Supplementary Information

Facile and efficient recycling of cathode materials of spent lithium manganate batteries

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Experiment Section

The spent LMO used in this study was purchased from Quzhou Huayou Cobalt New Material Co, Ltd, a local battery recycling company. The contents of the main elements (wt. %) in the waste LMO cathode material were 3.86% Li and 60.70% Mn. The reagents used in the study were of analytical grade, and the solutions were configured with deionized water.

The mass of LMO used in each experiment is 10 g. The amount of sodium persulfate and deionized water were chosen according to the oxidant dosage and L/S ratio, respectively. The mass of one time the theoretical dosage was obtained according to the reaction equation:

$$2LiMn_2O_4 + Na_2S_2O_8 = Na_2SO_4 + 4MnO_2 + Li_2SO_4 \#$$
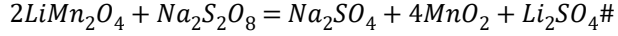
In this study, since m_0 was the mass of $LiMn_2O_4$ in the leaching experiments, one time the oxidant dosage was:

$$m_1 = \frac{m_0 \cdot M(Na_2S_2O_8)}{2M(LiMn_2O_4)} = 6.58g\#$$

All the solid materials were weighed using an electronic balance, and together with the deionized water, they were placed in a 250 mL beaker, which was used as a container for the reaction. The pre-weighed oxidant was added slowly and evenly and this process took about 5 minutes. Then the beaker is placed in a water bath preheated to 90°C accompanied by magnetic stirring. After the reaction, the samples were taken via a solid-liquid separation membrane with a pore size of 0.22 μm by a vacuum filter. Next, the leachate was used to measure the leaching rates of Li and Mn by ICP-OES (ICP-OES Optima 7000 DV, PerkinElmer Instruments, USA). The filter cake was dried in a drying oven for 24 hours.

In the production of Li_2CO_3, the leachate was first concentrated, increasing lithium concentration to ~10 g/L. Then the pH of concentrated solution was adjusted to 11 by solid NaOH. After the filtration of little solid impurities, sodium carbonate was added to precipitate Li^+ at 90 °C. The dosage of sodium carbonate is 1.1 times theoretical amount to precipitate the lithium in the solution. This process proceeded in the water bath for 2 hours with magnetic stirring. After that, the suspension was filtered and the filtration process needs to be as fast as possible and accompanied by hot water washing to prevent the dissolution of Li_2CO_3. Finally, the crystallized solid was dried to get Li_2CO_3 product.

To study the leaching mechanism, the leaching residues under different leaching times were analyzed by X-ray diffraction (XRD, RINT-TTR3, RIGAKU, Japan). The changes in functional groups during the leaching process were analyzed by Fourier transform infrared spectroscopy (FT-

IR, Bruker V70, Germany). X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi, United Kingdom) was also applied to analyze the valence state of Mn in leaching residue.

Thermodynamic analysis

Table S1 shows the Gibbs energy of components involved in the system [1-2]. The reactions that may occur in the system were listed in **Table S2**. Their balanced equation was then used in the calculating of the Nernst equation to describe the relationship between their potential and Gibbs free energy. The Nernst equation is shown as follow:

$$E = \frac{\Delta G^{\theta}}{zF} - \frac{RT}{zF} ln \frac{\Sigma a_{red}}{\Sigma a_{ox}} \#(1)$$

From these equations, the E-pH diagrams of the Li-Mn-H_2O system of 298 K and 363 K were drawn, respectively.

Table S1 Gibbs energy of components in Li−Mn−H_2O system at 363 K and 298 K

Component	$\Delta_r G^{\theta}_{363}$ (kJ/mol)	$\Delta_r G^{\theta}_{298}$ (kJ/mol)
Mn^{2+}	−229.521	−229.84
MnO_2	−453.314	−465.075
Mn_2O_3	−862.117	−879.658
MnO_4^{2-}	−465.806	−439.684
Li^+	−297.246	−292.61
$LiMnO_2$	−768.225	−792.85
Mn_3O_4	−1258.825	−1280.771
$Mn(OH)_2$	−597.369	−616.614
MnO_4^-	−425.909	−440.032
H_2O	−226.819	−237.19

LiMn$_2$O$_4$	−1374.795	−1315.61

Table S2 Equations of reactions in Li−Mn−H$_2$O system at 363 K (kJ/mol)

Reaction	$\Delta_r G^\theta_{363}$ (kJ/mol)	$\Delta_r G^\theta_{298}$ (kJ/mol)
Mn^{2+} + 2e = Mn	E=−1.19+0.036lg[Mn^{2+}]	E=−1.19+0.03lg[Mn^{2+}]
MnO$_2$ + 4H$^+$ + 2e = Mn^{2+} + 2H$_2$O	E=1.18−0.144pH−0.036lg[Mn^{2+}]	E=1.239−0.119pH−0.03lg[Mn^{2+}]
Mn^{2+} + 2H$_2$O = Mn(OH)$_2$ + 2H$^+$	pH=6.092−0.5lg[Mn^{2+}]	pH=7.68−lg[Mn^{2+}]
Mn(OH)$_2$ + 2H$^+$ + 2e = Mn + 2H$_2$O	E=−0.751−0.072pH	E=−0.737−0.06pH
Mn$_3$O$_4$ + 2H$_2$O + 2H$^+$ + 2e = 3Mn(OH)$_2$	E=0.422−0.072pH	E=0.491−0.06pH
Mn$_3$O$_4$ + 8H$^+$ + 2e = 3Mn^{2+} + 4H$_2$O	E=1.739−0.288pH−0.108lg[Mn^{2+}]	E=1.853−0.237pH−0.089lg[Mn^{2+}]
3Mn$_2$O$_3$ + 2H$^+$ + 2e = 2Mn$_3$O$_4$ + H$_2$O	E=0.805−0.072pH	E=0.828−0.0592pH
2MnO$_2$ + 2H$^+$ + 2e = Mn$_2$O$_3$ + H$_2$O	E=0.935−0.072pH	E=0.968−0.0592pH
Mn$_2$O$_3$ + 6H$^+$ + 2e = 2Mn^{2+} + 3H$_2$O	E=1.428−0.216pH−0.072lg[Mn^{2+}]	E=1.511−0.178pH−0.592lg[Mn^{2+}]
MnO$_4^-$ + 4H$^+$ + 3e = MnO$_2$ + 2H$_2$O	E=1.669−0.096pH+0.024lg[MnO$_4^-$]	E=1.725−0.079pH+0.02lg[MnO$_4^-$]
MnO$_4^{2-}$ + 4H$^+$ + 2e = MnO$_2$ + 2H$_2$O	E=2.284−0.144pH+0.036lg[MnO$_4^{2-}$]	E=2.311−0.118pH-0.02lg[MnO$_4^{2-}$]
MnO$_4^-$ + e = MnO$_4^{2-}$	E=0.441+0.072lg[MnO$_4^-$]−0.072lg[MnO$_4^{2-}$]	E=0.556+0.006lg[MnO$_4^-$]−0.059lg[MnO$_4^{2-}$]
LiMn$_2$O$_4$ + 8H$^+$ + 3e = 2Mn^{2+} + 4H$_2$O + Li$^+$	E=1.876−0.192pH−0.048lg[Mn^{2+}]−0.024lg[Li$^+$]	E=1.332−0.158pH−0.039lg[Mn^{2+}]−0.0197lg[Li$^+$]
3LiMn$_2$O$_4$ + 8H$^+$ + 5e = 2Mn$_3$O$_4$ + 4H$_2$O + 3Li$^+$	E=1.789−0.115pH−0.0432lg[Li$^+$]	E=0.915−0.095pH−0.036lg[Li$^+$]
LiMn$_2$O$_4$ + 4H$^+$ + 3e = 2Mn(OH)$_2$ + Li$^+$	E=1.291−0.096pH−0.024lg[Li$^+$]	E=0.726−0.079pH−0.02lg[Li$^+$]
2MnO$_4^{2-}$ + Li$^+$ + 8H$^+$ + 5e = LiMn$_2$O$_4$ + 4H$_2$O	E=2.183+0.014lg[Li$^+$]+0.029lg[MnO$_4^{2-}$]−0.115pH	E=2.04+0.095lg[Li$^+$]+0.024lg[MnO$_4^{2-}$]−0.118pH
2MnO$_4^-$ + Li$^+$ + 8H$^+$ + 7e = LiMn$_2$O$_4$ + 4H$_2$O	E=1.653+0.01lg[Li$^+$]+0.021lg[MnO$_4^-$]−0.082pH	E=1.616+0.085lg[Li$^+$]+0.017lg[MnO$_4^-$]−0.068pH
2MnO$_2$ + Li$^+$ + e = LiMn$_2$O$_4$	E=1.771+0.072lg[Li$^+$]	E=0.962+0.0592lg[Li$^+$]
LiMn$_2$O$_4$ + Li$^+$ + e = 2LiMnO$_2$	E=−1.405+0.072lg[Li$^+$]	E=−0.233+0.0592lg[Li$^+$]
LiMnO$_2$ + 2H$^+$ + e = Mn(OH)$_2$ + Li$^+$	E=2.566−0.144pH−0.072lg[Li$^+$]	E=1.206−0.118pH−0.0592lg[Li$^+$]
3LiMnO$_2$ + 4H$^+$ + e = Mn$_3$O$_4$ + 3Li$^+$ + 2H$_2$O	E=6.360−0.216lg[Li$^+$]−0.288pH	E=2.64−0.178lg[Li$^+$]−0.237pH

LiMn$_2$O$_4$+2H$^+$ + e = Mn$_2$O$_3$ + Li$^+$ + H$_2$O	E=2.280−0.072lg[Li$^+$]−0.144pH	E=1.009-0.059lg[Li$^+$]-0.118PH
4H$^+$ + O$_2$ + 4e = 2H$_2$O	E=1.175−0.072pH	E=1.23−0.059pH
2H$^+$ + 2e = H$_2$	E=−0.072pH	E=−0.059pH

Leaching kinetics

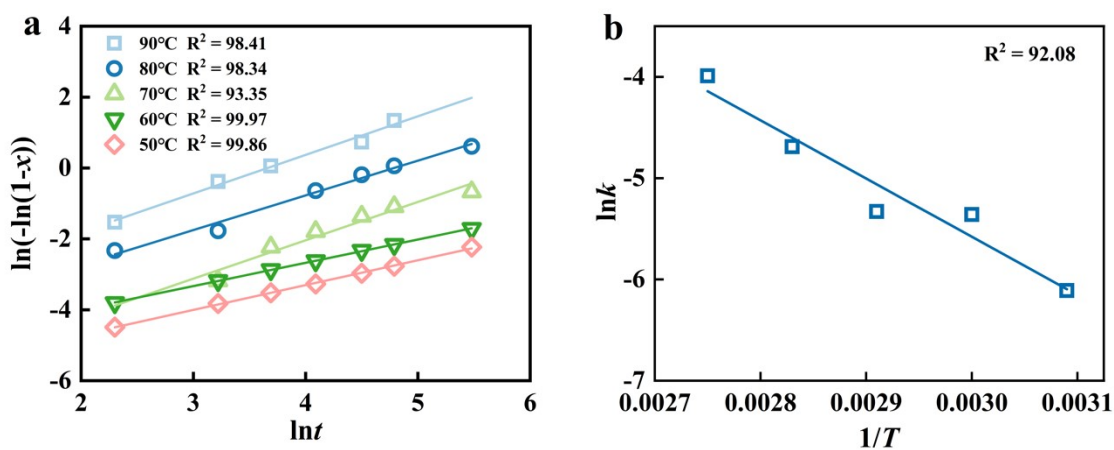**Fig. S1.** (a) Plots of ln(-ln(1-x)) vs. ln$t$ at different leaching temperatures. (b) Fitting of the Arrhenius equation.

(Leaching conditions: oxidant dosage = 2, L/S ratio= 5).
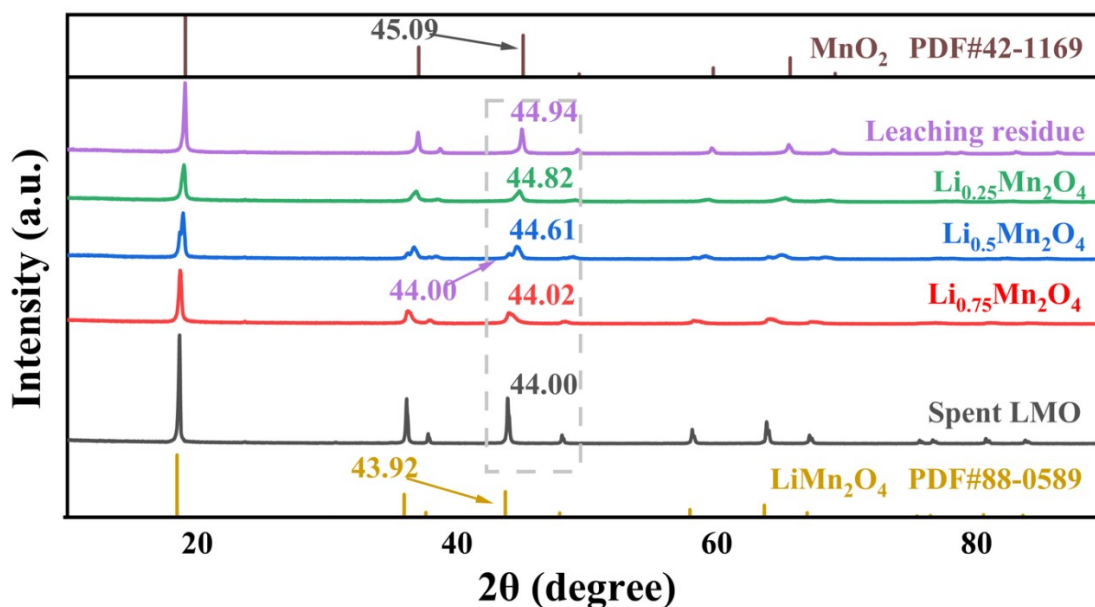
Characterization

Fig. S2. XRD pattern from 10 to 90 degrees

Table S3 ICP elemental compositions of the prepared Li_2CO_3

Element	Li_2CO_3	Mn	Na	Ca	F	Fe	Al	Cu	S
Wt. %	>99.5	0.02	0.09	0.04	0.04	<0.01	<0.01	<0.01	<0.01

Table S4 ICP elemental compositions of the leaching residue

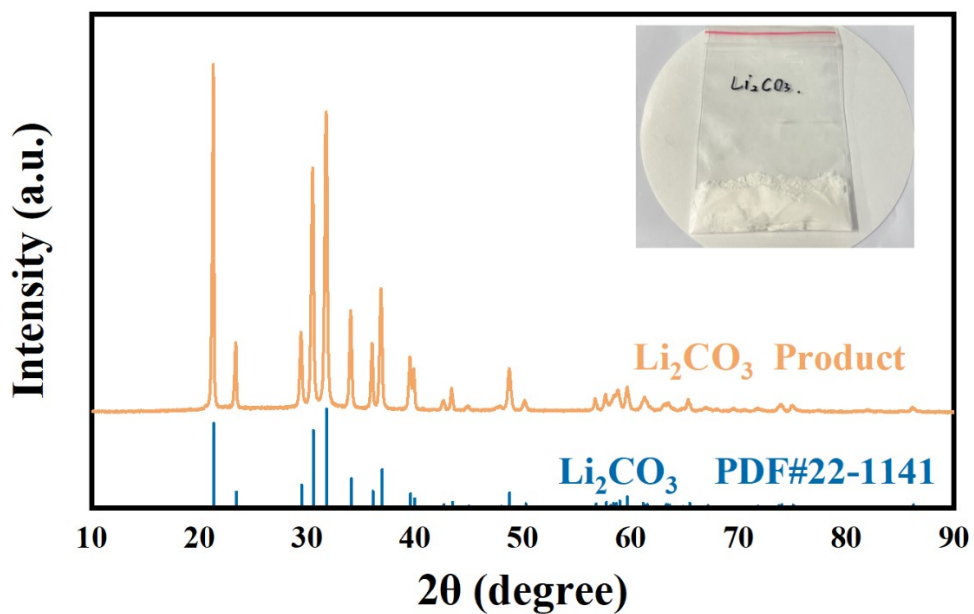| Element	Mn	Li	Na	Ca	F	Fe	Al	Cu	S
Wt. %	62.5	0.06	<0.01	<0.01	0.11	0.02	0.28	0.04	<0.01

Recovery process

Fig. S3. XRD parttern of the Li_2CO_3 product

Notes and references

[1] Z. Li, L. He, Z. W. Zhao, D. Wang and W. Xu, *ACS Sustainable Chemistry & Engineering*, 2019, **7**, 16738-16746.

[2] Z. Zhao, G. Huo, *China Nonferrous Metals*, 2004, **24**, 1296-1231.