Supporting Information

Highly Efficient Non-Nucleophilic $Mg(CF_3SO_3)_2$-Based Electrolyte for High-Power Mg/S Battery

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Results and Discussion

Table S1. Comparison of the costs of the electrolytes reported in Mg/S battery system

Electrolytes	Solubility (M)/solvents	Estimate Time	Materials	Materials Cost	Electrolytes Cost/100ml	Ref.
My work	0.2/DME	2 days	$Mg(CF_3SO_3)_2$	$ 45.65/25g (98%, Ourchem)	$195	
			$MgCl_2$	$ 92.80/50g (99.99%, Macklin)		
			$AlCl_3$	$ 227.69/25g (99.999%, Sigma-Aldrich)		
			DME	$ 127.38/100ml (99.5%, Sigma-Aldrich)		
HMDSMgCl-$AlCl_3$	0.4/THF	2-3 days	HMDS	$ 87.64/50ml (≥ 99.0%, Sigma-Aldrich)	$261	1
			EtMgCl	$ 49.79/100ml (2 M in THF, Sigma-Aldrich)		
			$AlCl_3$	$ 227.69/25g (99.999%, Sigma-Aldrich)		
			THF	$ 94.87/100ml (≥ 99.9%, Sigma-Aldrich)		
$(HMDS)_2Mg$-2$AlCl_3$	0.9/G2	> 3 days	$(HMDS)_2Mg$	$ 723.86/25g (97%, Sigma-Aldrich)	$1,383	2
			$AlCl_3$	$ 227.69/25g (99.999%, Sigma-Aldrich)		
			$MgCl_2$	$ 401.01/50g (99.9%, Sigma-Aldrich)		
			Diglyme	$ 198.67/100ml (99.5%, Sigma-Aldrich)		
$Mg(TFSI)_2$	0.3/DME-G2	< 1 day	$Mg(TFSI)_2$	$ 415.26/50g (99.5%, Solvionic)	$309	3
			DME	$ 127.38/100ml (99.5%, Sigma-Aldrich)		

			Diglyme	$ 198.67/100ml (99.5%, Sigma-Aldrich)		
$Mg(TFSI)_2$-$MgCl_2$	0.4/G4-DOL	< 1 day	$Mg(TFSI)_2$	$ 415.26/50g (99.5%, Solvionic)	$810	4
			$MgCl_2$	$ 499.25/50g (99.99%, Alfa Aesar)		
			Tetraglyme	$ 52.23/5ml (≥ 99.5%, Aladdin)		
			DOL	$ 111.35/100ml (99.8%, Sigma-Aldrich)		
$Mg(TFSI)_2$-$0.1I_2$	0.5/DME	< 1 day	$Mg(TFSI)_2$	$ 415.26/50g (99.5%, Solvionic)	$372	5
			I_2	$ 160.67/100g (≥99.8%, Sigma-Aldrich)		
			DME	$ 127.38/100ml (99.5%, Sigma-Aldrich)		
BCM (2THFPB-MgF_2)	0.05/DME	< 1 day	THFPB	$ 349.35/5g (95.0%, TCI)	$504	6
			MgF_2	$ 298.19/5g (99.99%, J&K Chemical Ltd.)		
			DME	$ 127.38/100ml (99.5%, Sigma-Aldrich)		
$Mg[B(hifp)_4]_2$	0.8/G2-G4	2-3 days	$Mg(BH_4)_2$	$ 231.03/1g (95%, Sigma-Aldrich)	$1,632	7
			$HOCH(CF_3)_2$	$ 150.64/1000g (≥ 99.7%, Sigma-Aldrich)		
			Diglyme	$ 198.67/100ml (99.5%, Sigma-Aldrich)		
			Tetraglyme	$ 52.23/5ml (≥ 99.5%, Aladdin)		
OMBB	0.5/DME	2 days	$B(HFP)_3$	$ 348.07/5g (95.0%, TCI)	$1,893	8
			$MgCl_2$	$ 92.80/50g (99.99%, Macklin)		
			DME	$ 127.38/100ml (99.5%, Sigma-Aldrich)		

The cost of magnesium/sulfur batteries will largely affect its development in practical applications, and electrolytes, as the key components of magnesium-sulfur batteries, have received much attention. We summarized the cost of previously reported electrolytes for Mg/S batteries (Table S1). The cost of Mg(TFSI)$_2$-based electrolytes are more than 300 US dollars per 100 ml, and boron-containing electrolytes are even more expensive. HMDSMgCl-AlCl$_3$ shows relatively low cost compared to above electrolytes but it still costs 261 US dollars per 100 ml, and the synthesis processes are complicated. Our work achieved a low-cost electrolyte using cost-effective Mg salts Mg(CF$_3$SO$_3$)$_2$, MgCl$_2$ and AlCl$_3$. As can be seen from the table S1, the price of our electrolyte is only 195 US dollars per 100 ml, which is cheaper than other electrolytes. And the preparation processes are relatively simple, which are of great significance for the practical application of magnesium-sulfur batteries.

Figure S1. Image of prepared MTB electrolyte. The electrolyte is clear and transparent, which remains clear and transparent after two months' stay.

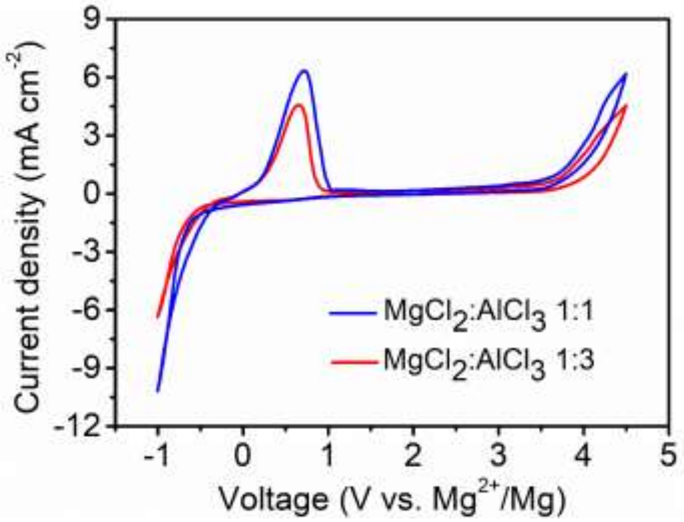

Figure S2. The cyclic voltammogram of the Mo electrode in the MTB electrolyte with different MgCl$_2$:AlCl$_3$ ratios at 50 mV s^{-1}.

The proportion of each component has a great influence on the performance of the electrolyte. The various contents of the Lewis acid $AlCl_3$ are shown in Figure S2, when the ratio of $MgCl_2$:$AlCl_3$ is 1:1, the electrolyte displays higher current density and Coulombic efficiency than that of the electrolyte with a ratio of 1:3. Under a ratio of 3:1, the electrolyte cannot completely dissolve $MgCl_2$ due to its poor solubility in DME and the incomplete acid-base reaction between $AlCl_3$ and $MgCl_2$. Hence, it is shown that the ratio of 1:1 is the most suitable ratio. In the subsequent experiments, we also prepared the electrolyte according to this ratio.

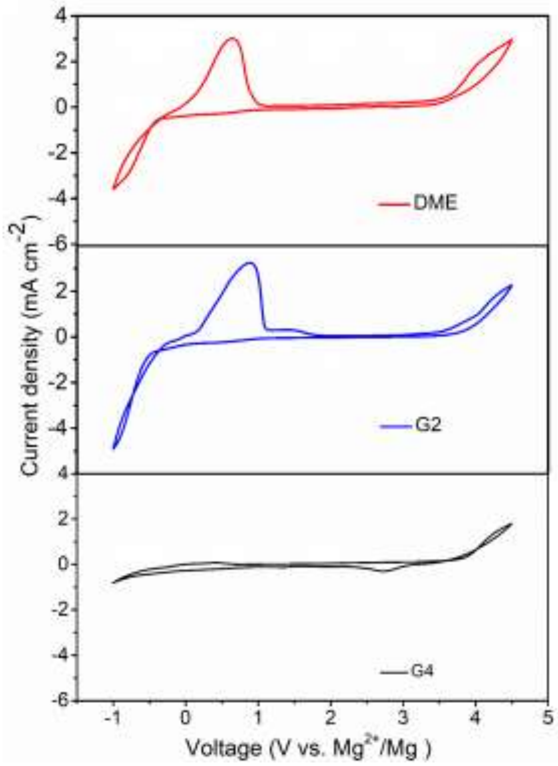

Figure S3. The CVs of the MTB electrolyte with different solvents at 50 mV s^{-1}.

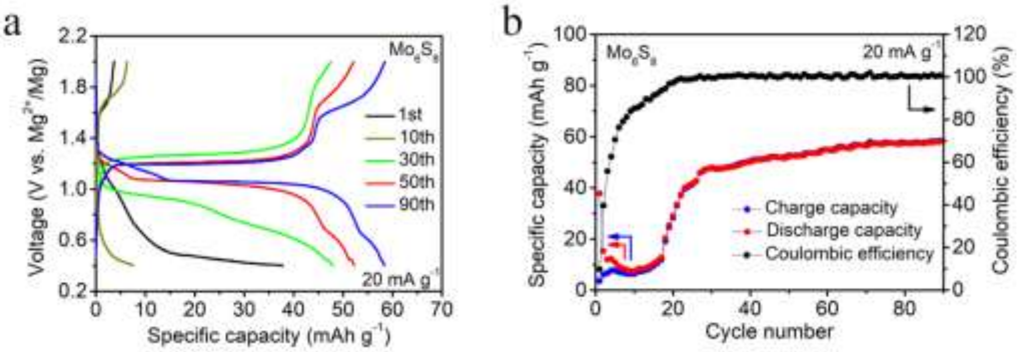

Figure S4. (a) The galvanostatic charge/discharge profiles and (b) cycling performance of the Mg/Mo_6S_8 battery at 20 mA g^{-1}.

Table S2. ICP analysis of Molar Mg:Al ratio in cycled MTB electrolyte

Sample	The concentration of Mg (mmol/L)	The concentration of Al (mmol/L)	Molar Mg:Al ratio
initial	4.498	2.642	1.702
20 cycles	4.007	1.871	2.142
50 cycles	4.807	1.696	2.834

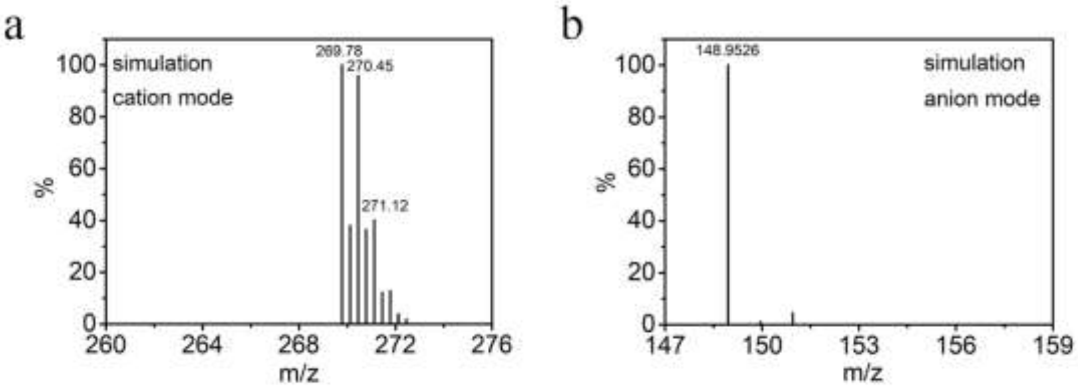

Figure S5. Simulated ESI-MS spectrums of (a) $[Mg_3(\mu_3\text{-}Cl)(\mu_2\text{-}Cl)_2(DME)_7]^{3+}$ and (b) $CF_3SO_3^-$.

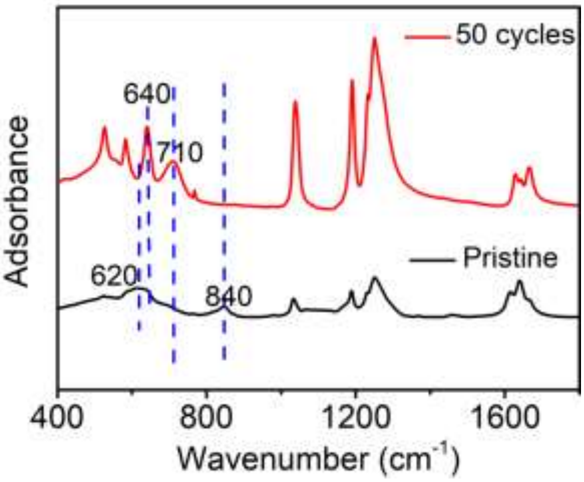

Figure S6. FTIR spectra of pristine MTB electrolyte and the electrolyte cycled for 50 cycles.

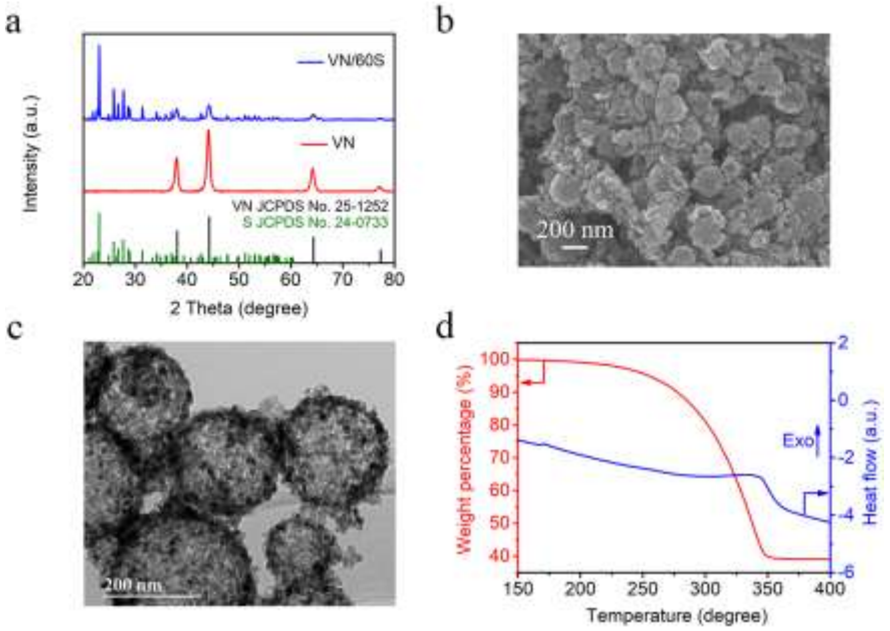

Figure S7. (a) XRD patterns, (b) SEM image, (c) TEM image and (d) TG analysis of VN/60S.

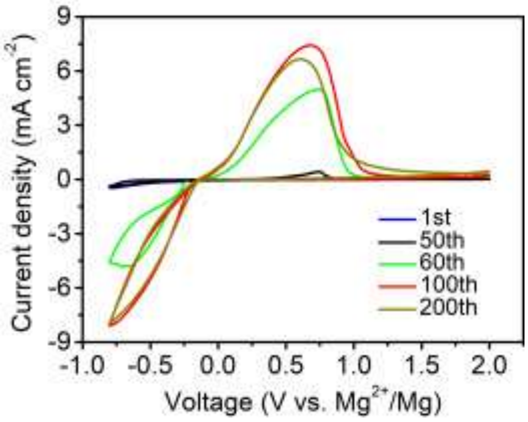

Figure S8. CVs of the Cu electrode in MTB electrolyte at 50 mV s^{-1}.

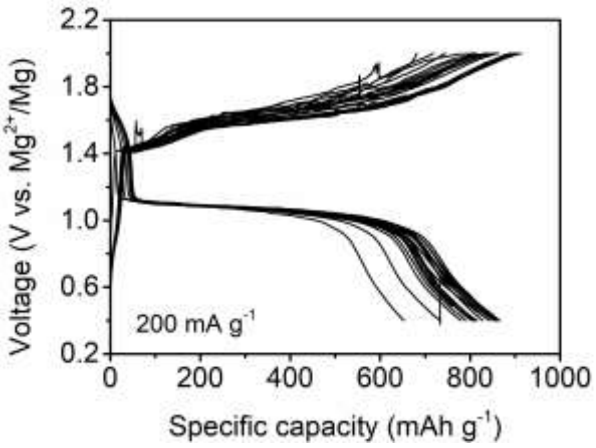

Figure S9. Galvanostatic charge/discharge profiles of the Mg-VN/60S battery after conditioning at a current density of 200 mA g^{-1}.

Table S3. Comparison of electrochemical performance for magnesium−sulfur batteries with previous reports

Electrolyte	Sulfur cathodes	Rate	The highest specific capacity / mAh g^{-1}	Overpotential / V	Cyclic performance	Ref.
My work	VN/60S	200 mA g^{-1}	866	0.58	844 mAh g^{-1} (20 cycles)	
		500 mA g^{-1}	575	0.58	450 mAh g^{-1} (100 cycles)	
$Mg(CF_3SO_3)_2$- $AlCl_3$-$MgCl_2$-anthracene/THF+TG	S@MC	84 mA g^{-1}	557	0.7	141 mAh g^{-1} (2 cycles)	9
HMDSMgCl-$AlCl_3$	S-carbon black	50 μA	1200	1.2	394 mAh g^{-1} (2 cycles)	1
$Mg(TFSI)_2$	CMK3-S	33 mA g^{-1}	250	1.5	259 mAh g^{-1} (4 cycles)	3
$Mg(TFSI)_2$-$MgCl_2$	S-C	28 mA g^{-1}	1320	0.65	650 mAh g^{-1} (4 cycles)	4
$Mg(TFSI)_2$-0.1I_2	ACC/S	168 mA g^{-1}	1200	0.55	550 mAh g^{-1} (10 cycles)	5
BCM (2THFPB-MgF_2)	S-C	50 mA g^{-1}	1081	0.4	930 mAh g^{-1} (30 cycles)	6
$Mg[B(hifp)_4]_2$	CMK3-S	168 mA g^{-1}	500	0.8	200 mAh g^{-1} (100 cycles)	7
OMBB	S-CNT	160 mA g^{-1}	1247	0.3	1019 mAh g^{-1} (100 cycles)	8
		500 mA g^{-1}	510	0.5	500 mAh g^{-1} (100 cycles)	

Reference

[1] Kim, H. S.; Arthur, T. S.; D. Allred, G.; Zajicek, J.; Newman, J. G.; Rodnyansky, A. E.; Oliver, A. G.; Boggess, W. C.; Muldoon, J.; Kim, H. S.; Arthur, T. S.; Allred, G. D. Structure and Compatibility of a Magnesium Electrolyte with a Cathode. Nat. Commun. 2011, 2, 427.

[2] Zhao-Karger, Z.; Zhao, X.; Di, W.; Diemant, T.; Behm, R. J.; Fichtner, M. Performance Improvement of Magnesium Sulfur Batteries with Modified Non-Nucleophilic Electrolytes. Adv. Energy Mater. 2015, 5(3), 1401155.

[3] Ha, S. Y.; Lee, Y. W.; Woo, S. W.; Koo, B.; Kim, J. S.; Cho, J.; Lee, K. T.; Choi, N. S. Magnesium(II) Bis(trifluoromethane sulfonyl) Imide-Based Electrolytes with Wide Electrochemical Windows for Rechargeable Magnesium Batteries. ACS Appl. Mater. Interfaces. 2014, 6, 6, 4063-4073.

[4] Robba, A.; Vizintin, A.; Bitenc, J.; Mali, G.; Arčon, I.; Kavčič, M.; Žitnik, M.; Bučar, K.; Aquilanti, G.; Martineau-Corcos, C.; Randon-Vitanova, A.; Dominko, R. Mechanistic Study of Magnesium−Sulfur Batteries. Chem. Mater. 2017, 29, 21, 9555-9564.

[5] Li, X.; Gao, T.; Han, F.; Ma, Z.; Fan, X.; Hou, S.; Eidson, N.; Li, W.; Wang, C. Reducing Mg Anode Overpotential via Ion Conductive Surface Layer Formation by Iodine Additive. Adv. Energy Mater. 2018, 8(7), 1701728.

[6] Zhang, Z.; Cui, Z.; Qiao, L.; Guan, J.; Xu, H.; Wang, X.; Hu, P.; Du, H.; Li, S.; Zhou, X.; Cui, G. Novel Design Concepts of Efficient Mg-Ion Electrolytes toward High-Performance Magnesium-Selenium and Magnesium-Sulfur Batteries. Adv. Energy Mater. 2017, 7(11), 1602055.

[7] Zhao-Karger, Z.; Bardaji, M. E. G.; Fuhr, O.; Fichtner, M. A New Class of Non-Corrosive, Highly Efficient Electrolytes for Rechargeable Magnesium Batteries. J. of Mater. Chem. A. 2017, 5 (22), 10815-10820.

[8] Du, A.; Zhang, Z.; Qu, H.; Cui, Z.; Cui, G. An Efficient Organic Magnesium Borate Based Electrolyte with Non-Nucleophilic Characteristic for Magnesium Sulfur Battery. Energy Environ. Sci., 2017, 10, 2616-2625.

[9] Yang, Y.; Wang, W.; Nuli, Y.; Yang, J.; Wang, J. High Active Magnesium Trifluoromethanesulfonate-Based Electrolytes for Magnesium-Sulfur Batteries. ACS Appl. Mater. Interfaces. 2019, 11, 9062-9072.