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## RECOVERY OF $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ FROM SPENT LITHIUM-ION BATTERY USING A SPECIALLY DESIGNED DEVICE

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### Abstract

Recycling of battery components for natural resources sustainability and consumer products has become an important endeavor that demands continuity through effective processes. In compliance with the need for waste management,  $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$  in the positive electrode of spent lithium-ion batteries has been recovered using specially designed device, consisting of two compartments separated with a plastic sieve of pore size 0.2mm. The upper compartment equipped with a mechanical stirrer contained the electrode pieces, while the lower compartment contained the powders recovered from the electrode pieces during the separation process. Both compartments were filled with a solvent such as N-N dimethyl formamide (DMF), N-dimethyl acetamide (DMAC) or dimethyl sulfoxide (DMSO) used to extract the binder in the electrode materials. The whole device was put in a hot bath maintained at a constant temperature. During the separation, the binder, polyvinylidene fluoride (PVDF) in the electrode dissolved in the solvent, which made the solid powders to fall off from the aluminium foils and then passed directly through the sieve pores into the lower compartment. This easy passage of the particles through the sieve pores without being adsorbed onto the foils made the separation much more efficient using the device. The XRD, SEM and the electrochemical performances results showed that the secondary use of the powder recovered in a new lithium-ion battery will be successful.

*Key words:* battery, extraction, recycle, separation, sieving

*Received:* July, 2013; *Revised final:* June, 2014; *Accepted:* July, 2014; *Published in final edited form:* May, 2018

### 1. Introduction

Lithium-ion batteries (LiBs) are of high energy density, low auto-discharge rate and excellent cycle life with no memory effect. Consequently, the use of LiBs has rapidly increased and substituting other batteries as power source in portable consumer electronic devices and electric vehicles (EVs). Although spent LiBs are not grouped as environmentally hazardous wastes, presence of flammable solvent mixture (dimethyl carbonate and ethylene carbonate), toxic polyvinylidene fluoride (PVDF) used as its binder and NMP often used as a solvent for the electrode active materials fabrication

may cause serious environmental problem. Besides, the LiBs used in portable electronic products are potential sources of hazardous metals adversely impacting environmental quality and human health. For environmental protection and resource development, recycling of LiBs is highly needed because daily use of mobile phones and other electronic appliances worldwide increases very rapidly with corresponding deposition of a startling quantity of waste batteries into the environment (Castillo et al., 2002; Dorella and Mansur, 2007; Jian et al., 2012; Kang et al., 2013; Kondás et al., 2006; Kurian, 2007; Notter et al., 2010; Zhou et al., 2010). Gaines et al. (2011) has recently shown that recycling

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of Li-ion battery will potentially enhance higher reduction in the material production energy, especially if the as-recovered active material is suitable for secondary use.

There have been methods to recover valuable metals and compounds in the spent LiBs. Usually, the first two steps are the same regardless of the methods. The batteries are fully discharged before dismantled to remove the case. According to the procedures after the first two steps, the methods can be divided into four groups. The first one involves treatment of the inner rolls of spent batteries with an organic solvent to dissolve the binder, polyvinylidene fluoride (PVDF) for the active materials to be easily separated from the copper or aluminium foils. For instance, Contestabile et al. reported that when N-methylpyrrolidone (NMP) was used as the solvent, the active materials were separated from the foils in 1 hour at 100 °C. The active materials which contained lithium cobalt oxide and carbon were treated with HCl to extract cobalt. The solution obtained was then treated with NaOH to produce cobalt hydroxide, which could be used to produce LiCoO<sub>2</sub> (Contestabile et al., 2001). The NMP toxicity (Robert, 2000) and gaseous chlorine produced during HCl treatment are the likely problems in this process. However, reports considered NMP with solubility of about 200 g kg<sup>-1</sup> the best solvent for PVDF (Contestabile et al., 2001; Li et al., 2007). This could possibly be the reason for using NMP in LiB industry. Li et al. (2010) also used NMP as a solvent for active materials recovery. The dried powders obtained were treated thermally to eliminate carbon and PVDF in the cathode active materials. It was further leached with citric acid and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) followed by determination of the content of the cobalt and lithium in the cathode. The cathode active material, LiCoO<sub>2</sub> containing Co<sub>3</sub>O<sub>4</sub> was finally obtained after sintering the sample recovered. Besides, process involving ultrasonic treatment with NMP, acid leaching, Fe-removing, precipitation of cobalt, nickel, manganese and lithium was also used successfully to recover mixture of LiCoO<sub>2</sub>, LiNi<sub>0.4</sub>Co<sub>0.2</sub>Mn<sub>0.4</sub>O<sub>2</sub>, LiFePO<sub>4</sub> and LiMn<sub>2</sub>O<sub>4</sub>. LiMn<sub>1/3</sub>Ni<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> was obtained as the product (Li et al., 2007). In a similar procedure, DMAC was used to recover LiCoO<sub>2</sub> (Liu et al., 2006).

The second group involves direct crushing and grinding of spent LiBs followed by magnetic separation and sieving to remove iron, aluminium, copper and plastic materials from the mixture. The fine powders obtained were leached with a mixture of an acid (H<sub>2</sub>SO<sub>4</sub>) and a reducing agent, H<sub>2</sub>O<sub>2</sub> to obtain solution of lithium and cobalt.

Meanwhile, the electrolyte lithium hexafluorophosphate (LiPF<sub>6</sub>) decomposed into lithium fluoride and phosphorus pentafluoride during crushing (Shin et al., 2005). Also, after subjecting the spent LiBs to physical treatment, the cobalt-containing powders were leached with H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>. Oxalic acid was added to the filtrate to produce crystalline CoC<sub>2</sub>O<sub>4</sub>.2H<sub>2</sub>O, which was then heated to produce Co<sub>3</sub>O<sub>4</sub> (Kang et al., 2010).

The third group involves the treatment of the batteries inner rolls with NaOH to dissolve the aluminium foil in order to separate the cathode material powders from other components. The cathode materials were burnt to remove organic adhesive (PVDF). The powder obtained was dissolved to obtain a solution of sulphates. Large quantity of cobalt in the solution was deposited as oxalate, while Acorga M5640 and Cyanex272 (di-(2,4,4 trimethyl pentyl) phosphoric acid) were used to selectively extract small quantities of Cu<sup>2+</sup>, Co<sup>2+</sup> (Nan et al., 2005) and Ni<sup>2+</sup> ions (Nan et al., 2006) in the solution.

The fourth group is bioleaching or biometallurgical process. Compared with the aforementioned pyrometallurgical and hydrometallurgical processes, bioprocesses have been reported to be of higher efficiency, low cost and environmentally compatible (Bernardes et al., 2004; Xin et al., 2009). For instance, both Xin et al. (2009) and Mishra et al. (2008) used a bioleaching process to recover Co and Li, while Freitas and Garcia (2007) used electrochemical techniques to recover Co. Lupi et al. (2005) combined electrochemical process with solvent extraction method to recover Co and Ni.

All the four groups of processes could successfully recover valuable metallic cobalt or their compounds. However, not all the processes are cost effective and environmentally compatible, especially when considering the use of many chemical reactions involving many chemicals which resulted in invaluable by-products. Consequently, we have carried out researches to eliminate by-products as well as overuse of chemicals. The principle employed was to use physical methods as much as possible to separate the batteries into their components followed by only chemical treatment of the active materials to obtain reactivated materials suitable for secondary use in new batteries (Lei et al., 2009; Lei, 2009). This research highly established the need for effective separation equipment to minimize serious environmental problem caused by hazardous metals in LiBs and therefore designed a simple but industrializable device for the recovery of the active materials from spent or low quality lithium-ion batteries.

## 2. Experimental

### 2.1. Pretreatment of the spent LiBs

Cylindrical spent LiBs with an average weight of 42.02 g used in this study were provided by a company in China, which used LiMn<sub>1/3</sub>Ni<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> as the positive electrode. The components of LiBs shown in Table 1 were obtained by calculating the average weights of different components of the LiBs supplied. The total weight of each battery was first estimated before dismantling it. After dismantling the battery, each component was weighed. This was done for many LiBs supplied before estimating the average weight of the battery used. However, weight of the electrolyte was estimated from the value obtained

since it has been washed into ethanol before weighing other components after air drying. The batteries were separated in the laboratory according to Fig. 1 as follows: (1) The potential difference of the batteries was checked to ascertain the need to discharge the spent LiBs to avoid self-ignition during dismantling and separation of the components; (2) The batteries were manually dismantled to remove the case and other components of the batteries; (3) The electrode rolls obtained were immediately manually uncurled, cut into pieces in a dry atmosphere, soaked in dry  $\text{C}_2\text{H}_5\text{OH}$  to extract the electrolyte. The electrolyte salt,  $\text{LiPF}_6$  was then converted to  $\text{Li}_2\text{SiF}_6$  according to report (Bankole and Lei, 2013) to reduce environmental pollution. The ethanol distillate obtained during the reaction was labelled solvent I; (4) The pieces were picked out and air dried; (5) The cathode electrode pieces were cut further into smaller pieces before putting them into the device (Fig. 2) and washed with organic solvent to separate the active material,  $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$  from the aluminium foils. Solvent II is the distillate of the organic solvent used (Fig. 1).

## 2.2. Description of the device

The device designed consists of two compartments separated with a plastic sieve of pore size 0.2 mm (Fig. 2). The upper compartment equipped with a mechanical stirrer contained the

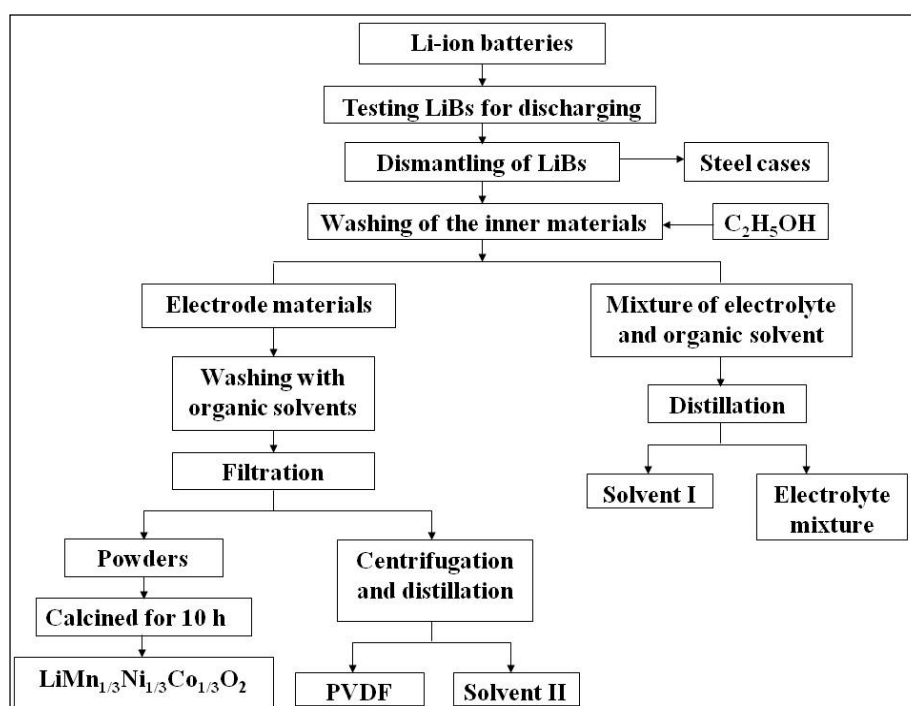
positive electrode pieces and a solvent. The lower compartment also contained the solvent used for the separation and the powders separated from the aluminium foils. The sieve separated the aluminium foils in the upper compartment from the powders in the lower compartment. The whole device was put in a hot bath maintained at a constant temperature.

## 2.3. Separation of the active materials from the aluminium foils

Ten grams of the positive electrode pieces was put into the device (Fig. 2) and separated with 250  $\text{cm}^3$  of N-Dimethyl acetamide (Lingpeng  $\geq 98.0\%$ ) with temperature maintained between 60  $^\circ\text{C}$  and 84  $^\circ\text{C}$ , and agitated at a constant speed of 300 rpm. During the process, the electrode powders separated from the aluminium foils passed directly through the sieve pores into the lower compartment, leaving the aluminium foils in the upper compartment. The separation was stopped when clean aluminium foils were obtained and then the time taken to complete the separation at 60, 70, 80 and 84  $^\circ\text{C}$  recorded. The powder obtained at different temperatures was immediately separated from the solvent by filtration at reduced pressure, dried at 60  $^\circ\text{C}$  for 24 h and then weighed. Similarly, N-N dimethyl formamide (Sinopharm  $\geq 99.5\%$ ) and dimethyl sulfoxide (Lingpeng  $\geq 99.0\%$ ) were used as solvents for the separation.

**Table 1.** Components of lithium-ion battery

Battery components	Anode electrode	Cathode electrode	Case	Electrolyte	Plastics	Rubber	Separator
Weight (g)	13.00	13.90	9.10	2.85	0.15	0.17	2.85



**Fig. 1.** Flowchart of the experimental procedures for the recycling of lithium-ion battery to recover valuable components

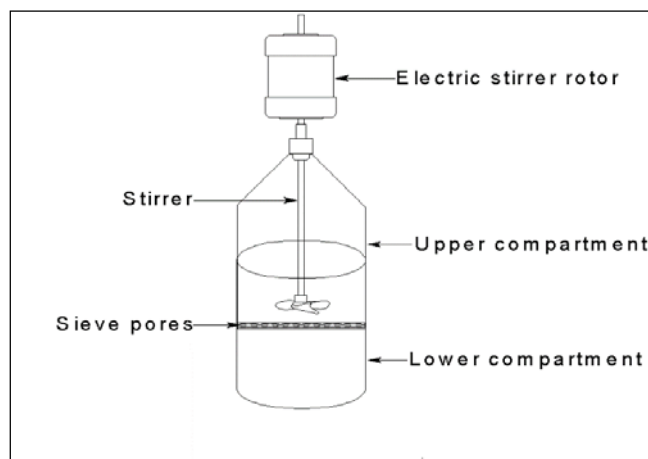


Fig. 2. Device for the recovery of the cathode active materials

To determine the rate of recovery in all the solvents selected, the above procedure was repeated with 10 g of the positive electrode pieces at 84 °C considered to be the best temperature for the recovery within the shortest possible time. Meanwhile, the electrode pieces were removed from the device every 5 mins, dried, weighed to a constant mass and then returned into the device for the next separation.

These steps were repeated until a constant mass of the aluminium foils was obtained. After the separation, the powder obtained was filtered, dried at 60 °C for 24 h and then weighed. The rate of mass loss during the recovery was calculated (Eq. 1):

$$\text{Rate} = (m_{n-1} - m_n) / t \quad (1)$$

where  $m_n$  and  $t$  represent the  $n^{\text{th}}$  mass of the electrode pieces in grams and time interval in minutes respectively.

#### 2.4. Powder and solvents characterization

The dried powders obtained were treated thermally to eliminate carbon in the cathode active materials. The as-recovered powder obtained after thermal treatment was characterized with powder X-ray diffraction using a Rigaku D/max 2000/PC X-ray diffractometer with a graphite monochromator and Cu  $K\alpha_1$  radiation operated at 5–90° and 0.02 °/s.

The web-like PVDF obtained, stock and distillates of the solvents used for the extraction called solvent II in Fig. 1 were characterized by potassium bromide (KBr) method using NICOLET 5700 FT-IR.

#### 2.5. Electrochemical performance of the as-recovered material

To ascertain the suitability of the active materials recovered for secondary use in battery formulation, the electrochemical characterization of the powder was performed using a CR2032 coin cell.

The cathode fabrication was prepared from the mixture of as-recovered  $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ , acetylene black and PVDF with one drop of DMSO. The homogeneous slurry obtained was pasted onto an aluminium coin current collector, dried in a vacuum at 100 °C for 24 h and then pressed at 10 MPa before assembling the cell in a dry argon-filled glove box for cell testing. The test cell consisted the cathode prepared, lithium metal anode, Cellgard 2300 film as the separator and the solution of electrolytes (1M  $\text{LiPF}_6$  dissolved in ratio 1:1 (v/v) mixture of dimethyl carbonate and ethylene carbonate). Capacity measurements and cycling tests of the coin-type cells were performed in LAND2001CT battery cyler over a voltage range 2–4.5 V at current density 0.2 mA and 0.1 C rate at room temperature.

### 3. Results and discussion

#### 3.1. Recovery efficiencies of solvents

Table 2 shows the time taken to separate cathode active materials from Al foils in all the organic solvents used at 60, 70, 80 and 84 °C. As shown, the best solvent is DMAC, while DMSO is the worst solvent. It is evident that higher temperature is better for the separation within the shortest possible time.

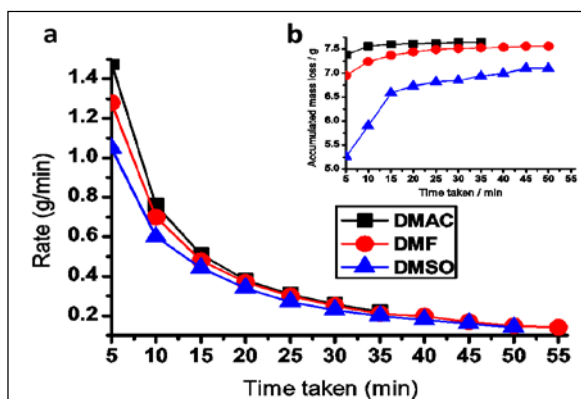
Table 2. Time-taken at varying temperatures for cathode active material separations

Temperature (°C)	Time-taken (min)		
	DMAC	DMF	DMSO
60	16	31	85
70	16	30	60
80	13	17	30
84	10	15	25

A clean Al foil can be obtained at 60 °C in 31 min. using DMF. Compared with the report of Zhou et al. (2010), which shows that it took 2h at 60°C for complete separation in DMF, this separation is more efficient. The efficiency of this recovery could be attributed to the effective separation of the particles from the foils by sieving in the device used in Fig. 2.

Fig. 3 shows the results of the recovery carried out using the device designed under different conditions. Fig. 3a shows the average mass loss rate of recovery versus time at 84°C calculated by Eq. (1). In the first 5 min, the average rates in DMAC, DMF and DMSO are 1.48, 1.28 and 1.05  $\text{g min}^{-1}$  respectively. Fig. 3b shows the accumulated mass loss from the electrode pieces. It can be seen that 7.38, 6.39 and 5.26 g are extracted from the electrode pieces in the first 5 mins at 84 °C in DMAC, DMF and DMSO respectively. If compared with the data in Table 2, it is evident that it takes more time to complete the separation in Fig. 3a. This could be attributed to the intermittent removal and drying of the electrode pieces every 5 mins to determine the mass loss. The drying certainly affects both the separation and time.

According to Fig. 3b, about 97%, 84% and 67% of the active material and other cathode electrode components (carbon and PVDF) are removed from the electrode pieces in the first 5 mins using DMAC, DMF and DMSO respectively. The general efficiency of the extraction with respect to solvents used follows the order  $\text{DMAC} > \text{DMF} > \text{DMSO}$ . This order is consistent with initial report for DMF and DMSO (Li et al., 2007).



**Fig. 3.** The curves of average rate of the extraction (a) and accumulated mass loss (b) versus time at 84 °C

### 3.2. Solvents and PVDF characterization

Fig. 4 shows the IR spectra of the organic solvents, DMF, DMAC and DMSO labelled “a”, “b” and “c” respectively, used for the separation as well as the PVDF labelled “d” obtained from the separation. The IR spectra were normalized to avoid problems caused by sampling method. As shown, the stock solution and distillate of DMF show characteristic absorption bands attributed to carbonyl bond (Kim and Park, 2002) at  $1659 \text{ cm}^{-1}$  and amide C-N bond at  $1389$

$\text{cm}^{-1}$ . As reported by Faghihi and Yazdi (2006), the stock solution and distillate of DMAC show absorption band attributed to C-O stretching of esters around  $1200\text{--}1000 \text{ cm}^{-1}$ , while both the stock solution and distillate of DMSO show characteristic absorption bands attributed to C-S and S-O bonds around  $701 \text{ cm}^{-1}$  and  $1030 \text{ cm}^{-1}$  respectively.

The IR spectra of PVDF extracted into DMF and DMSO, and the standard are comparatively the same. There are characteristic absorption bands attributed to H-O-H bending around  $1624 \text{ cm}^{-1}$  (Yu et al., 2009) and C-F stretching absorption peak at  $1182 \text{ cm}^{-1}$  (Kharitonov et al., 2005). This clearly shows that the solvents can effectively extract the PVDF in the electrode materials. The dissolution of PVDF in organic solvents will also reduce environmental pollution caused by burning the rolls of batteries (Nan et al., 2006). Considering the volume of the solvents before and after the separation, nearly 100 % of all the solvents can be recovered, indicating the stability of the solvents to materials during separation.

Fig. 5 shows the picture of the clean current collectors (aluminium foils) obtained after the separation. Comparatively, the best result is DMAC with the order of cleanness and brightness of the foils following  $\text{DMAC} > \text{DMF} > \text{DMSO}$ .

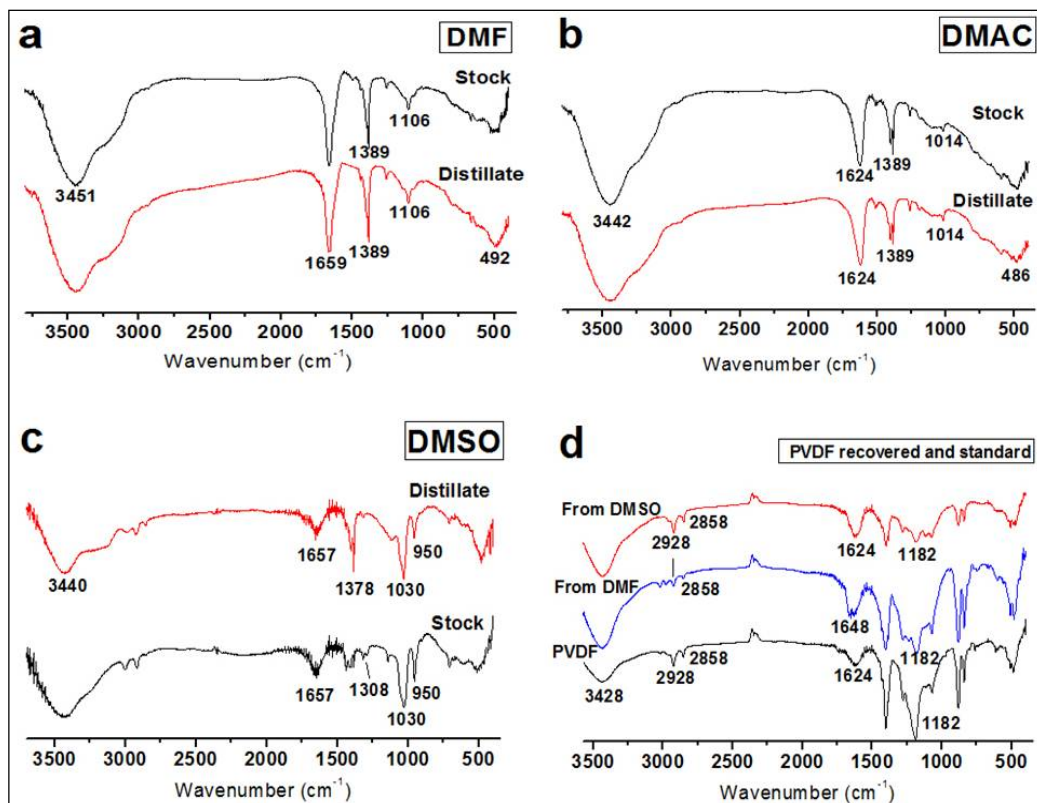
### 3.3. Characterization of the as-recovered materials

Fig. 6 shows the XRD patterns of the as-recovered powder obtained during the separation after sintered at 650°C and 900°C for 10 h. They have the same patterns with similar compound obtained by Belharouak et al. (2003). The similarity in the patterns recorded for the powders reveals that using different solvents have no significant effect on the crystalline structure of the powders. These are also similar to other patterns but have no impurities mentioned in the reports (Li et al., 2009; Li et al., 2010; Liu et al., 2006; Xin et al., 2009).

The lattice parameters shown in Table 3 were indexed on cells of  $\alpha\text{-NaFeO}_2$  type hexagonal structure with a space group of R-3M according to Oh et al. (2004) from the XRD patterns (Fig. 6). Though the order of the particle sizes follows  $\text{DMF} < \text{DMSO} < \text{DMAC}$  for the as-recovered  $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$  sintered at 650 °C, it is evident that there is neither significant difference in all the patterns nor impurity phases found in all the samples obtained from all the three solvents used. The c/a ratios of all the powders are around  $4.968 \pm 0.003$ , which comply with the value considered for the material having layered structures (Wu et al., 2010). The particle sizes were calculated by Scherrer equation according to the peak at about  $19^\circ$ .

### 3.4. Structure and morphology analysis

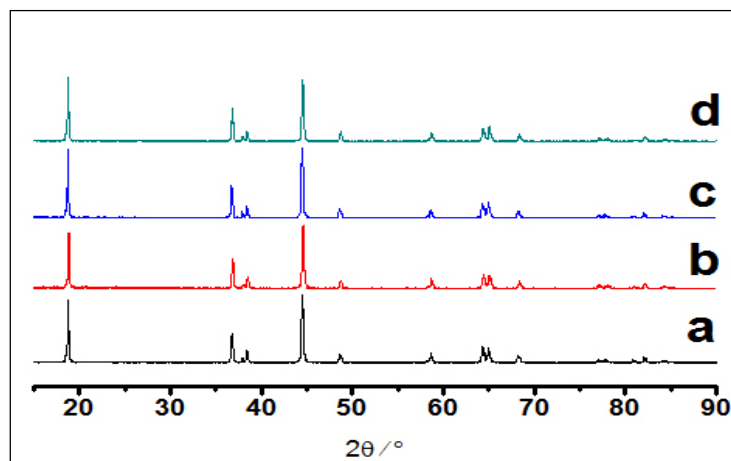
Fig. 7 shows the morphologies and particle sizes of the as-recovered  $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$  powders sintered at 650 °C and 900°C.



**Fig. 4.** The IR spectra of stock and distillate of (a) DMF, (b) DMAC, (c) DMSO, (d) PVDF



**Fig. 5.** The aluminum foils after extractions with DMF (F series), DMAC (C series) and DMSO (S series) at 60 °C, 80 °C and 84 °C (indicated as 1, 2 and 3 respectively)



**Fig. 6.** X-ray diffraction patterns of as-recovered  $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$  in (a) DMF (b) DMAC (c) DMSO sintered at 650 °C, and in (d) DMSO calcined at 900 °C for 10 h

**Table 3.** The lattice parameters of the powders obtained

Samples	<i>a</i> (Å)	<i>c</i> (Å)	<i>c/a</i>	Particle sizes (nm)
a	2.864	14.23	4.969	42.97
b	2.863	14.23	4.970	45.98
c	2.867	14.23	4.963	43.63
d	2.863	14.23	4.970	41.10

The larger aggregate particles are composed of smaller particle size ranges from 100 to 200 nm. The images show that the powders consist of well-crystallized particles. Sample 'b' has smaller particles size on the larger aggregate particles which are not observed in sample 'a'. This observation could account for the smaller particle size of 41.10 nm for sample 'd' sintered at 900°C compared with sample 'c' calcined at 650°C in Table 3. The difference in particle size observed in the samples does not comply with the effect of temperature on the particle size, which increases with the annealing temperature (Iqbal et al., 2008; Sclar et al., 2009).

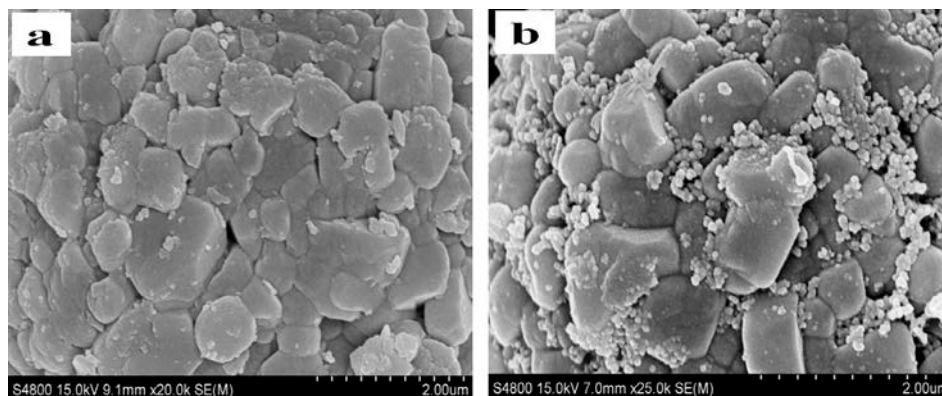
### 3.5. Electrochemical performance of the As-recovered material

Fig. 8 shows typical curves of electrochemical performance of sintered  $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$  recovered in this research. The sample sintered at

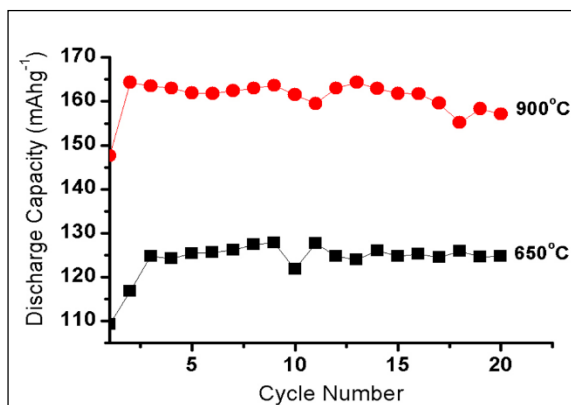
650°C delivers a much lower discharge capacity of 125  $\text{mAhg}^{-1}$  in the third cycle at a discharge rate of 0.1 C, while the sample sintered at 900°C delivers a better discharge capacity of about 160  $\text{mAhg}^{-1}$  at the same discharge rate. The higher values delivered by as-recovered sample sintered at 900°C can be attributed to its smaller particle size than sample sintered at 650 °C (Table 3, Fig. 7b). Report has shown that small particle size enhances a shorter lithium diffusion length with a resultant higher electrochemical performance (Zou et al., 2013). Though these values are lower than the 188  $\text{mAhg}^{-1}$  delivered by the same material (Ding et al., 2009), the reactivated powder reported delivered a higher discharge capacity of about 231  $\text{mAhg}^{-1}$  (Bankole et al., 2014). This shows that the  $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$  recovered will be suitable for secondary use in a new battery.

### 3.6. Measures used to eliminate exhaustion and toxicity

In this study, certain practical measures were taken to avoid excessive use of chemicals and reduce energy consumption. For instance, the solvents were used for at least three batches of separations until the concentration of PVDF was too high and then distilled to remove PVDF.



**Fig. 7.** SEM images of as-recovered  $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$  sintered at (a) 650 °C and (b) 900 °C for 10 h



**Fig. 8.** The plot of discharge capacity versus cycle number of  $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$  calcined at 650 °C and 900 °C for 10 h

The electrolyte mixture extracted into the ethanol reduced the possibility of polluting the environment with toxic organic solvents. Besides, the ethanol used instead of direct contact with water will also reduce the production and release of dangerous gases such as pentafluorophosphate and hydrogen fluoride from  $\text{LiPF}_6$  (Nan et al., 2006). Instead of producing dangerous gasses from the decomposition of the  $\text{LiPF}_6$ , it was rather converted to  $\text{Li}_2\text{SiF}_6$  during distillation process in glassware in a fume cupboard and then reported (Bankole and Lei, 2013). All the solvents were also re-used to reduce consumption costs.

#### 4. Conclusions

Effective separation of the valuable active cathode material,  $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$  from the aluminium foils and PVDF using specially designed device has been proposed for possible application to industrial scale-up. This can be used for all types of cathode active materials of spent or low quality lithium-ion batteries. The study shows that instead of burning to release HF into the environment, suitable organic solvent can be used to extract the PVDF in the electrode pieces. After dissolution of the PVDF, the easy passage of particles through the sieve pores without being adsorbed onto the foils makes the separation much more efficient within the shortest possible time.

The SEM images, XRD patterns and the electrochemical performance evaluations of the cathode active material,  $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$  recovered after thermal treatment to remove carbon evidently show that the cathode active material obtained is suitable for secondary use in new battery, while the aluminium foils can be used for other applications.

#### Acknowledgments

We appreciate the Highstar Batteries Group Company, Jiangsu China, for supplying the lithium-ion batteries used for the study. The supports received from Dr. Hu Meng, Xiao Dan and the School of Chemistry and Chemical Engineering, Southeast University, China is gratefully acknowledged.

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