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Study of spent battery material leaching process

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Abstract: The recovery of Ni, Co and Mn from spent battery material is very important to environment protection, utilization of resources and cost reduction of the material. The dissolution rates of Ni, Co and Mn with hydrochloric acid as leachant are all over 95% under the optimal conditions of initial hydrochloric acid of 6 mol/L, particle size of 120 μm for the exhausted scraps, molar ratio of H_2O_2 to MeS of 2, leaching temperature about 60 ℃, ratio of liquid to solid of 8, and leaching time of 2 h. The $Ni_xCo_yMn_z$ precursor for cathode material prepared from the purified leaching solution, can meet the demand of precursor by pure chemicals. The process is economic and feasible for base metals from spent battery material.

Key words: spent battery materials; nickel; cobalt; manganese; recovery; leaching

1 Introduction

Nickel and cobalt are very important in many fields, and the world's demand for them is progressively increasing. Due to the primary resources being depleted and the constraints by the laws and legislation related to the environment protection in the world, it becomes more and more important to recover these metals as the secondary resources. HU et al[1] extracted these metals from waste catalyst, GBOR et al[2] recovered Ni and Co from waste nickel smelt slag, and RABAH et al[3] recovered Ni, Co and some salts from spent Ni-MH batteries. Many methods have been applied for treatment of these spent materials and subsequent separation of impurities from leaching solution, such as leaching with different acids, chlorination, pyro- and hydro-metallurgical processes for extraction[4−9], and solvent extraction[10−11], ion exchange[12−14], sulfuration precipitation[15].

As cathode material for lithium ion battery, $Ni_xCo_yMn_z$ is widely applied in the battery industry[16]. Traditionally, the cathode material is prepared by using pure chemical reagents. To reduce the cost of the materials, it is essential to employ the secondary resources. LIU et al[17] prepared satisfactory $LiCoO_2$ from battery castoff. QIN et al[18] obtained lead sulfate powders from galena concentrates directly. The aim of this work is to recover nickel, cobalt, manganese and other metals from spent battery material by leaching treatment. The effects of various conditions, such as the ratio of liquid to solid(L/S), leaching temperature, molar ratio of H_2O_2 to MeS, acidity, oxidant concentration and particle size are investigated, and the precursor of $Ni_xCo_yMn_z$ cathode material is prepared directly from leaching solution.

2 Experimental

2.1 Materials

The composition of spent battery materials from a battery plant in Hunan Province, China, is shown in Table 1. The materials were mainly made of electrode castoffs including oxides of cobalt, nickel and manganese as well as their mixture with some alloy scraps used in production of battery; the acid insoluble components consisted of silica and refractory materials from electrode supplies in sintering. Fig.1 shows that XRD

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Table 1 Chemical composition of spent battery materials (mass fraction,%)

Ni	Fe	Cu	Co	Mn	Ca	Mg	Acid insoluble component
20	10	20	20	5	0.26	0.37	24.37

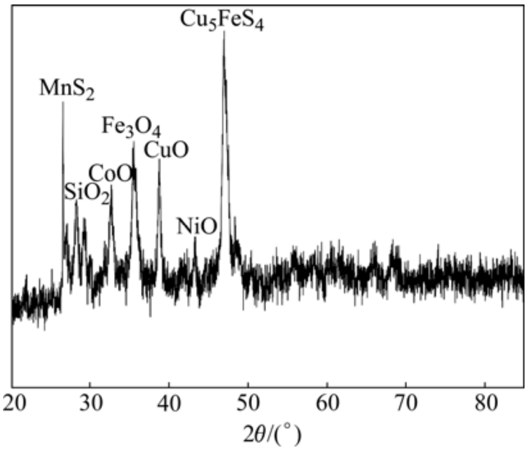

Fig.1 XRD pattern of spent battery material

pattern of the spent materials, where the main components are cobalt oxide, nickel oxide, manganese sulfide, ferric and ferrous oxide, copper oxide and copper iron sulfide. The samples were ground and sieved into four groups: 200, 150, 120 and 80 μm. Chemical grade hydrochloric acid was used in this study.

2.2 Principle

Some reactions occurring in the leaching process are as follows:

$$Fe_3O_4+8H^+=2Fe^{3+}+Fe^{2+}+4H_2O \quad (1)$$

$$CoO+2H^+=Co^{2+}+H_2O \quad (2)$$

$$NiO+2H^+=Ni^{2+}+H_2O \quad (3)$$

$$MnS_2+4H_2O_2=Mn^{2+}+SO_4^{2-}+4H_2O+S\downarrow \quad (4)$$

$$2Cu_5FeS_4+31H_2O_2+14HCl= 6CuSO_4+4CuCl_2+2FeCl_3+38H_2O+2S\downarrow \quad (5)$$

2.3 Procedure

The effects of leaching parameters such as initial HCl concentration, L/S ratio, temperature, molar ratio of H_2O_2 to MeS, particle size and leaching time on dissolution rate of the main metals in the samples were investigated. The prepared leaching solution with the desired hydrochloric acid concentration was placed into a 1 L round-bottom flask with 3 holes. Once the desired temperature was achieved, the dried sample was decanted to the flask from the feed opening and stirred at a constant speed by a Teflon coated magnet. The reaction temperature was controlled by an isothermal water bath with a digital thermometer (within ±1 ℃). The reaction mixture was agitated at a fixed rate of 250 r/min. The effect of leaching time on metallic extraction was calculated by Eq.(6). At the end of leaching, the leached residue was filtered and washed with distilled water using a Büchner funnel. The leaching rates of metals (Ni, Co, etc) were calculated by detecting the contents of metals in the filtrate.

$$X_{\mathrm{M},i}=\frac{\left(V-\sum_{i=1}^{i-1}V_i\right)C_{\mathrm{M},i}+\sum_{i=1}^{i-1}V_iC_{\mathrm{M},i}}{m(C_\mathrm{M}/100)} \quad (6)$$

where $X_{\mathrm{M},i}$ is the dissolution rate of M (Ni, Co, etc) in the sample i withdrawn each time, V the initial volume of the solution, V_i the volume of the sample i, $C_{\mathrm{M},i}$ the content of M in sample i, m the initial mass of waste (on dried basis) added in the reactor and C_M the content of M in waste.

2.4 Analysis

The contents of Co, Cu, Ni, Fe and Mn in samples and solution were analyzed by a chemical method and atomic absorption spectrophotometry (Ruili-wfx120). X-ray diffractometry (Rint-2000, Rigaku) was used to identify the components of the spent battery and leaching residue.

3 Results and discussion

3.1 Effect of initial HCl concentration

The effect of HCl concentration on the leaching of valuable metals is shown in Fig.2. It can be seen that the leaching rates increase gradually with the increase of initial HCl concentration. The increase in the amount of acid can increase the dissolution rate based on kinetics [19]. The maximum dissolution rate can reach 96.5%, 95.5%, 98.5%, 96.0% and 96.3% for nickel, cobalt, copper, manganese and iron, respectively. The maximum

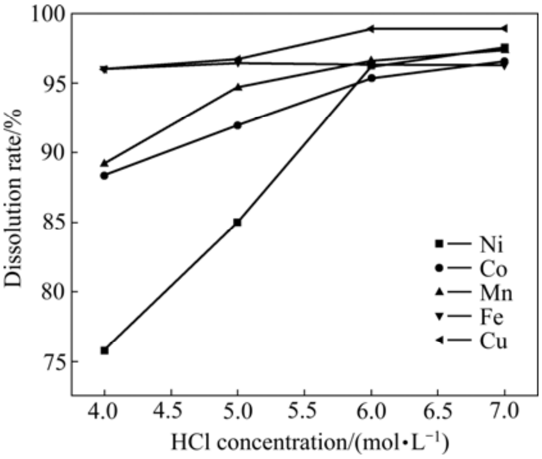

Fig.2 Effect of initial HCl concentration on dissolution rates of Ni, Co, Mn, Cu and Fe under conditions of L/S ratio of 8/1, molar ratio of H_2O_2 to MeS of 2, particle size of 120 μm at 60 ℃ for 120 min

rates of these metals except iron were increased little when the acid concentration was beyond 6 mol/L. This is probably because the determination of iron is interfered by its complex with chloride ion. The optimum initial HCl concentration is chosen to be 6 mol/L.

3.2 Effect of L/S ratio

Fig.3 shows that the dissolution rates increase obviously with the increase of L/S ratio but do not when the ratio is beyond 8:1. The increase in L/S ratio could decrease the concentration of metal ion in leaching solution, strengthen mass transfer and accelerate the leaching rate[19]. But too high L/S ratio would lead to the increase of leaching solution volume, which is not favorable to subsequent separation. Therefore, the L/S ratio of 8:1 is suitable.

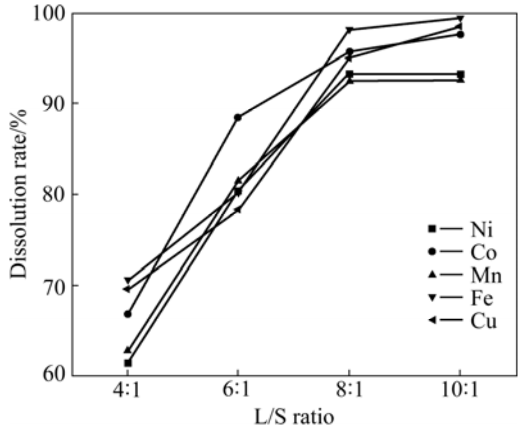

Fig.3 Effect of L/S ratio on dissolution rates of Ni, Co, Mn, Cu and Fe under conditions of initial HCl concentration of 6 mol/L, molar ratio of H_2O_2 to MeS of 2, particle size of 120 μm at 60 ℃ for 120 min

3.3 Effect of H_2O_2 content

It can be observed in Fig.4 that the content of oxidant H_2O_2 can affect the dissolution rate greatly. The dissolution rates of all metals increase with the increase of H_2O_2. In this leaching process, sulfide ion generates and reacts with metal ion and hydrogen ion to form insoluble sulfide and to release gas. To improve the dissolution rate, one way is to increase the acid concentration, which can be proved in Fig.2, the other is to add oxidant to make sulfide ion to form sulfate[20]. The dissolution rates of Fe, Mn and Cu increase more rapidly than those of Ni and Co as the oxidant content increases. This is because part of Fe, Mn and Cu exist in sulfide forms whilst Ni and Co exist in oxide form in waste as shown in Fig.1. When the molar ratio of H_2O_2 to MeS is more than 2, the maximum dissolution rate can be obtained.

3.4 Effect of temperature

The effect of temperature on dissolution rate is shown in Fig.5. It is clearly observed that the dissolution rate increases with temperature increasing from 20 to 60 ℃. The dissolution rate of Ni increases from 90% to 97%, Co from 86% to 95%, Mn from 82% to 96%, respectively. However, the dissolution rates of Ni and Co are not greatly affected by temperature. It is well known that Ni and Co mainly exist in samples as oxide form which can be easily dissolved by acid. But, parts of Fe, Cu and Mn as sulfides can be extracted in the presence of oxygen or some other oxidant[9]. Hence, the reactive activity of oxidants is intensified greatly when temperature increases. Although the dissolution rate can be improved with increase in temperature, the dissolution rates of Fe, Cu and Mn begin to descend at 90 ℃. Besides, at high temperature the operation cost increases and hydrochloric acid poignantly evaporates, which results in the operation conditions worse. So, 60 ℃ is chosen as an optimum temperature.

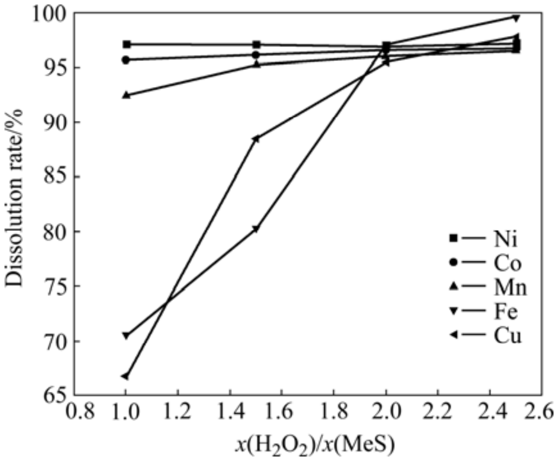

Fig.4 Effect of molar ratio of H_2O_2 to MeS on dissolution rates of Ni, Co, Mn, Cu and Fe for samples with particle size of 120 μm under conditions of initial HCl concentration of 6 mol/L, L/S ratio of 8/1 at 60 ℃ for 120 min

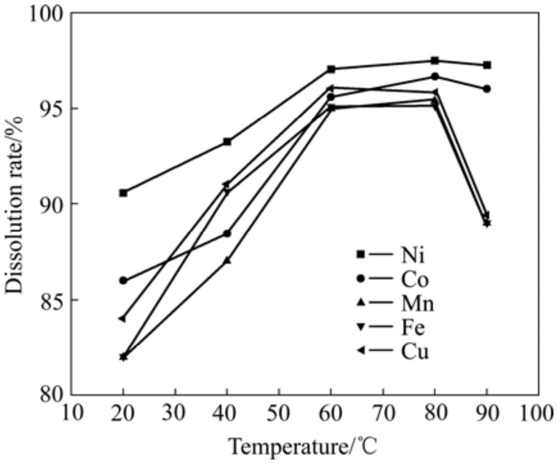

Fig.5 Effect of temperature on dissolution rates of Ni, Co, Mn, Cu and Fe under conditions of initial HCl concentration of 6 mol/L, particle size of 120 μm, molar ratio of H_2O_2 to MeS of 2 and L/S ratio of 8/1 for 120 min

3.5 Effect of particle size

The effect of particle size on the dissolution rates is presented in Fig.6. It is indicated that the dissolution rates of these metals are fairly similar, i.e. they increase with the decrease of particle size and reach about 95%. The decrease of particle size can increase the surface area of mineral, which increases the contact chance between solid and solution, leading to the increase of dissolution rate in given conditions. To acquire satisfactory leaching rate for the tested metals, it is necessary to keep particle size below 120 μm.

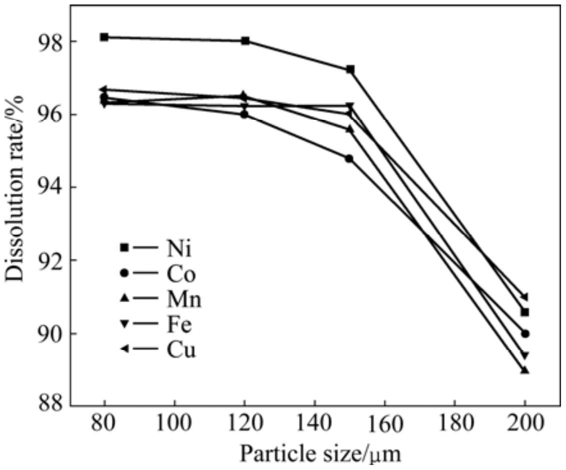

Fig.6 Effect of particle size on dissolution rates of Ni, Co, Mn, Cu and Fe under conditions of molar ratio of H_2O_2 to MeS of 2, initial HCl concentration of 6 mol/L, L/S ratio of 8/1 at 60 ℃ for 120 min

3.6 Effect of leaching time

The effect of leaching time on the dissolution rates is shown in Fig.7. It can be seen that the dissolution rates of Ni and Co can achieve a high value in 40 min and the maximum value of Ni is presented after leaching for 60 min. Because Ni and Co exist in oxide forms (Fig.8), the interaction of acid with relatively high concentration to oxides of Ni and Co is fast, and the leaching rates of them reach the maximum in relatively short leaching time[21]. For Fe and Co exist in oxide and sulfide forms (see Fig.8), the metal oxides can react with HCl, while the sulfides are oxidized by H_2O_2 in the initial period. As shown in Fig.7, with the leaching proceeding, the oxidized sulfides dissolve gradually, and the leaching rates of Fe and Cu increase continuously in the whole leaching process. MnS_2 reacts with H_2O_2 in acid solution, the Mn_2O_3 solid generates and dissolves gradually. It can be observed from the appearance and disappearance of X-ray diffraction peaks for the Mn_2O_3 at 2θ angle of 34.1° in Fig.8. Since both precipitation and dissolution occur simultaneously, a mediate plateau presents in the leaching rates curve of Mn, as shown in Fig.7.

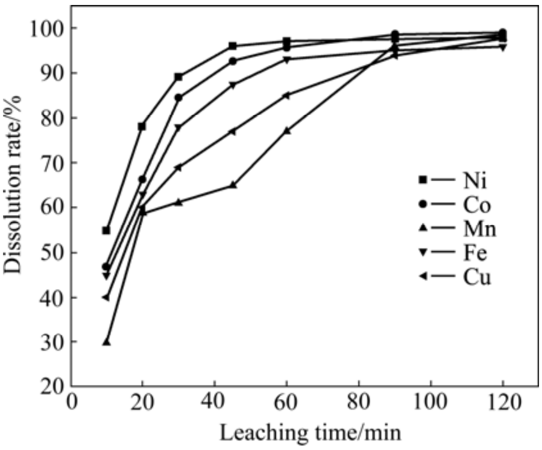

Fig.7 Effect of leaching time on dissolution rates of Ni, Co, Mn, Cu and Fe under conditions of molar ratio of H_2O_2 to MeS of 2, initial HCl concentration of 6 mol/L, L/S ratio of 8/1, particle size of 120 μm at 60 ℃

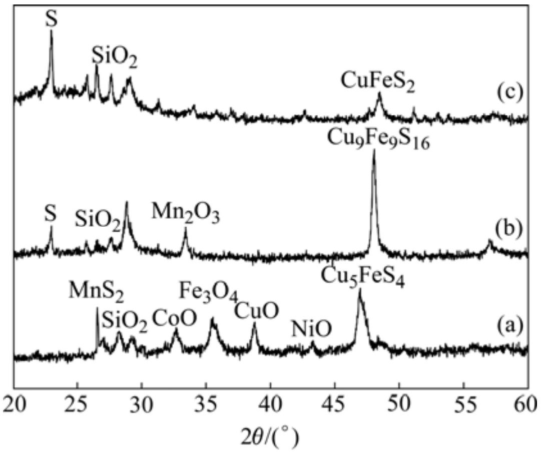

Fig.8 XRD patterns of material and leaching residue: (a) Material; (b) Leaching residue after 1 h; (c) Leaching residue after 2 h

4 Purification

There are large quantities of valuable metals, such as Ni, Co, Mn, Cu and Fe, as well as impurities in leaching solution. Cu was first removed through replacement by iron powder, then iron was removed by precipitation as goethite. After purification, the solution contains Ni 18.6 g/L, Co 18.1 g/L and Mn 4 g/L. According to $Ni_xCo_yMn_z$ ratio, the given amounts of chlorides of nickel, manganese and cobalt were added into the solution to prepare the precursor of the cathode material directly through co-precipitation with ammonium bicarbonate. The precursor can meet the demand of precursor by pure chemical.

5 Conclusions

To prepare battery material from secondary resources, the optimum leaching conditions were obtained with spent battery material as resources. The optimum leaching conditions for the spent battery material are: temperature 60 ℃, molar ratio of H_2O_2 to MeS 2, initial HCl concentration 6 mol/L, L/S ratio 8/1, particle size less than 120 μm and leaching time 120 min. The leaching solution after purification and separation of impurities can be used to prepare the precursor of $Ni_xCo_yMn_z$ cathode material directly. The precursor can be up to standard of precursor made by pure chemical, and is competitive of cost with the chemicals prepared from primary resources.

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