

# Electrochemical characteristics of $\text{LiFePO}_4/\text{LiCoO}_2$ mixed electrode for Li secondary battery

Hyun-Soo Kim · Mingzhe Kong · Ketaek Kim ·  
Ick-Jun Kim · Hal-Bon Gu

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**Abstract**  $\text{LiFePO}_4$  cathode active material was synthesized using a solid state method and a mixed cathode was prepared by adding  $\text{LiCoO}_2$ . A coin cell was prepared using the mixed cathode and its electrochemical performances were evaluated. The  $\text{LiFePO}_4$  material improved both in thermal stability and rate capability. The discharge capacity of the 5 wt.%  $\text{LiCoO}_2$ -added  $\text{LiFePO}_4$  material was 139.4 mAh/g at 0.2 C rate, and it showed a capacity retention of 64.2% even at 5 C rate in comparison to 0.2 C rate. The cycle performance of the bare  $\text{LiFePO}_4$  material was excellent, but the capacity fading of 20 wt.%  $\text{LiCoO}_2$ -added  $\text{LiFePO}_4$  material became significant during charge/discharge cycle. However, 5–10 wt.%  $\text{LiCoO}_2$ -added  $\text{LiFePO}_4$  material showed good thermal stability, high rate capability and good cycle performances.

**Keywords**  $\text{LiFePO}_4/\text{LiCoO}_2$  · Cathode material · Rate-capability · Capacity retention · Thermal stability

## 1 Introduction

Currently, the lithium ion battery (LIB) has been commercialized as a power source for electronic telecommunication devices. A layered structure  $\text{LiCoO}_2$  is used as a cathode active material in the LIB, due to the fact that  $\text{LiCoO}_2$  has ease of preparation, high energy density, high operational voltage, and good cycleability. However,  $\text{LiCoO}_2$  has high cost, toxicity, and low discharge capacity, so efforts are being made in attempts to find alternative materials [1, 2]. Currently, these alternative materials, such as  $\text{LiNiO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiN}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ , and  $\text{LiFePO}_4$ , and others are being researched and studied.

A. K. Padhi et al. [3] reported first that  $\text{Li}_{1-y}\text{FePO}_4$  with an olivine structure had been charged and discharged reversibly.  $\text{LiFePO}_4$  is being recognized as a new cathode material for high-power and large-scale lithium secondary batteries, because it has low cost, is not environmentally harmful, and has good thermal stability [4, 5]. Furthermore, it has a high discharge voltage of 3.4 V (vs.  $\text{Li}/\text{Li}^+$ ), a very long plateau during charge and discharge, and a high practical discharge capacity of 170 mAh/g, which is the theoretical discharge capacity.

Studies to commercialize this material as an alternative to  $\text{LiCoO}_2$  for the lithium secondary battery are being actively pursued [6, 7]. However, its drawbacks are that, at less than  $10^{-8}\text{S/cm}$  it has a low electrical conductivity, and also has a low diffusion of lithium ions, so consequently it shows low power performance [8].

There are various methods by which the poor electrical conductivity of  $\text{LiFePO}_4$  can be improved. Firstly, the particle size should be reduced to a nanometer size. To achieve this, there are two known methods: one is a top-down

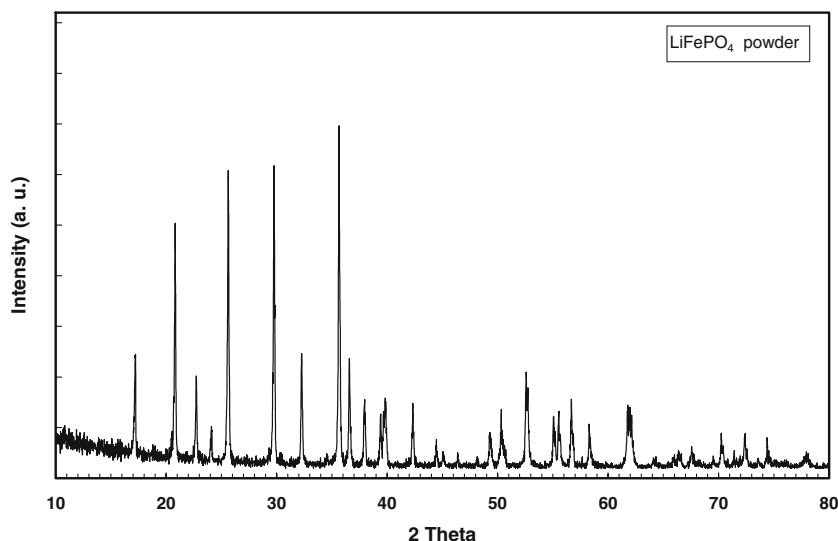
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H.-S. Kim · M. Kong · K. Kim · I.-J. Kim  
Korea Electrotechnology Research Institute,  
Changwon 641-120, South Korea

H.-B. Gu  
Chonnam National University,  
Gwangju 500-757, South Korea

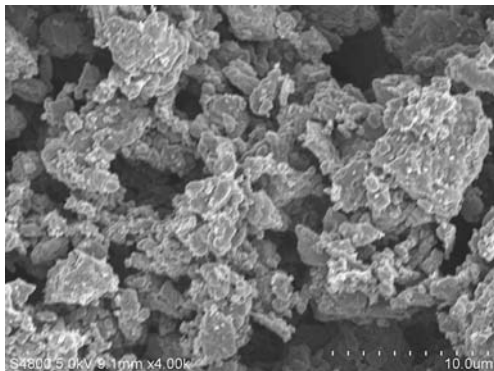
H.-S. Kim (✉)  
Battery Research Group,  
Korea Electrotechnology Research Institute,  
70 Bulmosan-gil,  
Changwon 641-120, South Korea  
e-mail: hskim@keri.re.kr

**Fig. 1** X-ray diffraction pattern of as-received  $\text{LiFePO}_4$  powder



method, whereby the particles are pulverized using a ball-mill, and the other is a bottom-up method by which nano-sized particles are synthesized using a hydrothermal method [9, 10]. Secondly, heterogeneous elements are doped into the material. For example, the cations may be doped, as in  $\text{Li}_x\text{C}_{1-x}\text{FePO}_4$  (C: alkali, alkali earth, transition metals) or the anions may be replaced, as in  $\text{LiFe}(\text{PO}_4)_x(\text{A})_{1-x}$  (A:  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^{2-}$ ,  $\text{N}^{3-}$ , and other anions) [11–13]. Thirdly, a coating is created on the surface of the active material, using carbon or Ag [14].

However, the low electric conductivity of  $\text{LiFePO}_4$  material could be easily improved by mixing it with  $\text{LiCoO}_2$  material [15]. In this study,  $\text{LiFePO}_4$  material was synthesized using a solid state method, and a mixed cathode was prepared by adding  $\text{LiCoO}_2$  in order to improve the poor electrical conductivity of  $\text{LiFePO}_4$ . A coin cell was prepared using the mixed cathode and a lithium metal anode. Its electrochemical performance was then evaluated.



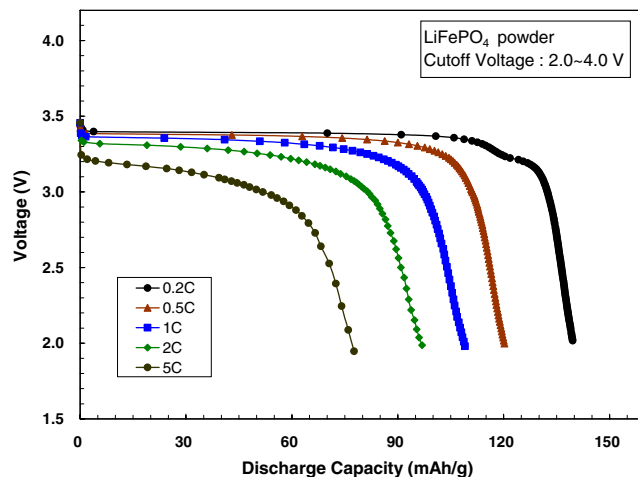
**Fig. 2** SEM photographs of as-received  $\text{LiFePO}_4$  powder

## 2 Experiment

$\text{LiFePO}_4$  powder was prepared through a solid state method, using  $\text{LiCo}_3$ ,  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , and  $(\text{NH}_4)_2\text{HPO}_4$ . After adding 0, 5, 10, 20 wt.% of  $\text{LiCoO}_2$  to  $\text{LiFePO}_4$  material to manufacture four mixed electrodes, samples were mixed for 2 h in an ethanol and then dried at  $50^\circ\text{C}$ .

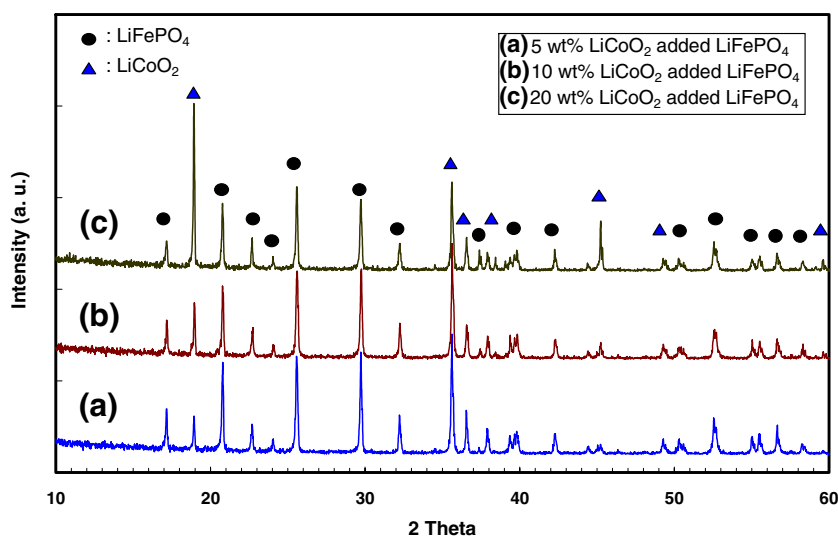
In order to understand the crystal structure of the active material, a Phillips X-ray Diffractometer PW 1830 was used. X-ray diffraction patterns were collected at a scan range of  $10\text{--}80^\circ$  and a scan step of  $0.02^\circ$ . The surface morphology of the as-prepared powder was examined using a Hitachi S-4800 scanning electron microscope (SEM).

To prepare a coin cell, the  $\text{LiFePO}_4/\text{LiCoO}_2$  as an active material, super p black as a conductor, and polyvinylidene



**Fig. 3** Voltage profiles of as-received  $\text{LiFePO}_4$  powder at various current rates

**Fig. 4** X-ray diffraction pattern of LiCoO<sub>2</sub>-added LiFePO<sub>4</sub> powder: (a) 5 wt% LiCoO<sub>2</sub> added LiFePO<sub>4</sub>, (b) 10 wt% LiCoO<sub>2</sub> added LiFePO<sub>4</sub>, and (c) 20 wt% LiCoO<sub>2</sub> added LiFePO<sub>4</sub>



fluoride as a binder were mixed at a ratio of 85:10:5 wt.%, respectively. A metal lithium was used for the anode, and an Asahi polypropylene was used for the separator. The ethylene carbonate/diethyl carbonate (1:1 vol.%) with 1.0 M LiPF<sub>6</sub> dissolved was used as an electrolyte and the 2032 type coin cell was prepared. The coin cell was assembled in a dry room, and the cell was aged for 24 h at room temperature.

To evaluate the thermal stability of the active material, TA's differential scanning calorimetry (DSC) Q 1000 was used. The samples were prepared by drying for 24 h at 80°C after charging up to 4 V (vs. Li/Li<sup>+</sup>). DSC measurements were performed at a heating rate of 10°C/min from 50°C to 500°C.

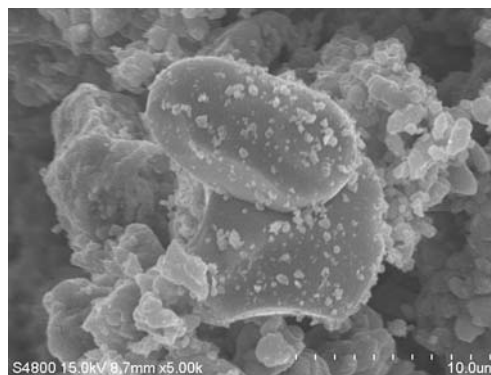
To evaluate the rate capabilities of the LiFePO<sub>4</sub>/LiCoO<sub>2</sub> mixed electrodes, each was charged at 0.2 C rate and discharged at current rates of 0.2, 0.5, 1.0, 2, and 5 C, respectively. The mixed cathode was charged and discharged at 0.5 C rate for 100 cycles at a voltage range of 2.0–4.0 V for the cycle performances.

### 3 Results and discussion

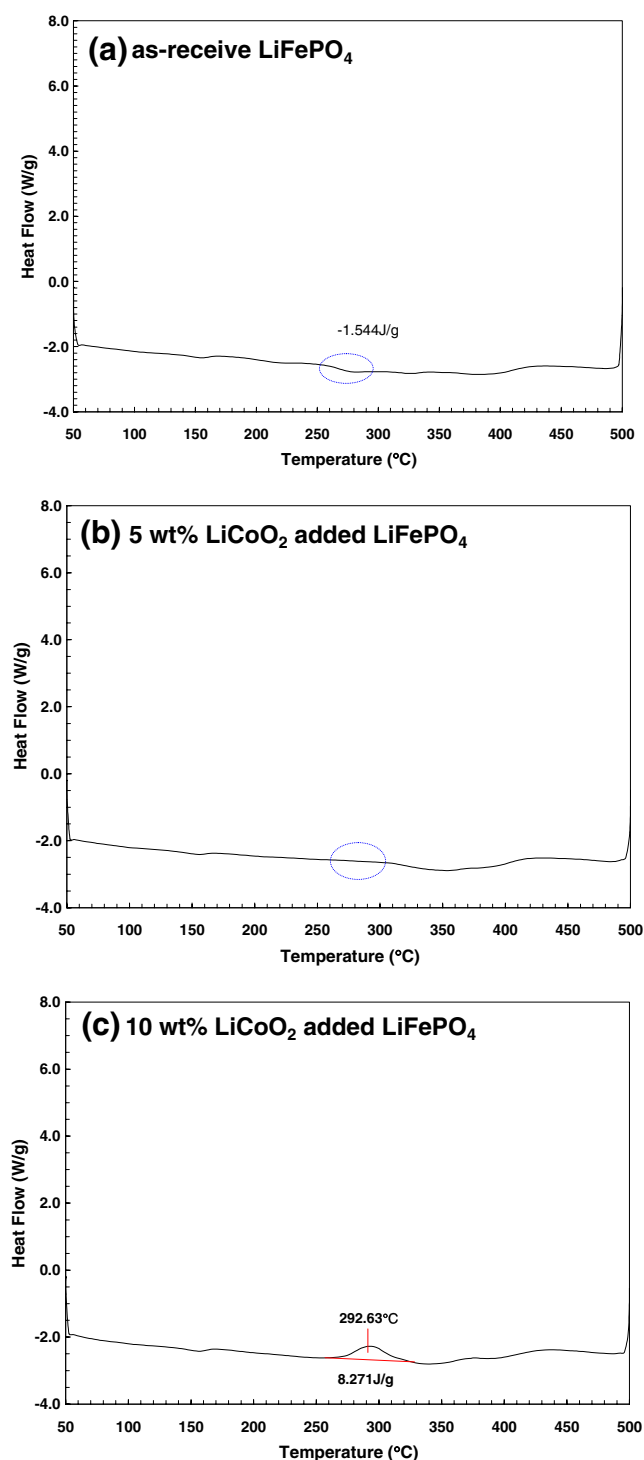
The XRD pattern of the synthesized LiFePO<sub>4</sub> powder is displayed in Fig. 1. The LiFePO<sub>4</sub> is in olivine structure with a space group of Pnma. The basic structure is hexagonal, but due to its lattice strain, it belongs to an orthorhombic system. Li and Fe occupy only octahedral sites, P occupies tetrahedral sites, and O atoms shared the apex and edge. The oxygen in the crystal structure forms a very strong covalent bond with the phosphoric acid element, which is advantageous in that it does not easily dissolve in the electrolyte [16, 17]. The morphology of the LiFePO<sub>4</sub>

powder synthesized through the solid state method is shown in Fig. 2. The size of the particle was approximately 5 μm.

The coin cell with the synthesized LiFePO<sub>4</sub> material was charged and discharged at a cut-off voltage of 2–4 V. The voltage profile of the synthesized LiFePO<sub>4</sub> powder is shown in Fig. 3. The voltage curve of the LiFePO<sub>4</sub> charges/discharges at 0.2 C rate shows a long plateau at approximately 3.4 V (vs. Li/Li<sup>+</sup>). The LiFePO<sub>4</sub> material showed a reversible discharge capacity of 139.6 mAh/g at 0.2 C rate, while at 5 C rate, it was 77.6 mAh/g, and therefore, it showed 55.5% capacity retention compared to its performance at 0.2 C rate. This is due to the fact that LiFePO<sub>4</sub> has a low electrical conductivity, and slow lithium ion diffusion. This is similar to the rate capability reported by Park et al. [18]. Therefore, in order to improve the poor rate capability of the bare LiFePO<sub>4</sub>, the LiCoO<sub>2</sub> was added in the preparation of the electrode, and its electrochemical performance was evaluated.



**Fig. 5** SEM photographs of 10 wt.% LiCoO<sub>2</sub>-added LiFePO<sub>4</sub> material

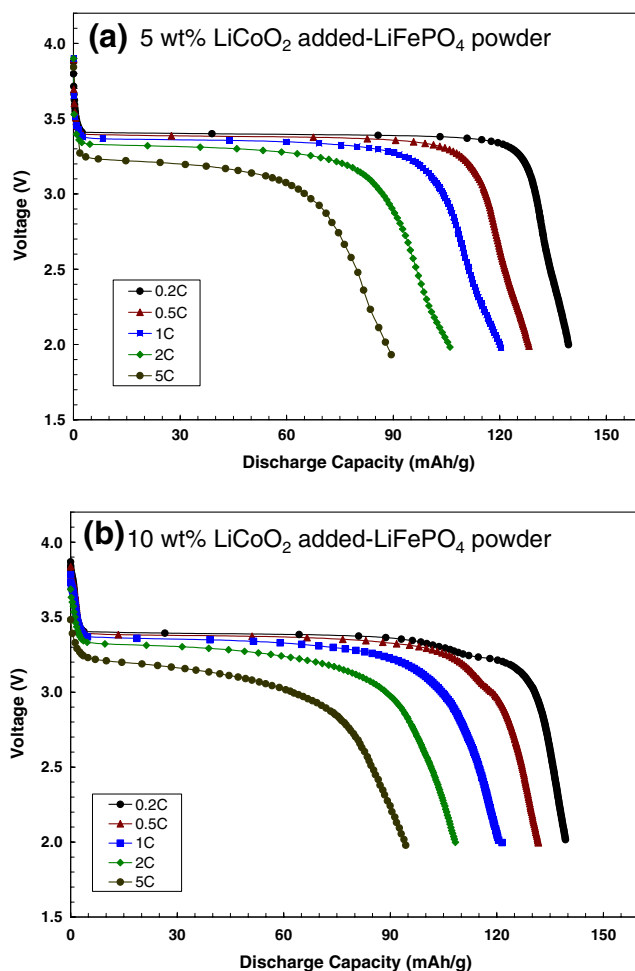


**Fig. 6** DSC profiles of as-received  $\text{LiFePO}_4$  and  $\text{LiCoO}_2$ -added  $\text{LiFePO}_4$  powder after charging to 4 V: (a) as-receive  $\text{LiFePO}_4$ , (b) 5 wt%  $\text{LiCoO}_2$  added  $\text{LiFePO}_4$ , and (c) 10 wt%  $\text{LiCoO}_2$  added  $\text{LiFePO}_4$

The XRD patterns of the mixed electrodes prepared from the  $\text{LiFePO}_4$  powder with 5, 10, 20 wt.% of  $\text{LiCoO}_2$  added, respectively, are shown in Fig. 4. When 5 wt.% of  $\text{LiCoO}_2$  was added, the (003) peak was observed around  $18^\circ$ , and when 10 wt.% was added, the (006)/(012), (108)/(110),

(101), (104) of the layered peak started to become observable [19]. However, the peak changes in XRD patterns do not indicate the formation of other compounds, but that two compounds were mixed physically with each other. This can be seen from the SEM photos. The morphology of the mixed electrode prepared from adding 10 wt.% of  $\text{LiCoO}_2$  is shown in Fig. 5. As can be seen from the figure, when 10 wt.% of  $\text{LiCoO}_2$  particles were added, it was evenly mixed with  $\text{LiCoO}_2$  particles with a size of  $10 \mu\text{m}$  [20].

The coin cell with the  $\text{LiFePO}_4/\text{LiCoO}_2$  mixed electrode was fully charged to 4 V, and the DSC measurement was conducted to evaluate its thermal behavior. DSC profiles of the as-received  $\text{LiFePO}_4$  and  $\text{LiCoO}_2$ -added  $\text{LiFePO}_4$  powder were shown in Fig. 6. As can be seen from the figure, in the bare- $\text{LiFePO}_4$  material, a small endothermic peak with a heat generation amount of 1.54 J/g was observed at around  $273.7^\circ\text{C}$ , but a exothermic peak could not be observed [21]. This thermal stability is actually excellent, considering that  $\text{LiCoO}_2$  and  $\text{LiCo}_{1/3}\text{Mn}_{1/3}\text{Ni}_{1/3}\text{O}_2$  show



**Fig. 7** Voltage profiles of  $\text{LiCoO}_2$ -added  $\text{LiFePO}_4$  powder at various current rates: (a) 5 wt%  $\text{LiCoO}_2$  added- $\text{LiFePO}_4$  powder and (b) 10 wt%  $\text{LiCoO}_2$  added- $\text{LiFePO}_4$  powder

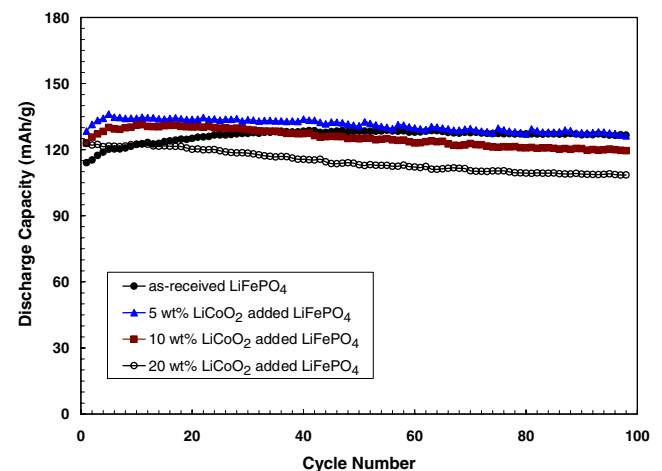
**Table 1** Discharge capacity and capacity retention of as-received LiFePO<sub>4</sub> and LiCoO<sub>2</sub>-added LiFePO<sub>4</sub> powder at various current rates.

Current rate	As-received LiFePO <sub>4</sub>		5 wt.% LiCoO <sub>2</sub> -added LiFePO <sub>4</sub>		10 wt.% LiCoO <sub>2</sub> -added LiFePO <sub>4</sub>		20 wt.% LiCoO <sub>2</sub> -added LiFePO <sub>4</sub>	
	Discharge capacity (mAh/g)	Capacity retention (%)	Discharge capacity (mAh/g)	Capacity retention (%)	Discharge capacity (mAh/g)	Capacity retention (%)	Discharge capacity (mAh/g)	Capacity retention (%)
0.2 C	139.6	100.0	139.4	100.0	139.4	100.0	137.0	100.0
0.5 C	120.2	86.1	128.2	92.0	131.7	94.5	129.5	94.5
1 C	109.1	78.1	120.3	86.3	121.5	87.2	125.2	91.4
2 C	96.9	69.4	106.0	76.1	108.4	77.7	112.7	82.2
5 C	77.6	55.6	89.5	64.2	94.4	67.7	98.0	71.5

exothermic peaks at 263.0°C and 292.0°C, respectively. This excellent thermal stability makes LiFePO<sub>4</sub> material applicable as a suitable active material in large-scale lithium ion batteries for hybrid electric vehicle application [22, 23]. In the 5 wt.% LiCoO<sub>2</sub> added electrode, the endothermic peak disappeared. When 10 wt.% of LiCoO<sub>2</sub> was added, a small exothermic peak was observed at 292.6°C, with a heat generation amount of 8.27 J/g. It is reported that the fully charged LiCoO<sub>2</sub> material shows an exothermic peak at 263.0°C, but if Al<sub>2</sub>O<sub>3</sub> is coated on the surface, the peak is shifted to a higher temperature of approximately 280°C [22]. Therefore, the small peak observed at 292.6°C is judged to have occurred due to the addition of LiCoO<sub>2</sub>. Therefore, even when 10 wt.% of LiCoO<sub>2</sub> is added to LiFePO<sub>4</sub> material, the thermal stability is maintained. When 20 wt.% of LiCoO<sub>2</sub> was added, the exothermal reaction was observed at 289.5°C.

To evaluate the rate capability of the mixed electrode, coin cells was charged and discharged with current rates of 0.2, 0.5, 1, 2, and 5 C, respectively. The examples of voltage curves obtained from the mixed electrodes with 5 and 10 wt.% of LiCoO<sub>2</sub> powder added to LiFePO<sub>4</sub> material are shown in Fig. 7. The discharge capacity and the capacity retention obtained from the mixed electrodes are summarized in Table 1. The discharge capacity of the bare-LiFePO<sub>4</sub> material was 139.6 mAh/g at 0.2 C rate and 77.6 mAh/g at 5 C rate, so the capacity retention at 5 C rate was 55.6% of the retention at 0.2 C rate. The discharge capacity of the LiFePO<sub>4</sub> material with 5 wt.% of LiCoO<sub>2</sub> added was 139.4 mAh/g at 0.2 C rate, and even at 5 C rate, the discharge capacity was 89.5 mAh/g, which is 64.2% of the capacity retention at 0.2 C. This means that the addition of LiCoO<sub>2</sub> improved the rate capacity of the LiFePO<sub>4</sub> material. When the amount of LiCoO<sub>2</sub> powder was increased to 10 and 20 wt.%, the rate capability of LiFePO<sub>4</sub> improved even further. This is due to the addition of LiCoO<sub>2</sub>, which has higher electric conductivity and lithium ion diffusion than LiFePO<sub>4</sub>.

The discharge capacities with charge/discharge cycle of the mixed material are shown in Fig. 8. The sample was charged and discharged at 0.5 C rate in a voltage range of 2.0–4.0 V for 100 cycles. As can be seen from the figure, the initial discharge capacity of the bare-LiFePO<sub>4</sub> material was maintained even after 100 cycles, proving its excellent cycle performance. And the mixed electrode added with 5 wt.% of LiCoO<sub>2</sub> also shows very good cycle performance, similar to the bare-LiFePO<sub>4</sub> active material. On the other hand, the mixed electrode with 10 wt.% of LiCoO<sub>2</sub> added still showed a very good cycle performance, although it did show a small decrease in discharge capacity during charge/discharge cycle. However, the 20 wt.% LiCoO<sub>2</sub>-added mixed electrode started to show slightly capacity fading after ten charge/discharge cycles. The reason why capacity fading increase on the 20 wt.% LiCoO<sub>2</sub>-added mixed electrode is that cycle performance of LiCoO<sub>2</sub> is lower than that of LiFePO<sub>4</sub>. So when all the above results are considered, one can conclude that the

**Fig. 8** Discharge capacity of as-received LiFePO<sub>4</sub> and LiCoO<sub>2</sub>-added LiFePO<sub>4</sub> powder with charge/discharge cycling at a current rate of 0.5 C

higher the ratio of  $\text{LiCoO}_2$ , up to 10 wt.%, that is added to the  $\text{LiFePO}_4$  material, the better the rate capability of the mixed electrode, and the more its thermal stability and cycle performance are degraded.

#### 4 Conclusions

In this study,  $\text{LiFePO}_4$  cathode active material was synthesized using a solid state method.  $\text{LiCoO}_2$  powder was added to the prepared- $\text{LiFePO}_4$  material, its electrochemical performance was evaluated, and the following results were obtained.

The synthesized  $\text{LiFePO}_4$  material was olivine in structure and consisted of a particle size of 5  $\mu\text{m}$ . The bare- $\text{LiFePO}_4$  material showed a small endothermic peak at around 273.7°C, and when the 5 wt.% of  $\text{LiCoO}_2$  was added, the endothermic peak disappeared and a slight exothermic peak was observed at 292.6°C.

The discharge capacity of the bare- $\text{LiFePO}_4$  material with 5 wt.% of  $\text{LiCoO}_2$  added was 139.4 mAh/g at the 0.2 C rate, while at 5 C it was 89.5 mAh/g, a 64.2% capacity retention compared to 0.2 C. When 10 and 20 wt.% of  $\text{LiCoO}_2$  powder were added, the rate capability of the  $\text{LiFePO}_4$  improved even further.

The cycle performance of the bare- $\text{LiFePO}_4$  material was excellent, but the mixed electrodes with 20 wt.% of  $\text{LiCoO}_2$  added tended to show slightly capacity fading with charge/discharge cycles. However, with up to approximately 10 wt.% of  $\text{LiCoO}_2$  powder addition, good cycle performance was achieved.

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