"ELECTRON-ASSISTED LEACHING OF COBALT AND MAGANESE FROM LIBS USING LFP AS REDUCTANT"

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Battery Industry

South Korea's Battery Recycling 2024

In 2024, South Korean major companies are actively involved in battery recycling. SK, LG, and Samsung have established partnerships and invested in recycling technologies and facilities. Additionally, POSCO and Doosan are also expanding their efforts in the battery recycling inductor.

recycling industry Key Players Status

- 1. SK Innovation
 - Developed lithium hydroxide recovery technology.
 - Recycling partnerships with EcoPro and Ascend Elements.
- 2. LG Energy Solution
 - Invested in Li-Cycle for nickel recycling.
 - Joint venture with Huayou Cobalt in China.
- 3. Samsung SDI
 - Collaborated with SungEel HiTech for recycling.
 - Established a closed-loop system in global plants.



Battery Recycling



Battery Industry

NCM Battery Recycling?: Sulfuric acid Leaching with H_2O_2 as reductant

Sulfuric acid Leaching

$$A \operatorname{LiNi}_{x}\operatorname{Mn}_{y}\operatorname{Co}_{z}\operatorname{O}_{2(s)} + 3/2A \operatorname{H}_{2}\operatorname{SO}_{4(aq)} + 1/6A \operatorname{H}_{2}\operatorname{O}_{2}) \longrightarrow Ax \operatorname{NiSO}_{4(aq)} + Ay \operatorname{MnSO}_{4(aq)} + Az \operatorname{CoSO}_{4(aq)} \\ + A/2 \operatorname{Li}_{2}\operatorname{SO}_{4(aq)} + 5/3A \operatorname{H}_{2}\operatorname{O}_{(aq)} + 1/3A \operatorname{O}_{2(g)} \\ Ax \operatorname{NiSO}_{4(aq)} + 5/3A \operatorname{H}_{2}\operatorname{O}_{(aq)} + 1/3A \operatorname{O}_{2(g)} \\ Ax \operatorname{NiSO}_{4(aq)} + 5/3A \operatorname{H}_{2}\operatorname{O}_{(aq)} + 1/3A \operatorname{O}_{2(g)} \\ Ax \operatorname{NiSO}_{4(aq)} + 5/3A \operatorname{H}_{2}\operatorname{O}_{(aq)} + 1/3A \operatorname{O}_{2(g)} \\ Ax \operatorname{NiSO}_{4(aq)} + 5/3A \operatorname{H}_{2}\operatorname{O}_{(aq)} + 1/3A \operatorname{O}_{2(g)} \\ Ax \operatorname{NiSO}_{4(aq)} + 5/3A \operatorname{H}_{2}\operatorname{O}_{(aq)} + 1/3A \operatorname{O}_{2(g)} \\ Ax \operatorname{NiSO}_{4(aq)} + 5/3A \operatorname{H}_{2}\operatorname{O}_{(aq)} + 1/3A \operatorname{O}_{2(g)} \\ Ax \operatorname{NiSO}_{4(aq)} + 5/3A \operatorname{H}_{2}\operatorname{O}_{2(aq)} + 1/3A \operatorname{O}_{2(g)} \\ Ax \operatorname{NiSO}_{4(aq)} + 5/3A \operatorname{H}_{2}\operatorname{O}_{2(aq)} + 1/3A \operatorname{O}_{2(g)} \\ Ax \operatorname{NiSO}_{4(aq)} + 5/3A \operatorname{N}_{2}\operatorname{O}_{2(q)} \\ Ax \operatorname{NiSO}_{4(aq)} \\ Ax \operatorname{NiSO}_{4(aq)} + 5/3A \operatorname{N}_{2}\operatorname{O}_{2(q)} \\ Ax \operatorname{NiSO}_{2(q)} \\ Ax \operatorname{NiSO}_{4(aq)} \\ Ax \operatorname{NiSO}_{4(aq)}$$

- Reductants are required to enhance the metal solubility especially Co, Mn by transforming from insoluble species Co(II) and Mn(IV) into soluble species Co(II) and Mn(II)
- H₂O₂ is main reducing agents to reduce the transition metals and Among the alternative, Iron ions can be used as reductants



Battery Industry

The LFP battery market is growing rapidly, driven by its safety and cost benefits. South Korea battery companies are actively developing and planning mass production to meet increasing global demand.



ALTA

Battery Industry

LFP Battery Recycling?: Metal value and Recycling viability

Battery Metal Values



Recycling of LFP



- Economic viability due to high metal prices and Potential decrease in value due to falling Li prices
- Low metal value made recycling uneconomical and lack of incentive for recycling LFP batteries
- For economic reasons, LFP batteries are being recycled through direct recycling or precursor recovery ALTA methods.

Battery Industry

LFP Battery Recycling?: LFP made from following materials

Structure of LFP Battery





Pretreatment: Physical separation of spent **LFP**



Results of Battery Recycling

Pretreatment: Information of NCM samples



(unit: v	wt%) NiO	MnO	Co ₂ O ₃	CuO	Al ₂ O ₃	Fe ₂ O ₃	P ₂ O ₅	SiO ₂
A(S)	26.52	13.95	9.17	7.60	6.05	1.65	0.57	0.25
B(H)	17.86	3.81	6.68	9.41	4.61	1.18	0.30	1.91



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Pretreatment: Heat treatment for removing organic and further process





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Results of Battery Recycling

Pretreatment: Heat treatment for removing organic and further process





Leaching part(i): Effect of Fe and Cu as reductant for sample A(-OH)



Experimental conditions: Concentration, 2M H₂SO₄; PD, 20%; Reductant(Cu, Fe), 25%/PD;
 Temp., 80 °C, Time, 6 H

Results of Battery Recycling

Leaching part(ii): Effect of Fe and Cu as reductant for sample $B(-O_2)$



evalta Experimental conditions: Concentration, 2M H₂SO₄; PD, 20%; Reductant(Cu, Fe), 25%/PD; 2024[©] Temp., 80 ℃, Time, 6 H

Leaching part(i): Effect of Cu dosage on NCM leaching



Experimental conditions: Concentration, 2M H₂SO₄; PD, 20%; Reductant(Cu), 1~20%/PD; Temp., 80 °C, Time, 6 H WALTA 🔮 2024

Results of Battery Recycling



ALTA 2024

Experimental conditions: Concentration, 2M H₂SO₄; PD, 20%; Reductant(Cu), 1~20%/PD; Temp., 80 °C, Time, 6 H

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Leaching part(i): Effect of Cu dosage on NCM leaching







Leaching part(i): Effect of Cu dosage on NCM leaching



Figure 3. The proposed concept of leaching behavior of copper from Cu metal by Cu^{2+} ions in sulfuric acid leaching: (a) without aeration and (b) with aeration.



Source: Yoo, K., et al. (2020)Improvement of copper metal leaching in sulfuric acid solution by simultaneous use of oxygen and cupric ions. Metals 2020, 10, 721

Cementation?

Reduction?

 Name
 Date
 Time
 HV
 Mag
 WD
 [mm]

 Residue oxidized 1500x 3430
 3/21/2024
 2:41:49 PM
 20.0 keV
 50x
 20.7 m

Leaching part(i): Effect of Cu dosage on NCM





- Cuprous ions are unstable in sulfuric acid solution, they immediately convert to cupric ions by losing one electron.
- Electron can easily reduce Co³⁺ and Mn³⁺, which have relatively high redox potentials, making Co and Mn easier to leach.

Results of Battery Recycling

Leaching part(i): Effect of Cu dosage on NCM



- Most of the cobalt and manganese have been leached, there are no more ions acting as oxidizing agents.
- The electrons released from the oxidation of Cu⁺ to Cu²⁺ are received by Cu⁺ ions, forming metallic copper precipitates.

Leaching parts: Effect of Iron ions on reducing of Co(III), Mn(III) to Co(II), Mn(II)



- Heat-treating LFP in an active atmosphere converts it into the Fe₂O₃ phase, incorporating trivalent iron ions (Fe³⁺).
- To obtain divalent iron ions (Fe²⁺) from Fe₂O₃, it is necessary to perform heat treatment in a reducing atmosphere. This process reduces Fe₂O₃ to FeO, providing the desired Fe²⁺ ions.





Results of Battery Recycling

Leaching parts: Effect of Iron ions on reducing of Co(III), Mn(III) to Co(II), Mn(II)



- Heat-treating LFP in an active atmosphere converts it into the Fe_2O_3 phase, incorporating trivalent iron ions (Fe^{3+}).
- To obtain divalent iron ions (Fe²⁺) from Fe₂O₃, it is necessary to perform heat treatment in a reducing atmosphere. This process reduces Fe₂O₃ to FeO, providing the desired Fe²⁺ ions. -0.28 -0.28 -0.44 -0.28 -0.44

Standard reduction potential [V] +1.82 \longrightarrow Co³⁺ + e⁻ \rightarrow Co²⁺

+1.51 → $Mn^{3+} + e^- \rightarrow Mn^{2+}$ +0.77 → $Fe^{3+} + e^- \rightarrow Fe^{2+}$ +0.34 → $Cu^{2+} + 2e^- \rightarrow Cu$ +0.15 → $Cu^{2+} + e^- \rightarrow Cu^+$ -0.28 → $Co^{2+} + 2e^- \rightarrow Co$ -0.44 → $Fe^{2+} + 2e^- \rightarrow Fe$

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Leaching part(iii): Effect of Fe(II)O as reductant for sample A(-OH) and $B(-O_2)$



Experimental conditions: Concentration, 2M H₂SO₄; PD, 20%; Reductant(FeO), 25%/PD; Temp., 80 °C, Time, 6 H 2024

Conclusions

' LFP(Fe, Cu) used as reductant for leaching of Co and Mn from LIBs

Co < 99%, Mn < 99%, Ni 99 %, Li 99% at 2M H2SO4, 80 °C, 6h, PD 20% with Cu or Fe as reductants

' Electron donation aids in Co, Mn leaching during conversion of Fe, Cu ions

Copper ions from monovalent to divalent (Cu⁺ to Cu²⁺) Iron ions should convert to FeO to reduce the ferric ion to ferrous (Fe³⁺ to Fe²⁺)

Phenomena clarified via direct methods (electrochemical analysis)

Investigate whether the electrons generated during the conversion of copper(I) ions to copper(II) ions are utilized in the reduction of cobalt and manganese



Thank you for your attention!



LIBs Recycling R&D

Previous Experiment: Efficient Separation Technology for Electrode Active Materials





Pretreatment: Heat treatment for removing organic and further process

Composition and potential environmental pollution of LIBs of

LIB battery								
Part	Composition	Main chemical properties	Potential pollution					
Cathode	Al+LiCoO ₂ / LiMn ₂ O ₄ /LiNiO ₂	Strong reaction with $\rm H_2O/acid/reductan$ ts/strong/oxidants, forming toxic oxide	Pollution of heavy metals					
	Cu + C(graphite)	Explosion when dust get fire or high te mperature	Dust pollution					
Electrolyte salts	LiPF ₆ /LiBF ₄ /LiAsF ₆	Strong corrosive, forming HF in $\rm H_2O$	Fluorine					
Electrolyte solvents	EC+PC+DC+DEC	Combustible	VOCs					
Organic se parator	PP/PE	Combustible	VOCs					
Binder	PVDF/VDF/EPD	Thermal decomposition produces HF	Fluorine					



Figure 5: Isocorrosion diagram of some plastic materials in sulphuric acid. The areas below the lines are suitable for these materials.

