

## Preparation of dense $\text{LiFePO}_4/\text{C}$ composite positive electrodes using spark-plasma-sintering process

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### Abstract

Composite positive electrodes  $\text{LiFePO}_4/\text{C}$ , applicable for rechargeable lithium-ion batteries cycled at high current density, were prepared using spark-plasma-sintering (SPS) technique.  $\text{LiFePO}_4/\text{C}$  composite positive electrodes with carbon content of 20 wt.% was synthesized at 600 °C in the SPS process, and it was found that  $\text{LiFePO}_4$  particles were covered with fine carbon particles and they formed agglomerates with the size of about 10  $\mu\text{m}$ . It resulted in higher electrode density. Charge/discharge tests for the cell using  $\text{LiFePO}_4/\text{C}$  composite positive electrodes showed superior cycle performance at the rates of 17–850  $\text{mAh g}^{-1}$  (0.1–5 C) compared with the cell using the conventionally blended  $\text{LiFePO}_4 + \text{C}$  composite positive electrodes. The improvement of the cell performance was attributed to strong binding between  $\text{LiFePO}_4$  and carbon powders. Consequently, the electrical network remained almost unchanged during electrochemical redox cycling, even at high current rates.

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**Keywords:** Composite electrodes; Spark-plasma-sintering;  $\text{LiFePO}_4$

### 1. Introduction

For the electrode materials in practical lithium-ion batteries, particularly those in electric vehicles, higher rate capability, in addition to higher energy density, is one of the most important characteristics [1]. However, lithium-ion cells cycled at relatively high current density exhibited a significant power loss, which is associated primarily with a rise of the cathode impedance; some active particles became electrically disconnected from the remaining part of the positive electrodes [1,2]. It could be attributed partly to mechanical stress caused by their volumetric changes during insertion/extraction of lithium ions, and/or partly to detachment of conductive additives from the positive electrode active particles. Therefore, the electrical disconnection during the redox cycling is a serious problem to be overcome, irrespective of the active materials.

Recently, olivine compound  $\text{LiFePO}_4$  has received a lot of attention as one of the promising positive electrode materials from the standpoints of its relatively high theoretical capacity (approximately 170  $\text{mAh g}^{-1}$ ), abundant resource of iron, and chemical stability, although it has poor electrical conductivity ( $10^{-9}$ – $10^{-10}$   $\text{S cm}^{-1}$ ) [3–5]. In order to overcome this disadvantage and utilize it as positive electrode material, two approaches have been widely in progress; minimizing the particle size and/or introducing conductive additives. Although minimizing the particle size of  $\text{LiFePO}_4$  improves the cycle performance [6], it causes less packing of the electrochemically active particles. The introduction of conductive additives, such as carbon coating on the surface of  $\text{LiFePO}_4$  or preparing  $\text{LiFePO}_4/\text{C}$  composite positive electrodes, has successfully improved the cell specific capacity even at higher current density [7].

In this work, we have applied spark-plasma-sintering (SPS) method [8] as one of the technique to prepare  $\text{LiFePO}_4/\text{C}$  composite electrodes. The SPS process makes

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use of a microscopic electrical discharge between particles [8,9], and it could generate strong binding between active particles and carbon additives and form dense composite positive electrodes. We have prepared  $\text{LiFePO}_4/\text{C}$  composite positive electrodes using the SPS process, and examined their tap densities, particle size distributions, and charge/discharge properties as compared with those of the conventionally blended  $\text{LiFePO}_4 + \text{C}$  powders.

## 2. Experimental

$\text{LiFePO}_4$  powder was prepared by hydrothermal method [10]. The mixed solution of  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ , and  $\text{NH}_4\text{H}_2\text{PO}_4$  with a molar ratio of 2.5:1:1 was subjected to the hydrothermal reaction at  $220^\circ\text{C}$  for 5 h.  $\text{Na}_2\text{SO}_3\cdot 7\text{H}_2\text{O}$  ( $\text{FeSO}_4:\text{Na}_2\text{SO}_3 = 1:0.2$ ) was introduced to protect ferrous iron from the oxidation. Thus obtained  $\text{LiFePO}_4$  was blended thoroughly with acetylene black in weight ratio of 8:2 and then allowed to the SPS treatment (SPS-515S, Sumitomo Coal Mining) at  $600^\circ\text{C}$  for 5 min, to form the  $\text{LiFePO}_4/\text{C}$  composites.

The samples were characterized by X-ray diffractometry (XRD; Rigaku Rotaflex RU-200B/RINT using monochromatic  $\text{Cu K}\alpha$  radiation), field-emission scanning electron microscopy (FE-SEM; Hitachi S-5000), laser diffraction and scattering measurements (Shimadzu SALD-2000), and  $^{57}\text{Fe}$  Mössbauer measurements (Model 222B, Topologic Systems, using  $\alpha\text{-Fe}$  as velocity calibration).

Electrochemical lithium insertion/extraction reactions were carried out using lithium coin-type cells. The working

electrode consisted of a mixture of 25 mg  $\text{LiFePO}_4/\text{C}$  sample and 0.5 mg Teflon powders pressed into a tablet of 15 mm diameter. The electrochemical test cells were constructed in a stainless steel coin-type configuration. The negative electrode was a 15 mm diameter and 0.2 mm thick disk of Li foil, and the separator was a microporous polyolefin sheet. The solution of 1 M  $\text{LiPF}_6$  in a 50:50 mixture of ethylene carbonate (EC) and diethylcarbonate (DEC) by volume (Tomiya Pure Chemical Industries Ltd., battery grade) was used as an electrolyte. Electrochemical measurements were carried out at  $30^\circ\text{C}$  after standing over night on open circuit, using a TOSCAT-3100 (Toyo System), with current densities of 34 and  $170\text{ mA g}^{-1}$  (0.2 and 1 C). Additional electrochemical measurements using carbon anode were also carried out under various current rates ranging from 17 to  $850\text{ mA g}^{-1}$  (0.1–5 C).

## 3. Results and discussion

The SPS-treated  $\text{LiFePO}_4/\text{C}$  composites were black in color, and their appearance was similar to that of the  $\text{LiFePO}_4 + \text{C}$  conventionally blended powder. Each XRD peak of  $\text{LiFePO}_4/\text{C}$  composites was indexed by the orthorhombic unit cell ( $Pmnb$ ), and the estimated lattice parameters ( $a = 6.00191(18)\text{ \AA}$ ,  $b = 10.3175(3)\text{ \AA}$ ,  $c = 4.69001(15)\text{ \AA}$ ) were in good agreement with those reported previously ( $a = 6.008(3)\text{ \AA}$ ,  $b = 10.334(4)\text{ \AA}$ ,  $c = 4.693(1)\text{ \AA}$ ) [3]. Any impurity peaks were not observable in  $\text{LiFePO}_4/\text{C}$  composites in XRD profiles.

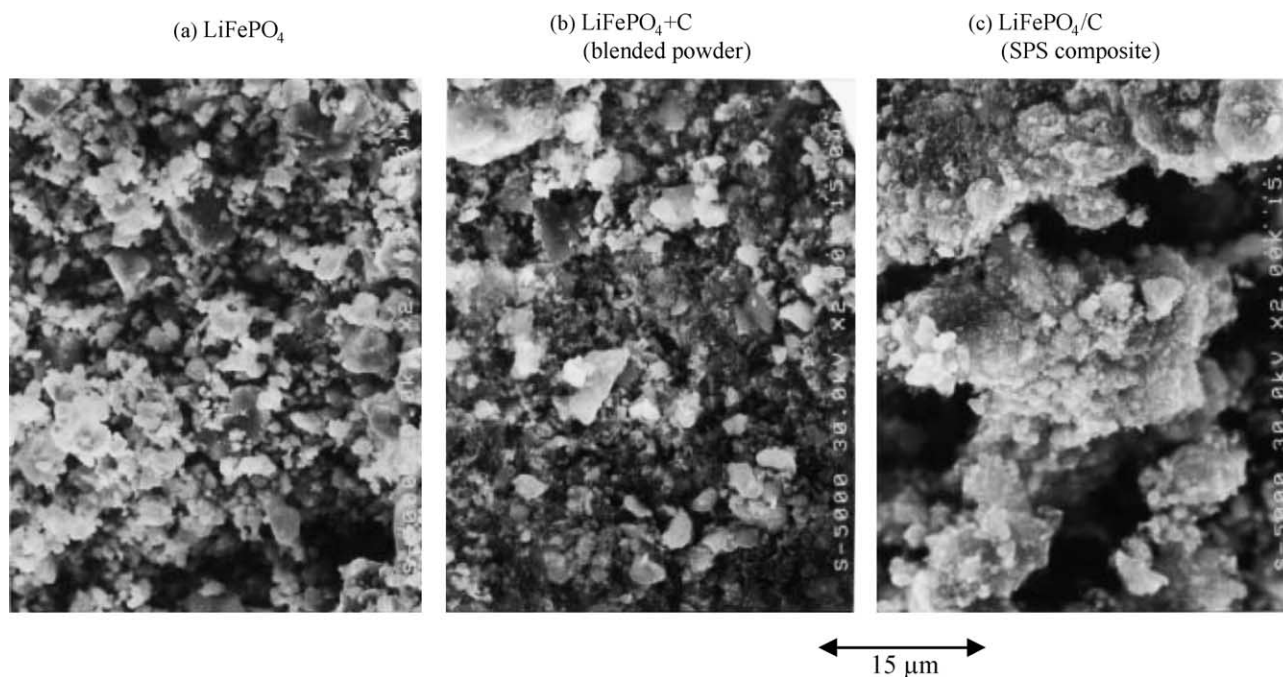


Fig. 1. SEM images of (a) initial  $\text{LiFePO}_4$  powder, (b)  $\text{LiFePO}_4 + \text{C}$  blended powder, and (c)  $\text{LiFePO}_4/\text{C}$  composite samples. Magnification is the same for each micrograph.

Fig. 1 shows typical SEM micrographs of the initial  $\text{LiFePO}_4$  powder,  $\text{LiFePO}_4 + \text{C}$  blended powder, and SPS-treated  $\text{LiFePO}_4/\text{C}$  composite. The initial  $\text{LiFePO}_4$  consisted of mainly micrometer-sized particles, and it remained nearly unchanged after blended with nanometer-sized acetylene black. After the SPS treatment,  $\text{LiFePO}_4$  and acetylene black formed agglomerates with the size of  $>10 \mu\text{m}$ , where  $\text{LiFePO}_4$  particles were connected each other via carbon particles. These SEM observations were consistent with the results of particle size distribution measured by laser diffraction and scattering method, Fig. 2. The initial  $\text{LiFePO}_4$  powder consisted of  $0.4\text{--}10 \mu\text{m}$  particles, and the average particle size, represented by the value at 50% cumulative population ( $d_{50\%}$ ), was  $1.6 \mu\text{m}$ . This distribution did not change significantly after blended with acetylene black, Fig. 2b, and it showed similar  $d_{50\%}$  value ( $1.5 \mu\text{m}$ ). After the SPS treatment, the population of larger particles of  $>10 \mu\text{m}$  drastically increased, resulting in larger  $d_{50\%}$  value ( $3.2 \mu\text{m}$ ), which is consistent with the presence of agglomerates of  $>10 \mu\text{m}$  in SEM observations. Although the presence of agglomerated active particles usually decreases tap density, the present SPS-treated composites showed relatively higher tap density; it increased from  $0.7$  to  $1.1 \text{ g cm}^{-3}$  by the SPS treatment ( $0.7 \text{ g cm}^{-3}$  is the value for the  $\text{LiFePO}_4 + \text{C}$  blended powder before the SPS treatment). This would be advantageous for preparing higher density electrodes, as described later. Thus, the densification and carbon contacts to  $\text{LiFePO}_4$  were simultaneously achieved by the present SPS treatment.

The oxidation state of Fe for the samples was checked by  $^{57}\text{Fe}$  Mössbauer spectroscopy. The spectra for both

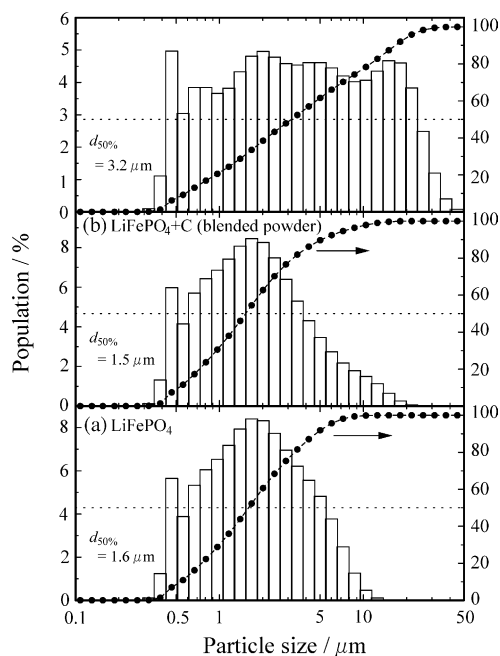


Fig. 2. Particle size distribution measured by laser diffraction and scattering method for (a) initial  $\text{LiFePO}_4$  powder, (b)  $\text{LiFePO}_4 + \text{C}$  blended powder, and (c)  $\text{LiFePO}_4/\text{C}$  composite samples. The average particle size is represented by the value at 50% cumulative population ( $d_{50\%}$ ).

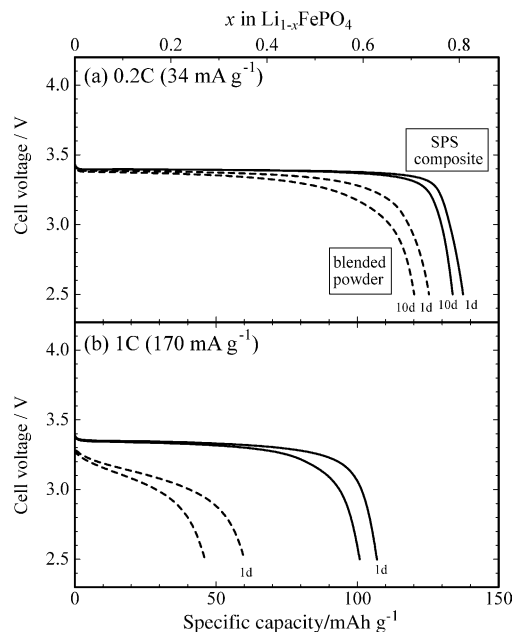


Fig. 3. Initial and 10th discharge profiles for  $\text{LiFePO}_4 + \text{C}$  blended powder and  $\text{LiFePO}_4/\text{C}$  composite sample cells.

$\text{LiFePO}_4 + \text{C}$  blended powder and  $\text{LiFePO}_4/\text{C}$  composite were analyzed as being composed of two doublets with isomer shifts (IS) of  $+1.22 \text{ mm s}^{-1}$ , which is consistent with the previously reported value ( $+1.22 \text{ mm s}^{-1}$ ) for high-spin  $\text{Fe}^{2+}$  in  $\text{LiFePO}_4$  [4], and  $\text{IS} = +0.3\text{--}+0.4 \text{ mm s}^{-1}$ , which is close to the value ( $+0.37 \text{ mm s}^{-1}$ ) for high-spin  $\text{Fe}^{3+}$  in  $\alpha\text{-LiFeO}_2$  [11]. A notable point is that the amount of the  $\text{Fe}^{3+}$ -containing phase, estimated by the area of the component, decreased after the SPS treatment (from 4 to 1%). The reductive condition during the SPS treatment resulted in such “purification” of the samples, and it could be advantageous for increasing charge/discharge capacity [4].

Fig. 3 shows the initial and 10th discharge curves for the cells with  $\text{LiFePO}_4 + \text{C}$  blended powder and SPS-treated  $\text{LiFePO}_4/\text{C}$  composite samples. The carbon contents, estimated by the Rietveld analyses of the respective XRD profiles using the program RIETAN-2000 [12], were nearly the same (approximately 17 wt.%) for both samples. The discharge capacities were enlarged by the SPS treatment, particularly at higher current density (1 C), and the capacity degradation rate with redox cycling was much reduced (from 23 to 6% for 1st–10th discharge at 1 C rate). Since the tap density of active particles increased by the SPS treatment, the effective volumetric discharge capacities were considerably enlarged by the SPS process. In addition, the discharge plateau around 3.4 V became longer by the SPS treatment. These improvements of the charge/discharge performance suggest that carbon powder was strongly bound to  $\text{LiFePO}_4$  particles in the composite samples and the electrical connection remained unchanged during the electrochemical redox cycling. Indeed, as shown in Fig. 4, the surfaces of  $\text{LiFePO}_4$  particles in the SPS composites were still covered with carbon

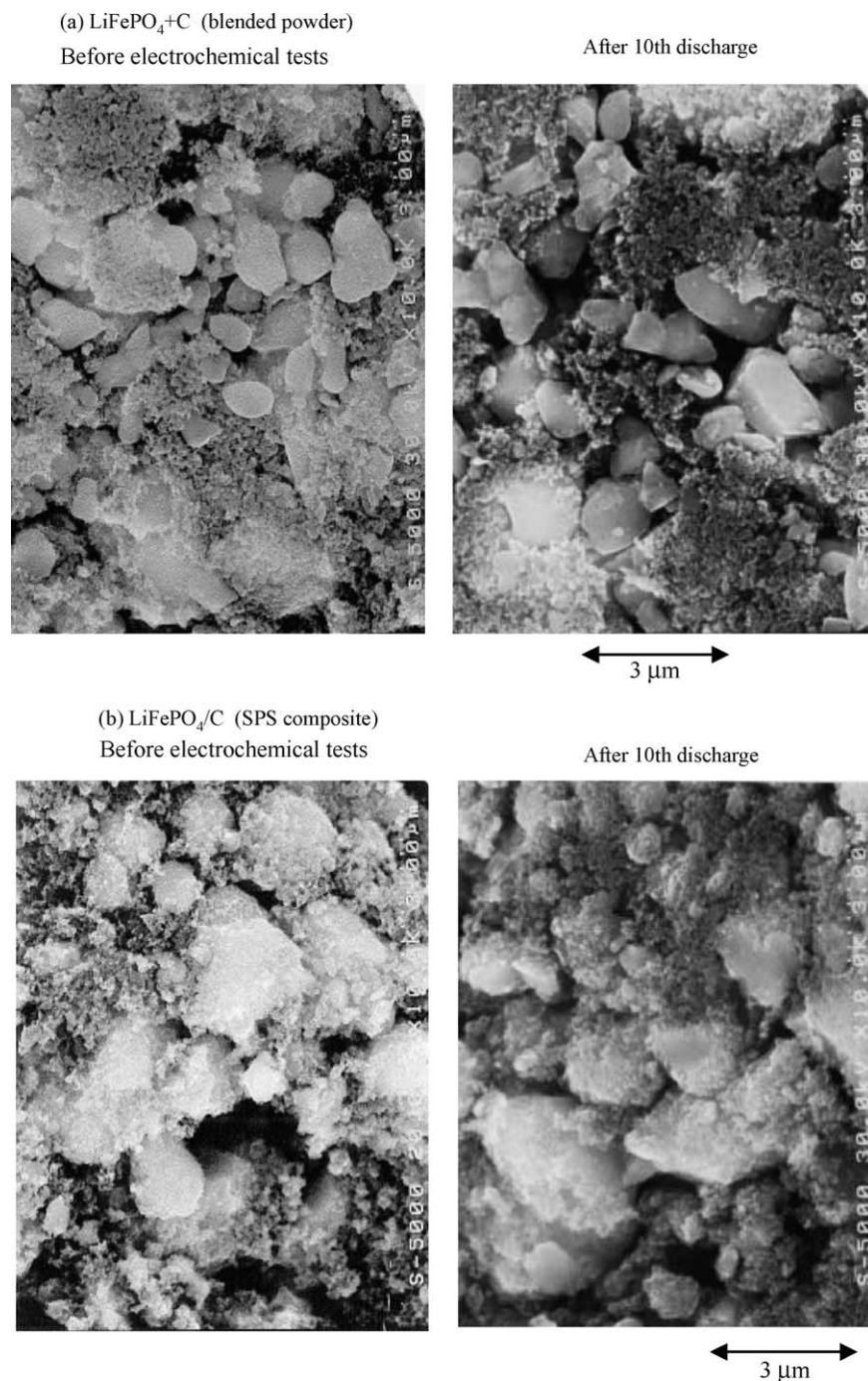


Fig. 4. SEM images of (a)  $\text{LiFePO}_4 + \text{C}$  blended powder and (b)  $\text{LiFePO}_4/\text{C}$  composite samples before electrochemical tests and after electrochemical tests over 10 cycles at a rate of  $34 \text{ mA g}^{-1}$ . Magnification is the same for each micrograph.

even after 10th discharging. This makes a clear contrast for the blended  $\text{LiFePO}_4 + \text{C}$  samples, where the surfaces of  $\text{LiFePO}_4$  particles seemed smooth and clear before and after electrochemical cycling, which indicates much less binding between  $\text{LiFePO}_4$  and carbon powders. Other contribution for the improvements in the charge/discharge performances for the SPS samples would be the decrease in the amount of  $\text{Fe}^{3+}$ -containing phase, as described above [4]. Also, heat treatment at  $600^\circ\text{C}$  during the SPS process may be advan-

tageous for removing detrimental chemical species on the surface of  $\text{LiFePO}_4$ , as in the case of  $\text{LiCoO}_2$  [13].

Using the present SPS-treated  $\text{LiFePO}_4/\text{C}$  composite samples, thin positive electrodes with the thickness of approximately  $60 \mu\text{m}$  were prepared, and rate capability tests were carried out. The electrode density and its electrical conductivity were listed in Table 1, with those for the electrodes prepared from  $\text{LiFePO}_4 + \text{C}$  blended powder for comparison. The electrode density increased by the SPS treatment; from

Table 1

Thickness ( $t/\mu\text{m}$ ), density ( $d/\text{g cm}^{-3}$ ), and electrical conductivity ( $\sigma/\text{S cm}^{-1}$ ) of the thin positive electrodes prepared from  $\text{LiFePO}_4 + \text{C}$  blended powder and  $\text{LiFePO}_4/\text{C}$  composites

	$t$ ( $\mu\text{m}$ )	$d$ ( $\text{g cm}^{-3}$ )	$\sigma$ ( $\text{S cm}^{-1}$ )
$\text{LiFePO}_4 + \text{C}$ blended powder	68	1.48	$2.91 \times 10^{-2}$
$\text{LiFePO}_4/\text{C}$ composites	57	1.80	$1.52 \times 10^{-2}$

The origin of slightly lower conductivity for  $\text{LiFePO}_4/\text{C}$  composites is unclear.

1.48 to  $1.80 \text{ g cm}^{-3}$ , increased by approximately 22%. This is consistent with the increase in the tap density, as described above, and is advantageous for improving the cell volumetric capacity. The electrode conductivity, which included that of Al substrate, showed slightly lower value for the  $\text{LiFePO}_4/\text{C}$  composites, and its origin was unclear. Fig. 5 shows the initial discharge curves with different current density ranging from 17 to  $850 \text{ mA g}^{-1}$  (0.1–5 C) for the cell with  $\text{LiFePO}_4/\text{C}$  composite electrodes. Even at higher current density ( $>1 \text{ C}$ ), the cell showed the redox cycling with the specific capacities of  $>90 \text{ mAh g}^{-1}$ . And the cell with thin positive electrodes showed relatively small capacity fading; the discharge capacities over 100 cycles were approximately 85% of the initial values when cycled at 1 C rate. These cycle performances, particularly at higher current density, would be attributed to strong binding between carbon and  $\text{LiFePO}_4$  particles, and their electrical connections remained unchanged even under higher rate electrochemical redox cycling. Thus, the electrochemical performance was improved by reinforcing the

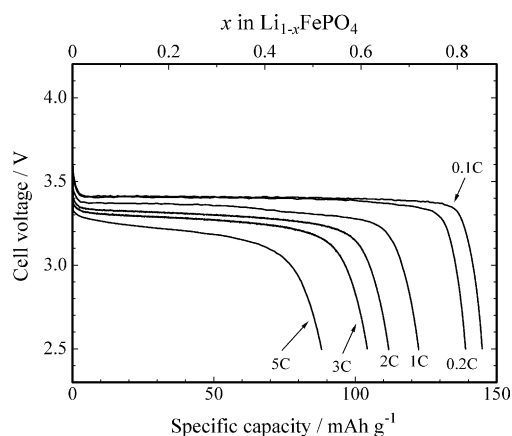


Fig. 5. Initial discharge profiles for the thin positive electrode cells prepared from  $\text{LiFePO}_4/\text{C}$  composite samples, cycled at different current density ranging from 17 to  $850 \text{ mA g}^{-1}$  (0.1–5 C) at room temperature using carbon anode.

interface connection between  $\text{LiFePO}_4$  and carbon particles, and this method would be applicable to other active materials.

#### 4. Conclusion

We have successfully prepared dense  $\text{LiFePO}_4/\text{C}$  composite electrodes using the SPS technique. The SPS-treated composites showed that  $\text{LiFePO}_4$  and carbon particles formed agglomerates with the size of about  $10 \mu\text{m}$ , which resulted in higher electrode density. Charge/discharge tests for the cells with the SPS-treated composites showed the improved cycle performance, particularly at higher current density, compared with those of the  $\text{LiFePO}_4 + \text{C}$  blended powder. These improvements of the cell performance were attributed to the strong binding between  $\text{LiFePO}_4$  and carbon powders, and these electrical connections remained unchanged during electrochemical redox cycling. Thus, the electrochemical performance was improved by reinforcing the interface connection between active particles and carbon powders.

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