Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

A novel magnesium electrolyte containing magnesium bis(diisopropyl)amide-magnesium chloride complex for rechargeable magnesium batteries

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Supporting Information

Table S1. Price comparison of three organic magnesium salts from Sigma-Aldrich.

Magnesium salts	Commercial cost	Calculated cost
$(HDMS)_2Mg$	671.81 $ / 25 g	26.87 $ / g
PhMgCl	408.59 $ / 2.0 mol L^{-1} in 800 mL THF	1.87 $ / g
Bu_2Mg	341.87 $ / 1.0 mol L^{-1} in 800 mL heptane	3.08 $ / g

Table S2. Input data of structure refinement for MBA.

0 1

Mg	0.00001900	0.00026000	-0.21897200
N	1.92280300	-0.21848800	-0.15952600
C	2.60549100	-1.20949400	0.67374100
H	3.63560100	-1.32781800	0.30291000
C	2.79259200	0.61194200	-0.98708700
H	3.46256000	-0.03900300	-1.57929200
C	1.92935100	-2.58428400	0.54903900
H	2.42737400	-3.34655200	1.15674900
H	0.88608800	-2.54029400	0.89475200
H	1.92406100	-2.92058600	-0.49058800
C	2.69229400	-0.80520600	2.15873500
H	3.26217500	-1.53276900	2.74795000
H	3.16283000	0.17214100	2.27735500
H	1.68878200	-0.74044200	2.59673500
C	1.94824200	1.40608100	-1.98915800
H	1.26733300	2.09893100	-1.47290100
H	2.56674200	2.01958900	-2.64896700
H	1.35668300	0.73989600	-2.62806700
C	3.69748000	1.57702700	-0.19596200
H	4.33614700	2.16349300	-0.86585200

H	3.09334500	2.27047000	0.39880800
H	4.35547100	1.03743700	0.48878400
N	-1.92281000	0.21864200	-0.15961700
C	-2.60583400	1.20929400	0.67379000
H	-3.63598700	1.32729400	0.30298300
C	-2.79231600	-0.61190900	-0.98735400
H	-3.46244700	0.03892500	-1.57949600
C	-1.93019400	2.58435200	0.54927300
H	-2.42856400	3.34638800	1.15699000
H	-0.88695200	2.54071100	0.89508800
H	-1.92490700	2.92073600	-0.49032700
C	-2.69250100	0.80476500	2.15872600
H	-3.26262900	1.53205300	2.74804200
H	-3.16271000	-0.17275800	2.27720000
H	-1.68897000	0.74027700	2.59672500
C	-1.94767700	-1.40564300	-1.98950300
H	-1.26656200	-2.09835500	-1.47333100
H	-2.56596700	-2.01924600	-2.64942100
H	-1.35631200	-0.73917800	-2.62830100
C	-3.69695500	-1.57738600	-0.19642000
H	-4.33542300	-2.16394000	-0.86642400
H	-3.09264300	-2.27074300	0.39827000
H	-4.35512800	-1.03808900	0.48838200

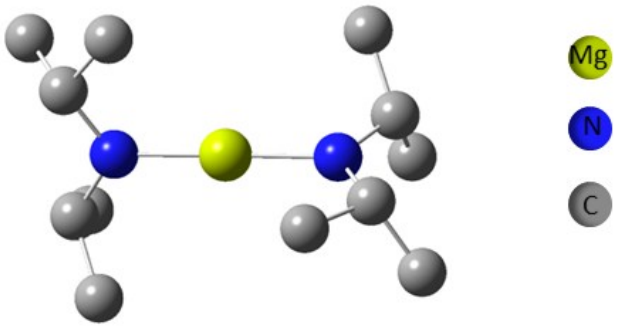

Figure S1. Molecular structure of MBA.

Table S3 Input data of structure refinement for $(C_3H_7)_2NMgCl$

0 1

Mg	-1.40434964	-0.21493209	0.00000000
Cl	-3.61080199	-0.31564072	0.00000000
N	0.51115125	-0.12750328	0.00000000
C	1.29926541	1.10379510	0.00000000
H	2.34119488	0.86146431	0.00000000
C	1.25752694	-1.38186839	0.00000000
H	0.57276822	-2.20312259	0.00000000

C	0.94588312	1.99160501	1.20768975
H	1.77154676	2.63427234	1.43165013
H	0.08563349	2.58395402	0.97532533
H	0.73493735	1.37344330	2.05520257
C	0.94588312	1.99160501	-1.20768975
H	1.77154676	2.63427234	-1.43165013
H	0.73493735	1.37344330	-2.05520257
H	0.08563349	2.58395402	-0.97532533
C	2.14628830	-1.40050055	1.25751980
H	2.47451918	-2.40103623	1.44750099
H	2.99649018	-0.76954219	1.10276734
H	1.58537128	-1.04386894	2.09602202
C	2.14628830	-1.40050055	-1.25751980
H	2.47451918	-2.40103623	-1.44750099
H	1.58537128	-1.04386894	-2.09602202
H	2.99649018	-0.76954219	-1.10276734

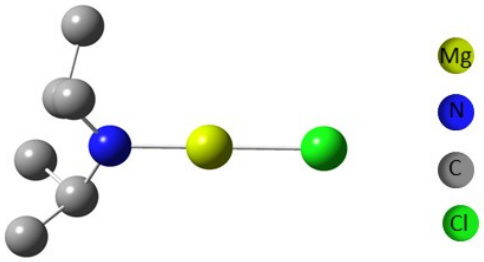

Figure S2. Molecular structure of $(C_3H_7)_2NMgCl$.

Table S4. Input data of structure refinement for $(C_3H_7)_2NMgCl_2$-MgCl.

0 1

Cl	1.34510400	1.35277000	-1.04285600
Cl	1.34485000	-1.35260400	1.04336900
Mg	-0.36027600	0.00009300	-0.00032200
Mg	2.97449100	-0.00003000	0.00056100
Cl	5.17470700	0.00035900	-0.00024000
N	-2.28057500	0.00009000	0.00004200
C	-3.04721400	-1.07853400	-0.61463500
H	-3.84517200	-0.66323200	-1.25229800
C	-3.04849200	1.07811400	0.61413100
H	-3.84685300	0.66213300	1.25084500
C	-3.71847800	-2.01294500	0.40963400
H	-4.33695500	-2.77113200	-0.08297700
H	-2.96261300	-2.52617000	1.01332300
H	-4.36666000	-1.45935300	1.09316600
C	-2.12756800	-1.88727300	-1.53586600
H	-2.64926500	-2.71628800	-2.02054900

H	-1.70850800	-1.25471200	-2.32627100
H	-1.30290000	-2.34280700	-0.96428000
C	-2.13035400	1.88724600	1.53650300
H	-1.30542200	2.34346100	0.96589900
H	-2.65322700	2.71568500	2.02091000
H	-1.71160200	1.25471100	2.32707300
C	-3.71928300	2.01223200	-0.41069300
H	-4.33859600	2.77006000	0.08142000
H	-2.96313000	2.52591700	-1.01363300
H	-4.36654700	1.45837200	-1.09488100

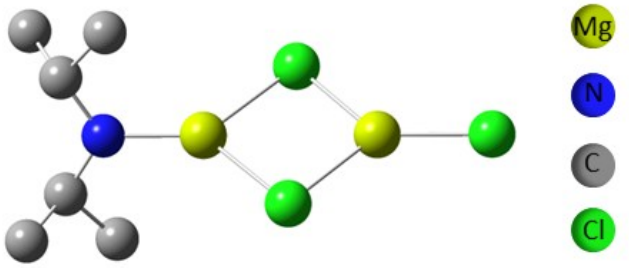

Figure S3. Molecular structure of $(C_3H_7)_2NMgCl_2$-MgCl.

Table S5. Input data of structure refinement for $[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+ \{[(C_3H_7)_2N]_2MgCl]\}^-$.

$Mg_2(\mu\text{-}Cl)_3(THF)_6^+$ +1 1

Mg	-0.0467983	0.0752845	1.5173959
Mg	-0.0344153	-0.0722872	-1.6711050
Cl	1.7137824	0.8989719	-0.0917589
Cl	-0.1104104	-1.9933345	0.0077205
Cl	-1.7519481	0.9938984	-0.1576103
C	2.5601314	0.0901068	3.3237761
C	1.7606495	-2.1357519	2.9446117
C	3.5837928	-0.9128755	3.8622410
H	2.9444162	0.6580417	2.4506327
C	3.2827890	-2.1715391	3.0317467
H	1.2877186	-2.5537977	3.8613275
H	4.6225739	-0.5476140	3.7470611
H	3.7274621	-2.0888386	2.0185587
C	-1.4958795	2.4058076	3.0453997
C	0.7120350	3.0688635	2.4050972
C	-1.5329905	3.8700258	2.6243554
H	-2.2630662	1.7792371	2.5543050
C	-0.0764741	4.3009027	2.8563585
H	1.6361382	2.8997722	2.9928570
H	-2.2647266	4.4602301	3.2092756

H	0.0993805	4.5111651	3.9316167
C	-2.7471154	-1.4263329	2.2893514
C	-1.5350525	-0.9430104	4.2065281
C	-2.8202437	-2.7159605	3.1140116
H	-3.6157529	-0.7562764	2.4768063
C	-2.1147931	-2.3523500	4.4519656
H	-0.4926769	-0.8013269	4.5467928
H	-2.2751050	-3.5262507	2.5924469
H	-1.3164326	-3.0812338	4.6889871
C	1.4354660	2.1412295	-3.4098713
C	-0.7305267	2.8180453	-2.9582019
C	1.6016877	3.5343482	-2.7868729
H	2.1998816	1.4091445	-3.0936500
C	0.1439839	4.0097241	-2.5286956
H	-1.1173907	2.9393636	-3.9944671
H	2.1593528	3.4541292	-1.8350865
H	-0.0091624	4.2341758	-1.4559858
C	1.3604929	-1.2962231	-4.3033368
C	2.6113362	-1.7034482	-2.2965882
C	2.7738202	-1.7309563	-4.6842383
H	0.6174706	-2.0964911	-4.5085552
C	3.2029238	-2.5274516	-3.4403730
H	3.2901685	-0.8978408	-1.9480988
H	2.7938760	-2.3254542	-5.6180560
H	2.7616279	-3.5453272	-3.4615026
C	-2.7863028	-0.2997118	-3.2955868
C	-1.8097423	-2.3721140	-2.9949437
C	-3.9031491	-1.1590349	-2.6787934
H	-2.7579498	0.7360949	-2.9142316
C	-3.2389846	-2.5488386	-2.4601930
H	-1.7299436	-2.6759765	-4.0633800
H	-4.7864821	-1.2058918	-3.3445586
H	-3.7673570	-3.3653540	-2.9887861
O	-0.1840545	1.9224632	2.6153116
O	-1.5447449	-0.7663283	2.7689638
O	1.4255954	-0.7130558	2.8598588
O	0.1500444	1.6619730	-2.9347176
O	1.4166013	-1.0616843	-2.8658833
O	-1.5476121	-0.9470605	-2.9063435
H	-2.6239397	-1.5725679	1.2016802
H	-3.8654341	-3.0511231	3.2582406
H	-2.8144321	-2.3441992	5.3101236
H	-2.1740417	-0.1560529	4.6650978
H	1.3344421	-2.6295552	2.0510529

H	3.6573857	-3.1038594	3.4969397
H	3.4140605	-1.1097625	4.9412153
H	2.1889954	0.7998498	4.0896976
H	-1.5685603	2.2900409	4.1497018
H	-1.8022320	3.9438762	1.5509589
H	0.2100649	5.2066761	2.2873912
H	0.9775905	3.0882518	1.3295398
H	-1.5658590	2.6071079	-2.2653136
H	-0.1163914	4.9203637	-3.1020905
H	2.1619901	4.2123366	-3.4592001
H	1.4035583	2.1871149	-4.5221317
H	1.0161055	-0.3640838	-4.7909981
H	3.4293833	-0.8469620	-4.8303988
H	4.3006754	-2.6385570	-3.3494380
H	2.2834522	-2.2940028	-1.4196609
H	-2.8369523	-0.2822299	-4.4070812
H	-4.2273476	-0.7246615	-1.7144311
H	-3.2104142	-2.8055941	-1.3842840
H	-1.0373993	-2.8901245	-2.3975468

$[(C_3H_7)_2N]_2MgCl]^-$ -1 1

Mg	0.2777503	-0.0056093	1.0889411
Cl	0.8413311	-0.0164115	3.3541286
N	0.1027299	1.7667872	0.1557417
N	-0.0102514	-1.7701495	0.1709474
C	0.2664519	1.8779868	-1.2878164
H	0.4587512	0.8441196	-1.6613978
C	-0.1100329	3.0215515	0.8747802
C	-0.7382612	-1.8473979	-1.0890888
H	-1.0221759	-0.8004029	-1.3499654
C	0.4207493	-3.0463693	0.7393656
H	0.2768922	-3.8658868	-0.0112594
C	1.1298297	3.4701022	1.6898653
H	1.3697724	2.7004366	2.4536633
H	2.0140445	3.5797229	1.0297557
H	0.9648036	4.4421253	2.2107575
C	1.4910113	2.7177457	-1.7424665
H	1.6235260	2.6955314	-2.8477404
H	1.3852120	3.7835787	-1.4452559
H	2.4177062	2.3288227	-1.2726483
C	-1.0070873	2.3640885	-2.0324997
H	-0.8726908	2.3686673	-3.1375841
H	-1.8646484	1.7048064	-1.7871976
H	-1.2810783	3.3980672	-1.7302912
C	0.1137897	-2.3627691	-2.2812210

H	0.4449467	-3.4116959	-2.1187751
H	-0.4492385	-2.3408879	-3.2415351
H	1.0235526	-1.7386514	-2.3947719
C	-2.0741004	-2.6364203	-1.0213265
H	-2.6327136	-2.5905489	-1.9829839
H	-1.9003939	-3.7102572	-0.7923000
H	-2.7223309	-2.2235162	-0.2211328
C	-0.3918968	-3.4498568	1.9956528
H	-1.4745888	-3.5061010	1.7613147
H	-0.0743738	-4.4365917	2.4054949
H	-0.2544483	-2.6837648	2.7884228
C	1.9277544	-3.0313227	1.0829571
H	2.5292526	-2.8026973	0.1790956
H	2.1319578	-2.2454734	1.8424825
H	2.2760819	-4.0025812	1.5020505
C	-1.3362617	2.9299031	1.8111189
H	-2.2482639	2.6748056	1.2330407
H	-1.1718166	2.1322944	2.5683551
H	-1.5207184	3.8791914	2.3633178
H	-0.3305256	3.8450286	0.1480079

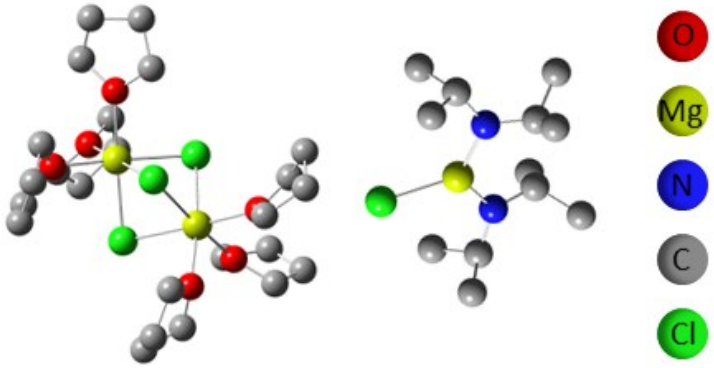

Figure S4. Molecular structure of $[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+ \{(C_3H_7)_2N]_2MgCl\}^-$.

Table S6. Input data of structure refinement for $MgCl_2$ and THF.

$MgCl_2$	0 1			
	Mg	-0.10620915	0.45751633	0.00000000
	Cl	2.24379085	0.45751633	0.00000000
	Cl	-2.45620915	0.45751633	0.00000000
THF	0 1			
	C	0.15130636	-0.45616465	1.15785979
	C	0.15130636	-0.45616465	-1.15785979
	C	-0.04799953	1.01378640	0.77506615
	H	-0.44669909	-0.78000622	2.00516041

C	-0.04799953	1.01378640	-0.77506615
H	1.20953891	-0.68593266	-1.33519656
H	-0.99807339	1.38226538	1.16312497
H	-0.99807339	1.38226538	-1.16312497
O	-0.28060892	-1.22078712	0.00000000
H	-0.44669909	-0.78000622	-2.00516041
H	0.73806986	1.63718665	-1.19657936
H	0.73806986	1.63718665	1.19657936
H	1.20953891	-0.68593266	1.33519656

Table S7. Calculated thermochemistry values from Gaussian. All values are in Hartrees.

	MBA	$MgCl_2$	THF	$(C_3H_7)NMgCl$	$(C_3H_7)NMgCl_2$-MgCl	$Mg_2(\mu\text{-}Cl)_3(THF)_6^+$	$[(C_3H_7)_2N]_2MgCl^-$
ε0	-783.925298	-1120.758053	-232.51	-952.34	-2073.1	-3176.3	-1244.3
εZPE	0.387070	0.002412	0.116855	0.194646	0.198757	0.719456	0.386496
Etot	0.407695	0.006715	0.121799	0.207179	0.216382	0.764962	0.409785
Hcorr	0.408639	0.007659	0.122743	0.208123	0.217327	0.765906	0.410729
Gcorr	0.339022	-0.022779	0.088001	0.154843	0.151929	0.633721	0.333852
ε0 +εZPE	-783.538229	-1120.755641	-232.395334	-952.146782	-2072.924262	-3175.556585	-1243.956214
ε0+ Etot	-783.517604	-1120.751339	-232.390390	-952.134250	-2072.906637	-3175.511080	-1243.932925
ε0+ Hcorr	-783.516660	-1120.750394	-232.389446	-952.133306	-2072.905693	-3175.510135	-1243.931980
ε0+ Gcorr	-783.586276	-1120.780833	-232.424188	-952.186586	-2072.971091	-3175.642321	-1244.008858

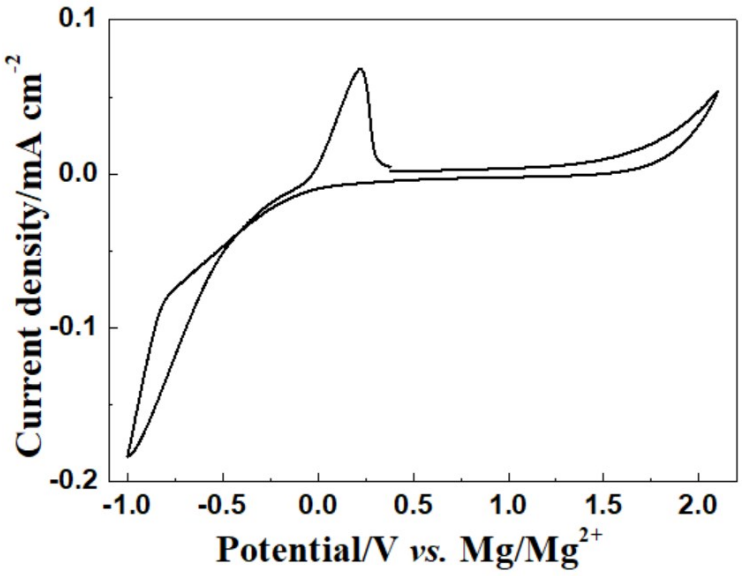

Figure S5. CVs of Mg electrochemical deposition-dissolution on Pt from the electrolyte of 0.6 mol L^{-1} MBA-2$MgCl_2$/THF at 25 mV s^{-1}.

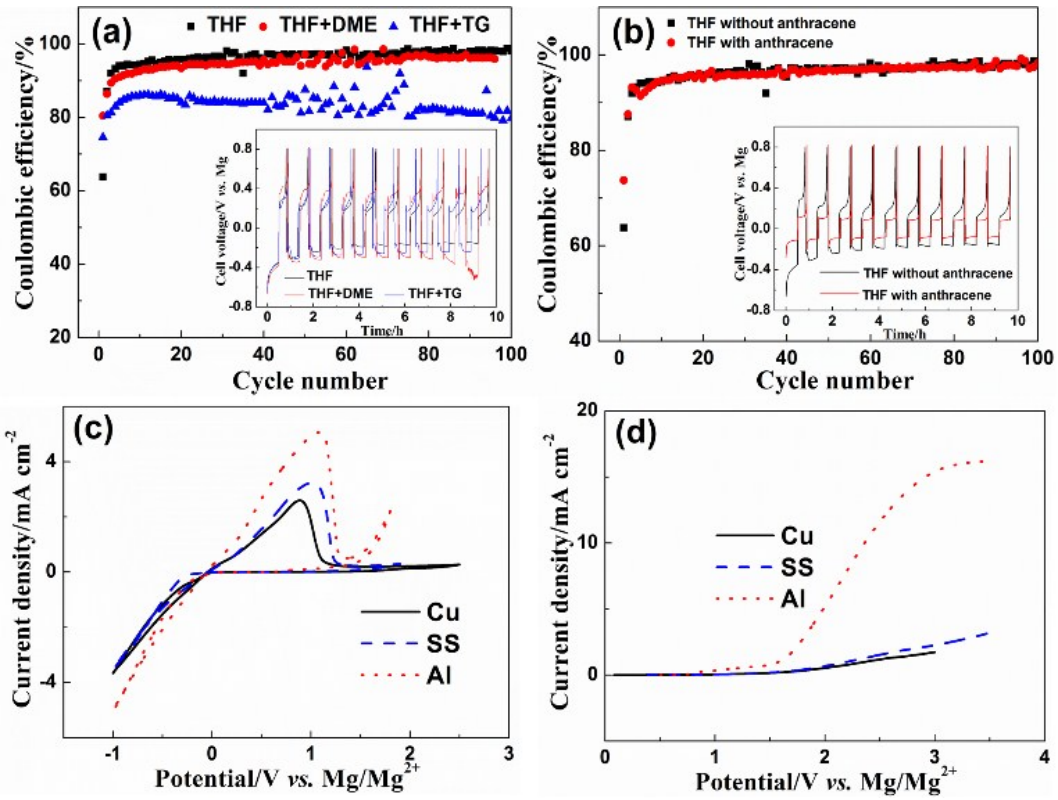

Figure S6. Coulombic efficiency of Mg deposition-dissolution upon cycling via SS|Mg coin-cells with the electrolytes of 0.6 mol L^{-1} MBA-2$MgCl_2$ in THF, THF+DME (1:1 volume ratio) and THF+TG (1:1 volume ratio) (a), 0.6 mol L^{-1} MBA-2$MgCl_2$ with or without anthracene in THF (b). CVs of Mg electrochemical deposition-dissolution (c) and the linear sweep voltammetry (d) from the electrolyte of 0.6 mol L^{-1} MBA-2$MgCl_2$+0.025 mol L^{-1} anthracene/THF on Cu, SS and Al disk electrodes at 25 mV s^{-1}.

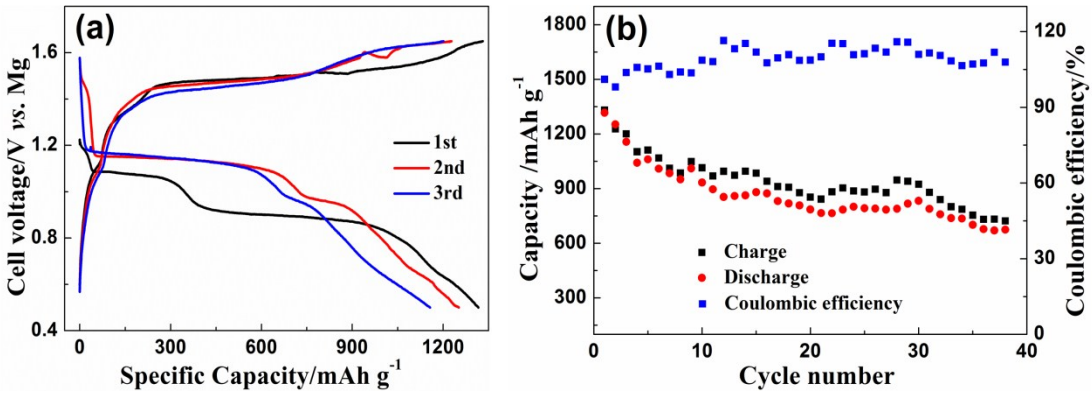

Figure S7. Discharge/charge voltage profile (a) and cycling performance (b) of the S@MC|Mg cells at 0.04 C, 0.6 mol L^{-1} MBA-2$MgCl_2$+0.4 mol L^{-1} $AlCl_3$/THF solution with the addition of 1.0 mol L^{-1} LiCl as the electrolyte.

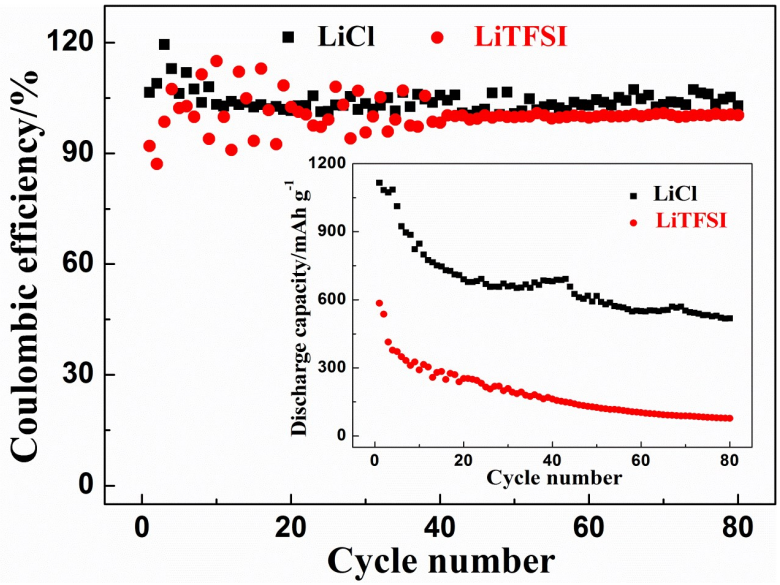

Figure S8. Comparison of cycling performance and Coulumbic efficiency of the S@MC|Mg cells at 0.1 C, 0.6 mol L^{-1} MBA-2$MgCl_2$+0.4 mol L^{-1} $AlCl_3$/THF solutions with the addition of 1.0 mol L^{-1} LiCl or LiTFSI as the electrolytes.

Table S8. Comparison of cycling and rate performance of Mg-S batteries reported in the literature with this work.

Cathode material	S content (wt%)	Electrolyte		Cycling performance			Rate performance		Ref.
				Current density (C, mA g^{-1}_S)	Discharge plateau (V *vs*. Mg)	Final discharge capacity (mAh g^{-1}_S)/cycle number	Current density (mA g^{-1}_S)	Average discharge capacity (mAh g^{-1}_S)	
S/CMK-3	55	1.2 mol L^{-1} $(HMDS)_2Mg$-$(AlCl_3)_2$-$MgCl_2$/PP14TFSI+diglyme	PVDF	20 mA g^{-1} (0.012 C)	1.65	about 150/20	/	/	12
			CMC		1.65	about 200/20	/	/	
		1.2 mol L^{-1} $(HMDS)_2Mg$-$(AlCl_3)_2$-$MgCl_2$/PP14TFSI+tetraglyme	PVDF		1.6	about 250/20	/	/	
			CMC		1.65	about 260/20	/	/	
S/rGO	49	1.8 mol L^{-1} $(HMDS)_2Mg$-$(AlCl_3)_2$-$MgCl_2$/tetraglyme		20 mA g^{-1} (0.012 C)	1.3~1.72 0.7~1.3	219/50	5	885	13
							10	530	
							15	285	
							25	180	
							35	130	
							45	108	
S/CNF	50	3.6 mol L^{-1} $(HMDS)_2Mg$-$(AlCl_3)_2$-$MgCl_2$/tetraglyme		0.02 C	about 1.55 0.85	about 750/20	/	/	14
S/CMK-3	69.3	0.3 mol L^{-1}		0.01 C	0.2	500/1	/	/	25

		$Mg(TFSI)_2$/glyme+diglyme						
S/ACC	/	0.25 mol L^{-1} $MgTFSI_2$+$MgCl_2$/DME	200 mA g^{-1} (0.12 C)	1.25~1.5	about 410/20	/	/	29
		1.0 mol L^{-1} $MgTFSI_2$+$MgCl_2$/DME	100 mA g^{-1} (0.06 C)	1~1.25	about 600/110			
S/C	85	0.5 mol L^{-1} THFPB+0.05 mol L^{-1} MgF_2/DME	50 mA g^{-1} (0.03 C)	1.05	about 980/30	/	/	41
S/C	/	0.5 mol L^{-1} THFPB+0.05 mol L^{-1} MgO/DME	10 mA g^{-1} (0.006 C)	1.1	1030/15	/	/	42
S/CMK-3	55	0.4 mol L^{-1} $Mg[B(hfip)_4]_2$/DME	0.1 C	1.25~1.5	200/100	/	/	43
S@MC	64.7	0.4 mol L^{-1} $(PhMgCl)_2$-$AlCl_3$/THF	20 mA g^{-1} (0.012 C)	1.4~1.5 1.1 0.9	270/50	/	/	54
		0.4 mol L^{-1} $(PhMgCl)_2$-$AlCl_3$+1.0 mol L^{-1} LiCl/THF	0.1 C	1.1 0.9	400/200	0.05 C	600	
						0.1 C	350	
						0.15 C	220	
						0.2 C	200	
S/ACC	15	0.1 mol L^{-1} $(HMDS)2Mg$-$(AlCl_3)_2$ + 1.0 mol L^{-1} LiTFSI/tetraglyme	1 C	1.75 1.2	1000/30	/	/	57
S@MC	55.8	0.6 mol L^{-1} MBA-2$MgCl_2$+0.4 mol L^{-1} $AlCl_3$/THF	0.05C	1.1 0.9	200/40	/	/	This work
		0.6 mol L^{-1} MBA-2$MgCl_2$+0.4 mol L^{-1} $AlCl_3$+1.0 mol L^{-1} LiCl/THF	0.1C		616/50 518/80	0.02 C	979	
						0.05 C	792	
			0.04C		880/25	0.1 C	586	
						0.15 C	397	
						0.2 C	287	