Re-synthesis and Electrochemical Characteristics of LiFePO₄ Cathode Materials Recycled from Scrap Electrodes

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This paper describes an environmentally friendly process for the recovery of LiFePO₄ cathode materials from scrap electrodes by a simple thermal treatment method. The active materials were easily separated from the aluminum substrate foil and polymeric binders were also decomposed at different temperatures (400 °C, 500 °C, 600 °C) for 30 min under nitrogen gas flow. The samples were characterized by X-ray diffraction (XRD), scanning electronic microscopy (SEM), Raman spectroscopy, Thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). The electrochemical properties of the recycled LiFePO₄ cathode were evaluated by galvanostatic charge and discharge modes. The specific charge/discharge capacities of the recycled LiFePO₄ cathode were similar to those of the original LiFePO₄ cathode. The LiFePO₄ cathode material recovered at 500 °C exhibits a somewhat higher capacity than those of other recovered materials at high current rates. The recycled LiFePO₄ cathode also showed a good cycling performance.

Key Words : LiFePO₄ cathode, Scrap electrode, Recycling process, Lithium-ion batteries

Introduction

In recent years, the recycling of lithium-ion batteries has become important because of the need to dispose of them safely in a manner that is consistent with environmental preservation.[1,2] This is especially important as current levels of battery consumption are quite high. For instance, in the USA and Europe, the consumption of batteries is estimated to be 8 billion units per year.[3] In Japan, around 6 million batteries were produced in 2004, while almost 1 billion units are consumed every year in Brazil.[4]

The recycling process should reduce scrap volume, separate battery components, enrich valuable metals, and eliminate the danger of battery waste to the environment. Two basic classes of recycling processes, including physical and chemical processes, have been applied for the separation or the recovery of cobalt, nickel, lithium and other components from spent lithium-ion batteries. These physical processes mainly involve mechanical processes, thermal treatment, mechanochemical processes and dissolution processes. Chemical processes mainly involve acid leaching or base leaching, bio leaching, solvent extraction, chemical precipitation and electrochemical processes. The re-synthesis of electrode active materials or the synthesis of other reactive materials from the spent lithium-ion batteries has been also studied through many investigations.[5-8] Although there has been a great deal of research achievements developed for the recycling technologies of lithium-ion batteries, most of them are still based on hydrometallurgical chemistry and have been developed with industrial process in mind.[9,10]

This paper introduces, a recycling process, a simple thermal treatment to recover materials from scrap LiFePO₄ cathodes, and the electrochemical performances of the recovered LiFePO₄. In addition, the original LiFePO₄ cathodes were compared in view of feasibility for recycling lithium-ion batteries.

Experimental

The scrap LiFePO₄ samples were prepared by cutting original LiFePO₄ cathodes manufactured the industrial field. The scrap LiFePO₄ cathodes were initially thermally treated at different temperatures (400 °C, 500 °C, 600 °C) for 30 min under nitrogen gas flow. The heat-treated LiFePO₄ cathode active materials were then allowed to naturally cool down to room temperature and separate from the aluminum foil substrate. Secondly, the separated active materials were ground and then sieved to completely remove residual aluminum powder. The experimental procedure is illustrated in Figure 1.

The recycled cathodes, including conductors from the scrap, were prepared by mixing the recovered LiFePO₄ active materials (96.86 wt %), the mixture of styrene butadiene rubber (40 wt % in water, Sigma) and sodium carboxymethyl cellulose (1 wt % in water, Zeon) binder (3.14 wt %). The slurry was mixed at 5,000 rpm for 30 min in a homogenizer and then cast on an aluminum foil by a doctor blade. The cathodes were dried at 80 °C in a vacuum oven for 24 h to remove residual solvent and pressed using a rolling machine. These cathodes were assembled along with a lithium metal foil anodes using CR2032 coin cells in a dry room (dew point: −60 °C). A microporous polypropylene separator (Celgard 2400) was used. The electrolyte used was 1 M LiPF₆ in a solvent mixture of ethylene carbonate, ethyl-methyl carbonate, and dimethyl carbonate (1:1:1 by volume

Figure 1. Flow diagram of the recycling process of LiFePO₄ cathode materials.

Figure 2. TGA and DSC curves of CMC and SBR binders.

ratio). The structure of the recycled LiFePO₄ powders and heat-treated binders was analyzed by X-ray diffraction (XRD, Rigaku D/MAX-2500V) and dispersive Raman spectroscopy (Nicolet Almega XR dispersive Raman Spectrometer, Thermo Scientific Corp.), respectively. The carbon contents of the LiFePO₄ cathodes were analyzed by elemental analyzer (LECO TC-136). The results showed that the final carbon amounts for the original LiFePO₄, 400 °C, 500 °C, and 600 °C were 12.4, 13.7, 13.3, and 12.8 wt %, respectively. The thermal properties of the binder were analyzed by DSC/TGA (TG Instrument, Q600). The morphology of the powders was examined by scanning electron microscope (SEM, Hitachi 4300). The cyclic properties of the cells were performed by galvanostatic modes in the voltage range of 2.5 to 4.3 V *vs* Li/Li$^+$ using a Maccor cycle system (S 4000 series).

Figure 3. XRD pattern of the recycled LiFePO₄ and the original LiFePO₄ cathode materials (a): original LiFePO₄, (b): recycled LiFePO₄ at 400 °C, (c): 500 °C, (d): 600 °C).

Results and Discussion

Figure 2 shows the DSC-TGA curves of the SBR and CMC binders with a heating rate of 10 °C min^{-1} from room temperature to 600 °C under nitrogen gas flow to protect the oxidation of the LiFePO₄. There is one exothermic peak at near 290 °C on the DSC curve, which is associated with a sharp weight loss on the TGA curve, which is related to the carbonization of the polymeric binders. The TGA curve indicates that the change of sample weight remains constant above 500 °C. Therefore, we can conclude that the carbonization of the binders will be completed when temperature is about 500 °C. Based on the above result, the thermal treatment conditions of recycling were also conducted at around 500 °C for 30 min under nitrogen gas flow.

As seen in Figure 3, the XRD patterns of the recycled LiFePO₄ and the original LiFePO₄ powders demonstrate that they have the same olivine structure (JCPDS card no. 40-1499). There are also no impurity phases such as Li₃PO₄ and Fe^{3+}-related compounds in the recycled LiFePO₄ cathode material. Figure 4 shows the SEM morphologies of the recycled LiFePO₄ and the original LiFePO₄ powders, respec-

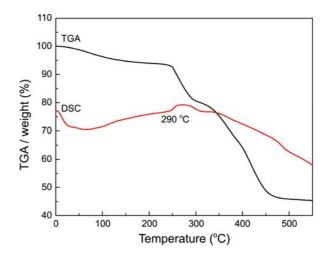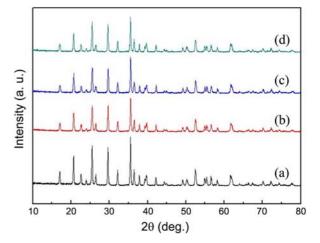**Figure 4.** SEM images of the recycled LiFePO₄ and the original LiFePO₄ cathode materials (a): original LiFePO₄, (b): recycled LiFePO₄ at 400 °C, (c): 500 °C, (d): 600 °C).
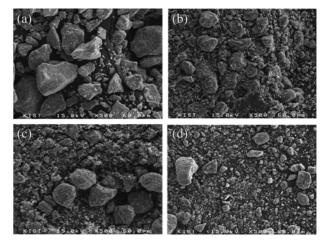
tively. The recycled LiFePO₄ powder shows fine particle having a spherical feature of about 2-10 μm in diameter
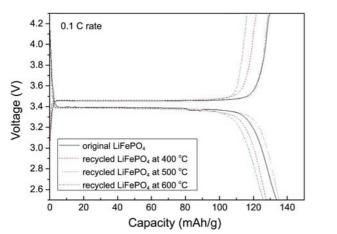
Figure 5. The charge/discharge voltage curves of the recycled LiFePO₄ and the original LiFePO₄ cathode at 0.1C rate.

compared to the original LiFePO₄ powder, which is coarse and irregular feature. In addition, the smaller particles seem to be the carbon phases formed from the decomposition of polymeric binders and the acetylene black conductor in the original cathode.

Figure 5 shows the charge/discharge voltage curves of the recycled LiFePO₄ and original LiFePO₄ cathode at 0.1C rate. A flat charge discharge curve at around 3.45 V over a large compositional range implies that the two-phase redox reaction proceeds *via* a first-order transition between LiFePO₄ and FePO₄.[11] The small voltage difference of about 0.05 V between the charge and discharge plateaus is representative of the recycled LiFePO₄ cathode's good kinetics. The specific capacity of LiFePO₄ treated at 500 ºC was somewhat higher than that of the original LiFePO₄ cathode. The cyclic efficiency of the recycled LiFePO₄ cathodes was similar to that of the original LiFePO₄ cathode. The related electrochemical results of the LiFePO₄ cathodes are presented in Table 1.

Figure 6 shows the charge/discharge voltage curves of the recycled LiFePO₄ and the original LiFePO₄ cathodes at 1C rate. The LiFePO₄ cathode treated at 500 ºC also showed the highest specific discharge capacity of 112 mAh/g among the LiFePO₄ cathodes. The difference between the charge and discharge average potential is 0.2 V and the cyclic efficiency is more than 98% at even a high rate. The detailed electrochemical data are summarized in Table 2. This effect may be attributed to the increased electrical conductivity of the active material by carbonization of CMC and SBR binders at 500 ºC.

Table 1. The electrochemical results of the recycled LiFePO₄ and the original LiFePO₄ cathode at 0.1C rate

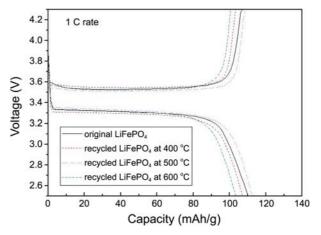|	Original	400 ºC	500 ºC	600 ºC
Charge specific capacity (mAh/g)	134.52	128.48	136.58	123.44
Discharge specific capacity (mAh/g)	133.58	127.52	135.02	122.68
Charge-discharge efficiency (%)	99.30	99.25	98.85	99.38
Average charge voltage (V)	3.45	3.45	3.45	3.45
Average discharge Voltage (V)	3.40	3.40	3.40	3.40

Figure 6. The charge/discharge voltage curves of the recovered LiFePO₄ and the original LiFePO₄ cathode at 1C rate.

Table 2. The electrochemical results of the recycled LiFePO₄ and the original LiFePO₄ cathode at 1C rate

	Original	400 ºC	500 ºC	600 ºC
Charge specific capacity (mAh/g)	112.87	108.58	114.31	105.46
Discharge specific capacity (mAh/g)	110.15	107.22	112.36	103.51
Charge-discharge efficiency (%)	97.59	98.74	98.29	98.15
Average charge voltage (V)	3.55	3.55	3.55	3.55
Average discharge Voltage (V)	3.35	3.35	3.35	3.35

In order to gain a better understanding of this phenomenon, the pyrolyzed CMC and SBR binder were analyzed using the Raman spectroscopy. This spectrum was recorded with a 532 nm laser excitation line as shown in Figure 7. The two peaks at 1355 cm⁻¹ and 1582 cm⁻¹ are related to the carbon phase due to the thermal decomposition of the polymer binders. In the spectrum of a pure carbon film, the position of D (disordered carbon) and G (graphitic carbon) bands were 1355 cm⁻¹ and 1582 cm⁻¹.[12,13] The positions and relative intensities of the G and D bands provide more
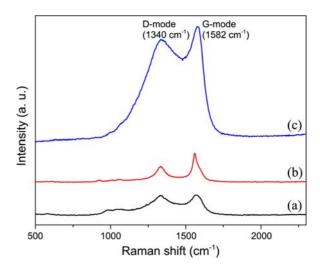

Figure 7. Raman spectrum of CMC and SBR binder decomposed at different temperatures (a): 400 ºC, (b): 500 ºC, (c): 600 ºC.
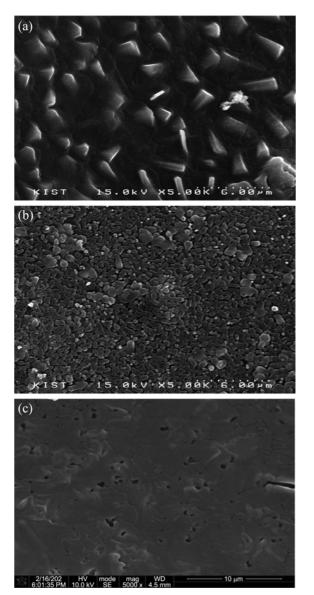
Figure 8. SEM images of CMC and SBR binders pyrolyzed at different temperatures (a): 400 °C, (b): 500 °C, (c): 600 °C).

Figure 9. The cycling performances of the recycled LiFePO$_4$ and the original LiFePO$_4$ cathode.

information on the structure and domain size of a carbon material. The two peaks indicate that the carbon layer is composed of crystalline carbon and disordered carbon phase.[14] Especially, the graphitic carbon increases the electrical conductivity of the cathode. The Raman peaks indicated that the binders could be carbonized to the crystalline carbons and disordered carbon by thermal treatment process. The peak of the G band is more intensive than that of the D band at 500 °C, whereas the disordered carbon phase is well developed at 400 °C and 600 °C. Although the intensity of Raman peak is higher at 600 °C, the G mode/D mode ratio is low compared to that of binder pyrolyzed at 400 °C. The increased electrochemical activity thus attributed to the increased G mode in Raman peaks. Figure 8 shows SEM images of the binders pyrolyzed at different temperatures. The morphology of the pyrolyzed binders exhibited different features. The size of the bin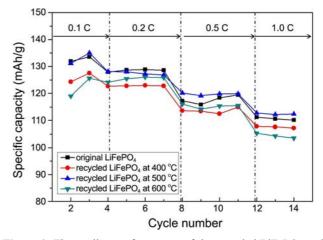ders pyrolyzed at 500 °C is much smaller than that of other pyrolyzed binders and is distributed homogeneously. Therefore, the enhanced electrochemical properties of the recycled LiFePO$_4$ cathode could be attributed to the increased crystallinity and uniformed size of the carbon phase formed from the thermal decomposition of binders at this temperature.

Figure 9 shows the cycling performances of the recycled LiFePO$_4$ and the original LiFePO$_4$ cathode at various rates. There is a slightly different rate capability between the recycled LiFePO$_4$ and the original LiFePO$_4$ cathodes. The LiFePO$_4$ cathode treated at 500 °C showed a good cycling performance without capacity fading at all rates. This excellent cycling stability of the recycled LiFePO$_4$ could be due to the high stability of the olivine structure and the minor lattice adjustments upon cycling.[15]

Conclusion

The technology of recycle and synthesis of LiFePO$_4$ from the scrap cathode of lithium secondary batteries was studied. The active material containing CMS and SBR binders can be separated from the aluminum foil and the LiFePO$_4$ cathode materials were recovered successfully by a thermal decomposition reaction. The recycled LiFePO$_4$ cathode materials showed higher specific capacity than the original LiFePO$_4$ cathode materials. This effect may be attributed to the increased electrical conductivity of LiFePO$_4$ active material by carbonization of CMC and SBR binders at 500 °C. These recycled LiFePO$_4$ cathodes also exhibited good cycling performances without capacity fading even at high rates.

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