

Short communication

## LiFePO<sub>4</sub>-based electrode using micro-porous current collector for high power lithium ion battery

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### Abstract

In order to improve the power performance of the lithium ion battery based on lithium iron phosphate (LiFePO<sub>4</sub>), a new methodology using a three-dimensional micro-porous current collector was described. The three-dimensional current collector was manufactured based on foamed polyurethane and nickel–chromium alloy. The cell using the three-dimensional current collector exhibited a superior high-rate discharge capability as compared to a conventional-type cell using the aluminum foil current collector. Furthermore, impedance analysis revealed the size reduction of a semicircle for the charge-transfer resistance by applying the three-dimensional current collector, which indicates a superior current collecting ability for the developed substrate.

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**Keywords:** Lithium iron phosphate; Positive electrode; Three-dimensional current collector; High-power application

### 1. Introduction

Lithium iron phosphate (LiFePO<sub>4</sub>) has been extensively studied because of its superior properties such as a high thermal stability at the charged state, low toxicity, and large theoretical capacity (170 mAh g<sup>-1</sup>) [1–7]. Recently, the LiFePO<sub>4</sub>-based battery attracts attention as a power source for hybrid electric vehicles (HEVs) owing to its many advantages described above. However, LiFePO<sub>4</sub>-based batteries generally exhibit poor high-rate performances, since LiFePO<sub>4</sub> itself shows low conductivity ( $\sim 10^{-9}$  S cm<sup>-1</sup>) compared with the conventional LiCoO<sub>2</sub> ( $\sim 10^{-3}$  S cm<sup>-1</sup>) [2,3]. In order to improve the high-rate performance of the LiFePO<sub>4</sub>-based batteries, the enhancement in the electric conductivity of the active materials by doping with other elements [2,3] or by coating with electronic conductive materials on the particles [4,5] has been widely performed. The size reduction of the active material particle has been also reported to be an effective way [6,7]. In this paper, we propose a new method-

ology using a three-dimensional porous current collector made from nickel–chromium alloy. The influence of the structure of the current collector on the high-rate discharging performance was discussed.

### 2. Experimental

The three-dimensional current collector was manufactured by alloying the conventional foam-type nickel substrate with metallic chromium powder. The foam-type nickel substrate was manufactured by nickel plating on foamed polyurethane followed by a heat treatment to remove the inner polyurethane. Onto the resultant foam-type nickel substrate, metallic chromium powder was then adsorbed, which was reheated to initiate the alloy formation. X-ray diffraction (XRD) measurements were used to confirm the alloy formation. The chromium ratio was determined to be approximately 35% by X-ray fluorescence (XRF) (ZSX Primus II, Rigaku Corp.) and inductively coupled plasma emission spectrophotometer (ICP) (IRIS RP Advantage, Nippon Jarrell-Ash Co. Ltd.) measurements. The morphology of the substrate was examined with a scanning electron microscope (SEM) (VE-9800, Keyence Corp.). Analytical data of the substrate such as weight, thickness, porosity, average pore diameter,

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and specific surface areas were  $450 \text{ g m}^{-2}$ ,  $1.4 \text{ mm}$ ,  $96\%$ ,  $85 \mu\text{m}$ , and  $0.2 \text{ m}^2 \text{ g}^{-1}$ , respectively. The corrosion resisting property of the developed substrate was estimated by using the cyclic voltammetric (CV) measurement with an electrochemical analyzer (SI 1280B, Solartron). The voltammogram was recorded at a scan speed of  $0.1 \text{ mV s}^{-1}$ , with a potential range of  $2.0\text{--}5.0 \text{ V}$  versus a lithium ( $\text{Li}^+/\text{Li}$ ) reference electrode.

Carbon layer deposited  $\text{LiFePO}_4$  (primary particle diameter:  $70\text{--}100 \text{ nm}$ ) was provided by Mitsui Engineering & Shipbuilding Co. Ltd. [8]. The slurry for the positive electrode was prepared by mixing carbon layer deposited  $\text{LiFePO}_4$ , ketchen black as the conductive additive, and polyvinylidene fluoride (PVdF) as the binder in a weight ratio of  $86:2:12$  with *N*-methyl-2-pyrrolidone (NMP). The prepared slurry was loaded into the three-dimensional substrate ( $\phi 12 \text{ mm}$ ); and the resultant electrode was dried, and then roll-pressed to the thickness of  $160 \mu\text{m}$ . For a comparison, a conventional-type electrode was also prepared by using aluminum foil as the current collector (electrode thickness:  $110 \mu\text{m}$ ). Both positive electrodes were prepared such that they have approximately the same capacity densities of  $2.4\text{--}2.5 \text{ mAh cm}^{-2}$  (deposited amount of the cathode material:  $15\text{--}16 \text{ mg cm}^{-2}$ ). The prepared each electrode and lithium sheet as a negative electrode were placed into an R2032 coin type cell case with a glass filter. After an electrolyte of the mixed solution of ethylene carbonate and diethyl carbonate (1:1) containing lithium hexafluorophosphate of  $1.0 \text{ mol L}^{-1}$  was added, the cell case was sealed.

Prior to a high-rate discharging test, a charge/discharge pattern was applied for the prepared cells several times using a current density of  $0.2 \text{ C}$  rate with a voltage range of  $2.5\text{--}4.0 \text{ V}$ . The high-rate discharging capabilities of the cells were examined by using a pulse-type discharging for  $2 \text{ s}$  at various current densities ranging from  $0.2$  to  $30 \text{ C}$  rates. In the pulse-type test, the state of charge (SOC) of the cells was controlled to be  $50\%$  since the actual battery in the HEV system is managed to have a partially charged state during driving to facilitate both charging and discharging [9]. All of the charge/discharge tests were performed at  $25^\circ \text{C}$  with a computer-controlled charge/discharge system (BLS series, Keisokuki Center Co. Ltd.). The electrochemical impedance spectra of the cells were recorded with a frequency response analyzer (SI 1280B, Solartron) at the discharged states. The frequency range from  $2 \times 10^{-1}$  to  $2 \times 10^4 \text{ Hz}$  with an alternative current signal of  $0.1 \text{ mA}$  amplitude was used for the measurement.

### 3. Results and discussion

Fig. 1 shows an SEM image of the developed three-dimensional substrate. The substrate has a three-dimensional framework structure based on the foamed polyurethane as seen in the image. The active material particles can be filled uniformly in the inner pore space of the three-dimensional current collector. Besides, the substrate has a large surface area due to its characteristic structure. The surface area per apparent unit area calculated from the value obtained by the BET method was approximately  $100 \text{ m}^2 \text{ m}^{-2}$ , which can improve the current collecting ability of the substrate. In the electrochemical toler-

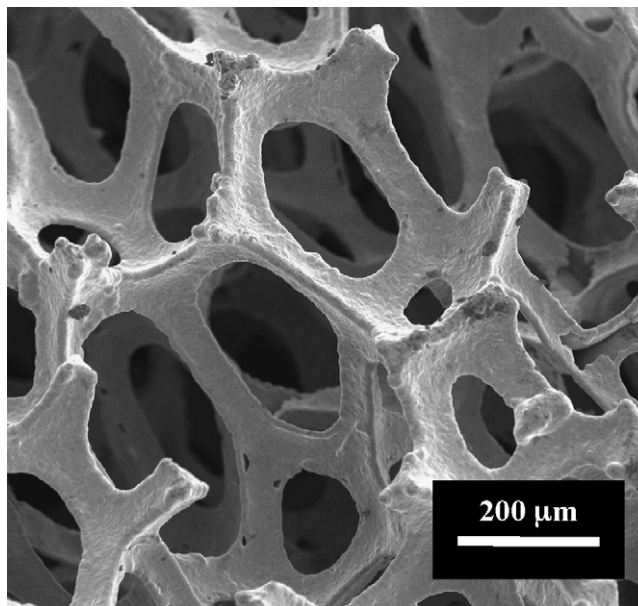


Fig. 1. SEM image of the foam-type three-dimensional current collector.

ance test using the CV measurement, a high anodic potential was observed for the developed substrate compared with a pure nickel substrate. The pure nickel substrate exhibits a growing current curve above around  $4.0 \text{ V}$  owing to corrosion. In contrast, the developed substrate exhibits a small anodic peak at around  $4.7 \text{ V}$  during the first cycle. Besides, the substrate shows no peak after that cycle in a voltage range of  $2.0\text{--}5.0 \text{ V}$ . This polarization behavior is attributed to the formation of a passivation film on the surface, which will improve the electrochemical tolerance of the substrate.

Fig. 2 shows a comparison of the charge–discharge curves at the  $0.2 \text{ C}$  rates for the cells using the three-dimensional, and the foil-type substrates as the current collectors. Both cells exhibit almost the same discharge capacity of approximately  $150 \text{ mAh g}^{-1}$ , which are comparable value for actual capacity of  $\text{LiFePO}_4$  at this discharge current [2,8]. In our preparatory experiment, the  $\text{LiFePO}_4$ -based cell with a pure nickel substrate did not show sufficient cycle stability probably due to the corrosion of nickel. On the other hand, the cell using the three-dimensional substrate made of nickel–chromium alloy exhibited stable charge–discharge behavior due to the improved corrosion resistance property of the alloy. In addition, the cell using the substrate exhibits a comparable cycle-life performance to the cell using the aluminum foil substrate as shown in Fig. 3, which also indicates the improved durability of the developed substrate.

Considering HEV usage of the cell, a pulse-type high-rate discharge test was applied for the cells. For the battery in the HEV system, high performance in a transient discharging is strongly required for the battery to facilitate rapid acceleration of the vehicle [9]. Fig. 4 shows the relationship between the voltages after  $2 \text{ s}$  discharge at the  $50\%$  SOC of the cells, and the discharging currents as the current–voltage ( $I\text{--}V$ ) curves with the closed circles and squares. The power output curves are also shown in the figure using the open ones. The cell using the three-dimensional substrate exhibits superior performance in

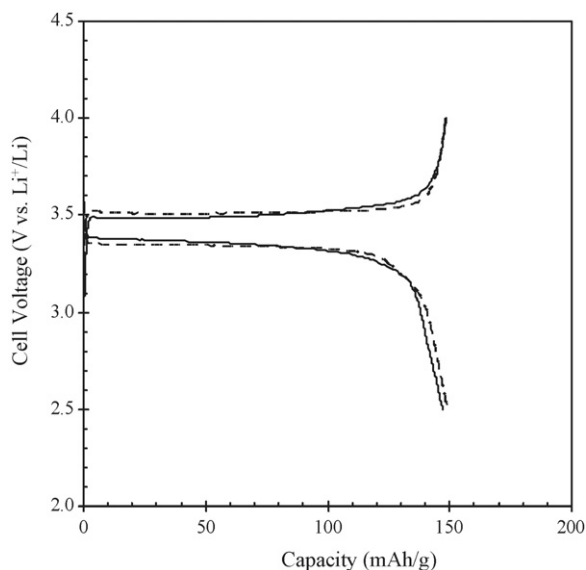


Fig. 2. Charge and discharge curves of the cells using the foam-type three-dimensional substrate (solid line) and the conventional foil-type aluminum substrate (broken line). Current densities of 0.2 C rates were applied for both charge and discharge.

almost all the current rates compared with the conventional cell using the foil-type substrate. At a current of about  $60 \text{ mA cm}^{-2}$  (25 C rate), the voltage of the cell using the foil-type substrate falls to 0 V versus Li<sup>+</sup>/Li, while that of the cell using the three-dimensional substrate exhibits much higher value of 2.4 V versus Li<sup>+</sup>/Li at this current. Furthermore, the cell using the three-dimensional substrate exhibits more than three times larger power maximum value than the conventional cell using the foil-type substrate. In general, the electrode for high-power application is manufactured to be thin [10–12]. Actually, the carbon layer deposited LiFePO<sub>4</sub> itself used in this paper exhibits an

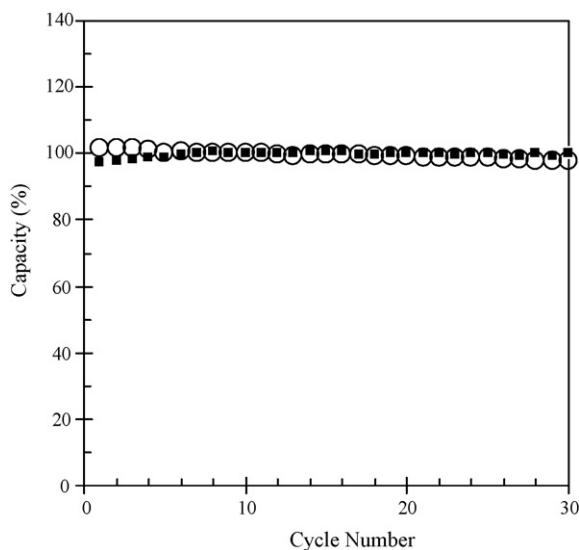


Fig. 3. Cycle-life performance of the cells using the foam-type three-dimensional (○) and the foil-type Al (■) substrates at 25 °C. Charge/discharge current: 0.2 C rate, potential range: 2.5–4.0 V.

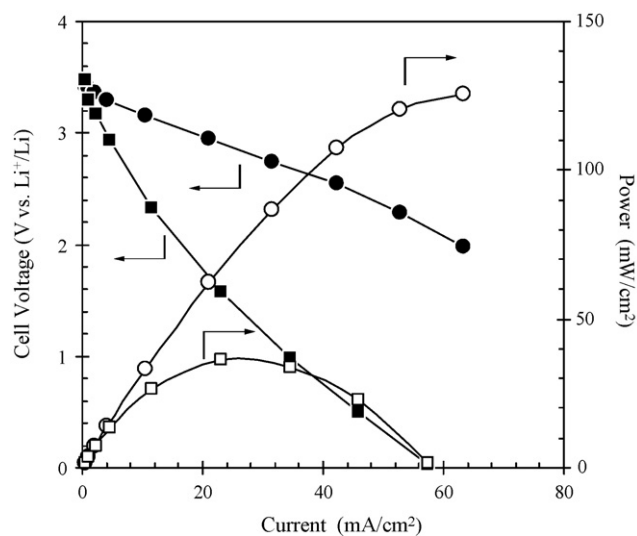


Fig. 4. Current–voltage plots of the cells at 50% SOC. The relationships between the current and the calculated power are also presented. The voltages after 2 s were used for the calculation of the power. The closed circles (●) and the open circles (○) represent the voltage and the power of the cell using the foam-type three-dimensional substrate, respectively. The closed squares (■) and the open squares (□) represent the voltage and the power of the cell using the foil-type substrate, respectively.

excellent high-rate performance at high-rate discharge [8] when it is prepared in a thin electrode condition. However, the thin electrode requires a large net volume of other materials such as separator and substrate, which decreases the total capacity as a result. Therefore, the development of the thick electrode exhibiting high-power has been strongly desired. In our case, the cell using the three-dimensional substrate showed an excellent high-rate performance in spite of having used an electrode thicker than 100 μm, which is considered to be due to the superior current collecting ability of the substrate as compared to the conventional foil-type one.

The preparation of the thick electrodes usually requires much amount of chemical binder such as PVdF, which would become additional electric resistance components of the electrodes. In particular, this tendency becomes noticeable in the case using small particles as active material. By applying the three-dimensional substrate, the amount of the chemical binder can be reduced because of the high retention ability of the substrate for the active materials, which would also lead to much improvement in the high-power capability of the LiFePO<sub>4</sub>-based electrode.

To investigate the observed difference in the pulse-type discharging test in detail, the electrochemical impedance measurement was also applied for the cells. The Nyquist plots and the Bode plots of the cells are shown in Fig. 5a and b, respectively. In the Nyquist plots, each curve consists of a semicircle in the high-frequency regions and a tilted straight line in the low-frequency regions. This observed impedance behavior is a typical pattern for Li-ion batteries and is expressed using an equivalent circuit shown in the inset of Fig. 5a. In this equivalent circuit,  $R_O$ ,  $R_{CT}$ ,  $Z_W$ , and CPE represent the total ohmic resistance of the cell components, the charge-transfer resistance of the electrodes, the Warburg impedance, and the

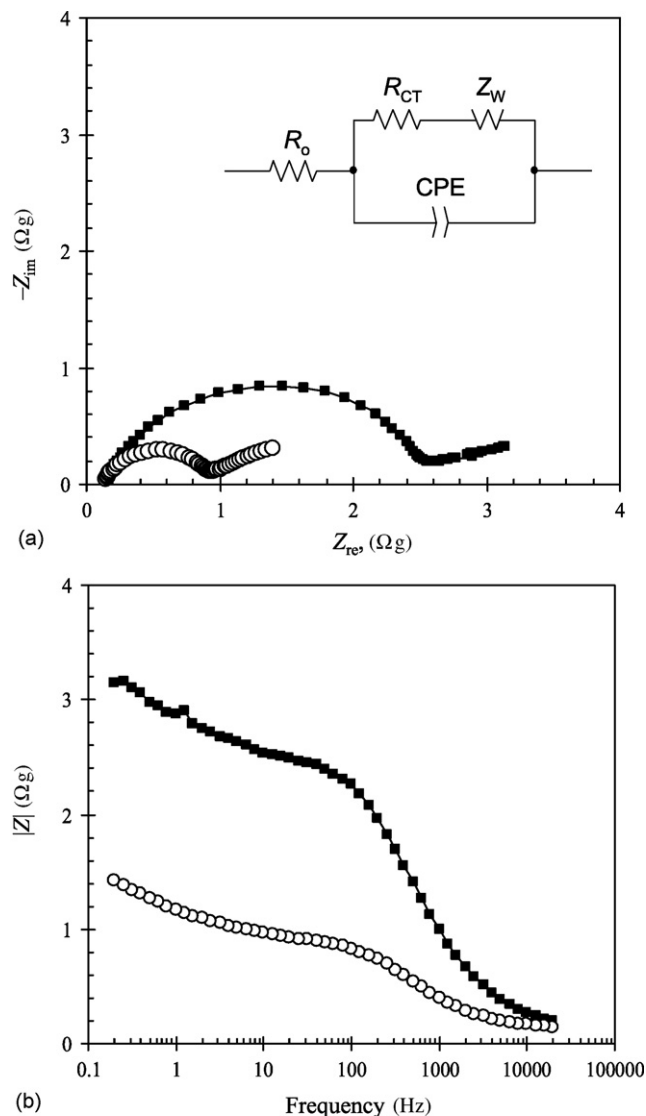


Fig. 5. Nyquist plots (a) and Bode plots (b) of the cells using the foam-type three-dimensional (○) and the foil-type (■) substrates. The inset shows the corresponding equivalent circuit.

capacitive constant-phase element, respectively. In the Nyquist plot, the semicircle observed in high frequency region and the tilted straight line in low frequency region correspond to the charge-transfer process, and the diffusion process in electrochemical reaction, respectively.

In Fig. 5a, both curves start from approximately the same point on the real axis in the high-frequency region, which indicates that both cells have almost the same ohmic resistances. However, a clear difference is observed in the size of the semicircle: the cell using the three-dimensional substrate shows a smaller charge-transfer resistance than the cell using the foil-type substrates. Their sizes were estimated to be 0.8 and 2.4  $\Omega \text{g}$ , respectively, by the fitting of the semicircles. In the Bode plots, the cell using the three-dimensional substrate also shows smaller impedance than the cell using the foil-type substrate in the wide frequency range.

Several groups have reported similar decreases in the charge-transfer resistance by the addition of conductive materials into the positive electrodes [13,14] or by modifying the morphology of the substrate surface [15]. These studies indicate that there exists a close relationship between the charge-transfer resistance and the current collecting ability of the electrode. In our case, the observed difference in the size of the semicircles for the charge-transfer resistances can be ascribed mainly to the differences in the structure of the current collector. A large effective contact area between the active material particles and the current collector due to the characteristic three-dimensional structure contributes to reducing the charge-transfer resistance of the positive electrode, which is considered to improve the high-rate discharge performance of the LiFePO<sub>4</sub> cell.

#### 4. Conclusions

A three-dimensional substrate that exhibits high tolerance in organic electrolytes was prepared as the current collector for the lithium ion battery by using foamed polyurethane and nickel–chromium alloy. In the power output measurement of the prepared LiFePO<sub>4</sub>-based cells, the one using the three-dimensional substrate exhibited an approximately three-times larger value than the conventional one using the foil-type aluminum current collector, which is considered to be due to the characteristic current collecting ability of the three-dimensional substrate. In the electrochemical impedance measurement, the charge-transfer resistance for the positive electrode was considerably reduced on applying the three-dimensional substrate as the current collector, which also indicates the excellent current collecting property of the three-dimensional substrate.

The methodology using a three-dimensional current collector was revealed to improve the high-rate discharge performance of the LiFePO<sub>4</sub>-based lithium ion battery. By designing the structure of the three-dimensional substrate, it would lead to much more improvement of the high-power battery.

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