Supplementary Materials

Green and Sustainable Recycling of Spent Lithium Batteries: Synergistic Leaching of SLFP and SLMO for Valuable Metal Extraction and Environmental Benefit

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Principles and method of plotting E-pH diagrams

Generally, the electrochemical reactions occurring in an aqueous solution have the following typical half-reaction equations[1]:

$$m\ \mathrm{A} + n\ \mathrm{H}+ + z\ \mathrm{e} = b\ \mathrm{B} + c\ \mathrm{H_2O} \qquad \text{(S1)}$$

According to Gibbs free energy of the half-reaction ($\Delta_r G_T^\Theta$) and the Nernst relationship between and emf of the half-reaction (E) and $\Delta_r G_T^\Theta$, we have:

$$\Delta_r G_T = \Delta_r G_T^\theta = \mathrm{RTInQ} \qquad \text{(S2)}$$

$$E = E^\theta - \frac{RT}{zF}\mathrm{InQ} \qquad \text{(S3)}$$

Where, $Q=\frac{a_B^b \cdot a_{H_2O}^c}{a_A^m \cdot a_{H^+}^n}$ —the reaction quotient; α—the activity of each species in aqueous; R—gas constant, 8.314 J mol^{-1} K^{-1}; T—Temperature, K;

F—Faraday constant, 96485 C·mol^{-1}, respectively.

Substituting the Nernst equation into the above isothermal equation can yield the relationship between the electrode potential E and the pH value:

$$E = -\frac{\Delta_r G_T^\theta}{zF} - \frac{2.303RT}{zF}\lg\frac{a_B^b}{a_A^m} - \frac{2.303nRT}{zF}\mathrm{Ph} \qquad \text{(S4)}$$

Table S1. The E-ph data of the equilibrium reactions in the Li-Fe-P-H_2O system at 298K [2]

No.	Reaction equations	E~pH relationships
1	$2H_2O = O_2 + 4H^+ + 4e^-$	$E = 1.229 - 0.0592\ pH$
2	$2H^+ + 2e^- = H_2$	$E = - 0.0592\ pH$
3	$LiFePO_4 + 2H^+ = Li^+ + Fe^{2+} + H_2PO_4^-$	$E = - 0.1184\ pH$
4	$Fe^{3+} + e^- = Fe^{2+}$	$E = 0.7696 - 0.0592\ lg[Fe^{2+}]/[Fe^{3+}]$
5	$FePO_4{\cdot}2H_2O + 3H^+ = Fe^{3+} + H_3PO_4 + 2H_2O$	$pH = -3.482 - 1/3\ lg[Fe^{3+}][H_3PO_4]$
6	$FePO_4{\cdot}2H_2O + 3H^+ + e^- = Fe^{2+} + H_3PO_4 + 2H_2O$	$E = 0.1515 - 0.0592\ lg[Fe^{2+}][H_3PO_4] - 0.1775\ pH$
7	$LiFePO_4 + 3H^+ = Fe^{2+} + Li^+ + H_3PO_4$	$pH = 0.6137 - 1/3\ lg[L^{i+}]\ [Fe^{2+}][H_3PO_4]$
8	$FePO_4{\cdot}2H_2O + Li^+ + e^- = LiFePO_4 + 2H_2O$	$E = 0.1083 - 0.0197\ lg[H_3PO_4] - 0.0592\ pH$
9	$Fe^{2+} + PO_4^{3-} = FePO_4 + e^-$	$E = 0.0426 + 0.0592\ lg[Li^+]$
10	$Li_3PO_4 + Fe(OH)_3 + 3H^+ = FePO_4{\cdot}2H_2O + 3Li^+ + H_2O$	$pH = 6.0831 - lg[Li^+]$
11	$Fe(OH)_3 + Li_3PO_4 + 3H^+ + e^- = LiFePO_4 + 2Li^+ + 3H_2O$	$E = 1.1224 - 0.1183\ lg[Li^+] - 0.1775\ pH$
12	$Fe(OH)_2 + Li_3PO_4 + 2H^+ = LiFePO_4 + 2H_2O + 2Li^+$	$pH = 7.4167 - lg[Li^+]$
13	$Fe(OH)_3 + H^+ + e = Fe(OH)_2 + H_2O$	$E = 0.2447 - 0.0592\ pH$
14	$Fe(OH)_2 + 2H^+ = Fe^{2+} + 2H_2O$	$pH = 5.3515 - 1/2\ lg[Fe^{2+}]$
15	$Fe(OH)_3 + 3H^+ = Fe^{3+} + 3H_2O$	$pH = 0.6103 - 1/3\ lg[Fe^{3+}]$
16	$Li_3PO_4 + 3H^+ = H_3PO_4 + 3Li+$	$pH = 1.9905 - lg[Li^+] - 1/3\ lg[H_3PO_4]$
17	$Li_3PO_4 + 2H^+ = H_2PO_4^- + 3Li+$	$pH = 4.5827 - 3/2\ lg[Li^+]$

Table S2. The E-ph data of the equilibrium reactions in the Li-Mn-H_2O system at 298K [3]

No.	Reaction equations	E~pH relationships
1	$Mn^{2+} + 2e^{-} = Mn$	$E = -1.191 + 0.02958\ lg[Mn^{2+}]$
2	$MnO_2 + 4H^{+} + 2e^{-} = Mn^{2+} + 2H_2O$	$E = 1.239-0.1192pH – 0.02958\ lg[Mn^{2+}]$
3	$Mn^{2+} + 2H_2O=Mn(OH)_2 + 2H^{+}$	$pH=7.675 - ln[Mn^{2+}]$
4	$Mn(OH)_4^{2-} + 4H^{+} + 2e^{-} = Mn + 4H_2O$	$E = 0.2375 - 0.1183\ pH + 0.02958\ lg[Mn(OH)_4^{2-}]$
5	$Mn_3O_4 + 2H_2O + 2H+ + 2e = 3Mn(OH)_2 + 2H_2O$	$E = 0.4907 - 0.05916\ pH$
6	$Mn_3O_4 + 8H^{+} + 2e^{-} = 3Mn^{2+} + 4H_2O$	$E = 1.8528 - 0.2366\ pH - 0.08874\ lg[Mn^{2+}]$
7	$Mn_3O_4 + 8H_2O + 2e^{-} = 3Mn(OH)_4^{2-} + 4H^{+}$	$E = - 2.4331-0.1183\ pH - 0.1183\ lg[Mn(OH)_4^{2-}]$
8	$MnO_2 + 2H^{+} + 2e^{-} = Mn_2O_3 + H_2O$	$E = 0.9675 - 0.05916\ pH$
9	$Mn_2O_3 + 5H_2O + 2e^{-} = Mn(OH)_4^{2-} + 2H+$	$E = - 1.3461-0.05916\ pH - 0.1183\ lg[Mn(OH)_4^{2-}]$
10	$Mn_2O_3 + 6H^{+} + 2e^{-} = 2Mn^{2+} + 3H_2O$	$E = 1.51116-0.1775\ pH - 0.5916\ lg[Mn^{2+}]$
11	$MnO_4^{-} + 4H^{+} + 3e^{-} = MnO_2 + 2H_2O$	$E = 1.7254 - 0.07888\ pH + 0.01972\ lg[MnO_4^{-}]$
12	$MnO_4^{2-} + 4H^{+} + 2e^{-} = MnO_2 + 2H_2O$	$E = 2.3107 - 0.1183\ pH - 0.01972\ lg[MnO_4^{-}]$
13	$MnO_4^{-} + e^{-}= MnO_4^{2-}$	$E = 0.5561 + 0.05916\ lg[MnO_4^{-}]-0.05916\ lg[MnO_4^{2-}]$
14	$Mn(OH)_2 + 2H_2O = Mn(OH)_4^{2-} + 2H^{+}$	$pH = 16.4750 - 0.5\ lg[Mn(OH)_4^{2-}]$
15	$LiMn_2O_4 + 8H^{+} + 3e^{-} = 2Mn^{2+} + 4H_2O + Li^{+}$	$E = 1.332 - 0.1578\ pH - 0.03944\ lg[Mn^{2+}] - 0.019\ 72\ lg[Li^{+}]$
16	$3LiMn_2O_4 + 8H^{+} + 5e = 2Mn_3O_4 + 4H_2O + 3Li^{+}$	$E = 0.9147 - 0.09466\ pH - 0.03550\ lg[Li^{+}]$
17	$LiMn_2O_4 + 4H^{+} + 3e^{-} = 2Mn(OH)_2 + Li^{+}$	$E = 0.7263 - 0.07888\ pH - 0.01972\ lg[Li^{+}]$
18	$LiMn_2O_4 + 4H_2O + 3e^{-} = 2Mn(OH)_4^{2-} + Li^{+}$	$E = - 0.5732 - 0.01972\ lg[Li^{+}] - 0.03944\ lg[Mn(OH)_4^{2-}]$
19	$MnO_4^{2-} + Li^{+} + 8H^{+} + 5e^{-} = LiMn_2O_4 + 4H_2O$	$E = 2.0405 - 0.09466\ pH + 0.02366\ lg[Mn(OH)_4^{2-}] + 0.01183\ lg[Li^{+}]$
20	$2MnO_2 + Li^{+} + e^{-} = LiMn_2O_4$	$E = 0.9623 + 0.05916\ lg[Li^{+}]$
21	$LiMn_2O_4 + Li^{+} + e^{-} = 2LiMnO_2$	$E = - 0.2334 + 0.05916\ lg[Li^{+}]$
22	$LiMnO_2 + 2H^{+} + e^{-} = Mn(OH)_2$	$E = 1.2060 – 01183\ pH - 0.05916\ lg[Li^{+}]$
23	$2H_2O = O_2 + 4H^{+} + 4e^{−}$	$E = 1.229 - 0.0592\ pH$
24	$2H^{+} + 2e^{−} = H_2$	$E = - 0.0592\ pH$

According to the data in Table S1 and Table S2, combined with the software (HSC Chemistry 6.0), the E-pH diagrams of the Li-Fe-P-H_2O system and the Li-Mn-H_2O system at 298 K can be respectively plotted.

Table S3. The fixed parameter values of different conditional factors

Figure sequence	Fixed parameter value
4(a)	Temperature(℃): 60, Time(min): 120, SLFP:SLMO(mol): 1, Slurry Density(g/L): 100
4(b)	H_2SO_4 concentration(mol/L): 0.6, Time(min): 120, SLFP:SLMO(mol): 1, Slurry Density(g/L): 100
4(c)	H_2SO_4 concentration(mol/L): 0.6, Time(min): 120, Temperature(℃): 40, Slurry Density(g/L): 100
4(d)	H_2SO_4 concentration(mol/L): 0.6, Time(min): 120, Temperature(℃): 40, SLFP:SLMO(mol): 1
4(e)	H_2SO_4 concentration(mol/L): 0.6, Slurry Density(g/L): 100, Temperature(℃): 40, SLFP:SLMO(mol): 1
5(a)	Temperature(℃): 60, Time(min): 120, SLFP:SLMO(mol): 1, Slurry Density(g/L): 100
5(b)	H_2SO_4 concentration(mol/L): 0.6, Time(min): 120, SLFP:SLMO(mol): 1, Slurry Density(g/L): 100
5(c)	H_2SO_4 concentration(mol/L): 0.6, Time(min): 120, Temperature(℃): 40, Slurry Density(g/L): 100
5(d)	H_2SO_4 concentration(mol/L): 0.6, Time(min): 120, Temperature(℃): 40, SLFP:SLMO(mol): 1
5(e)	H_2SO_4 concentration(mol/L): 0.6, Slurry Density(g/L): 100, Temperature(℃): 40, SLFP:SLMO(mol): 1

References

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