Supporting Information

Evaluating the Synthesis of $Mg[Al(hfip)_4]_2$ Electrolyte for Mg Rechargeable Batteries: Purity, Electrochemical Performance and Costs

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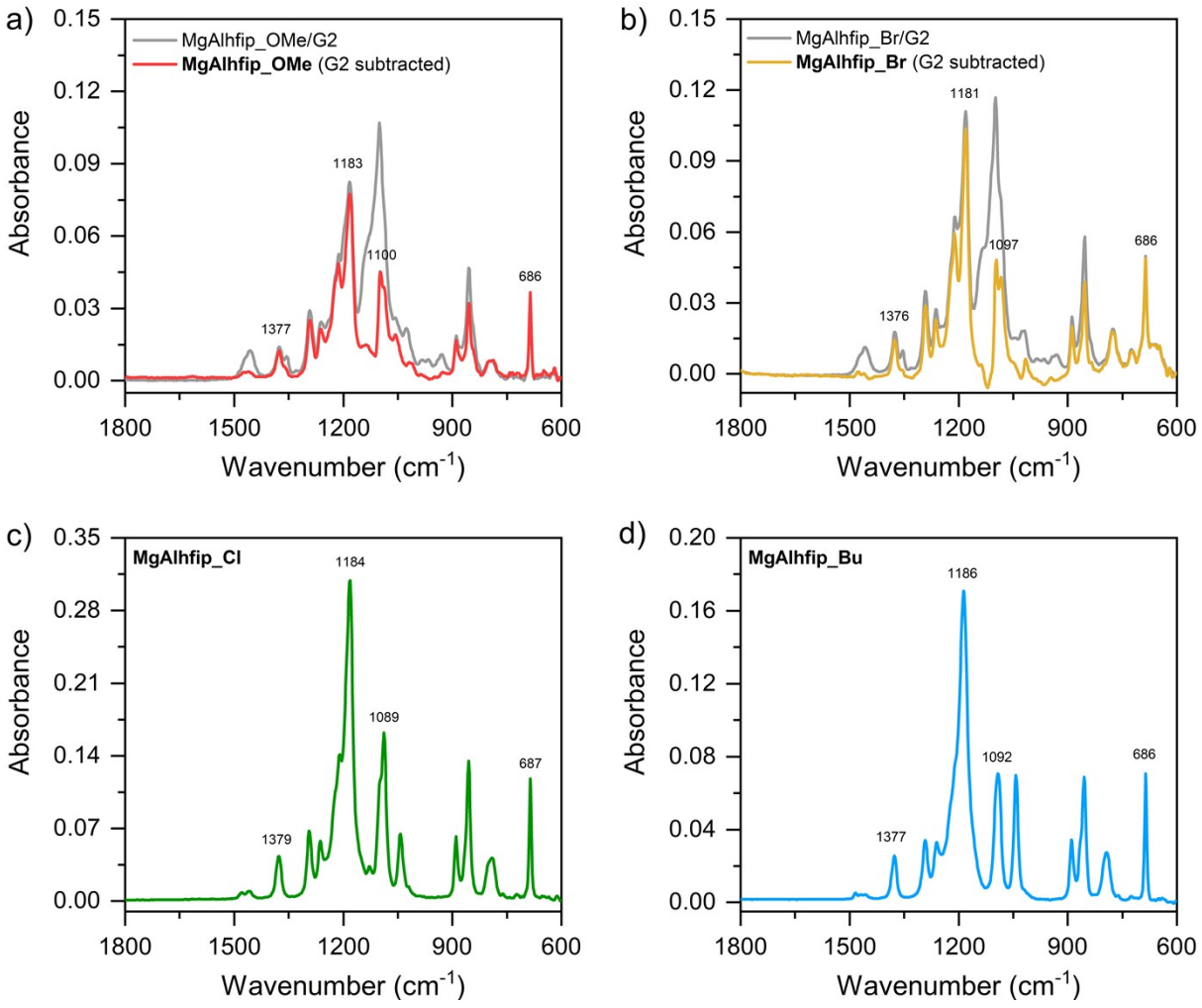

Figure S1: IR spectra of MgAlhfip salts synthesized by different procedures with marked characteristic peaks**.** Grey curves on **a)** and **b)** graphs represent spectra of MgAlhfip_OMe and MgAlhfip_Br *in situ* electrolytes in G2, from which solvent spectrum was subtracted, to extract the signals belonging to the MgAlhfip salts (red and yellow curve, respectively).

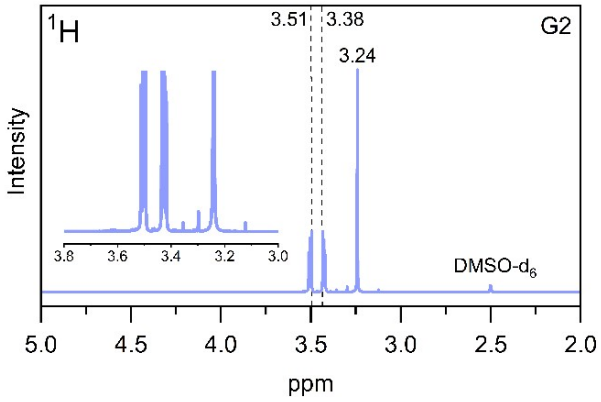

Figure S2: ^{1}H NMR of G2 solvent.

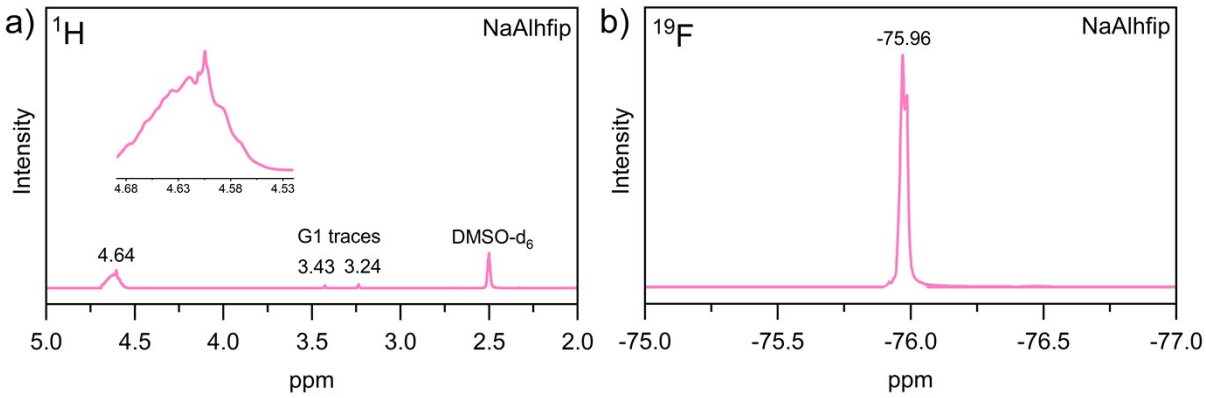

Figure S3: **a)** ^{1}H and **b)** ^{19}F NMR of NaAlhfip salt.

Table S1: ICP-OES analysis of MgAlhfip samples.

MgAlhfip product	Expected Mg [%]	Measured Mg* [%]	Expected Al [%]	Measured Al* [%]
MgAlhfip_OMe	1.443	1.444	3.203	3.012
MgAlhfip_Br		1.078		3.842
MgAlhfip_Cl		1.337		2.830
MgAlhfip_Bu		1.481		3.229

**The relative standard deviation for the presented results is within 2%.*

Table S2: Determination of impurities in MgAlhfip_Br and MgAlhfip_Cl with ICP-OES.

MgAlhfip product	Impurities		
	Na [%]	Cl [ppm]	Br [ppm]
MgAlhfip_Br	1.338	/	< 0.623
MgAlhfip_Cl	1.858	33.8	/

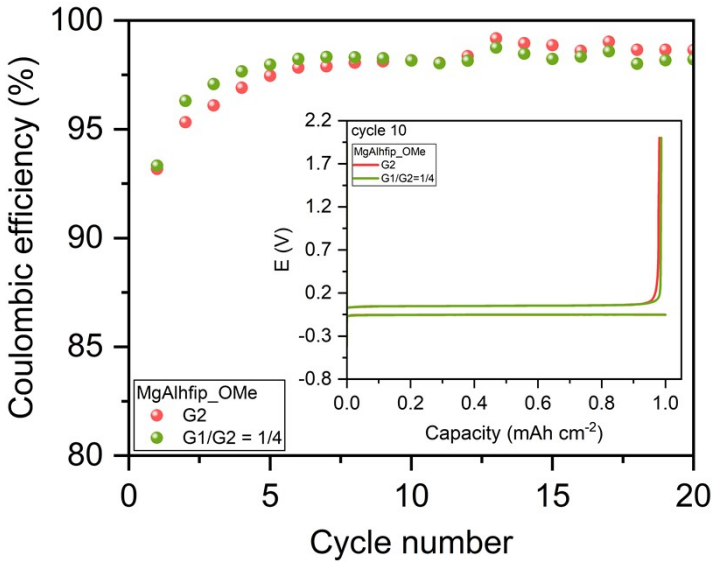

Figure S4: Coulombic efficiency of Mg plating/stripping in MgAlhfip_OMe electrolyte in G2 and in G1/G2 = 1/4 solvent mixture. Corresponding galvanostatic curves of the 10th cycle are shown as insets.

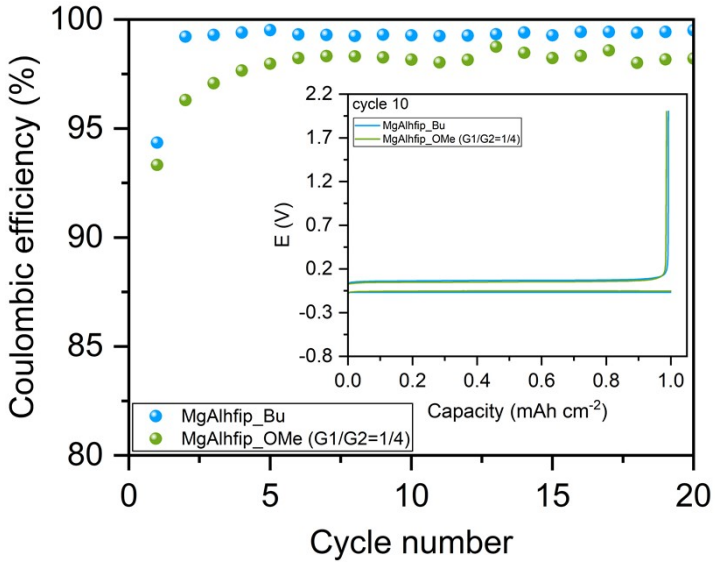

Figure S5: Coulombic efficiency of Mg plating/stripping in MgAlhfip_Bu and MgAlhfip_OMe electrolytes with a comparable solvent composition of G1/G2 = 1/4. Corresponding galvanostatic curves of the 10th cycle are shown as insets.

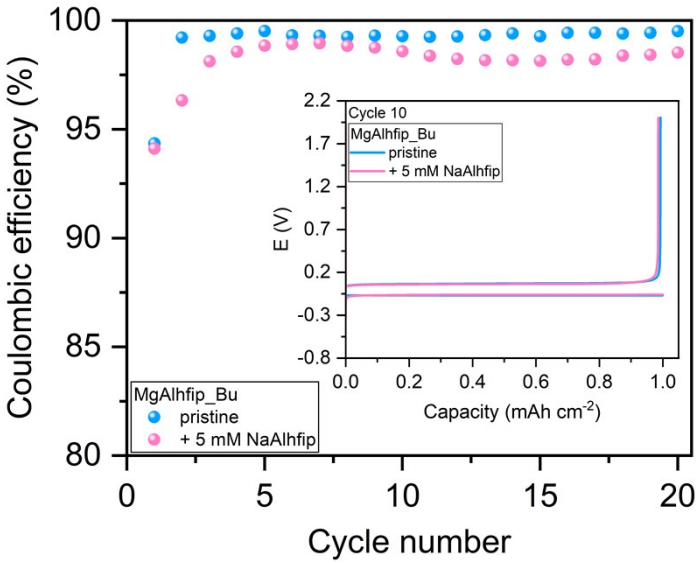

Figure S6: Coulombic efficiency of Mg plating/stripping in 0.4 M MgAlhfip_Bu electrolyte in G2 with and without the addition of NaAlhfip (5 mM). Corresponding galvanostatic curves of the 10th cycle are shown as insets.

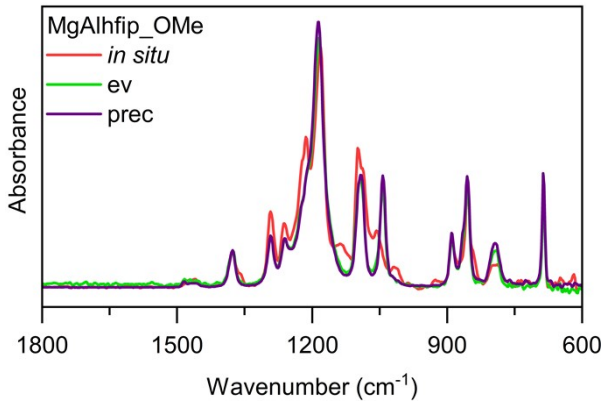

Figure S7: IR spectra of MgAlhfip_OMe salts of different purities.

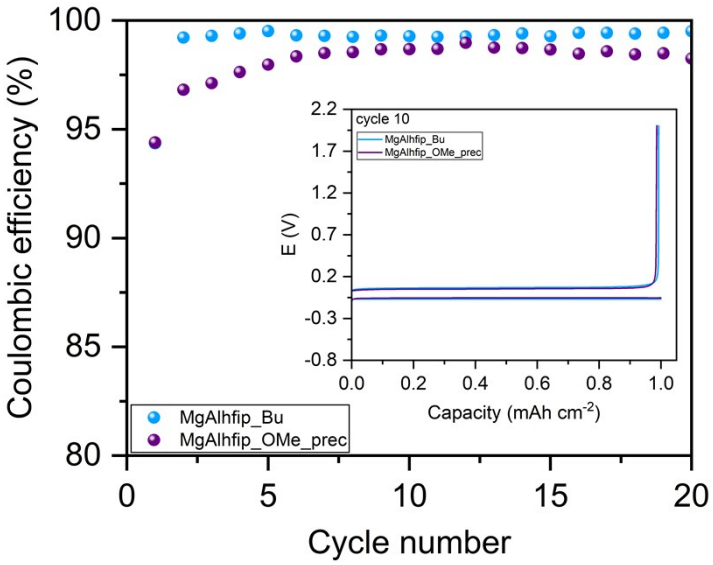

Figure S8: Coulombic efficiency of Mg plating/stripping in MgAlhfip_Bu and MgAlhfip_OMe_prec electrolytes. Corresponding galvanostatic curves of the 10th cycle are shown as insets.

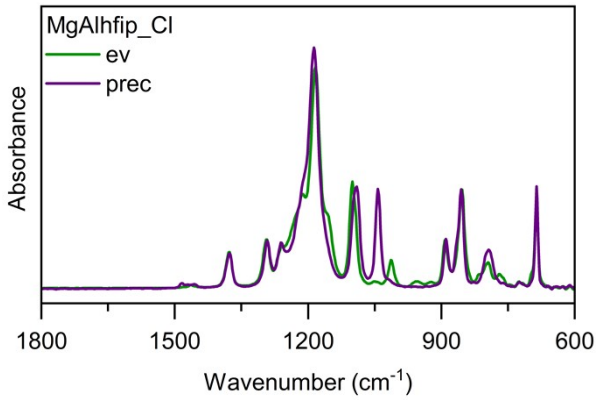

Figure S9: IR spectra of MgAlhfip_Cl salts of different purities.

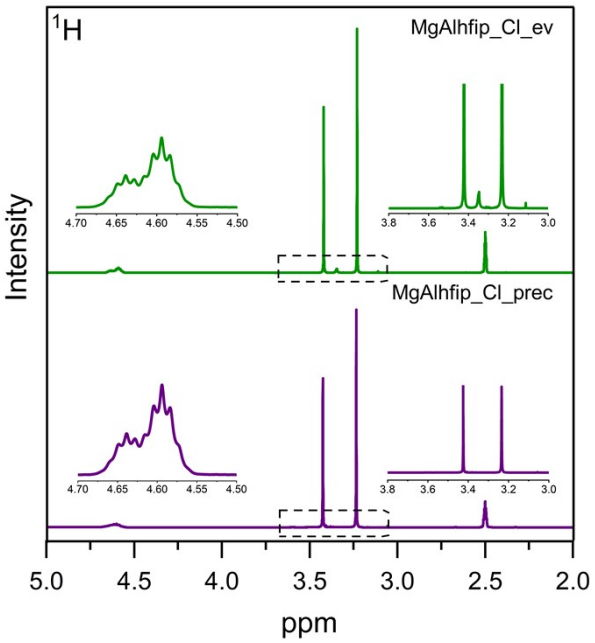

Figure S10: ^{1}H NMR spectra of MgAlhfip_Cl salts of different purities.

Table S3: ICP-OES analysis of MgAlhfip_Cl samples.

MgAlhfip product	Expected Mg [%]	Measured Mg [%]	Expected Al [%]	Measured Al [%]
MgAlhfip_Cl_ev	1.443	1.337	3.203	2.830
MgAlhfip_Cl_prec		1.439		3.095

**The relative standard deviation for the presented results is within 2%.*

Table S4: Determination of contaminants in different purities of MgAlhfip_Cl samples with ICP-OES analysis.

MgAlhfip product	Contaminants	
	Na [%]	Cl [ppm]
MgAlhfip_Cl_ev	1.858	33.8
MgAlhfip_Cl_prec	1.932	35.8

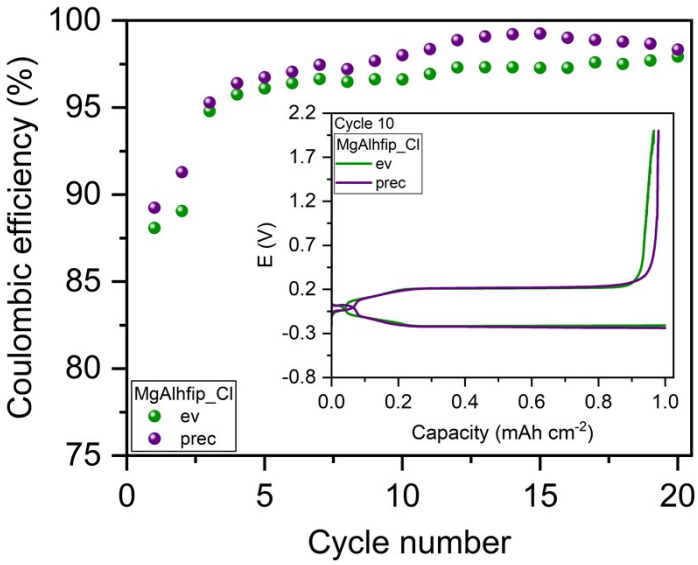

Figure S11: Coulombic efficiency of Mg plating/stripping in MgAlhfip_Cl electrolytes of different purities. Corresponding galvanostatic curves of the 10th cycle are shown as insets.

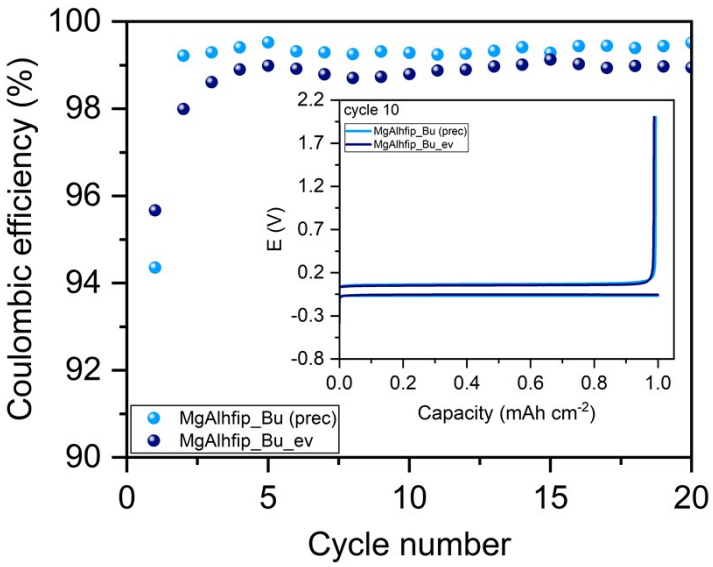

Figure S12: Coulombic efficiency of Mg plating/stripping in MgAlhfip_Bu electrolytes of different purities. Corresponding galvanostatic curves of the 10th cycle are shown as insets.

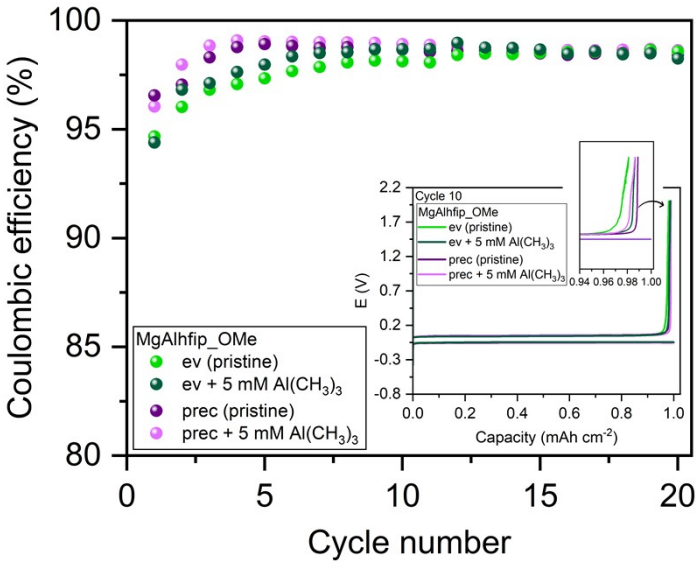

Figure S13: Coulombic efficiency of Mg plating/stripping in MgAlhfip_OMe electrolytes of different purities with and without the $Al(CH_3)_3$ additive. Corresponding galvanostatic curves of the 10th cycle are shown as insets.

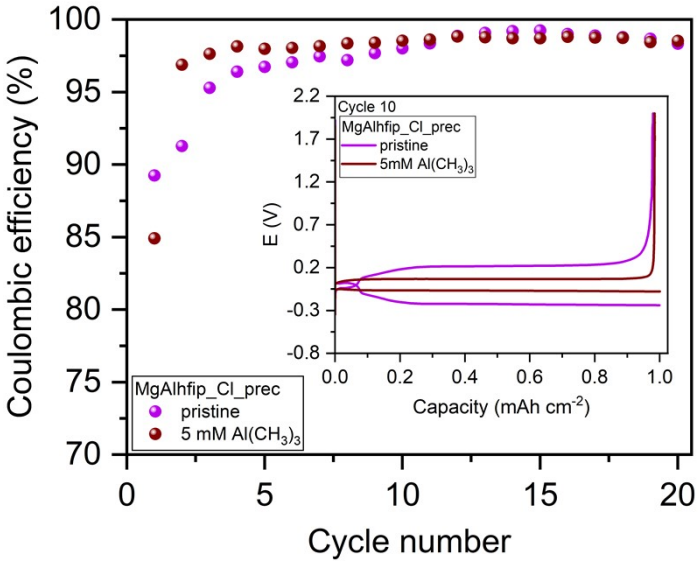

Figure S14: Coulombic efficiency of Mg plating/stripping in MgAlhfip_Cl_prec electrolyte with and without the $Al(CH_3)_3$ additive. Corresponding galvanostatic curves of the 10th cycle are shown as insets.

Table S5: Estimated time for each step of different synthesis procedures of MgAlhfip electrolytes. The overall time does not include time for drying solvents (5–7 days per solvent) and HFIP alcohol (4 days).

Electrolyte	Synthesis steps	Time [h]
MgAlhfip_OMe	Synthesis and drying of $Mg(hfip)_2$	48
	Synthesis and drying of $Al(hfip)_3$	24
	Formation of *in situ* electrolyte	96
	3	**168 (7 days)**
MgAlhfip_Br	$NaAlH_4$ purification	48
	Synthesis of $Na[Al(hfip)_4]$	48
	Formation of *in situ* electrolyte	24
	3	**120 (5 days)**
MgAlhfip_Cl	$NaAlH_4$ purification	48
	Synthesis of $Mg(AlH_4)_2$	24
	Synthesis of $Mg[Al(hfip)_4]_2$	
	Salt drying	48
	4	**120 (5 days)**
MgAlhfip_Bu	Synthesis of $Mg[Al(hfip)_4]_2$	24
	Salt drying	48
	2	**72 (3 days)**

Estimation of chemicals cost

Costs (**Figure S15**) are calculated based on the prices of the specific chemicals we used to perform the syntheses and prepare the electrolytes, listed in **Table S6**. Prices of the chemicals were collected from online catalogs of the selected suppliers in May 2023. Calculations refer to the preparation of 1 mL of 0.4 M MgAlhfip electrolytes in G2 solvent (0.4 mmol of salt) – the composition of electrolytes that was used to perform the electrochemical experiments within this work. Calculations consider the excess amounts of reactants utilized during the reactions, as well as the yield of each synthesis step.

Table S6: Specific reagents used in the experimental procedures, including purity, packaging, and supplier information.

Chemical	Purity	Packing	Supplier
6–10 % $Mg(OCH_3)_2$/methanol	-	500 mL	Sigma Aldrich
$MgBr_2$	98%	10 g	Sigma Aldrich
$MgCl_2$	99.9%, ultra-dry	25 g	Alfa Aesar
1.0 M *n*-Bu_2Mg/heptane	-	100 mL	Sigma Aldrich
$NaAlH_4$	97%	10 g	Sigma Aldrich
2.0 M $Al(CH_3)_3$/toluene	-	100 mL	Sigma Aldrich
HFIP	99%	1 kg	Fluorochem
THF	>99.9%, for HPLC	2.5 L	Honeywell
G1	99.9%, for HPLC	1 L	Sigma Aldrich
G2	99%	2.5 L	Acros Organics
hexane	>95%	2.5 L	Carl Roth

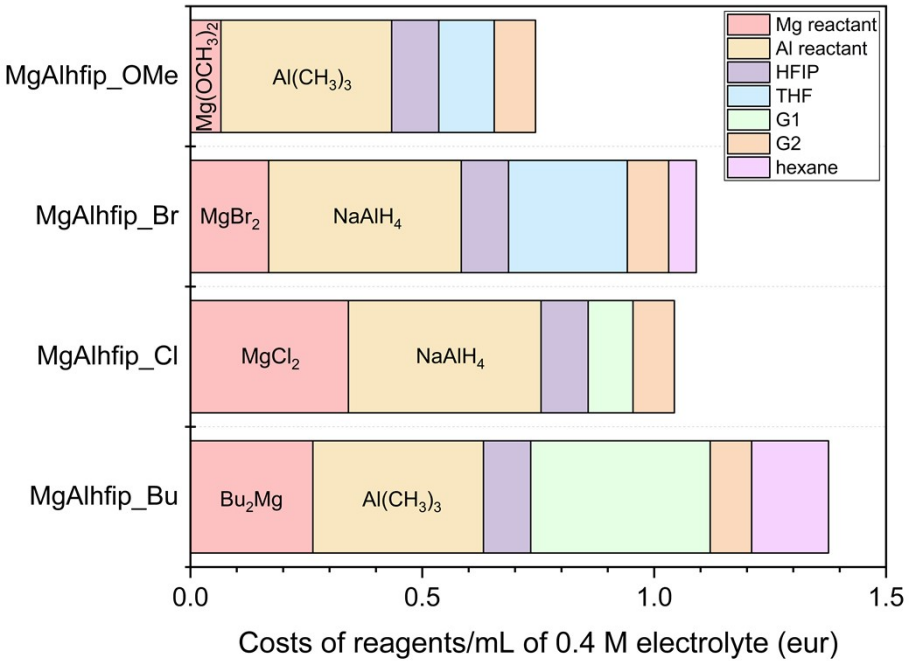

Figure S15: Chemicals cost estimation for different synthesis procedures of MgAlhfip electrolytes.

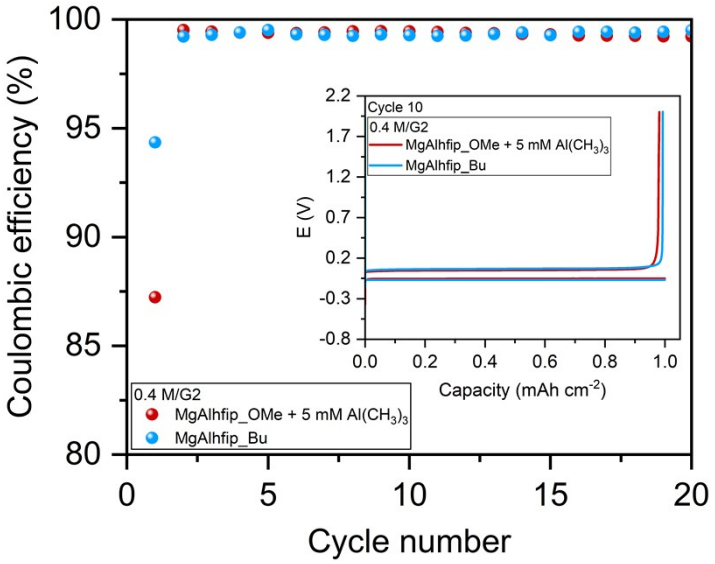

Figure S16: Comparison of electrochemical performance in MgAlhfip_OMe electrolyte with the addition of $Al(CH_3)_3$ and MgAlhfip_Bu electrolyte. Corresponding galvanostatic curves of the 10th cycle are shown as insets.

REFERENCES

1. Herb, J. T., Nist-Lund, C. A. & Arnold, C. B. A Fluorinated Alkoxyaluminate Electrolyte for Magnesium-Ion Batteries. *ACS Energy Lett.* **1**, 1227–1232 (2016).

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5. Mandai, T., Youn, Y. & Tateyama, Y. Remarkable electrochemical and ion-transport characteristics of magnesium-fluorinated alkoxyaluminate-diglyme electrolytes for magnesium batteries. *Mater. Adv.* **2**, 6283–6296 (2021).

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