



Current collectors as reducing agent to dissolve active materials of positive electrodes from Li-ion battery wastes



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ABSTRACT

This study evaluates the electrochemical effect of mineral, organic and metallic reducing agents to promote $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC) dissolution in acidic media. The main aim is to compare the reactivity of metallic current collectors (Cu and Al) to more conventional reducing agents such as organic acids and hydrogen peroxide. In a more applied perspective, this work points out the economic interest to use current collectors as an alternative chemical reagent for an efficient NMC dissolution as they are inherently present in the fraction treated by an hydrometallurgical approach. It demonstrates that galvanic interactions are suitable to leach the transition metal oxides from spent LIBs without heating and emission unlike carboxylic acid solutions, allowing the development of low ecological footprint processes. In a more fundamental framework, the results obtained clear several parts of the dissolution NMC mechanism. A fast first step is controlled by the solution pH with a low influence of redox reactions on the kinetic. A slower second stage is subjected to the electrochemical processes with a surface-controlled dissolution.

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1. Introduction

Spent lithium-ion batteries contain attractive valuable resources such as nickel, cobalt and lithium usually considered as potential environmental contaminants. Recent national and international regulations (in European Union, North America or Channel Islands) define requirements to reduce environmental pollution from spent Li-ion batteries (LIBs). The European 2006/66/CE directive drives manufacturers to improve the recycling efficiency of LIBs. Economic, environmental, health and safety issues need paying attention to batteries recycling as well.

Pyrometallurgical, hydrometallurgical or combined pyro-hydrometallurgical processes can be used to recycle spent LIBs. The high temperature pyrometallurgical technique allows treating a large volume of spent LIBs (Georgi-Maschler et al., 2012; Cheret and Santen, 2007) but involves a loss of materials (organic materials), emission of hazardous gases (HF), dusts and a high energy consumption. In general, metals such as cobalt, copper and nickel are recovered as alloys. Lithium, manganese and aluminum end up in the slag and need specific complementary treatments to be recovered and the produced alloys need an additional refining step to get higher purity metals. Hydrometallurgical routes represent an alternative to recover pure compounds from spent LIBs with a low energy need. Currently, investigations to treat spent

LIBs mainly focus on conditions to leach positive electrodes such as LiCoO_2 (LCO), LiMn_2O_4 (LMO), $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA), $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC) or $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) (Li et al., 2010a,b; Wang et al., 2009; Li et al., 2009; Swain et al., 2007; Nan et al., 2005; Shin et al., 2005; Zhang et al., 1998; Joulié et al., 2014; Sun and Qiu, 2011). This kind of transition metal oxides requires usually acidic solutions, thermal energy and a suitable reducing agent for efficient dissolution. Extensive research focuses on the nature of reducing agents, and many of them introduce hydrogen peroxide in strong acidic media such as HCl, H_2SO_4 and HNO_3 (Swain et al., 2007; Shin et al., 2005; Sun and Qiu, 2011; Chen et al., 2011; Kang et al., 2010; Ferreira et al., 2009; Paulino et al., 2008; Lee and Rhee, 2002, 2003; Li et al., 2011; Weng et al., 2013). For the last decade, intense effort has been made to improve conditions, using environmental friendly reducing reagents such as carboxylic acids such as citric (Li et al., 2010b), malic (Li et al., 2010a), oxalic (Sun and Qiu, 2012; Zeng et al., 2015), aspartic (Li et al., 2013) and ascorbic acids (Li et al., 2012) or glucose (Granata et al., 2012) to leach LIBs active materials. Despite the large number of reactants evaluated, metallic compounds such as LIBs collectors have never been considered to treat spent LIBs. Galvanic leaching was reported to leach ores (Nakazawa et al., 2016) or electronic wastes (Nakazawa et al., 2013, 2016).

Physical pre-treatments (grinding, sieving) aim at separating the lithium metal mixed oxides from the main fraction of other solid elements (collectors, membranes) (Li et al., 2010a,b; Chen et al., 2011;

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Kang et al., 2010). This partition is partially done and the remaining collector material fraction is considered as negative, whereas they can have a beneficial impact on the dissolution step.

Often unconsidered in the literature, the interaction between cathodic materials and metals coming from collectors is investigated as an alternative chemical reagent for an efficient NMC dissolution. This study compares the leaching of NMC electrode by a well-known conventional approach with usual reducing solution (citric, oxalic, formic acids and hydrogen peroxide). An experimental design is first implemented to define the best conditions for the NMC dissolution under low reducing conditions. Effects of temperature, concentration and time are evaluated by this approach. Further, a comparative study between conventional reducing agents and collector metals (Cu and Al) focused on the leaching showing a promising efficiency of collectors with an “environmental friendly” behavior.

2. Materials and methods

2.1. Material leaching

NMC MX6 electrode material is supplied by Umicore. The particles mean size of NMC powder measured by laser grading with Malvern Mastersizer 2000 is $7.68 \pm 0.05 \mu\text{m}$. The specific surface area measured by BET method with Beckman Coulter SA3100 surface area analyzer is $0.4 \text{ m}^2/\text{g}$. A complete dissolution of material in acidic media (50 vol% of HNO_3 4 M and 50 vol% of HCl 4 M) is achieved assisted by a microwave digestion system (Multiwave 3000, Perkin Elmer, Anton Paar). The chemical analysis performed by an Induced Coupled Plasma Optical Emission Spectrometer (Agilent Technologies 700 Series ICP-OES) indicates a composition of $\text{Li}_{1.043}\text{Ni}_{0.333}\text{Mn}_{0.296}\text{Co}_{0.328}\text{O}_2$ (8.1 wt% Li, 22 wt% Ni, 18.3 wt% Mn and 21.8 wt% Co). The chemical reactants and the metallic powders (aluminum and copper) are reagent grade supplied by Sigma Aldrich. The Cu and Al metals were fed as a powder to simulate the presence of current collectors. The cathode material is leached in a 100 mL neck glass reactor equipped with a vapor condenser and placed into an oil bath to control the reaction temperature. The solution is stirred at 500 rpm. Before complete filtration a 1 mL was drawn and filtered for analysis through $0.2 \mu\text{m}$ syringe filters in Teflon®. The unleached material is filtered with a paper filter (VWR Folded qualitative filter paper, 313, particle retention 5–8 μm). Concentrations of Li, Ni, Mn, Co, Al and Cu in the leaching liquor are measured by ICP-OES. The solid residue is analyzed by X-ray diffraction with X-ray diffractometer Bruker D8 Advance.

2.2. Experimental design

Experiments are conducted to determine the most efficient leaching conditions using two non-reducing acids, hydrochloric and sulfuric acid by a 23 factorial design.

Factors tested (levels in parentheses) are: acid concentration C (1 and 3 M), temperature T (30 and 90 °C), and time t (3 and 18 h). The solid to liquid (S/L) ratio is fixed at 4 w/v%. Table 1 gathers experimental conditions of each performed treatment. The regression equation of the

Table 1
Experimental conditions of 23 full factorial design.

Experiment	X1 (C)	X2 (T)	X3 (t)	C (M)	T (°C)	t (h)
1	+	+	+	3	90	18
2	–	+	+	1	90	18
3	+	–	+	3	30	18
4	–	–	+	1	30	18
5	+	+	–	3	90	3
6	–	+	–	1	90	3
7	+	–	–	3	30	3
8	–	–	–	1	30	3

above matrix can be represented by Eq. (1).

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{123}X_1X_2X_3 \quad (1)$$

Y is the percentage of metal dissolved, b is the empirical model coefficients, N is the test number and X_1, X_2, X_3 are dimensionless coded factors for respectively acid concentration, temperature, and time. The relation between the coded and actual values is $X_j = +1$ if the factor is set at high level, and $X_j = -1$ if the factor is set at low level. Eqs. (2), (3) and (4) allow to calculate regression coefficients quantifying the effect of each parameter.

$$b_0 = (\sum Y_i)/N \quad (2)$$

$$b_j = (\sum X_j X_i)/N \quad (3)$$

$$b_{nij} = (\sum X_{ni} X_{ji} Y_i)/N \quad (4)$$

3. Results

The dissolution rate has thermodynamic and kinetic implication. Positive electrodes from LIBs have a high chemical stability. Their chemical and electrochemical reactivities evolve with the solid-state properties (structure and composition). The NMC material presents a layered structure including mixed-metal oxides with lithium intercalation. As first approximation, the NMC can be assimilated to a stack of transition metal oxides. From this point of view, NMC is composed of NiO , MnO_2 and Co_2O_3 with inserted lithium. E-pH diagrams of transition metals show a high potential in acidic condition (Pourbaix, 1963). On a thermodynamic point of view, many reducing agents could efficiently leach the NMC material. Table 2 gathers standard potentials, solubility product constants and complexation constants in tested acids.

Table 2

Complexation constants pKi (Charlot, 1983; Ringbom, 1967), solubility product constants pKs (Haynes and Lide, 2011) and standard potentials E^0 (Haynes and Lide, 2011) in the five tested acids for each metal composing NMC material.

Media	Metal	pKi	pKs	E^0 (SHE)
HCl	Li(+I)	–	–2.6	Cl_2/Cl^-
	Ni(+II)	0.9 (Cl^-)	–2.8	1.359 V
	Mn(+II)	0.6 (Cl^-); 0.8 (2Cl^-); 0.4 (3Cl^-)	–3	
	Co(+II)	2.4 (Cl^-)	–2.5	
H_2SO_4	Li(+I)	0.6 (SO_4^{2-})	–2.1	$\text{S}_2\text{O}_8^{2-}/\text{HSO}_4^-$
	Ni(+II)	2.3 (SO_4^{2-})	–0.8	2.123 V
	Mn(+II)	2.3 (SO_4^{2-})	–1.3	
	Co(+II)	2.4 (SO_4^{2-})	–0.8	
$\text{C}_6\text{H}_8\text{O}_7$ (H_4L)	Li(+I)	–	–3.6	$\alpha\text{-C}_5\text{H}_6\text{O}_5/\text{C}_6\text{H}_8\text{O}_7$
	Ni(+II)	17.5 (H_3L^-); 3.3 (H_2L_2^-); 5.1 (HL_3^-); 14.3 (L_4^-)	–	–0.38 V
	Mn(+II)	2.1 (H_2L_2^-); 3.5 (HL_3^-)	–	
	Co(+II)	1.25 (H_3L^-); 3.2 (H_2L_2^-); 4.8 (HL_3^-); 12.5 (L_4^-)	7.2	
$\text{C}_6\text{H}_8\text{O}_7$ (H_4L)	Li(+I)	–	–3.6	$\alpha\text{-C}_5\text{H}_6\text{O}_5/\text{C}_6\text{H}_8\text{O}_7$
	Ni(+II)	17.5 (H_3L^-); 3.3 (H_2L_2^-); 5.1 (HL_3^-); 14.3 (L_4^-)	–	–0.38 V
	Mn(+II)	2.1 (H_2L_2^-); 3.5 (HL_3^-)	–	
	Co(+II)	1.25 (H_3L^-); 3.2 (H_2L_2^-); 4.8 (HL_3^-); 12.5 (L_4^-)	7.2	
HCO_2H	Li(+I)	–	–	$\text{H}_2\text{CO}_3/\text{HCO}_2\text{H}$
	Ni(+II)	–	–	–0.156 V
	Mn(+II)	–	–	
	Co(+II)	–	0.8	
$\text{H}_2\text{C}_2\text{O}_4$	Li(+I)	–	–	$\text{H}_2\text{CO}_3/\text{H}_2\text{C}_2\text{O}_4$
	Ni(+II)	5.2 ($\text{C}_2\text{O}_4^{2-}$); 1.3 ($2\text{C}_2\text{O}_4^{2-}$)	8.2	–0.386 V
	Mn(+II)	4.0 ($\text{C}_2\text{O}_4^{2-}$); 1.4 ($2\text{C}_2\text{O}_4^{2-}$)	5.3	
	Co(+II)	4.8 ($\text{C}_2\text{O}_4^{2-}$); 2.1 ($2\text{C}_2\text{O}_4^{2-}$); 1.4 ($3\text{C}_2\text{O}_4^{2-}$)	7.2	

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