Supplementary Information (SI) for RSC Mechanochemistry.

Supplementary information to the manuscript

Mechanistic investigation of the mechanochemical reduction of $LiCoO_2$ with Al in the context of lithium-ion battery recycling

Raphael Sieweck (a), Arseniy Bokov (a, b), Oleksandr Dolotko (a, b), Thomas Bergfeldt (a), Udo Geckle (a), Michael Knapp (a), Helmut Ehrenberg (a, b)

(a) Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Karlsruhe, Germany.
(b) Helmholtz-Institute Ulm for Electrochemical Energy Storage (HIU), P.O. Box 3640, D-76021 Karlsruhe, Germany

Kinematic equations and respective parameters

The kinematic equations used in the article were derived by Burgio, who expressed velocities, accelerations, collision frequency and energies as functions of system parameters and experimental parameters of a planetary ball mill.[1] The equations 1-9 were adapted by Kessler to the Pulverisette 7 (Fritsch).[2] The kinetic energy ΔE_b transferred from a ball to the powder by a single collision between the ball and the wall of the milling jar can be calculated after equation 1. K_a is a constant reflecting the elasticity of an impact. It can be assumed as fully inelastic and is set to 1. v_b and v_s represent the ball velocity before and after the collision respectively and m_b is the mass of a ball. ω_j and ω_p are the angular velocity in rad/s of the milling jar and of the plate respectively. ω_j is fixed at -2ω_p and ω_p can be obtained from the set rotation speed v_R as $\omega_p = 2\pi * v_R/60$. R_J and R_P are the radius of the milling jar and of the plate respectively and d_b is the diameter of the milling balls.

ΔE_b should be corrected by the yield coefficient φ_b which depends on the number and size of the balls in relation to the volume and surface area of the milling jar. It takes the ball-to-ball interaction in account and was calculated according to equations 5-7.

The collision frequency f_b is given by equation 8, where K is related to the time which is required for the energy transferred to the powder. It can be assumed to be close to one and cancels out in subsequent equations.

Equations for kinematic calculations:

$$\Delta E_b = \frac{1}{2} K_a m_b \left(v_b^2 - v_s^2\right)$$

$$= -m_b \left(\frac{\omega_J^3 \left(R_J - \frac{d_b}{2}\right)}{\omega_P} + \omega_P \omega_J R_P \right) \left(R_J - \frac{d_b}{2}\right)$$

$$= 8 m_b \left(\frac{\pi v_R}{60}\right)^2 \left(4\left(R_J - \frac{d_b}{2}\right)^2 + R_P\left(R_J - \frac{d_b}{2}\right)\right)$$

(1)[2]

$$\omega_P = \frac{2\pi\, v_R}{60}$$

(2)[2]

$$\omega_J = -2\omega_P$$

(3)[2]

$$\Delta E_b^* = \varphi_b \Delta E_b$$

(4)[2]

$$\varphi_b = 1 - \left(\frac{N_b}{N_{bv}}\right)^{\varepsilon}$$

(5)[2]

$$N_{bs} = \frac{\pi\left(2R_J - d_b\right) H_J}{3 d_b^2}$$

(6)[2]

$$\varepsilon = \log_{10}(0.05) / \log_{10}\left(\frac{N_{bs}}{N_{bv}}\right)$$

(7)[2]

$$f_b = \frac{K\left(\omega_P - \omega_J\right)}{2\pi} = \frac{K v_R}{20}$$

(8)[2]

$$N_{tot} = N_b * f_b * t_{ig}$$

(9)[2]

$$D_{ig} = \frac{N_b f_b t_{ig} \Delta E_b^*}{m_p}$$

(10)[3]

$$D_{ig}^* = \frac{N_b f_b t_{ig}\left(\Delta E_b^* - E_0\right)}{m_p}$$

(11)[3]

$$d_{drum} = \frac{v_b^2}{2\,g} * \frac{1}{0{,}55}$$

(12)[4]

Table S 1: parameters for kinematic calculations.

Variable	Name	Value
ΔE_b	Energy transferred to the powder by an impact	Equation 2
K_a	Constant for elasticity of a collision	1
m_b	Ball mass	Table S 2
v_b	Ball velocity at impact	
v_s	Ball velocity after impact	
ω_p	Angular velocity of the plate	Equation 2
ω_j	Angular velocity of the milling jar	Equation 3
v_R	Rotation speed of the plate	Set between 200 – 950 rpm
R_J	Radius of milling jar	0.02315 m
R_P	Radius of the plate	0.07 m
d_b	Diameter of a ball	Table S 2
ΔE_b^*	Corrected Energy transferred to the powder by an impact	Equation 4
φ_b	Yield coefficient	Equation 5
N_b	Number of balls	Counted
N_{bv}	Number of balls to completely fill the milling jar	Counted, Table S 2
N_{bs}	Number of balls to cover 1/3 of the milling jar´s wall	Equation 6, Table S 2
ε	Parameter	Equation 7, Table S 2
H_J	Height of the milling jar	0.0453 m
f_b	Collision frequency of one ball	Equation 8
K	Constant	Cancels out (close to 1)
N_{tot}	Number of total collisions	Equation 9
t_{ig}	Milling time until the spike in pressure	Measured
m_p	Mass of the powder	Measured
D_{drum}	Diameter of a drum mill	Equation 12

Table S 2: Values for kinematic calculations depending on the ball size.

d_b [mm]	m_b [g]	N_{bv}	N_{bs}	ε
3	0.109	3223	228.2	1.131
6.35	1.011	314	47.0	1.577
12.7	8.202	32	9.88	2.550

Table S 3: Experimental and calculated data presented in Figure 1. Milling of LCO with Al at different rotation speeds.

rotation speed [rpm]	ball diameter [mm]	total ball mass [g]	powder mass [g]	ignition time [s]	number of balls	$\frac{10^{-8}}{N_{tot}}$	ΔE_b^* [mJ]	D_{ig} [J]	D_{ig}^* [J]
200	6.35	65.69	2.19	28841	65	5.33	2.43	20842	3718
200	6.35	65.33	2.18	19505	65	7.89	2.43	14173	2529
200	6.35	65.28	2.17	21148	65	7.27	2.43	15402	2748
350	6.35	65.89	2.20	1669	65	52.7	7.46	6444	4716
350	6.35	65.28	2.18	1731	65	50.8	7.46	6746	4936
350	6.35	65.29	2.18	1695	65	51.9	7.46	6605	4833
500	6.35	65.77	2.19	447	65	138	15.21	5041	4378
500	6.35	65.34	2.18	452	65	136	15.21	5131	4457
500	6.35	65.37	2.18	457	65	135	15.21	5188	4506
650	6.35	60.12	2.00	194	59	269	26.04	4835	4464
650	6.35	65.47	2.18	182	65	260	25.71	4530	4177
650	6.35	65.60	2.19	193	65	245	25.71	4794	4421
800	6.35	65.59	2.19	84	65	458	38.95	3890	3691
800	6.35	65.41	2.18	84	65	458	38.95	3901	3701
800	6.35	65.34	2.18	87	65	442	38.95	4045	3838
950	6.35	65.58	2.19	53	65	611	54.92	4111	3962
950	6.35	65.37	2.18	63	65	514	54.92	4903	4724
950	6.35	65.58	2.18	60	65	540	54.92	4667	4497

Table S 4: Experimental and calculated data presented in Figure 2: Milling of LCO with Al at different SBR using small balls.

Rotation speed [rpm]	ball diameter [mm]	total ball mass [g]	powder mass [g]	SBR	ignition time [s]	number of balls	$\frac{10^{-8}}{N_{tot}}$	ΔE_b^* [mJ]	Dig [J]
650	3	65.40	1.31	0.020	153	601	33.5	2.9	6645
650	3	65.41	1.31	0.020	158	601	32.4	2.9	6861
650	3	60.16	1.20	0.020	150	553	37.1	3.0	6619
650	3	65.49	1.32	0.020	160	602	31.9	2.9	6899
650	3	60.82	2.00	0.033	241	559	22.8	2.9	6447
650	3	65.45	2.18	0.033	251	601	20.4	2.9	6536
650	3	65.45	2.18	0.033	261	601	19.6	2.9	6796
650	3	65.45	2.18	0.033	221	601	23.2	2.9	5755
650	3	60.12	2.00	0.033	217	552	25.7	3.0	5741
650	3	60.09	4.00	0.067	673	552	8.3	3.0	8919
650	3	65.38	4.36	0.067	564	601	9.1	2.9	7351
650	3	65.38	4.36	0.067	699	601	7.3	2.9	9111
650	3	65.37	4.36	0.067	554	600	9.3	2.9	7213
650	3	60.07	4.00	0.067	623	552	8.9	3.0	8249
650	3	60.18	6.02	0.100	636	553	8.7	3.0	5612
650	3	65.42	6.54	0.100	456	601	11.2	2.9	3960
650	3	65.42	6.54	0.100	462	601	11.1	2.9	4012
650	3	65.40	6.54	0.100	643	601	8.0	2.9	5585
650	3	60.11	6.01	0.100	552	552	10.1	3.0	4869
650	3	65.44	8.17	0.125	546	601	9.4	2.9	3795
650	3	60.19	7.52	0.125	536	553	10.4	3.0	3783
650	3	60.19	7.52	0.125	741	553	7.5	3.0	5229
650	3	65.42	8.18	0.125	543	601	9.4	2.9	3772
650	3	65.39	8.18	0.125	554	601	9.2	2.9	3849

Table S 5: Experimental and calculated data presented in Figure 2: Milling of LCO with Al at different SBR using medium balls.

Rotation speed [rpm]	ball diameter [mm]	total ball mass [g]	powder mass [g]	SBR	ignition time [s]	number of balls	$\frac{10^{-7}}{N_{tot}}$	ΔEb* [mJ]	Dig [J]
650	6.35	65.74	1.315	0.020	123	65	38.5	25.7	5082
650	6.35	65.78	1.316	0.020	127	65	37.3	25.7	5243
650	6.35	60.51	1.210	0.020	126	60	40.7	26.0	5276
650	6.35	65.34	1.307	0.020	112	65	42.3	25.7	4655
650	6.35	60.12	2.004	0.033	194	59	26.9	26.0	4835
650	6.35	60.90	2.030	0.033	185	60	27.7	26.0	4618
650	6.35	65.78	2.193	0.033	185	65	25.6	25.7	4583
650	6.35	65.60	2.187	0.033	193	65	24.5	25.7	4794
650	6.35	65.47	2.182	0.033	182	65	26.0	25.7	4530
650	6.35	65.90	4.393	0.067	354	65	13.4	25.7	4377
650	6.35	60.73	4.049	0.067	307	60	16.7	26.0	3843
650	6.35	65.17	4.345	0.067	386	64	12.5	25.8	4762
650	6.35	60.78	6.078	0.100	681	60	7.5	26.0	5678
650	6.35	65.28	6.528	0.100	567	65	8.3	25.7	4718
650	6.35	65.24	6.524	0.100	635	65	7.5	25.7	5287
650	6.35	60.13	7.516	0.125	706	59	7.4	26.0	4691
650	6.35	65.81	8.227	0.125	765	65	6.2	25.7	5051
650	6.35	65.29	8.162	0.125	800	65	5.9	25.7	5324

Table S 6: Experimental and calculated data presented in Figure 2: Milling of LCO with Al at different SBR using large balls.

Rotation speed [rpm]	ball diameter [mm]	total ball mass [g]	powder mass [g]	SBR	ignition time [s]	number of balls	$\frac{10^{-6}}{N_{tot}}$	ΔE_b^* [mJ]	Dig [J]
650	12.7	65.73	1.300	0.020	144	8	26.7	170.1	4898
650	12.7	65.48	1.310	0.020	134	8	28.7	170.1	4525
650	12.7	65.49	1.310	0.020	119	8	32.3	170.1	4017
650	12.7	65.46	2.182	0.033	156	8	24.7	170.1	3161
650	12.7	65.62	2.187	0.033	190	8	20.2	170.1	3841
650	12.7	65.72	2.191	0.033	175	8	22.0	170.1	3532
650	12.7	65.73	4.382	0.067	295	8	13.0	170.1	2977
650	12.7	65.48	4.366	0.067	281	8	13.7	170.1	2846
650	12.7	65.44	4.362	0.067	270	8	14.2	170.1	2737
650	12.7	65.66	6.566	0.100	274	8	14.0	170.1	1845
650	12.7	65.49	6.549	0.100	327	8	11.8	170.1	2208
650	12.7	65.54	6.555	0.100	505	8	7.6	170.1	3407
650	12.7	65.41	6.541	0.100	424	8	9.1	170.1	2867
650	12.7	65.50	8.187	0.125	508	8	7.6	170.1	2744
650	12.7	65.51	8.189	0.125	440	8	8.7	170.1	2376
650	12.7	65.53	8.191	0.125	526	8	7.3	170.1	2840

Additional figures

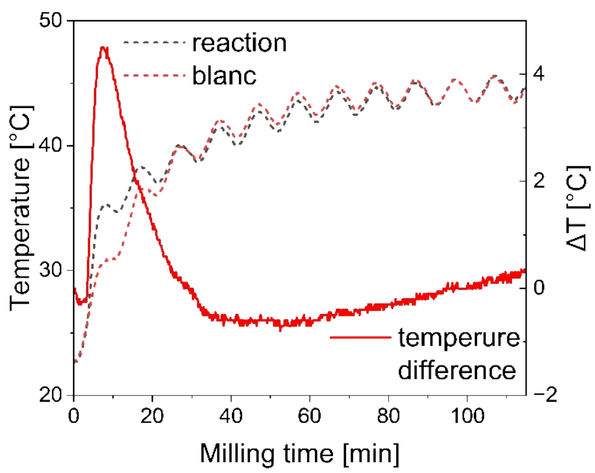

Figure S 1: Temperature profile of the mechanochemical reduction of LCO with Al at 650 rpm using 60 balls (6.35 mm), 2.0 g of powder, LCO/Al =1.0 and a SBR of 0.033 using repeating cycles of 5 minutes milling and 5 min resting.

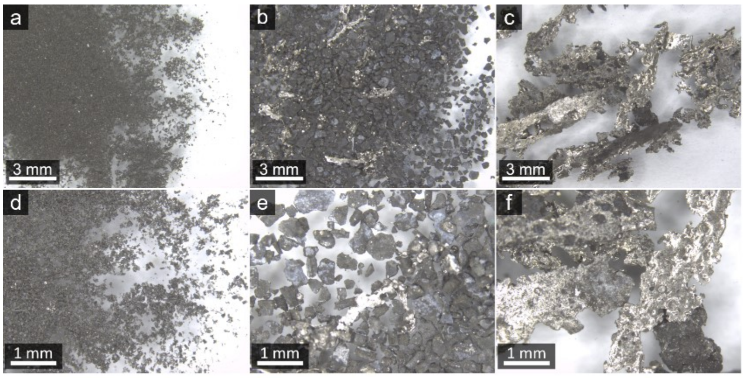

Figure S 2: Light microscopy images of Sample III, after sieving. The fractions belong to 90 µm and less (a,d), 90-500 µm (b,e), and larger than 500 µm (c,f). The sample was collected after 3.2 min, when the spike in pressure was observed in the mechanochemical reaction between LCO and Al at 650 rpm with 60 balls (6.35 mm), 2.0 g of powder, LCO/Al =1.0 and a SBR of 0.033

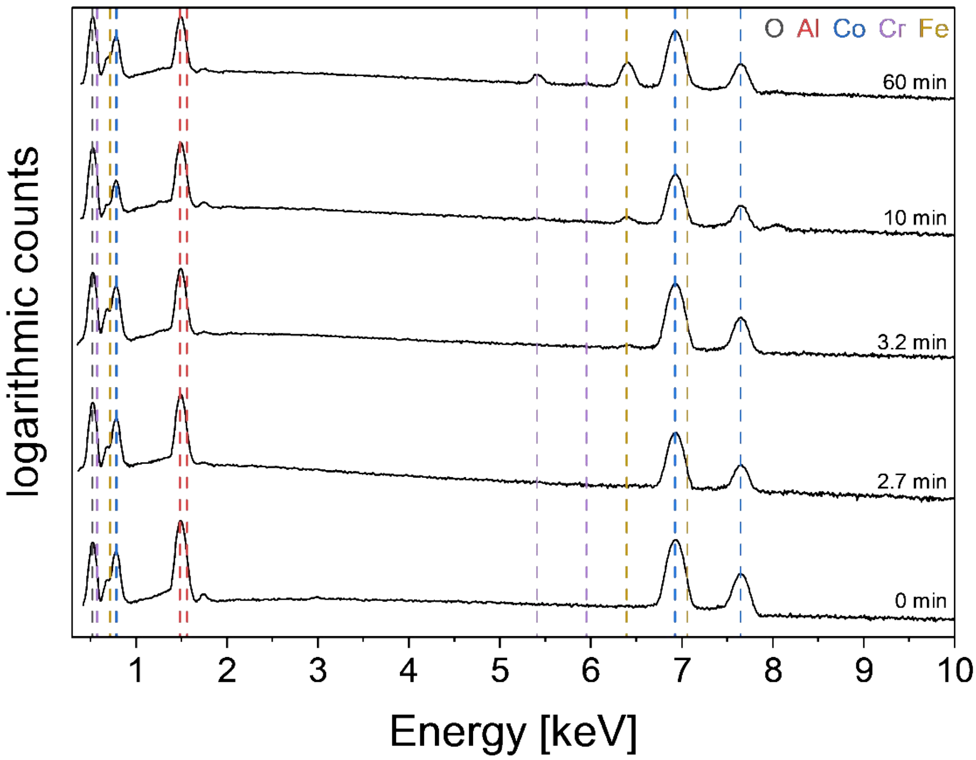

Figure S 3: EDX spectra of samples collected from the mechanochemical reaction between LCO and Al at 650 rpm with 60 balls (6.35 mm), 2.0 g of powder, LCO/Al =1.0 and a SBR of 0.033 using repeating cycles of 5 minutes milling and 5 min resting

Table S 7: Elemental composition, determined by ICP-OES, of Products obtained after mechanochemical reaction between LCO and Al at 650 rpm using 60 balls (6.35 mm), 2.0 g of powder, LCO/Al =1.0 and a SBR of 0.033 using repeating cycles of 5 minutes milling and 5 min resting. A large metallic piece was obtained milling was stopped after 3.2 min, directly after the spike in pressure was observed. A homogenous powder was analyzed after 60 min of total milling.

Element	metallic piece [wt.%]	LCO milled with Al for 1h [wt.%]
Li	0.01	4.56
Al	0.24	17.12
Co	97.00	39.44
Cr	N.A.	0.44
Fe	N.A.	2.72
Sum	**97.25**	**64.28**

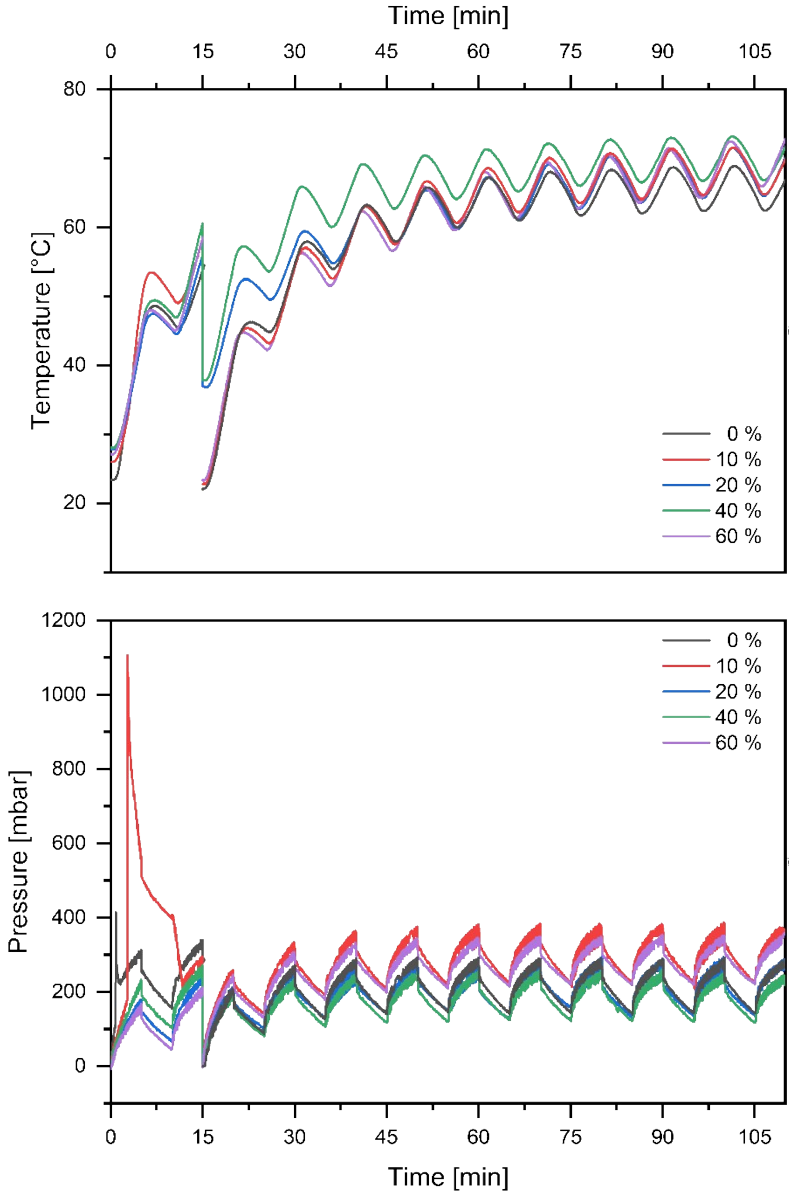

Figure S 4: Recorded temperature and pressure profiles of the mechanochemical reduction of LCO with Al in the presence of different amounts of graphite (0-60 wt%). Experiments were performed at 950 rpm using 2.0 g powder, 60 balls of 6.35 mm diameter, a SBR of 0.033 and alternating cycles of 5 min milling and resting.

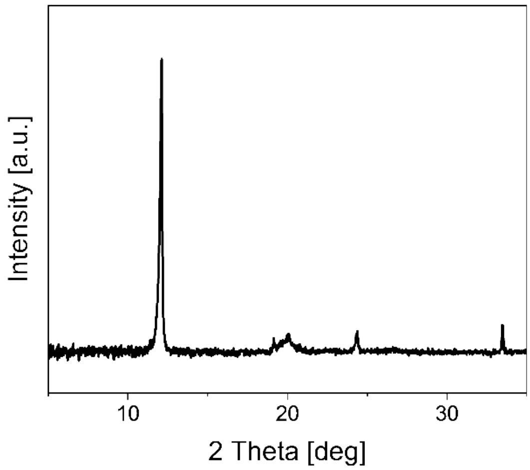

Figure S 5: XRD pattern of pristine graphite.

References

1 N. Burgio, A. Iasonna, M. Magini, S. Martelli and F. Padella, *Il Nuovo Cimento D*, 1991, **13**, 459–76.
2 M. Kessler and R. Rinaldi, *Front. Chem.*, 2022, **9**, 816553.
3 L. Caggiu, S. Enzo, L. Stievano, R. Berthelot, C. Gerbaldi, M. Falco, et al., *Batteries*, DOI:10.3390/batteries6030043.
4 H. Zoz, H. Ren, R. Reichardt and H. U. Benz, High Energy Milling / Mechanical Alloying / Reactive Milling, https://group.zoz.de/zoz.main/pdf_content/publications/v14.pdf, (accessed October 24, 2024).