

Supplementary Materials for: Solvent-Free Mechanochemical Approach Towards Thiospinel MgCr₂S₄ as a Potential Electrode for Post-Lithium Ion Batteries

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Table 1. Crystallographic parameters obtained by the Rietveld analysis for the system MgH₂ + 2Cr + 4S after mechanical treatment (with 8 g ball and 875 rpm).

0.5 h BM										
	a (Å)	b (Å)	c (Å)	β (°)	γ (°)	Volume Lattice (Å ³)	Space Group	Crystallite size (Å)	Microstrain	Weight fraction
Cr	2.887	-	-	-	-	24.062	Im-3m	505	1.39 · 10 ⁻³	0.383
MgH ₂	4.519	3.022	-	-	-	61.713	P42/mnm	1212	4.74 · 10 ⁻⁴	0.108
S	10.469	12.872	24.499	-	-	3301.411	Fddd:2	1249	5.67 · 10 ⁻⁴	0.509

1 h BM										
	a (Å)	b (Å)	c (Å)	β (°)	γ (°)	Volume Lattice (Å ³)	Space Group	Crystallite size (Å)	Microstrain	Weight fraction
Cr	2.887	-	-	-	-	24.062	Im-3m	491	1.32 · 10 ⁻³	0.405
MgH ₂	4.519	3.021	-	-	-	61.693	P42/mnm	958	7.60 · 10 ⁻⁴	0.088
S	10.468	12.870	24.496	-	-	3300.179	Fddd:2	1365	5.73 · 10 ⁻⁴	0.507

2 h BM

	a (Å)	b (Å)	c (Å)	β (°)	γ (°)	Volume Lattice (Å ³)	Space Group	Crystallite size (Å)	Microstrain	Weight fraction
Cr	2.887	-	-	-	-	24.062	Im-3m	428	$1.02 \cdot 10^{-3}$	0.417
MgH ₂	4.519	3.022	-	-	-	61.713	P42/mnm	659	$7.97 \cdot 10^{-4}$	0.094
S	10.469	12.873	24.499	-	-	3301.667	Fddd:2	1289	$4.56 \cdot 10^{-4}$	0.489

4 h BM

	a (Å)	b (Å)	c (Å)	β (°)	γ (°)	Volume Lattice (Å ³)	Space Group	Crystallite size (Å)	Microstrain	Weight fraction
Cr	2.887	-	-	-	-	24.062	Im-3m	460	$1.08 \cdot 10^{-3}$	0.448
MgH ₂	4.520	3.021	-	-	-	61.720	P42/mnm	418	$7.67 \cdot 10^{-4}$	0.90
S	10.469	12.873	24.499	-	-	3301.667	Fddd:2	1180	$5.50 \cdot 10^{-4}$	0.462

MSR event (5h)

	a (Å)	b (Å)	c (Å)	β (°)	γ (°)	Volume Lattice (Å ³)	Space Group	Crystallite size (Å)	Microstrain	Weight fraction
Cr ₃ S ₄	5.955	3.433	11.359	90.99	-	232.183	C2/m	666	$3.27 \cdot 10^{-3}$	0.360
MgS	5.189	-	-	-	-	139.718	Fm-3m	426	$2.51 \cdot 10^{-3}$	0.297
S	10.486	12.898	24.524	-	-	3316.832	P42/mnm	1180	$5.50 \cdot 10^{-4}$	0.040
MgCr ₂ S ₄	10.195	-	-	-	-	1059.648	Fd-3m	194	$3.38 \cdot 10^{-3}$	0.303

	a (Å)	b (Å)	c (Å)	β (°)	γ (°)	Volume Lattice (Å ³)	Space Group	Crystallite size (Å)	Microstrain	Weight fraction
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Cr₂S₃	5.933	-	11.16 8	-	120	340.451	P-31 C	293	$6.84 \cdot 10^{-3}$	0.717
MgS	5.185	-	-	-	-	139.395	Fm-3m	2267	$3.20 \cdot 10^{-3}$	0.115
MgCr₂S₄	10.09 4	-	-	-	-	1029.995	Fd-3m	405	$4.77 \cdot 10^{-3}$	0.168

MSR event + TT

8 h BM

	a (Å)	b (Å)	c (Å)	β (°)	γ (°)	Volume Lattice (Å ³)	Space Group	Crystallite size (Å)	Microstrain	Weight fraction
Cr₃S₄	5.954	3.407	11.352	90.875	-	230.252	C2/m	160	$5.64 \cdot 10^{-3}$	0.522
MgS	5.161	-	-	-	-	137.468	Fm-3m	811	$9.50 \cdot 10^{-3}$	0.328
MgCr₂S₄	10.088	-	-	-	-	1026.633	Fd-3m	81	$4.86 \cdot 10^{-3}$	0.150

Table S2. Crystallographic parameters obtained from the Rietveld analysis for the system Mg + 2Cr + 4S after mechanical treatment (with 8 g ball and 875 rpm).

1 h BM

	a (Å)	b (Å)	c (Å)	β (°)	γ (°)	Volume Lattice (Å ³)	Space Group	Crystallite size (Å)	Microstrain	Weight fraction
Cr	2.887	-	-	-	-	24.062	Im-3m	468	$1.28 \cdot 10^{-3}$	0.366
Mg	3.210	5.212	-	-	12 0	46.510	P63/mm c	1629	$7.52 \cdot 10^{-4}$	0.141
S	10.468	12.871	24.494	-	-	3300.165	Fddd:2	1229	$5.07 \cdot 10^{-4}$	0.493

2 h BM

	a (Å)	b (Å)	c (Å)	β (°)	γ (°)	Volume Lattice (Å ³)	Space Group	Crystallite size (Å)	Microstrain	Weight fraction
Cr	2.887	-	-	-	-	24.062	Im-3m	483	$1.30 \cdot 10^{-3}$	0.421
Mg	3.211	5.213	-	-	12	46.548	P63/mm	1489	$9.71 \cdot 10^{-4}$	0.110

					0		c			
S	10.470	12.873	24.498	-	-	3301.848	Fddd:2	1345	$7.61 \cdot 10^{-4}$	0.469

4 h BM

	a (Å)	b (Å)	c (Å)	β (°)	γ (°)	Volume Lattice (Å ³)	Space Group	Crystallite size (Å)	Microstrain	Weight fraction
Cr	2.888	-	-	-	-	24.087	Im-3m	473	$1.29 \cdot 10^{-3}$	0.464
Mg	3.212	5.216	-	-	120	46.604	P63/mmc	726	$6.35 \cdot 10^{-4}$	0.102
S	10.472	12.879	24.504	-	-	3304.827	Fddd:2	1232	$6.94 \cdot 10^{-4}$	0.434

MSR event (6 h 20 min)

	a (Å)	b (Å)	c (Å)	β (°)	γ (°)	Volume Lattice (Å ³)	Space Group	Crystallite size (Å)	Microstrain	Weight fraction
Cr ₃ S ₄	5.970	3.413	11.439	91.317	-	233.015	C2/m	213	$5.26 \cdot 10^{-3}$	0.593
MgS	5.181	-	-	-	-	139.072	Fm-3m	740	$8.56 \cdot 10^{-3}$	0.240
S	10.486	12.898	24.524	-	-	3316.832	P42/mnm	1180	$5.50 \cdot 10^{-4}$	0.034
MgCr ₂ S ₄	10.108	-	-	-	-	1032.751	Fd-3m	137	$8.72 \cdot 10^{-3}$	0.133

8 h BM

	a (Å)	b (Å)	c (Å)	β (°)	γ (°)	Volume Lattice (Å ³)	Space Group	Crystallite size (Å)	Microstrain	Weight fraction
Cr ₃ S ₄	5.986	3.399	11.486	91.499	-	233.619	C2/m	182	$5.07 \cdot 10^{-3}$	0.497
MgS	5.174	-	-	-	-	138.509	Fm-3m	786	$9.64 \cdot 10^{-3}$	0.330
S	10.486	12.898	24.524	-	-	3316.832	P42/mnm	1180	$5.50 \cdot 10^{-4}$	0.016

MgCr ₂ S	10.10	-	-	-	-	1030.301	Fd-3m	100	6.63 · 10 ⁻³	0.157
₄	0									

16 h BM

	a (Å)	b (Å)	c (Å)	β (°)	γ (°)	Volume Lattice (Å ³)	Space Group	Crystallite size (Å)	Microstrain	Weight fraction
Cr ₃ S ₄	5.952	3.398	11.483	91.626	-	232.149	C2/m	83	1.25 · 10 ⁻⁴	0.627
MgS	5.159	-	-	-	-	137.308	Fm-3m	779	1.36 · 10 ⁻³	0.216
MgCr ₂ S	9.824	-	-	-	-	948.124	Fd-3m	32	1.39 · 10 ⁻³	0.157
₄										

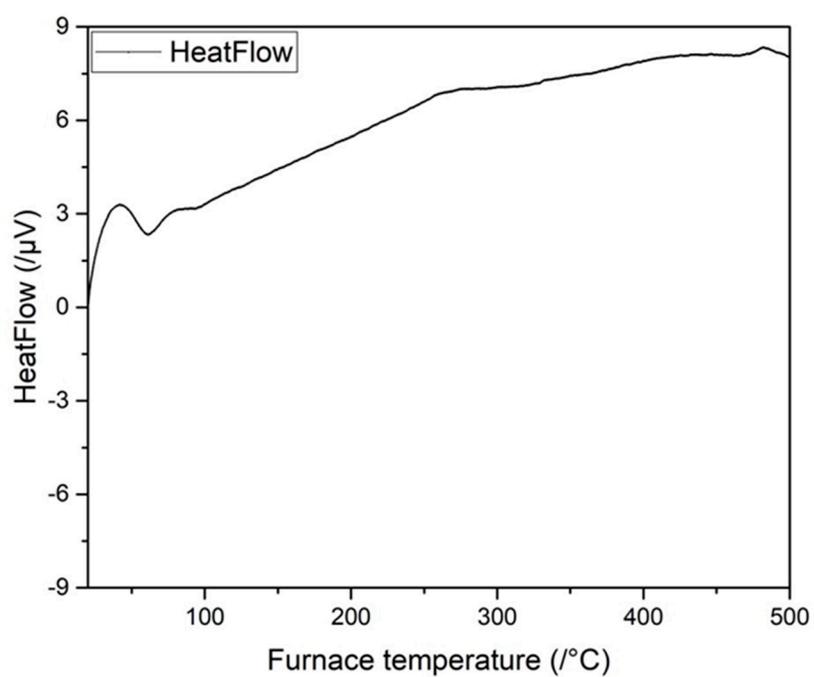


Figure S1. DSC profile of the system MgH₂ + 2Cr + 4S collected at the ignition time of 5 h BM.

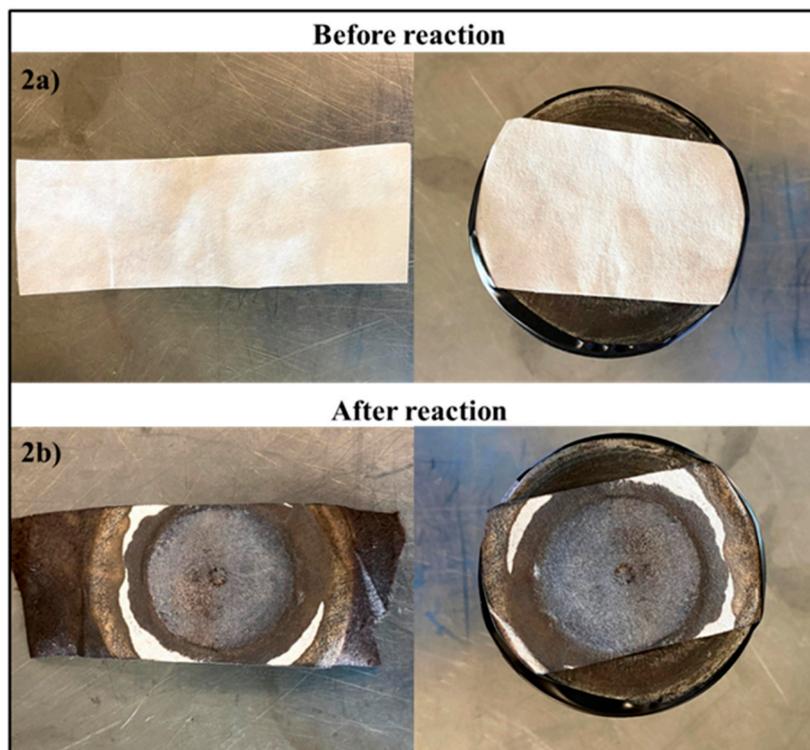


Figure S2. Pictures captured before (2a) and after (2b) the MRS reaction. The white lead acetate paper (2a) becomes dark (b) upon BM for 5 h proving the H₂S evolution.

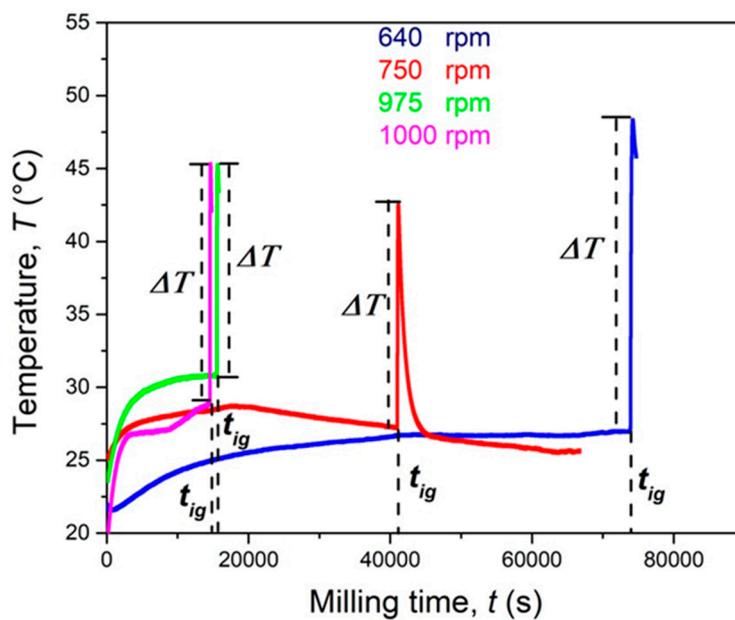


Figure S3. Temperature profiles acquired during the experiments carried out at increasing milling speed from 640 to 1000 rpm.

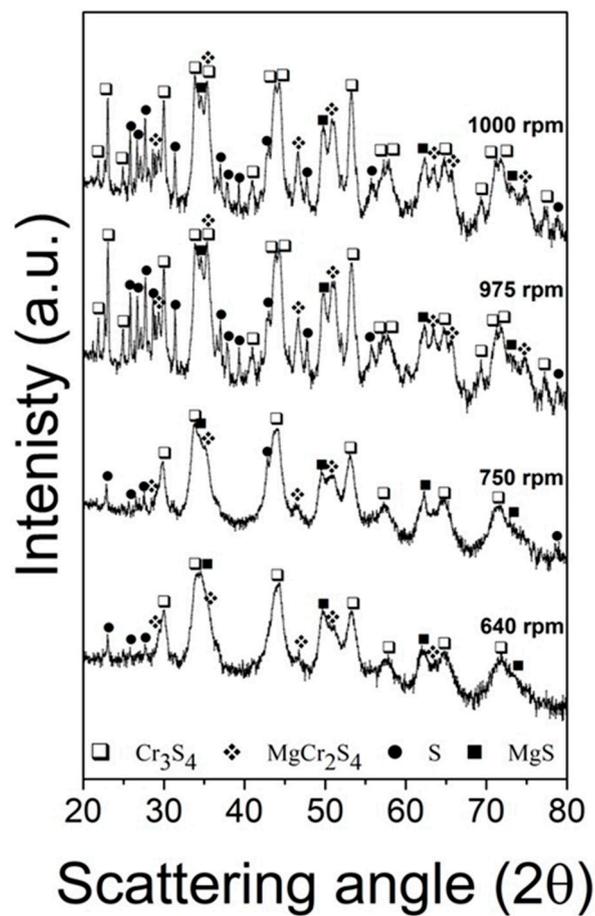


Figure S4. XRD patterns of the powders milled at different rotation speed and collected after the combustive reaction.

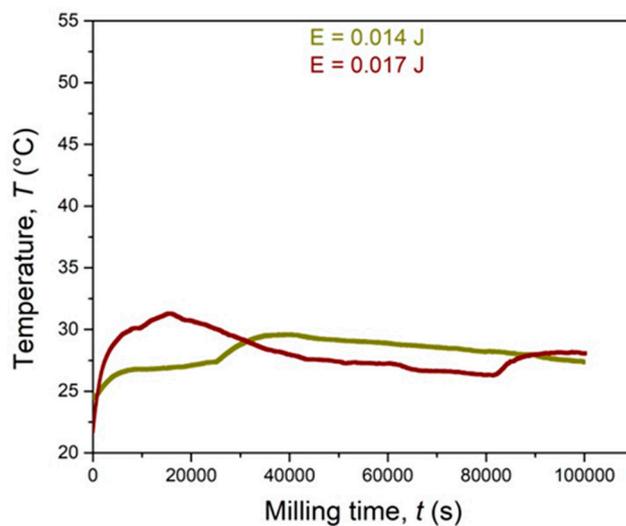


Figure S5. Temperature profiles acquired during the experiments carried out varying the operative condition: 550 rpm with 8 g ball ($E = 0.014 \text{ J}$) and 875 rpm with 2 g ball ($E = 0.017 \text{ J}$).

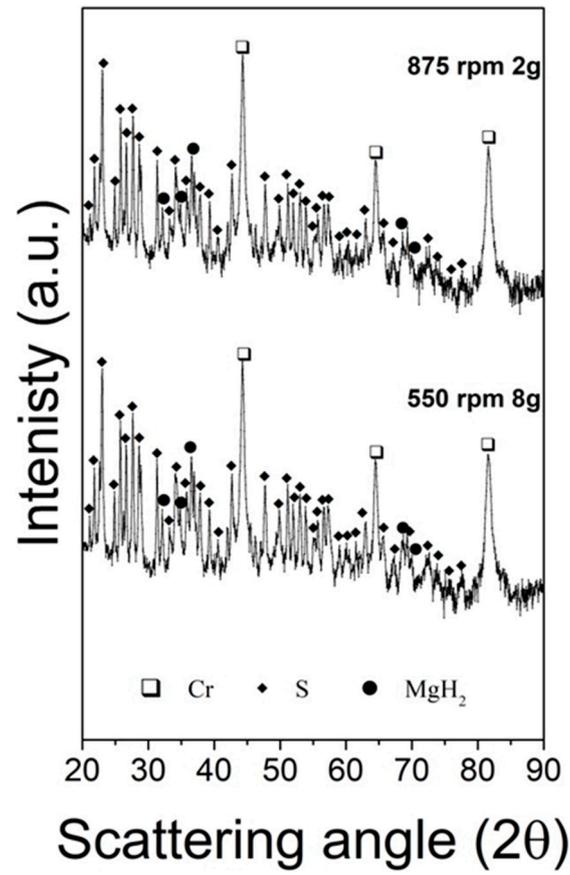


Figure S6. XRD patterns acquired during the syntheses at 550 rpm with 8 g ball and 875 rpm with 2 g ball.