Recovery of Cobalt Metal from Waste Lithium-ion Batteries as Sensor Materials

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In this study, tartaric acid was used to extract the valuable metals lithium (Li), cobalt (Co), nickel (Ni), and manganese (Mn) from the anodes of waste Li-ion batteries. The effects of various factors, namely, acid concentration, the amount of the reducing agent added, temperature, solid-to-liquid (S/L) ratio, and time, on leaching efficiency were explored in order to determine the best conditions for metal recovery. First, Taguchi methods were used to obtain the initial parameters and the factor weights affecting leaching efficiency. Finally, the optimal leaching parameters were obtained through confirmation experiment. For optimal leaching rates, the acid concentration was 2 mol L^{-1}, the time was 30 min, the S/L ratio was 10 g L^{-1}, the temperature was 90 °C, and the amount of hydrogen peroxide (H_2O_2) added was 1.0 vol.%, resulting in leaching efficiencies of Li, Co, Ni, and Mn of 87.29, 80.51, 95.78, and 99.99%, respectively. The valuable metal Co can be used as a sensor material.

1. Introduction

In recent years, people have been paying significantly more attention to resource depletion and environmental protection issues,[1] which has prompted the active development of renewable energy. Lithium (Li)-ion batteries are undoubtedly a key alternative to reduce the current dependence on fossil fuel resources, as the demand for electric vehicles increases yearly.[2] However, the number of waste Li-ion batteries will also increase. Therefore, owing to safety and economic considerations, waste Li-ion batteries should not be disposed in landfills,[3] but the valuable metals Li, cobalt (Co), nickel (Ni), and manganese (Mn) should be extracted through resource recycling[4,5] and repurposed into reusable products.

Generally, methods of separating and recovering metals from waste Li-ion batteries are divided into three categories, namely, hydrometallurgy, pyrometallurgy, and biometallurgy.[6,7] Compared with pyrometallurgy and biometallurgy, hydrometallurgy has the following advantages: higher purity of product obtained, lower energy consumption, and less gas emissions. Therefore, we will use hydrometallurgical methods for metal recovery in this study.

From research on leaching, most studies use inorganic acids such as sulfuric acid,[8–10] hydrochloric acid,[6,11] and nitric acid[12,13] for leaching, and a small number of studies focus on organic acid leaching. Using tartaric acid at a temperature of 80 °C and a time of 3 to 4 h, Nayaka *et al*.[14] successfully recovered Co from waste Li-ion battery cathode material ($LiCoO_2$). He *et al*.[15] used 2 M tartaric acid to recover metals from waste Li-ion batteries, a solid-to-liquid (S/L) ratio of 17 g/L, a temperature of 70 °C, a time of 30 min, and 4 vol.% hydrogen peroxide (H_2O_2) to leach the metals Li, Co, Ni, and Mn by Taguchi methods. In comparison with the above two studies,[14,15] tartaric acid has the advantages of low cost and high acidity compared with other organic acids in terms of re-acid solution. Therefore, the Taguchi methods will be used to study the positive anode leaching of Li-ion batteries. We successfully reduced the acid concentration and the amount of H_2O_2 added. According to the research of Ribeiro *et al*.,[16] the Co metal leached in this study can be used as an electrochemical sensor material to improve the performance of the electrochemical sensor.

2.   Materials and Methods

2.1   Materials

The material used for this study is the anode of a waste Li-ion battery (NMC111), which is fully digested with aqua regia to obtain each metal. As shown in Table 1, the Li, Co, Ni, and Mn contents of the anode are relatively high, so in this research, these metals are mainly recovered.

Nitric acid (HNO_3, 70%) and hydrochloric acid (HCl, 37%) for aqua regia digestion were purchased from PanReac. Tartaric acid for leaching was purchased from Eco Chemical.

2.2   Leaching

First, the L_{16} (4^5) orthogonal array was used to reduce the number of experiments and determine the effects of acid concentration, reducing agent addition, temperature, S/L ratio, and time on leaching efficiency. The selection factors and levels are as follows. As shown in Table 2,

Table 1
Metal contents in anode materials of waste Li-ion batteries.

Element	Al	Mn	Fe	Co	Ni	Li
wt.%	0.1	18.1	0.1	31.3	30.0	18.0

Table 2
Control factors and selection levels.

Factors	Temperature	S/L ratio	Time	Acid	H_2O_2
Unit	°C	$g\,L^{-1}$	min	$mol\,L^{-1}$	vol.%
Level 1	60	10	15	0.5	0
Level 2	70	20	30	1.0	0.5
Level 3	80	30	45	1.5	1.0
Level 4	90	40	60	2.0	1.5

after the completion of the orthogonal array experiment, factor effect analysis can be performed to understand each factor weight affecting the leaching efficiency, and finally, the best leaching parameters are obtained through experiment confirmation.

3. Results and Discussion

3.1 Orthogonal array

A tartaric acid orthogonal array experiment was conducted to determine the effects of temperature, S/L ratio, time, tartaric acid concentration, and the amount of H_2O_2 added on the leaching rate of Li-ion battery anode materials under different parameter conditions. The results are shown in Table 3.

3.2 Factor analysis

The results of the orthogonal array experiment were analyzed to determine the weights of factors that affect the efficiency of leaching. The results are shown in Table 4. The order of effect on Li leaching efficiency is as follows: temperature > time > acid > S/L > H_2O_2. The order of effect on Co leaching efficiency is acid > S/L > time > temperature > H_2O_2, the order of effect on Ni leaching efficiency is acid > S/L > time > temperature > H_2O_2, whereas the order of effect on Mn leaching efficiency is acid > time > S/L > temperature > H_2O_2. Then, we scored each order; the first is five points, the second is four points, and so on. Then, we added the scores and sorted them. Finally, the factor effects of the four metals were integrated, and the order that best affects the overall leaching efficiency was concluded as acid > time > S/L > temperature >

Table 3
Orthogonal array experiment results.

No.	Temp.	S/L ratio	Time	Acid	H_2O_2	Li	Co	Ni	Mn
Unit	°C	g L^{-1}	min	mol L^{-1}	vol.%	%	%	%	%
1	60	10	15	0.5	0	9.84	5.29	6.30	10.63
2	60	20	30	1.0	0.5	27.33	16.99	20.02	35.27
3	60	30	45	1.5	1.0	41.28	30.31	34.33	49.03
4	60	40	60	2.0	1.5	52.15	40.54	42.19	58.29
5	70	10	30	1.5	1.5	72.57	53.47	63.20	77.07
6	70	20	15	2.0	1.0	36.18	23.08	27.64	38.27
7	70	30	60	0.5	0.5	44.81	21.88	32.37	40.86
8	70	40	45	1.0	0	42.13	21.90	27.22	36.64
9	80	10	45	2.0	0.5	83.88	62.03	78.66	85.19
10	80	20	60	1.5	0	64.40	48.39	64.36	70.37
11	80	30	15	1.0	1.5	46.57	41.02	46.45	62.14
12	80	40	30	0.5	1.0	46.93	6.57	16.00	19.84
13	90	10	60	1.0	1.0	85.90	58.93	87.99	84.13
14	90	20	45	0.5	1.5	66.38	6.68	25.23	26.36
15	90	30	30	2.0	0	63.35	32.67	51.99	58.67
16	90	40	15	1.5	0.5	50.41	28.63	37.50	48.37

Table 4
Factor response table.

	Effect factor	Temp. (%)	Time (%)	Acid (%)	H_2O_2 (%)	S/L (%)		Effect factor	Temp. (%)	Time (%)	Acid (%)	H_2O_2 (%)	S/L (%)
Li	K1	32.65	35.75	41.99	44.93	63.05	Ni	K1	25.71	29.47	19.98	37.47	59.04
	K2	48.92	52.54	50.48	51.61	48.57		K2	37.61	37.80	45.42	42.14	34.31
	K3	60.45	58.42	57.16	52.57	49.00		K3	51.37	41.36	49.85	41.49	41.29
	K4	66.51	61.81	58.89	59.42	47.90		K4	50.68	56.73	50.12	44.27	30.73
	Extreme deviation	33.86	26.06	16.90	14.49	15.15		Extreme deviation	25.66	27.25	30.15	6.80	28.31
	Priority order	temperature > time > acid > S/L > H_2O_2						Priority order	acid > S/L > time > temperature > H_2O_2				
Co	K1	23.28	24.50	10.10	27.06	44.93	Mn	K1	38.31	39.85	24.42	44.08	64.25
	K2	30.08	27.43	34.71	32.38	23.78		K2	48.21	47.72	54.55	52.42	42.57
	K3	39.50	30.23	40.20	29.72	31.47		K3	59.39	49.30	61.21	47.82	52.68
	K4	31.73	42.43	39.58	35.43	24.41		K4	54.38	63.41	60.11	55.97	40.79
	Extreme deviation	16.22	17.93	30.10	8.37	21.15		Extreme deviation	21.08	23.56	36.79	11.89	23.47
	Priority order	acid > S/L > time > temperature > H_2O_2						Priority order	acid > time > S/L > temperature > H_2O_2				

H_2O_2, and an acid concentration of 1.5 mol L^{-1}, a time of 60 min, a S/L ratio of 10 g L^{-1}, a temperature of 80 °C, and 1.5 vol.% H_2O_2 were selected as preliminary optimal production parameters.

3.3 Confirmation experiments

The factor effect analysis results were used to conduct experiments ranging from the most to the least effective parameters that affect the overall leaching efficiency. Part 1 is the effect of tartaric acid concentration on leaching efficiency. The results are shown in Fig. 1(a). When the acid concentration is increased from 0.5 to 2 mol L^{-1}, the leaching efficiencies of Li, Co, Ni, and Mn increase from 81.66, 70.10, 86.41, and 99.99% to 84.34, 75.93, 90.29, and 99.99%, respectively. If the acid concentration is increased again, the leaching efficiency will not increase significantly. Therefore, the acid concentration of 2 mol L^{-1} was selected as the optimal leaching parameter.

Part 2 is the impact of time on leaching efficiency, and the results are shown in Fig. 1(b). When the time is extended from 15 to 30 min, the leaching efficiencies of Li, Co, Ni, and Mn increase from 61.91, 54.28, 57.69, and 84.13% to 80.69, 73.32, 82.10, and 99.99%, respectively. If the leaching time is extended, the leaching efficiency does not significantly increase, so the time of 30 min was selected as the best leaching parameter.

Part 3 is the impact of S/L ratio on leaching efficiency, and the results are shown in Fig. 1(c). When the S/L ratio is increased from 5 to 10 g L^{-1}, the leaching efficiencies of Li, Co, Ni, and Mn change slightly from 78.86, 81.38, 77.64, and 95.24% to 78.83, 75.56, 78.00, and 99.99%, respectively. When the S/L ratio is increased to 15 g L^{-1}, the leaching efficiencies of Li, Co, Ni, and Mn decrease to 77.25, 65.58, 71.81, and 93.59%, and the leaching effect is less than ideal. Therefore, the S/L ratio of 10 g L^{-1} was selected as the best leaching parameter.
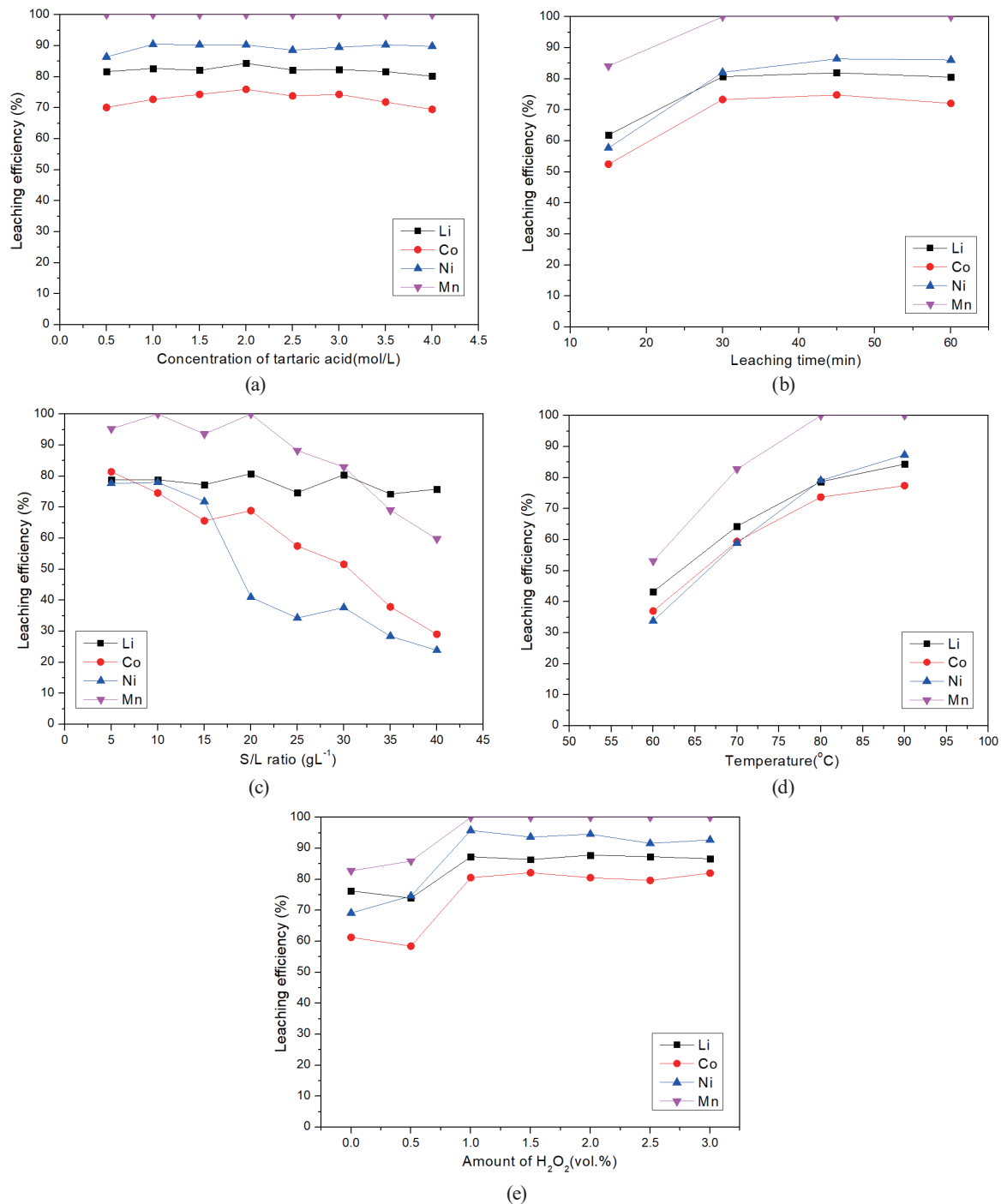
Fig. 1.   (Color online) Effects of (a) acid concentration, (b) time, (c) S/L ratio, (d) temperature, and (e) amount of H$_2$O$_2$ added on leaching efficiency.

Part 4 is the impact of temperature on leaching efficiency, with the results shown in Fig. 1(d). When the temperature is increased from 80 to 90 °C, the leaching efficiencies of Li, Co, Ni, and Mn increase from 78.71, 73.69, 79.00, and 99.99% to 84.37, 77.42, 87.33, and 99.99% respectively, so the temperature of 90 °C was selected as the best leaching parameter.

Part 5 is the impact of the amount of H_2O_2 added on leaching efficiency. The results are shown in Fig. 1(e). When the amount of H_2O_2 added is increased from 0.5 to 1.0 vol.%, the leaching efficiencies of Li, Co, Ni, and Mn increase from 73.92, 58.43, 74.62, and 85.89% to 87.29, 80.51, 95.78, and 99.99%, respectively. If it is further increased, the addition of H_2O_2 does not increase the leaching efficiency significantly, so 1.0 vol.% H_2O_2 is selected as the best leaching parameter.

Finally, the best leaching parameters are the tartaric acid concentration of 2 mol L^{-1}, the time of 30 min, the S/L ratio of 10 g L^{-1}, the temperature of 90 °C, and 1.0 vol.% H_2O_2, resulting in the best leaching efficiencies of Li, Co, Ni, and Mn of 87.29, 80.51, 95.78, and 99.99%, respectively.

4.   Conclusion

In this study, Taguchi methods were used to explore the effects of acid concentration, time, S/L ratio, temperature, and the amount of H_2O_2 added on leaching efficiency. First, orthogonal array experiment results were used to analyze the results, and the optimal order of the overall leaching efficiency was obtained as acid > time > S/L > temperature > H_2O_2. The acid concentration of 1.5 mol L^{-1}, the time of 60 min, the S/L ratio of 10 g L^{-1}, the temperature of 80 °C, and 1.5 vol.% H_2O_2 were selected as the preliminary optimal manufacturing parameters. Finally, the optimal leaching parameters obtained by confirmation experiment were the acid concentration of 2 mol L^{-1}, the time of 30 min, the S/L ratio at 10 g L^{-1}, the temperature of 90 °C, and 1.0 vol.% H_2O_2 for the optimal leaching rates of Li, Co, Ni, and Mn of 87.29, 80.51, 95.78, and 99.99%, respectively. The recovered Co metal can be used as a sensor material. In this study, 80.51% Co was successfully leached, which can be used as an electrochemical sensor material and improve the electrochemical performance of the electrochemical sensor.

Acknowledgments

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