Supporting information to the manuscript

Revealing the mechanism of reductive, mechanochemical Li recycling from $LiFePO_4$

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Table S1: Fit parameters used to describe the Fe Mössbauer spectra of LFP ball-milled for up to 5 h with Al metal foil (1:3 molar ratio of LFP to Al): isomer shift (IS), quadrupole splitting (QS), Hyperfine field (B_{hf}), line width (Γ), and area fraction. IS, QS, and Γ are given in mm/s. B_{hf} is given in T.

sample		IS	QS	B_{hf}	Γ	area frac.
pristine	Fe^{2+}	1.28 ± 0.01	3.13 ± 0.01	-	0.31 ± 0.01	94.0 %
	Fe^{3+}	0.79 ± 0.05	0.41 ± 0.26	-	0.40 ± 0.30	6.0 %
0.25 h	Fe^{2+}	1.28 ± 0.01	3.10 ± 0.01	-	0.35 ± 0.01	79.2 %
	Fe^{3+}	0.45 ± 0.02	0.78 ± 0.03	-	0.67 ± 0.04	20.8 %
0.5 h	Fe^{2+}	1.28 ± 0.01	3.11 ± 0.01	-	0.34 ± 0.01	76.4 %
	Fe^{3+}	0.43 ± 0.01	0.85 ± 0.01	-	0.61 ± 0.02	23.6 %
1 h	Fe^{2+}	1.47 ± 0.01	2.71 ± 0.03	-	0.33 ± 0.04	6.7 %
	Fe^{x+}	0.65 ± 0.01	0.44 ± 0.01	-	0.45 ± 0.02	27.4 %
	Fe^{y+}	0.18 ± 0.01	-	-	0.07 ± 0.01	65.9 %
2 h	Fe^{x+}	0.45 ± 0.01	0.78 ± 0.01	-	0.41 ± 0.02	27.3 %
	Fe^{y+}	0.29 ± 0.01	0.30 ± 0.01	-	0.64 ± 0.01	72.7 %
3 h	Fe^{x+}	0.41 ± 0.01	0.64 ± 0.02	-	0.60 ± 0.02	65.8 %
	Fe^{y+}	0.22 ± 0.02	0.34 ± 0.03	-	0.48 ± 0.04	34.2 %
5 h	Fe^{x+}	0.43 ± 0.01	0.64 ± 0.01	-	0.51 ± 0.01	53.7 %
	Fe^{y+}	0.20 ± 0.01	0.41 ± 0.01	-	0.43 ± 0.01	29.7 %
	Fe^{0}	-0.00 ± 0.02	0.06 ± 0.03	31.3 ± 0.1	1.13 ± 0.05	16.6 %

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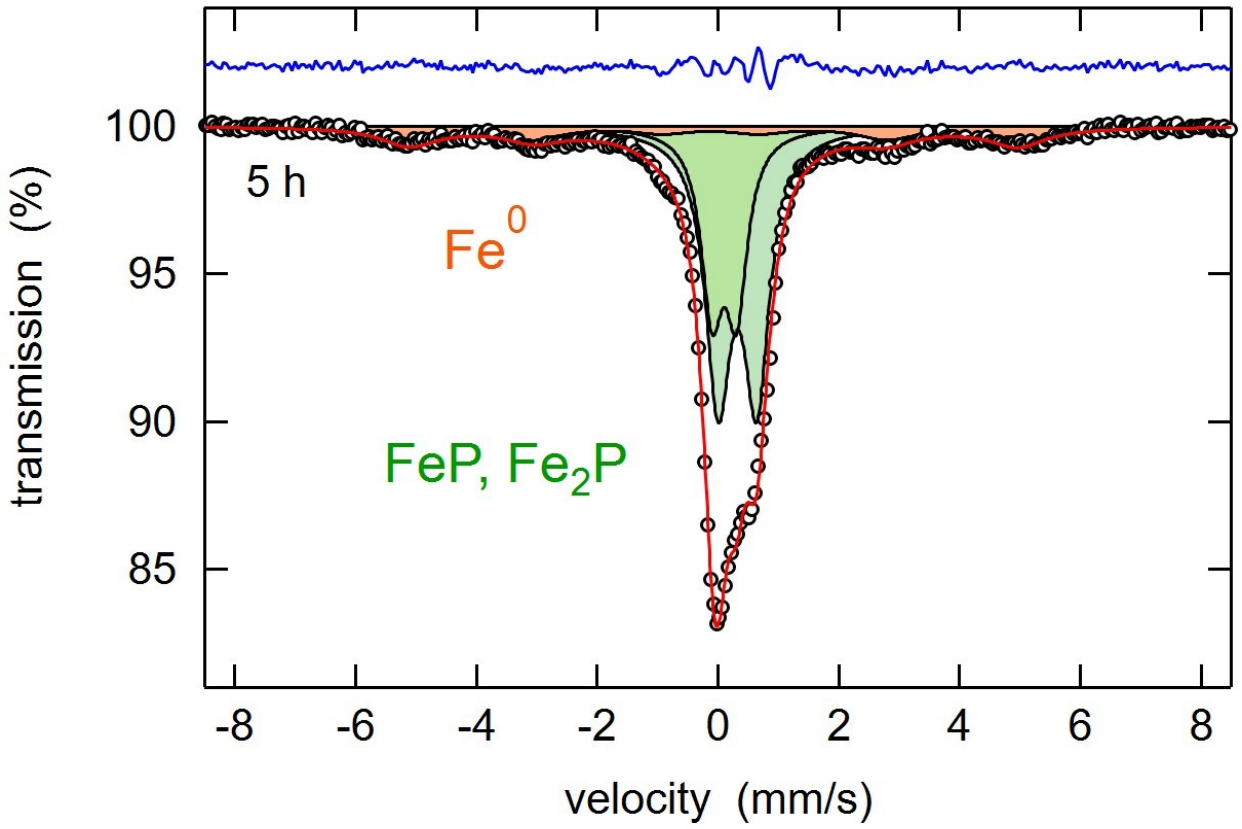

Figure S1: Mössbauer spectrum of LFP ball-milled with Al for 5 h (1:3 molar ratio of LFP to Al).

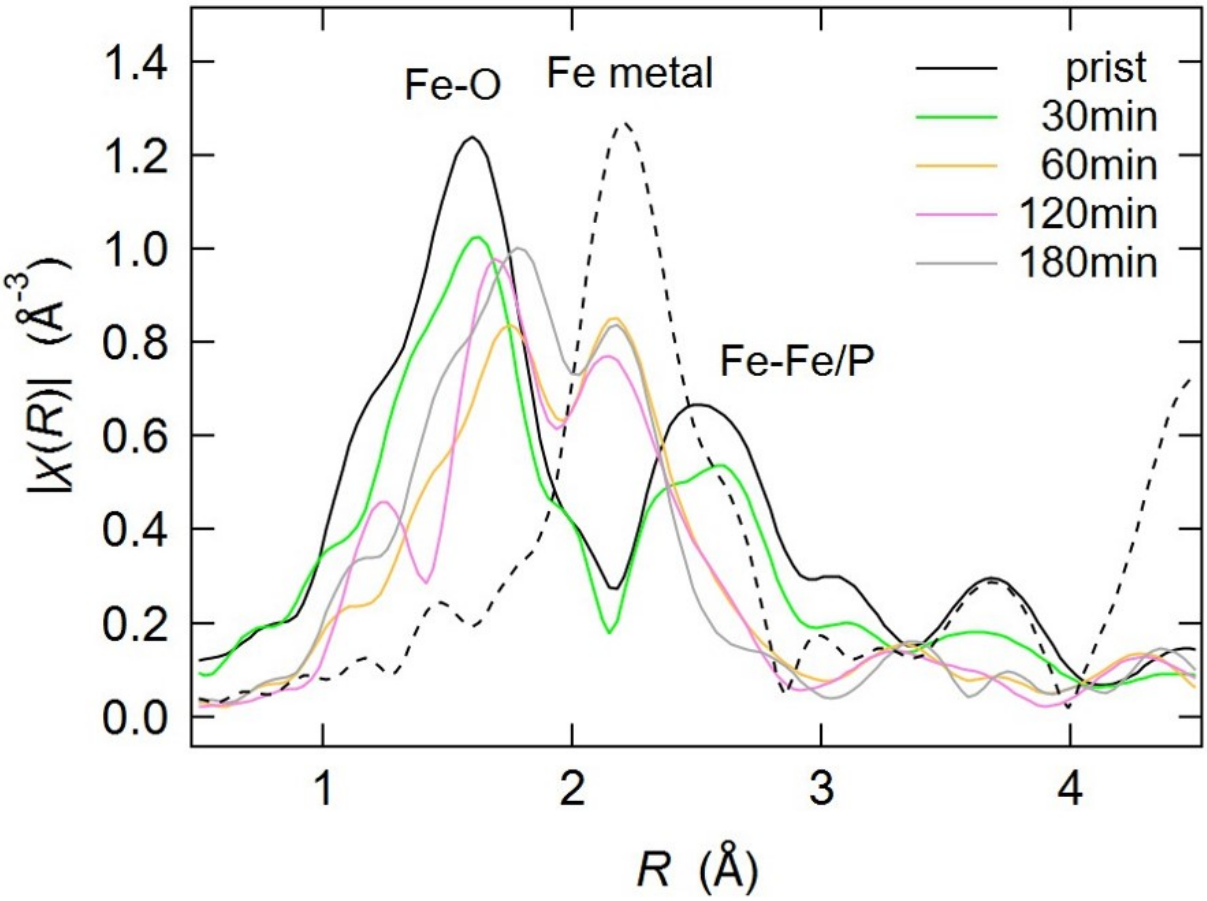

Figure S2: Fourier-transformed Fe K-edge extended X-ray absorption fine structure (EXAFS) spectra of pristine LFP and LFP ball-milled with Al metal foil for 0.5 h to 5 h (1:3 molar ratio of LFP to Al). The radial distribution function of elemental iron was plotted for comparison.

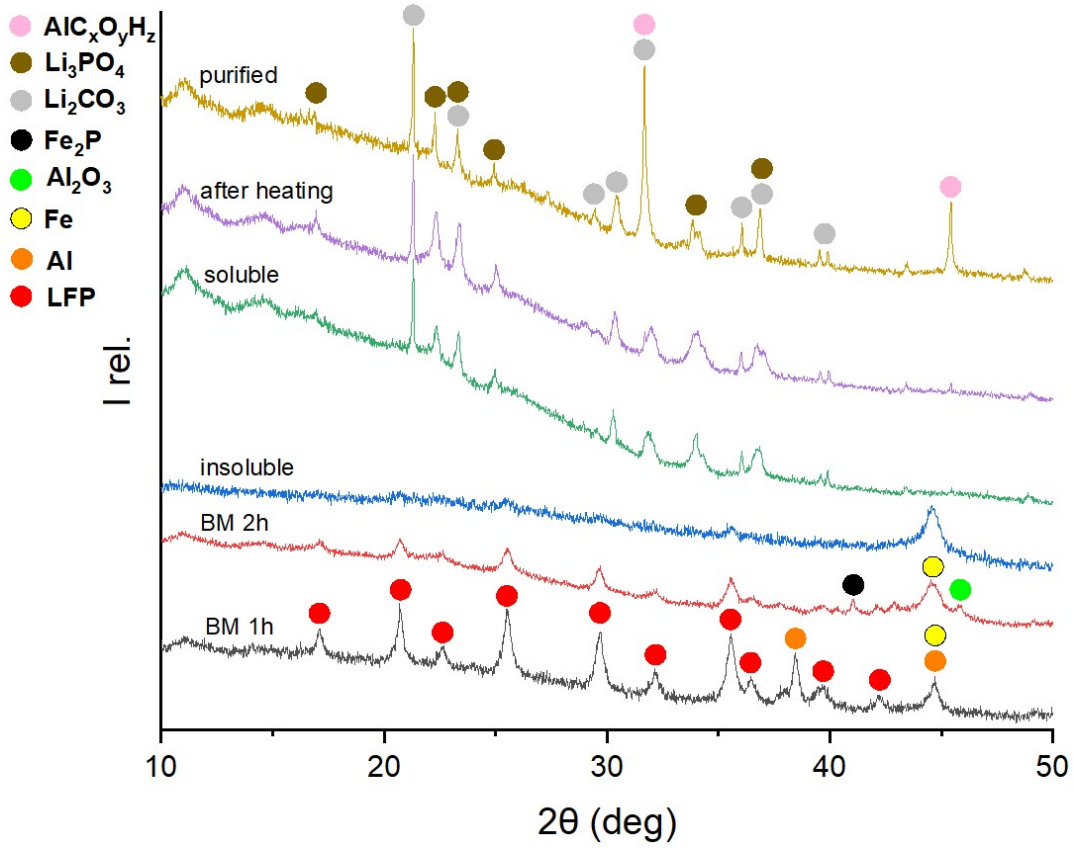

Figure S3: XRD patterns of the products after ball-milling, leaching and purification process obtained from a 1:1 molar mixture of LFP and Al. The most intense Bragg-reflections are assigned to different phases for analysis.

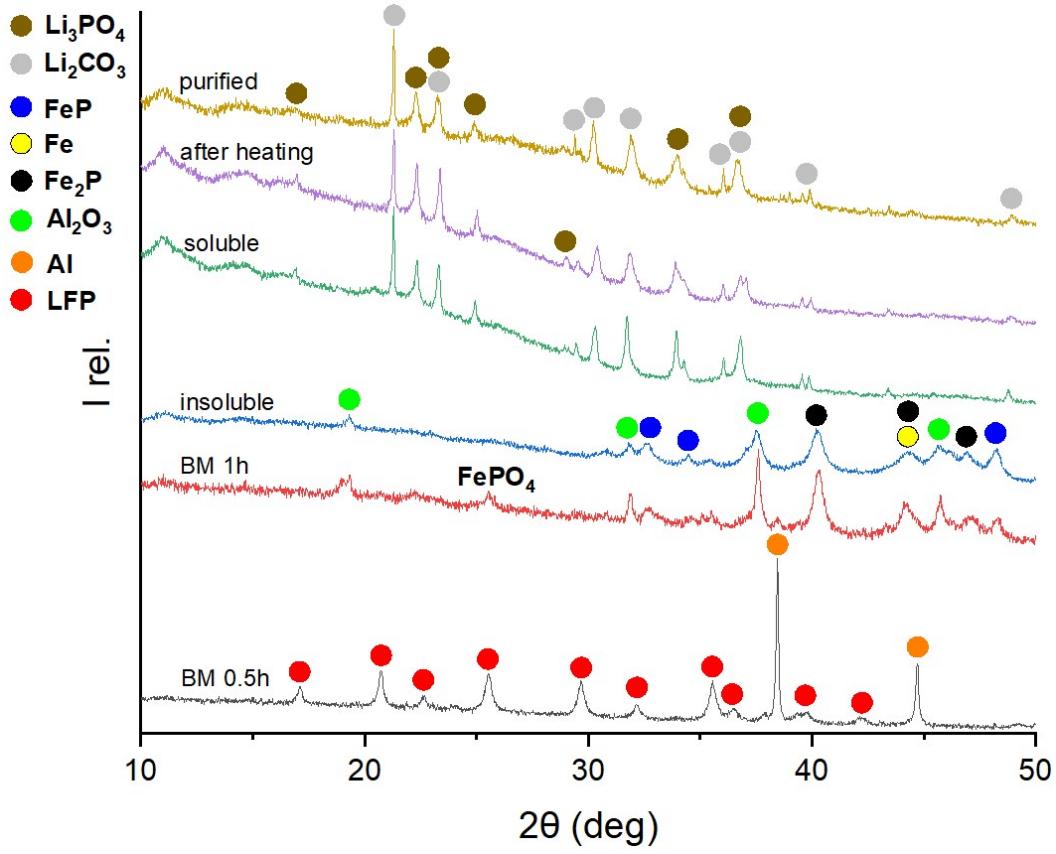

Figure S4: XRD patterns of the products after ball-milling, leaching and purification process obtained from a 1:2 molar mixture of LFP and Al. The most intense Bragg-reflections are assigned to different phases for analysis.

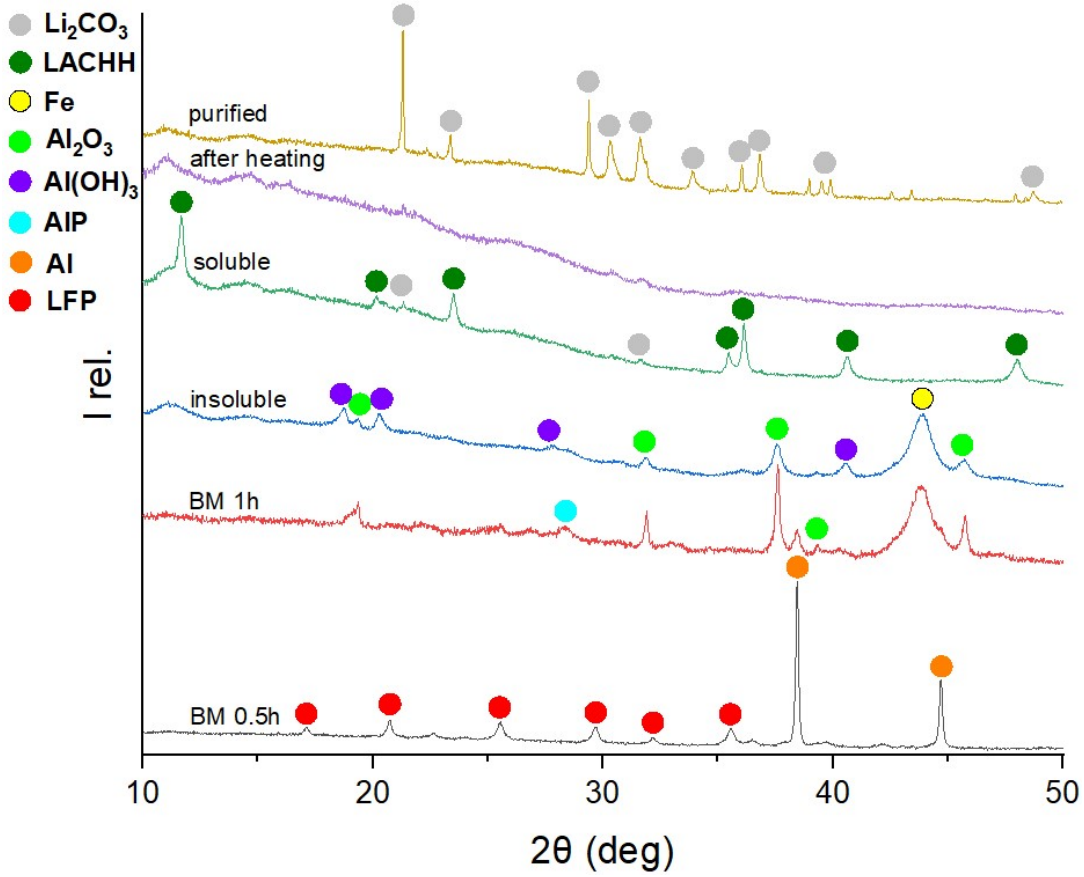

Figure S5: XRD patterns of the products after ball-milling, leaching and purification process obtained from a 1:5 molar mixture of LFP and Al. The most intense Bragg-reflections are assigned to different phases for analysis.

Calculation of Li_2CO_3 purity and Lithium lost in the insoluble parts

Li_2CO_3 purity:

The purity as well as the amount of impurities was determined using the results obtained by ICP-OES measurements. To calculate the Li_2CO_3 purity, the weight percentage (wt-%) of Li was used to determine a stochiometric wt-% of carbon and oxygen. Li_2CO_3 purity was then obtained by adding these wt-% to the wt-% of Li. Impurities were stated as received from the measurement except oxygen. For oxygen the oxygen contained in the Li_2CO_3 was subtracted.

Lithium lost in the insoluble parts:

To calculate the Li loss the insoluble part was weighted before ICP-OES measurement. The weight was multiplied by the wt-% of Li measured. The resulting mass of Li is transformed to a molar amount and compared to the theoretical Li amount obtained from yield calculation. The calculation is summarized in Eq. S1.

$$Lithium\ loss\ [\%] = \frac{m(insoluble) \cdot wt\%\ Li}{M(Li) \cdot n(Li\ yield\ theo.)} \qquad (Eq.\ S1)$$