Improvement in Electrochemical Performance of LiCoPO₄/C Using Furnace Blacks with High Surface Areas as a Carbon-based Composite Material

Shoma KONISHI,a Dai MURAYAMA,a Atsushi ITADANI,a,b Kazuyoshi UEMATSU,a Kenji TODA,a Mineo SATO,c,* Nozomi ARIMITSU,d Takayuki AOKI,d and Togo YAMAGUCHId

© The Electrochemical Society of Japan, All rights reserved.

ABSTRACT

LiCoPO₄-carbon composites (LiCoPO₄/C) were synthesized via a solid state reaction with a new furnace black, CB1, which was developed by Asahi Carbon Co., Ltd. The CB1 used here has superiority physico-chemical properties, e.g., ultrafine particle sizes, high specific surface areas, and high "structure", the degree of linkage among carbon particles. The particle growth of LiCoPO₄ was suppressed by the addition of CB1 to the LiCoPO₄ precursors and then followed by calcination. CB1 was dispersed among LiCoPO₄/C particles successfully to form conductive paths. Consequently, a high electrochemical capacity was achieved in aid of the presence of CB1.

1. Introduction

For a few decades, the layered rock salt LiCoO₂, LiNiO₂ and manganese-spinel framework LiMn₂O₄ have been used for positive active materials, which showed moderate high energy density and rechargeable cyclability as electrode materials for lithium ion secondary batteries (LIBs). However, those oxides have some problems like stability in a hot environmental condition and emergence of over-charged state in practical use for commercial secondary batteries. For the solution of these matters and with an eye to the future in the era of electric vehicles, Padhi et al. carried out the study on ordered olivine-type compounds LiMPO₄ (M = Fe, Mn, Co and Ni), and many studies relating to this field have been done by a number of researchers. The leading theme of these challenges is the improvement in electronic conductivity, where carbon materials are used in a variety of ways in synthesis steps for the olivine-type compounds. That is because the olivine-type active materials have characteristics of poor electronic conductivity and low lithium ion diffusivity due to limitations of lithium ion mobility in its crystal structure.

In our previous work, we showed significant improvement in the electrochemical properties of the carbon coated LiFePO₄ using polystyrene (PS) and newly developed carbon black “CB1” as carbon sources by a solid state reaction. The carbon black labeled as “CB1” developed by Asahi Carbon Co., Ltd., Japan has excellent characteristics of the smaller sized primary particles with a diameter of 10 nm and has a relatively large specific surface area of 336 m²g⁻¹ (dibutyl phthalate (DBP) absorption number: 206 ml (100 g)⁻¹), in comparison with the commercially available acetylene black (AB) (primary particle size: 35 nm; surface area: 68 m²g⁻¹; DBP absorption number: 175 ml (100 g)⁻¹). Therefore, CB1 can adhere to the active material particles to make contacts among active materials ease. However, with the consideration for expansion of rechargeable batteries to electric vehicles, the active material for LIBs is preferable to being higher energy density to get a further cruising radius. From this perspective, LiCoPO₄, which has a higher redox potential (4.8 V vs. Li/Li⁺) as well as a modest theoretical capacity (167 mAh g⁻¹), is one of the prospective cathode material candidates. In this communication, we investigated the synthesis of LiCoPO₄ carbon composite (LiCoPO₄/C) using polystyrene and CB1 via a solid state reaction by a method similar to our earlier study for LiFePO₄. The several electrochemical measurements for the synthesized cathode materials were conducted to clarify the effect of CB1 to the olivine-type LiCoPO₄.

2. Experimental

The carbon-coated LiCoPO₄ samples were synthesized via a solid state reaction with PS as carbon sources to elucidate the possibility and the effect of the carbon coating for LiCoPO₄. For the pyrolysis process of LiCoPO₄ raw materials, stoichiometric amounts of Li₂CO₃ (Kanto Chemical Co., Inc.), CoC₂O₄·2H₂O (Kanto Chemical Co., Inc.), and NH₄H₂PO₄ (Kanto Chemical Co., Inc.) were mixed by ball milling with toluene (Kanto Chemical Co., Inc) as a mixing solvent for 3 h. The mixture was heated at 375°C for 8 h in an air atmosphere in a tubular furnace. Then, PS (Wako Pure Chemical Industries, Ltd.) was added 20 wt% relative to the weight of the LiCoPO₄ precursor prepared. The precursors were mixed using the ball mill with toluene as a solvent for 2 h.

The carbon-coated LiCoPO₄/C samples prepared using PS and CB1 were synthesized to estimate the suitable additive amount of CB1. First, CB1 was added to a LiCoPO₄ precursor by mixing with the ball mill under a dry condition for 1 h. Then, an appropriate amount of CB1 was added to the precursor with the ratios of 7, 20,
and 40 wt%, respectively, to pyrolyze the material. Moreover, PS was added as mentioned above, and mixed with toluene for 1 h. To compare the feature of CB1 with that of AB, the samples with AB (Denka Co., Ltd.) and PS were also synthesized with the same technique as in the way of the sample with CB1 and PS. The sample with AB and PS was synthesized with 20 wt% of AB.

Finally, these mixtures of the precursors and the carbon sources were heated at 750°C for 12 h in an Ar atmosphere. Hereafter, the samples obtained are abbreviated as LCP/C for sample carbon-coated with PS only, LCP/C-CB1-A for sample carbon-coated with PS and CB1 (A: weight percent of CB1), and LCP/C-AB-A for carbon-coated with AB and PS (A: weight percent of AB), respectively.

Powder X-ray diffraction (XRD) profiles were collected using a D2 Phaser diffractometer (Bruker Co., Ltd.) with a monochromatic CuKα radiation (λ = 0.154056 nm) under 10 mA and 30 kV. Rietveld refinement was carried out using RietanFP software. The elemental analysis of the carbon-coated LiCoPO4 samples was performed with a CHN corder (Micro corder JM10, J-Science Lab Co., Ltd.). Transmission electron microscopy (TEM) images for the carbon-coated LiCoPO4 samples were taken using a Tecnai G2 20ST (FEI Company).

To clarify the electrochemical properties of carbon-coated LiCoPO4 samples, a LiCoPO4 cathode was prepared by a slurry-coating technique by mixing 85 wt% acquired carbon-coated LiCoPO4, 8 wt% acetylene black, and 7 wt% polyvinylidene difluoride (PVDF) in an N-methyl-2-pyrrolidone (NMP) solvent (Kureha Co.). The slurry obtained was coated onto an aluminum foil. The lithium metal foil and 1 M LiPF6 in an ethylene carbonate: dimethyl carbonate (1:1 v/v) solution (Kishida Chemical Co., Ltd.) were used as a counter electrode and an electrolyte, respectively. The galvanostatic charge-discharge cycles at 30°C were carried out at 0.05 C with cut-off voltage ranges of 3.0 to 5.0 V versus Li/Li+ using a PFX2011S charge-discharge unit (Kikusui Electronics Co.).

3. Results and Discussion

The XRD measurements confirmed all the samples prepared to be well crystalline with a single phase. Rietveld refinement was performed using these data to obtain crystalline size of products, and the results are listed in Table 1. The crystalline size of LCP/C, LCP/C-CB1-7 and LCP/C-CB1-20 are approximately the same, but their sizes of LCP/C-CB1-40 and LCP/C-AB-20 are a bit larger. In this study, to verify the amount of the carbon substances generated by PS resource (PS-derived carbons) in obtained samples, a no-carbon coated LiCoPO4 sample was synthesized. By investigating the product mass change between the obtained samples before and after calcination at 750°C, the possible mass reduction of the no-carbon coated LiCoPO4 is estimated to be 8.0 wt%. For example, by adding 7.0 wt% of CB1 to LCP/C-CB1-7 precursor before calcination at 750°C, the resulting amount of CB1 in LCP/C-CB1-7 obtained is calculated to be 7.6 wt%. In addition, calcining under an inert atmosphere, the combustion of carbon black does not likely occur. Therefore, the mass ratio of PS-derived carbons in LCP/C-CB1-7 is estimated to be 0.98 wt%, lower than half of that of LCP/C. It is understandable to consider that the reduction of PS-derived carbons is caused by an addition of carbon with high specific surface area. The carbon mass fractions measured by the CHN corder measurements and the estimated from the starting material compositions for LiCoPO4 calcined at 750°C are listed in Table 2. Except for LCP/C-CB1-40, there is little difference between the theoretical and the measured results, being within the experimentally acceptable range. The CB1 ratio of LCP/C-CB1-40 was 8.6, respectively. The galvanostatic charge-discharge cycles at 30°C versus Li/Li+ were carried out at 0.05 C with cut-off voltage ranges of 3.0 to 5.0 V versus Li/Li+ using a PFX2011S charge-discharge unit (Kikusui Electronics Co.).

Table 2. Carbon mass fractions measured from CHN corder measurements and estimated from starting material composition of LiCoPO4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ratio of carbon (wt%)</th>
<th>Estimated amount of carbon blacks (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCP/C</td>
<td>2.3</td>
<td>—</td>
</tr>
<tr>
<td>LCP/C-CB1-7</td>
<td>8.6</td>
<td>7.6</td>
</tr>
<tr>
<td>LCP/C-CB1-20</td>
<td>19.3</td>
<td>21.7</td>
</tr>
<tr>
<td>LCP/C-CB1-40</td>
<td>28.8</td>
<td>43.5</td>
</tr>
<tr>
<td>LCP/C-AB-20</td>
<td>19.6</td>
<td>21.7</td>
</tr>
</tbody>
</table>

Table 1. Results of Rietveld refinements and estimated crystalline sizes of LiCoPO4 obtained.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rwp (%)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCP/C</td>
<td>6.39</td>
<td>178</td>
</tr>
<tr>
<td>LCP/C-CB1-7</td>
<td>2.00</td>
<td>178</td>
</tr>
<tr>
<td>LCP/C-CB1-20</td>
<td>6.34</td>
<td>177</td>
</tr>
<tr>
<td>LCP/C-CB1-40</td>
<td>2.62</td>
<td>188</td>
</tr>
<tr>
<td>LCP/C-AB-20</td>
<td>2.09</td>
<td>209</td>
</tr>
</tbody>
</table>

Figure 1. TEM images of (a) LCP/C, (b) LCP-CB1-7, (c) LCP/C-CB1-20, (d) LCP/C-CB1-40, and (e) LCP/C-AB-20.
estimated from CHN corder measurements, however, disagrees with the theoretical one. This seems to be caused by inadequate cohesion of ball-milled LiCoPO$_4$ precursors. In other words, insufficient collection of re-solidified PS in a ball mill jar after milling process causes for underestimation of the carbon mass fraction.

To make clear the states of primary particles of prepared LiCoPO$_4$ and existing carbon materials, TEM observations of samples were conducted. The particle diameters of five samples are in the range of about 50–400 nm. The sizes of active materials calcined with PS and CB1 are reduced to some extent compared to LCP/C, calcined without CB1. Referring to the reports$^{10-13}$ made recently, the particle sizes are in the range of 100 nm, the sizes of our samples being at the same and/or a little smaller. In our previous study,$^7$ when CB1 and PS were used in calcination of LiFePO$_4$ precursor, it was found that CB1 promotes the reduction in particle size. This fact proofs that CB1, used together with PS in synthesis of active materials, inhibits particle growth occurring in calcination. The TEM image of LCP/C are shown in Fig. 1(a). Although PS-derived carbons is dispersed among LiCoPO$_4$ primary particles, graphitized carbons on the surface of active materials are rarely found. Figure 1(b) and (c) show that CB1 is dispersed moderately among active materials in LCP/C-CB1-7 and LCP/C-CB1-20, even though graphitized carbon materials on or around active materials are little or not. As shown in Figs. 1(d) and (e), the active materials in LCP/C-CB1-40 are surrounded by excess amounts of CB1, aggregated AB particles being isolated from the active materials in LCP/C-AB-20. Thus, the graphitized carbons on the active materials are rarely found in both samples. The TEM observations declare that the deposition of PS-derived carbons (as carbon layers) on LiCoPO$_4$ particles, especially the samples to which carbon blacks are added at calcination, is not an easy thing. This result is consistent with the fact mentioned previously that the samples added with carbon blacks have less amount of PS-derived carbons than the samples without carbon blacks. Therefore, the deposition of PS-derived carbons on LCP/C-CB1-20, LCP/C-CB1-40 and LCP/C-AB-20 seems to be few.

The charge/discharge measurements of all the samples were conducted for 5 cycles at a C rate of 0.05, and their profiles are shown in Fig. 2. LCP/C-CB1-20 exhibited the highest discharge capacity in all the samples, the second-highest capacity being observed for LCP/C. In the charge/discharge measurement of LCP/C-CB1-7, an abrupt decrease of capacity is observed at the second cycle. In any cycle for both of LCP/C-AB-20 and LCP/C-CB1-40, no good cycle performance is obtained. On the other hand, the samples synthesized with CB1 and PS have good capacity performance, where the capacity increases in progress of cycle. An excellent charge/discharge cycle performance is achieved in LCP/C-CB1-20.

![Figure 2. (Color online) Charge and discharge curves of (a) LCP/C, (b) LCP/C-CB1-7, (c) LCP/C-CB1-20, (d) LCP/C-CB1-40, and (e) LCP/C-AB-20, and coulombic efficiency are noted below the caption of its cycle number: (black) first cycle; (red) second cycle; (blue) third cycle; (green) fourth cycle and (orange) fifth cycle.](Image)
4. Conclusions

LCP/C-CB1-20 showed the best electrochemical performance in all the synthesized materials. Although there is no crucial difference in the active particle diameter as well as in estimated amounts of PS-derived carbons among all the samples, there is a large difference in the electrochemical performance. The considerable factor for such a difference can be due to the additive amounts of CB1 to active material precursors. As seen in Fig. 2(c) for LCP/C-CB1-20, an appropriate amount of CB1 are dispersed in the LiCoPO4 particles, giving improvement in the electrochemical properties of LiCoPO4. The possible factor of such improvement is attributed to the enhancement in the electrical conductivity between dispersed CB1 particles and LiCoPO4 particles.

However, the charge/discharge capacity of LCP/C-AB-20 and LCP/C-CB1-40 are considerably lower than that of LCP/C-CB1-20. As shown in the TEM images, the active materials in LCP/C-CB1-40 are fully surrounded by excess or agglomerated carbon blacks. This fact suggests that large agglomerates, composed of carbon blacks and LiCoPO4 particles, reduce the number of their conductive path sites among neighboring particles or the current collector of electrodes, causing an abrupt deterioration of charge/discharge capacity. LCP/C-CB1-7 shows a marked trend that the charge/discharge capacity decreases abruptly at the second cycle. The result implies that, in the synthesis of LiCoPO4 carbon composites, a certain amount of CB1 is needed to obtain adequate electronic conductivity.

In conclusion, the hybridization of active material LiCoPO4 and CB1 with ultrafine particle sizes, high specific surface areas, and high “structure” is a quite usable method to bring out the potential electrochemical performance of LiCoPO4.

References