# Supplementary information for:

# Reduction of dinitrogen to ammonium through a magnesium-based electrochemical process at close-to-ambient temperature

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# ALTERNATIVE MEDIATORS FOR N<sub>2</sub> ELECTROREDUCTION

Clearly, a mediator system should have  $E^0$  significantly more positive than that for the Li<sup>0/+</sup> mediator (-3.04 V vs. SHE).<sup>1</sup> From this perspective, K<sup>0/+</sup>, Rb<sup>0/+</sup>, and Cs<sup>0/+</sup> do not seem to present significant prospects due to very negative  $E^0$  (Table S1).<sup>1</sup> Moreover, K<sub>3</sub>N was reported to decompose at temperatures above -10 °C.<sup>2</sup> The standard potential for Na<sup>0/+</sup> is more positive than that for Li<sup>0/+</sup> by *ca*. 0.3 V, but the formation of Na<sub>3</sub>N is thermodynamically unfavourable under standard conditions, where the free energy of formation ( $\Delta G$ ) of this compound is positive.<sup>3</sup>

Metal	<i>E</i> <sup>0</sup> / V <i>vs</i> . SHE <sup>a</sup>	ΔG° <sub>f</sub> / kJ mol⁻ <sup>1 b</sup>	Experimentally reported M <sub>x</sub> N <sub>y</sub> <sup>c</sup>	Reactivity against H <sub>2</sub> O <sup>d</sup>
Li	-3.04	-154.8	Li <sub>3</sub> N	Yes
Na	-2.71	65.61 <sup>e</sup>	Na₃N	n.a. <sup>e</sup>
К	-2.94	n.a.	K <sub>3</sub> N	n.a.
Rb	-2.94	n.a.	n.a.	n.a.
Cs	-3.03	n.a.	n.a.	n.a.
Ве	-1.97	-533.0	Be <sub>3</sub> N <sub>2</sub>	No
Mg	-2.36	-401.2	Mg <sub>3</sub> N <sub>2</sub>	Yes
Ca	-2.87	-410.0	Ca <sub>3</sub> N <sub>2</sub> (Ca <sub>2</sub> N, CaN <sub>2</sub> )	Yes
Sr	-2.90	-322.2	"Sr <sub>3</sub> N <sub>2</sub> " (Sr <sub>2</sub> N, SrN, SrN <sub>2</sub> )	n.a.
Ва	-2.91	-305.4	"Ba <sub>3</sub> N <sub>2</sub> " (Ba <sub>2</sub> N, BaN <sub>2</sub> )	n.a.

Table S1. Properties of alkali and alkaline-earth metal nitrides.

<sup>a</sup> Standard potential for the M<sup>*n*+/0</sup> process against standard hydrogen electrode;<sup>1</sup> note that this potential is different from a thermodynamically predicted potential for a (6/*n*)M<sup>*n*+</sup> + 6e<sup>-</sup> + N<sub>2</sub>  $\rightleftharpoons$  2M<sub>3/*n*</sub>N half-reaction. <sup>b</sup> Standard free energy of the formation of alkali (M<sub>3</sub>N) and alkali earth (M<sub>3</sub>N<sub>2</sub>) stoichiometric ionic nitrides.<sup>3-5</sup> <sup>c</sup> Experimentally reported metal-nitrogen compounds (subnitrides, nitride-diazenides, and diazenides are in parenthesis).<sup>2, 6-12</sup> <sup>d</sup> Reactivity of stoichiometric M<sub>3</sub>N or M<sub>3</sub>N<sub>2</sub> nitrides at room temperature to water.<sup>7, 13</sup> <sup>e</sup> Not available/applicable.

Among alkaline-earth metals,  $Ca^{0/2+}$ ,  $Sr^{0/2+}$  and  $Ba^{0/2+}$  are unlikely to be highly promising mediators due to the very negative potentials required for their reduction (Table S1). Besides, these metals tend to form not only stoichiometric salt-like nitrides  $M_3N_2$ , but also subnitrides, nitride-diazenides and diazenides, with the tendency to form diazenide increasing in the sequence  $Ca < Sr < Ba.^8$ Nevertheless, a recent demonstration of the possibility of the  $Ca^{0/2+}$ -mediated NRR by Chorkendorff and colleagues presents a significant fundamental contribution to the field.<sup>14</sup> The existence of "Sr<sub>3</sub>N<sub>2</sub>" and "Ba<sub>3</sub>N<sub>2</sub>" was questioned recently due to the lack of reliable data;<sup>10</sup> crystallographically confirmed phases are Sr<sub>2</sub>N, SrN, SrN<sub>2</sub>, Ba<sub>2</sub>N, BaN<sub>2</sub>.<sup>9-11</sup> From the perspective of energy efficiency, Be<sup>0/2+</sup> mediator with the least negative  $E^0$  of -1.97 V vs. SHE among examined candidates is clearly the most appealing. However, Be<sub>3</sub>N<sub>2</sub> has been reported to undergo very slow protonation with the release of ammonia in contact with boiling acids only.<sup>13</sup> Strong toxicity of beryllium compounds is also a significant concern. Thus, an arguably most promising redox mediator alternative to lithium is  $Mg^{0/2+}$ . Magnesium is a highly abundant and non-toxic element,<sup>15</sup> and is well known to form a stoichiometric  $Mg_3N_2$  nitride, which is sensitive to moisture, hydrolyses quickly in water, and decomposes rapidly in air to  $NH_3$  and  $Mg(OH)_2$ .<sup>7, 13</sup> Recognising these advantageous properties, Jin and co-workers have recently described a high-temperature process for the electrosynthesis of  $NH_3$  from  $N_2$  based on three consecutive separated reaction steps: (1) electroplating  $Mg^0$  from a molten mixture of  $MgCl_2$ -NaCl-KCl at 700 °C and *ca* 2.6 V, (2) reacting  $Mg^0$  with  $N_2$  at 700 °C to produce  $Mg_3N_2$ , and (3) reacting  $Mg_3N_2$  with  $NH_4Cl$  to produce  $NH_3$  and recover  $Mg^{2+}$  at 500 °C.<sup>16</sup> The approach is conceptually similar to the one previously reported for a  $Li^{0/+}$ -based cycle,<sup>3</sup> but requires lower voltage of the electrolysis cell as expected based on the differences in the standard potentials of the two mediators.

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# **EXPERIMENTAL**

### Materials

1,2-Dimethoxyethane (glyme; DME) (anhydrous, 99.5%), lithium borohydride (≥90%), magnesium ribbon (≥99.5%), salicylic acid (99.0%), sodium nitroprusside (99%), maleic acid (>99%), ammonium chloride (99.5%), sodium hypochlorite aqueous solution (5.3 wt.% solution) and zeolite beads (1.5–2.5 mm beads with an average pore size of 0.3 nm average pore size) were obtained from Sigma-Aldrich. Sodium hydroxide (analytical grade) and tri-sodium citrate dihydrate (analytical grade) were purchased from Merck. Sulfuric acid (99.8%) was purchased from Univar. Magnesium(II) bis-(trifluoromethylsulfonyl)imide (Mg(NTf<sub>2</sub>)<sub>2</sub> also known as Mg(TFSI)<sub>2</sub>; 99.5%) was purchased from Solvionic. Concentrated aqueous HCI solution (32 wt.%) was obtained from Ajax Finechem. Copper wires (99.8%, Ø 1.6 and 1.25 mm) were purchased from Fisher Scientific. Dimethyl sulfoxide-d6 (DMSO-d6; D, 99.9%; chemical purity 99.5%) was obtained from Cambridge Isotope Laboratories Inc. All starting non-aqueous reagents and solutions were stored and handled in a glovebox (KOREA KIYON glovebox system) under high-purity argon atmosphere (99.997%, O<sub>2</sub> < 1 ppm, H<sub>2</sub>O < 1 ppm; sourced from BOC). High-purity deionised water with a measured resistivity of 18.2 MΩ cm at 24 ± 1 °C derived from a Sartorius Arium Comfort I purification system equipped with a SARTOPORE 2 150 filter was used for all procedures requiring water.

DME was dried over cleaned (washed several times with water and acetone) and dried (48 h at 300 °C in air) zeolite inside the Ar-filled glovebox. The water concentration in the dried DME was measured by the Karl–Fischer method to be less than 0.3 mM. Mg(NTf<sub>2</sub>)<sub>2</sub> was dried under vacuum at 80 °C for 48 h prior to introduction into the glovebox, while LiBH<sub>4</sub> was used as received.

### **Electrochemical experiments**

BioLogic VMP electrochemical workstation operated in a three-electrode mode was used for all experiments. Working electrode was either a custom-made copper metal disk ( $\emptyset$  0.16 cm; geometric surface area *ca* 0.02 cm<sup>2</sup>) embedded in a polyether ether ketone (PEEK) sheath or a copper wire (geometric surface area *ca* 0.18 cm<sup>2</sup>). The Cu disk working electrode was polished using a polishing emery paper and an aqueous slurry of 0.3 µm Al<sub>2</sub>O<sub>3</sub> powder; the surface of the electrode was further cleaned by rinsing with water and acetone, wiped over the clean polishing emery paper, washed again with acetone, and finally dried in a vacuum oven at 60 °C. The Cu wire electrode was pre-treated by oxidative electropolishing in concentrated orthophosphoric acid solution (at 4 A current for 2 min) using the setup and following the procedure described in the literature [S. Johnston, L. Kemp, B. Turay, A. N. Simonov, B. H. R. Suryanto and D. R. MacFarlane, *ChemSusChem*, 2021, **14**, 4793]. After pre-treatment, the electrode was rinsed with water, washed with ethanol, and dried in a vacuum oven at 60 °C before it was introduced into the glovebox. A Pt wire counter and a Mg ribbon (*ca* 70 mm × 3.4 mm × 0.2 mm) were used as auxiliary and reference electrodes, respectively. The magnesium ribbon was scraped with a scalpel to clean the surface and obtain a fresh electrode surface prior to each experiment.

High-pressure electrochemical cell with a polyether ether ketone (PEEK) body (Figure S1a) was used for the experiments, which were run under static atmosphere of either 1 bar Ar + 14 or 15 bar N<sub>2</sub> (for the N<sub>2</sub> reduction tests), 1 bar Ar + 15 bar of the [<sup>14</sup>N<sub>2</sub> + <sup>15</sup>N<sub>2</sub>] mixture with <sup>14</sup>N<sub>2</sub> : <sup>15</sup>N<sub>2</sub> = 5.6 : 1 or 2.9 : 1 (for the <sup>15</sup>N<sub>2</sub> controls), or 1 bar Ar (for blank experiments). The cell was assembled and loaded with the electrolyte solution inside the glove box under Ar atmosphere, hermetically sealed, and transferred outside to be filled with N<sub>2</sub> as required. To avoid air penetration, the gas lines were filled with nitrogen gas before filling the cell using a two-valve system (Figure S1b).



### Figure S1. Experimental setup.

(a-b) Photographs of the (a) pressurised electrochemical cell, and (b) gas-purging line used for filling the cell with  $N_2$ . (c) Evolution of temperature within the electrolyte solution inside a fully-assembled cell during heating.

Electrolyte solutions were prepared inside the argon-filled glove box. For each experiment, 2 mL of the DME electrolyte solution containing the required concentrations of Mg(NTf<sub>2</sub>)<sub>2</sub> (0.1–0.4 M) and LiBH<sub>4</sub> (0.2–0.8 M) were prepared in a 20 mL scintillation vial and transferred into the cell. During electrochemical experiments the electrolyte solution was not stirred due to its small volume. The cell was heated using a heating belt and the temperature was measured in the headspace inside of the cell directly above the electrolyte solution. Prior to commencing the experiments, the fully assembled cell was pre-heated for 10 minutes (all data for 14 bar <sup>14</sup>N<sub>2</sub> and a test at a decreased distance between the working and auxiliary electrodes at 15 bar <sup>14</sup>N<sub>2</sub>) or 120 minutes (<sup>14</sup>N<sub>2</sub> + <sup>15</sup>N<sub>2</sub> experiments, and experiment at 15 bar <sup>14</sup>N<sub>2</sub> where electrodes were not positioned very close to each other). The temperature was found to stabilise at 33 ± 1, 46 ± 1 and 60 ± 1 °C after *ca* 60-90 minutes under the conditions employed (Figure S1c), but the key experiments undertaken at 33 ± 1 °C after pre-heating for 10 and 120 minutes produced similar results. All potentials reported herein are raw values measured against the magnesium ribbon reference electrode, which was assumed to correspond to the Mg<sup>0/2+</sup> redox process under the conditions employed. All currents reported herein are normalised to the geometric surface area of the working electrode.

### Spectrophotometric quantification of ammonium

The modified Berthelot spectrophotometric test and the method of standard additions were used for routine quantification of ammonium after dissolving the electrochemically generated solids in 2, 4, or 6 mL (depending on the amount of solid) of aqueous 0.1 M HCl under ambient conditions over 20 min. In a typical procedure, five 0.200 mL aliquots were withdrawn from each of the freshly prepared analyte solutions, added to 2 mL Axygen boil-proof microtubes and mixed with different known amounts of the 0.132 mM NH<sub>4</sub>Cl aqueous solution and water (total 0.200 mL). Next, 0.400 mL solution containing 5 wt.% salicylic acid and 5 wt.% trisodium citrate in 1 M NaOH, 0.100 mL of 0.05 M NaClO<sub>(aq.)</sub> and 0.030 mL of 1 wt.% sodium nitroferricyanide in water were added. The resulting mixtures were incubated in the dark for 1 h at ambient temperature ( $22 \pm 2$  °C). Absorption spectra of derivatised solutions were recorded in the 500–1000 nm range using polystyrene/polystyrene 10 mm cuvettes (Sarstedt) and a Cary UV–vis spectrophotometer. A typical analysis procedure is exemplified in Figure S2.





Solution for analysis was derived from adding 0.1 M  $HCl_{(aq.)}$  to an electrodeposit generated by the reduction of 0.2 M Mg(NTf<sub>2</sub>)<sub>2</sub> + 0.4 M LiBH<sub>4</sub> (DME) at -0.8 V vs. Mg<sup>2+/0</sup> and 33 ± 1 °C for 10 h. Plots show standard-additions dependence of the absorbance and absorption spectra (optical pathlength 1 cm); inset shows a photograph of the derivatised samples (*green*), and reference (*yellow*).

### <sup>1</sup>H NMR quantification of ammonium

For selected experiments, including those using <sup>15</sup>N<sub>2</sub>, ammonium was additionally quantified by <sup>1</sup>H NMR spectroscopy, following the procedure described by Hodgetts *et al.* [ACS Energy Lett., 2020, **5**, 736-741; doi: 10.1021/acsenergylett.9b02812].

For the experiments under 14 bar <sup>14</sup>N<sub>2</sub>, analysis was undertaken on the solutions derived from the dissolution of the electrochemically generated solids as described above for the Berthelot analysis. In this case, the <sup>1</sup>H NMR data were recorded on a Bruker Avance III 600 MHz (<sup>1</sup>H at 600.27 MHz) spectrometer at ambient temperature, using the lc1pncwps pulse sequence (504 scans, d1 = 1.5 s). For the experiments under 15 bar <sup>14</sup>N<sub>2</sub> and [<sup>14</sup>N<sub>2</sub> + <sup>15</sup>N<sub>2</sub>], 8-9 mL 0.1 M HCl was added directly to the cell to ensure that all solid species, even the most highly-dispersed, are dissolved. Further, 0.125 mL aliquot of the acidified solution was mixed with 0.050 mL of 4 M H<sub>2</sub>SO<sub>4</sub> in DMSO-d6, 0.125 mL of

0.050 or 0.500 mM maleic acid in DMSO-d6, 0.010 mL of water, and 0.740 mL of DMSO-d6 (the total volume of the mixture was 1.050 mL). For these samples, the data were collected on a Bruker Avance III 400 MHz NanoBay instrument, using a pulse sequence noesygppr1d (256 scans, d1 = 2 s). These data are easily recognised as the distinctive *J* coupling for the ammonium signal is 1.5 times broader (0.135 and 0.18 ppm for the <sup>14</sup>NH<sub>4</sub> triplet and <sup>15</sup>N<sub>2</sub> doublet, respectively) as compared to those obtained with a 600 MHz spectrometer.

For quantitative analysis, integrals of the ammonium signals ( $I_{1^4NH_4^+}$  or  $I_{1^5NH_4^+}$ ) were normalised to those of the maleic acid internal standard ( $I_{MA}$ ).

For the 600 MHz data, the calibration dependence was

 $c_{{}^{14}\mathrm{NH}_4{}^+} = (2.19 \pm 0.03) (I_{{}^{14}\mathrm{NH}_4{}^+} / I_{\mathrm{MA}}) - (0.08 \pm 0.14).$ 

For the 400 MHz data, the calibration dependencies were

 $c_{^{14}\mathrm{NH_4^+}} =$  (11.12  $\pm$  0.02) ( $I_{^{14}\mathrm{NH_4^+}}$  /  $I_\mathrm{MA})$  – (1.0  $\pm$  0.8), and

 $c_{15}_{NH_4^+} = (11.84 \pm 0.02) (I_{15}_{NH_4^+} / I_{MA}) - (7.9 \pm 0.2).$ 

Examples of the <sup>1</sup>H NMR analysis of experiments under 14 bar <sup>14</sup>N<sub>2</sub> are shown in Figure S3, while the data for  $[^{14}N_2 + {}^{15}N_2]$  are provided in Figure 4a in the main text.





(a) Calibration plot for the determination of  $[NH_4^+]$  in samples by <sup>1</sup>H NMR spectroscopy based on the NH<sub>4</sub><sup>+</sup> signal normalised to that of the maleic acid internal standard. (b) <sup>1</sup>H NMR spectra for the analysis of ammonium in solutions derived from dissolving electrodeposits generated by chronoamperometric reduction of 0.2 M Mg(NTf<sub>2</sub>)<sub>2</sub> + 0.4 M LiBH<sub>4</sub> (DME) solutions with 0.1 M HCl<sub>(aq.)</sub>; the data are shown for a control experiment under argon (0.3 µmol NH<sub>4</sub><sup>+</sup>; *red*) and the experiments undertaken with 14 bar N<sub>2</sub> producing low (1.7 µmol NH<sub>4</sub><sup>+</sup>; *light blue*) and the highest (17 µmol NH<sub>4</sub><sup>+</sup>; *blue*) ammonium yields. Corresponding experimental data are provided in Table S2.

### **Physical Characterisation**

**X-ray Diffraction (XRD)** measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu K<sub> $\alpha$ </sub> radiation (1.5406 Å) operated at 40 mA and 40 kV. Deposit from the bottom of the electrolytic cell was decanted in the glove box and, without washing, placed on a XRD sample holder for analysis. The sample contacted air during transfer to the diffractometer and during the analysis.

**X-ray photoelectron spectroscopic (XPS)** analysis was undertaken using a Thermo Scientific Nexsa Surface Analysis System equipped with a hemispherical analyser and an X-ray source providing a monochromatic Al K<sub> $\alpha$ </sub> X-ray (1486.6 eV) incident radiation (72 W, 6 mA, 12 kV; 400  $\mu$ m × 250  $\mu$ m spot). The pressure in the analysis chamber was below 5.0 × 10<sup>-9</sup> mbar. Survey and high-resolution spectra were recorded at analyser pass energies of 150 and 50 eV and step sizes of 1.0 and 0.1 eV, respectively. Surface charging was compensated using a low-energy dual-beam (ion and electron) flood gun. Avantage software (version 5.9921) was used for data processing, and the binding energy scale was referenced to the aliphatic C 1s signal of carbon at 284.8 eV. Prior to XPS measurements samples (the electrode with deposit and the material deposited at the bottom of the electrolytic cell) were washed with small amount of DME and were mounted into a vacuum transfer module inside the glove-box before being transferred to the XPS instrument, avoiding any explosion to air.

The key reference materials for the XPS analysis were the magnesium and lithium salts constituting the electrolyte solution, which spectra were recorded using a Cu wire that was kept in contact with an Ar-saturated 0.2 M  $Mg(NTf_2)_2 + 0.4 M LiBH_4$  (DME) solution for 10 hours and then dried under vacuum without preliminary washing.

**Scanning electron microscopic (SEM)** data were recorded using a FEI Nova NanoSEM 450 with a field emission gun at an accelerating voltage of 5 kV for EDS analysis and using spot size 2.0. Samples for the analysis were prepared by electroreduction of N<sub>2</sub>-saturated (14 bar) 0.4 M Mg(NTf<sub>2</sub>)<sub>2</sub> + 0.8 M LiBH<sub>4</sub> (DME) solutions using a Cu wire electrode with an active geometric surface area of

+ 0.8 M LiBH<sub>4</sub> (DME) solutions using a Cu wire electrode with an active geometric surface area of *ca* 0.05 cm<sup>2</sup> at 33 ± 1 °C. The chronoamperometry was run for 0.5 h, which enabled a significant increase in the current density up to *ca* 0.64 A cm<sup>-2</sup> and corresponding to *ca* 31 C of the reductive charge (*ca* 20% Mg<sup>2+</sup> reduction), but was before the peak current density was achieved at -0.8 V vs. Mg<sup>0/2+</sup>. This was done to visualise the morphology of the deposit in its hypothesised active state. For consistency, the same duration of the experiment was used for -0.3 V vs. Mg<sup>0/2+</sup> (*ca* 16 C reductive charge passed). After electroreduction, the electrodes were intensively washed with DME to remove the majority of the electrolyte salts, which resulted in partial detachment of the fragile, high-surface area dendrites from the sample obtained at -0.8 V vs. Mg<sup>0/2+</sup>, and little loss of the material prepared at -0.3 V vs. Mg<sup>0/2+</sup>. This observation provides additional evidence for the significantly more compact morphology, and hence lower surface area, of the deposits produced at lower Mg<sup>0/2+</sup> overpotential. After washing, the samples were sealed in a hermetically sealed Ar-filled vessel (2 mL total volume), into which *ca* 0.3 mL of air was slowly injected to passivate the Mg<sup>0</sup> surface and avoid its vigorous oxidation when exposed to air. Finally, the electrodes were mounted onto SEM stubs using a double-sided carbon sticky tape, removed from the glove-box and transferred to the microscope.

# SUMMARY OF EXPERIMENTAL DATA

[Mg(NTf <sub>2</sub> ) <sub>2</sub> ] / M	<i>T /</i> ℃	<i>P</i> <sub>N2</sub> / bar	-Q / C <sup>b</sup>	Mg <sup>2+</sup> reduced / % <sup>c</sup>	NH₄⁺ yield / µmol	FE / % <sup>d</sup>	Yield rate / nmol s <sup>-1</sup> cm <sup>-2</sup>
0.1	33 ± 1	14	38	98	1.0	0.8	0.9
			36	93	0.9	0.8	0.8
			33	86	4.5	4.0	3.8
			32	83	1.5	1.4	1.3
			44	110	12	8.0	10
0.2	33 ± 1	14	63	82	1.7	0.8	1.9
			71	92	1.3	0.6	1.9
			66	85	2.0	0.9	2.8
			56	73	1.2	0.6	1.7
			63	82	2.7	1.3	3.8
			78 <sup>e</sup>	100	7.2	2.7	5.0
			91	120	17	5.5	24
		0	74	96	0.3	0.1	0.5
			61	79	0.2	0.1	0.3
			53	69	0.2	0.1	0.3
	46 ± 1	14	58	75	2.0	1.0	2.7
	60 ± 1	14	40	52	2.2	1.6	3.0
0.3	33 ± 1	14	126	110	2.4	0.6	3.3
			106	92	4.6	1.2	6.3
			143	120	4.0	0.8	5.6
			89	77	4.3	1.4	5.9
0.4	33 ± 1	£1 14	170 <sup>e</sup>	110	9.1	1.6	6.3
			184	120	4.8	0.8	6.6
			152	98	9.2	1.7	13
			238	150	13	1.6	18
			140	91	9.5	2.0	13
			198	130	48	7.0	66
			846 <sup>f</sup>	111	48	1.7	33
		15	168	109	5.2	0.9	7.2
			286 <sup>g</sup>	185	22	2.3	31
			159 <sup>g,h</sup>	103	11 (5.7 : 1)	2.0	15
			582 <sup>g,i</sup>	377	93 (2.7 : 1)	4.6	129

### Table S2. Performance of Mg<sup>0/2+</sup>-mediated N<sub>2</sub> reduction under different conditions.<sup>a</sup>

<sup>a</sup> Reduction was undertaken using a Cu disc electrode in N<sub>2</sub>- or Ar-saturated 2 mL DME solutions containing Mg(NTf<sub>2</sub>)<sub>2</sub> at defined concentration and twice higher concentration of LiBH<sub>4</sub> at -0.8 V vs. Mg<sup>0/2+</sup> for 16.5 (0.1 M Mg(NTf<sub>2</sub>)<sub>2</sub>) or 10 h (all other concentrations, unless stated otherwise); chronoamperograms are shown in Figures S10-S12. NH<sub>4</sub><sup>+</sup> was obtained by reacting electrochemically produced solids with aqueous 0.1 M HCl under ambient conditions over 20 min. <sup>b</sup> Charge passed during the electroreduction stage. <sup>c</sup> Coulombic efficiency of Mg<sup>2+</sup> reduction to Mg<sup>0</sup> calculated as Q [C] / (2 × 96485.3 [C mol<sup>-1</sup>] × N<sub>Mg<sup>2+</sup></sub> [mol]), where N<sub>Mg<sup>2+</sup></sub> is the amount of Mg<sup>2+</sup> introduced into the electrolyte solution. <sup>d</sup> Faradaic efficiency of the N<sub>2</sub> to ammonium conversion calculated using the charge passed and amount of NH<sub>4</sub><sup>+</sup> produced; Ar control experiments are highlighted in green. <sup>e</sup> Experiments were conducted for 20 h. <sup>f</sup> Experiment was conducted for 20 h using 10 mL of the electrolyte solution. <sup>g</sup> Experiments were undertaken at a decreased distance between the working and auxiliary electrodes. <sup>h-i</sup> Experiments used <sup>14</sup>N<sub>2</sub> + <sup>15</sup>N<sub>2</sub> gas mixtures with ratios of 5.6 : 1<sup>h</sup> or 2.9 : 1<sup>i</sup>; values in brackets in the "NH<sub>4</sub><sup>+</sup> yield" column show the <sup>14</sup>NH<sub>4</sub><sup>+</sup> : <sup>15</sup>NH<sub>4</sub><sup>+</sup> ratios.

# **EXTENDED DATA**



Figure S4. Voltammetry under N<sub>2</sub> and Ar.

Cyclic voltammograms (1<sup>st</sup> cycles, scan rate v = 0.020 V s<sup>-1</sup>) of a Cu disk electrode (0.02 cm<sup>2</sup>) in contact with a 0.2 M Mg(NTf<sub>2</sub>)<sub>2</sub> + 0.4 M LiBH<sub>4</sub> (DME) solution under 1 bar Ar (*red*) and 1 bar Ar + 14 bar N<sub>2</sub> (*blue*) at 33 ± 1 °C. Dashed line shows j = 0 mA cm<sup>-2</sup>. Currents are normalised to the geometric surface area of the electrode.





Current density transient recorded during electroreduction of 0.4 M LiBH<sub>4</sub> (DME) solution under 14 bar N<sub>2</sub> + 1 bar Ar using a Cu disc electrode (0.02 cm<sup>2</sup>) at -0.8 V vs. Mg<sup>0/2+</sup> and 33 ± 1 °C. Dashed line shows j = 0 mA cm<sup>-2</sup>. Currents are normalised to the geometric surface area of the electrode.





Current density transients recorded during electroreduction of 0.2 M Mg(NTf<sub>2</sub>)<sub>2</sub> + 0.4 M LiBH<sub>4</sub> (DME) solutions under 1 bar Ar (*red*) and 14 bar N<sub>2</sub> + 1 bar Ar (*blue*) using a Cu disc electrode (0.02 cm<sup>-2</sup>) at -0.8 V vs. Mg<sup>0/2+</sup> and 33 ± 1 °C. Dashed line shows j = 0 A cm<sup>-2</sup>. Currents are normalised to the geometric surface area of the electrode.



### Figure S7. Effects of potential on potentiostatic Mg<sup>2+</sup> reduction under N<sub>2</sub>.

Current density transients recorded during electroreduction of 0.2 M Mg(NTf<sub>2</sub>)<sub>2</sub> + 0.4 M LiBH<sub>4</sub> (DME) solutions under 14 bar N<sub>2</sub> + 1 bar Ar using a Cu disc electrode (0.02 cm<sup>2</sup>) at 33 ± 1 °C and at -0.8 (*blue*),-0.5 (*teal*) and -0.3 V vs. Mg<sup>0/2+</sup> (*orange*). Dashed line shows j = 0 A cm<sup>-2</sup>. Currents are normalised to the geometric surface area of the electrode. Table shows corresponding performance metrics (as defined in Table S2).





Data were collected for the Cu wire (0.05 cm<sup>2</sup>) electrodes after 0.5 h of electroreduction at (a) -0.3 and (b) -0.8 V vs.  $Mg^{0/2+}$  of a N<sub>2</sub>-saturated (14 bar) 0.4 M  $Mg(NTf_2)_2$  + 0.8 M LiBH<sub>4</sub> (DME) solution. Prior to analysis, the electrodes were intensively washed with DME to remove the electrolyte salts from the surface.



# Figure S9. XPS of the deposit produced by long-term electroreduction of Mg<sup>2+</sup> under N<sub>2</sub>.

Data were collected for a deposit detached from the Cu disk (0.02 cm<sup>2</sup>) electrode surface after reduction of N<sub>2</sub>-saturated (14 bar) 0.2 M Mg(NTf<sub>2</sub>)<sub>2</sub> + 0.4 M LiBH<sub>4</sub> (DME) solution at -0.8 V vs. Mg<sup>0/2+</sup> for 10 h (*blue*) at 33 ± 1 °C. Prior to analysis the sample was washed with DME. Reference data for Mg(NTf<sub>2</sub>)<sub>2</sub> + LiBH<sub>4</sub> electrolyte dried on a Cu wire surface are shown as *black* curves.



Figure S10. XPS of the deposit produced by voltammetric reduction of  $Mg^{2+}$  under  $N_2$ .

Data were collected for a Cu wire electrode (0.18 cm<sup>2</sup>) after recording 10 voltammetric cycles (0.020 V s<sup>-1</sup>; as in Figure S4) stopping at -0.8 V vs. Mg<sup>0/2+</sup> and resting for 10 h in N<sub>2</sub>-saturated (14 bar) 0.2 M Mg(NTf<sub>2</sub>)<sub>2</sub> + 0.4 M LiBH<sub>4</sub> (DME) solution at 33 ± 1 °C. The electrode was washed with DME (*purple*), and then additionally etched by argon ion beam for 30 min (*blue*). Data reported previously [*ACS Appl. Mat. Int.* 2022, 14, 34552-34561; doi: 10.1021/acsami.2c04073] for a sample electrodeposited in the same manner but in the Ar-saturated (1 bar) solution at 23 ± 2 °C are shown as *red* curves. Reference data for Mg(NTf<sub>2</sub>)<sub>2</sub> and LiBH<sub>4</sub> dried on a Cu wire surface are shown as *black* curves.





Examples of current density transients recorded during reduction (-0.8 V vs. Mg<sup>0/2+</sup>) of DME solutions containing 0.4 Mg(NTf<sub>2</sub>)<sub>2</sub> + 0.8 LiBH<sub>4</sub> under 14 bar N<sub>2</sub> + 1 bar Ar using a Cu disc electrode (0.02 cm<sup>2</sup>) at 33 ± 1 (*blue*), 46 ± 1 (*teal*) and 60 ± 1 °C (*orange*). Dashed line shows j = 0 A cm<sup>-2</sup>. Currents are normalised to the geometric surface area of the electrode.

In principle, the lack of improvement in the performance with increasing the temperature from  $33 \pm 1$  to  $46 \pm 1$  and  $60 \pm 1$  °C (Table S2) correlates with the appearance of the chronoamperograms recorded under these conditions. Indeed, the data demonstrate commencement of the rapid Mg<sup>2+</sup> reduction peak at approximately the same time, although the magnitude is slightly lower at elevated temperatures. This suggests comparable time allowed for the electrodeposited Mg<sup>0</sup> to react with dissolved N<sub>2</sub>. It is also noted that significant pitting of the Cu electrode surface was observed after electroreduction at  $60 \pm 1$  °C, which precluded us from further exploration of the electroreduction at temperatures higher than  $33 \pm 1$  °C at this stage. Future work might explore the use of more robust electrode materials to achieve faster kinetics provided by higher temperatures.





Examples of current density transients recorded during reduction (-0.8 V vs. Mg<sup>0/2+</sup>) of DME solutions containing different concentrations of Mg(NTf<sub>2</sub>)<sub>2</sub> + LiBH<sub>4</sub> (1 : 2 mol.) under 14 bar N<sub>2</sub> + 1 bar Ar using a Cu disc electrode (0.02 cm<sup>2</sup>); data are shown for the experiments where visually complete detachment of the deposit from the electrode surface occurred and the highest NH<sub>4</sub><sup>+</sup> yields at each concentration were achieved, *viz.* 12, 17 and 48 µmol at [Mg<sup>2+</sup>] = 0.1 (*orange*), 0.2 (*teal*) and 0.4 M (*blue*), respectively. Corresponding experimental data are provided in Table S2. Dashed line shows j = 0 A cm<sup>-2</sup>. Currents are normalised to the geometric surface area of the electrode.



Figure S13A. Chronoamperograms (33 ± 1 °C, -0.8 V vs.  $Mg^{0/2+}$ ) for experiments in Table S2. Data are shown for the experiments using the DME solutions containing 0.1, 0.2 and 0.3 M Mg(NTf<sub>2</sub>)<sub>2</sub> along twice higher concentrations of LiBH<sub>4</sub> saturated with either 14 bar N<sub>2</sub> + 1 bar Ar or 1 bar Ar, except for the highest-performance tests shown in Figure S12. Currents are normalised to the geometric surface area of a Cu disk electrode (0.02 cm<sup>2</sup>).



**Figure S13B. Chronoamperograms (33 ± 1 °C, -0.8 V vs. Mg**<sup>0/2+</sup>) for experiments in Table S2. Data are shown for the experiments using the DME solutions containing 0.4 M Mg(NTf<sub>2</sub>)<sub>2</sub> + 0.8 M LiBH<sub>4</sub> saturated with either 14 bar N<sub>2</sub> + 1 bar Ar or 15 bar N<sub>2</sub> + 1 bar Ar, except for the high-performance test shown in Figure S12. Currents are normalised to the geometric surface area of a Cu disk electrode (0.02 cm<sup>2</sup>).



### Figure S14. Photographs of the electrode assemblies after the experiments.

Experiments were undertaken with the Pt wire auxiliary electrode positioned (a) further and (b) closer to the working electrode. In panel a, the electrodeposit essentially completely exfoliated from the electrode surface and was dispersed in the electrolyte solution. In panel b, part of the electrodeposit remained on the electrode surface and might have touched the Pt auxiliary electrode.