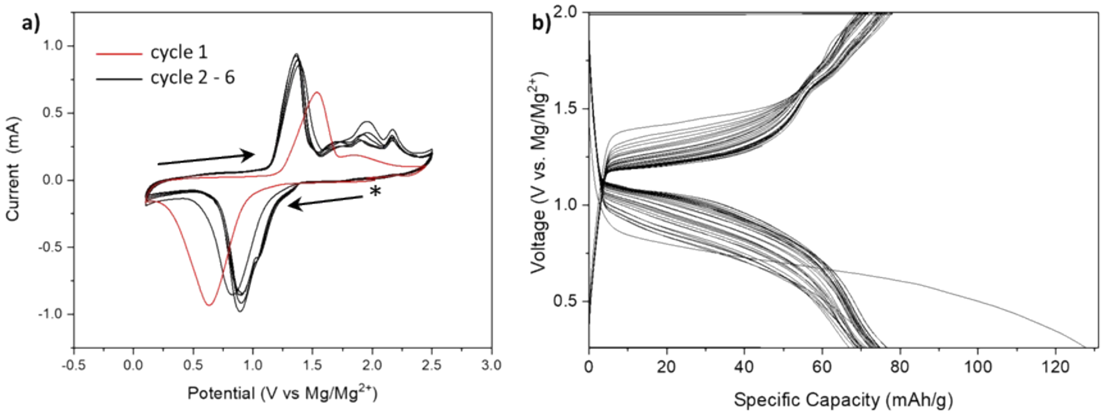


Figure S2: a) CV and b) C/10 charge/discharge profile (30 cycles) of a Mg/Mo_6S_8 cell using isolated crystals of $[(HMDS)AlCl_3]^-$ $[Mg_2Cl_3{\cdot}6THF]^+$ (0.175 M in THF). Arrows indicate the CV sweeping direction and * indicates the starting point of the CV cycles.

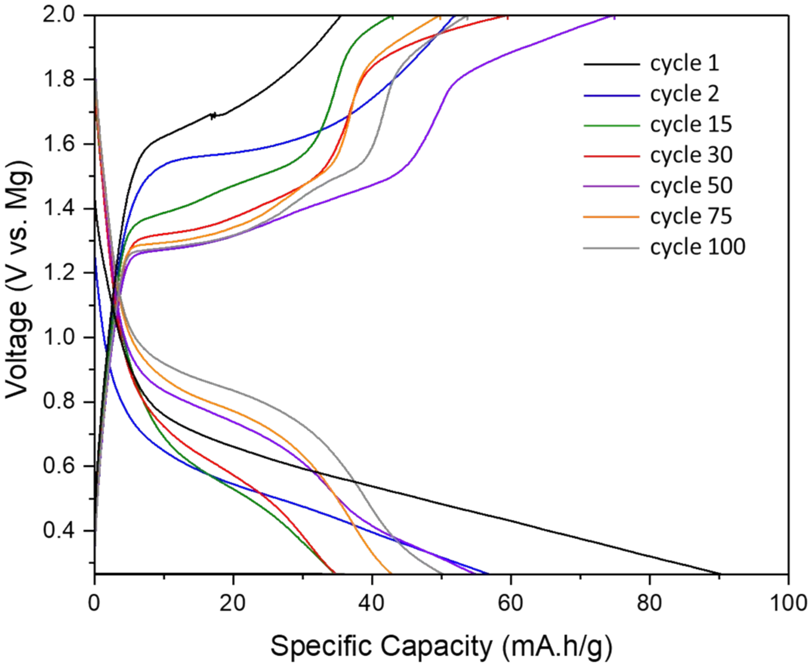


Figure S3: C/10 charge/discharge profile of a Mg/Mo_6S_8 cell using 0.35 M MCE in THF.

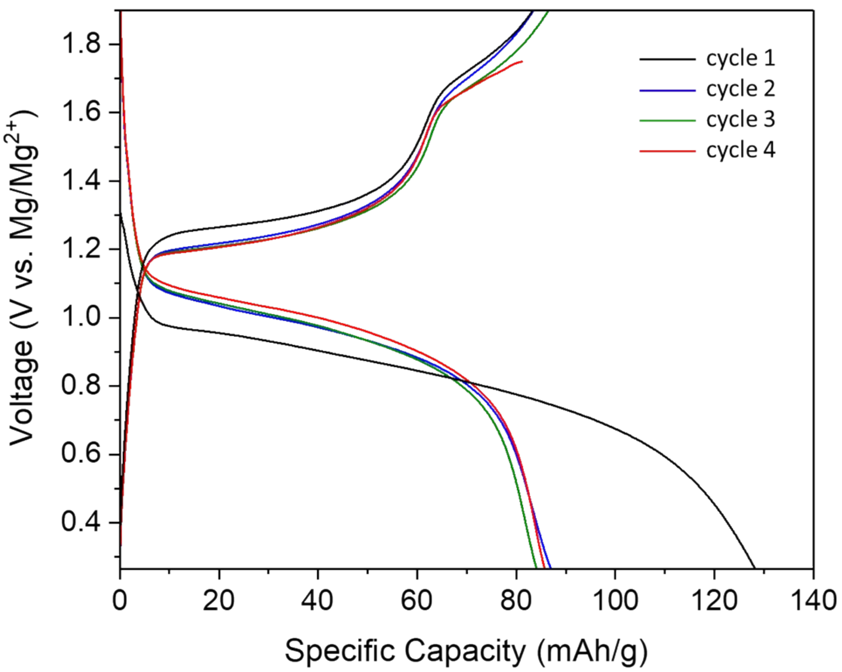


Figure S4: C/10 charge/discharge profile of a Mg/Mo_6S_8 cell using 0.175 M DCE in THF.

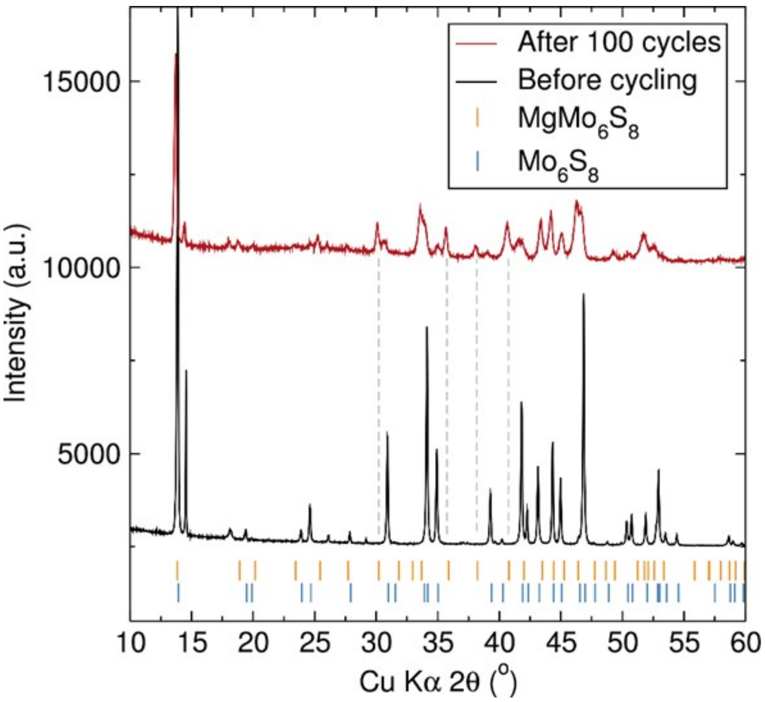


Figure S5: *Ex-situ* PXRD of the Mo_6S_8 electrode before and after cycling. Vertical tick marks indicate position of Bragg reflections for the Mo_6S_8 phase (blue) and magnesiated $MgMo_6S_8$ phase (orange). Dash lines indicate the major additional peaks arising from Mg insertion into the Mo_6S_8 electrode.

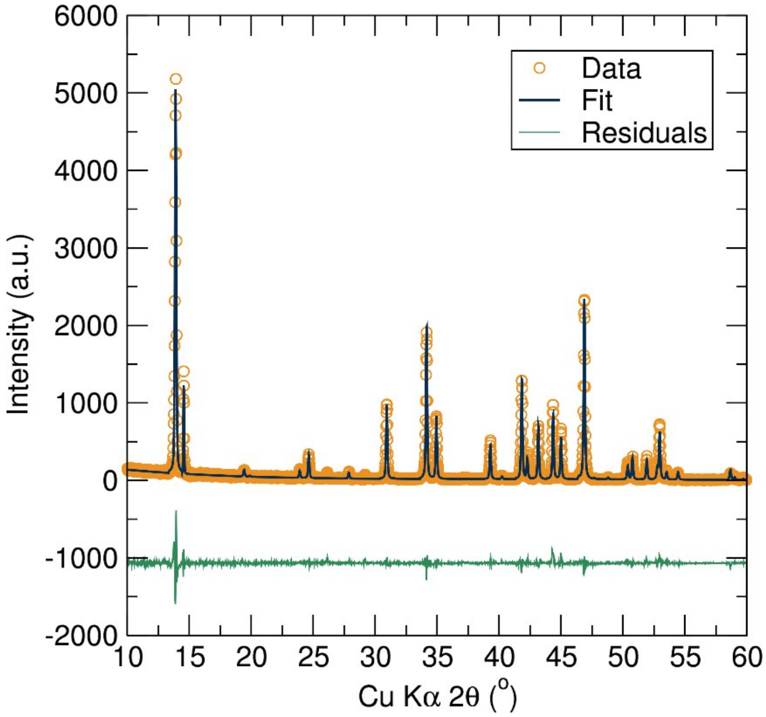


Figure S6: Rietveld Refinement to PXRD of the as-synthesised Mo_6S_8 Chevrel phase with $R\bar{3}$ space group. *a* and *b* = 9.1950(1) Å and *c* = 10.8876(2) Å. R_{wp} = 0.1639, R_p = 0.1159 and X^2 =2.505. A MoS_2 (*R*3m) secondary phase was added to the refined resulting in a 3.2% in weight contribution to the diffraction pattern.

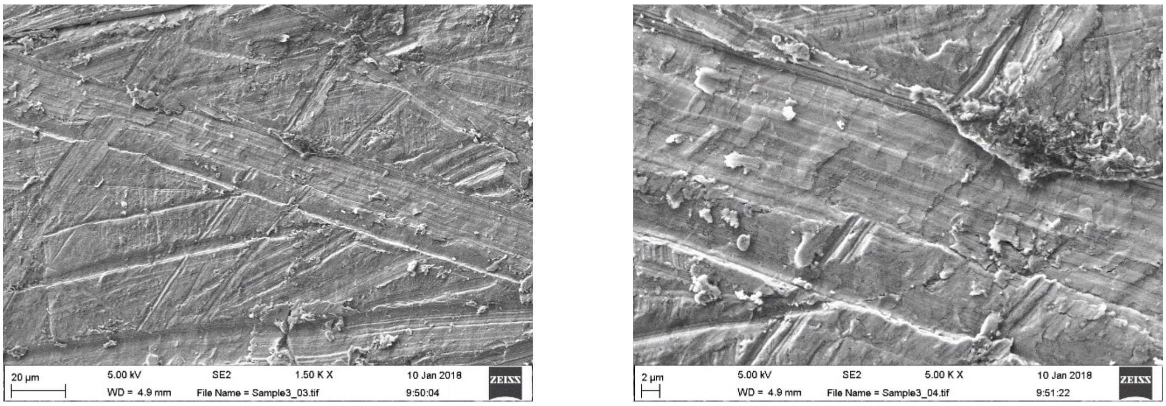
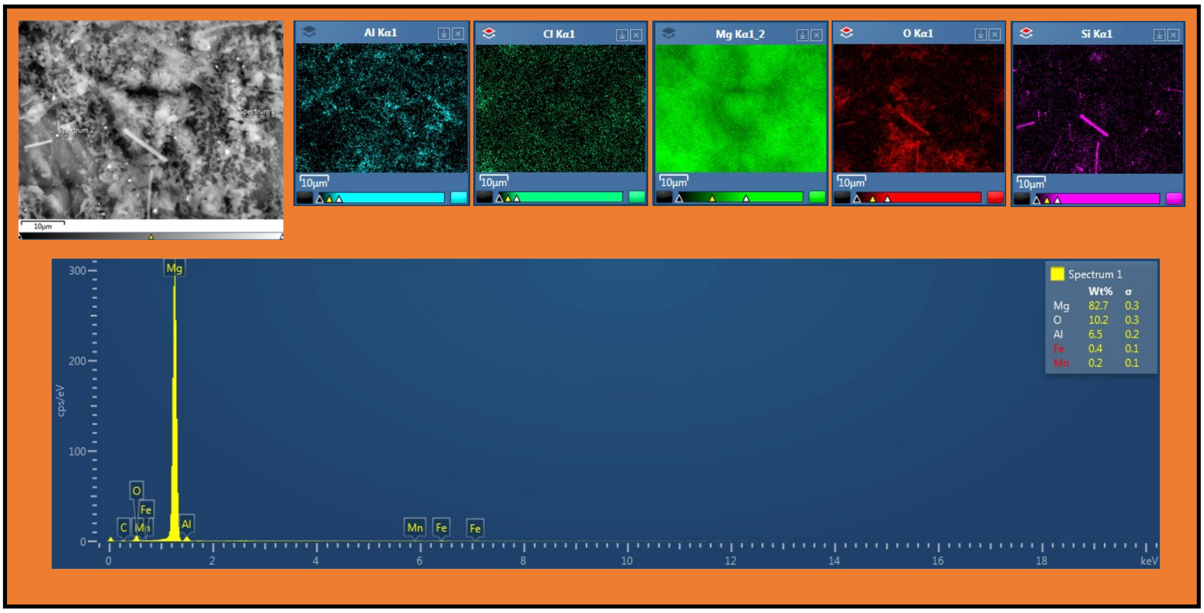
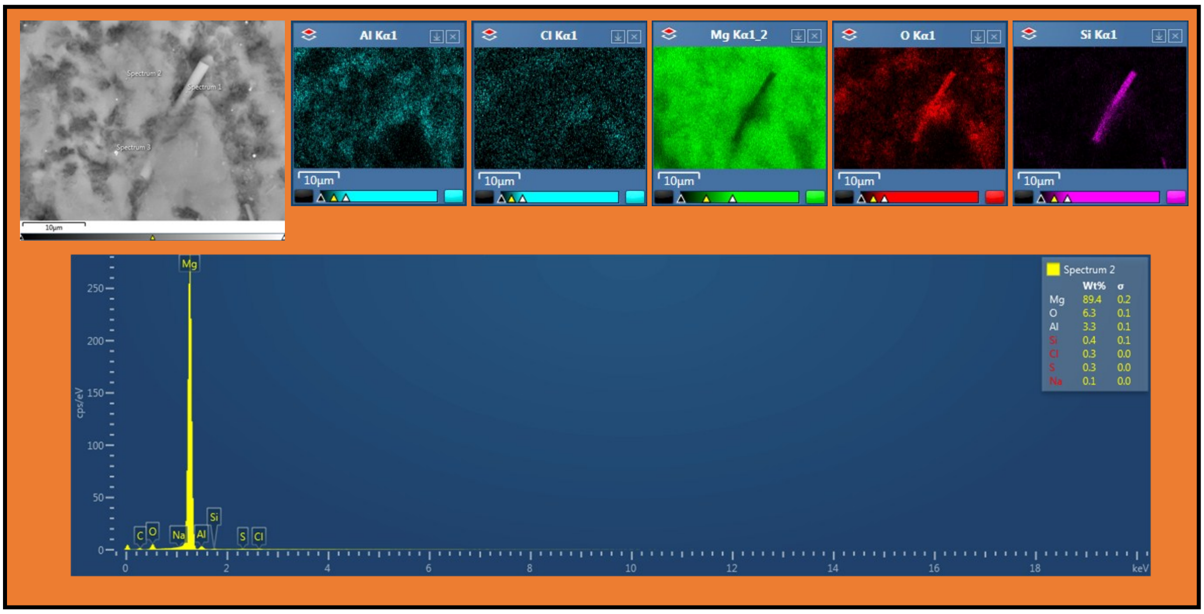


Figure S7: SEM micrographs of pristine Mg metal surface after being scratched by sandpaper.



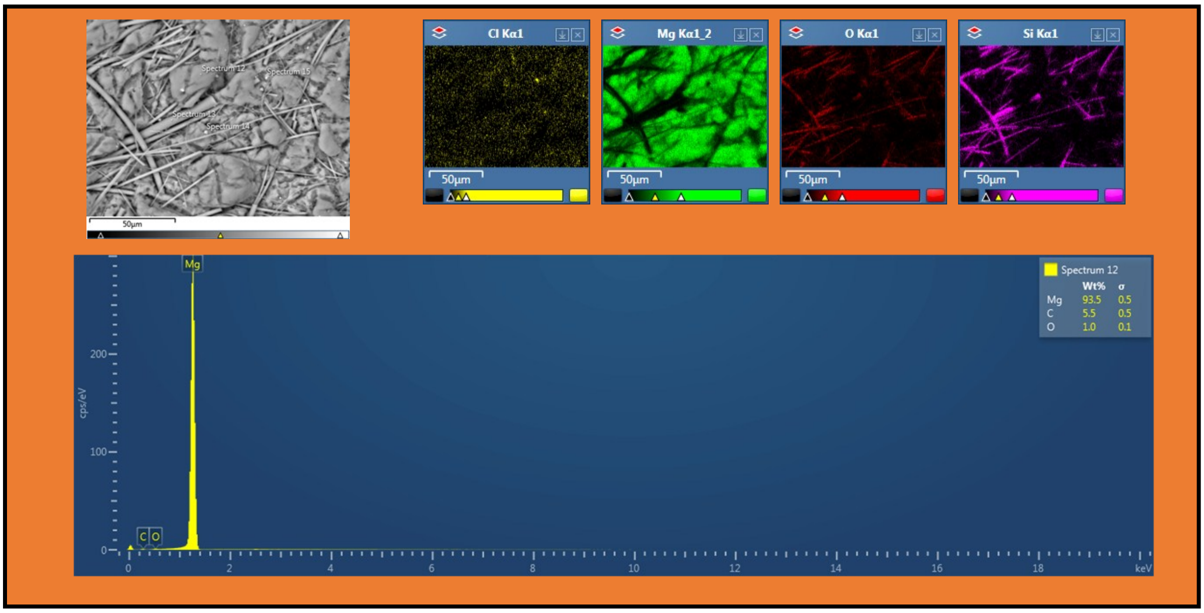
Spectrum 1	Wt%	σ
Mg	82.7	0.3
O	10.2	0.3
Al	6.5	0.2
Fe	0.4	0.1
Mn	0.2	0.1

Figure S8: EDX mapping of a Mg electrode from a cell using MCE as the electrolyte after 100 cycles.



Spectrum 2	Wt%	σ
Mg	89.4	0.2
O	6.3	0.1
Al	3.3	0.1
Si	0.4	0.1
Cl	0.3	0.0
S	0.3	0.0
Na	0.1	0.0

Figure S9: EDX mapping of a Mg electrode from a cell using DCE as the electrolyte after 100 cycles.



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	Wt%	σ
Mg	93.5	0.5
C	5.5	0.5
O	1.0	0.1

Figure S10: EDX mapping of a Mg electrode from a cell using TCE as the electrolyte after 100 cycles.

References:

[1] E. V. Brouillet, A. R. Kennedy, K. Koszinowski, R. McLellan, R. E. Mulvey and S. D. Robertson, Exposing elusive cationic magnesium–chloro aggregates in aluminate complexes through donor control, *Dalton Trans.*, 2016, **45**, 5590.

[2] P. Saha, P. H. Jampani, M. K. Datta, D. Hong, B. Gattu, P. Patel, K. S. Kadakia, A. Manivannan and P. N. Kumta, A rapid solid-state synthesis of electrochemically active Chevrel phases (Mo_6T_8; T = S, Se) for rechargeable magnesium batteries, *Nano Res.*, 2017, **10**, 4415.