Electrochemical Performance of LiMn$_{0.7}$Fe$_{0.3}$PO$_4$/C Secondary Particles in Various Cathode Compositions

リチウムイオン電池用正極材 LiMn$_{0.7}$Fe$_{0.3}$PO$_4$/C 造粒体における電極配合が電気化学的特性に与える影響

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平山愉子*, 山下弘樹*, 大神剛章**

ABSTRACT

The effects of cathode compositions including 90–99 wt.% active material on the electrochemical performance of lithium-ion batteries were studied. The cathodes were comprised of LiMn$_{0.7}$Fe$_{0.3}$PO$_4$/C secondary particles as the active material, acetylene black (AB) as the conductive additive, and polyvinylidene fluoride (PVDF) as the binder in N-methyl-2-pyrrolidone. The area ratio of the active material on the cathode surface analyzed by backscattered electron imaging was found to decrease with the increase in the AB content in the cathodes. The electrical conductivity of the cathodes increased with the increase in the weight ratio of AB and the decrease in the weight ratio of the active material in the cathodes. The discharge capacity of the cathodes including 90–99 wt.% active material was between 153.1–157.3 mAh g$^{-1}$ at a current rate of 0.2 C, showing an increase with the decrease in the weight ratio of the active material. Their energy density was found to be between 560.5–592.0 Wh kg$^{-1}$. In addition, the capacity retention rate of the cathodes having 90–98 wt.% active material was between 79.8–91.5% at current rates of 5/0.2 C, showing an increase with the decrease in the weight ratio of the active material in the cathodes. This was likely due to the low $R_{ct}$ associated with the decreasing weight ratio of the active material. Among the cathode compositions with an AB/PVDF weight ratio of 1/3, 1 and 3, those with AB/PVDF=1 were found to achieve the lowest $R_{ct}$ and thus the best rate capability with any active material ratios.
要        旨
90wt.%以上の活物質を含む正極において, 電極配合がリチウムイオン電池の電気化学的特性に与える影響を評価した. 正極は, 活物質としてLiMn_{0.7}Fe_{0.3}PO_4/C造粒体, 導電助剤としてアセチレンブラック(AB), 結着剤としてポリフッ化ビニリデン(PVDF)を使用し, N-メチル-2-砒ロリドンと混合して作製した. 反射電子像より解析した正極表面の活物質面積率は, AB量の増加に伴い減少した. 正極の導電率は, AB量の増加, 活物質量の減少に伴い増加した. 90−99wt.%の活物質を含む正極の0.2Cにおける放電容量は153.1−157.3mAh g⁻¹を示し, 活物質量の減少に伴い増加した.このときエネルギー密度は560.5−592.0Wh kg⁻¹であった.また, 90−98wt.%の活物質を含む正極の5/0.2Cにおける容量維持率は79.8−91.5%を示し, 活物質量の減少に伴って増加した. これは, 電荷移動抵抗の低下によるものと考えられる. 90−99wt.%の活物質比率において, AB/PVDF比=1/3, 1, 3のうち1が最も低い電荷移動抵抗および最も高いレート特性を示した.

キーワード : リチウムイオン電池, 正極活物質, リン酸マンガン鉄リチウム, 造粒体

1. INTRODUCTION
Lithium-ion batteries (LIBs) are used in electronic devices, such as smartphones and electric vehicles, among others. Recently, their market has expanded.①②Active material for LIBs provides higher power density, energy density, and safety; thus, investigation in this area has been on for the last decades.③④Olivine-structured lithium transition metal phosphates (LiMPO_4 (M = Fe, Mn, Ni, or Co)), an active material, have environmental benignity, low cost, and superior safety compared to the conventional transition-metal oxide active material, such as LiNi_{x}Mn_{y}Co_{2}O_2.⑤ However, lithium manganese iron phosphates (LiMn_{1−x}Fe_xPO_4) have been considered to be promising active material for next-generation LIBs due to their higher energy density than conventional lithium iron phosphates (LiFePO_4).⑤⑥ The electrochemical performance of LiMn_{1−x}Fe_xPO_4 has been improved by several researchers since first reported by J. B. Goodenough et al.⑦ However, few studies have focused on cathode compositions. Discharge capacities of LiMn_{1−x}Fe_xPO_4 for various cathode compositions in previous reports are summarized in Table 1. Hao Yang et al.⑧ reported the electrochemical performance of LiMn_{0.5}Fe_{0.5}PO_4 on a cathode consisting of 80 wt.% active material (LiMn_{0.5}Fe_{0.5}PO_4), 10 wt.% ketjen black, and 10 wt.% polyvinylidene fluoride (PVDF). They showed a high discharge capacity of 169 mAh g⁻¹ at a current rate of 0.2 C. It was almost equal to the theoretical capacity of LiMn_{1−x}Fe_xPO_4 (170 mAh g⁻¹). Jianlong Li et al.⑨ reported the CNT'embedded LiMn_{0.5}Fe_{0.5}PO_4 on the cathode composed of 80 wt.% active material (LiMn_{0.5}Fe_{0.5}PO_4), 15 wt.% acetylene black (AB),
and 5 wt.% water-soluble binder. They showed high rate capability, such as 90.3% of capacity retention at current rates of 5/0.2 C. In 2019, we reported cathodes including 90 wt.% active material (LiMn$^{1-x}$Fe$^x$PO$_4$, $x = 0.2$, 0.3, and 0.4) 9). The active material content of our report was higher than that of previous reports on LiMn$^{1-x}$Fe$^x$PO$_4$ (Table 1). The result showed a high rate capability, such as 85.3–92.2% of capacity retention at current rates of 5/0.2 C.

The mixing ratios of LiMn$^{1-x}$Fe$^x$PO$_4$ material in cathodes were all less than 90 wt.% in the previous reports on LiMn$^{1-x}$Fe$^x$PO$_4$ (Table 1). These mixing ratios are lower than those of conventional cathodes of LiNi$^x$Co$^y$Mn$^z$O$_2$ 10) 11) and LiNi$^x$Co$^y$Al$^z$O$_2$ 12), as shown in Table 1. The weight ratio of LiMn$^{1-x}$Fe$^x$PO$_4$ in cathodes should be as high as that of conventional active material of LiNi$_x$Mn$_y$Co$_z$O$_{2+2}$ 10) 11) and LiNi$_x$Co$_y$Al$_z$O$_{2-2}$ 12) to obtain satisfactory electrochemical performance. Since

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Chemical composition of active material</th>
<th>Cathode composition</th>
<th>Discharge capacity (mA h g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Active material (wt.%)</td>
<td>Conductive additive (wt.%)</td>
</tr>
<tr>
<td>14</td>
<td>LiMn$<em>{0.8}$Fe$</em>{0.2}$PO$_4$</td>
<td>80</td>
<td>CB</td>
</tr>
<tr>
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<td>AB</td>
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<td>AB</td>
</tr>
<tr>
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<td>AB</td>
</tr>
<tr>
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<td>80</td>
<td>CB</td>
</tr>
<tr>
<td>16</td>
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<td>CB</td>
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<tr>
<td>17</td>
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<td>80</td>
<td>AB</td>
</tr>
<tr>
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<td>80</td>
<td>AB</td>
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<tr>
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<tr>
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<td>CB</td>
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<tr>
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<tr>
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<tr>
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<td>AB</td>
</tr>
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<td>AB</td>
</tr>
<tr>
<td>8</td>
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<td>80</td>
<td>KB</td>
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<tr>
<td>10</td>
<td>LiNi$<em>{0.6}$Co$</em>{0.2}$Mn$_{0.2}$O$_2$</td>
<td>94.4</td>
<td>CB</td>
</tr>
<tr>
<td>11</td>
<td>LiNi$<em>{0.3}$Co$</em>{0.3}$Mn$_{0.2}$O$_2$</td>
<td>96</td>
<td>CB</td>
</tr>
<tr>
<td>12</td>
<td>LiNi$<em>{0.3}$Co$</em>{0.1}$Al$_{0.5}$O$_2$</td>
<td>94</td>
<td>CB</td>
</tr>
</tbody>
</table>
the gravimetric discharge capacity of lithium-ion battery cells typically increases with an increase in the weight ratio of active material in cathodes.\textsuperscript{13}

However, enhancing the discharge capacity of LIBs requires investigating the ratio of conductive additive to polymer binder in the cathodes. Yoon Koo Lee et al.\textsuperscript{13} reported that cycling performance improved in proportion with the decreasing ratio of the conductive additive to polymer binder in LiMn\textsubscript{2}O\textsubscript{4}.

In this study, we study the effects of the mixing ratio of cathodes, containing 90 wt.% or more active material (LiMn\textsubscript{0.7}Fe\textsubscript{0.3}PO\textsubscript{4}), on the electrochemical performance of LIBs.

2. EXPERIMENTAL

2.1 Preparation of cathodes

The active material used in this experiment is the LiMn\textsubscript{0.7}Fe\textsubscript{0.3}PO\textsubscript{4}/C material synthesized using the method in our previous work\textsuperscript{9}. The SEM image of the active material is shown in Fig. 1. The active material secondary particles are spherical and the size is 13 μm, whereas the primary nanoparticle size is 100 nm. The physical and chemical properties of the active material are summarized in Table 2. The BET-specific surface area of the active material was higher than that of a conventional active material (LiNi\textsubscript{0.8}Co\textsubscript{0.15}Al\textsubscript{0.05}O\textsubscript{2}) for LIBs.\textsuperscript{12}

Cathode slurries were made by mixing the active material, acetylene black (Denka Co. Ltd., Li-100) as the conductive additive, and polyvinylidene fluoride (Kureha Corp., L\#9305) as the binder in N-methyl-2-pyrrolidone (Fujifilm Wako Pure Chemical Corp., Special grade). The cathode slurries were coated onto aluminum foil (Hohsen Corp., thickness 20 μm) by a doctor blade and dried at 80°C for 12 h in a vacuum oven. The prepared cathodes were pressed at 16 MPa and punched into 14-mm diameter disks as cathodes.

Cathode compositions are summarized in Table 3. The cathodes possessing 90–99 wt.% active material and AB/PVDF weight ratio of 1/3, 1, and 3 were prepared. The cathode compositions are referred to as Lot No. (Table 3).
To eliminate factors associated with the cathode composition, the cathodes were made by setting up target values described below:

- cathode mass loading: 6 mg cm$^{-2}$
- thickness of the cathode: 35 μm
- porosity of the cathode: 45 vol.%

where the porosity of the cathode was calculated using the following equations:

\[
\text{Actual density (g cm}^{-3}\text{)} = \frac{\text{Cathode mass loading (mg cm}^{-2}\text{)}}{\text{Cathode thickness (μm)}} \times 10
\]

\[
\text{Theoretical density (g cm}^{-3}\text{)} = \frac{1}{\sum \left(\frac{\text{Materials (wt.%)}}{\text{Materials true density (g cm}^{-3}\text{)} \times 100}\right)}
\]

\[
\text{Porosity (%) } = \left(1 - \frac{\text{Actual density (g cm}^{-3}\text{)}}{\text{Theoretical density (g cm}^{-3}\text{)}}\right) \times 100
\]

where Materials are each component of the cathodes (active material, AB, and PVDF). The true densities of the active material (LiMn$_{0.7}$Fe$_{0.3}$PO$_4$), AB, and PVDF are 3.4 g cm$^{-3}$, 1.94 g cm$^{-3}$, and 1.78 g cm$^{-3}$, respectively.

### 2.2 Characterization of cathodes

Surface morphologies of the cathodes were observed using a field emission scanning electron microscope (FE-SEM) using a JSM-7001F (JEOL Ltd.) set at an accelerating voltage of 15 kV. The actual active material ratios of cathode surface were calculated using backscattered electron images using an image processing software NS2K-Pro (Nanosystem Corporation). A smoothing processing$^{22}$ was conducted on the backscattered electron images. A binarization processing$^{23}$ was done on the images. Area measurement of black and white areas was conducted on the binarized images.

Electrical conductivities of the cathode mixture peeled off from the cathodes were measured by a four-probe method$^{24}$ using a powder resistivity measurement system MCP–PD51 (Nittoseiko Analytech Co., Ltd.).

### 2.3 Electrochemical measurements

Electrochemical performances of the cathodes were evaluated using CR-2032 coin-type cells. 15-mm diameter disks were punched out from metallic lithium foils (Honjo Chemical Corp.) and used as counter electrodes, while 17-mm diameter disks were punched out from polyethylene (W-Scope Corp., COD-20-B) and used as separator. The cells were assembled with the prepared electrodes, separators, and 1 M LiPF$_6$ dissolved in a 3:7 (v/v) mixture of ethylene carbonate and ethyl-methyl carbonate (Kishida Chemical Co., Ltd.) as the electrolyte solution in argon-filled glove box (dewpoint < −90°C, O$_2$ level < 0.2 ppm).

Electrochemical measurements were conducted using a battery testing system (Hokuto–Denko Co., Model: HJ1001SM8A). The fabricated cells were cycled at 30°C in the voltage range of 2.0–4.5 V using a constant-current voltage charge and a constant-current voltage discharge protocol at current rates of 34, 170, 510, and 850 mA g$^{-1}$.

The electrochemical impedance spectroscopy (EIS) measurements of the cells after cycling were conducted at frequency range of 100 kHz–0.01 Hz using a VersaSTAT4 system (Princeton Applied Research Co.).

### 3. RESULTS AND DISCUSSION

#### 3.1 Characterization of cathodes

The effects of cathode compositions on the cathode properties were evaluated. Backscattered electron images of the surface of the cathodes are shown in Fig. 2A. White, gray, and black areas of backscattered electron images were assigned to the active material, AB, and voids, respectively. For cathodes having 90–94 wt.% active material, AB and voids were unevenly distributed, whereas, for cathodes having 98–99 wt.% active material, AB and voids could not be recognized.
This is due to a small amount of AB in the cathodes. Lot No. 98-1.5 could not be measured because of electrode peeling.

Binary images by the corresponding backscattered electron images (Fig. 2A) are shown in Fig. 2B. The binary images were made by separating active material area (white area) from other areas (gray and black areas) of backscattered electron images. The area ratios of the active material to all areas calculated using the binary images are shown in Fig. 2C. The area ratio of the active material decreased with an increase in the AB content in the cathode. This result suggests that active material, AB and PVDF are mixed uniformly.

Electrical conductivities of the cathodes as a function of AB content are shown in Fig. 3A. The electrical conductivities increased with increasing the weight ratio of AB in the cathodes. This result is due to two reasons: the uniform distribution of the active material, AB and PVDF in the cathodes and the influence of AB content on the conductive path and AB network in the cathode.\(^{21}\) The electrical conductivities of the cathodes as a function of AB/PVDF (weight ratio) are shown in Fig. 3B. The electrical conductivities increased with decreasing the weight ratio of active material. This is because the electrical conductivity of the active material, LiMn\(_{0.7}\)Fe\(_{0.3}\)PO\(_4\)C \((2.0E-5 \text{ S cm}^{-1})\), is lower than that of AB \((5.0E+1 \text{ S cm}^{-1}))^{13}\).
Fig. 2B  Binary images of the surface of the cathodes

Fig. 2C  Plot of area ratio of the active material (AM) against AB content of the cathodes

Fig. 3A  Plot of electrical conductivity (S cm⁻¹) of the cathode mixture having 90–99 wt.% active material (AM) against AB content of the cathodes
3.2 Electrochemical performance

(1) Weight ratio of active material

Electrochemical performances of the cathodes with different weight ratios of active material in the cathodes were evaluated. First charge–discharge curves of Lot No. 90-5, 94-3, 98-1, and 99-0.5 at a current rate of 0.2 C (current density of 34 mA g\(^{-1}\)) are shown in Fig. 4. The charge–discharge curves had two plateaus, where the voltages were flat, at 3.5–3.6 V of Fe\(^{2+/3+}\) and 4.0–4.1 V of Mn\(^{2+/3+}\) redox couples.\(^{25}\) The discharge capacities of Lot No. 90-5, 94-3, 98-1, and 99-0.5 at a current rate of 0.2 C were 157.3, 156.3, 155.6, and 153.1 mAh g\(^{-1}\), respectively. The discharge capacity increased with decreasing the weight ratio of the active material. This is because electrical conductivities of the cathodes increase with a decrease in the weight ratio of active material as shown in Fig. 3B. However, this result was different from that of LiMn\(_2\)O\(_4\) in the previous report\(^{13}\). This difference is due to fewer AB content (0.5–5 wt.%) in the cathodes in this report than that of the previous one (2.9–7.5 wt.%). Moreover, the discharge capacities of the cathodes with much number of active material in this report were not inferior to those of the cathodes with fewer active material in previous reports (Table 1). These results are due to high electrical conductivities of the cathodes caused by the LiMn\(_{0.7}\)Fe\(_{0.3}\)PO\(_4\) secondary particles (Fig. 1). The effective surface area (an index of absorption of solvent in cathode slurry) of the LiMn\(_{0.7}\)Fe\(_{0.3}\)PO\(_4\) secondary particles seems to be lower than that of nanoporous\(^{28}\) or nanoparticle\(^{6,14,20,27}\) LMFP in previous reports. The lower effective surface area of active material, the easier the mixing of the active material and AB, and the higher electrical conductivities of the cathodes, even with a few AB and PVDF content.\(^9\)

Rate capabilities of the cathodes were evaluated. The discharge curves of Lot No. 90-5, 94-3, 98-1, and 99-0.5 at current rates of 0.2, 1, 3, and 5 C (current densities of 34, 170, 510, and 850 mA g\(^{-1}\), respectively) are shown in Fig. 5. The polarization of Lot No. 90-5 and 94-3 was almost the same, whereas the polarization of Lot No. 94-3, 98-1, and 99-0.5 improved with decreasing the weight ratio of active material. These results are because the electrical conductivities of the cathodes increase with a decrease in the weight ratio of active material, as shown in Fig. 3B. The discharge capacities as a function of the current rate of Lot No. 90-5, 94-3, 98-1, and 99-0.5 are shown in Fig. 6. The discharge capacities of Lot No. 90-5, 94-3, 98-1, and 99-0.5 at a current rate of 5 C were 144.0, 142.2, 124.1, and 57.4 mAh g\(^{-1}\), respectively. Their corresponding capacity retention rates at current rates of 5/0.2 C were 91.5, 91.0, 79.8, and 37.5%, respectively. The capacity retention rate increased with a decrease in the weight ratio of active material in the
Fig. 5 Discharge curves of (a) 90-2.5, (b) 90-5, (c) 90-7.5, (d) 94-1.5, (e) 94-3, (f) 94-4.5, (g) 98-0.5, (h) 98-1, and (i) 99-0.5 at current rates of 0.2, 1, 3, 5 C.
cathodes. This result is because the electrical conductivity of the cathodes increases with decreasing the weight ratio of active material, as shown in Fig. 3B. In addition, the cathodes having 90–98 wt.% active material exhibited higher rate capability than those of the previous reports in Table 1. These results are due to the high electrical conductivities of the cathodes fabricated using LMFP secondary particles, as mentioned above. Energy densities of the cathodes are shown in Fig. 7. The energy densities of Lot No. 90-5, 94-3, 98-1, and 99-0.5 were 592.0, 588.6, 580.8, and 560.5 Wh kg\(^{-1}\) at a current rate of 0.2 C, and 458.1, 447.2, 370.8, and 134.9 Wh kg\(^{-1}\) at a current rate of 5 C, respectively. The energy density increased with a decrease in the weight ratio of active material. This result is due to the higher electrical conductivity of the cathodes with decreasing the weight ratio of active material, as shown in Fig. 3B.

To clarify the cause of the capacity deterioration, the resistances of the cells after cycling were measured. EIS are shown in Fig. 8. All spectra in Fig. 8 consisted of semicircles in high and moderate frequency regions and straight lines in the low frequency region. They can be fitted with the equivalent circuit model\(^{25}\) in Fig. 8, consisting of the resistance of the solution (R\(_{Ω}\)), charge–transfer (R\(_{ct}\)), corresponding constant phase element, and Warburg impedance (Z\(_w\)).\(^{17,25}\) R\(_{Ω}\) were almost the same, despite the weight ratio of active material in the cathodes. This result indicates that there is no effect of electrolyte solution resistance on the cathode composition. R\(_{ct}\) (a diameter of semicircle) decreased with a decreasing ratio of active material. The decreased R\(_{ct}\) causes improvement of the electrical conductivity and rate capability with the decreasing weight ratio of active material, as shown in Figs. 3B and 6.

(2) Weight ratio of AB/PVDF

The influence of the AB/PVDF weight ratio of the cathodes on rate capability was evaluated. The cathode composition having the best rate capability among AB/PVDF weight ratios of 1/3, 1, and 3 was AB/PVDF weight ratio of 1 for each ratio of active material, as shown in Fig. 5. Where the influence of AB/PVDF weight ratio on the
discharge capacities of the cathodes having 90 and 94 wt.% active material was different from that of the cathodes having 98 wt.% active material. For the cathodes having 90 and 94 wt.% active material, the discharge capacity decreased from AB/PVDF weight ratio of 1 to 1/3. The polarizations worsened from the AB/PVDF weight ratio of 1 to 1/3. These results are due to the lower electrical conductivity from the AB/PVDF weight ratio of 1 to 1/3, as shown in Fig. 3B. However, the discharge capacity also decreased from AB/PVDF weight ratio of 1 to 3. The polarizations worsened from the AB/PVDF weight ratio of 1 to 3. These results are due to a reduction in PVDF that keeps the AB particles together as a network. For the cathodes with 98 wt.% active material, the discharge capacity did not decrease from AB/PVDF weight ratio of 1 to 1/3. This result is due to the lower electrical conductivity from cathode content of 94 wt.% to 98 wt.%, as shown in Fig. 3B. The polarizations declined from the AB/PVDF weight ratio of 1 to 1/3. This decline is due to weaker conductive paths with decreasing AB/PVDF ratio.

EIS are shown in Fig. 9. All spectra in Fig. 9 can be fitted with the equivalent circuit model in Fig. 8. As mentioned above, \( R_\Omega \) were almost the same despite cathode compositions. This result indicates that there is no influence on the electrolyte solution resistance. However, \( R_{ct} \) increased from AB/PVDF weight ratio of 1 to 1/3. The \( R_{ct} \) trend corresponds to that of the electrical conductivity to the weight ratio of AB, as shown in Fig. 3A. Moreover, \( R_{ct} \) increased from AB/PVDF weight ratio of 1 to 3. This result is due to the shortage of PVDF that keeps the AB particles together as a network. Increased \( R_{ct} \) causes lower rate capability by AB/PVDF weight ratio of 1 to 3.

![Fig. 9](image-url)  
Fig. 9  Electrochemical impedance spectra of the cathodes having AM of (a) 90 wt.%, (b) 94 wt.%, and (c) 98 wt.%)
4. CONCLUSION

In summary, we studied the effects of the mixing ratio of cathodes containing ≥90 wt.% active material (LiMn$_{0.7}$Fe$_{0.3}$PO$_4$/C) on the electrochemical performance of LIBs. The major findings are summarized below:

(1) The cathodes with 90–99 wt.% of LiMn$_{0.7}$Fe$_{0.3}$PO$_4$/C material at a current rate of 0.2 C exhibited high discharge capacities of 153.1–157.3 mAh g$^{-1}$ and high energy densities of 560.5–592.0 Wh kg$^{-1}$. The discharge capacity increased with a decrease in the weight ratio of LiMn$_{0.7}$Fe$_{0.3}$PO$_4$/C material. In addition, the cathodes with 90–98 wt.% of LiMn$_{0.7}$Fe$_{0.3}$PO$_4$/C material exhibited high capacity retention rates of 79.8–91.5% at current rates of 5/0.2 C. The capacity retention rate increased with decreasing the weight ratio of LiMn$_{0.7}$Fe$_{0.3}$PO$_4$/C material in the cathodes because of low R$_{ct}$. Moreover, they exhibited high energy densities of 370.8–458.1 Wh kg$^{-1}$ at a current rate of 5 C.

(2) The cathode composition with the best rate capability among AB/PVDF weight ratio of 1/3, 1, and 3 was AB/PVDF weight ratio of 1 for each ratio of LiMn$_{0.7}$Fe$_{0.3}$PO$_4$/C material: this is due to the low R$_{ct}$.

Based on the above results, the cathode with ≥90 wt.% LiMn$_{0.7}$Fe$_{0.3}$PO$_4$/C material exhibited high discharge capacity. Therefore, it is expected that the gravimetric and volume energy density of lithium-ion battery cells will improve in the future.

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