Electrolyte dependent deposition morphology on magnesium metal utilizing MeMgCl, Mg[B(hfip)4]2 and Mg(HMDS)2-2AlCl3 electrolytes

Leon Leuppert, [†a] Adam Reupert, [†*a] Thomas Diemant, [a] Tom Philipp, [b] Christine Kranz, [b] Zhenyou Li, [ac] and Maximilian Fichtner *[ad]

a. *Helmholtz Institute Ulm (HIU), Electrochemical Energy Storage, Helmholtzstr. 11, D-89081 Ulm, Germany.*
b. *Institute of Analytical and Bioanalytical Chemistry (IABC), Ulm University, Albert-Einstein-Allee 11, 89081 Ulm, Germany.*
c. *Qingdao New Energy Shandong Laboratory, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, No. 189 Songling Road, Laoshan District, Qingdao, 266101 China*
d. *Institute of Nanotechnology (INT), Karlsruhe Institute of Technology, P.O. Box 3640, D-76021 Karlsruhe, Germany.*

Karl-Fischer titration / Water content analysis:

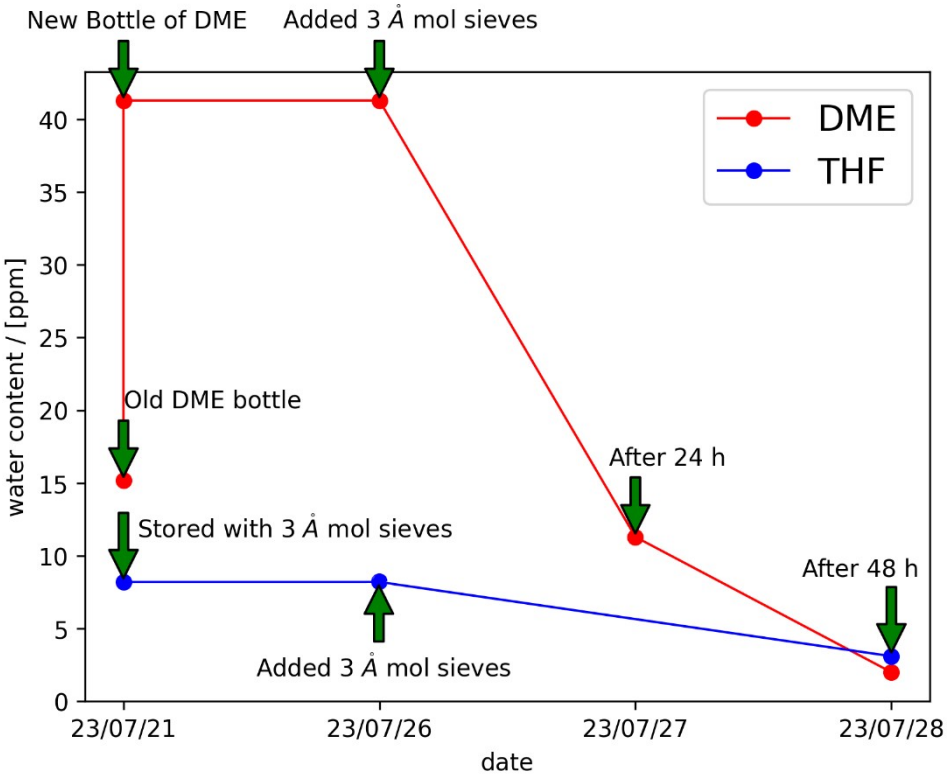

Figure 1: Karl-Fischer titration experiments of the typical drying procedure of THF & DME. The values were determined three months after performing the magnesium deposition experiments in the main article. The initial values of DME and THF were 15 ppm and 8.2 ppm, respectively, indicating higher trace levels of water in the used electrolytes. A normal drying process would lower it down to 2.0 ppm for DME and 3.1 ppm for THF.

Research data management:

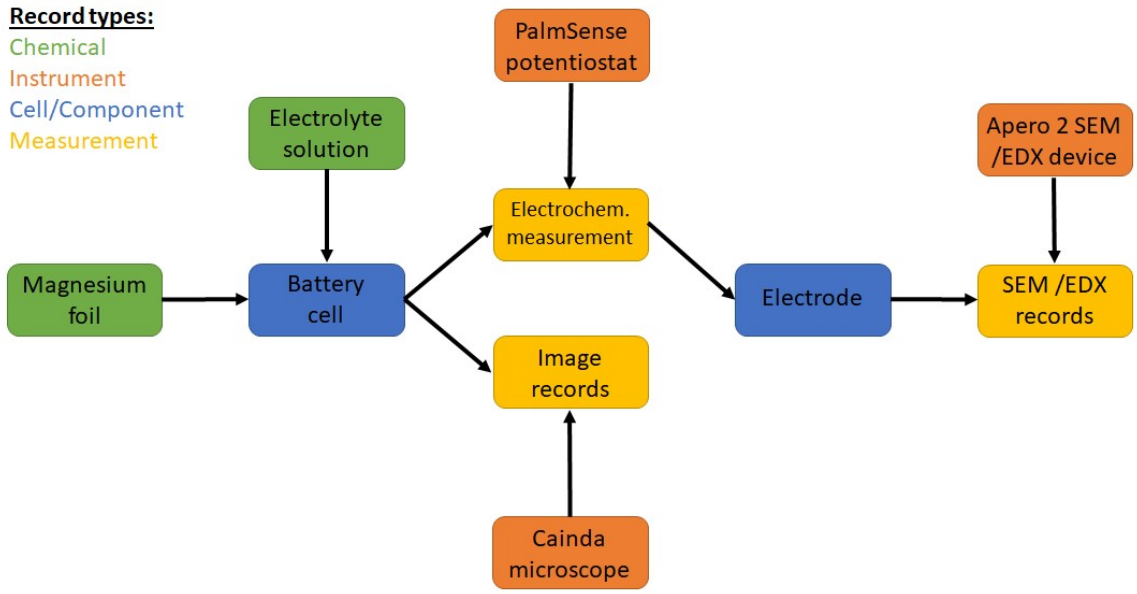

Figure 2: Exemplary research data management structure of records and measurment data that were generated during this work.

Deposition morphologies

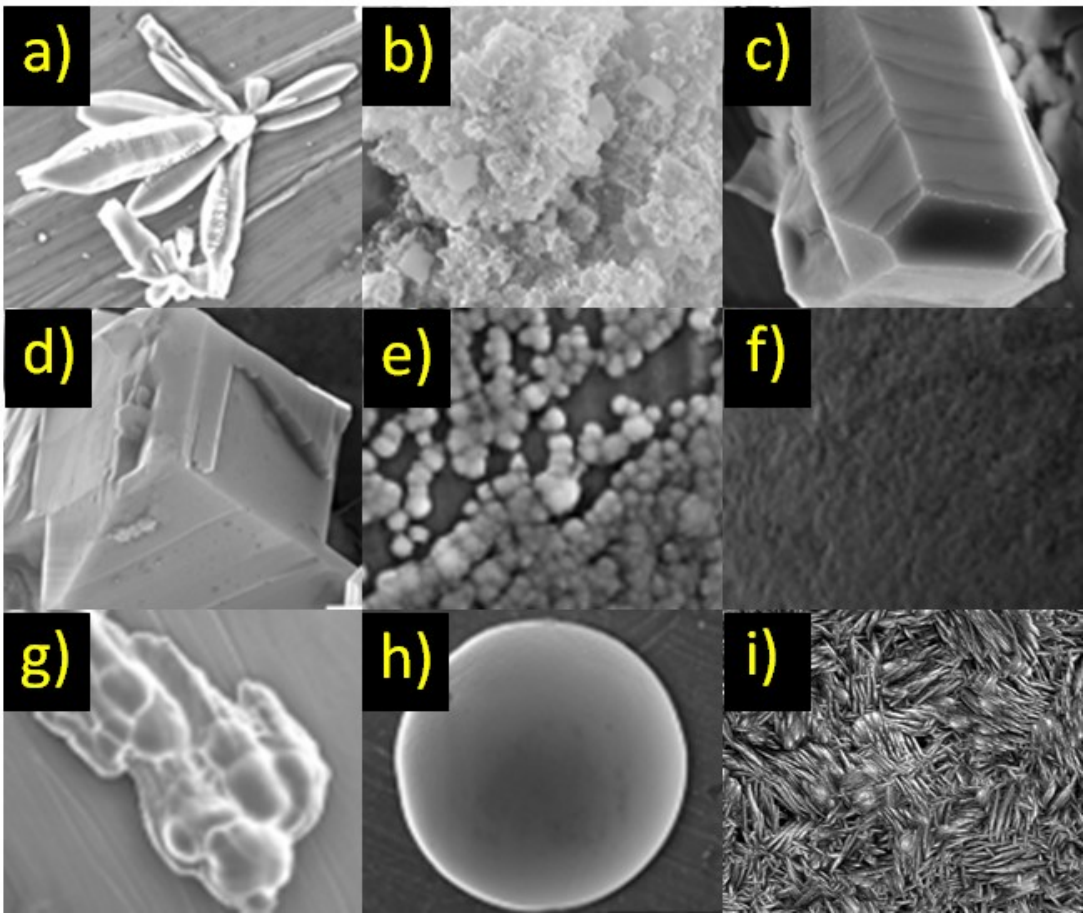

Figure 3: a) root-growing: branching directly on the electrode surface then unidirectional growth in electrolyte direction, b) mossy: no smooth surface, spherical shape, no clear direction of growth, c) unidirectional: smooth surface, single crystal, one direction of growth, d) crystalline: single crystal, smooth surface, no clear direction of growth, e) small nucleation: on the electrode surface, numerous, small in diameter, f) smooth surface: no surface structure, g) grown together: no original nucleation sites recognizable, h) spherical: spherical shape, one large nucleation spot, i) needle-like: small, long, thin

The area of the electrode to set the current density was computed as the average of the area of both electrodes.

Table 1: Dimensions of the electrodes [mm] used in the MeMgCl in THF experiments.

	0.307 mA cm^{-2}		0.921 mA cm^{-2}		1.54 mA cm^{-2}	
	1	2	1	2	1	2
0.25 M	3.98 x 3.38	3.88 x 3.30	3.39 x 3.63	3.49 x 3.51	3.88 x 3.45	3.90 x 3.45
0.3 M	3.56 x 3.28	3.65 x 3.32	3.80 x 3.64	3.78 x 3.53	3.63 x 3.74	3.60 x 3.63
0.5 M	3.86 x 3.13	3.82 x 3.13	3.69 x 2.82	3.66 x 2.83	3.31 x 2.98	3.36 x 2.95

Table 2: Dimensions of the electrodes [mm] used in the Mg[HMDS]2-2AlCl3 in THF experiments.

	0.307 mA cm^{-2}		0.921 mA cm^{-2}		1.54 mA cm^{-2}	
	1	2	1	2	1	2
0.1 M	3.54 x 2.93	3.46 x 2.88	3.56 x 3.56	3.60 x 3.53	3.50 x 2.65	3.44 x 2.55
0.2 M	3.60 x 3.60	3.61 x 3.49	3.68 x 3.66	3.69 x 3.65	3.40 x 3.16	3.44 x 3.09
0.3 M	3.35 x 3.28	3.38 x 3.31	3.52 x 2.83	3.54 x 2.93	3.58 x 2.84	3.52 x 2.85

Table 3: Dimensions of the electrodes [mm] used in the Mg[B(hfip)4]2 in DME experiments.

	0.307 mA cm^{-2}		0.921 mA cm^{-2}		1.54 mA cm^{-2}	
	1	2	1	2	1	2
0.1 M	3.01 x 2.78	3.07 x 2.63	3.84 x 3.44	3.64 x 3.64	3.41 x 2.39	3.44 x 2.35
0.2 M	4.07 x 3.22	4.04 x 3.25	4.35 x 3.49	4.38 x 3.65	3.74 x 3.65	3.75 x 3.64
0.3 M	3.66 x 3.35	3.57 x 3.44	3.74 x 3.35	3.82 x 3.39	4.00 x 3.34	4.12 x 3.29

Additiv: 0.1 M, 0.921 mA cm^{-2}: 3.81 x 3.67, 3.76 x 3.50

Table 4: Conductivity measurements in mS cm^{-2} of all investigated electrolytes.

	MeMgCl in THF	*$Mg[HMDS]_2$-2$AlCl_3$ in THF*	*$Mg[B(hfip)_4]_2$ in DME*	*$Mg[B(hfip)_4]_2$ in THF*
0.1 M		1.523	5.962	4.806
0.2 M		2.347	8.043	6.421
0.25 M	0.062			
0.3 M	0.092	2.915	7.867	4.976
0.5 M	0.199			

EDX results

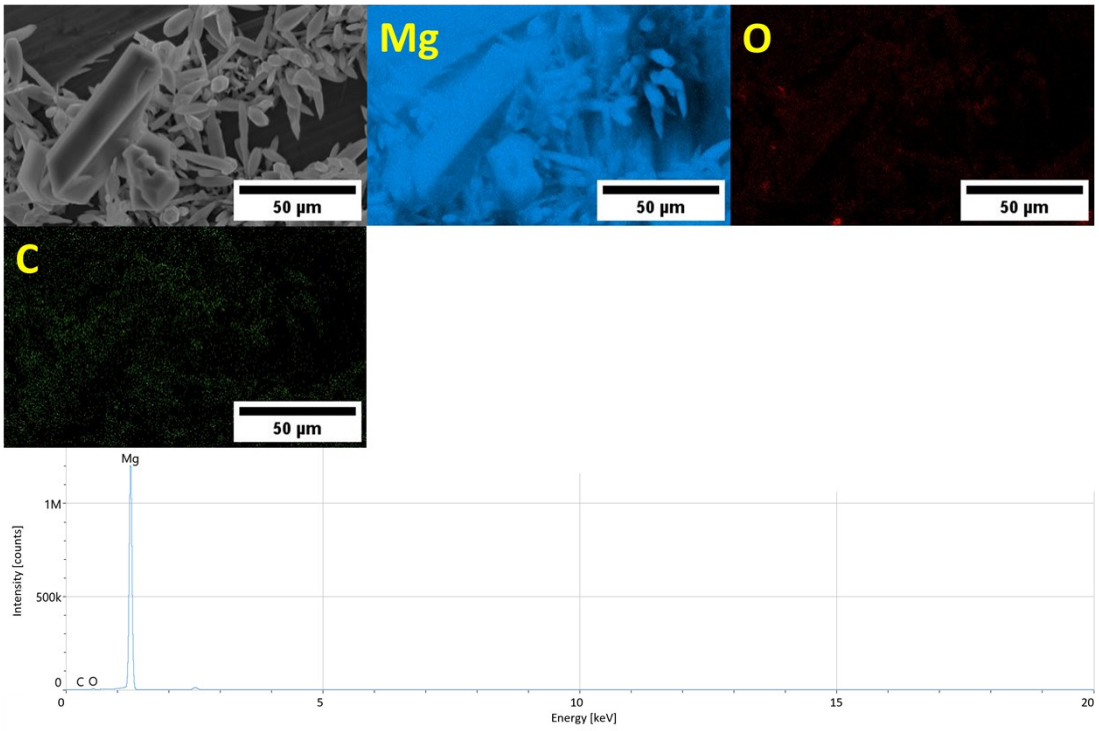

Figure 4: SE image and EDX maps of Mg, O and C with corresponding sum spectrum of a Mg deposition obtained from a 0.25 M solution of MeMgCl in THF at a current density of 0.307 mA cm^{-2}.

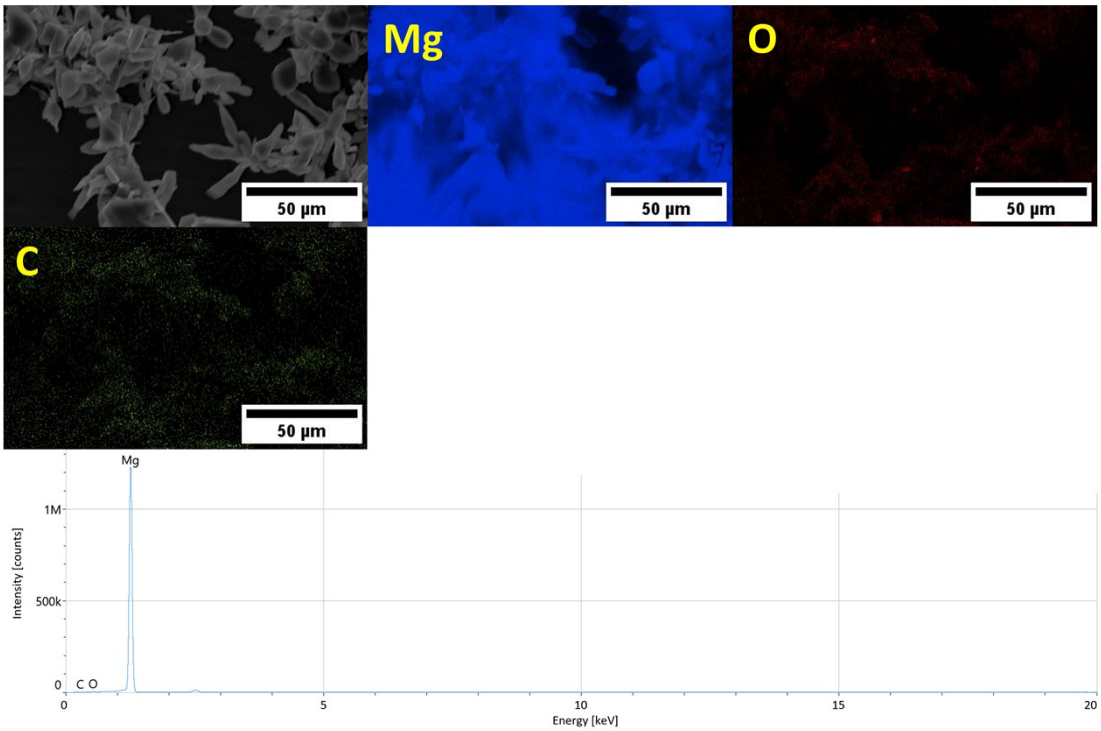

Figure 5: SE image and EDX maps of Mg, O & C with corresponding sum spectrum of a Mg deposition obtained from a 0.25 M solution of MeMgCl in THF at a current density of 0.921 mA cm^{-2}.

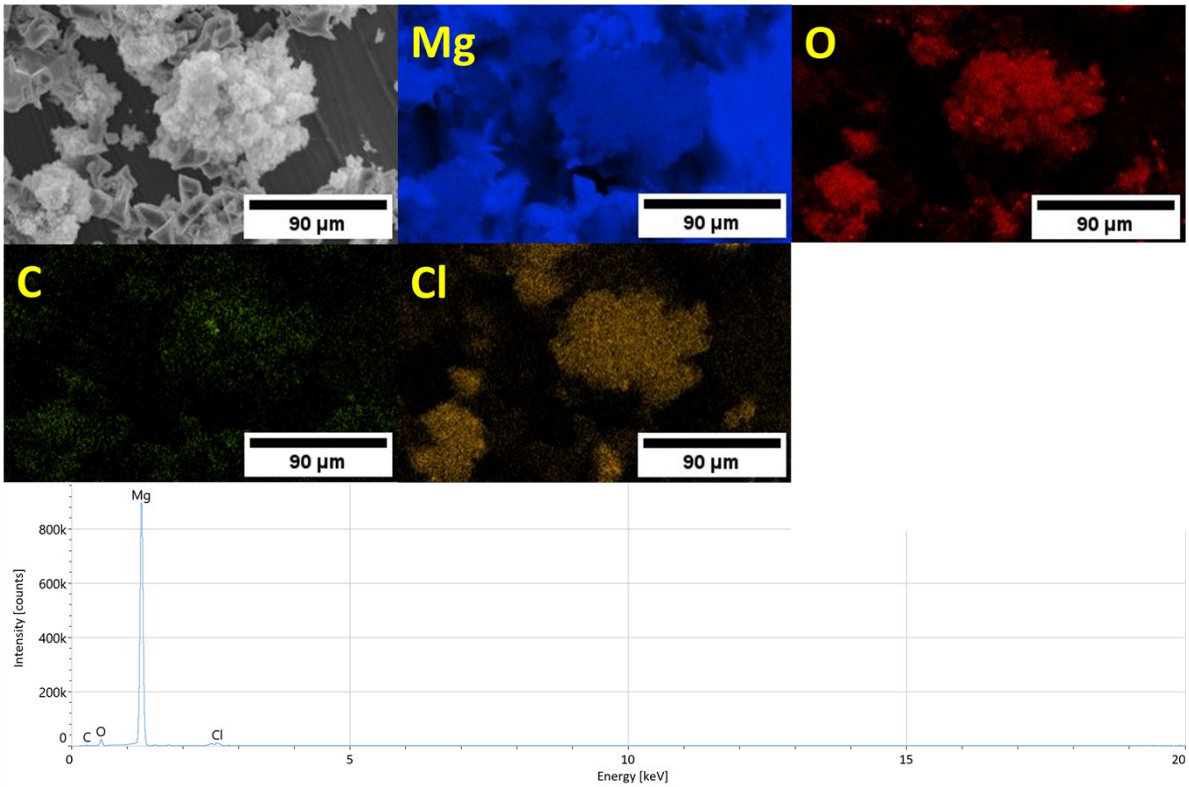

Figure 6: SE image and EDX maps of Mg, O, C & Cl with corresponding sum spectrum of a Mg deposition obtained from a 0.25 M solution of MeMgCl in THF at a current density of 1.54 mA cm^{-2}.

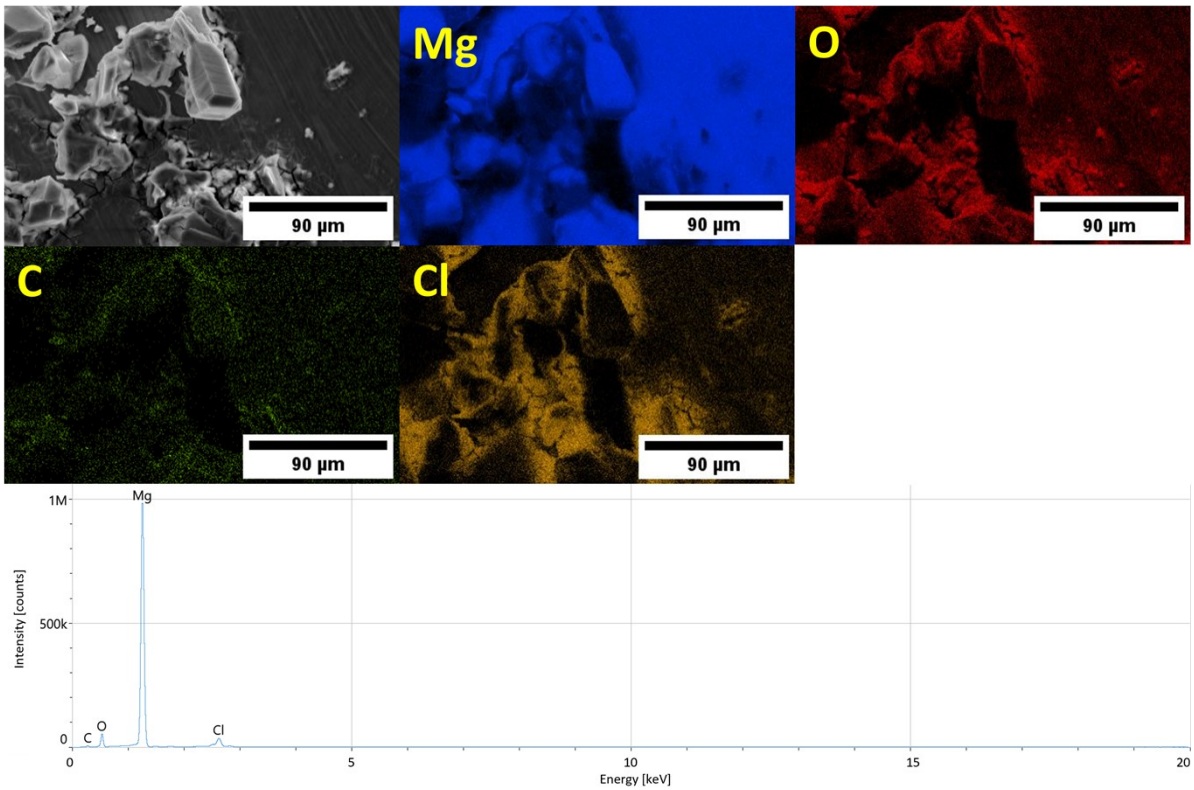

Figure 7: SE image and EDX maps of Mg, O, C & Cl with corresponding sum spectrum of a Mg deposition obtained from a 0.3 M solution of MeMgCl in THF at a current density of 0.307 mA cm^{-2}.

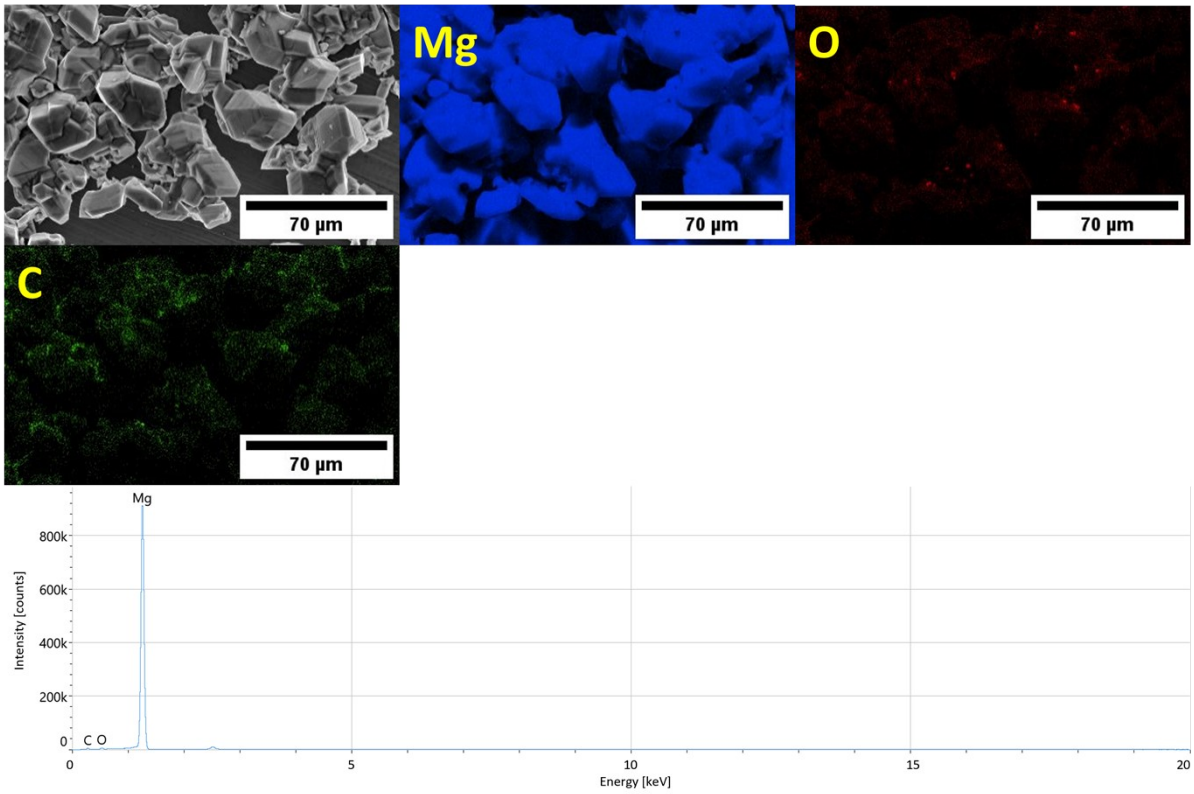

Figure 8: SE image and EDX maps of Mg, O and C with corresponding sum spectrum of a Mg deposition obtained from a 0.3 M solution of MeMgCl in THF at a current density of 0.921 mA cm^{-2}.

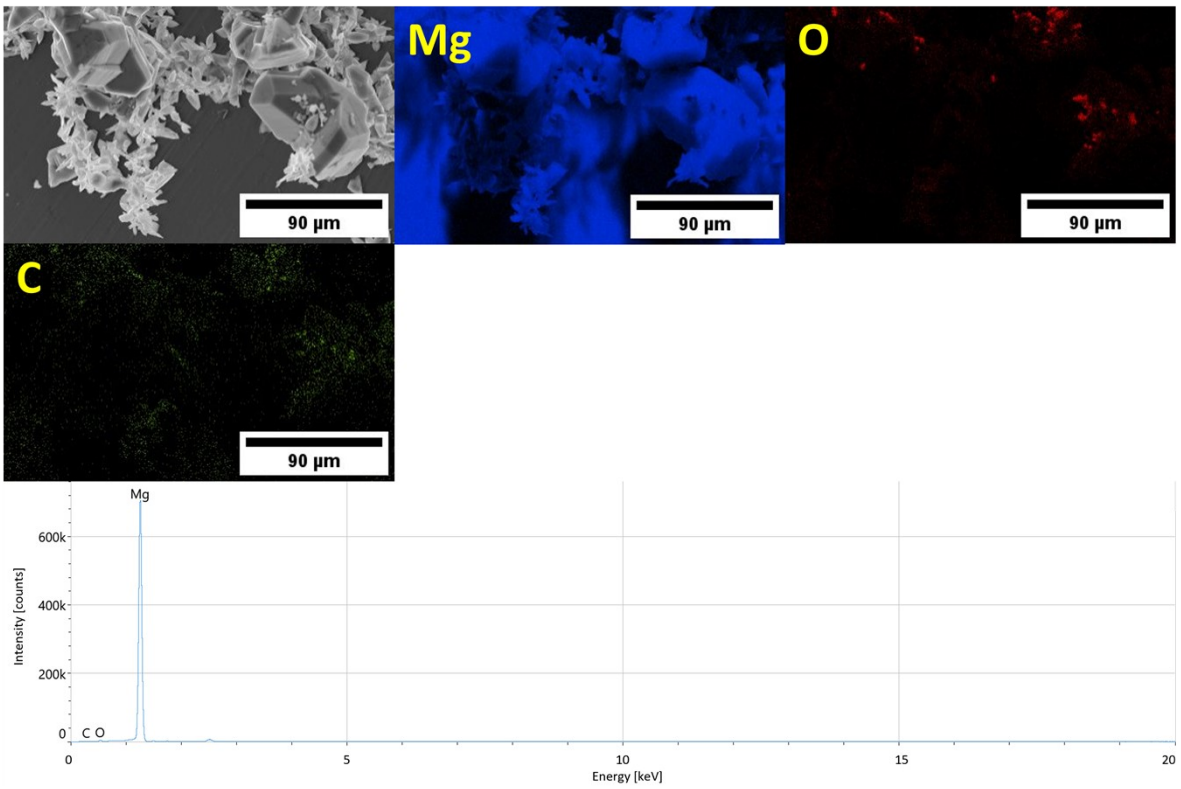

Figure 9: SE image and EDX maps of Mg, O & C with corresponding sum spectrum of a Mg deposition obtained from a 0.3 M solution of MeMgCl in THF at a current density of 1.54 mA cm^{-2}.

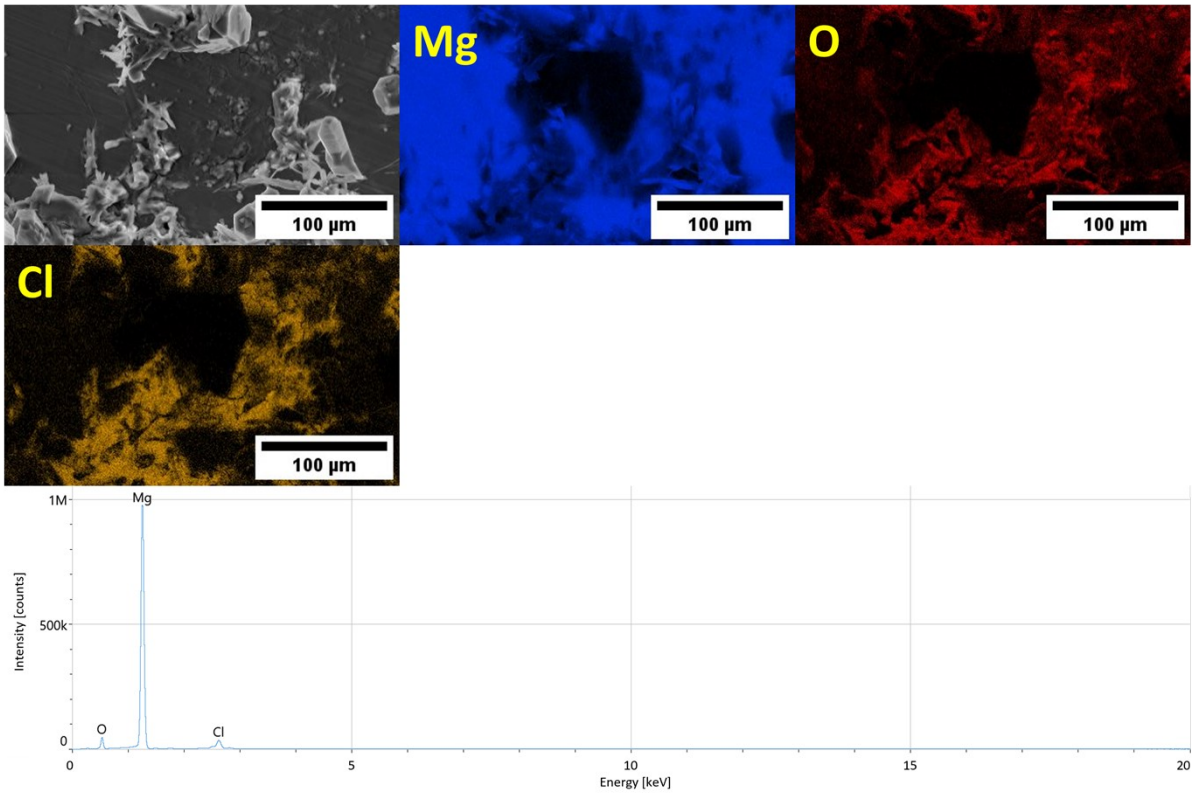

Figure 10: SE image and EDX maps of Mg, O & Cl with corresponding sum spectrum of a Mg deposition obtained from a 0.5 M solution of MeMgCl in THF at a current density of 0.307 mA cm^{-2}.

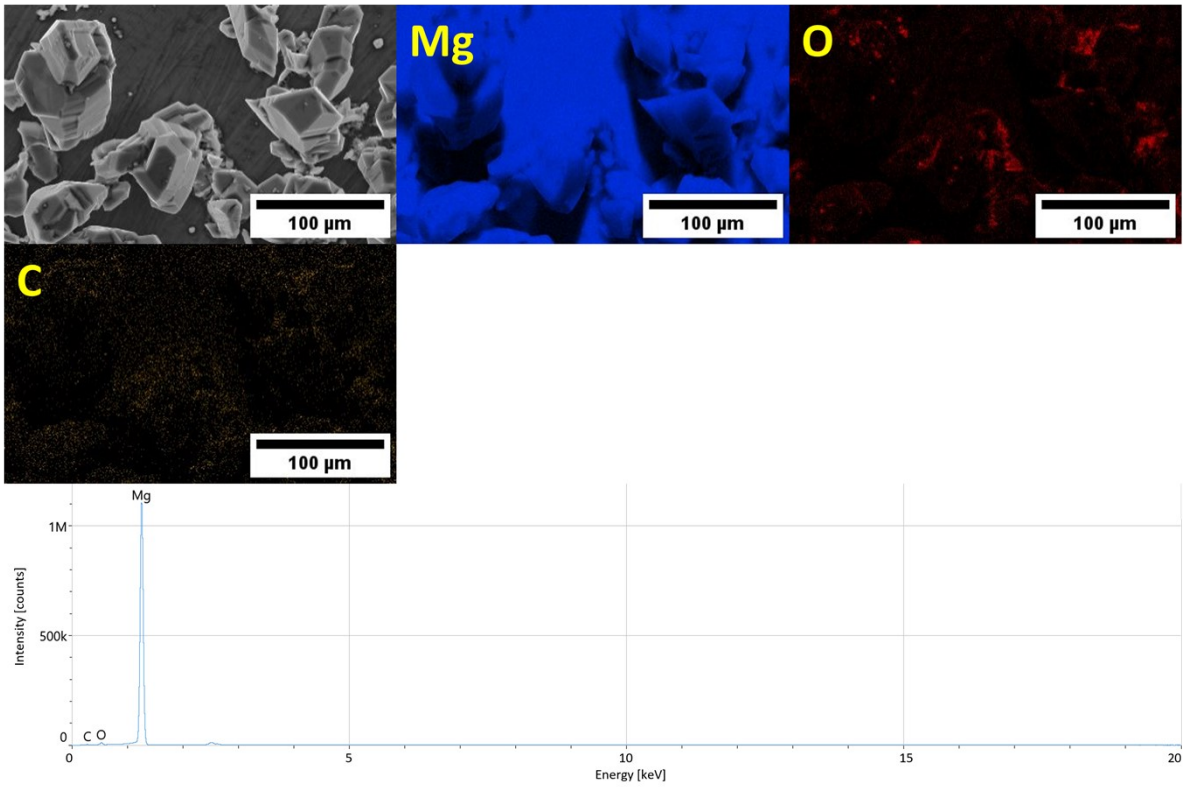

Figure 11: SE image and EDX maps of Mg, O & C with corresponding sum spectrum of a Mg deposition obtained from a 0.5 M solution of MeMgCl in THF at a current density of 0.921 mA cm^{-2}.

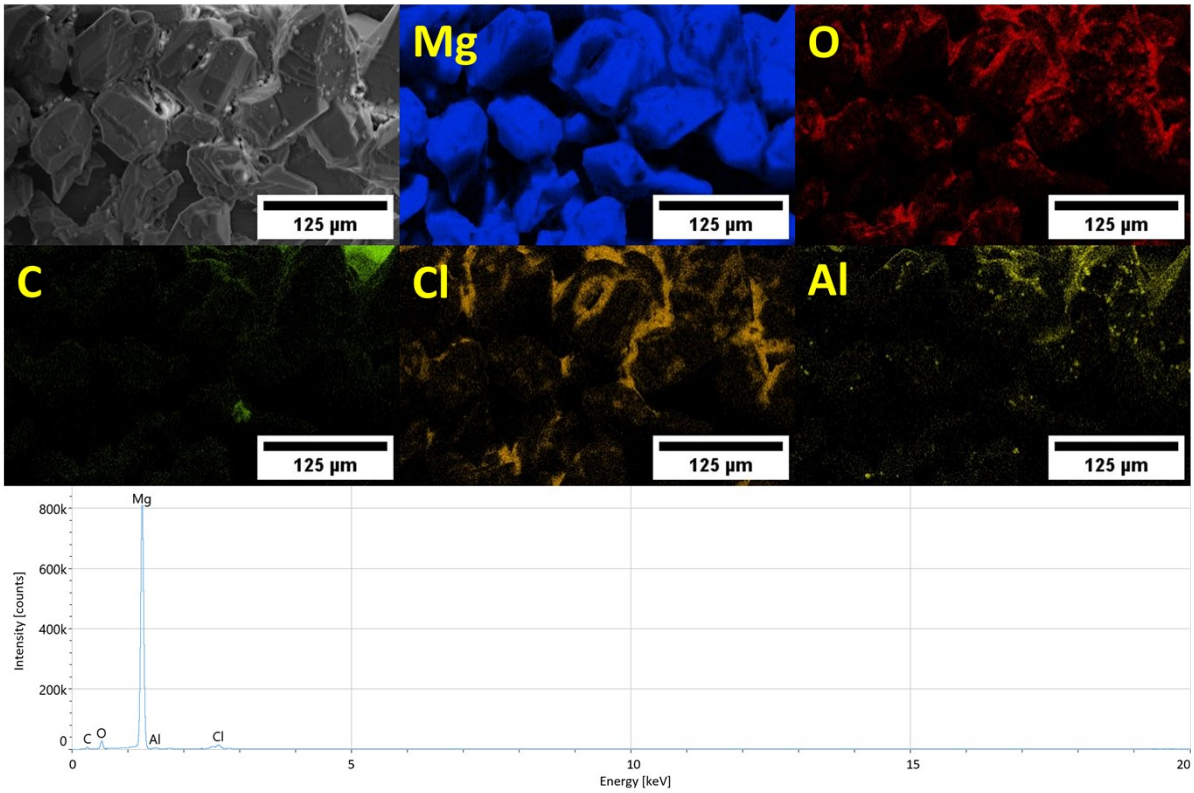

Figure 12: SE image and EDX maps of Mg, O, C, Cl & Al with corresponding sum spectrum of a Mg deposition obtained from a 0.5 M solution of MeMgCl in THF at a current density of 1.54 mA cm^{-2}.

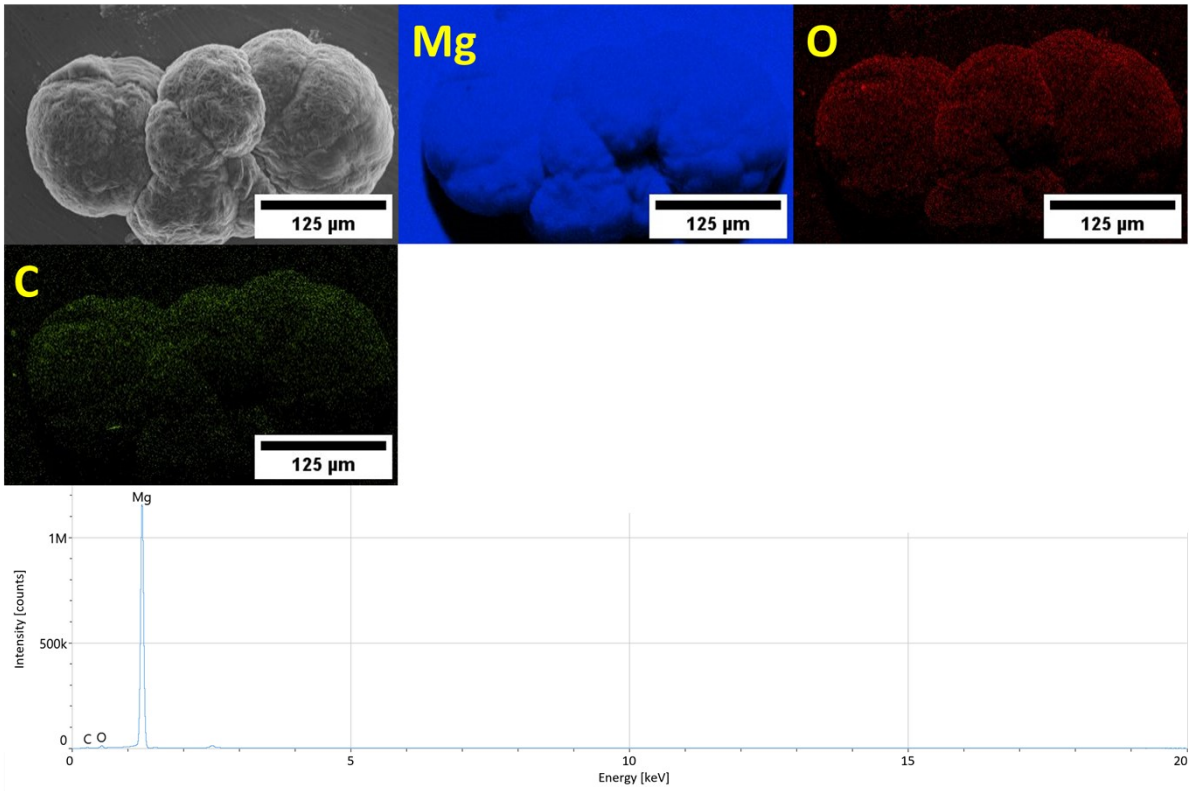

Figure 13: SE image and EDX maps of Mg, O & C with corresponding sum spectrum of a Mg deposition obtained from a 0.1 M solution of Mg(HMDS)$_2$-2AlCl$_3$ in THF at a current density of 0.307 mA cm^{-2} after 8 h.

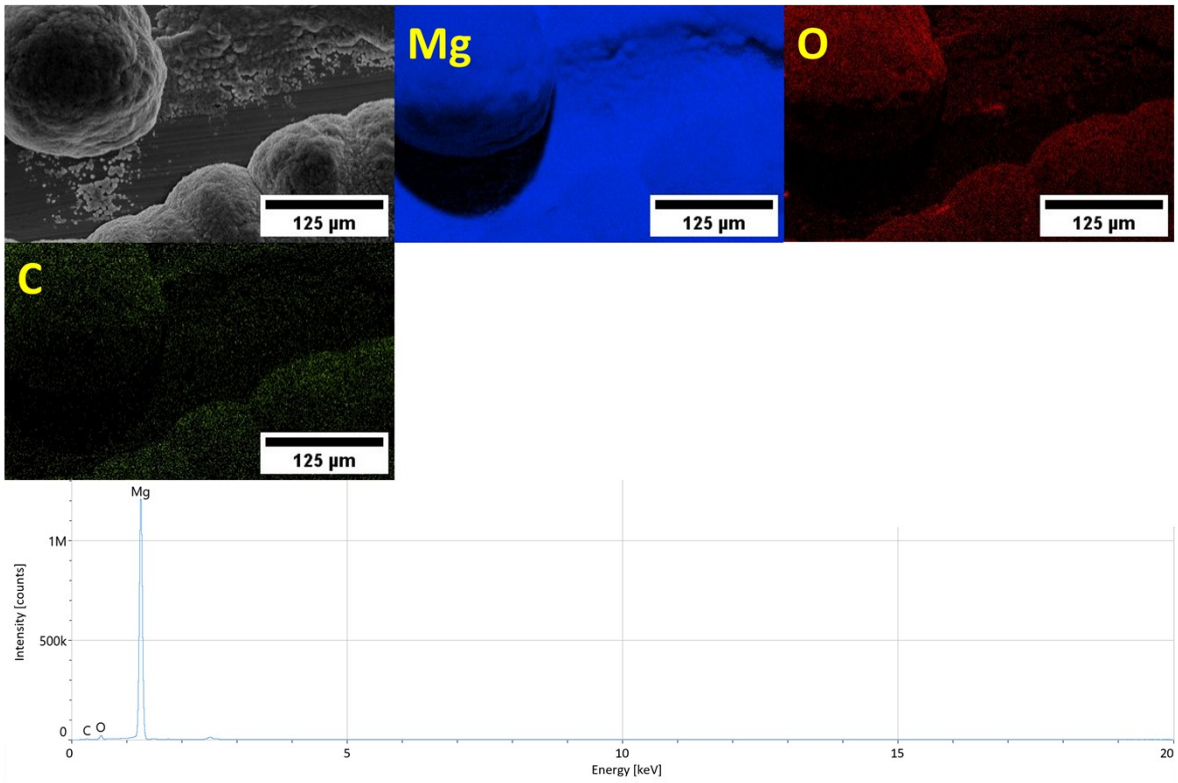

Figure 14: SE image and EDX maps of Mg, O & C with corresponding sum spectrum of a Mg deposition obtained from a 0.1 M solution of $Mg(HMDS)_2$-$2AlCl_3$ in THF at a current density of 0.921 mA cm^{-2} after 8 h.

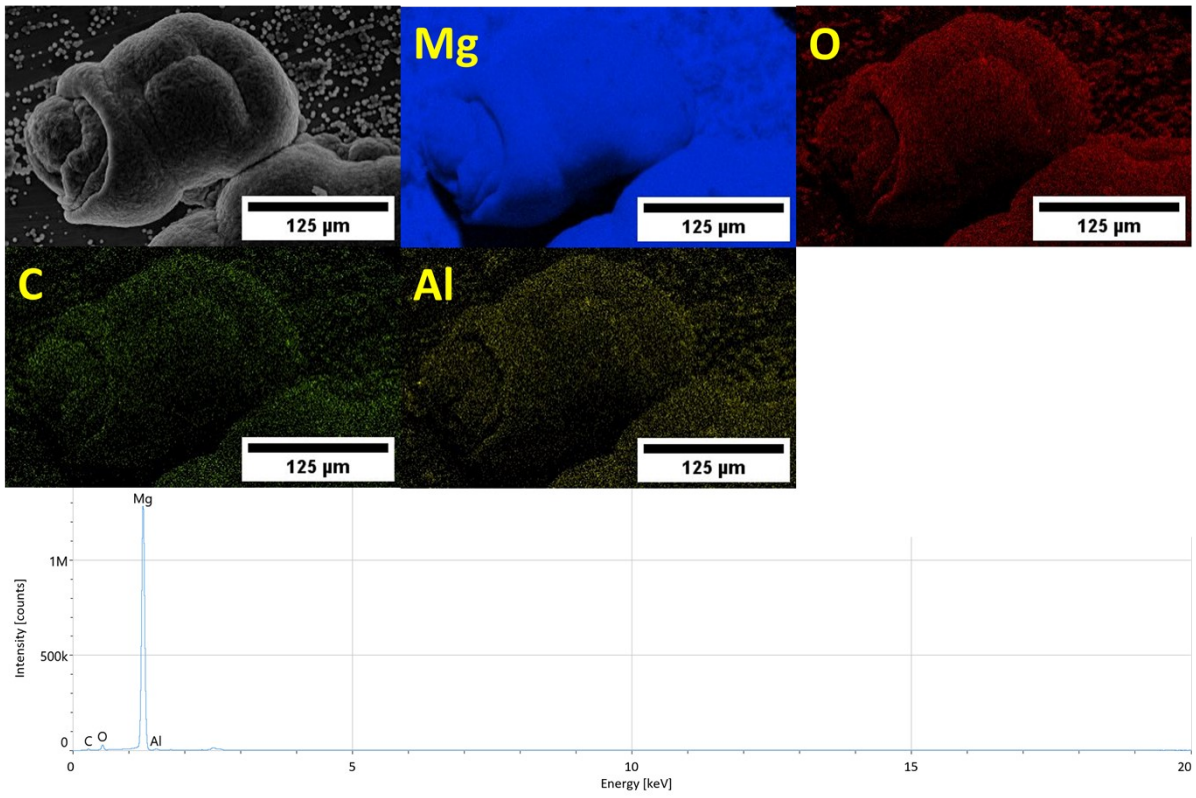

Figure 15: SE image and EDX maps of Mg, O, C & Al with corresponding sum spectrum of a Mg deposition obtained from a 0.1 M solution of $Mg(HMDS)_2$-$2AlCl_3$ in THF at a current density of 1.54 mA cm^{-2} after 8 h.

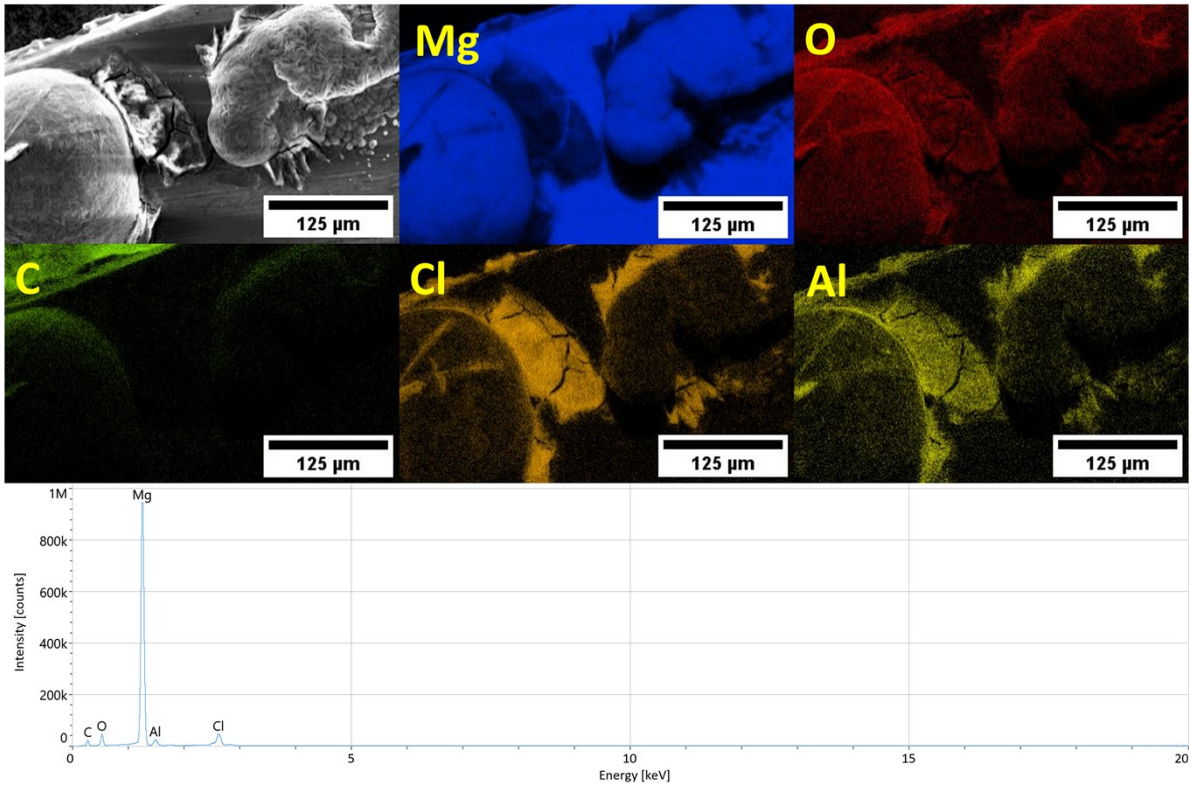

Figure 16: SE image and EDX maps of Mg, O, C, Cl & Al with corresponding sum spectrum of a Mg deposition obtained from a 0.2 M solution of $Mg(HMDS)_2$-$2AlCl_3$ in THF at a current density of 0.307 mA cm^{-2} after 8 h.

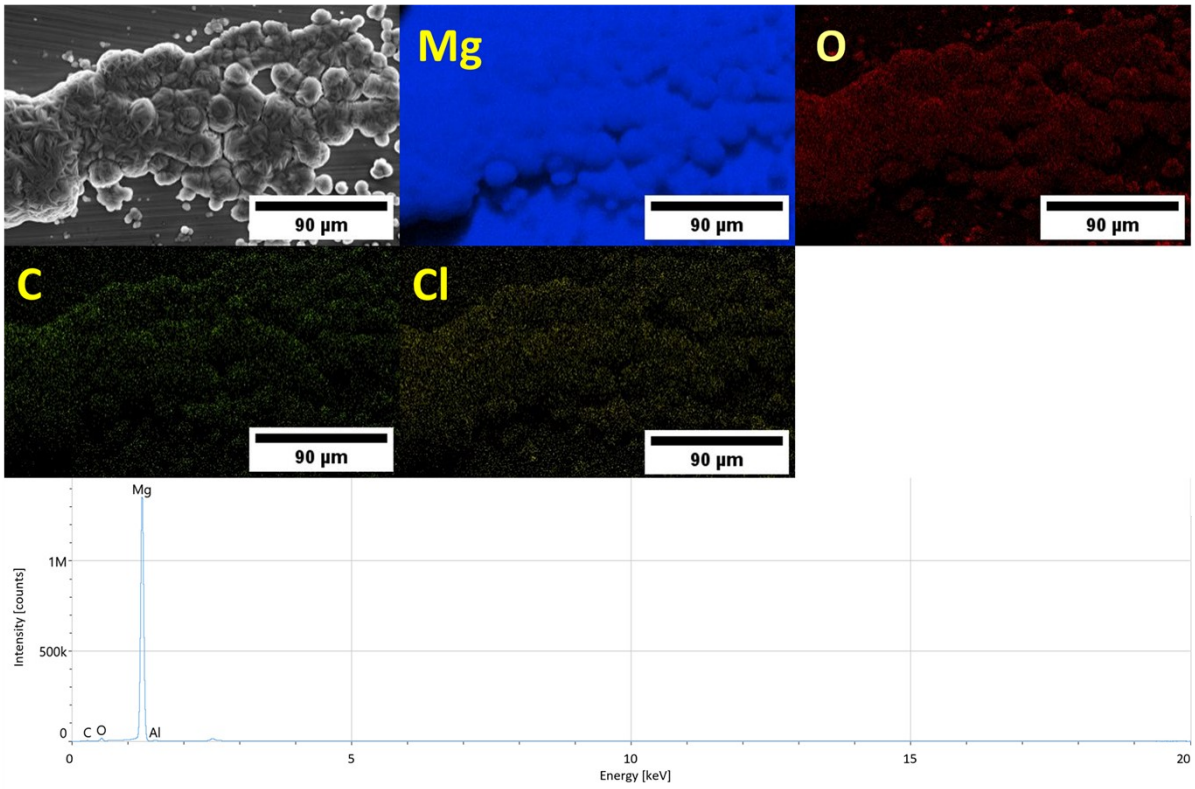

Figure 17: SE image and EDX maps of Mg, O, C, Cl with corresponding sum spectrum of a Mg deposition obtained from a 0.2 M solution of $Mg(HMDS)_2$-$2AlCl_3$ in THF at a current density of 0.921 mA cm^{-2} after 8 h.

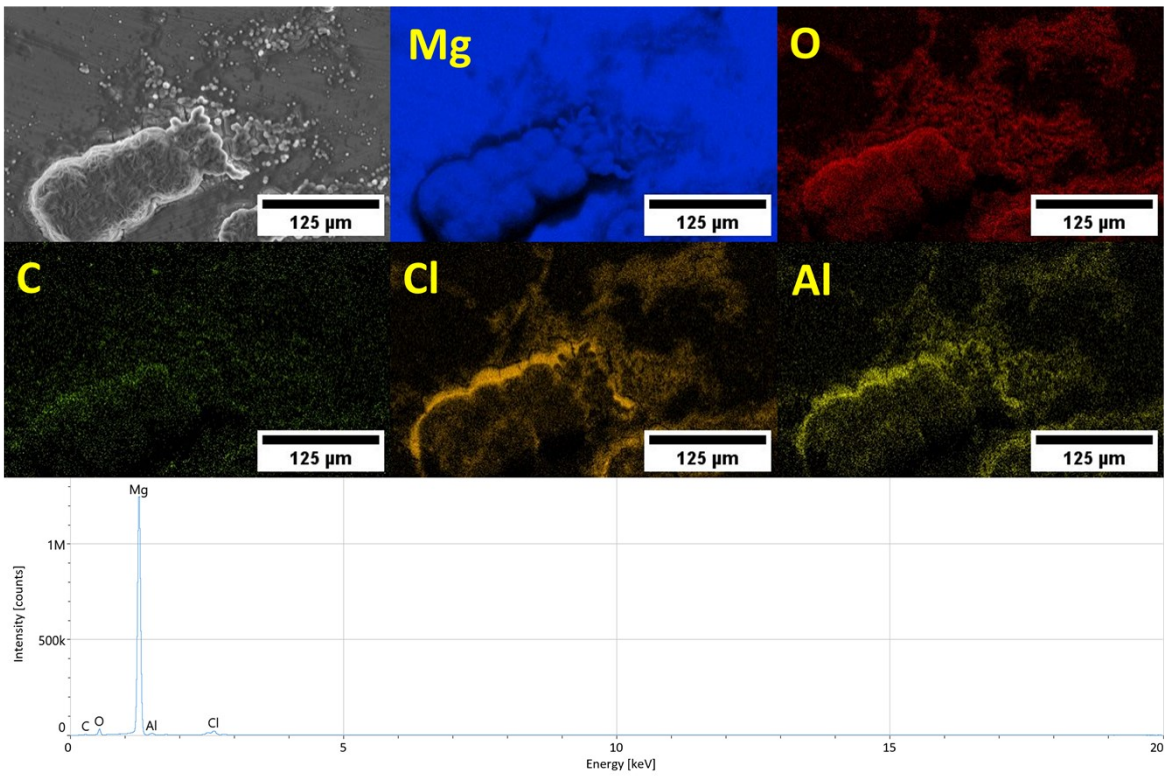

Figure 18: SE image and EDX maps of Mg, O, C, Cl & Al with corresponding sum spectrum of a Mg deposition obtained from a 0.2 M solution of $Mg(HMDS)_2$-$2AlCl_3$ in THF at a current density of 1.54 mA cm^{-2} after 8 h.

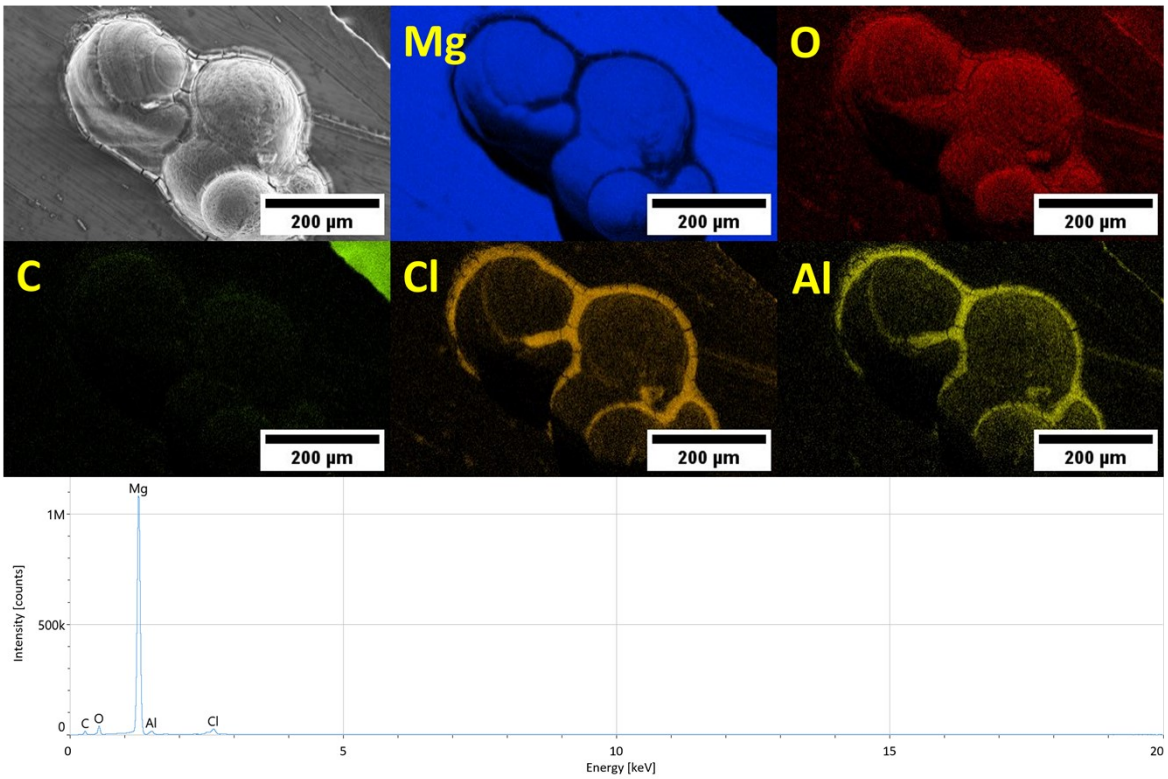

Figure 19: SE image and EDX maps of Mg, O, C, Cl & Al with corresponding sum spectrum of a Mg deposition obtained from a 0.3 M solution of $Mg(HMDS)_2$-$2AlCl_3$ in THF at a current density of 0.307 mA cm^{-2} after 8 h.

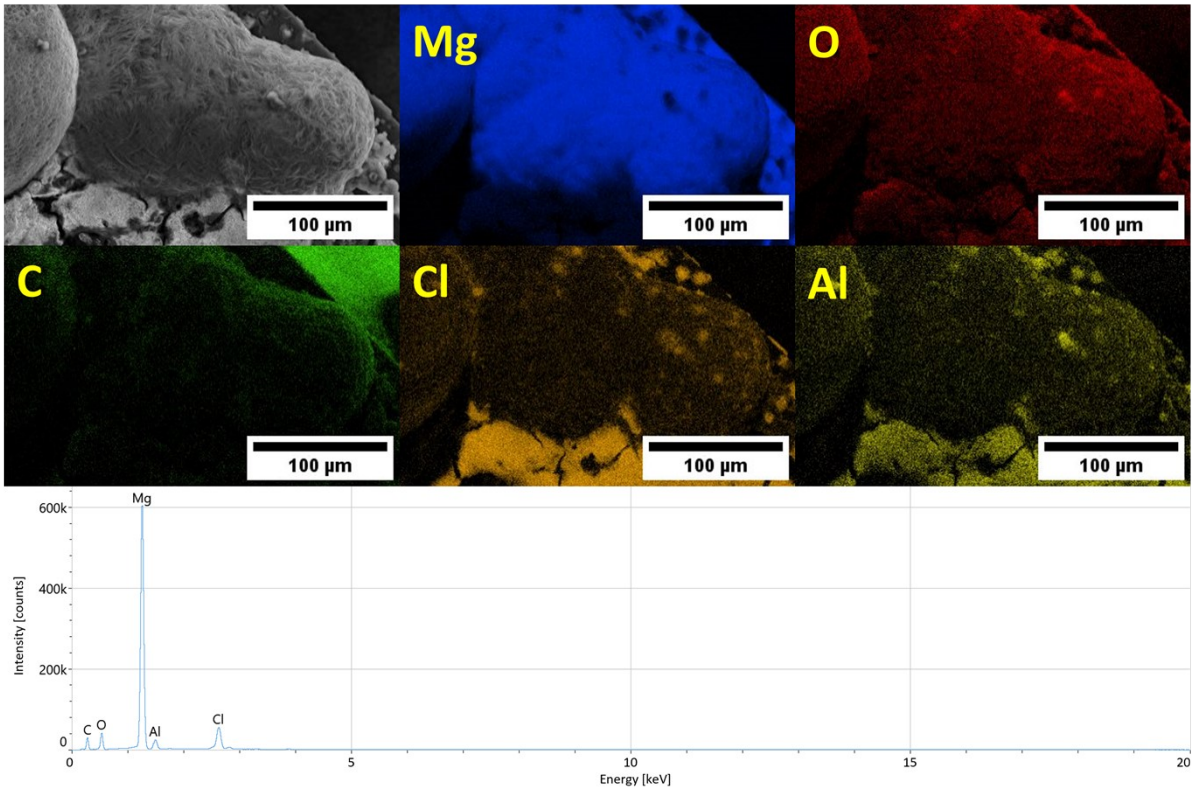

Figure 20: SE image and EDX maps of Mg, O, C, Cl & Al with corresponding sum spectrum of a Mg deposition obtained from a 0.3 M solution of $Mg(HMDS)_2$-$2AlCl_3$ in THF at a current density of 0.921 mA cm^{-2} after 8 h.

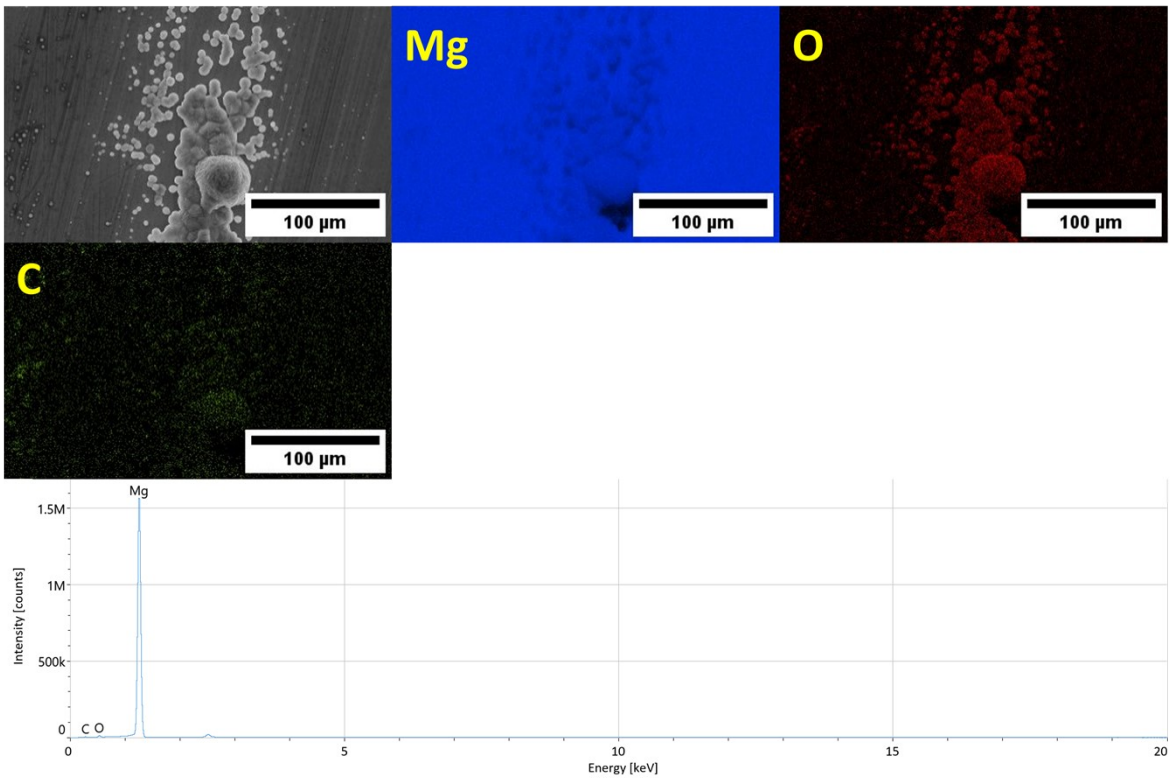

Figure 21: SE image and EDX maps of Mg, O & C with corresponding sum spectrum of a Mg deposition obtained from a 0.3 M solution of $Mg(HMDS)_2$-$2AlCl_3$ in THF at a current density of 1.54 mA cm^{-2} after 8 h.

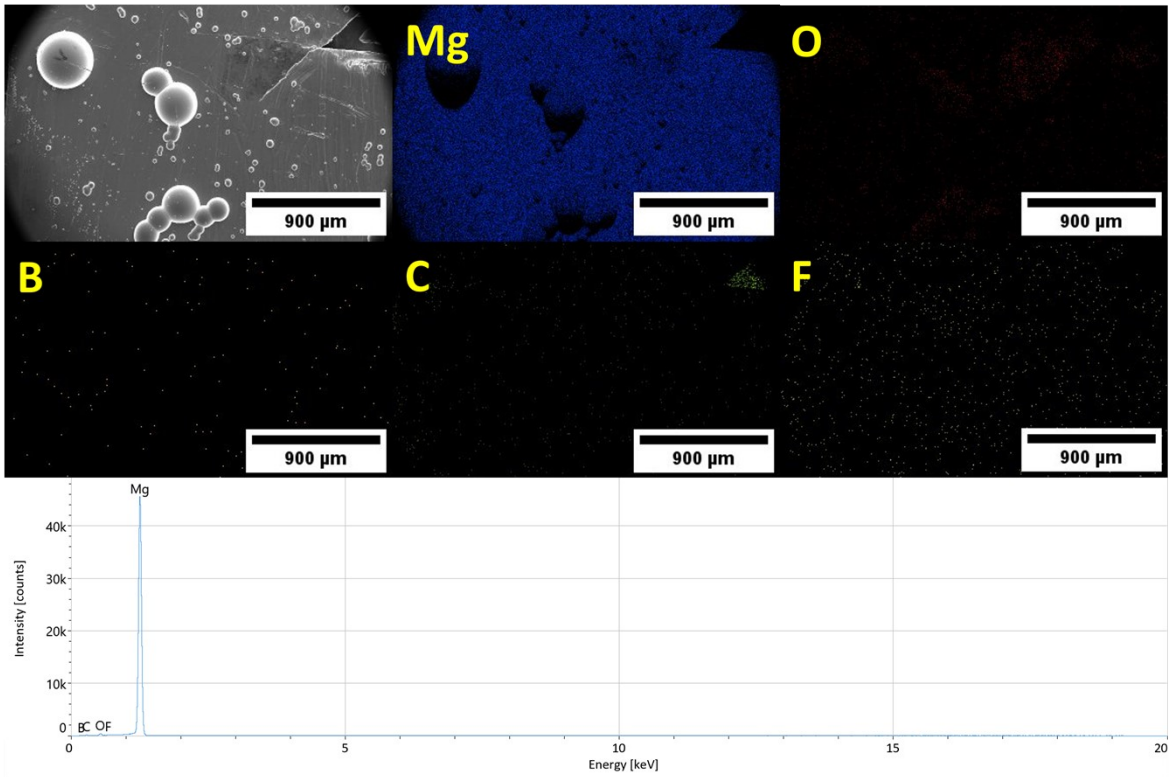

Figure 22: SE image and EDX maps of Mg, O, B, C & F with corresponding sum spectrum of a Mg deposition obtained from a 0.1 M solution of $Mg[B(hfip)_4]_2$ in DME at a current density of 0.307 mA cm^{-2} after 8 h.

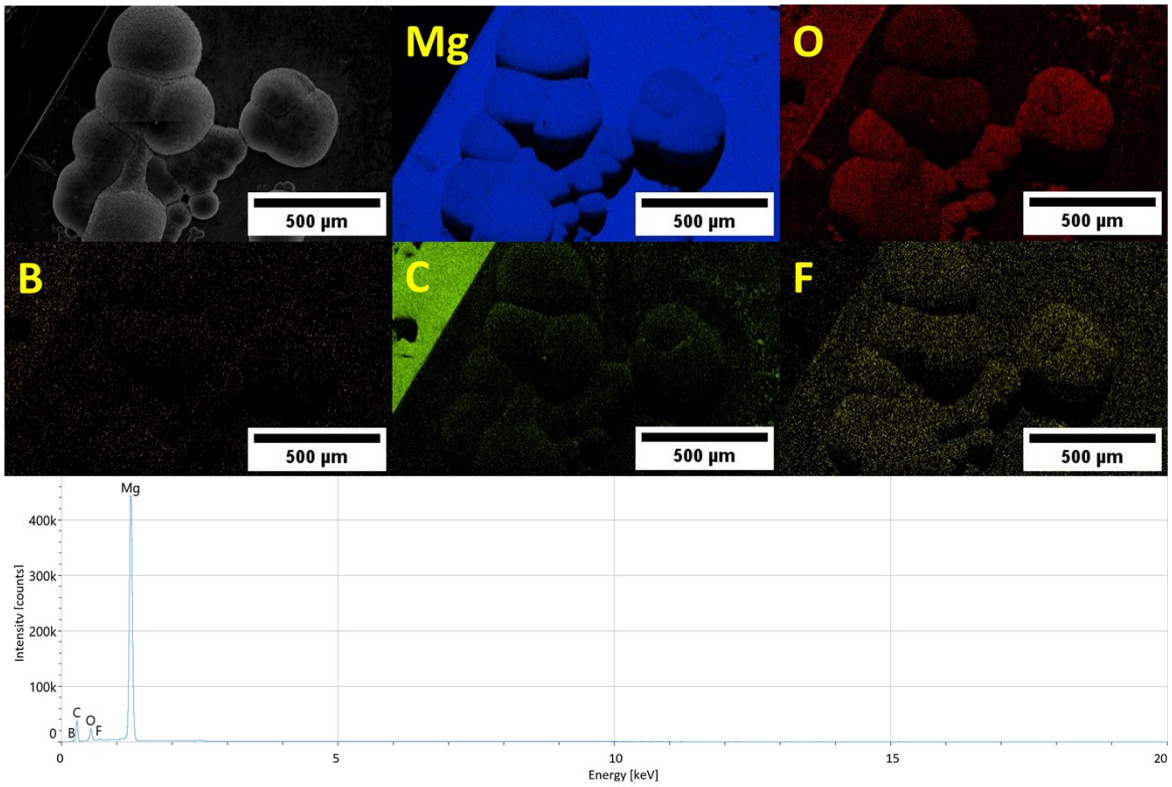

Figure 23: SE image and EDX maps of Mg, O, B, C & F with corresponding sum spectrum of a Mg deposition obtained from a 0.1 M solution of $Mg[B(hfip)_4]_2$ in DME at a current density of 0.921 mA cm^{-2} after 8 h.

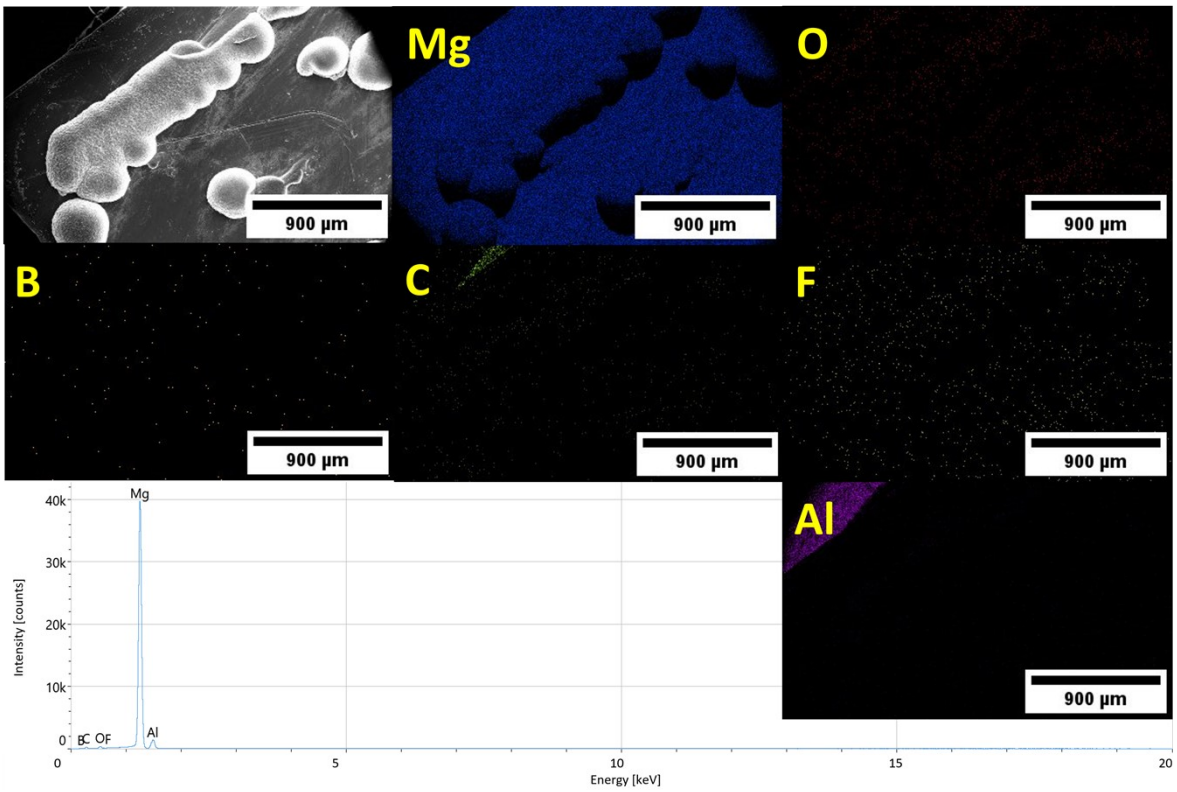

Figure 24: SE image and EDX maps of Mg, O, B, C, F & Al with corresponding sum spectrum of a Mg deposition obtained from a 0.1 M solution of $Mg[B(hfip)_4]_2$ in DME at a current density of 1.54 mA cm^{-2} after 8 h.

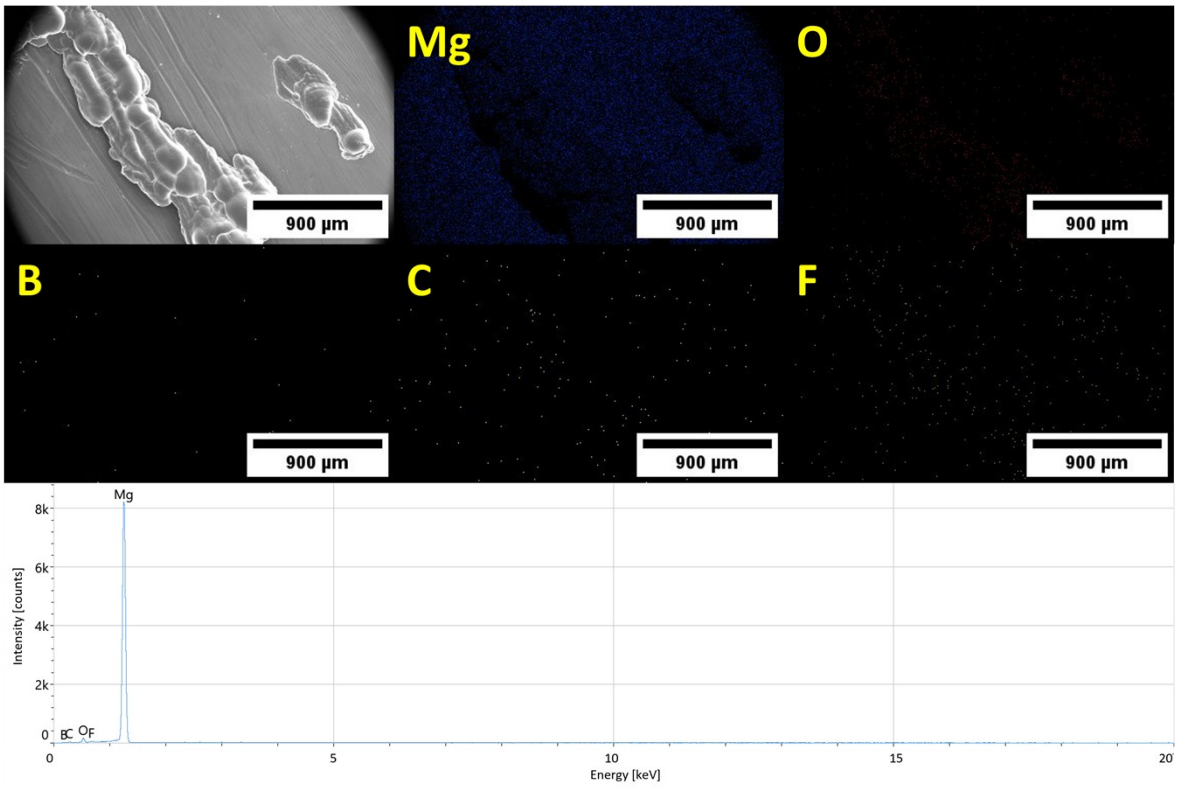

Figure 25: SE image and EDX maps of Mg, O, B, C & F with corresponding sum spectrum of a Mg deposition obtained from a 0.2 M solution of $Mg[B(hfip)_4]_2$ in DME at a current density of 0.307 mA cm^{-2} after 8 h.

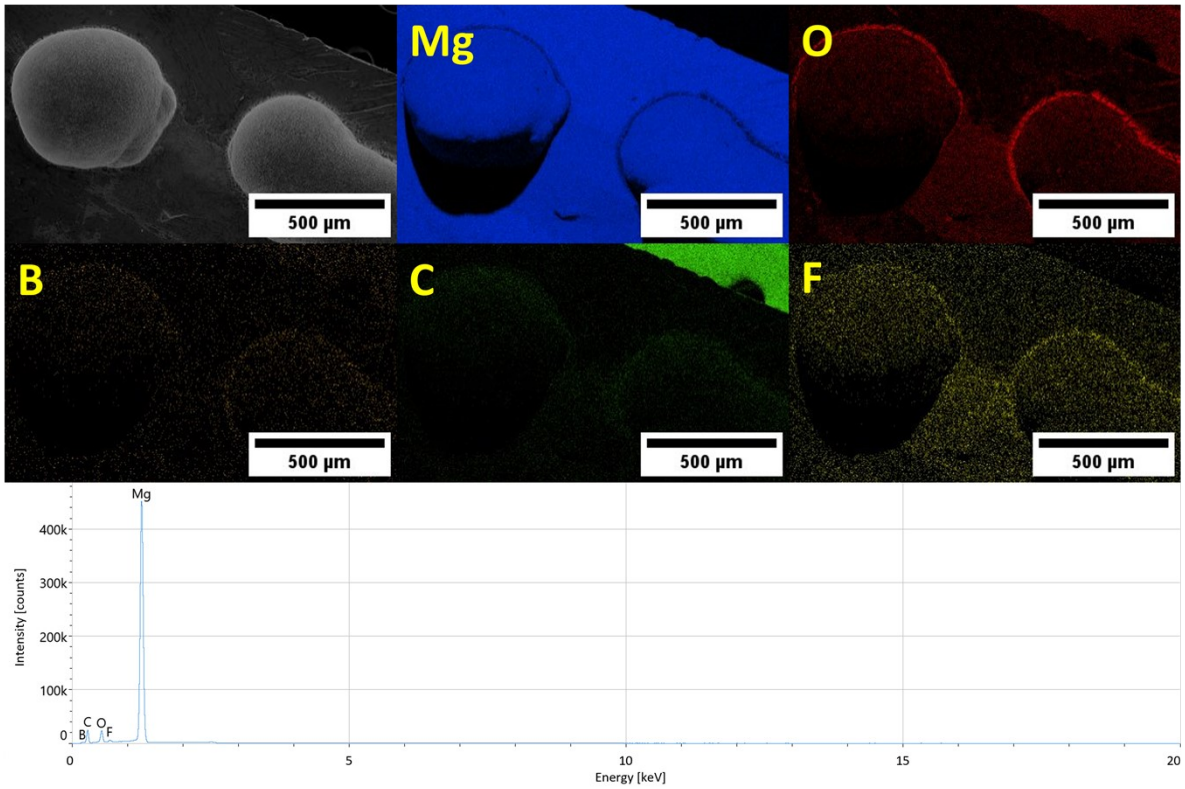

Figure 26: SE image and EDX maps of Mg, O, B, C & F with corresponding sum spectrum of a Mg deposition obtained from a 0.2 M solution of $Mg[B(hfip)_4]_2$ in DME at a current density of 0.921 mA cm^{-2} after 8 h.

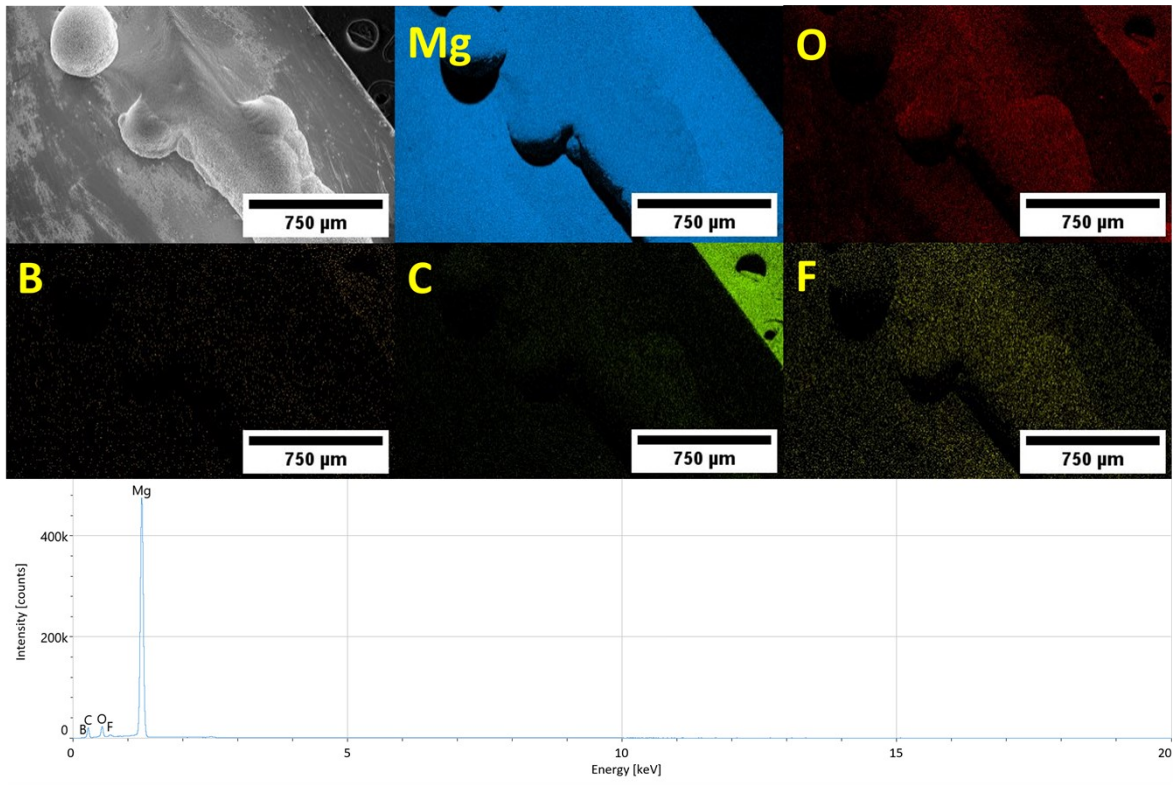

Figure 27: SE image and EDX maps of Mg, O, B, C & F with corresponding sum spectrum of a Mg deposition obtained from a 0.2 M solution of $Mg[B(hfip)_4]_2$ in DME at a current density of 1.54 mA cm^{-2} after 8 h.

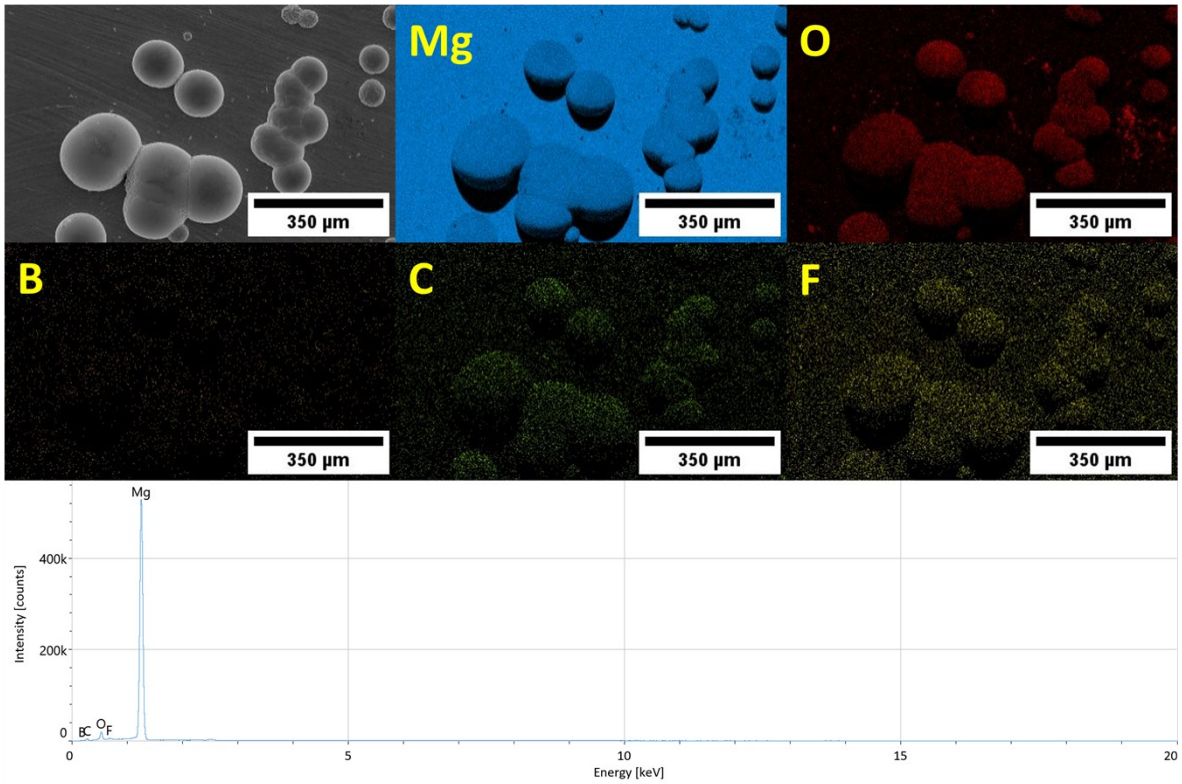

Figure 28: SE image and EDX maps of Mg, O, B, C & F with corresponding sum spectrum of a Mg deposition obtained from a 0.3 M solution of $Mg[B(hfip)_4]_2$ in DME at a current density of 0.307 mA cm^{-2} after 8 h.

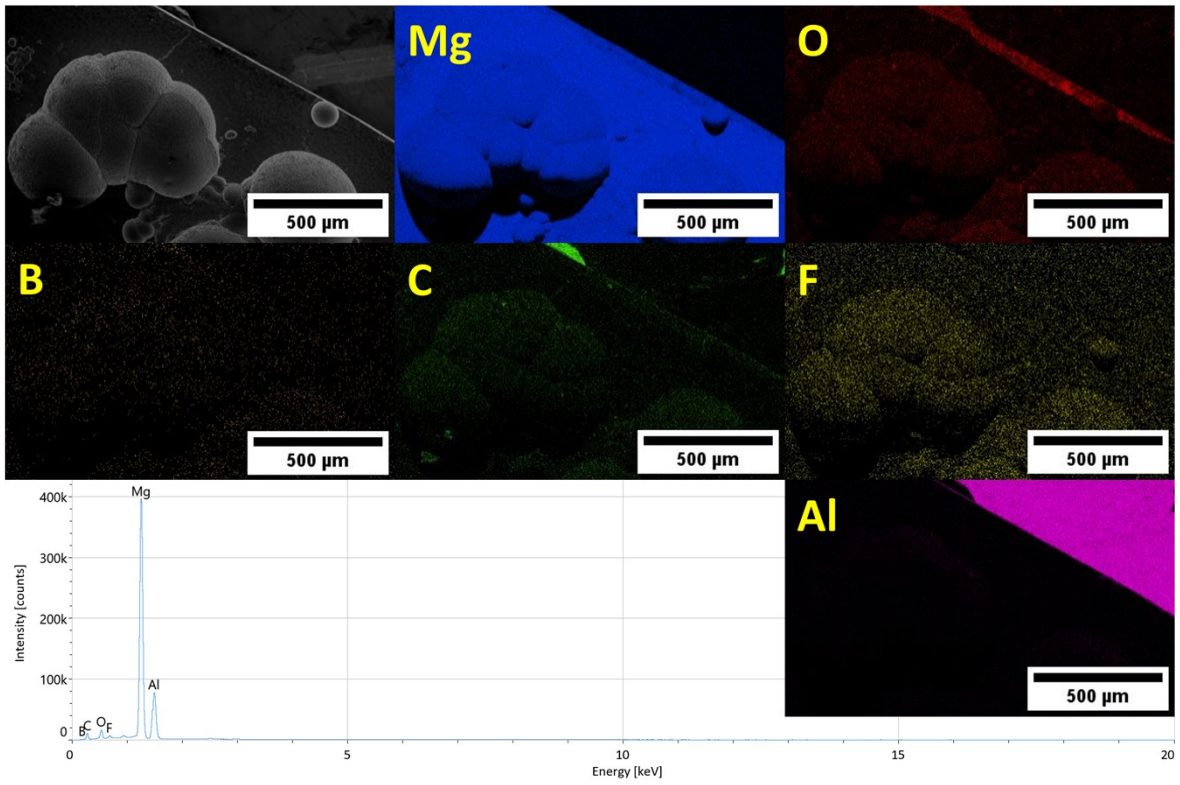

Figure 29: SE image and EDX maps of Mg, O, B, C, F & Al with corresponding sum spectrum of a Mg deposition obtained from a 0.3 M solution of $Mg[B(hfip)_4]_2$ in DME at a current density of 0.921 mA cm^{-2} after 8 h.

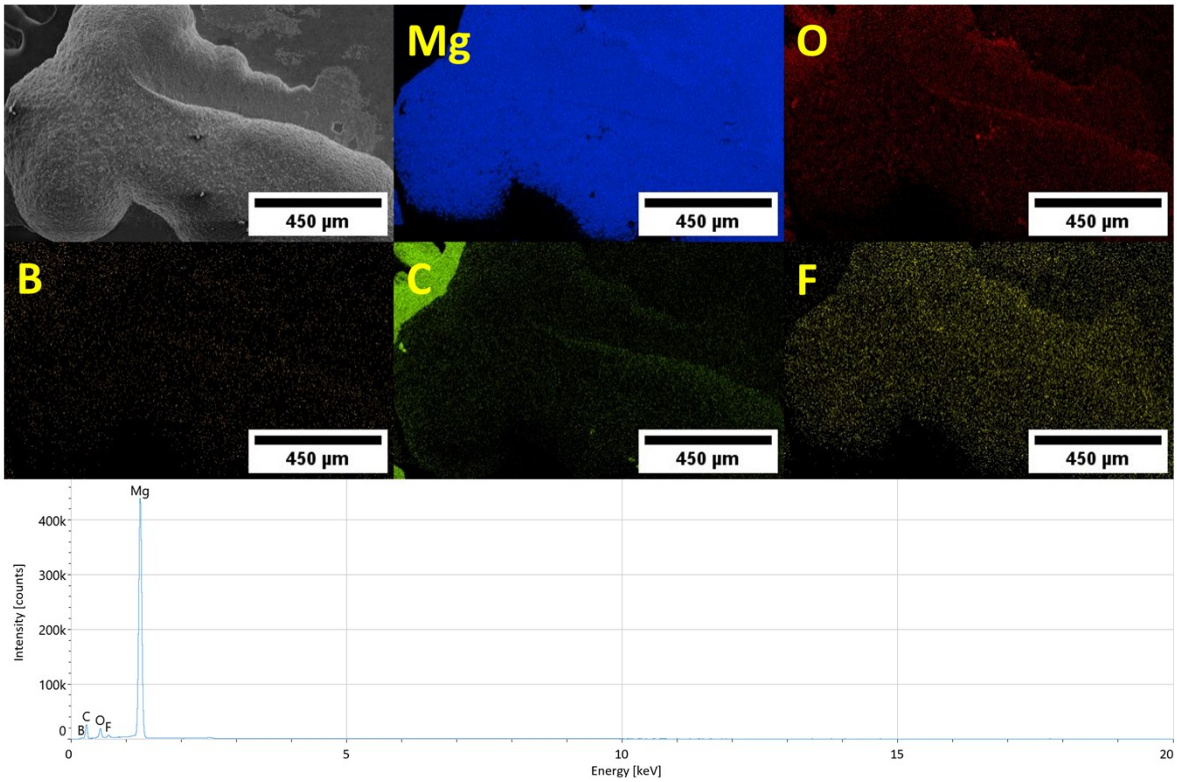

Figure 30: SE image and EDX maps of Mg, O, B, C & F with corresponding sum spectrum of a Mg deposition obtained from a 0.3 M solution of $Mg[B(hfip)_4]_2$ in DME at a current density of 1.54 mA cm^{-2} after 8 h.

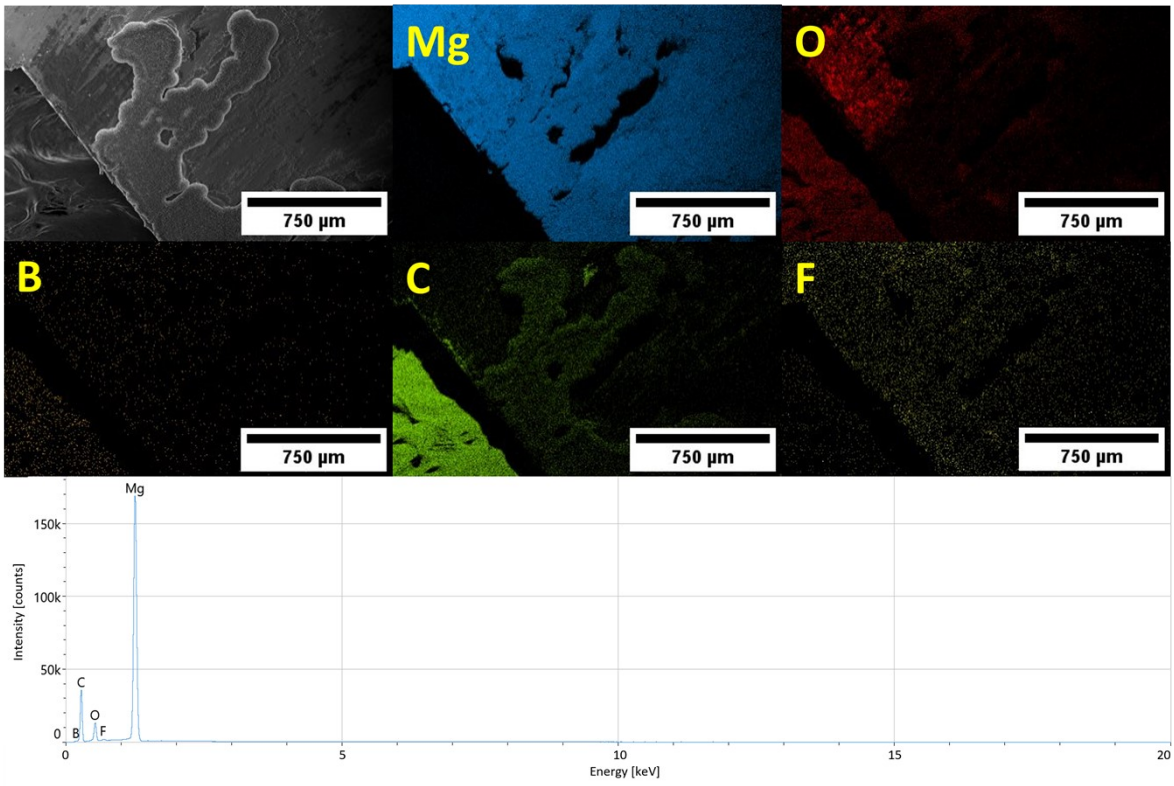

Figure 31: SE image and EDX maps of Mg, O, B, C & F with corresponding sum spectrum of a Mg deposition obtained from a 0.1 M solution of $Mg[B(hfip)_4]_2$ and 5 mM $Mg(BH_4)_2$ in DME at a current density of 0.921 mA cm^{-2} after 8 h.

Deposition experiments of Mg[B(hfip)4]2 in THF with 15 ppm water

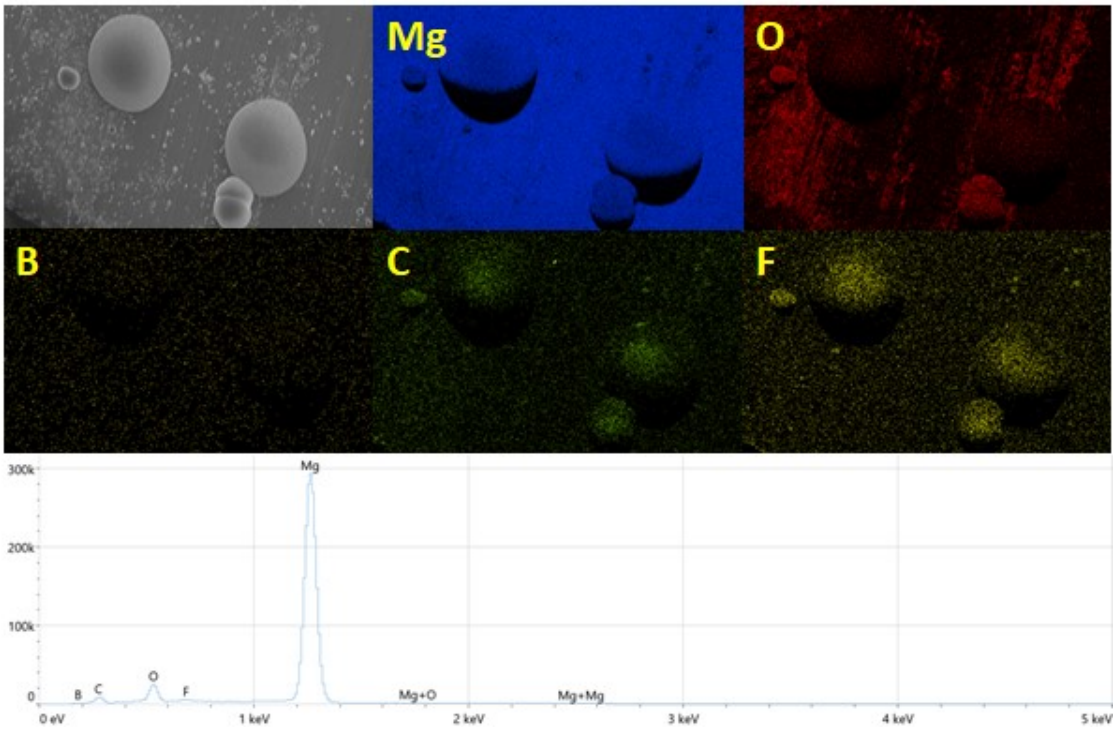

Figure 32: SE image and EDX maps of Mg, O, B, C & F with corresponding sum spectrum of a Mg deposition obtained from a 0.1 M solution of $Mg[B(hfip)_4]_2$ in THF with 15 ppm water at a current density of 1.54 mA cm^{-2} after 8 h.

Deposition experiments of Mg[B(hfip)4]2 in THF with 1.2 ppm water

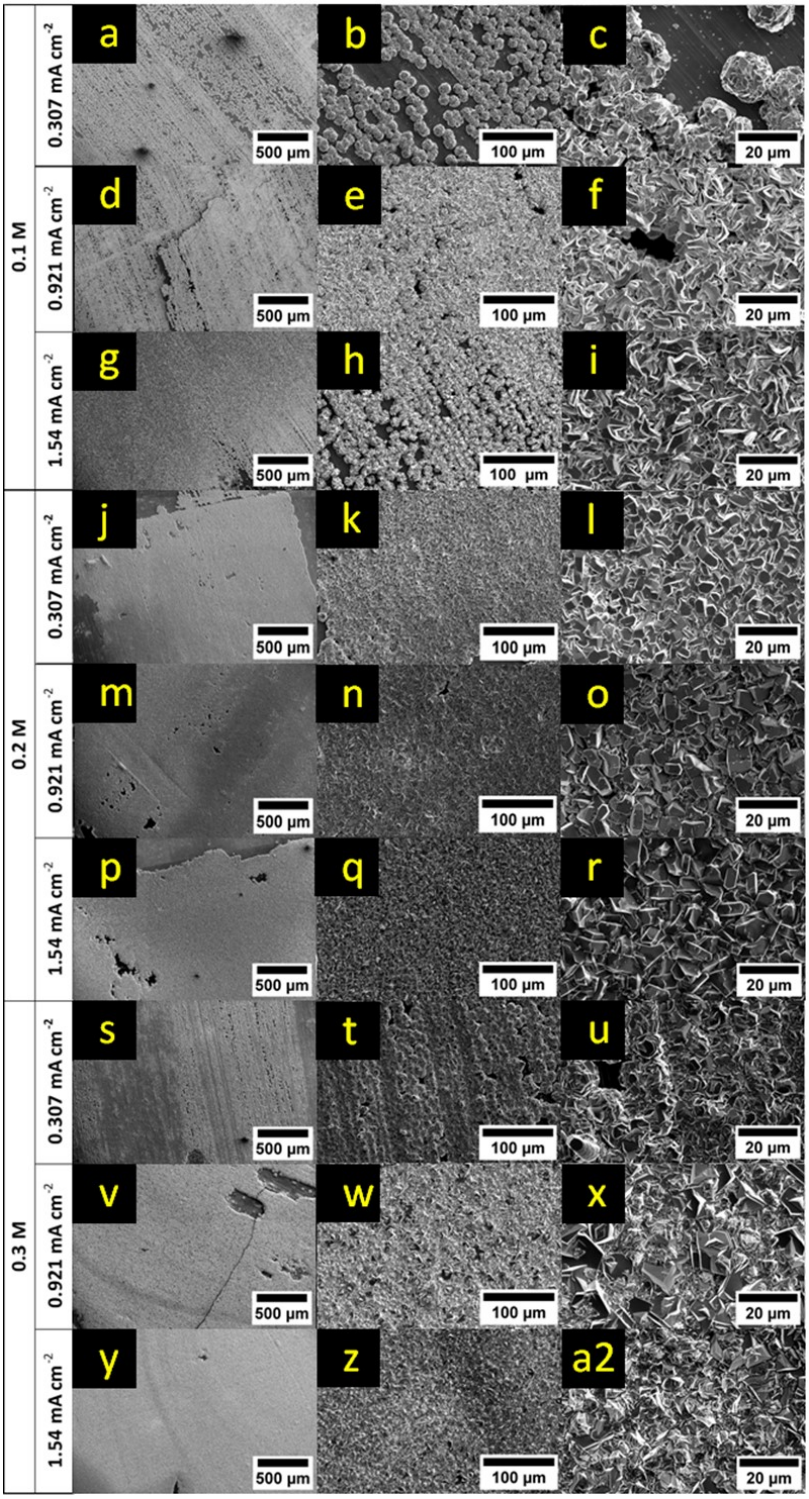

Figure 33: Magnesium deposition morphologies using different concentrations and current densities. SEM images were taken after 8 h of deposition. Utilization of THF with lower water content led to the formation of a uniform deposition, consisting of individual crystallites, growing into each other along the whole electrode. Higher current led to denser deposition. No observable dendrite formation under any, here applied, condition.

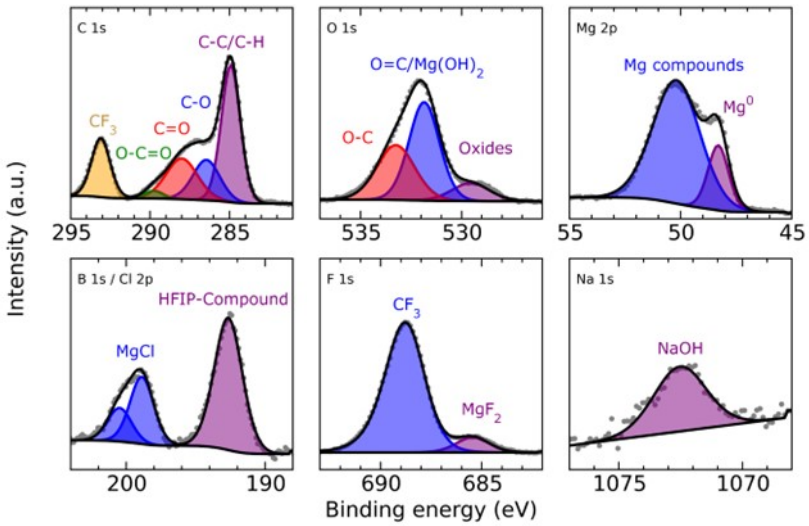

Figure 34: XPS results of Mg depositions from $Mg[B(hfip)_4]_2$ in THF in 1.2 ppm water. The attributed species are identical to the species found in the DME based $Mg[B(hfip)_4]_2$ electrolyte.