



# A copper-catalyzed bioleaching process for enhancement of cobalt dissolution from spent lithium-ion batteries

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## ABSTRACT

A copper-catalyzed bioleaching process was developed to recycle cobalt from spent lithium-ion batteries (mainly  $\text{LiCoO}_2$ ) in this paper. The influence of copper ions on bioleaching of  $\text{LiCoO}_2$  by *Acidithiobacillus ferrooxidans* (*A.f*) was investigated. It was shown that almost all cobalt (99.9%) went into solution after being bioleached for 6 days in the presence of 0.75 g/L copper ions, while only 43.1% of cobalt dissolution was obtained after 10 days without copper ions. EDX, XRD and SEM analyses additionally confirmed that the cobalt dissolution from spent lithium-ion batteries could be improved in the presence of copper ions. The catalytic mechanism was investigated to explain the enhancement of cobalt dissolution by copper ions, in which  $\text{LiCoO}_2$  underwent a cationic interchange reaction with copper ions to form  $\text{CuCo}_2\text{O}_4$  on the surface of the sample, which could be easily dissolved by  $\text{Fe}^{3+}$ .

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## 1. Introduction

The usage of lithium-ion batteries (LIBs) has rapidly increased as they are widely used as electrochemical power sources in mobile telephones, personal computers, video cameras and other modern-life appliances [1]. However, the spent LIBs contain many metal values such as nickel, cobalt, and lithium, which may also have a potential hazard to the ecosystem and human health [2–4]. Recycling of the major components of spent cells appears to be a beneficial way to prevent environmental pollution and raw material consumption. In addition, it meets the new legal requirements [5,6]. Therefore, the development of recycling technologies for spent LIBs has attracted great attention.

Although many methods have been used to recycle the spent LIBs, there is no efficient recycling method as yet [7]. Bioleaching is a mineral bio-oxidation process assisted by microorganisms, during which insoluble metal sulfides are converted into water-soluble metal sulfates. Bioleaching technique shows competitive advantages owing to environment friendly and low cost process. However, due to its slow kinetics, the commercial application of bioleaching in metal extraction is limited relatively [8,9]. Therefore, different methods, such as improvement of bacteria culture,

accession of metal ions, and addition of surfactants, have been carried out in order to enhance the bioleaching rate [10–13].

Recently, it has been observed that metal dissolution rate in bioleaching process can be improved by using catalytic ions in the solution [14–16], which shows great significance for optimizing the bioleaching processes [17,18]. Although the bioleaching process using catalysts has been indicated to be an effective technology for metals dissolution from minerals, high cost metals such as Ag, Bi, Ru and Hg were normally used [19,20]. Thus, it is very important to find a cheaper effective metal catalyst applied in bioleaching process for industrial application.

Bioleaching process using  $\text{Cu}^{2+}$  catalyst was firstly carried out by Scott and Dyson [21], who applied some metal ions, such as Cu, Bi, Ru, Mo and Fe, as catalysts to accelerate the dissolution rate of zinc sulfide. They found that copper ions made the best effects. Dutrizac [22] investigated the leaching effect by applying cupric chloride on sintered chalcopyrite in ferric chloride solution and found that  $\text{CuCl}_2$  could substantially accelerate the leaching rate. Furthermore, it was shown that the percentage of metal leached was enhanced with additional amounts of metal catalyst [23]. The main feature of the copper-catalyzed mechanism for the dissolution of synthetic magnetite is the electron transfer between  $\text{Cu}^+$  and a surface  $\text{Fe}^{3+}$  species. The electron transfer process is proposed to proceed through an inner sphere mechanism, in which the surface hydroxyl ligand functions as a bridging ligand between the surface Fe and the Cu reductant species [24]. However, the role of metal catalysts in the chalcopyrite bioleaching has been attributed to the formation of a metal sulfide on the chalcopyrite surface, which dissolves the original sulfide material by galvanic reaction [25–27].

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**Table 1**  
Chemical compositions of cathode material in lithium-ion batteries.

	Chemical compositions				
	Li	Co	Mn	Ki	Fe
Contents (%)	3.37	48.5	23.9	24.1	0.14

Meanwhile, it has been reported that the catalytic mechanism of  $\text{Cu}^{2+}$  is due to the formation of  $\text{CuS}$  on the surface of realgar, which was then dissolved by  $\text{Fe}^{3+}$  [28]. Chen et al. [29] reported a positive effect of marmatite bioleaching in the presence of copper ions. Iron sulfide, elemental sulfur and jarosite are formed on the mineral surface during bioleaching which become barrier for bioleaching of marmatite, and the copper ions catalyze the bio-oxidation of elemental sulfur and thus eliminate the barrier to bioleaching.

Copper ion was found to efficiently catalyze the bioleaching of metal sulfides. However, the spent  $\text{LiCoO}_2$  is a kind of metal oxide different from metal sulfides, consequently, the catalytic mechanism of the  $\text{LiCoO}_2$  may differ from that of metal sulfides [30–32]. Besides, it is still lack of studies on the bioleaching process of  $\text{LiCoO}_2$  catalyzed by catalytic ions, and for the first time copper ion was applied for bioleaching of  $\text{LiCoO}_2$  from spent batteries.

The main objective of this paper is to investigate the catalytic effect of copper ions on the dissolution of  $\text{LiCoO}_2$ , and to propose a mechanism to account for the catalytic effect. These results are helpful to improve the recovery of Co from spent lithium-ion batteries and to find an appropriate method to solve the problem of low efficiency.

## 2. Experimental

### 2.1. Materials

The spent lithium-ion batteries used in the experiments were provided by Youteli Co. Ltd. in Jiangxi Province of China, which were manually separated into many portions: plastic shell, cathode material, anode material and aluminum foil. Then the cathode material was grinded into powder and sieved to 0.075 mm, oversize material was pulverized and added to the undersize fraction. EDX analysis of the powder was carried out, and chemical compositions were shown in Table 1.

### 2.2. Microorganisms and culture

*Acidithiobacillus ferrooxidans* (A.f) were applied in the experiments. The original bacteria were collected and isolated from the acidic mine drainage taken from Dexing Mine, Jiangxi Province, China. The bacteria were cultured in the 9K medium (g/L):  $(\text{NH}_4)_2\text{SO}_4$  3.0, KCl 0.1,  $\text{K}_2\text{HPO}_4$  0.5,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  0.5,  $\text{Ca}(\text{NO}_3)_2$  0.01 and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  44.8. The medium was adjusted to pH value 2.0 by sulfuric acid ( $3 \text{ mol L}^{-1}$ ). Erlenmeyer flasks of 250 mL were used, containing 200 mL culture medium, and inoculum were 10% (v/v), and flasks were shaken at 160 rpm on an orbital shaker at 35 °C. The only energy source for bacteria growth was  $\text{FeSO}_4$ , and the isolates were identified as *A. ferrooxidans*. Before the bioleaching period of the experiment, these bacteria had been sub-cultured in medium containing 1% spent battery samples at 35 °C for three months, so that they could adapt to the spent lithium-ion batteries circumstance faster. These cultures were also adapted to the catalytic ions of copper ion 10 g/L for a month.

### 2.3. Bioleaching procedure

The bioleaching experiments were carried out in a constant-temperature shaker at 160 rpm using 250 mL Erlenmeyer flasks at

35 °C. In each bioleaching experiment, the pulp density was kept at 1% (s/v) in 250 mL flasks with 200 mL medium while the volume fraction of inoculation was 5% (v/v). When the bacteria were cultured for about 2 days and in the log phases, the  $\text{LiCoO}_2$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  were added into the process simultaneously, and the concentrations of copper ion were 0.01, 0.1, 0.25, 0.50, 0.75, 1.0 and 10 g/L, respectively. A controlled experiment was performed in parallel without copper ion for comparison. All experiments were carried out for 10 days. During the bioleaching experiment, 1 mL of solution was sampled every 24 h, the solution filtered through a 0.45  $\mu\text{m}$  membrane was used for Co and Cu concentrations determination. By the end of the experiment, leaching solution were also filtered through a 0.45  $\mu\text{m}$  membrane, and the residues dried in vacuum dry oven at 35 °C for X-ray diffraction (XRD), energy spectrum analysis (EDX) and scanning electron microscopy (SEM) analyses, the solution after separation were used for pH and redox potential determination.

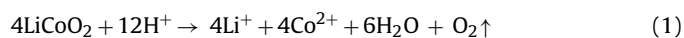
### 2.4. Measurement and analysis

The bacteria in solution were counted by direct counting, using a counting chamber (Neubauer) with phase contrast microscope (LEICA DMI 3000B). The concentration of dissolved  $\text{Co}^{2+}$  in solution was analyzed by atomic absorption spectroscopy (Varian AA-400). The solid residues were air dried and samples were taken for X-ray diffraction (D8ADVANCE), energy spectrum analysis (INCA) and scanning electron microscopy (SEM, Quanta 200) analyses. The pH value and redox potential were measured at room temperature with a pH meter (PHSJ-3F) and a Pt electrode with reference to an Ag/AgCl electrode, respectively.

## 3. Results and discussion

### 3.1. Variations of pH and redox potential

Variations of pH during the bioleaching at different  $\text{Cu}^{2+}$  concentrations are shown in Fig. 1(a). A maximum pH value was obtained at the  $\text{Cu}^{2+}$  concentration of 0.75 g/L. However, with more copper addition of 1.0 g/L and 10 g/L, the pH value was decreased because high  $\text{Cu}^{2+}$  concentrations have toxic effect on the bacteria growth and activity. On the other hand, the pH increased apparently and showed similar behavior when copper ion was added, which could be attributed to the catalytic effect of copper ions, because the  $\text{LiCoO}_2$  was dissolved by the reaction (Eq. (1)), and the presence of copper ions accelerated the reaction rate, resulting in the increase of pH.



Initially, all of the pH curves were observed to have the trends of declining, which could be attributed to the bacteria growth that ferrous iron was oxidized to ferric iron. Since the ferric iron increased, the hydrolysis of ferric iron was also enhanced. Meanwhile, the quantity of acid production was much more than acid consumption, this resulted in the pH decreased. After four days, the pH in the solution is in rising trends, which could be contributed to the acid consumption was much more than the acid production, and finally, the acid was reduced and pH was increased.

As the experiments continue, the pH in the leaching solution was decreased when the copper addition were 0.25, 0.50, 0.75 and 1.0 g/L, which indicated that almost all of the  $\text{LiCoO}_2$  in the solution has been dissolved, so the acid in solution would not be consumed. Thus, the pH value decreased. However, the pH in solution showed inconspicuous changes when the copper ions were 0.01, 0.1 and 10 g/L, which indicated

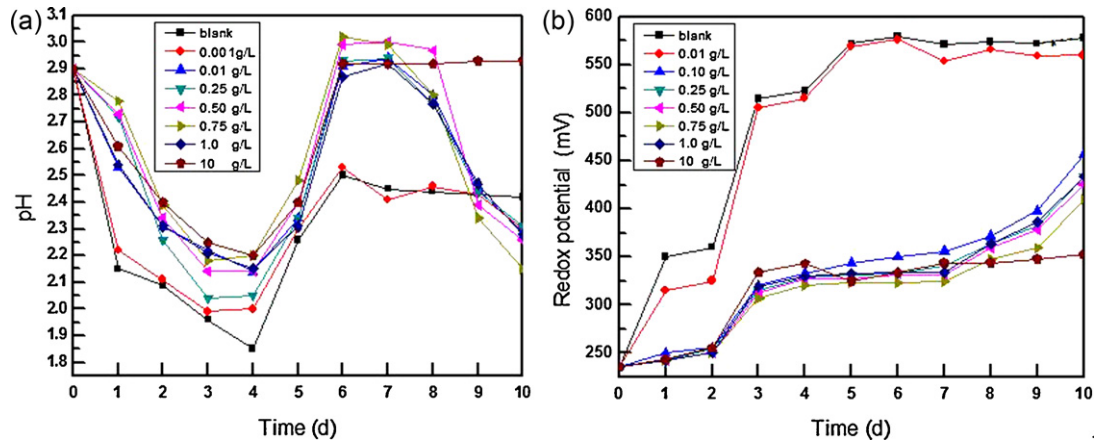


Fig. 1. Variations of pH and redox potential during the bioleaching at different  $\text{Cu}^{2+}$  concentrations: (a) pH variations and (b) redox potential variations.

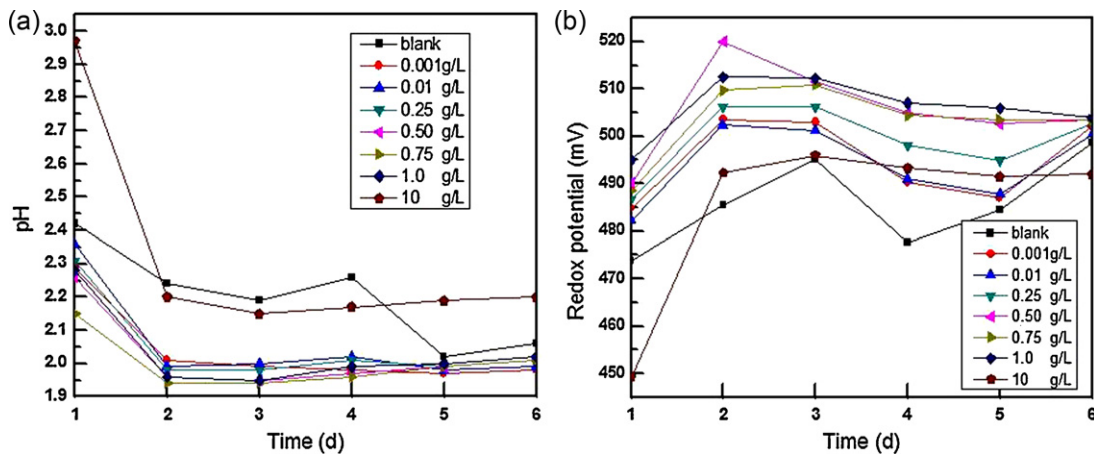


Fig. 2. Variations of pH and redox potential after the removing of the sediment at different  $\text{Cu}^{2+}$  concentrations: (a) pH variations and (b) redox potential variations.

that the  $\text{LiCoO}_2$  in the leaching solution has not been entirely dissolved.

Variations of redox potential during the bioleaching at different  $\text{Cu}^{2+}$  concentrations are shown in Fig. 1(b). Big difference was clearly observed in the presence and absence of copper ions, the redox potential in solution decreased quickly when copper ions were added into the bioleaching processes, and a minimum redox potential was achieved at 327 mV when  $\text{Cu}^{2+}$  concentration was 0.75 g/L. However, when the addition of  $\text{Cu}^{2+}$  concentrations were 0 g/L and 0.01 g/L, the corresponding redox potential were 578 mV and 560 mV, respectively. The redox potential in the solution represents the concentration ratio of the couple  $\text{Fe}^{3+}/\text{Fe}^{2+}$ , which was affected by the presence of copper ions. When copper ions were added into the bioleaching solution, the ferric iron concentration was decreased accordingly, so that the redox potential in solution decreased, which indicated that the addition of copper ions accelerate reduction rate of ferric ion.

Variations of pH and redox potential after the removing of the sediment at different  $\text{Cu}^{2+}$  concentrations are shown in Fig. 2. The pH curves (Fig. 2(a)) and redox potential (Fig. 2(b)) show similar trends, both of the pH and redox potential changed greatly on the first day, and the balance was almost achieved from the second day to the end of the experiments. On the other hand, bacteria growth still existed in the processes after separation, and there were no remarkable differences of the pH and redox potential in the presence and absence of copper ions. So it can be concluded that the addition of copper will not change the balance of bacteria growth, but only accelerate the balance rates.

### 3.2. Cobalt dissolution

The dissolution percentages of cobalt catalyzed under different  $\text{Cu}^{2+}$  concentrations are shown in Fig. 3, which show that copper ion has an important catalytic effect on the dissolution rate and cobalt dissolution percentage. The best catalytic effect was obtained using 0.75 g copper/L at 6 days, cobalt dissolution percentage increased

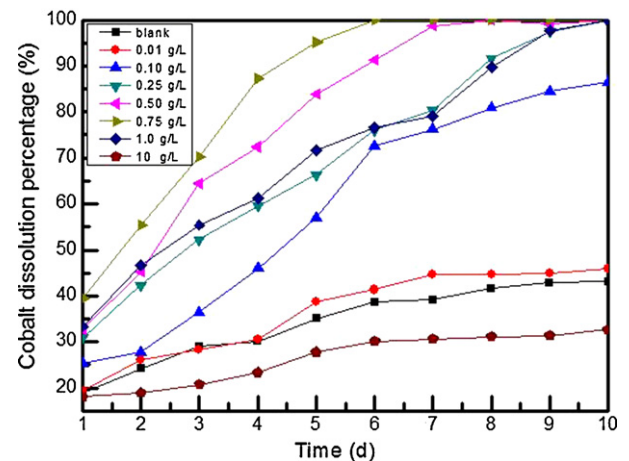


Fig. 3. The dissolution percentage of copper catalyzed process under different  $\text{Cu}^{2+}$  concentrations.



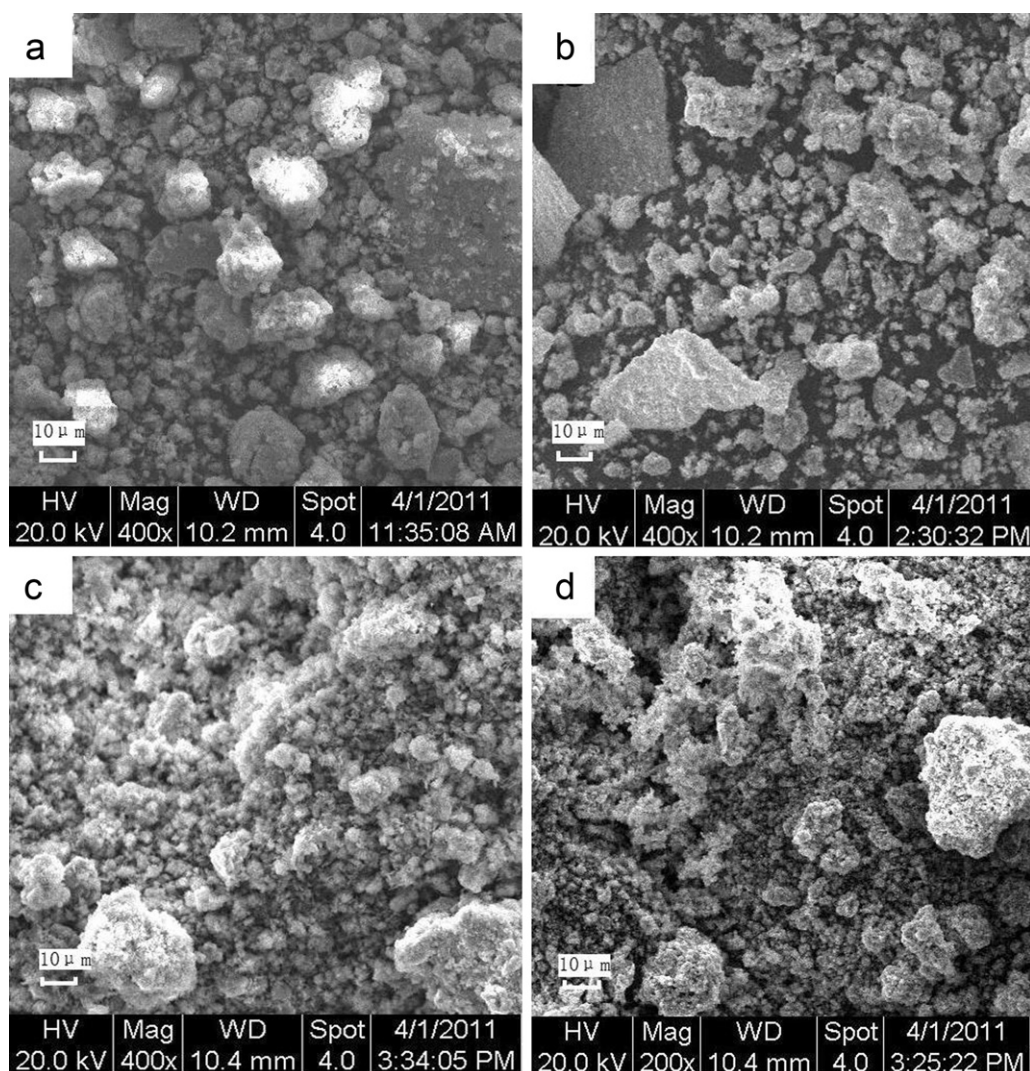


Fig. 4. SEM micrographs of leaching residues (a, blank; b, 0.01 g/L; c, 0.75 g/L; d, 10 g/L).

from 43.1% in the absence of copper ions to 99.9% at the copper concentration of 0.75 g/L, and the corresponding Co concentration was 4.8 g/L. However, when the copper ions concentrations were 0.01, 0.1 and 10 g/L, cobalt dissolution percentages were 46.0%, 86.4% and 32.7%, respectively. It shows that additional amounts of  $\text{Cu}^{2+}$  increased the percentage of leached cobalt, which is in agreement with the previous study. Ballester et al. [18] reported that the microbiological dissolution of the sphalerite improves considerably when using  $\text{Ag}^+$  and  $\text{Cu}^{2+}$  as catalysts, with zinc dissolution of 90%. Furthermore, it showed that additional amounts of  $\text{Cu}^{2+}$  increased the percentage of metal leached.

For the bioleaching process, the pH is expected to be decreased and the redox potential is expected to be increased to achieve higher metal solubilization [33–35]. However, according to Fig. 1(a), when the metal solubilization was higher, the pH was also in a relative higher level. It is just due to the addition of copper ions catalyzed the  $\text{LiCoO}_2$  dissolution rates and increased acid consumption, this resulted the pH in a relative higher level, or not due to the higher pH increased the metal solubilization. Similarly, the redox potential was in lower level according to Fig. 1(b), because the addition of copper ions accelerated the hydrolysis of  $\text{Fe}^{3+}$ , this maintained the redox potential in a relative lower level.

EDX analyses was further used for determining the surplus quantity of  $\text{LiCoO}_2$  in the residues, the contents of Co, Fe, O, S and Cu

are shown in Table 2. When the  $\text{Cu}^{2+}$  concentration was 0.75 g/L, the percentage of Co in the residues was only 0.09%, it indicated that almost all of the  $\text{LiCoO}_2$  were dissolved in the solution, which was accorded with the high cobalt dissolution percentage (Fig. 3). On the other hand, great differences of Co contents were observed in the residues, the content of Co was lowest when the copper ion concentration was 0.75 g/L, it indicates that the copper ions not only catalyzed the leaching efficiencies of  $\text{LiCoO}_2$ , but also resulted in more cobalt dissolution from spent lithium-ion batteries. The  $\text{Cu}^{2+}$  concentrations in the overall processes were determined, and  $\text{Cu}^{2+}$  concentrations in the solution were almost kept at the initial concentrations. Besides, copper was not detected in the residues.

Table 2

Residual element content in the sediment catalyzed under different copper concentrations.

Copper added (g/L)	Co (%)	O (%)	S (%)	Fe (%)	Cu (%)
0.00	8.19	38.58	10.63	31.39	0
0.01	7.61	38.78	10.27	33.70	0
0.10	4.49	38.47	11.01	41.21	0
0.75	0.09	38.51	11.52	46.67	0
1.0	2.01	38.58	12.04	44.06	0
10	3.41	36.94	12.14	41.80	0

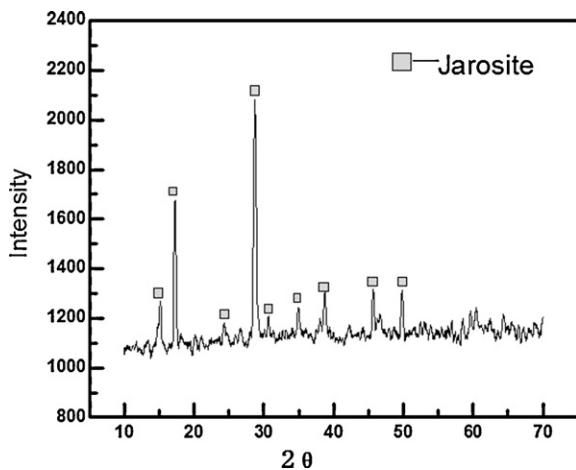


Fig. 5. XRD analyses of the leaching residues (0.75 g/L Cu<sup>2+</sup>).

These results indicated that copper existed in the leaching solution and did not precipitate in the residues.

SEM was used to characterize the particle size and morphology changes of LiCoO<sub>2</sub> (Fig. 4). Clear differences of the residues morphologies in the presence of different copper ion concentrations were observed. When the experiment was performed in the absence of copper ion (Fig. 4(a)) and with copper concentration of 0.001 g/L, residues surface were coated with a solid product layer, a relative larger particle size of the residues was observed. However, when the experiment was performed at Cu<sup>2+</sup> concentration of 0.75 g/L, a extreme exiguous particle was observed in Fig. 4(c). Associated with the EDX analysis results that little Co contents in the presence of Cu<sup>2+</sup> concentration of 0.75 g/L, and also the XRD results (Fig. 5) show that only jarosite was existed in the residues. So the observed particles were jarosite, and almost no LiCoO<sub>2</sub> particles remained. These results are also in good agreement with the dissolution percentage curves.

According to these results, it can be deduced that the catalytic effect of copper ions on the LiCoO<sub>2</sub> bioleaching is obviously, and the reason for greatest efficiency achieved in 0.75 g copper/L concentrate lies in the lower level of jarosite precipitation in solution, since the bacteria were not hindered from attacking the LiCoO<sub>2</sub>.

### 3.3. Bacteria growth

The bacterial growth at different copper ion concentrations during the bioleaching process is shown in Fig. 6. When the copper

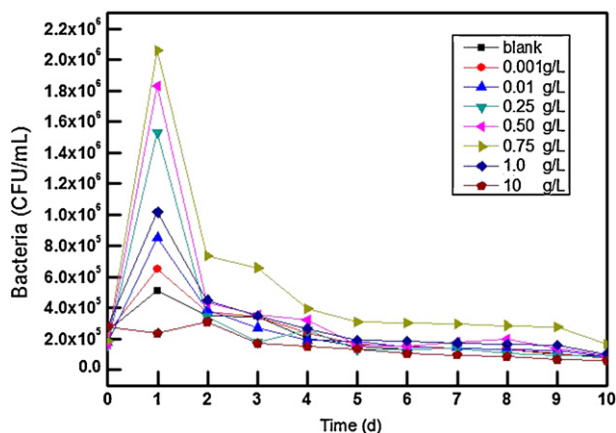


Fig. 6. Bacterial growth at different Cu<sup>2+</sup> concentrations during the bioleaching process.

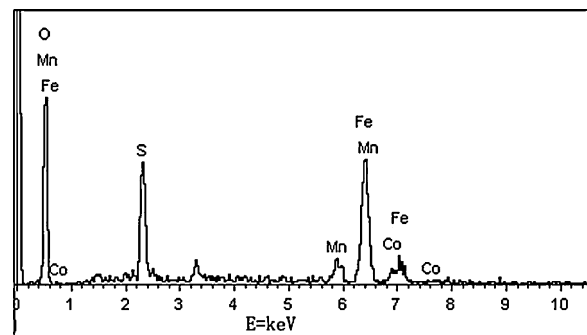
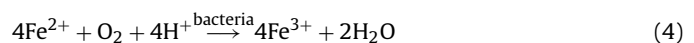
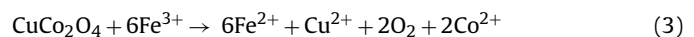
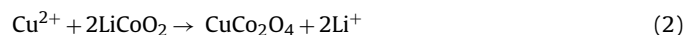


Fig. 7. EDX analyses of leaching residues (0.75 g/L Cu<sup>2+</sup>).

concentration was less than 0.75 g/L, the addition of copper ions in the bioleaching process caused a slight enhancement in bacterial growth. However, when the copper ions were greater than 0.75 g/L, the bacteria was inhibited owing to the toxic effect on the bacteria growth. When the copper ion was 10 g/L, there were also some bacteria in the solution. It can be concluded the growth were not totally inhibited at high copper concentration. On the other hand, the bacteria were firstly counted at the initial of log phase, so an obvious growth was observed on the first day. Later, a sharp decrease of the bacterial was shown in the curves since the bacteria were in stationary phase. Compared with the results of cobalt dissolution in Fig. 3, a conclusion can be drawn to explain the relationship between bacteria number and leaching efficiency, the more bacteria, the higher leaching efficiency. These results were in good agreement with the work reported by Chen and Lin [32], who also found the bacterial growth of *A. ferrooxidans* and *Acidithiobacillus thiooxidans* were enhanced by the addition of 30 mg/L silver in the batch bioleaching experiment, and the leaching efficiency was also improved.

### 3.4. Catalytic mechanism

When the copper ion was added into the bioleaching process, EDX analyses shows that Fe, K, S and O were contained in the residues, while copper was not detected in the residues (Fig. 7), which indicated that the copper ion did not precipitate in the residues and it supposed to exist in the solution. Thus, it is difficult to confirm its existing form, and it may exist as CuCo<sub>2</sub>O<sub>4</sub>. Similar work has been proposed, Chen et al. [29] indicated that Cu<sup>2+</sup> had catalytic effect on the bioleaching of marmatite, the catalytic mechanism was intermediate products CuS accelerated the process. Many researchers reported that Ag<sub>2</sub>S is formed on the particle surface when the silver ion was added in the bioleaching process, and then dissolution rates were enhanced [32,36,37]. Thus, the possible catalytic mechanisms are proposed in Eqs. (2)–(4):



The main requirement for metal ion to exhibit catalytic activity appears to be the formation of such intermediate products (CuCo<sub>2</sub>O<sub>4</sub>), which are oxidized by leaching solution so that catalytic ion is reproduced. Firstly, CuCo<sub>2</sub>O<sub>4</sub> is formed on the particle surface when the copper ion was added in the bioleaching process (Eq. (2)). Based on the reaction, Cu<sup>2+</sup> is regenerated through the oxidation of CuCo<sub>2</sub>O<sub>4</sub> by ferric iron (Eq. (3)). Subsequently, ferric ion is produced from the ferrous ions according to Eq. (4). These results indicated that CuCo<sub>2</sub>O<sub>4</sub> has high performance on catalyze aspect, and also has ability to catalyze hydrolysis of ferric iron, and then

enhance the acid production. Consequently, the dissolution rate of  $\text{LiCoO}_2$  is accelerated.

#### 4. Conclusions

Bioleaching of Co from spent lithium-ion batteries was studied using low cost copper ions as catalyst for the first time. Cobalt dissolution percentage was increased from 43.1% in the absence of copper ion within 10 days to 99.9% at copper concentration of 0.75 g/L after 6 days, indicating that the copper ions could enhance not only the oxidation rate of  $\text{LiCoO}_2$ , but also the leaching amount of cobalt from spent lithium-ion batteries. A probable catalytic mechanism was proposed to explain the catalytic effect of copper ions on bioleaching of Co from spent lithium-ion batteries. Thus, the primary leaching efficiency problem of Co recovery from lithium ion batteries was solved by applying a low cost copper ions as catalysis, which is very important for recycling of spent lithium-ion batteries.

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