Emulsion Drying Preparation of $LiFePO_4$/C Composite and Its Enhanced High-rate Performance at 50 °C

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$LiFePO_4$/C composite was successfully synthesized by an emulsion drying method. As confirmed by X-ray diffraction and scanning transmission electron microscopic observation, the prepared particle size of $LiFePO_4$ was of about 300 nm and the powder was modified by conductive carbon. Consequentially, the existence of carbon increased the electronic conductivity of $LiFePO_4$/C composite to ca. 10^{-4} S cm^{-1} at 25 °C. Because of smaller particle size and enhanced conductivity, the composite showed higher capacity about 140 mA h g^{-1} (20 mA g^{-1}), excellent cyclability and superior rate capability at 50 °C, i.e., over 90 mA h (g-phosphate)$^{-1}$ at a current density of 1000 mA g^{-1}.

Since the discovery of $LiFePO_4$ by Padhi et al.[1] in 1997, it has been believed that $LiFePO_4$ could be used as a cathode material for Li-ion battery. In fact, orthorhombic olivine type $LiFePO_4$ is very attractive material, because iron is much more abundant, cheaper, less toxic than other transition metals in our surrounding. Even though olivine type $LiFePO_4$ shows a relatively high capacity and good cyclability, a significant drawback is a poor rate capability. As a higher current density was applied across a $LiFePO_4$ electrode, the resulting capacity decreased abruptly, because $LiFePO_4$ is intrinsically electrical insulator.[1] In previous attempts to enhance the electronic conductivity, $LiFePO_4$/C composite seemed to be very promising to overcome the limited rate capability, because improvement of electronic conductivity provides pathway for electron transport.[2–4] Iron component is cheaper than other transition metals; however, relatively expensive divalent iron compounds were usually selected as a starting material to synthesize $LiFePO_4$.[1,3–10]

When conventional ceramic methods were employed to prepare olivine compound, several recalcinations and subsequent regrindings were required to improve homogeneity of the final products.[1,5–10] These repeated heat-treatments result in a significant crystal growth in the final product.[5–8] According to previous reports, $LiFePO_4$ having smaller particle size shows a beneficial effect on improvement of capacity.[5–10]

From the above reviews, one can understand that preparation of carbon containing $LiFePO_4$ with smaller particle size would be preferred to improve capacity as well as limited rate capability of $LiFePO_4$. For these reasons, we selected an emulsion drying method.[11] With help of this method, we have successfully synthesized $LiFePO_4$/C composite. On cycling $LiFePO_4$ electrode at elevated temperatures, it showed capacity decrease, as reported by Takahashi et al.[5,6] and Andersson et al.[7] Here, we would like to show that $LiFePO_4$/C composite electrode exhibits up to 90 mA h g^{-1} at a high current density of 1000 mA g^{-1} at 50 °C.

$LiFePO_4$/C composite was prepared by the emulsion drying method. Stoichiometric amounts of $LiNO_3$ (Kanto), $Fe(NO_3)_3 \cdot 9H_2O$ (Kanto) and $(NH_4)_2HPO_4$ (Wako) were dissolved in distilled water. Then, the aqueous solution was mixed with kerosene (Kanto) and Tween 85 (surfactant, Kanto) to prepare homogeneous water-in-oil type emulsion, in which cations are distributed very uniformly in atomic scale. Detailed routes of the emulsion drying method were described previously.[11] The emulsion-dried precursor was burned out at 300 °C for several minutes in air. Sequentially, the burned out powders were calcined at 750 °C for 48 h in an Ar atmosphere. X-ray diffractometry (XRD, Rigaku Rint 2200), transmission electron microscopy for SEM, STEM and EDS elemental mapping (STEM; 200 kV, Hitachi, H-800), CHN analyzer (MT-5, Yanaco) were employed to characterize the prepared powders. The collected intensity data of XRD were analyzed by the Rietveld refinement program, *Fullprof* 2000.[12] Conductivity measurement was made on disc-shaped pellet by four-point d.c. method at 25 °C. A gold paste was pasted on the surface of disc (13 mm diameter and 2 mm thickness).

The prepared powders were blended with acetylene black and polyvinylidene fluoride (75:20:5) in *N*-methylpyrolidinon. The slurry was pasted onto Al foil disc. A coin cell (2032) consisted of the cathode, lithium foil as an anode and 1 M $LiPF_6$ in ethylene carbonate–diethyl carbonate (1:1 in volume) as an electrolyte. The cells were charged and discharged between 2.7 and 4.5 V vs Li by applying various current densities at 50 °C.

The prepared w/o type emulsion is composed of oil phase (aqueous:oil phase = 2:8). After burning out the emulsion-dried precursor at 300 °C in air, though most of oil components were removed from the precursor, carbon and some organic compounds formed by decomposition of the oily phase remained with low crystalline $LiFePO_4$ powders.[13] Because the precursor is once ignited, CO_2 gas and carbons are generated or contained in the resultant, where the carbon makes a strong reducing atmosphere. At this stage, it is likely that most of Fe^{III} in the precursor was readily reduced to Fe^{II} by only burning-out the oily components.[13]

The burned out powder was calcined at 750 °C for 48 h in Ar. Figure 1 shows Rietveld refinement results of XRD data of the prepared powders. All peaks can be indexed as olivine $LiFePO_4$ phase without any observable secondary phase. A space group of *Pnmb* was chosen as the best refinement model. The observed and calculated patterns fit well. In inset of Figure 1, a broad hill observed at 2 theta = 22–28° in the difference pattern is due to the

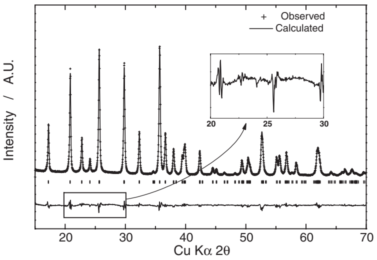

Figure 1. Rietveld refinement of XRD pattern of olivine type $LiFePO_4$/C calcined at 750 °C for 48 h in an Ar atmosphere. Lattice parameters: $a = 10.320(24)$ Å, $b = 6.002(13)$ Å and $c = 4.690(12)$ Å. R_{wp}: 9.37%, R_{Bragg}: 2.97% and R_f: 2.06%.

presence of low crystalline or amorphous carbon, because such hill is usually observed in amorphous material. The amount of carbon in $LiFePO_4$/C was of about 15% in weight by CHN analyzer, and the electronic conductivity of the $LiFePO_4$/C composite was ca. 10^{-4} S cm^{-1} at 25 °C, of which the value is much higher than that of pure $LiFePO_4$ (ca. 10^{-8} S cm^{-1}).[14] It is significantly notable that carbon containing high crystalline olivine $LiFePO_4$ was very easily prepared using relatively cheap Fe^{III} source as a starting material by the emulsion drying method.

Figure 2 illustrates SEM, STEM images and the corresponding Fe mapping of the prepared the $LiFePO_4$/C composite. The prepared powders are homogeneous and the particle size is estimated to be of about 300 nm in Figures 2a and 2b. The distribution of Fe is very homogeneous in Figure 2b. Comparing with Figures 2a and 2b, the olivine powders are covered with carbon. From Figure 2c, it is clear that some parts marked by arrows in Figure 2c are empty, which are clearly filled with some particles in Figures 2a and 2b. From higher magnification TEM observation, those spaces are due clearly to the existence of nanosized carbon in $LiFePO_4$/C composite. The presence of carbon would inhibit the crystal growth of $LiFePO_4$ during heat treatment. The distribution of carbon for overall $LiFePO_4$ powders may play an important role to enhance electronic conductivity of $LiFePO_4$.

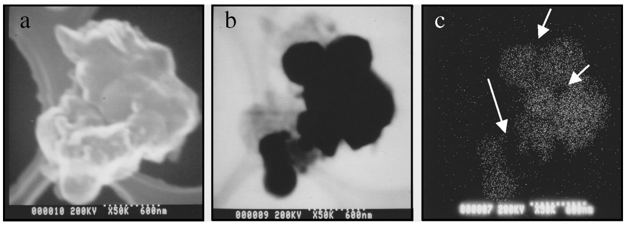

Figure 2. (a) SEM, (b) STEM images and (c) corresponding EDS elemental map for Fe of $LiFePO_4$ observed by TEM.

Figure 3 shows charge-discharge profiles of $LiFePO_4$/C composite cell cycled between 2.7 and 4.5 V by applying a current density of about 20 mA g^{-1} at 50 °C. And, the obtained capacity was compared with that of room temperature operation in inset of Figure 3. The cell voltage profile shows a flat plateau at 3.4 V from the first charge, and 0.98 mol of Li^+ ions calculated from the obtained capacity was extracted from the host structure. During the first discharge, a long flat plateau indicates that two-phase redox reaction proceeds via the first transition between $FePO_4$ and $LiFePO_4$.[1] A slight capacity difference between charge and discharge capacities would be ascribed to the first transition. From the second cycle, the coulombic efficiency between charge and discharge became higher, comparing to the first cycle. When we look at the capacity at 25 and 50 °C in the inset of Figure 3, somewhat higher capacity is obviously seen at the elevated temperature operation. According to reports by Takahashi et al.[5,6] and Andersson et al.,[7] the capacity increased at elevated temperatures, but performance at the elevated temperatures showed a large capacity decrease by electrochemical cycling of $LiFePO_4$ electrode. In our case, the higher capacity of about 140 mA h g^{-1} was maintained upon cycling, as can be seen in inset of Figure 3. The capacity retention was over 98%.

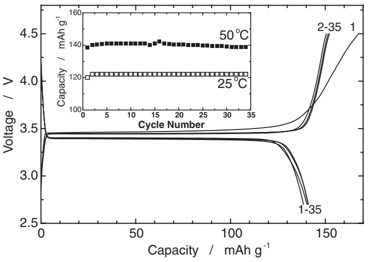

Figure 3. Charge-discharge curves of $LiFePO_4$/C fired at 750 °C for 48 h in an Ar atmosphere. Applied current density was 20 mA g^{-1} at 25 and 50 °C. Inset means the corresponding cyclability of the $LiFePO_4$/C composite electrode at 25 and 50 °C.

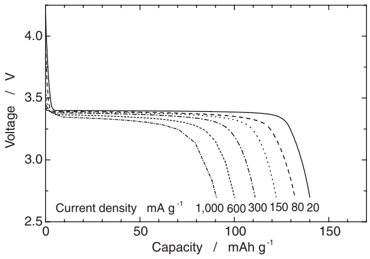

Figure 4. Rate capability of $LiFePO_4$/C composite electrode at 50 °C.

As mentioned above, one of the serious demerits of olivine $LiFePO_4$ is poor rate capability. The limitation can be overcome by preparation of $LiFePO_4$/C composite, as shown in Figure 4. The cell was discharged at various currents at 50 °C. As current density increases, voltage of the cell decreases. When the applied current density across the cathode was of about 1000 mA g^{-1} (11 C), the delivered capacity was over 90 mA h g^{-1} showing an average voltage of about 3.3 V vs Li. To our knowledge, the high capacity at the high rate (90 mA h g^{-1} at 11C) has not been achieved ever. The superior cyclability and rate capability are considered to be due to the coexistence of carbon with $LiFePO_4$ powders. Distribution state of the nanosized carbon around $LiFePO_4$ is to be investigated in order to understand the origin of excellent cyclability as well as rate capability of $LiFePO_4$/C composite. We believe that $LiFePO_4$/C prepared by the emulsion drying is an excellent candidate for the cathode of coming generation of high capacity material to be applied for Li-ion secondary battery.

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