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Recycling Metal from Waste Lithium-ion Batteries for Use as Electrochemical Sensor Material

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With the development of electric vehicles, the number of discarded lithium (Li)-ion batteries is expected to increase in the future. Waste Li-ion batteries contain cobalt (Co), nickel (Ni), and Li, which are valuable metals and, if not appropriately handled, will cause irreparable harm to the environment. Therefore, the recycling of waste Li-ion batteries is an important topic. In this study, we employed the Taguchi method to explore the impact of temperature, solid-to-liquid (S/L) ratio, time, acid concentration, and the amount of added hydrogen peroxide (H_2O_2) on the leaching rate. The optimized process parameters were initially obtained by the Taguchi method to be a S/L ratio of 10 g L^{-1}, H_2O_2 addition of 1.5 vol.%, an acid concentration of 2 mol L^{-1}, a temperature of 60 °C, and a time of 45 min. Because interactions may occur between the various factors, confirmation experiments were carried out according to the order of importance of the effect of the five parameters on the leaching rate. The optimum leaching parameters were ultimately found to be a S/L ratio of 25 g L^{-1}, H_2O_2 addition of 1.5 vol.%, an acid concentration of 2 mol L^{-1}, a temperature of 60 °C, and a time of 15 min. For these parameters, the leaching rates of Li, Co, Ni, and Mn were 96.41, 82.53, 89.25, and 99.99%, respectively. Finally, through kinetic analysis, we found that the activation energies of Li, Co, Ni, and Mn were 3.74, 24.81, 37.82, and 24.01 kJ mol^{-1}, respectively. Co obtained by leaching can be used in electrochemical sensors.

1. Introduction

Lithium (Li)-ion batteries are mainly composed of metals, organic chemicals, and plastics, and contain about 5–20% cobalt (Co), 5–10% nickel (Ni), 5–7% Li, 15% organic chemicals, and 7% plastics, depending on the manufacturer.(1) Owing to the advantages of Li-ion batteries, i.e., high battery voltage, high energy density, low self-discharge rate, and wide operating temperature range,(2) they are often used as power sources for mobile phones, notebook computers, and other electronic devices. Recently, with the development of hybrid and electric vehicles,(3) the production of Li-ion batteries has also increased, increasing the importance of recycling waste Li-ion batteries.

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According to the U.S. Geological Survey,(4–8) the global production of Li, Co, Ni, and manganese (Mn) in 2019 was about 86000, 144000, 2610000, and 19600000 metric tons, respectively. In 2019, Li-ion batteries used in the production of electric vehicles consumed approximately 17000, 19000, 65000, and 22000 metric tons of Li, Co, Ni, and Mn, respectively. It is estimated that by 2030, there will be 245 million electric vehicles on the road in the world, requiring over 185000, 180000, 925000, and 177000 metric tons of Li, Co, Ni, and Mn per year, respectively.(9) In 2020, China produced about 500000 tons of Li-ion batteries, with a recycling rate of less than 5%, and it is estimated that by 2030, 2 million tons of Li-ion batteries will be discarded worldwide annually.(9) Therefore, if the valuable metals of Li, Co, Ni, and Mn can be recovered from discarded Li-ion batteries, not only can the waste problem be reduced, but also a more circular economy can be realized.

In this study, we examine the use of sulfuric acid to leach Li-ion batteries. Chen and Ho(10) used 2 mol/L sulfuric acid, 10 vol.% hydrogen peroxide (H_2O_2), a solid-to-liquid (S/L) ratio of 30 ml/g, and a temperature of 70 ℃ for 90 min to successfully leach metal from Li-ion batteries They obtained leaching rates of 99.76, 98.46, 98.56, and 98.62% for Li, Co, Ni, and Mn, respectively. Yang *et al.*(11) used 3 mol/L sulfuric acid, 3 vol.% H_2O_2, a S/L ratio of 20 g/L, and a temperature of 80 ℃ for 60 min to successfully leach metal from Li-ion batteries. They obtained leaching rates of 97.8, 96.5, 98.1, and 97.0% for Li, Co, Ni, and Mn, respectively. He *et al.*(12) used 1 mol/L sulfuric acid, 1 vol.% H_2O_2, a S/L ratio of 40 g/L, and a temperature of 40 ℃ for 60 min to successfully leach about 99.7% of Li, Co, Ni, and Mn from Li-ion batteries.

The above studies all adopted a one-factor-at-a-time approach, making it impossible to know the effect of each parameter on the leaching rate. The effects of factors are relative to the calculated values under specific reference experimental conditions. Although the Li-ion battery materials in the above studies were different, the maximum difference in the leaching temperature was up to 30 ℃ and other factors also varied.

In this study, we used the Taguchi method to obtain useful statistical information from fewer experiments by performing full-factorial experiments. First, the weight of each parameter's effect on the leaching rate was confirmed, and then the impact weights were arranged in descending order to search for optimized process parameters for leaching. According to the research of Ribeiro *et al.*,(13) the Co leached in this study can be used as an electrochemical sensor material to improve the performance of electrochemical sensors.

2. Materials and Methods

2.1 Materials

Anode materials from waste Li-ion batteries were used in this study. Table 1 lists the contents of the elements in the anode materials after digestion with aqua regia and analysis by atomic absorption spectrometry. Among these elements, Li, Co, Ni, and Mn are the main target metals for leaching in the study. Nitric acid (HNO_3, 70%) for aqua regia digestion, hydrochloric acid (HCl, 37%) for aqua regia digestion, and sulfuric acid (H_2SO_4, 96%) for leaching were purchased from PanReac.

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

2.2 Leaching

The five control factors that may affect the leaching rate are temperature (60 to 90 °C), S/L ratio (10 to 40 g L^{-1}), time (15 to 60 min), acid concentration (0.5 to 2.0 mol L^{-1}), and H_2O_2 volume (0 to 1.5 vol.%). The L_{16} (4^5) orthogonal table was introduced for experimental planning, which allows the five control factors to have four levels, and the optimal parameters were finally obtained through factor response analysis and confirmation experiments. Table 2 lists the control factors selected in this experiment and their levels.

3. Results and Discussion

3.1 Sulfuric acid leaching

First, we performed a sulfuric acid leaching experiment to determine the degree of impact of the temperature, S/L ratio, time, acid concentration, and H_2O_2 addition on the leaching of the anode of the waste Li-ion battery. The leaching rates of Li, Co, Ni, and Mn are shown in Table 3. It can be seen from the experimental results that all five control factors affect the leaching rate.

3.2 Factor analysis

The response table is displayed in Table 4 and the response graph is shown in Fig. 1. The results show that the order of importance of factors affecting the Li leaching rate is S/L ratio > temperature > acid concentration > H_2O_2 addition > time. For the Co leaching rate, the order is H_2O_2 addition > S/L ratio > acid concentration > time > temperature. For the Ni leaching rate, the order is acid concentration > S/L ratio > H_2O_2 addition > time > temperature. For the Mn leaching rate, the order is H_2O_2 addition > S/L ratio > temperature > acid concentration > time. Finally, it is considered that the order of importance of factors affecting the total leaching rate is S/L ratio > H_2O_2 addition > acid concentration > temperature > time. The optimal process

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

Table 3
Leaching rates of Li, Co, Ni, and Mn under different control factor levels.

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	76.54	33.89	40.74	40.37
2	60	20	30	1.0	0.5	79.29	61.78	54.50	75.66
3	60	30	45	1.5	1.0	85.75	69.44	75.77	86.19
4	60	40	60	2.0	1.5	89.31	74.16	77.24	90.35
5	70	10	30	1.5	1.5	93.22	83.50	96.35	94.71
6	70	20	15	2.0	1.0	80.12	81.45	68.66	96.56
7	70	30	60	0.5	0.5	70.74	50.49	43.98	53.85
8	70	40	45	1.0	0	68.95	34.06	30.75	29.59
9	80	10	45	2.0	0.5	90.39	76.42	92.24	76.72
10	80	20	60	1.5	0	56.45	35.30	49.65	29.51
11	80	30	15	1.0	1.5	59.60	61.45	45.46	72.08
12	80	40	30	0.5	1.0	61.91	51.61	42.07	57.89
13	90	10	60	1.0	1.0	89.51	78.04	91.99	76.54
14	90	20	45	0.5	1.5	58.60	82.32	41.29	90.21
15	90	30	30	2.0	0	65.44	38.42	57.49	27.43
16	90	40	15	1.5	0.5	66.22	43.48	61.79	44.71

Table 4
Response table of factors for each metal.

	Effect factor	Temp. (%)	Time (%)	Acid (%)	H_2O_2 (%)	S/L (%)		Effect factor	Temp. (%)	Time (%)	Acid (%)	H_2O_2 (%)	S/L (%)
Li	K1	82.72	70.62	66.95	66.85	87.41	Ni	K1	62.06	54.16	42.02	44.66	80.33
	K2	78.26	74.97	74.34	76.66	68.62		K2	59.94	62.60	55.67	63.13	53.53
	K3	67.09	75.92	75.41	79.32	70.38		K3	57.35	60.01	70.89	69.62	55.67
	K4	69.94	76.50	81.32	75.18	71.60		K4	63.14	65.72	73.91	65.08	52.96
	Extreme deviation	15.64	5.88	14.37	12.48	18.80		Extreme deviation	5.79	11.55	31.89	24.97	27.37
	Order of importance	S/L > temperature > acid > H_2O_2 > time						Order of importance	acid > S/L > H_2O_2 > time > temperature				
Co	K1	59.82	55.07	54.58	35.42	67.96	Mn	K1	73.14	63.43	60.58	31.73	72.09
	K2	62.37	58.83	58.83	58.05	65.21		K2	68.68	63.93	63.47	62.74	72.99
	K3	56.20	65.56	57.93	70.13	54.95		K3	59.05	70.68	63.78	79.30	59.89
	K4	60.56	59.50	67.61	75.36	50.83		K4	59.73	62.56	72.77	86.84	55.63
	Extreme deviation	6.18	10.49	13.03	39.94	17.13		Extreme deviation	14.09	8.11	12.18	55.11	17.35
	Order of importance	H_2O_2 > S/L > acid > time > temperature						Order of importance	H_2O_2 > S/L > temperature > acid > time				

parameters are the addition of 1.5 vol.% of H_2O_2, an acid concentration of 2 mol L^{-1}, a temperature of 60 °C, a S/L ratio of 10 g L^{-1}, and a time of 45 min.

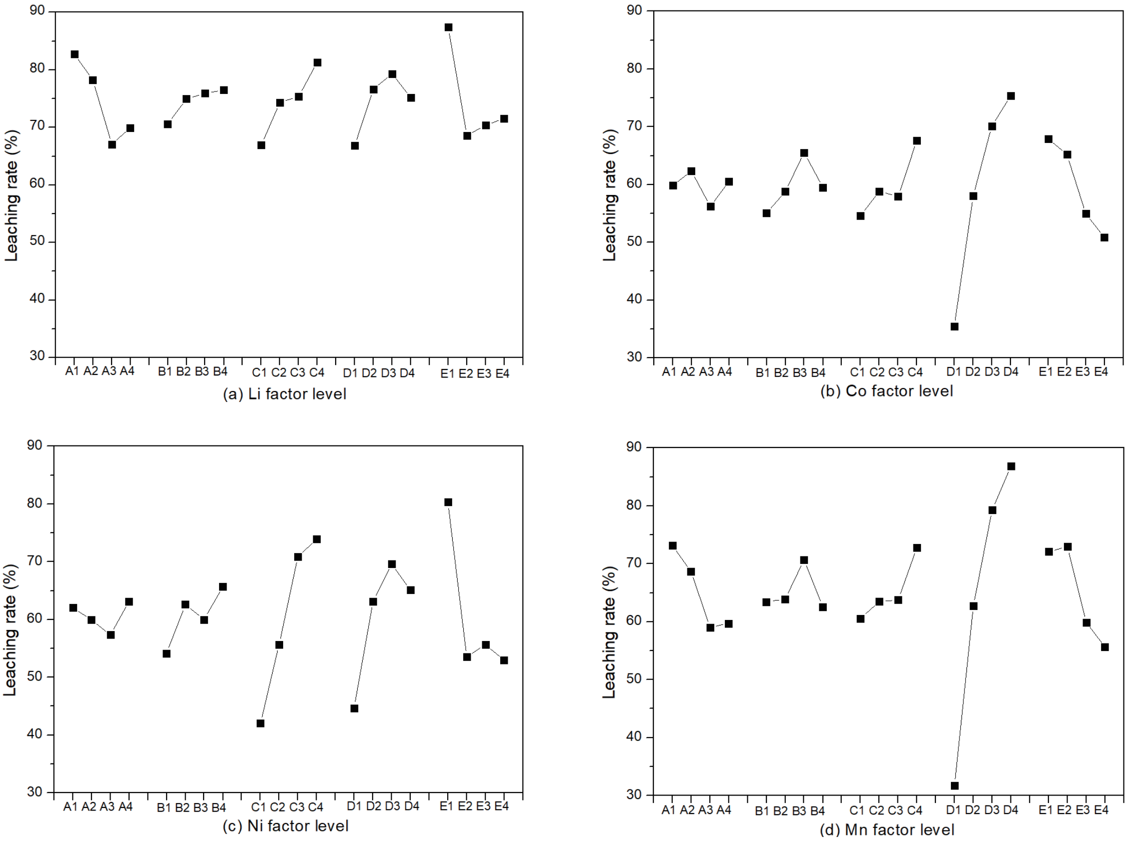

Fig. 1. (a) Li, (b) Co, (c) Ni, and (d) Mn factor levels vs leaching rate.

3.3 Confirmation experiments

3.3.1 Effect of S/L ratio

Figure 2(a) shows that the S/L ratio affects the leaching rate. The leaching effect is considered when the amount of added H_2O_2 is 1.5 vol.%, the acid concentration is 2 mol L^{-1}, the temperature is 60 °C, and the time is 45 min. A S/L ratio of 25 g L^{-1} is selected as the optimal parameter, for which the leaching rates of Li, Co, Ni, and Mn are 99.86, 89.27, 84.99, and 99.99%, respectively.

3.3.2 Effect of amount of H_2O_2

It can be seen from Fig. 2(b) that the amount of added H_2O_2 affects the leaching rate. Under the conditions of 2 mol L^{-1} acid concentration, a S/L ratio of 25 g L^{-1}, a temperature of 60 °C, and a time of 45 min, the leaching rates of the four metals increase with the amount of added H_2O_2. The leaching rate is highest when the amount of added H_2O_2 is 1.5 vol.%. This amount of H_2O_2 is selected as the optimal parameter, for which the leaching rates of Li, Co, Ni, and Mn are 91.91, 87.88, 82.51, and 99.99%, respectively.

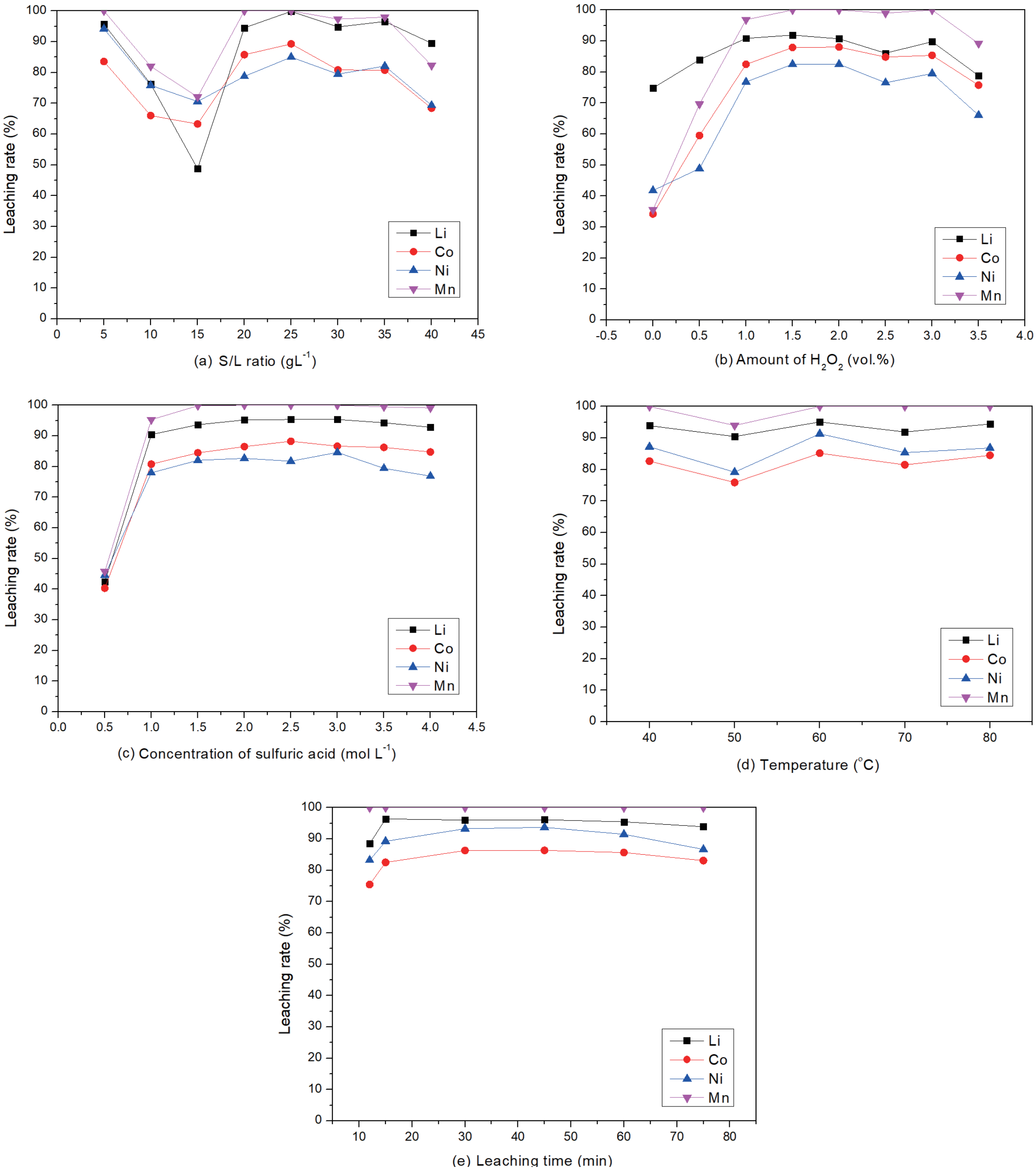

Fig. 2. (Color online) Effects of (a) S/L ratio, (b) amount of added H_2O_2, (c) sulfuric acid concentration, (d) temperature, and (e) time on the leaching rates under optimized parameters.

3.3.3 Effect of acid concentration

Figure 2(c) shows the effect of acid concentration on the leaching rate. When the S/L ratio is 25 g L^{-1}, the amount of added H_2O_2 is 1.5 vol.%, the temperature is 60 °C, and the time is 45 min, the leaching rates of the four metals increase with the acid concentration. The leaching rate is highest when the acid concentration is 2 mol L^{-1}, and any subsequent increase in the acid concentration does not increase the leaching rate. Therefore, the acid concentration of 2 mol L^{-1} is selected as the best parameter, for which the Li, Co, Ni, and Mn leaching rates are 95.22, 86.50, 82.66, and 99.99%, respectively.

3.3.4 Effect of temperature

Figure 2(d) shows the effect of temperature on the leaching rate. When the S/L ratio is 25 g L^{-1}, the amount of added H_2O_2 is 1.5 vol.%, the acid concentration is 2 mol L^{-1}, and the time is 45 min, the leaching rates of the four metals do not change markedly with the temperature. The leaching rate is highest when the temperature is 60 ℃ and is about 4% higher than that at 40 ℃. Therefore, the temperature of 60 ℃ is selected as the optimal parameter. For this temperature, the leaching rates of Li, Co, Ni, and Mn are 95.09, 85.16, 91.31, and 99.99%, respectively.

3.3.5 Effect of time

Figure 2(e) shows the effect of time on the leaching rate. When the S/L ratio is 25 g L^{-1}, the amount of added H_2O_2 is 1.5 vol.%, the acid concentration is 2 mol L^{-1}, and the temperature is 60 ℃, the leaching rates of the four metals increase with time. When the leaching time is 12 min, the leaching rates of Li, Co, Ni, and Mn are 88.47, 75.43, 83.23, and 99.97%, respectively. When the leaching time is 15 min, the leaching rates of Li, Co, Ni, and Mn are highest (96.41, 82.53, 89.25, and 99.99%, respectively). Further increasing the leaching time does not affect the leaching rate; thus, the optimal leaching time is 15 min.

3.3.6 Optimizing process parameters

The finally selected process parameters are a S/L ratio of 25 g L^{-1}, H_2O_2 addition of 1.5 vol.%, an acid concentration of 2 mol L^{-1}, a temperature of 60 ℃, and a time of 15 min, for which the leaching rates of Li, Co, Ni, and Mn are 96.41, 82.53, 89.25, and 99.99%, respectively.

3.4 Kinetic analysis

Kinetic analysis was performed for a S/L ratio of 25 g L^{-1}, H_2O_2 addition of 1.5 vol.%, an acid concentration of 2 mol L^{-1}, temperatures of 60 to 90 ℃, and times of 0.5 to 75 min. The obtained leaching rates are shown in Fig. 3.

Metal leaching from an anode material is a solid-liquid heterogeneous reaction, which has been successfully explained by shrinking-core models. These models can be further subdivided into three types: chemical reaction control, diffusion process control, and hybrid control models.(14) The results of this study are shown in Fig. 4, which are mainly in line with the hybrid control model [Eq. (1)]. The kinetic parameters are shown in Table 5.

$$\text{Hybrid control: } \frac{1}{3}\ln\left(1-x\right)+\left[\left(1-x\right)^{\frac{1}{3}}-1\right]=kt \tag{1}$$

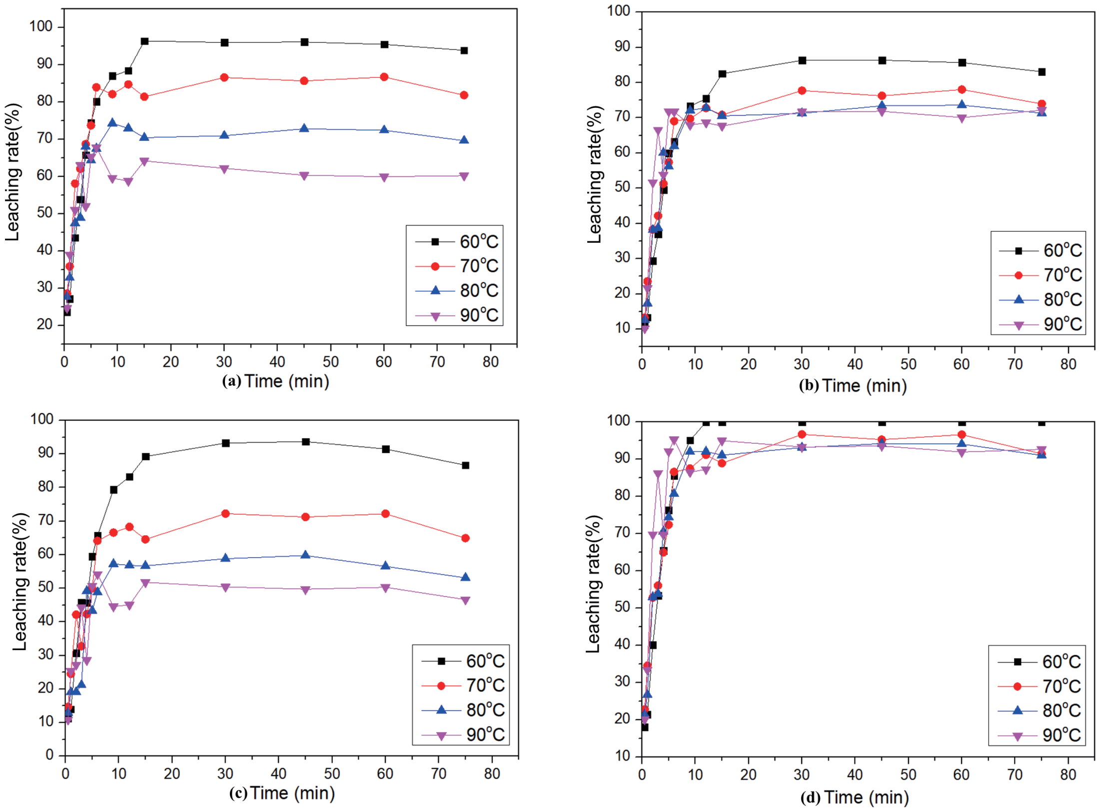

Fig. 3. (Color online) Effect of reaction temperature and time on the leaching rates of (a) Li, (b) Co, (c) Ni, and (d) Mn.

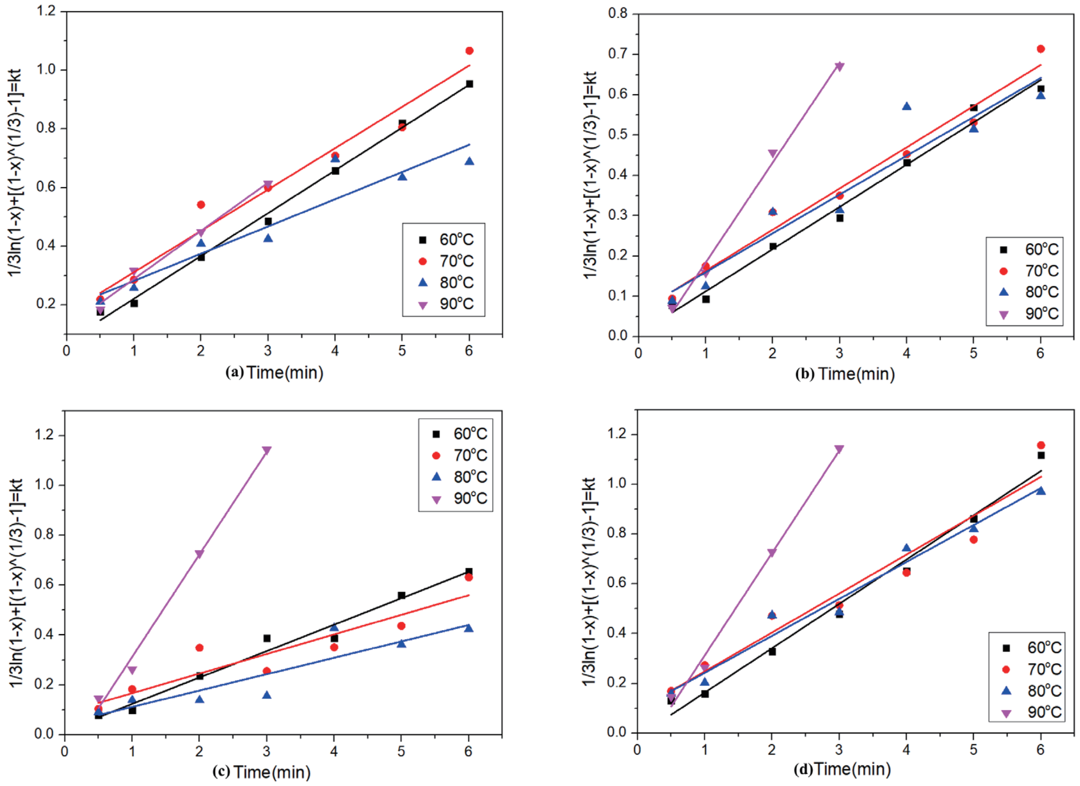

Fig. 4. (Color online) Fitting of leaching kinetics of (a) Li, (b) Co, (c) Ni, and (d) Mn for hybrid control model.

Table 5
Kinetic parameters of Li, Co, Ni, and Mn.

	Li		Co		Ni		Mn	
T (°C)	*k*	R^2	*k*	R^2	*k*	R^2	*k*	R^2
60	0.146	0.996	0.105	0.988	0.106	0.977	0.178	0.986
70	0.141	0.967	0.102	0.977	0.078	0.857	0.156	0.942
80	0.145	0.891	0.097	0.909	0.066	0.816	0.149	0.974
90	0.164	0.987	0.248	0.994	0.411	0.993	0.411	0.993

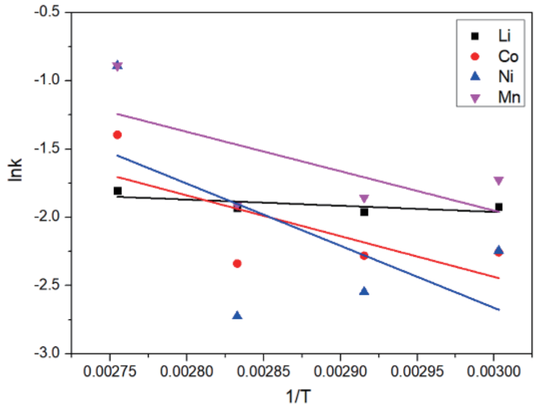

Fig. 5. (Color online) Fitting of leaching kinetics of Li, Co, Ni, and Mn using Arrhenius formula.

Table 6
Activation energies of Li, Co, Ni, and Mn.

Metal	R^2	E_a (kJ mol^{-1})
Li	0.507	3.74
Co	0.502	24.81
Ni	0.341	37.82
Mn	0.419	24.01

Finally, the Arrhenius formula [Eq. (2)]$^{(14)}$ was used to analyze the metal leaching. The results are shown in Fig. 5 and Table 6. The activation energies of Li, Co, Ni, and Mn were found to be 3.74, 24.81, 37.82, and 24.01 kJ moL^{-1}, respectively.

$$\text{Arrhenius formula: } k = Ae^{\frac{-E_a}{RT}} \tag{2}$$

4. Conclusion

In this study, the Taguchi method was used to explore the effect of sulfuric acid on the leaching rate of the anode of waste Li-ion batteries. The effects of five control factors were considered: temperature, S/L ratio, time, acid concentration, and H_2O_2 addition. An L_{16} (4^5) orthogonal table was used for experimental planning. From the experimental results, the order of importance of the weighting factors affecting the leaching rate was S/L ratio > H_2O_2 addition > acid concentration > temperature > time. A S/L ratio of 10 g L^{-1}, H_2O_2 addition of 1.5 vol.%, an acid concentration of 2 mol L^{-1}, a temperature of 60 °C, and a time of 45 min were initially selected as the optimal process parameters. Finally, a confirmation experiment was carried out. The results showed that when the S/L ratio was 25 g L^{-1}, the amount of H_2O_2 addition was 1.5 vol.%, the acid concentration was 2 mol L^{-1}, the temperature was 60 °C, and the time was 15 min, the Li, Co, Ni, and Mn leaching rates were 96.41, 82.53, 89.25, and 99.99%, respectively;

thus, metals can be effectively leached from the anodes of waste Li-ion batteries. As a result of dynamic analysis, a hybrid control model was successfully fitted. The results showed that the activation energies of Li, Co, Ni, and Mn were 3.74, 24.81, 37.82, and 24.01 kJ moL^{-1}, respectively. In this study, 82.53% of the Co was successfully leached, which can be used as an electrochemical sensor material to improve the performance of electrochemical sensors.

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