

Investigating Ternary Li-Mg-Si Zintl Phase Formation and Evolution for Si anodes in Li-ion Batteries with Mg(TFSI)₂ Electrolyte Additive

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Supporting Information:

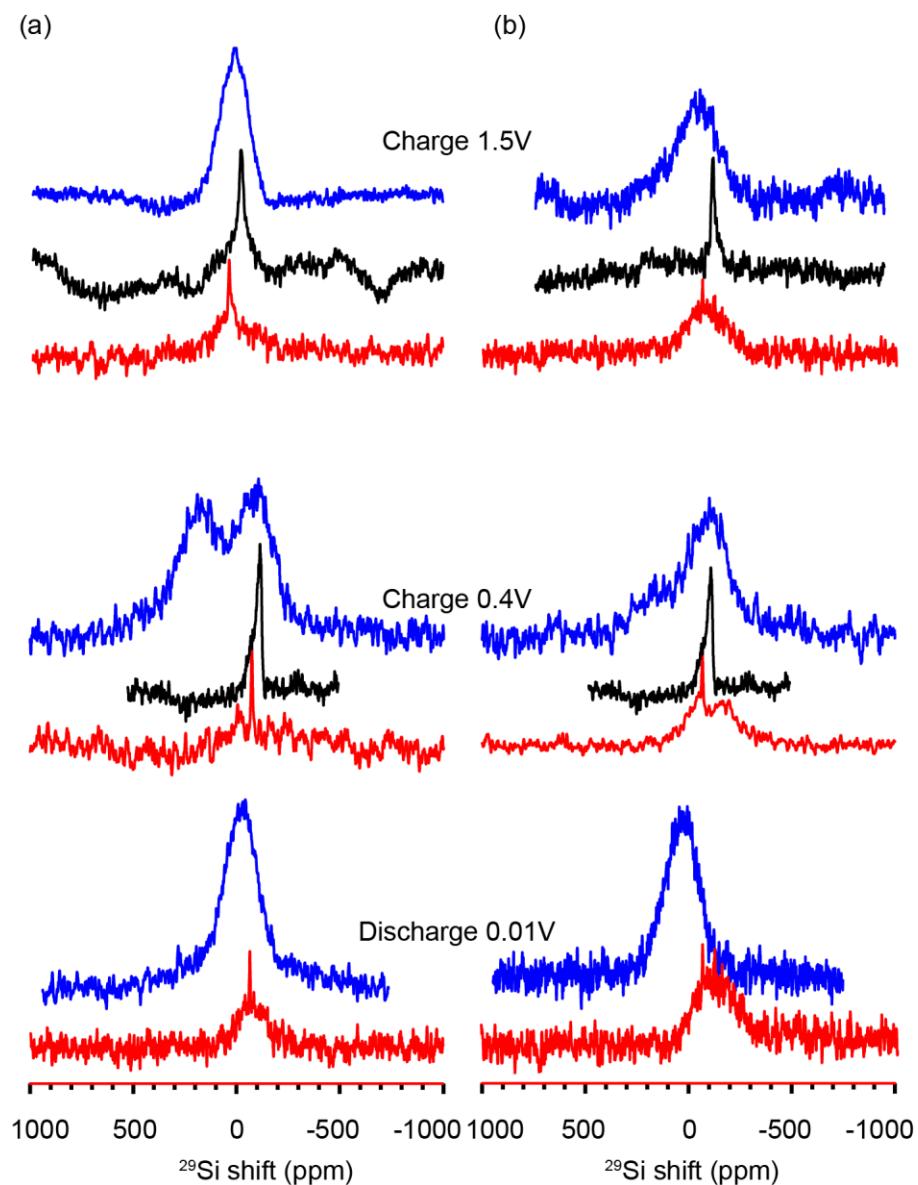


Figure S1. One pulse, Hahn echo, and Li-Si CP NMR on GFM(a) and GF(b) at 10 mV, 400 mV, and 1500 mV.

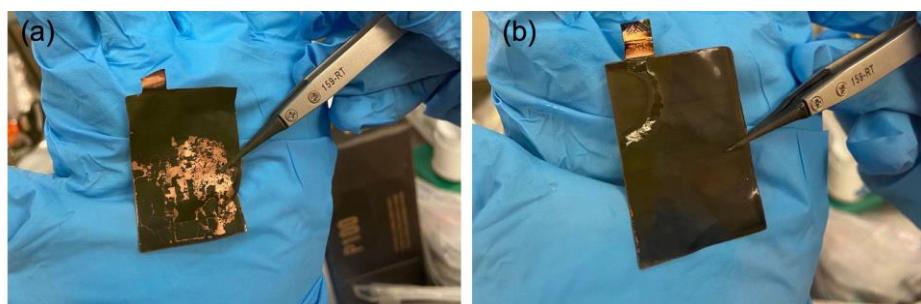


Figure S2. Delamination comparison after 270 cycles between GF (a) and GFM (b) in full cell testing. (detailed results are beyond the scope of this work and will be presented in a separate study) The electrodes are the same as those used in pouch half cells but with different sizes, so it's representative of the level of delamination.

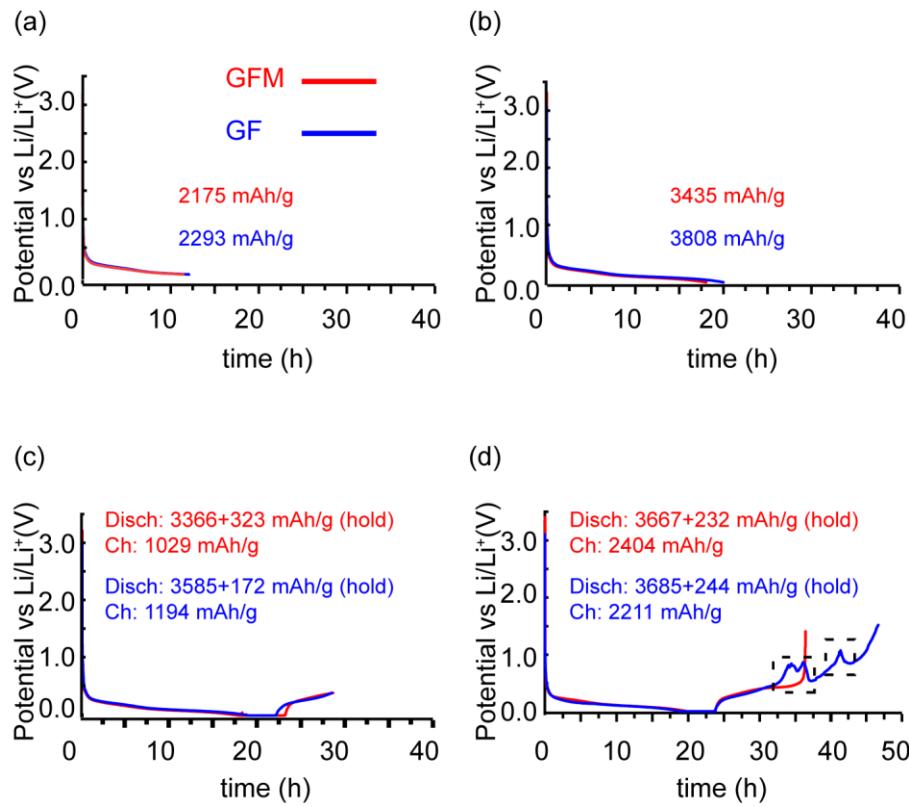


Figure S3. Electrochemical profiles of GF and GFM pouch cells. At the fully delithiated state, the GF cell exhibits abnormal fluctuating charge curve. Given that all the half cells were cycled without additional pressure. It is possibly due to severe delamination of the Si electrode, especially when some of the lithiated Si particles occasionally detach from current collector and obtain contact again.

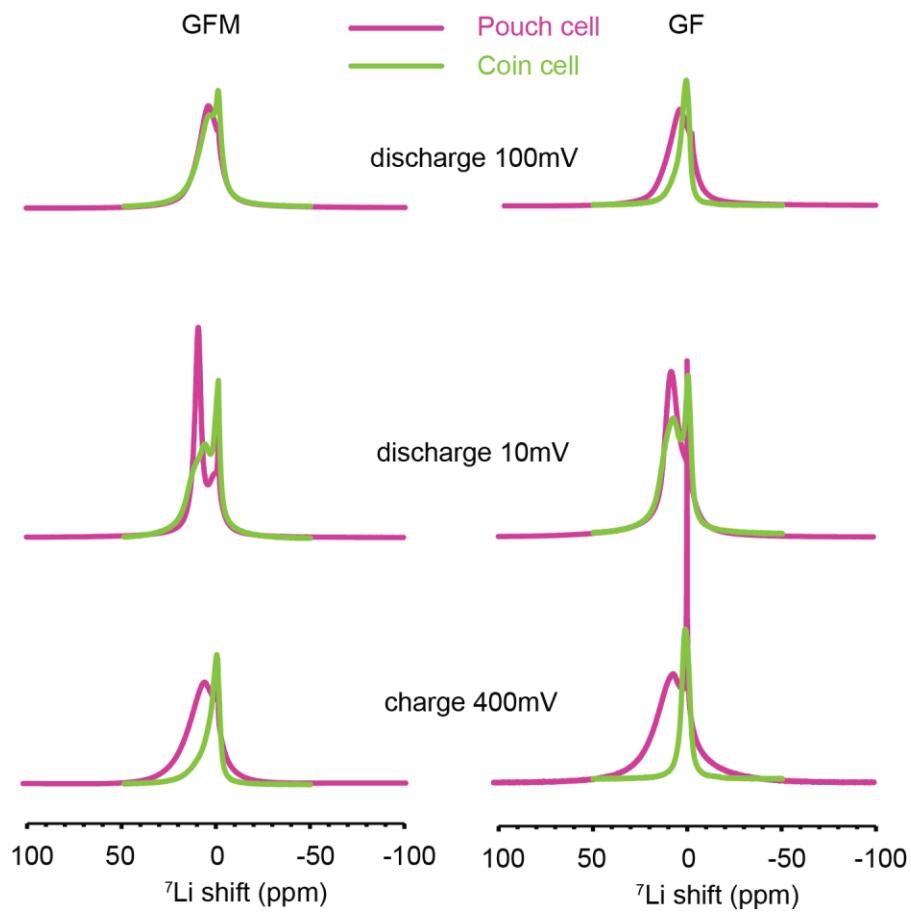


Figure S4. ${}^7\text{Li}$ NMR spectra comparison between pouch cells(purple) and coin cells(yellow) for GFM and GF.

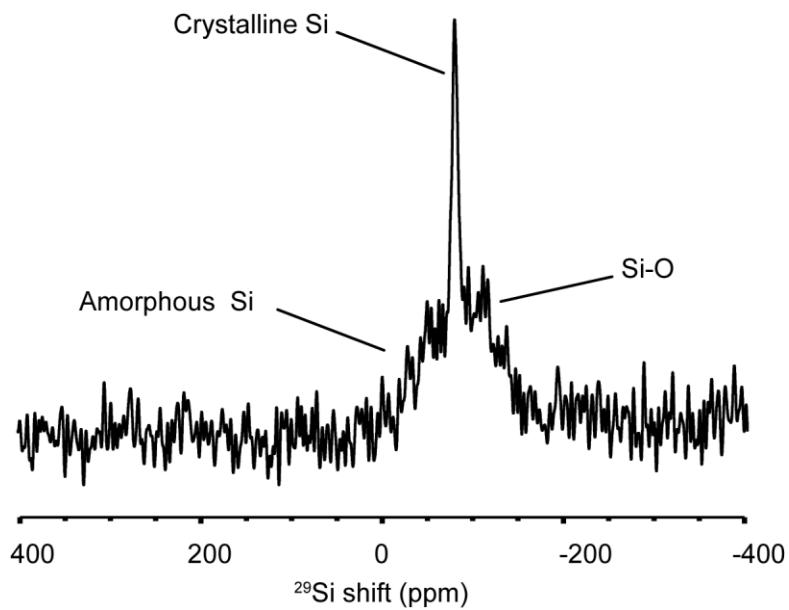


Figure S5. ^{29}Si NMR spectrum of pristine Si powder.

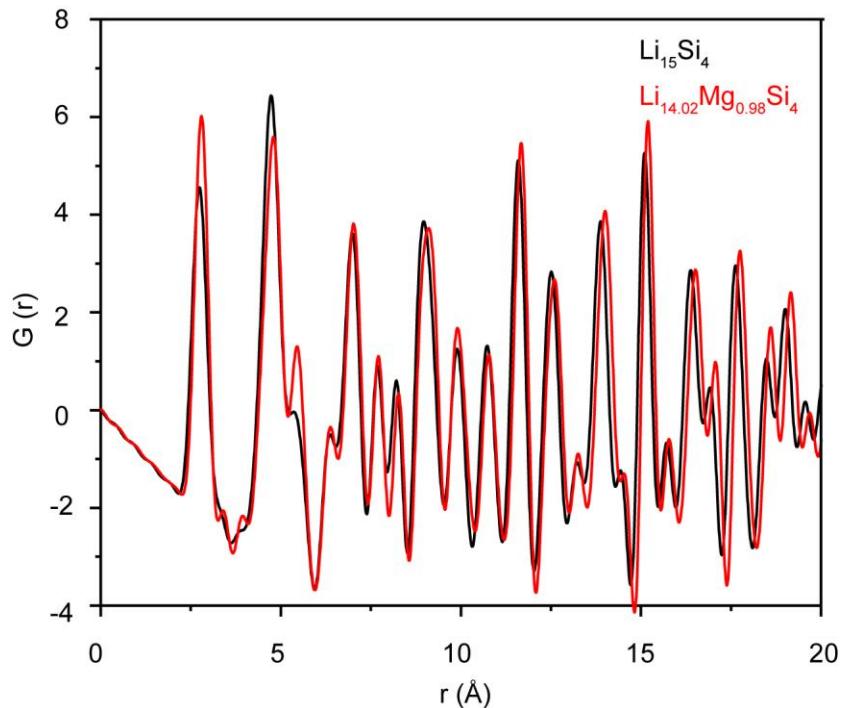


Figure S6. Calculated PDFs of $\text{Li}_{15}\text{Si}_4$ and $\text{Li}_{14.02}\text{Mg}_{0.98}\text{Si}_4$ structure models.

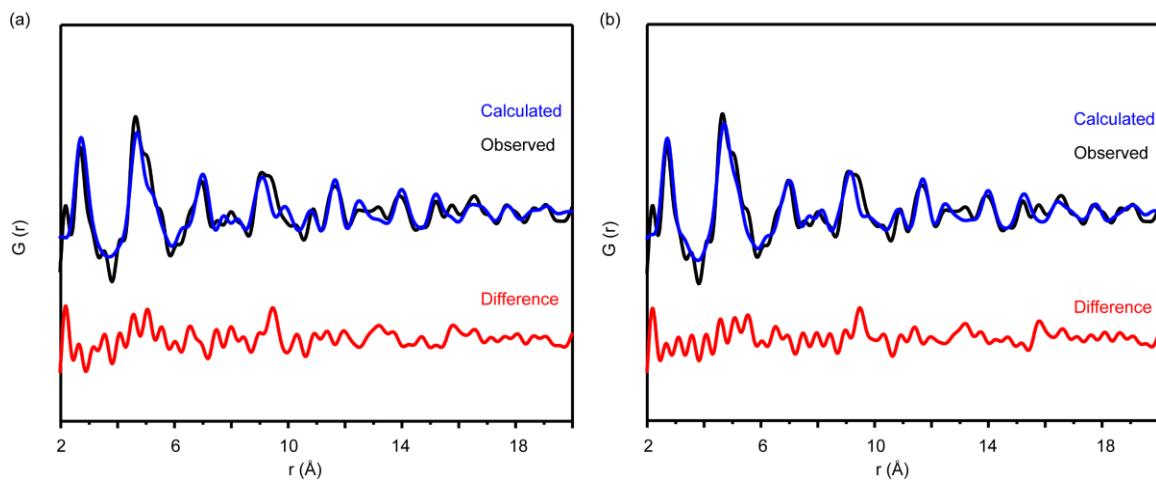


Figure S7. PDF fit of silicon anode discharged to 10 mV against $\text{Li}_{14.02}\text{Mg}_{0.98}\text{Si}_4$ (a) and $\text{Li}_{15}\text{Si}_4$ (b) model in GFM electrolyte.

Table S1. ^7Li NMR spectra deconvolution parameters of GF coin cells.

	shift/ppm	LB/Hz	xG/(1-x)L	%
1st dis 0.2V	-0.92	500	0.2	0.588
	0.22	270	0.3	0.284
	1.4	500	0.5	0.128
0.15V	-0.75	500	0.2	0.288
	0.4	450	0.8	0.171
	2.2	700	0.1	0.541
0.1V	-0.2	650	0.2	0.419
	1.7	600	0.3	0.445
	4.25	1000	0.2	0.136
0.01V	-0.4	500	0.1	0.197
	1.7	600	0.1	0.065
	7.5	2000	0.45	0.567
	12.8	2000	0.1	0.171
1st ch 0.4V	0.2	640	0.5	0.429
	2.4	600	0.3	0.178
	5	1600	0.3	0.337
	12.5	2000	0.1	0.056
2nd dis 0.01V	-0.1	400	0.2	0.194
	1.4	600	0.3	0.104
	5.1	1700	0.23	0.573
	13.3	2000	0.5	0.228
	-1.6	400	0.2	0.095

Table S2. ^7Li NMR spectra deconvolution parameters of GFM coin cells

	shift/ppm	LB/Hz	xG/(1-2)L	%
1st dis 0.35V	-0.98	110	0.4	0.202
	-1.2	500	0.1	0.798
0.2V	-0.15	600	0.5	0.921
	1.5	1000	0.5	0.079
0.15V	0.55	850	0.1	0.465
	1.7	1500	0.1	0.535
0.1V	-0.95	500	0.2	0.133
	16	2500	0.1	0.095
	4.25	2400	0.6	0.759
	1.4	500	0.5	0.013
0.05V	-0.3	400	0.5	0.165
	4.7	2000	0.3	0.535
	15	2500	0.3	0.228
	1.6	500	0.5	0.072
0.01V	-0.5	400	0.1	0.145
	1.2	600	0.1	0.116
	6.2	1650	0.1	0.387
	12.5	2000	0.1	0.322
	25	2500	0.2	0.03
1st ch 0.2V	-0.4	300	0.3	0.133
	1	600	0.2	0.244
	5	1600	0.2	0.395

	11	2000	0.5	0.207
	25	2500	0.5	0.022
0.3V	-0.85	300	0.3	0.045
	0.6	550	0.1	0.197
	4.7	2000	0.7	0.485
	12.6	2000	0.2	0.242
	25	2500	0.5	0.03
0.4V	-0.15	550	0.6	0.243
	1.8	700	0.4	0.172
	4.2	2000	0.6	0.426
	12.5	2000	0.1	0.117
	22	2500	0.1	0.042
1.5V	-0.7	360	0.1	0.415
	0.58	370	0.15	0.352
	4.2	1500	0.4	0.053
	1.5	700	0.7	0.18
2nd dis 0.1V	-0.9	500	0.3	0.166
	0.2	330	0.15	0.116
	1.6	600	0.35	0.286
	4.7	1500	0.3	0.344
	11.5	2000	0.3	0.088
dis 0.01V	-0.1	400	0.1	0.1
	1.3	650	0.1	0.115
	5.8	1700	0.3	0.314
	13.7	2000	0.5	0.283

	28.5	3500	0.15	0.05
	-1.5	400	0.2	0.05
	-6	2500	0.3	0.087

Table S3. ^7Li NMR spectra deconvolution parameters of GF pouch cells

	Shift/ppm	LB/Hz	xG/(1-x)L	%
dis 100 mV	5.2	1695	0.46	0.979
	-1.2	205	0.64	0.021
	8.2	1000	0.5	0.664
10 mV	-0.5	1000	0.2	0.241
	-1.4	100	0.2	0.004
	22	2500	0.2	0.091
	6.4	2228	0.3	0.855
char 400 mV	-2	1000	0.1	0.084
	-1.72	50	0.5	0.061
	10.6	1900	0.3	0.713
	-0.6	1215	0.1	0.274
1500 mV	-1.72	45	8	0.013

Table S4. ^7Li NMR spectra deconvolution parameters of GFM pouch cells

	shift	LB	x	%
100mV	4	1400	0.35	0.979
	-1.37	200	0.6	0.021
10mV	9	460	0.41	0.529
	13	1300	0.29	0.106

	0.3	1020	0.33	0.334
	-1.8	65	0.11	0.031
400	4.97	1686	0.84	0.577
	15.81	2316	0.54	0.247
	-1.4	98	0.13	0.03
	0.173	2177	0.23	0.146
1500	3.3	1000	0.21	0.763
	-1.75	50	0.13	0.055
	13	1300	0.33	0.086
	-3	800	0.28	0.097

Table S5. ^{29}Si NMR spectra deconvolution parameters of GF pouch cells.

	shift/ppm	CSA	η	LB/kHz	GB/kHz	%
dis 100 mV	-10	70	0.8	11000	4000	0.861
	220	200	0.1	5000	3000	0.107
	-75	165	0.2	700	900	0.031
10 mV	30	150	0.7	10000	2000	1
char 400 mV	180	150	0.7	4000	4500	0.116
	-70	300	0.5	500	500	0.009
	-65	260	0.8	13000	2000	0.875

Table S6. ^{29}Si NMR spectra deconvolution parameters of GFM pouch cells.

	shift/ppm	CSA	η	LB/kHz	GB/kHz	%
dis 100 mV	-80	80	0.2	700	800	0.065

	-18	280	0.7	13000	2000	0.868
	225	140	0.2	2000	800	0.066
10 mV	-25	90	0.5	11500	2000	1
char 400 mV	-63	110	0.2	500	300	0.007
	-72	200	0.8	11000	2000	0.48
	180	85	0.7	13000	2000	0.514
char 1500 mV	-90	300	-0.4	7000	9600	0.936
	-85	300	0.4	700	500	0.006
	140	167	0.4	4000	5000	0.059

Table S7: Refined parameters for discharged Si anode against Li₁₅Si₄ and Li_{14.02}Mg_{0.98}Si₄.

Phase	Scale Factor	Delta2	a (Å)
Li ₁₅ Si ₄	0.4720	0.9934	10.7231
Li _{14.02} Mg _{0.98} Si ₄	0.4627	0.9504	10.7095