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Influences of Solution pH and Redox Potential on the Bioleaching of LiCoO$_2$ from Spent Lithium-ion Batteries

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Abstract The influences of solution pH and redox potential on bioleaching of LiCoO$_2$ from spent lithium-ion batteries using *Acidithiobacillus ferrooxidans* were investigated. Bioleaching at different initial pH and ferrous ion (Fe^{2+}) concentrations were carried out, and electrochemical behavior of LiCoO$_2$ dissolution was examined to study the effect of solution redox potential on the bioleaching process. The results showed maximum cobalt dissolution at initial pH of 1.5 and initial Fe^{2+} concentration of 35 g/L, and cobalt dissolution showed only slight relationship with pH of solution. Nonetheless, there was improvement of cobalt dissolution at higher redox potential. The cyclic voltammograms showed that dissolution rates increase when the solution potentials are higher than 0.4 V, and rapid decrease at 1.3 V. The anodic polarization curves indicated that the corrosion, primary passive, and passivation potentials were 0.420, 0.776 and 0.802 V, respectively.

Keywords *Acidithiobacillus ferrooxidans* · bioleaching · redox potential · spent lithium-ion batteries

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Introduction

There is fast growth in the use of lithium-ion batteries (LIBs) worldwide since 2000. Due to characteristics such as light-weight, high-energy, and good performance, they are widely used as power sources in mobile telephones, personal computers, video-cameras, and other modern-life appliances (Watling, 2006; Giaveno et al., 2007; Li et al., 2009, 2010). However, metals in LIBs such as nickel, cobalt, copper, and lithium are potentially hazardous to the ecosystem and human health. Furthermore, it would be wasteful if the metals were disposed without being recycled (Third et al., 2002; Watling, 2006; Aral and Angelica, 2008). From the environmental and economical viewpoint, it is beneficial to recover the major components of spent LIBs such as electrode material LiCoO$_2$. To comply with new legal requirements (Paulino et al., 2008; Dewulf et al., 2010), it is necessary to develop suitable recycling technologies for the handling of spent LIBs.

Although many methods have been used to treat spent LIBs, there is no recycling plant as yet (Dewulf et al., 2010). Bioleaching is a kind of process for mineral biooxidation assisted by microorganisms, during which insoluble metal sulfides are converted into water-soluble metal sulfates. Bioleaching processes are environment-friendly and low-cost, and have been successfully applied in treatment of low-grade ores, showing remarkable advantages over other traditional methods (Giaveno et al., 2007; Petersen and Dixon, 2007). The extraction of metals from spent LIBs by bioleaching processes have been investigated (Modak et al., 1996; Xin et al., 2009). It was reported that the pH and redox potential of leaching solution have influences on the bioleaching processes. Olson et al. (2002) reported that redox potential was a key factor in determining the efficiency of bioleaching by *Acidithiobacillus ferrooxidans*. It was pointed out that with increase of solution redox potential during microbial oxidation of ferrous ions (Fe^{2+}), there was an enhancement in bacterial activity.

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Modak *et al.* (1996) also reported that the oxidation of Fe^{2+} provided energy for bacterial growth, and the oxidation-reduction potential (ORP) of Fe^{3+}/Fe^{2+} couple was monitored and considered as a criterion for bacterial activity or bioleaching effectiveness (Hansford and Vargas, 2001). In addition, it was pointed out that there was improvement in bioleaching efficiency with rise of solution potential (Mahmood and Turner, 1985; Mishra et al., 2008). Gericke et al. (2010) discovered that a redox potential between 500 and 600 mV favored the dissolution of low-grade chalcopyrite, and suggested a new method for bioleaching. $LiCoO_2$ is a kind of metal oxide, and the pH and redox potential of bioleaching process should differ from those adopted in bioleaching of minerals (Chen and Lin, 2009; Wang et al., 2009). Thus, it is necessary to determine the effect of solution pH and redox potential on the bioleaching of $LiCoO_2$.

In the present study, we investigated the influence of solution pH and redox potential on $LiCoO_2$ bioleaching from anode of spent LIBs by varying the initial pH and Fe^{2+} addition. The cyclic voltammograms and anodic polarization curves were recorded to understand the influence of redox potential on the bioleaching process. The results are helpful to improve the recovery of Co from spent LIBs and to tackle the problem of low efficiency in bioleaching.

Materials and Methods

Materials. The spent LIBs were kindly provided by Youteli Co. Ltd. (China). They were manually separated into plastic shell, cathode material, anode material, and aluminum foil. The cathode material was then ground into powder and sieved to 0.075 mm, and oversize material was also included after being pulverized. Finally, energy-dispersive X-ray spectroscopy (EDX) analysis of the powder was carried out, and contents of chemical compositions can be seen as follows (%): Li, 3.37; Co, 48.5; Mn, 23.9; Ni, 24.1; Fe, 0.14.

Microorganism. *A. ferrooxidans* were used in the present study. The original bacterium was collected and isolated from the acidic mine drainage taken from Dexing Mine, Jiangxi Province, China. The bacteria were cultured in 9K medium (g/L): $(NH_4)_2SO_4$, 3.0; KCl 0.1, K_2HPO_4, 0.5; $MgSO_4 \cdot 7H_2O$, 0.5; $Ca(NO_3)_2$, 0.01; and $FeSO_4 \cdot 7H_2O$, 44.8 (Yelloji et al., 1997). The medium was adjusted to pH 2.0 by sulfuric acid (3 M). Erlenmeyer asks of 250 mL containing 200 mL of culture medium and inoculum (10%, v/v) were used, and the flasks were shaken at 160 rpm on an orbital shaker at 35°C. The only energy source for bacteria growth was $FeSO_4$, and the isolates were confirmed to be *A. ferrooxidans*. Before being applied in a bioleaching experiment, the bacteria were sub-cultured in a 9K medium containing 1% spent battery at 35°C for three months for fast adaptation to the circumstance of spent LIBs.

Bioleaching procedures. Bioleaching experiments were carried out using 250 mL Erlenmeyer flasks in a constant-temperature
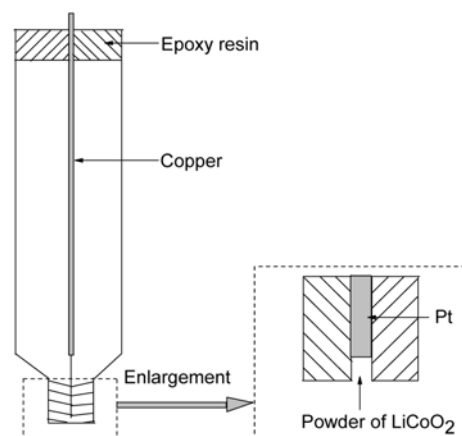

Fig. 1 Powder microelectrode of $LiCoO_2$

shaker at 160 rpm and 35°C in 9K medium, and the experimental period was 7 days. The pulp density was kept at 1% (s/v) with 200 mL medium, whereas the volume fraction of inoculation was 5% (v/v). When the bacteria were cultured for about 2 days in the log phase, the cathode powder was added. Experiments were performed at different initial pH values as well as at different initial Fe^{2+} concentrations. During the seven day-period, 1 mL of solution was sampled at intervals of 24 h, and the solution was subjected to filtration through a 0.45-μm membrane before being analyzed for the determination of Co^{2+} contents.

Electrochemical measurements. The test was conducted by using a self-designed powder microelectrode, which is a combination of a copper wire (diameter =1 mm) and a platinum wire (diameter =45 μm). The electrode was polished with aqueous sandpapers (10−14 μm), metallograph sandpapers, 5−7 μm metallograph sandpapers, and finally with 0.03 μm aluminium oxide powder. The construction of the $LiCoO_2$ powder microelectrode is illustrated in Fig. 1.

A standard three-electrode electrochemical system was used with the $LiCoO_2$ powder microelectrode as working electrode, platinum wires as counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The electrolyte employed for the electrochemical test was the same as the medium used in the bioleaching experiments. Electrochemical measurements were performed on an electrochemical workstation (Chi660d, China) at 25°C.

Analytical methods. The Co^{2+} concentration in the solution was determined by atomic absorption spectroscopy (Varian AA-400, Germany). The pH value and redox potential were measured at room temperature with a pH meter (PHSJ-3F), and a Pt electrode together with Ag/AgCl as reference electrode.

Results and discussion

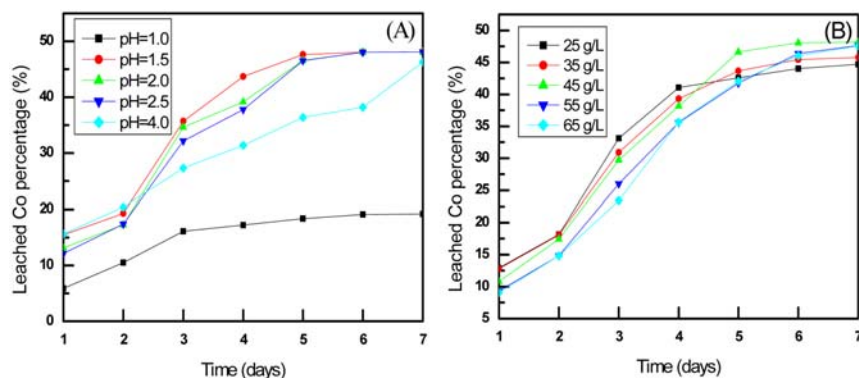**Cobalt dissolution.** The dissolution percentages of cobalt at

Fig. 2 Percentages of leached Co versus time (days) at (A)-different initial pH values, (B)-different initial Fe^{2+} concentrations
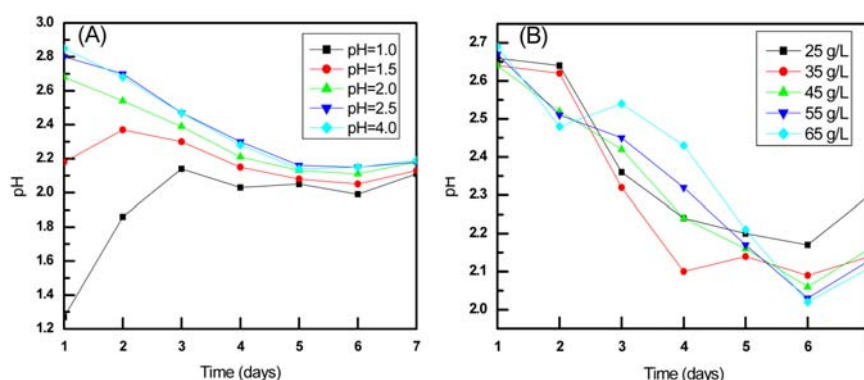

Fig. 3 Variations in pH of solution versus time (days) at (A)-different initial pH values, (B)-different initial Fe^{2+} concentrations
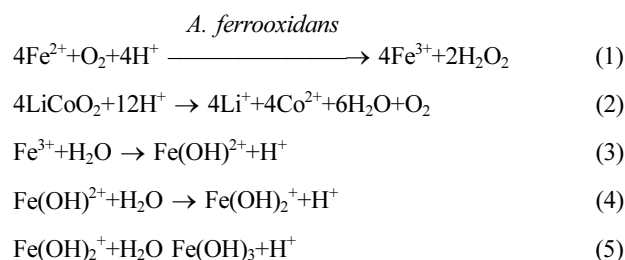
different initial pH values are shown in Fig. 2A. A maximum cobalt dissolution percentage of 47.6% was achieved on the 5th day when the initial pH was 1.5. There was no significant difference in terms of cobalt dissolution when the initial pH was varied from 1.5 to 4.0, and further $LiCoO_2$ dissolution was insignificant after day 5. The results indicated that an initial pH of 1.5 was suitable for the bioleaching process.

The cobalt dissolution percentages at different initial Fe^{2+} concentrations are shown in Fig. 2B. During the first four days, higher cobalt dissolution was observed at a relative lower Fe^{2+} concentration. On the contrary, after day 4, higher cobalt dissolution was observed at a relative higher Fe^{2+} concentration, and the highest cobalt dissolution percentage of 48.2% was achieved at the end of experiments when initial Fe^{2+} concentration was 45 g/L.

Variations of solution pH at different initial pH values are shown in Fig. 3A. The initial pH (1.0) of the solution was the lowest compared with those of the other initial pH values. Referring to the corresponding cobalt dissolution curves (Fig. 2A), the cobalt dissolution obtained with initial pH=1.0 was also the lowest. However, despite that the solution pH was the highest with initial pH=4.0, the corresponding cobalt dissolution level was relatively lower than those obtained with initial pH=1.5, 2.0, and 2.5. Thus, it is deduced that the pH of leaching solution has little influence on cobalt dissolution.

In the overall process, the pH values of the leaching solutions gradually stabilized at around 2.1. Because the oxidation of Fe^{2+} (Eq. 1) and $LiCoO_2$ (Eq. 2) are proton-consumption process, there should be a rise in pH values. However, in the hydrolysis of ferric ions (Fe^{3+}), the generation of H^+ (Eqs. 3, 4, and 5) was observed. Hence, the pH of the leaching solution is a net result of H^+ formation and consumption.

$$4Fe^{2+}+O_2+4H^+ \xrightarrow{\quad A.\ ferrooxidans \quad} 4Fe^{3+}+2H_2O_2 \qquad (1)$$

$$4LiCoO_2+12H^+ \rightarrow 4Li^++4Co^{2+}+6H_2O+O_2 \qquad (2)$$

$$Fe^{3+}+H_2O \rightarrow Fe(OH)^{2+}+H^+ \qquad (3)$$

$$Fe(OH)^{2+}+H_2O \rightarrow Fe(OH)_2^++H^+ \qquad (4)$$

$$Fe(OH)_2^++H_2O\ Fe(OH)_3+H^+ \qquad (5)$$

The variations of solution pH versus time with different initial Fe^{2+} concentrations are shown in Fig. 3B. There is no obvious difference in solution pH across the Fe^{2+} initial concentrations, and the pH of the solutions gradually stabilized at around 2.1 at the end of the experiments. The results are in good agreement with those of Fig. 3A, in that there is little relation between cobalt dissolution and solution pH values.
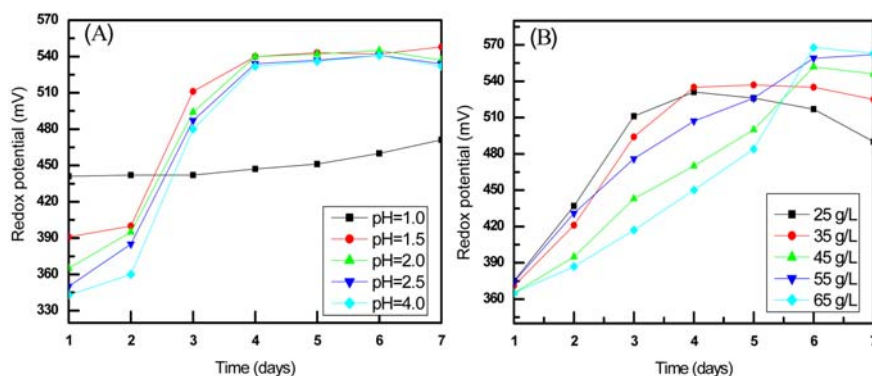
Fig. 4 Variations in redox potential of solution versus time at (A)-different initial pH, (B)-different initial Fe^{2+} concentration

The variations of solution redox potential versus time with different initial pH values are shown in Fig. 4A. The tendency of variation is similar to that of cobalt dissolution curves depicted in Fig. 2A. It is hence deduced that the higher cobalt dissolution can be associated with the higher redox potential. It is believed that an increase in redox potential would result in enhanced cobalt dissolution. A high redox potential of around 525 mV was observed on the 5th day when the initial pH was set at or above 1.5. However, when the initial pH was 1.0, the redox potential only varied between 435 to 465 mV throughout the seven day-period, a phenomenon that could be interpreted as poor bacteria activity in oxidizing Fe^{2+}. When the initial pH was set between 1.5 to 4.0, there was a rapid rise in redox potential on the third day, indicating that the bacteria was in exponential phase as reflected by the rise of Fe^{2+} oxidation rate; similar observation was reported by other researchers (Gericke et al., 2010; Third et al., 2002).

The variations of solution redox potential versus time at different initial Fe^{2+} concentrations are shown in Fig. 4B, and the curves exhibited tendency similar to that of cobalt dissolution curves (Fig. 2A). At the beginning, a relative higher redox potential at an initial Fe^{2+} concentration of 25 g/L would result in higher cobalt dissolution. After day 5, a slight decline in redox potential was observed when initial Fe^{2+} concentrations were 25 and 35 g/L, and was accompanied by a decrease of cobalt dissolution. These results demonstrated that cobalt dissolution was enhanced due to the rise of redox potential, and the main factor that influences cobalt dissolution is the redox potential of solution.

Eh-pH diagram of Li-Co-H₂O system. The bioleaching percentage of $LiCoO_2$ in the solution is mainly limited by two factors, that is solution redox potential and pH value. According to experimental results, maximum pH range in the bioleaching process was 1.0–3.0, and the corresponding redox potential was 0.3−0.6 V. As shown in the Eh-pH diagram of Li-Co-H₂O system (Fig. 5) (Wen et al., 2005), $LiCoO_2$ was transformed into Co^{2+} and Li^+ when the redox potentials ranged from −0.3 to 1.8 V and the pH values were below 7.8. In other words, the conditions of bioleaching are contained in this area. The results indicated that the leached cobalt in the solution exists as Co^{2+} rather than CoO_2,
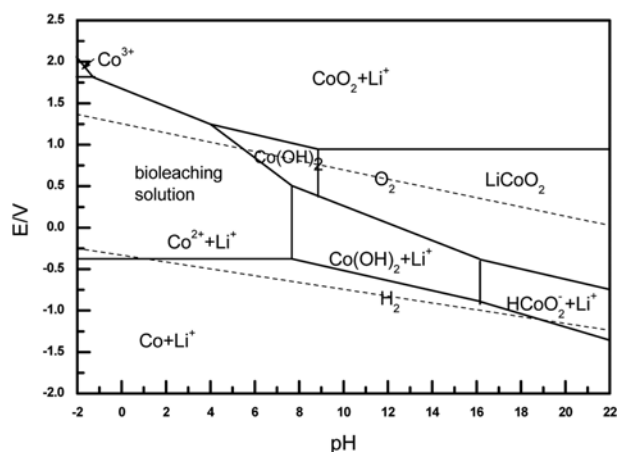

Fig. 5 E-pH diagram of Li-Co-H₂O system (ion concentrations in solution are all $10^{-3} \, mol \, L^{-1}$)

$Co(OH)_2$, Co^{3+} or Co.

Electrochemical behavior of bioleaching LiCoO₂. Electrochemical method with microelectrode was applied to study the oxidation processes and the related mechanisms. Compared with the typical Carbon Paste Electrode, the powder microelectrode identifies peaks more readily. In other words, the latter generates current density higher than that of the former, and is more precise and sensitive in signal determination (Li et al., 2006).

The cyclic voltammograms were obtained in bioleaching tests with a self-designed $LiCoO_2$ powder microelectrode in the presence or absence of *A. ferrooxidans*. As shown in Fig. 6, on the anodic scanning, a selective dissolution of $LiCoO_2$ (A_2) at 400 mV was detected accordingly to Eq. 6:

$$2LiCoO_2 + 3H_2O \rightarrow 2Co(OH)_2 + 2LiOH + 1/2O_2 + 2e$$
$$E^0 = 0.632V \text{ (VS. SCE)} \tag{6}$$
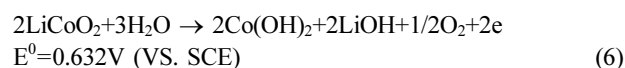
During anodic scanning, a rapid decrease of current density was observed at potential of 1.3 V; suggesting the formation of a thin passive film on the surface of $LiCoO_2$ that would prevent Co dissolution. One can see that there was fast increase of dissolution
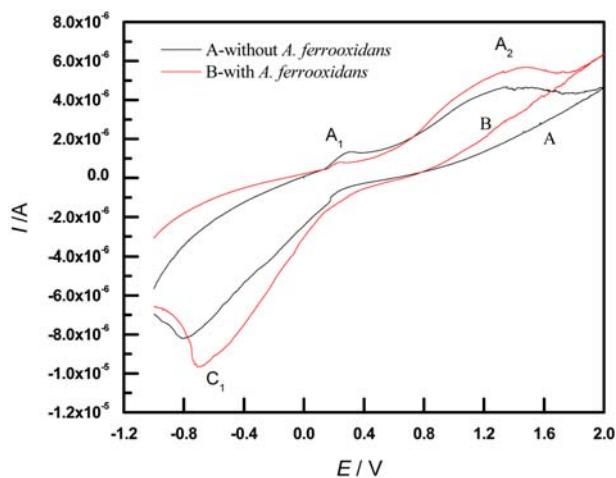
Fig. 6 Cyclic voltammograms of $LiCoO_2$ powder microelectrode in the presence and absence of *A. ferrooxidans* (T=298 K, SR=50 mV s^{-1})
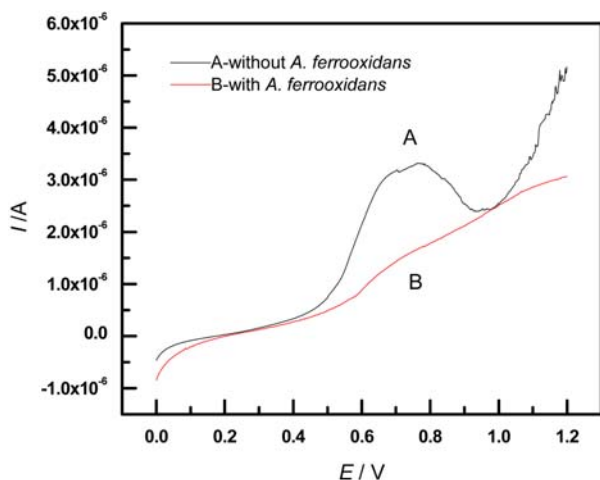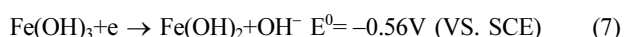

Fig. 7 Anodic polarization curves of $LiCoO_2$ powder microelectrode in the absence and presence of *A. ferrooxidans* (T=298 K, SR=10 mV s^{-1})

rate at 0.4 V, and the highest current density was achieved at 1.3 V. During the inverse scan, a signal (C_1) was recorded, and the possible reactions are listed as follows:

$$Fe(OH)_3 + e \rightarrow Fe(OH)_2 + OH^- \quad E^0 = -0.56V \text{ (VS. SCE)} \quad (7)$$
$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \quad E^0 = 0.401V \text{ (VS. SCE)} \quad (8)$$

Nonetheless, there is no definite difference between the two CV curves depicted in Fig. 6, and the only difference is that current density at the high level in the presence of bacteria, which indicates that *A. ferrooxidans* enhanced the reaction rate of cationic interchange, and consequently cobalt dissolution was promoted.

Anodic polarization curves (linear scanning rate =10 mV/s) of $LiCoO_2$ powder microelectrode in the absence or presence of *A. ferrooxidans* are shown in Fig. 7. There is a rapid rise of potential at 0.420 V, where the current density also increased. In other

words, there should be a rise in Co dissolution rate at the potential of 0.420 V, because current density gives a direct indication of cobalt dissolution rate. It is obvious that the current density in the presence of bacteria is much higher than that in the absence of bacteria.

When the electrode was positively scanned to 0.776 V, a rapid decline in current was observed, indicating the formation of a passive film on the surface of $LiCoO_2$. However, when scanned to 0.802 V, the passive film was punctured and a rise in current was observed. According to the results, at scanning rate of 10 mV · s^{-1}, the corrosion potential is 0.420 V, the primary passive potential is 0.776 V and the passivation potential is 0.802 V.

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