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Environmentally friendly recycling and effective repairing of cathode powders from spent $LiFePO_4$ batteries

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Extensive use of $LiFePO_4$ batteries will bring a lot of spent $LiFePO_4$ batteries, which can not be recycled properly in traditional processes at present. If these spent $LiFePO_4$ batteries are thrown away without recycling properly, it is not only a severe waste of valuable resources, but also leads to serious environmental pollution. In this paper, a completely green recycling process and a small scale model line are developed to recycle cathode powders from spent $LiFePO_4$ batteries for the first time. Part of $LiFePO_4$ host particles in spent $LiFePO_4$ batteries decompose to $FePO_4$, Fe_2O_3, P_2O_5 and Li_3PO_4 after numerous charge-discharge cycles, resulting in poor electrochemical performance of freshly recycled cathode powders for Li-ion batteries. To repair decomposed $LiFePO_4$ host particles, recycled cathode powders are heat-treated at different temperatures. After heat-treatment at high temperatures, especially at 650 °C, cathode powders are effectively repaired and can be reused for Li-ion batteries.

1.Introduction

With the increasing use of electric vehicles (EV) all over the world, the consumption of $LiFePO_4$ batteries also increases sharply. Therefore, there will be a large number of spent $LiFePO_4$ batteries need to be disposed in the near future. In order to make full use of these spent $LiFePO_4$ batteries, echelon use as Li-ion storage batteries is the preferred option. However, for those damaged or used in echelon $LiFePO_4$ batteries, recycling valuable materials after dismantling is the only option. If these spent $LiFePO_4$ batteries are thrown away without recycling properly, it is not only a severe waste of valuable resources, but also leads to serious environmental pollution.

At present, some recycling processes have been developed to recycle valuable materials from spent Li-ion batteries. For example, spent LCO type batteries are recycled with a typical process as follows, (a) dismantling batteries and separating cathode plates from others, (b) calcining and sieving cathode plates to separate cathode powders from Al foil, (c) leaching cathode powders with inorganic acid to form solution containing Co^{2+}, Li^{+}, (c) recycling lithium and cobalt elements in the form of Li_2CO_3, $CoSO_4$, CoC_2O_4, $Co(OH)_2$, Co with extraction method, chemical precipitation method or electrolysis method[1-13].

These recycling processes are widely used, but there are still some defects, (a) generating a large amount of electrolyte exhaust gas, which may cause atmospheric pollution, (b) using a large amount of inorganic acid and organic extraction agent, which also may cause wastewater pollution, (c) having complicated steps, high equipment requirement, low added-value and high cost. Consequently, these processes are only applicable to spent Li-ion batteries containing cobalt or nickel elements (such as LCO type, LNO type, NCM type and NCA type, etc.), and not applicable to spent $LiFePO_4$ batteries. Therefore, considering the resource utilization and environment protection, developing a new and green recycling process of spent $LiFePO_4$ batteries is necessary.

In this paper, a new recycling process and a small scale model line are developed to recycle cathode powders from spent $LiFePO_4$ batteries for the first time. In this recycling process and small scale model line, no toxic reagent is used, no toxic exhaust gas or wastewater is leaked into environment, operators do not exposure to toxic exhaust gas and wastewater, so it can be considered

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as a completely green recycling process for both environment and operators. Recycled cathode powders in this recycling process are further repaired by heat-treatment at different temperatures and reused for Li-ion batteries. Effects of heat-treatment temperature on strcture, tap densities and electrochemical performances of recycled cathode powders are investigated in detail.

2.Experimental

2.1 Recycling and heat-treatment of cathode powders

A green recycling process (Fig. 1) and a small scale model line with the recycling capacity of 100 Kg per day (Fig. 2) are developed to recycle spent $LiFePO_4$ batteries. In this experiment, a 20 Ah soft package spent $LiFePO_4$ battery after used in EV (provided by Wanxiang A123 systems Asia Co., Ltd.) (Fig. 3) was recycled as this process in the small scale model line. After discharged to 2.0 V at first, spent battery was dismantled and soaked in dilute alkaline solution (pH=10-11), then plate lugs and aluminium-plastic films could be directly recycled. Cathode plates, separator and anode plates were separated using special equipment, respectively.

To obtain coarse cathode powders, cathode plates needed to be further treated in the seal box as the process shown in Fig. 2. After ball-milled, sieved and heat-treated coarse cathode powders for 1 h under Ar/H_2 flow, repaired cathode powders were finally obtained.

Cathode powders heat-treated at 150 °C, 200 °C, 250 °C, 300 °C, 350 °C, 600 °C, 650 °C, 700 °C, 750 °C and 800 °C for 1 h were designated as "S-150, S-200, S-250, S-300, S-350, S-600, S-650, S-700, S-750 and S-800 cathode powders", respectively. For comparison, unused cathode powders were prepared by mixing unused $LiFePO_4$/C and acetylene black with the same ratio as recycled cathode powders.

2.2 Compositional and structural characterization of recycled cathode powders

Surface configuration and crystal structure of recycled cathode powders were characterized by scanning electron microscope (SEM, JMS-6700F, JEOL) and X-ray diffraction (XRD, Rigaku D/MAX-2500). Particle size distribution and tap density were measured with particle size analyzer (OMEC, LS-POP (6)) and ZS tap density meter (ZS-201).

2.3 Electrochemical tests of recycled cathode powders

The content of $LiFePO_4$/C and acetylene black in recycled cathode powders was calculated based on the parameters provided by battery manufacturer. According to the content of $LiFePO_4$/C and acetylene black, 2.89 g recycled cathode powders were mixed with 0.26 g acetylene black and 0.35 g PVDF in NMP to ensure the proportions of three components were 8:1:1 in weight. Electrochemical tests were conducted using a 2032 type coin cell with lithium foil as anode and 1 M $LiPF_6$ in ethylene carbonate diethyl carbonate (1:1 in volume) as electrolyte. The cells were charged and discharged between 2.5-4.2 V (versus Li^+/Li) by applying a current density of 0.2 C (1 C=150 mA g^{-1}) at 25 °C. It should be noted that the calculation of specific capacity is based on the mass of $LiFePO_4$/C in recycled cathode powders.

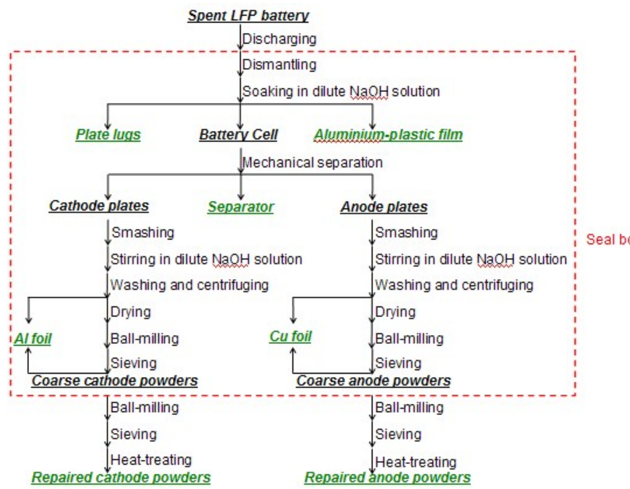

Fig. 1 Recycling process flow diagram of soft package spent $LiFePO_4$ battery.

Fig. 2 Small scale model line developed by ourselves.

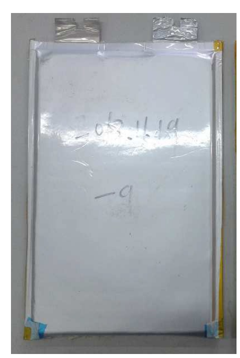

Fig. 3 20 Ah soft package spent $LiFePO_4$ battery after used in EV.

3.Results and discussion

3.1 Green recycling of cathode powders

Fig. 1 shows the recycling process flow diagram of soft package spent $LiFePO_4$ battery. Most of the recycling process is conducted inside a sealed box, ensuring electrolyte exhaust gas can not be leaked into environment before three-level spray purification with DMF+KOH solution, KOH solution and water. After soaking in dilute alkaline solution, most electrolyte in dismantled battery will be hydrolyzed gradually as the reactions (1) (2) (3) (4).

$$LiPF_6 + 7NaOH \rightarrow 5NaF + LiF + Na_2HPO_4 + 3H_2O \quad (1)$$
$$C_3H_4O_3\,(EC) + H_2O \rightarrow CO_2 + C_2H_6O_2 \quad (2)$$
$$C_3H_6O_3\,(DMC) + H_2O \rightarrow CO_2 + 2CH_4O \quad (3)$$
$$C_4H_8O_3\,(EMC) + H_2O \rightarrow CO_2 + CH_4O + C_2H_6O \quad (4)$$

Waste NaOH solution generated during soaking and stirring processes can be reused after adding a certain mount of concentrated NaOH solution. After repeated use, waste NaOH solution containing NaF, LiF, Na_2HPO_4, CH_4O, C_2H_6O and $C_2H_6O_2$ is sold to recycling company. Compared with the reported recycling processes[14-19], no electrolyte exhaust gas or wastewater is leaked into environment in this recycling process, most of this recycling process is conducted inside the sealed box through the gloves and operators do not exposure to electrolyte exhaust gas and waste NaOH solution, so it can be considered as a completely green recycling process for both environment and operators.

Total mass of spent $LiFePO_4$ battery is 569 g. After recycling, 176 g cathode powders ($LiFePO_4$/C + acetylene black) and 84 g anode powders (graphite + acetylene black) are obtained with high recovery ratios of over 93% for both (Parameters of this $LiFePO_4$ battery are provided by battery manufacturer). Meanwhile, five kinds of recycling byproducts (32 g separator, 17 g aluminium-plastic film, 4 g plate lugs, 79 g Cu foil and 37 g Al foil) are also obtained with high recovery ratios of more than 95% after a rough calculation. Moreover, all the five kinds of byproducts have high purity (Fig. 4). Except electrolyte, all the rests of spent $LiFePO_4$ battery can be recycled in this recycling process.

Fig. 4 Five kinds of recycling byproducts. (a) Separator, (b) Aluminium-plastic film, (c) Plate lugs, (d) Cu foil and (e) Al foil.

3.2 Heat-treatment of cathode powders at low temperatures

Fig. 5 shows SEM images of cathode powders heat-treated at low temperatures. Compared with unused cathode powders, obvious agglomeration is observed in unheat-treated and S-150 cathode powders. As heat-treatment temperature increases, the agglomeration degree of cathode powders significantly decreases, but it is observed that agglomeration dose not completely disappear in S-350 cathode powders.

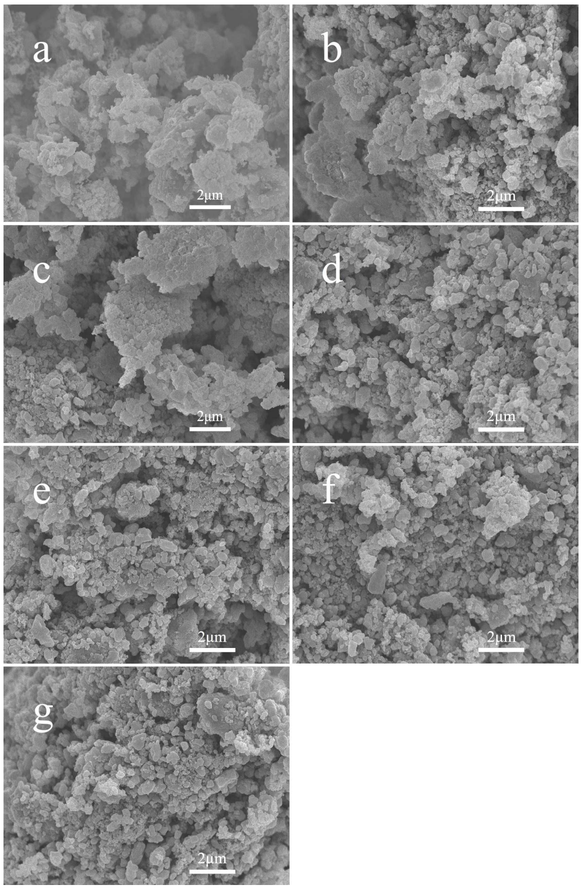

Fig. 5 SEM images of cathode powders heat-treated at low temperatures. (a) Unused, (b) Unheat-treated, (c) S-150, (d) S-200, (e) S-250, (f) S-300 and (g) S-350.

Fig. 6 shows XRD patterns of cathode powders heat-treated at low temperatures. Compared with unused cathode powders, some weak peaks of $FePO_4$, Fe_2O_3, P_2O_5 and Li_3PO_4 except for $LiFePO_4$ are observed in unheat-treated ones. However, as heat-treatment temperature increases, $FePO_4$, Fe_2O_3, P_2O_5 and Li_3PO_4 peaks become weaker gradually and then disappear.

In order to clarify the source of these substances, an unused $LiFePO_4$ battery with the same type is recycled in this recycling process. From XRD patterns, no $FePO_4$, Fe_2O_3, P_2O_5 and Li_3PO_4 peaks are found in cathode powders recycled from this unused $LiFePO_4$ battery, so it can be concluded that $FePO_4$, Fe_2O_3, P_2O_5 and Li_3PO_4 in unheat-treated ones derive from the decomposition of $LiFePO_4$ host particles after numerous charge-discharge cycles. This conclusion also explains the reason for performance degradation of $LiFePO_4$ battery after numerous charge-discharge cycles.

After heat-treatment under Ar/H_2 flow, new $LiFePO_4$ is gradually re-synthesized from $FePO_4$, Fe_2O_3, P_2O_5 and Li_3PO_4, so the intensities of $FePO_4$, Fe_2O_3, P_2O_5 and Li_3PO_4 peaks decrease as heat-treatment temperature increases.

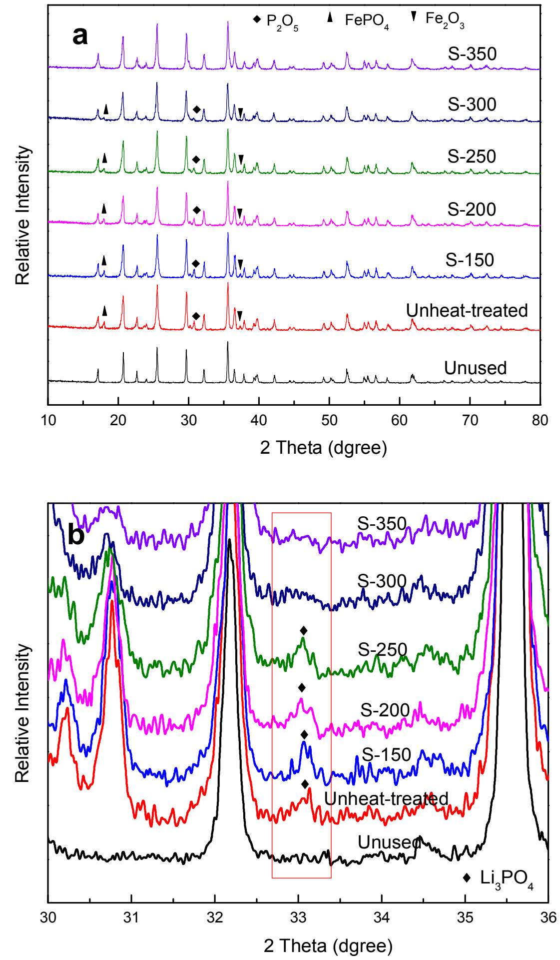

Fig. 6 XRD patterns of cathode powders heat-treated at low temperatures. (b) is a local enlargement of (a).

Generally, high tap density is corresponding to excellent processing property of electrode powders. From Table 1, tap densities of heat-treated cathode powders are lower than that of unused ones (mixtures of $LiFePO_4/C$ and acetylene black), but gradually increase as heat-treatment temperature increases from 150 °C to 350 °C. The reason for this change can be explained as follows, as heat-treatment temperature increases, PVDF binder begins to fail and decompose, leading to the decreasing agglomeration and the increasing tap densities. But PVDF binder dose not completely decompose even at 350 °C, so tap density of S-350 cathode powders is still lower than that of unused ones. This explaination can be proved by SEM images in Fig. 5. In addition, almost identical tap densities of commercial $LiFePO_4/C$ (without PVDF binder) before and after heat-treated (Table S1) can also prove the above explaination.

Table 1 Tap densities of cathode powders heat-treated at low temperatures.

Cathode powders	Tap density (g cm^{-3})
Unused	0.851
Unheat-treated	0.766
S-150	0.733
S-200	0.739
S-250	0.745
S-300	0.787
S-350	0.793

Cycle performances of cathode powders heat-treated at low temperatures are displayed in Fig. 7. Due to the partial decomposition of $LiFePO_4$ host particles, unheat-treated cathode powders display lower maximum discharge capacity (~139 mAh g^{-1}) than unused ones (~147 mAh g^{-1}) at 0.2 C. S-150 and S-200 cathode powders also display similar discharge capacities. However, as heat-treatment temperature further increases, the discharge capacities of S-250, S-300 and S-350 cathode powders gradually decrease. Among them, the initial discharge capacity of S-350 cathode powders is only 38 mAh g^{-1}, which is far below others. With the increasing charge-discharge cycles, crystallinity of re-synthesized $LiFePO_4$ gradually develops improved, so the discharge capacities increase over cycle number for all cathode powders heat-treated at low temperatures.

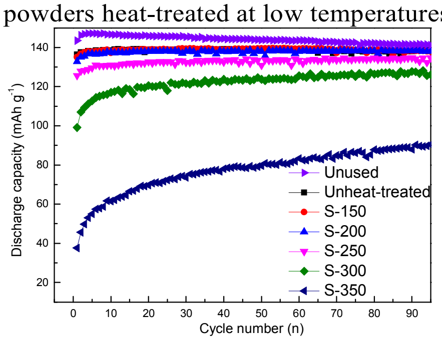

Fig. 7 Cycle performances of cathode powders heat-treated at low temperatures at 0.2 C (2.5 - 4.2 V).

Fig. 8 displays charge-discharge curves of cathode powders heat-treated at low temperatures. Charge-discharge curves of unused, unheat-treated, S-150 and S-200 cathode powders are stable at both 5th cycle and 95th cycle. By contrast, there is a significant polarization in charge-discharge curves of S-250, S-300 and S-350 cathode powders at 5th cycle. This polarization phenomenon significantly reduces but still exists at 95th cycle.

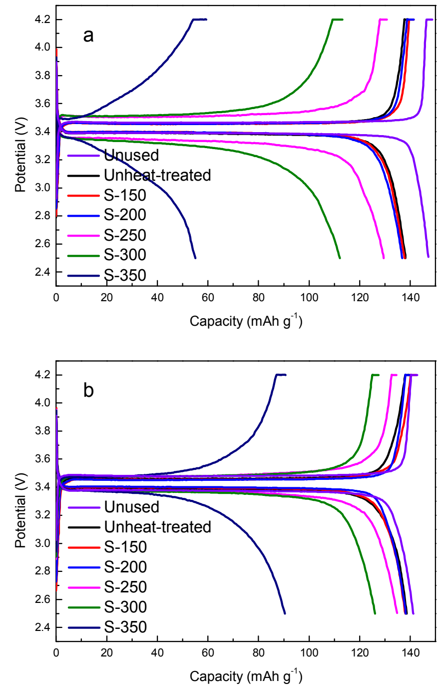

Fig. 8 Charge-discharge curves of cathode powders heat-treated at low temperatures at 0.2 C (2.5 - 4.2 V). (a) 5th cycle, (b) 95th cycle.

As shown in Fig. 9, median voltages of unused, unheat-treated, S-150 and S-200 cathode powders are stable during charge-discharge cycles. By contrast, as heat-treatment temperature further increases, median voltages S-250, S-300 and S-350 cathode powders significantly decrease, despite increase gradually along with the increasing cycles. The change of median voltages is consistent with that of charge-discharge curves displayed in Fig. 8.

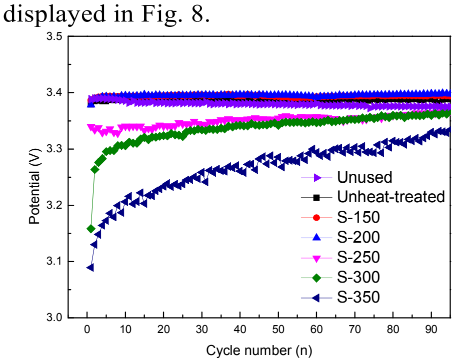

Fig. 9 Median voltages of cathode powders heat-treated at low temperatures at 0.2 C (2.5 - 4.2 V).

In summary, as heat-treatment temperature of recycled cathode powders increases from 150 °C to 350 °C, (a) new $LiFePO_4$ is gradually re-synthesized from $FePO_4$, Fe_2O_3, P_2O_5 and Li_3PO_4. (b) tap densities gradually increase, but are still lower than that of unused ones. (c) discharge capacities gradually decrease and polarization gradually increase.

After analyzing the synthesis temperature of commercial $LiFePO_4$/C[20, 21], it can be concluded that re-synthesized $LiFePO_4$ at low temperature has poor crystallinity, conductivity and electrochemical performance, which certainly leads to low discharge capacities and serious polarization of cathode powders. Higher heat-treatment temperature results in more re-synthesized $LiFePO_4$, which leads to lower discharge capacities and more serious polarization of cathode powders.

Based on the above conclusion and the synthesis temperature of commercial $LiFePO_4$/C, high heat-treatment temperatures (600 °C-800 °C) are adopted in the following experiments to re-synthesize new $LiFePO_4$ with high crystallinity, conductivity and electrochemical performance from $FePO_4$, Fe_2O_3, P_2O_5 and Li_3PO_4 in recycled cathode powders.

3.3 Heat-treatment of cathode powders at high temperatures

When heat-treatment temperature is higher than 600 °C, agglomeration of cathode powders caused by PVDF binder completely disappears (Fig. S1), $FePO_4$, Fe_2O_3, P_2O_5 and Li_3PO_4 peaks are not observed (Fig. S2). Consequentially, tap densities hardly change from 600 °C to 800 °C and are much higher than that of ones heat-treated at low temperatures (Table 2).

Table 2 Tap densities of cathode powders heat-treated at high temperatures.

Cathode powders	Tap density (g cm^{-3})
Unused	0.851
S-600	0.894
S-650	0.891
S-700	0.899
S-750	0.897
S-800	0.916

Compared with S-350 cathode powders, cathode powders heat-treated at high temperatures display improved discharge capacities and cycle performances (Fig. 10a). Discharge capacities gradually increase from 600 °C to 650 °C, but gradually decrease as heat-treatment temperature further increases. Among those cathode powders, S-650 cathode powders display the highest discharge capacities and rate performances, which are comparative with unheat-treated ones (at 0.2 C) and unused ones (at 5 C).

As shown in Fig. 10b, polarization phenomenon still exists in S-600 cathode powders, but it is significantly reduced compared with S-350 cathode powders. As heat-treatment temperature increases from 650 °C to 750 °C, polarization phenomenon disappears, and cathode powders display improved median voltages compared with the unused ones. When heat-treatment temperature increases to 800 °C, polarization phenomenon appears again, which may be caused by the decomposition of $LiFePO_4$ host particles at this temperature.

In order to comprehensively compare the electrochemical performances of cathode powders heat-treated at high temperatures, specific energy densities are calculated according to discharge capacities and median voltages. From Fig. 10c, specific energy densities of S-650 cathode powders are lower than that of unused ones at 0.2 C, but the gaps are gradually reduced as discharge current density increases. It is worth noting that specific energy densities of S-650 cathode powders are even higher than those of unused ones at 2 C and 5 C.

These results indicate re-synthesized $LiFePO_4$ from $FePO_4$, Fe_2O_3, P_2O_5 and Li_3PO_4 at 650 °C has fine crystallinity, conductivity and electrochemical performance, so S-650 cathode powders display almost the same discharge capacities and specific energy densities as unused ones at high discharge current densities and can be reused for Li-ion batteries.

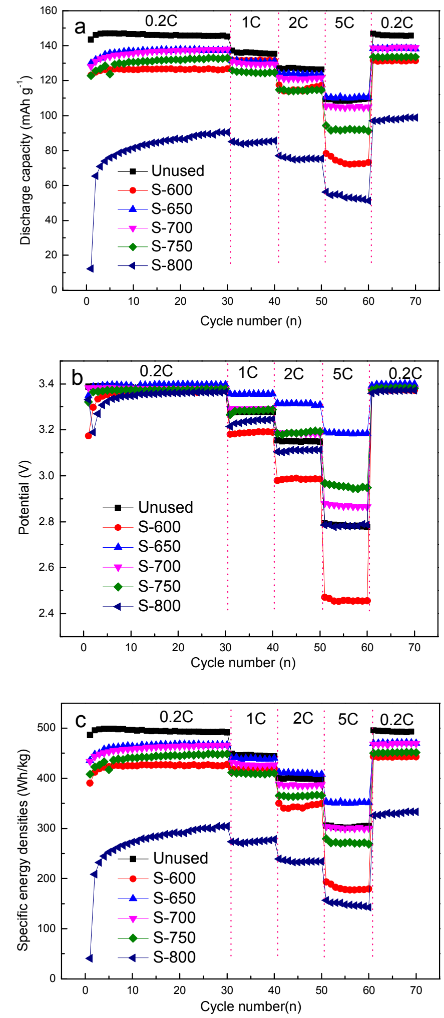

Fig. 10 Cycle performances (a), median voltages (b) and specific energy densities (c) of cathode powders heat-treated at high temperatures at 0.2 C (2.5 - 4.2 V) and 1-5 C (2.0 - 4.2 V).

4. Conclusions

A green recycling process and a small scale model line are developed to recycle cathode powders from spent $LiFePO_4$ batteries for the first time, and recycled cathode powders are modified for reuse by heat-treatment at different temperatures. Residue of PVDF binders and decomposition of $LiFePO_4$ host particles lead to low tap density and poor electrochemical performance of unheat-treated cathode powders. As heat-treatment temperature increases from 150 °C to 350 °C, tap densities gradually increase, but discharge capacities gradually decrease due to poor crystallinity and electrochemical performance of re-synthesized $LiFePO_4$ from $FePO_4$, Fe_2O_3, P_2O_5 and Li_3PO_4. As heat-treatment temperature increases from 600 °C to 800 °C, all the cathode powders display improved tap densities and discharge capacities compared with heat-treated ones at low temperature. Among them, S-650 cathode powders display almost the same discharge capacities and specific energy densities as unused ones at high discharge current densities. These results indicate that recycled cathode powders from spent $LiFePO_4$ batteries can be reused for Li-ion batteries after heat-treated at proper temperature. In addition, recycled anode powders with this process can also be reused for Li-ion batteries, and the detailed data will be reported in the follow paper.

This research provides a green, simple and high-yield strategy to recycle and reuse electrode powders from spent $LiFePO_4$ batteries, which cannot be recycled in traditional processes at present. This research is of great significance, not only for resource reuse, but also for environmental protection.

Acknowledgements

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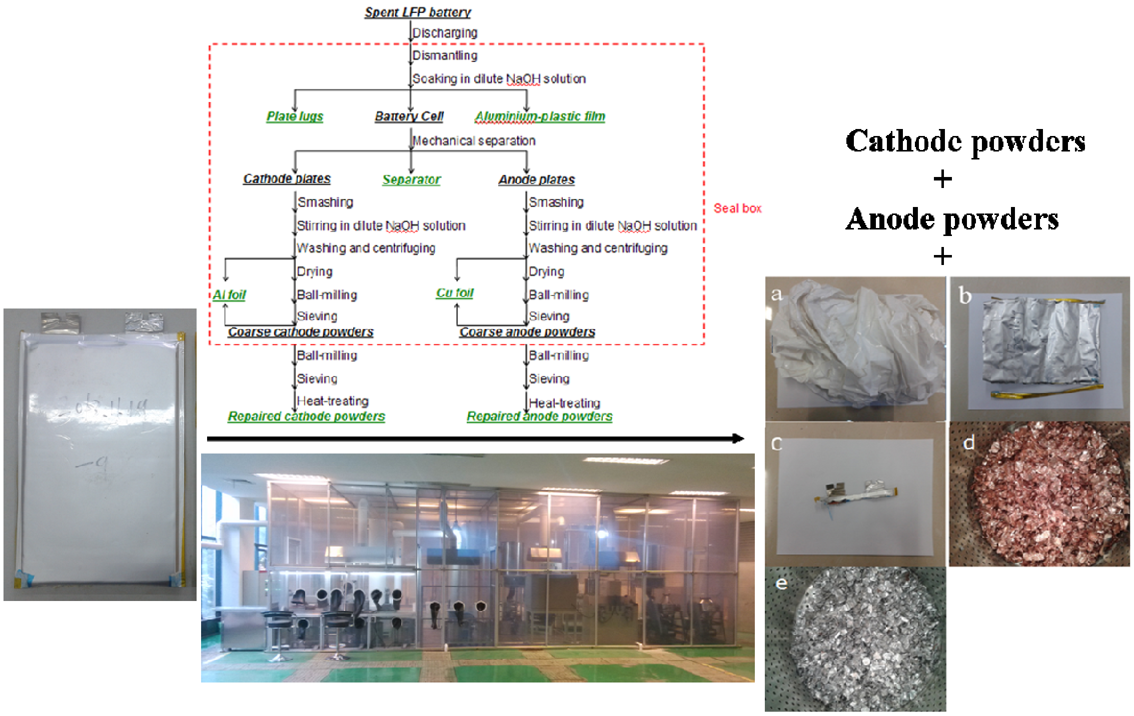
Spent LFP battery
Discharging
Dismantling
Soaking in dilute NaOH solution
Plate lugs
Battery Cell
Aluminium-plastic film
Mechanical separation
Cathode plates
Separator
Anode plates
Smashing
Stirring in dilute NaOH solution
Washing and centrifuging
Drying
Ball-milling
Sieving
Al foil
Cu foil
Coarse cathode powders
Coarse anode powders
Seal box
Ball-milling
Sieving
Heat-treating
Repaired cathode powders
Repaired anode powders
Cathode powders
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Anode powders
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