



Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Recycling of spent lithium-ion battery with polyvinyl chloride by mechanochemical process

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ARTICLE INFO

Article history:

Received 12 February 2017

Revised 25 April 2017

Accepted 6 May 2017

Available online xxx

Keywords:

Spent lithium-ion batteries

Waste polyvinyl chloride

Mechanochemical method

Lithium recovery

Cobalt ferrite

ABSTRACT

In the present study, cathode materials (C/LiCoO₂) of spent lithium-ion batteries (LIBs) and waste polyvinyl chloride (PVC) were co-processed via an innovative mechanochemical method, i.e. LiCoO₂/PVC/Fe was co-grinded followed by water-leaching. This procedure generated recoverable LiCl from Li by the dechlorination of PVC and also generated magnetic CoFe₂O₄ from Co. The effects of different additives (e.g. alkali metals, non-metal oxides, and zero-valent metals) on (i) the conversion rates of Li and Co and (ii) the dechlorination rate of PVC were investigated, and the reaction mechanisms were explored. It was found that the chlorine atoms in PVC were mechanochemically transformed into chloride ions that bound to the Li in LiCoO₂ to form LiCl. This resulted in reorganization of the Co and Fe crystals to form the magnetic material CoFe₂O₄. This study provides a more environmentally-friendly, economical, and straightforward approach for the recycling of spent LIBs and waste PVC compared to traditional processes.

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1. Introduction

Lithium-ion batteries (LIBs) are an attractive energy storage option due to their high energy density, high energy storage performance, long discharge period, and excellent circulation performance (Goodenough and Park, 2013). Recently, there has been a large increase in the number of spent LIBs due to the gradual upgrading of electrical and electronic products and the continued promotion of new energy automobiles. In China alone, the total quantity and weight of discarded LIBs are estimated to reach 25 billion units and 500 thousand tons, respectively by 2020 (Zeng et al., 2012b; Zeng et al., 2015a). Therefore, developing approaches to safely collect and dispose of spent LIBs has become a priority in the scientific community.

Owing to the lack of adequate policy and feasible technology, there are only limited recycling plants to recycle the spent LIBs in some countries such as China. As a consequence, the most wasted batteries including the spent LIBs entered into the approach of municipal solid waste treatment and disposal. LIBs are discarded at the end-of-life phase, and the recycling mainly rely on small workshops since lacking of specific collection system (Zeng et al., 2014). Some recyclers and scavengers only collect the most valuable parts of spent batteries and discard the rest, which

not only results in a waste of resources, but also causes pollution (Chen et al., 2017). The European Union issued a battery directive in 2004 that requires all battery products to be recycled and producers and retailers to assume responsibility for the recycling and disposal of spent batteries (Directive, 2006). In China, “waste battery pollution control technology policy” has completed the document of the draft with the purpose to control the pollution prevention during the period of battery recycling and regeneration.

Prior work on recycling spent LIBs has focused on the recovery of valuable metals cobalt (Co) and lithium (Li) from the cathode materials using recovery processes such as pyrometallurgy, hydrometallurgy and biometallurgy (Zeng et al., 2014). Table 1 summarized recent works (2011–2016) focusing on the recovery of metals from spent LIBs. While these methods have been successful, there are practical limitations for their use in industry. Pyrometallurgy requires a large amount of energy and emits harmful fumes, while hydrometallurgy requires strong acids, organic acids, and expensive reagents, and produces an abundant amount of liquid waste (Ordoñez et al., 2016).

In recent years, the chlorination metallurgical process has been widely used for the recovery of metals from waste materials. Polyvinyl chloride (PVC) has been used in these processes because it contains 58% Cl by weight and is an excellent chlorine atom donor. Moreover, the disposal of waste PVC has become a major problem as the production of PVC rises steadily (Yu et al., 2016). In our previous work, a subcritical water process was proposed for the

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Table 1
A summary of different processes used to recover metals from spent LIBs (2011–2016).

Process	Types	Reagents	Temperature (°C)	Time (h)	Metal recovery rates (%)	Reference
Pyrometallurgy	LiCoO ₂	None	1000	0.5	95.72%Co, 98.93% Li	Li et al. (2016)
Hydrometallurgy	LiNi _{0.8} Co _{0.15} Al _{0.05} O ₂	1–4 M H ₂ SO ₄ /HNO ₃ /HCl	25–90	3–18	100% Li, 100% Co, 99.99%Ni	Joulié et al. (2014)
	LiCoO ₂ , Li ₂ CoMn ₃ O ₈ and (Li _{0.85} Ni _{0.05}) (NiO ₂)	1 M H ₂ SO ₄ + 50 g/L pulp density	95	4	93.4% Li, 66.2% Co, 96.3% Ni, 50.2% Mn.	Meshram et al. (2015b)
	LiCoO ₂	3 M HCl	90	1.5	99.4% Li	Guo et al. (2016)
	LiCoO ₂ , Li ₂ CoMn ₃ O ₈ and (Li _{0.85} Ni _{0.05}) (NiO ₂)	1 M H ₂ SO ₄ + 0.075 M NaHSO ₃	95	4	96.7% Li, 91.6% Co, 96.4% Ni, 87.9% Mn.	Meshram et al. (2015a)
	LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂	1 M H ₂ SO ₄ , 1 vol% H ₂ O ₂	40	1	Li, Ni, Co, and Mn reached 99.7%	He et al. (2017)
	LiCoO ₂	H ₂ SO ₄ /HCl/citric acid + 0.55MH ₂ O ₂	60	5	100% Li, 96% Co	Li et al. (2014)
	LiCoO ₂	1.0 M Oxalate + H ₂ O ₂	80	2	Li/Co > 98%	Sun and Qiu (2012)
	LiCoO ₂	1.0 M Oxalate + H ₂ O ₂	95	2.5	98% Li, 97% Co	Zeng et al. (2015b)
	LiCoO ₂	(0.5–2.0 M) Citric acid/Malic acid/Aspartic acid + (1.0–6.0)vol.% H ₂ O ₂	90	2	100% Li, 90% Co	Li et al. (2013)
	LiCoO ₂	1.25 M Ascorbic acid + H ₂ O ₂	70	1/3	98.5% Li, 94.8% Co	Li et al. (2012)
	LiCoO ₂	1.5 M Succinic acid + 1.0vol.%H ₂ O ₂	70	2/3	96% Li, 100% Co	Li et al. (2015)
	LiCoO ₂	1 M iminodiacetic acid + 0.02 M maleic acid + ascorbic acid	80	6	99% Li, 91% Co	Nayaka et al. (2016a)
	LiCoO ₂	1.5 mol/L phosphoric acid 0.02 mol/L glucose	80	2	98% Co, 100% Li	Meng et al. (2017)
	LiCoO ₂	0.5 M Glycine + 0.02 M ascorbic acid	80	6	100% Li, 95% Co	Nayaka et al. (2016b)
LiMn ₂ O ₄ , LiCo _x Mn _y Ni _z O ₂ and Al ₂ O ₃	NH ₃ ⁺ (NH ₄) ₂ SO ₃ ⁻ (NH ₄) ₂ CO ₃	80	1	100%Co, 100%Cu 0%Al, 0%Mn, 40%Ni	Ku et al. (2016)	
LiCoO ₂	PVC	350	0.5	98% Li, 95% Co	Liu and Zhang (2016)	
Biometallurgy	LiCoO ₂	0.75 g/LCuSO ₄ + Acidithiobacillus ferrooxidans + 1%pulp density	Constant temperature	144	99.9% Co (With Cu ²⁺) 43.1%Co (WithoutCu ²⁺)	Zeng et al. (2012a)
	LiCoO ₂	Citric, malic and gluconic acid produced by Aspergillus niger	Constant temperature	336	100% Cu, 100% Li, 77% Mn, 75% Al, 64% Co, 54% Ni	Bahaloo-Horeh and Mousavi (2017)
	LiNi _{0.8} Co _{0.15} Al _{0.05} O ₂	Citric acid/Gluconic acid/Oxalic acid + Aspergillus niger + 1% pulp density	Constant temperature	72–336	100% Cu, 95% Li, 70% Mn, 65% Al, 45% Co, 38% Ni	Horeh et al. (2016)
	LiFePO ₄ , LiMn ₂ O ₄ and LiNi _x Co _y Mn _{1-x-y} O ₂	H ⁺ /H ⁺ + Fe ²⁺ /H ⁺ + Fe ³⁺ + Sulfur-oxidizing bacteria/iron (II)-oxidizing bacteria + 1% pulp density	Constant temperature	0–216	95%Li, 96%Co, 96%Mn, 97%Ni	Xin et al. (2016)

co-treatment of spent LIBs and waste PVC. Li and Co from C/LiCoO₂ powder can be successfully leached into subcritical water using PVC as an acid source. The disadvantages of this process include requirements of high temperature and pressure, generation of corrosive hydrochloric acid, and subsequent separation of Li and Co (Liu and Zhang, 2016).

Recently, many research groups have focused their efforts on the recovery of metals by mechanochemical methods (Lee et al., 2013; Yuan et al., 2012). During the milling process, mechanical forces act on reactants in order to induce changes in their structural and physiochemical properties, thereby facilitating chemical reactions (Day, 1984; James et al., 2012). Mechanochemical reactions are driven by mechanical energy rather than heat energy, thus they can occur at room temperature and atmospheric pressure. This could largely reduce the energy and cost. Moreover, the solid-solid reaction does not depend on water as a medium, hence there is no liquid waste produced by this process (Guo et al., 2010). However, using this method to recover metals from spent LIBs has not been extensively explored. In our previous work, mechanochemical method was applied for the recovery of Co and Li through LiCoO₂ co-grinded with EDTA (Wang et al., 2016). However, this process cannot selectively separate of Co and Li; and the high price of EDTA also limits its further application. In another work by Saito, LiCoO₂ was subjected to co-grinding with PVC using

a planetary ball mill to form Co- and Li-chlorides mechanochemically in the product (Saeki et al., 2004). The co-grinding of the mixture caused the mechanochemical reaction to form soluble Li and Co-chlorides in the ground product. However, the separation of lithium chloride and cobalt chloride in the aqueous phase remains a difficult problem.

In this study, we developed an innovative mechanochemical method for the co-processing of cathode materials (C/LiCoO₂) from spent LIBs and waste PVC. Ferrous powder was used as a co-grinding reagent for the dechlorination of PVC. Li in LiCoO₂ was recovered by reaction with organic chlorine in PVC. The residual Co was recombined with Fe and converted into magnetic material CoFe_xO_y after calcination. The operating parameters were optimized, and the mechanochemical residues were characterized. The reaction mechanisms of the co-grinding of PVC/LiCoO₂ with different additives are discussed in detail.

2. Experimental

2.1. Materials and reagents

Spent LIBs were supplied by XIAMEN OASIS Sources Co., Ltd. The LIBs were completely discharged by addition of a 5 wt% NaCl

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