

A novel method to recycle mixed cathode materials for lithium ion batteries†

Cite this: *Green Chem.*, 2013, **15**, 1183

Haiyang Zou, Eric Gratz, Diran Apelian and Yan Wang*

The rechargeable lithium ion (Li-ion) battery market was \$11.8 billion in 2011 and is expected to increase to \$50 billion by 2020. With developments in consumer electronics as well as hybrid and electric vehicles, Li-ion batteries demand will continue to increase. However, Li-ion batteries are not widely recycled because currently it is not economically justifiable (in contrast, at present more than 97% lead-acid batteries are recycled). So far, no commercial methods are available to recycle Li-ion batteries with different cathode chemistries economically and efficiently. Considering our limited resources, environmental impact, and national security, Li-ion batteries must be recycled. A new low temperature methodology with high efficiency is proposed in order to recycle Li-ion batteries economically and thus commercially feasible regardless of cathode chemistry. The separation and synthesis of cathode materials (the most valuable material in Li-ion batteries) from the recycled components are the main focus of this study. The results show that the developed recycling process is practical with high recovery efficiencies, and that it is viable for commercial adoption.

Received 23rd January 2013,
Accepted 27th February 2013

DOI: 10.1039/c3gc40182k

www.rsc.org/greenchem

Introduction

Li-ion batteries have attracted more attention than any other battery technology since Sony made the first commercial cell in 1991.^{1,2} Two decades later, they remain widely used and account for about 60% of worldwide sales of portable batteries. Li-ion batteries are currently the system of choice, offering high energy density, flexibility and lightweight design, and long lifespan in comparison to competing battery technologies.^{3–5} Li-ion battery technologies are superior to other types of batteries with respect to energy density, which is a critical parameter for portable electronics, as well as hybrid and electric vehicles.^{6–8}

The working principle of Li-ion batteries can be explained by examining the electrolytic cell. When charging, Li-ions transfer from cathode materials to anode materials through the electrolyte, and electrons are transferred from the cathode to the anode *via* the external circuit. When discharging, Li ions will transfer from anode materials to cathode materials through the electrolyte, and electrons are transferred from the anode to the cathode through the external circuit. With every cycle of charging and discharging, Li ions traverse back and forth between the anode and the cathode. It is for this reason that a Li-ion battery is also called a rocking chair battery.

The working voltage is more than 3 V (allowing higher energy/power), which is one of the most important advantages compared to batteries with aqueous solution.⁹

Li-ion batteries include anodes, cathodes, current collectors, separators, liquid electrolytes, containers and sealing parts. Normally, Li-ion batteries consist of heavy metals, organic chemicals and plastics,¹⁰ and the composition varies with different manufacturers. The anode is made of graphite, conductive carbon and a polyvinylidene fluoride (PVDF) binder. The anode current collector is made of Cu foil. The cathode consists of conductive carbon, a PVDF binder and a Li compound. LiCoO₂, LiMn₂O₄, LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂, and LiFePO₄ are the most commonly used compounds for the cathode. A cathode current collector is made of Al foil. The separator is made of polypropylene (PP) or polyethylene (PE). The common electrolyte is lithium hexafluorophosphate (LiPF₆) dissolved in ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC) or a mixture of these. The cell container is made of metal or plastics and sealing parts are made of plastics. With the development of new chemistries for electrode materials and incorporation of new manufacturing technologies, the composition and proportion of the various components varies greatly.

Currently, Li-ion batteries are mostly used for portable applications such as laptops and cell phones. As we look into the near future, Li-ion batteries are gradually being used for large scale applications, such as hybrid or electrical cars and grid level power systems.¹¹ For these latter applications, the battery pack size is much larger.

Mechanical Engineering, Worcester Polytechnic Institute, 100 Institute Road, Worcester, MA, USA. E-mail: yanwang@wpi.edu; Fax: +1 5088315178; Tel: +1 5088315453

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c3gc40182k

Currently, most of the Li-ion batteries are not recycled because it is not economically justifiable to recycle the small Li-ion batteries used in cell phones and laptops. We believe that such an open loop industrial cycle is not sustainable; it is our strong conviction that we must develop and establish viable Li-ion battery recycling methodologies. The first justification is based on economic reasons. The materials used in Li-ion batteries are expensive; the cathode materials for most Li-ion batteries in laptops and cell phones are LiCoO₂. Li and Co are not renewable materials and Co is relatively expensive; therefore it makes sense to recycle them. The second reason is for environmental concerns. Although Li-ion batteries are called “green batteries”, the solvent is flammable, and toxic HF can be released when the batteries burn. Therefore, recycling Li-ion batteries is important and necessary for environmental and economic considerations.

Academia, national laboratories, and industries have addressed the subject of recycling Li-ion batteries. However, there are significant gaps in the methodologies developed to date with respect to efficiency and their effectiveness. Many of the recycling processes that have been pursued consider LiCoO₂ as the only cathode material.^{12–14} In a recent review paper by Xu *et al.*,¹⁵ existing recycling methods consider LiCoO₂ as the cathode material. However, this is not the case in the commercial world. Cathode materials in commercial Li-ion batteries include LiCoO₂, LiMn₂O₄, LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ and LiFePO₄. Table 1 shows the cathode composition of the 2012 battery market. Thus previously developed methods cannot effectively recycle Li-ion batteries with such varying chemistries of the cathode; when extracting Co from used Li-ion batteries, other elements including Fe, Ni, and Mn can also be extracted. Some work has been carried out which considers recycling of Li-ion batteries with varying cathode chemistries;^{16,17} however they are complex and commercially not feasible.

Industrially, companies such as Umicore, Recupyl Battery Solutions, and Toxco do recycle Li-ion batteries. Umicore uses an ultrahigh temperature smelting technology^{18,19} and does offer a closed loop solution for high value metals such as Co and Ni. Less valuable metals such as Mn, Fe, Li, Al are ‘down-cycled’, meaning that they are not recovered and reused in battery applications. In order to lower battery prices, there is a strong drive to reduce the use of Co and Ni containing compounds. For example, LiMn₂O₄ is used as the cathode material for GM Volt batteries, and LiFePO₄ is used as the cathode material in A123 batteries. Thus the need is to recover all cathode materials regardless of battery composition.

The cathode material is the most expensive part of a Li-ion battery, and many different cathode materials are being used in commercial batteries. The challenge is to recycle Li-ion

batteries with differing cathode chemistries, as it is difficult to separate Fe, Ni, Co, and Mn due to their similar properties. Impure materials have a less value in the commercial sector. In this study we have developed a new methodology to successfully recycle mixed cathode materials including LiCoO₂, LiMn₂O₄, LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂, and LiFePO₄. A novel method is adopted to separate Fe from Ni, Co and Mn in solution. The mixture of Ni(OH)₂, Co(OH)₂, and Mn(OH)₂ with recovered Li₂CO₃ is used to synthesize LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂. The recycling process is practical, has a high recovery efficiency, and commercially viable.

Experimental

Mixed cathode materials including LiCoO₂, LiMn₂O₄, LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂, and LiFePO₄ were employed in the recovery process. The cathode materials including LiCoO₂ and LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ were obtained from Umicore; and LiMn₂O₄ and LiFePO₄ from MTI. 30 wt% Hydrogen peroxide was purchased from Columbus Chemical Industries Inc; and Li₂CO₃ from Alfa Aesar Company. All of the reagents were utilized as received without any further purification.

The separation and synthesis process for mixed cathode materials is shown in Fig. 1.

Step 1: Mixed cathode materials were leached using 4 M sulfuric acid and 30 wt% hydrogen peroxide for about 2–3 hours at 70–80 °C. Residual LiFeO₄ was filtered out. The metals of interest were transferred into the aqueous solution.

Step 2: NaOH solution was added to adjust the pH number to deposit Fe(OH)₃ which has a much lower solubility constant, and Mn²⁺, Co²⁺, and Ni²⁺ were kept in solution.

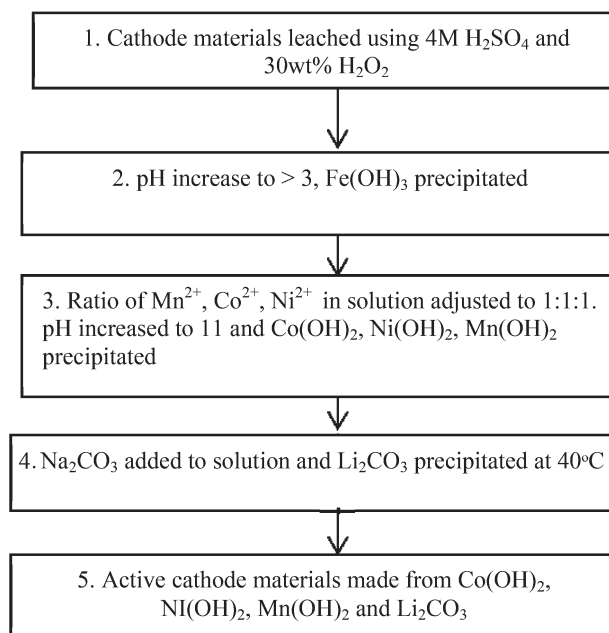


Fig. 1 Flow chart for the separation and synthesis process for mixed cathode material.

Table 1 World market size with different cathode materials (2012/Forecast in Volume)¹⁸

LiNi _{0.33} Mn _{0.33} Co _{0.33} O ₂	LiCoO ₂	LiNiO ₂	LiMn ₂ O ₄	LiFePO ₄
29.00%	37.20%	7.20%	21.40%	5.20%

Step 3: The concentration of Mn^{2+} , Co^{2+} , Ni^{2+} in solution was tested, and their ratios were adjusted to 1 : 1 : 1 with additional CoSO_4 , NiSO_4 , and MnSO_4 ; the solution was stirred for 2 hours. NaOH solution was further added to increase the pH number to 11, and the mixture of $\text{Co}(\text{OH})_2$, $\text{Ni}(\text{OH})_2$, $\text{Mn}(\text{OH})_2$ with a 1 : 1 : 1 molar ratio could be fully co-precipitated. The mixture was rinsed with distilled water.

Step 4: Na_2CO_3 was added to the solution to deposit Li_2CO_3 at about 40 °C. After filtration, recovered Li_2CO_3 is used to synthesize the active cathode material $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ in the next step.

Step 5: The co-precipitate including $\text{Co}(\text{OH})_2$, $\text{Mn}(\text{OH})_2$, $\text{Ni}(\text{OH})_2$ and recovered Li_2CO_3 with additional Li_2CO_3 in a molar ratio of 1.1 : 1 of Li versus M (M = the sum of Ni, Mn, and Co) were mixed and ground in the mortar. The precursor was subjected to ball-milling for 48 hours and pressed into pellets (pressure = 15 000 lbs, 12.96 mm diameter). The pellets were then sintered at 900 °C for 15 h in air, and the temperature was increased at a rate of 9 °C min^{-1} from room temperature. The reaction product was ground into powder using a mortar and pestle.

The crystal structure was characterized using an X-ray diffractometer (Bruker D8 Focus; S/N 203207 with copper $\text{K}\alpha$ radiation, Cu target; S/N 07/03-1120). An X-ray scintillation detector SD 650 NaI (TI) was used. The concentration of metal ions in solution was tested by atomic absorption spectroscopy (Perkin-Elmer AA Analyst 300). The scanning electron microscopy (SEM) images and energy dispersion spectroscopy (EDS) results were obtained with a JEOL JSM-7000F electron microscope. The pH of the solution was tested by a Milwaukee MW102 pH meter.

The synthesized $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ was used to make the cathode, which was prepared by the typical procedure of mixing the electroactive $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ with conductive carbon and a PVDF binder. Subsequently, the slurry was cast on the Al current collector and dried and pressed. The electrode was electrochemically tested against Li foil in a Swagelok cell with stainless-steel current collectors. A piece of Li foil was pressed onto a collector, two pieces of a Celgard 2500 microporous separator placed over it, a piece of the cathode centered over the separator, and the cell was sealed with pressure to ensure good contact between the electrode and the other collector. 1 M LiPF_6 electrolyte solution in ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC) (1 : 1 : 1) was used to fabricate cells. Each cell was tested with a galvanostat/potentiostat/impedance analyzer (Bio-logic VMP3).

Constant current charging and discharging were used at different rates in the voltage range of 2.5–4.6 V.

Results and discussion

Materials separation

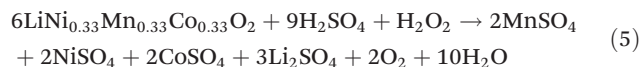
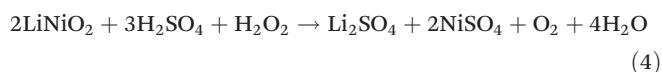
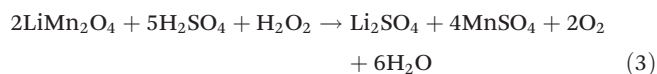
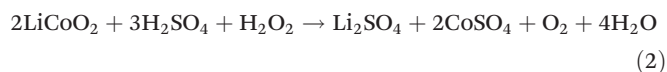
Acid leaching. Leaching of the mixed cathode materials has been investigated with leaching agents H_2SO_4 , HCl and HNO_3 ; Table 2 summarizes leaching operational conditions for different acidic media. The leaching reaction for LiCoO_2 with HCl is as follows:



Although HCl has a better leaching rate,²⁰ it results in serious environmental problems and requires special equipment for treating chlorine (Cl_2) gas, which will contribute to the recycling cost. Our approach was to leach cathode materials by the use of H_2SO_4 with the addition of H_2O_2 as a reduction/oxidation agent.

Vu *et al.* studied the dissolution of LiCoO_2 in acid solution.²⁹ In their experiments, H_2SO_4 concentration was 2 M and the pulp density was 50 g L^{-1} , the leaching temperature was 75 °C with an agitation of 300 rpm. Increasing the H_2O_2 concentration leads to higher leaching rates and efficiencies. H_2O_2 has been shown to help the dissolution of cobalt, manganese and nickel, and in the transfer of $\text{Co}(\text{III})$ to $\text{Co}(\text{II})$.³⁰

In our work, the mixed cathode powder consisting of LiCoO_2 , LiMn_2O_4 , LiFePO_4 and $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ was put into 4 M H_2SO_4 acid with 30 wt% H_2O_2 . The reactions are:



As-received batteries for recycling may be in different charged/discharged states and the valence of the metallic

Table 2 Summary of some operational conditions for the leaching of spent Li-ion secondary rechargeable batteries by different acidic media¹⁷

References	Sample	Leaching agent	Temperature (°C) + Time	Reduction agent
Zhang <i>et al.</i> (1998) ²¹	LiCoO_2	4 M HCl	80 + 1 h	
Castillo <i>et al.</i> (2002) ²²	Li, Mn, Ni	2 M HNO_3	80 + 2 h	
Lee and Rhee (2003) ²³	LiCoO_2	1 M HNO_3	75 + 1 h	1.7 vol% H_2O_2
Bok <i>et al.</i> (2004) ²⁴	LiCoO_2	35% HNO_3 + 18% H_2SO_4 + 5% HCl	Room temp. + 24 h	
Shin <i>et al.</i> (2005) ²⁵	LiCoO_2	H_2SO_4	75 + 10 min	15 vol% H_2O_2
Nan <i>et al.</i> (2005) ²⁶	LiCoO_2	3 M H_2SO_4	70 + 4 h	
Aktas <i>et al.</i> (2006) ²⁷	LiCoO_2	4 M H_2SO_4	80 + 4 h	H_2O_2
Nan <i>et al.</i> (2006) ²⁸	LiCoO_2	3 M H_2SO_4	70 + 5 h	3 wt% H_2O_2

elements may differ. Hydrogen peroxide transferred all Co, Mn, Ni, and Fe to Co(II), Mn(II), Ni(II), and Fe(III), respectively. These were verified by our experiments, and are provided in the ESI.†

All Mn, Ni, Co, Li are in solution and only a part of LiFePO₄ can be dissolved in the solution with H₂SO₄ and H₂O₂. This is because of the high bonding energy of Fe–P–O. Undissolved LiFePO₄ can be filtered out.

Separating Fe. Iron was the only impurity in the work described herein. By controlling the pH iron ions can be completely separated from solution. The solubility of a metal hydroxide, M(OH)_n, is related to the solubility equilibrium and the pH according to the following equations:

$$K_{sp} = [M^{n+}][OH^-]^n \quad (6)$$

$$K_w = [H^+][OH^-] = 10^{-14} \quad (7)$$

$$pH = -\log 10(H^+) \quad (8)$$

Assume $C_{min}(M^+) = 10^{-5}$ M as the concentration of M^{n+} when all M^{n+} ions fully precipitate out, and $C_{max}(M^+)$ as M^{n+} begins to precipitate. According to the chemical reactions given above, the maximum ion concentration of metal ions $C_{max}(M^+)$ for Fe, Ni, Co, and Mn are 1 M, 2.667 M, 2.667 M, and 3.2 M, respectively, when the concentration of sulfuric acid is 4 M. Table 3 shows that the pH number of metal ions starting to precipitate and precipitating fully.

As shown in Fig. 2, if all Fe ions exist in the state of +3, while all other metal ions (Mn, Ni, Co) are in a divalent state, then controlling the pH of the leaching solution between 2.815 and 5.156 (this number varies slightly with the concentration of Co in the solution) can separate all iron from the solution. The materials in the as-received batteries can either be in the

Table 3 The pH number for the start and end of precipitating various metal ions³¹

Substance	K _{sp}	C _{max} (M)	C _{min} (M)	pH _{start}	pH _{end}
Fe(OH) ₃	2.79×10^{-39}	1.00	1×10^{-5}	1.149	2.815
Al(OH) ₃	3.00×10^{-30}		1×10^{-5}		4.49
Cu(OH) ₂	2.00×10^{-20}		1×10^{-5}		6.65
Ni(OH) ₂	5.48×10^{-15}	2.667	1×10^{-5}	5.156	8.869
Co(OH) ₂	5.92×10^{-15}	2.667	1×10^{-5}	6.673	9.386
Mn(OH) ₂	2.00×10^{-13}	3.200	1×10^{-5}	7.398	10.151
Fe(OH) ₂	4.87×10^{-17}	1.00	1×10^{-5}	5.844	8.344

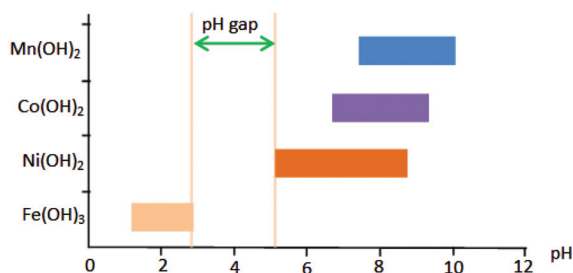


Fig. 2 pH number of the start and end of precipitation for different metal ions.

oxidation state or reduction state. The valence of Co, Ni and Mn can be +3 or +4, and the valence of Fe can be +2 or +3 based on their charging or discharging state. As mentioned above, H₂O₂ can help transfer all Fe(II) to Fe(III), and other metal ions to divalent state, which will help separate Fe from the solution effectively.

Separating Al and Cu. Aluminum and copper are not present in this study, however, in recycled spent Li-ion batteries there will be Al and Cu ion impurities leached into solution. The aluminum reaches C_{min} at a pH of 4.49 and is therefore not a major concern. Copper on the other hand reaches the C_{min} concentration at a pH of 6.65. For this reason the Ni ion concentration must be kept low (>1 M) or Ni ions will be lost in the impurity removal step. Thankfully, Ni is the least common metal in Li-ion batteries today, Table 1.

Precipitating Co, Ni and Mn hydroxide. With Co, Mn and Ni ions coexisting in the solution after removing the Fe, the appropriate amounts of NiSO₄, MnSO₄, CoSO₄ are added to adjust the molar ratio of Ni, Mn, and Co to 1 : 1 : 1. One of the innovations in this process is that Co, Mn, and Ni are recycled and re-introduced into the battery production chain without separation, and they are directly utilized to synthesize the cathode material LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂, which saves significant amounts of labor cost and time. Also since the properties of Mn, Co, Ni are similar it is difficult to separate these elements efficiently.

NaOH was further added to co-precipitate Ni, Mn and Co as Ni(OH)₂, Mn(OH)₂, and Co(OH)₂, which was utilized to synthesize LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂. Fig. 3 shows the relationship between the metal ion concentration in the solution and the pH number. Almost 100% of metal ions can co-precipitate when the pH value equals to 11 or above. After filtration, the precipitate was rinsed with distilled water to remove impurities and alkaline solution. The co-precipitate was used as starting materials to synthesize LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂. During the precipitation process, the mixture of Ni(OH)₂, Mn(OH)₂, and Co(OH)₂ was distributed evenly, which is beneficial to synthesize high performance LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂. Various

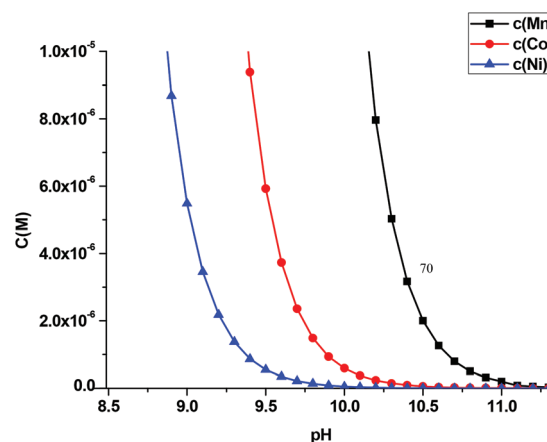
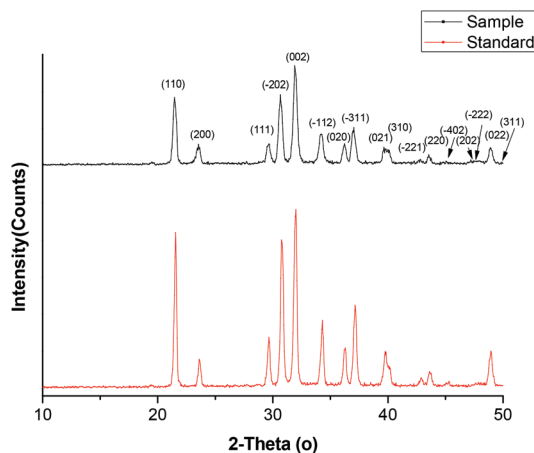
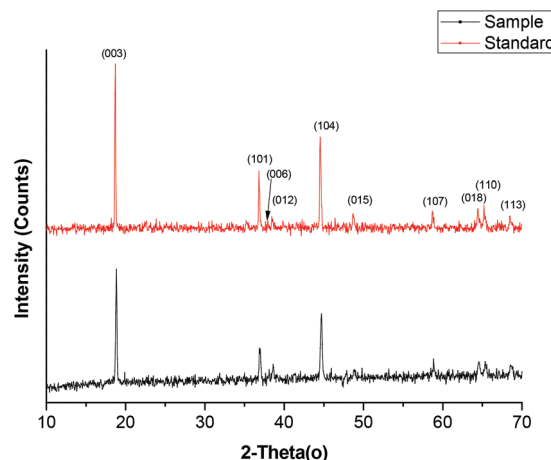


Fig. 3 Concentration of different metal ions left in solution for various pH numbers.

Table 4 Variation in solubility of different substances in water at various temperatures, at 1 atm pressure; the unit of solubility is given in g/100 g H₂O

Compound	0 °C	10 °C	20 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C	100 °C
LiOH	11.9	12.1	12.3	\	12.7	\	13.2	14.6	16.6	17.8	19.1
Na ₂ CO ₃	7	12.5	21.5	39.7	49	\	46	\	43.9	43.9	\
Li ₂ CO ₃	1.54	1.43	1.33	1.26	1.17	\	1.01	\	0.85	\	0.72

**Fig. 4** XRD patterns of recycled Li₂CO₃ filtered from solution compared to the commercial sample from Alfa Aesar.**Fig. 5** XRD patterns of LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ compared to the commercial sample from Umicore.

LiNi_xMn_yCo_{1-x-y}O₂ compounds can be synthesized if the ratio of Ni, Mn, and Co is adjusted by controlling the added amount of NiSO₄, MnSO₄, and CoSO₄.

Lithium recovery. After co-precipitating Ni, Mn and Co, the leaching solution was treated with Na₂CO₃ solution at about 40 °C to precipitate Li as Li₂CO₃, since the solubility of Li₂CO₃ in an aqueous solution is inversely proportional to its temperature (Table 4). The appropriate amount of Na₂CO₃ is directly added to the leaching solution. Li₂CO₃ is recovered and washed by hot water to remove the residual alkali.

The results show that about 80% lithium was recovered as a precipitate, because aqueous solution dissolves some Li₂CO₃. This is similar to the recovery ratio reported by Wang *et al.*¹⁷ The maximum recycling efficiency of Li ions recovered from LiCoO₂ is 80.3%. The result is the same for LiNiO₂ and LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂. Lithium recovery from LiMn₂O₄ is 67.2%. The hot water used to rinse the recycled Li₂CO₃ will slightly lower the efficiency. Concentrating the solution by evaporating water will increase the recovery efficiency.

Fig. 4 shows the XRD patterns of recycled Li₂CO₃ compared to the standard pattern from commercial material. The lattice parameters are $a = 8.34802$ Å, $b = 4.96058$ Å, $c = 6.1819$ Å, which proves that the recycled Li₂CO₃ is of high purity.

Materials characterization and electrochemical performance of synthesized LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂

Compared to LiCoO₂, LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ provides lower cost as well as greater safety and performance. When charged to 4.6 V and then discharged to 2.5 V, the specific capacity can

reach 200 mA h g⁻¹,³² which is higher than LiCoO₂ without sacrificing cycle life. LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ also has much less heat flow and higher onset temperature than LiCoO₂.

Homogeneous precursors can not only accelerate the formation of LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂, but also significantly improve its electrochemical performance.³³ During the recycling process, precipitates of Ni(OH)₂, Mn(OH)₂, and Co(OH)₂ can help the starting materials distribute uniformly. Precursors were ground by a mortar and pestle, and ball-milled for 3 days to ensure they were mixed well.

Fig. 5 shows XRD patterns of synthesized LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ and the standard LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ product from Umicore. Lattice parameters of samples were calculated from the d -value of 10 strong diffraction peaks. The sample peaks can be indexed as α -NaFeO₂ structures with a space group of $R\bar{3}m$. Distinct splitting of (006)/(012) and (018)/(110) peaks indicates that the sample possesses a well-developed layered-structure.³⁴ No impurity peaks are present in either pattern, which suggests that LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ is of high purity.

SEM images of LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ at different magnifications are shown in Fig. 6. Homogenous particles are well distributed throughout without any agglomeration; the particle size ranges from 100 to 200 nm. Uniform particle size and homogenous particles are critical factors for high quality materials. Smaller particle size allows a shorter lithium diffusion length, which in turn provides higher performance.

The first two cycles of the cell were charged and discharged at 0.0729C (11.67 mA g⁻¹, $C = 160$ mA h g⁻¹). The discharge capacity for the first two cycles was 173.96 mA h g⁻¹ and

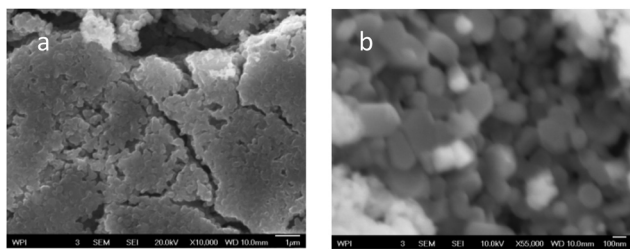


Fig. 6 SEM images of $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ at different magnifications sintered at 900 °C for 15 h in air, (a) low magnification, (b) high magnification.

$172.92 \text{ mA h g}^{-1}$, respectively. The coulombic efficiency is the discharge capacity over charge capacity, for the first two cycles it was 81.07% and 94.86%, respectively. These results are in line and similar to published results.^{35–37}

Rate-capability test results for the $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ electrode are shown in Fig. 7(a) and (b). The cell was charged up to 4.6 V and then discharged to 2.5 V at (a) 11.67, (b) 23.33, (c) 46.67, (d) 116.67, and (e) 233.34 mA g^{-1} . As shown in Fig. 7(a) and (b), discharge capacity decreases with increasing C rate. From SEM images, we note that particles are interconnected together, and are not separated or distinct. Although single particles are nearly nanoscale, the diffusion length of the tightly connected particles remains high. Well ground powders might have had a better performance.

Fig. 7(c) shows specific capacity and coulombic efficiency as a function of the cycle for the cell with recycled $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ (voltage range of 2.5–4.6 V at 46.6 mA g^{-1}). The initial capacity is $130.20 \text{ mA h g}^{-1}$, and the reversible capacity after 50 cycles is $107.29 \text{ mA h g}^{-1}$ (82.40% of the first discharge capacity). The decrease of the capacity is probably due to the increase of the impedance of lithium foil.³⁸ The coulombic efficiency is nearly 100%, which clearly demonstrates that the synthesized $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ has good electrochemical properties.

Comparative analysis

It is widely accepted that the cathode materials in lithium ion batteries determine the batteries performance. Currently, LiCoO_2 is widely used as a cathode material, it is simple to produce, has high specific capacity and a long cycle life. However LiCoO_2 is a relatively expensive cathode material, thus the need to consider other cathode materials such as $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$, LiFePO_4 , LiMn_2O_4 , and LiNiO_2 . Table 5 compares the performance characteristics for various cathode materials.

LiCoO_2 has been a successful cathode material. Compared with other cathode materials, LiCoO_2 has better performance in reversibility, capacity, charging efficiency, and voltage stability. However, cobalt is a near critical material, expensive, and there are environmental issues to consider.

The performance of LiNiO_2 is similar to LiCoO_2 , though it is less expensive than the latter. Furthermore LiNiO_2 needs to be synthesized and the operating window for synthesis is quite tight. Slight processing variations may lead to

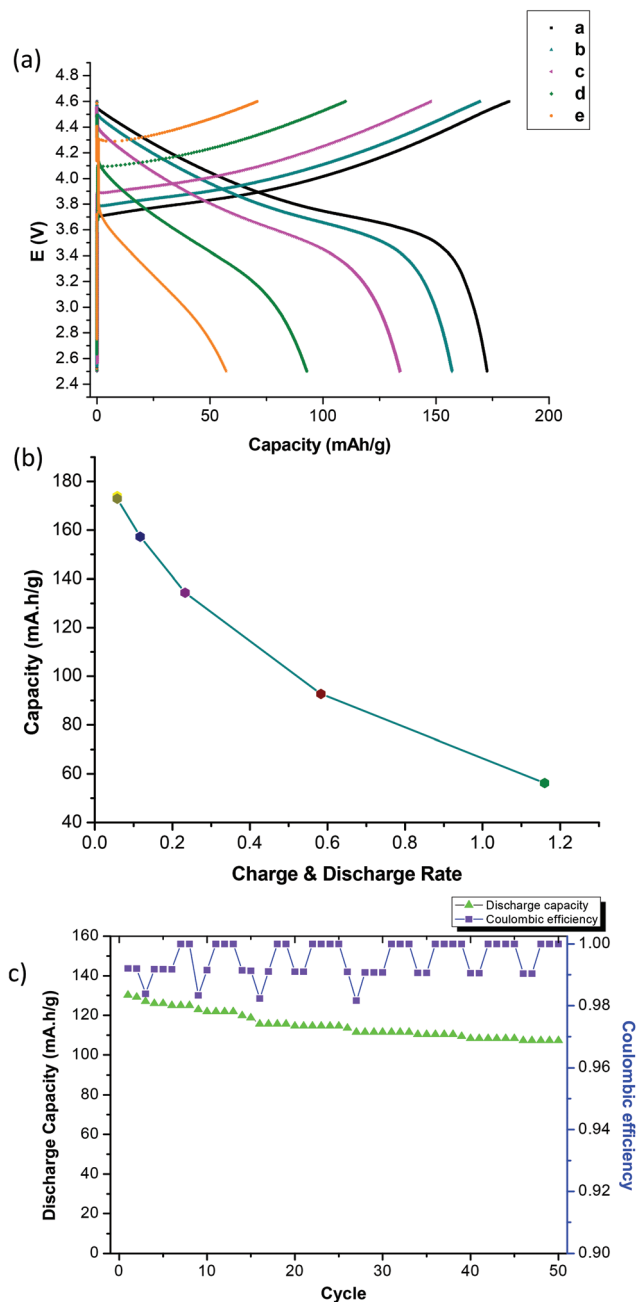


Fig. 7 Electrochemical performance of synthesized $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$, (a) charge and discharge curves for different rates (a 11.67, b 23.33, c 46.67, d 116.67, e 233.34 mA g^{-1}), (b) discharge capacity as a function of rate, (c) cycle test at a current density of 46.6 mA g^{-1} and voltage of 2.5–4.6 V.

Table 5 Performance of various commercial cathode materials

Electrode material	Average potential difference (V)	Specific capacity (mA h g^{-1})	Specific energy (kW h kg^{-1})
LiCoO_2	3.7	140	0.518
LiMn_2O_4	4.0	148	0.592
LiNiO_2	3.5	180	0.630
LiFePO_4	3.3	170	0.495
$\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$	3.6	160	0.576

Table 6 Price and cost to recycle one-ton cathode materials from spent Li-ion batteries⁴²

Substance	Price (\$/ton)	Cost (\$)
MnSO ₄ ·H ₂ O	600	265
NiSO ₄ ·6H ₂ O	6000	4831
CoSO ₄ ·7H ₂ O	7500	0
H ₂ O ₂ , 30%	500	62
Na ₂ CO ₃	300	222
NaOH	350	400
Li ₂ CO ₃	8000	2621
H ₂ SO ₄	150	210
Total		8611

nonstoichiometric LiNiO₂, in which lithium and nickel are randomly distributed, giving rise to poor electrochemical performance and lower energy density. In addition, because the decomposition temperature of the product after desertion of lithium is low, much heat and oxygen is released during decomposition. This may cause fire and/or explosion when LiNiO₂ is overcharged; not an acceptable scenario.

As iron is plentiful and cheap, LiFePO₄ has the advantage of being the least expensive cathode material. It also has high thermal stability (better than LiCoO₂), and is environmentally more friendly. The problem with LiFePO₄ is its relatively low energy density and low electronic conductivity. Surface coating and doping technologies have been utilized to increase its conductivity.^{39–41}

LiMn₂O₄ cathode materials have the same advantages as LiFePO₄: low cost, resource availability, and both are environmentally friendly. However, at high temperatures, manganese dissolves in the electrolyte. The dissolved manganese is no longer considered active battery material and the battery capacity is reduced leading to reduced performance.

LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ combines lower cost as well as greater safety and performance. In addition, heat flow was much less and a higher onset temperature than LiCoO₂ was observed.

According to a report on the Li-ion battery market from Yano Research Institute, market share of various cathode materials in 2012 is dominated by LiCoO₂ followed by LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂; see Table 1. Additionally, in 2011 the LiCoO₂ market share was 42% and the LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ market share was 25.6%. Thus the trend is that LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ continues to increase its market share in the lithium ion battery market. Considering the 2012 distribution of the market share, a representative lot of 1000 kg of cathode material obtained from recycled batteries would contain 290 kg LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂, 372 kg LiCoO₂, 72 kg LiNiO₂, 214 kg LiMn₂O₄, and 52 kg LiFePO₄. Based on the reactions for material separation, the price and cost of chemicals for recycling in our process [Fig. 1] are given in Table 6; prices obtained from Alibaba website.⁴²

The recycled products include 0.047 tons LiFePO₄, and 1.39 tons LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂. More than one ton of active LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ is obtained since both MnSO₄·H₂O and NiSO₄·6H₂O are added to solution to precipitate out the Co(OH)₂, Ni(OH)₂ and Mn(OH)₂ at a 1 : 1 : 1 ratio.

Table 7 Prices and cost of virgin materials used to produce LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ by co-precipitation

	Price (\$/ton)	Cost (\$)
MnSO ₄ ·H ₂ O	600	487
NiSO ₄ ·6H ₂ O	6000	7575
CoSO ₄ ·7H ₂ O	8000	10 801
Li ₂ CO ₃	8000	4259
Total		23 121

Energy consumption. The complete process to process the recycled Li-ion batteries is described in ESI.† The energy required to recycle Li-ion batteries with the approach described is considerably less than the high temperature pyrometallurgical methods in use today. Energy is required to power the shredder, heat the batteries and acid to 70 °C for 1 hour during the leaching step, and heat the solution to 40 °C for 1 hour during the Li₂CO₃ precipitation step.

Waste products. The only waste product generated during the leaching step is water, eqn (2)–(5). When the metal hydroxides are precipitated sodium sulphate is generated according to eqn (9) and (10).



Since the process generates relatively benign waste products and relies primarily on acid base chemistry it is believed to be an environmentally friendly method of recycling Li-ion batteries.

Comparison of recycled versus virgin materials. The cost of using virgin materials instead of recycled materials to synthesize LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ by co-precipitation has been calculated; see Table 7.

The cost of synthesizing LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ is \$16 635 /ton (\$23 121/1.3899 ton) using virgin materials. While using recycled materials, the cost is only \$6195/ton (\$8610/1.3899 ton). The cost differential is \$10 440/ton (\$16 635/ton – \$6195/ton), which is significant. Dewulf *et al.*⁴³ studied resource savings that can be accrued when recycling Li-ion batteries. There are implications other than just fiscal. Recycling resulted in natural resource savings by decreasing mineral ore dependency and reduced fossil resource and energy demand. The analysis results clearly show that recycling can not only save the cost of production, but also save energy and reduce resource consumption.

Global impact. This process is dependent on the demand for the recovered LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ cathodes in Li-ion batteries. Since LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ cathodes are used in ~30% of the Li-ion batteries produced today and that the number keeps on increasing,¹⁸ it is believed that the process is commercially viable and would have a noticeable impact on a global scale.

Conclusions

A novel approach that combines synthesis of LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂, with a recycling process that does not separate

different elements (Mn, Ni, Co) and is dedicated to recovering all spent commercial Li-ion batteries has been developed. Cathode materials from different battery chemistries, such as LiCoO_2 , LiMn_2O_4 , $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ and LiFePO_4 , are recovered with high efficiency in the form of marketable materials or are directly utilized to synthesize the new materials. Analysis results show that almost 100% of Ni, Mn, Co are recovered, and experiments demonstrate that about 80% Li are recycled in the form of Li_2CO_3 . The electrochemical performance tests showed that the synthesized $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ shows excellent electrochemical performance.

It is believed that synthesizing $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ using recycled materials can save \$10 440/ton in chemicals not including energy savings. There are additional economic benefits from recycling in that the Cu current collector, the electrolyte, and carbon may be recovered. The Li-ion battery industry is growing fast, and new types of Li-ion batteries will be presented in the market. However, this might not challenge our method since it is anticipated that the major elements will still be the same. Even with additional elements, some process steps can be adjusted to the new chemical composition.

One of the most daunting challenges we face is sustainable development in the 21st century. With population increasing at a 1.4% annual rate and energy demand increasing at a 1.7% annual rate, the need for recycling is pivotal. The Li-ion battery market is posed to grow, and we must establish closed loop systems to ensure sustainable development.

Acknowledgements

This work was supported by WPI start-up funds for Dr Wang, the Center for Resource Recovery & Recycling (CR^3) and the National Science Foundation (NSF).

Notes and references

- W. V. Schalkwijk and B. Scrosati, *Advances in Lithium Ion Batteries Introduction*, Springer, 2002.
- M. S. Whittingham, *Chem. Rev.*, 2004, **104**, 4271–4301.
- M. Armand and J. M. Tarascon, *Nature*, 2008, **451**, 652–657.
- J. M. Tarascon and M. Armand, *Nature*, 2001, **414**, 359–367.
- Y. M. Chiang, *Science*, 2010, **330**, 1485–1486.
- J. M. Tarascon and M. Armand, *Nature*, 2001, **414**, 359–367.
- W. A. van Schalkwijk and B. Scrosati, *Advances in lithium-ion batteries*, Springer, New York, 2002.
- D. Linden and T. B. Reddy, *Handbook of Batteries*, McGraw-Hill, 3rd edn, 2002.
- M. Winter and R. J. Brodd, *Chem. Rev.*, 2004, **104**, 4245–4269.
- S. M. Shin, N. H. Kim, J. S. Sohn, D. H. Yang and Y. H. Kim, *Hydrometallurgy*, 2005, **79**, 172–181.
- P. B. Balbuena and Y. X. Wang, *Lithium-ion batteries: solid-electrolyte interphase*, Imperial College Press, London, 2004.
- W. J. McLaughlin, Method for the neutralization of hazardous materials, *US Patent* 5,345,033, 1994.
- M. Contestabile, S. Panero and B. Scrosati, *J. Power Sources*, 2001, **92**, 65–69.
- J. M. Nan, D. M. Han and X. X. Zuo, *J. Power Sources*, 2005, **152**, 278–284.
- J. O'M. Bockris, N. Bonciocat and F. Gutmann, *An introduction to Electrochemical Science*, Wykeham Publications Ltd., 1974.
- S. Castillo, F. Ansart, C. L. Robert and J. Portal, *J. Power Sources*, 2002, **112**, 247–254.
- R. C. Wang, Y. C. Lin and S. H. Wu, *Hydrometallurgy*, 2009, **99**, 194–201.
- Yano Research Institute, Lithium-ion Battery Market: Cell and Components, 2011. p. 16; D. Chéret, Recycling of rechargeable batteries Li-ion – NiMH, in *ICBR – International Congress for Battery Recycling*, Como, June 2004.
- C. Siret and G. Van Damme, Umicore and SAFT closing the battery loop – Recycling lowers environmental impact: The case of Li-ion batteries, in *EBR – Electronics & Battery Recycling*, Toronto, June 2008.
- P. B. Balbuena and Y. X. Wang, *Lithium-ion batteries: solid-electrolyte interphase*, Imperial College Press, 2004.
- P. Zhang, T. Yokoyama, O. Itabashi, T. M. Suzuki and K. Inoue, *Hydrometallurgy*, 1998, **47**, 259–271.
- S. Castillo, F. Ansart, C. Laberty-Robert and J. Portal, *J. Power Sources*, 2002, **112**, 247–254.
- C. K. Lee and K. I. Rhee, *Hydrometallurgy*, 2003, **68**, 5–10.
- J. S. Bok, J. H. Lee, B. K. Lee, D. P. Kim, J. S. Rho, H. S. Yang and K. S. Han, *Solid State Ionics*, 2004, **169**, 139–144.
- S. M. Shin, N. H. Kim, J. S. Sohn, D. H. Yang and Y. H. Kim, *Hydrometallurgy*, 2005, **79**, 172–181.
- J. Nan, D. Han and X. Zuo, *J. Power Sources*, 2005, **152**, 278–284.
- S. Aktas, D. J. Fray, O. Burheim, J. Fenstad and E. Acma, Mineral processing and extractive metallurgy, *Trans. Inst. Min. Metall. C*, 2006, **115**, 95–100.
- J. Nan, D. Han, M. Yang and M. Cui, *J. Electrochem. Soc.*, 2006, **153**, 101–105.
- C. Vu, K. N. Han and F. Lawson, *Hydrometallurgy*, 1980, **6**, 75–87.
- CRC Handbook of Chemistry and Physics, in *Solubility Product Constants*, ed. W. M. Haynes, 93 edn, 2012, pp. 196–198.
- M. J. Lain, Recycling of lithium ion cells and batteries, *J. Power Sources*, 2001, **97–98**, 736–738.
- N. Yabuuchi and T. Ohzuku, *J. Power Sources*, 2003, **119–121**, 171–174.
- W. Lai, C. K. Erdonmez, T. F. Marinis, C. K. Bjune, N. J. Dudney, F. Xu, R. Wartena and Y. M. Chiang, *Adv. Mater.*, 2010, **22**, 139–144.
- L. Q. Zhang, X. Q. Wang, T. Muta, D. C. Li, H. Noguchi, M. Yoshio, R. Z. Ma, K. Takada and T. Sasaki, *J. Power Sources*, 2006, **162**, 629–635.
- R. Guo, P. F. Shi, X. Q. Cheng and C. Y. Du, *J. Alloys Compd.*, 2009, **473**, 53–59.

- 36 J. Liu, W. Qiu, L. Y. Yu, G. H. Zhang, H. L. Zhao and T. Li, *J. Power Sources*, 2007, **174**, 701–704.
- 37 P. Yue, Z. X. Wang, W. J. Peng, L. J. Li, W. Chen, H. J. Guo and X. H. Li, *Powder Technol.*, 2011, **214**, 279–282.
- 38 K. M. Shaju, G. V. Subba Rao and B. V. R. Chowdari, *Electrochim. Acta*, 2003, **48**, 1505–1514.
- 39 R. Dominko, M. Bele, M. Gaberscek, M. Remskar, D. Hanzel, S. Pejovnik and J. Jamnik, *J. Electrochem. Soc.*, 2005, **152**, A607–A610.
- 40 D. Wang, H. Li, S. Shi, X. Huang and L. Chen, *Electrochim. Acta*, 2005, **50**, 2955–2958.
- 41 S. Chung, J. Bloking and Y. Chiang, *Nat. Mater.*, 2002, **1**, 123–128.
- 42 <http://www.alibab.com>, http://www.alibaba.com/chemicals_p8, Accessed September 17, 2012.
- 43 J. Dewulf, G. V. Vorst, K. Denturck, H. V. Langenhove, W. Ghyoot, J. Tytgat and K. Vandeputte, *Resour., Conserv. Recycl.*, 2010, **54**, 229–234.