

LEACHING PROCESS FOR THE RECOVERY OF VALUABLE METALS FROM SPENT LITHIUM-NICKEL-COBALT-MANGANESE-OXIDE-BASED LITHIUM-ION BATTERIES

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Abstract

This study focused on the leaching process for the recycling of Li, Ni, Co, and Mn from the $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM) cathodes of spent lithium-ion batteries (LIBs). Eh–pH diagrams were used to analyze suitable leaching conditions. Operating variables, such as the concentration of H_2SO_4 (0.5–2.5 M), concentration of H_2O_2 (0–1 vol%), temperature (10–50 °C), stirring speed (400–800 rpm), and solid/liquid ratio (0.03–0.2 g·mL⁻¹), were investigated to determine the most efficient conditions for leaching. The results indicated that the leaching efficiencies of Ni, Co, and Mn in $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ were almost identical and significantly lower than that of Li. Possible reaction mechanisms were proposed to explain the leaching efficiencies of the various elements. Under optimum leaching conditions, complete leaching was achieved for Li, Ni, Co, and Mn. Moreover, the leaching kinetics of $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ is controlled by the rate of the leaching reaction, and not by that of the diffusion. Based on the characteristics of the leaching kinetics, the “cubic rate law” was revised to optimally characterize the leaching process.

Keywords

Lithium-ion batteries, Recycling, Leaching, Kinetics, $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$

Introduction

Lithium-ion batteries (LIBs) have been widely used in portable electronic devices and being considered the most suitable battery for powering electric vehicles (EVs). From the perspectives of environmental conservation and resources recovery, the recycling of spent LIBs is worthy of investigation. $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM) has many advantages over LiCoO_2 , such as a higher reversible capacity, a higher thermal stability, and a lower cost. Therefore, the market share of NCM keeps significantly increasing year by year. In 2012, NCM has surpassed LiCoO_2 as the most widely used cathode material of LIBs. However, the leaching behavior (including kinetics

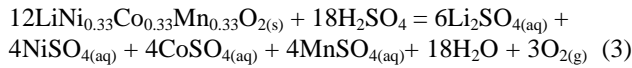
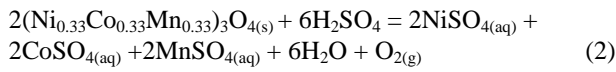
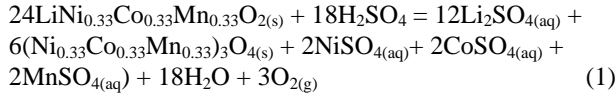
aspects) of NCM cathode was rarely reported. Many researchers only focus on the leaching of Li and Co from the LiCoO_2 cathode materials during the recycling of spent LIBs and neglect other metals, which will result in environmental pollution (Ni is a toxic metal) and a waste of resources. Thus, a detailed investigation of the leaching behavior of NCM cathode materials is quite necessary.

Conclusions

In the leaching process of LiCoO_2 , the intermediate of Co_3O_4 was formed (Ferreira et al., 2009). Similarly, the

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leaching reaction of $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ may involve two steps: the conversion of $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ to $(\text{Ni}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33})_3\text{O}_4$, which remains in the solid phase at first, as shown in Eq. (1), after which the solid phase $(\text{Ni}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33})_3\text{O}_4$ further dissolves in H_2SO_4 , as shown in Eq. (2). The reaction rate of Eq. (1) seems faster than that of Eq. (2). Therefore, the leaching efficiency of Li was higher than that of Ni, Co, and Mn. The possible reactions can be expressed as follows:



The thermodynamics data can be used to predict the feasibility and equilibrium of the leaching reaction. According to the Eh–pH diagrams, the solid phase $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ can effectively convert to the aqueous phases of Li^+ , Ni^{2+} , Co^{2+} , and Mn^{2+} in acidic solutions (pH < 6.1) under appropriate Eh conditions. However, even after increasing the H_2SO_4 concentration and temperature, the leaching efficiency was still found to be low (80% for Li, and 40% for Ni, Co, and Mn).

From a kinetics perspective, the leaching efficiency depends on the rate of the leaching reaction and that of mass transfer. Experimental results show that an increase in stirring speed has no obvious effect on the leaching efficiencies for any of the metals. Moreover, the leaching of $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ involves the conversion of Ni^{2+} , Co^{3+} , and Mn^{4+} in the solid phase (determined by XPS) to Ni^{2+} , Co^{2+} , and Mn^{2+} in the aqueous phase. H_2O_2 was found to act as a reducing agent to significantly improve the leaching efficiency. Therefore, the leaching kinetics of $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ is controlled by the rate of the leaching reaction, and not by that of the diffusion.

Finally, the leaching efficiencies of Li, Ni, Co, and Mn achieved 100% under the optimum leaching conditions: a H_2SO_4 concentration of 1 M, a temperature of 40 °C, a H_2O_2 concentration of 1 vol%, an S/L ratio of 1/15 $\text{g}\cdot\text{mL}^{-1}$, and a leaching time of 1 h.

Based on the results of SEM and the characteristics of leaching kinetic curves (shown in Figure 1), “cubic rate law” (Segal and Sellers, 1982) was used to characterize the leaching process. However, the experimental results were found to be slightly different from those predicted by using the equation. This is probably because the cubic rate law did not consider the variation of the weight fraction of

metal in the solid phase during the leaching process. Therefore, the cubic rate law was corrected to be:

$$(1-f)^{1/3} = \left(\frac{w}{w_0}\right)^{1/3} \left(1 - \frac{kt}{r_0\rho}\right) = \theta_{(t)} \left(1 - \frac{kt}{r_0\rho}\right) \quad (4)$$

Compared to the initial cubic rate law, $(1-f)^{1/3} = 1 - kt/r_0\rho$, and Eq. (4) added a $\theta_{(t)}$ term, which is a function of time and can characterize the variation of the weight fraction of the metal in the solid phase. If the weight fraction of the metal in this phase, w , is maintained constant during the leaching process, then $\theta_{(t)} = 1$, and Eq. (4) can be simplified to the initial cubic rate law.

Using the experimental data, a plot of $(1-f)^{1/3}$ vs. t is shown in the inset of Figure 1. The leaching of $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ can be divided into two stages, and the function of $\theta_{(t)}$ can be approximated to a constant in each stage. For the first stage (0–15 min), $\theta = 0.832$, $k_{obs} (= k/r_0\rho) = 0.027 \text{ min}^{-1}$ for Li and $\theta = 0.962$, $k_{obs} = 0.027 \text{ min}^{-1}$ for Ni, Co, and Mn. For the slow second stage, $\theta = 0.782$, $k_{obs} = 0.022 \text{ min}^{-1}$ for Li, and $\theta = 0.773$, $k_{obs} = 0.017 \text{ min}^{-1}$ for Ni, Co, and Mn.

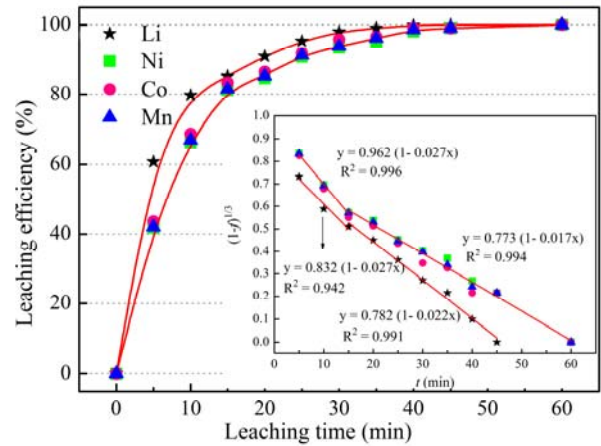


Figure 1. Leaching kinetic curves of Li, Ni, Co, and Mn from $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$. $[\text{H}_2\text{SO}_4] = 1 \text{ M}$; $T = 40 \text{ }^\circ\text{C}$; $[\text{H}_2\text{O}_2] = 1 \text{ vol\%}$ and $S/L = 1/15 \text{ g}\cdot\text{mL}^{-1}$. Inset shows Cubic rate law plots.

Acknowledgments

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