Short communication

Liquid-phase synthesis of highly dispersed NaFeF$_3$ particles and their electrochemical properties for sodium-ion batteries

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ABSTRACT

Highly dispersed NaFeF$_3$ particles were prepared at 280 °C by liquid-phase synthesis using high-boiling-point organic solution, and their electrochemical properties were studied by charge and discharge measurements. TEM observation clarified that the resultant NaFeF$_3$ particles had uniform particle sizes of ca. 10–20, 100–200, and 500–600 nm, which could be controlled by the composition of the synthetic solution. The discharge capacities were higher for NaFeF$_3$ that had smaller particle sizes, particularly at a rate of 0.1 C or higher, while the discharge capacities obtained at a rate of 0.01 C between 1.5 and 4.5 V were almost the same in the range 170–181 mAh g^{-1} regardless of the particle size of NaFeF$_3$. These results clearly indicate that the use of well-dispersed nano-sized NaFeF$_3$ particles should effectively improve the rate performance of NaFeF$_3$.

1. Introduction

Li-ion batteries have been considered as possible power sources in electric vehicles and electric power storage devices, due to their high energy densities. However, before Li-ion batteries can be used in such large-size and/or high-power applications, their performance still needs to be improved with regard to battery cycle life, rate capability, and safety. In addition, such high-performance Li-ion batteries need to be manufactured at reasonably low cost, particularly for large-scale applications. Commercially available Li-ion batteries generally use lithium 3d-transition metal oxides such as LiCoO$_2$ as a positive electrode material, and non-aqueous organic solvents containing lithium salts as an electrolyte solution. LiCoO$_2$ works at around 3.9 V and shows an acceptably large capacity of around 140 mAh g^{-1}. However, sources of lithium and cobalt are relatively costly. In addition, LiCoO$_2$ is known to decompose at elevated temperature to release oxygen, particularly in a charged state, i.e. Li$_x$CoO$_2$ ($x < 1$) [1]. The organic solvents used in the electrolyte should be decomposed exothermally by the generated oxygen, and hence the temperature of the batteries can be further increased [2]. Organic solvents are flammable, and therefore the thermal stability of Li$_x$CoO$_2$ should be improved to enhance the safety of Li-ion batteries. Based on these facts, oxygen-free active materials that can be prepared from relatively inexpensive metal resources are required. Among them, iron-based fluorides seem to be a possible candidate as an alternative to LiCoO$_2$ and its analogs [3–7]. Badway et al. [8] reported that FeF$_3$/C (85/15 wt.%) composite electrodes showed a high discharge capacity of about 200 mAh g^{-1} at ca. 3.3 V vs. Li metal in 1 mol dm^{-3} LiPF$_6$ dissolved in a mixture of ethylene carbonate and dimethyl carbonate, which corresponds to 99% of the theoretical specific capacity (238 mAh g^{-1}) based on FeF$_3$ content. On the other hand, our group previously reported that FeF$_3$/C composite electrodes showed a discharge capacity of 100 mAh g^{-1} vs. Na metal in 1 mol dm^{-3} NaClO$_4$ dissolved in propylene carbonate (PC) [9]. Thus, charge and discharge reactions at FeF$_3$ can take place in both Li and Na cells. However, the active materials of the positive electrodes need to contain mobile ions, such as Li-ion or Na-ion, when pristine carbonaceous materials are used as a negative electrode. Unfortunately, to the best of our knowledge, the synthesis of LiFeF$_3$ and its electrochemical properties have not yet been reported. We previously reported that NaFeF$_3$ prepared by mechanochemical synthesis could give a discharge capacity of 120 mAh g^{-1} at around 2.7 V, but this corresponds to only about 61% of the theoretical capacity (197 mAh g^{-1}) [10]. While the resultant NaFeF$_3$ particles were agglomerated (ca. 6 μm), the primary particles should be nano-sized. Fluoride-based materials usually show poor electronic conductivity due to the ionic character of the metal/fluorine bond. The use of fine particles of fluoride-based materials provides short conductive paths for electrons within them, and therefore the apparent electronic resistance should be low. Based on the above considerations, fine particles of NaFeF$_3$ should be very useful for achieving apparent high Na-ion diffusion.

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Various synthetic methods have been developed to produce monodisperse nano-sized particles with a controlled size, shape, and composition. Among them, wet-chemical synthesis is suited to the preparation of uniform nano-sized particles because nucleation and subsequent growth processes upon the formation of particles can be well controlled in a solution phase. In fact, high-quality nanocrystals of inorganic materials, such as metal, metal alloy, oxide, sulfide, fluoride and phosphate, have been prepared by liquid-phase synthesis using high-boiling-point organic solutions [11–13]. We previously reported the liquid-phase synthesis of uniform nano-sized $LiMnPO_4$ particles (ca. 7 nm) and their unique charge and discharge characteristics [14].

In this study, we prepared highly dispersed uniformly sized perovskite $NaFeF_3$ by liquid-phase synthesis using a high-boiling-point organic solution, and investigated its electrochemical properties by charge and discharge measurements.

2. Experimental

Oleic acid (90%, OA), oleylamine (70%, OAm), 1-octadecene (90%), iron powder (97%), trifluoroacetic acid (99%), sodium trifluoroacetate (98%), ethanol (99.5%) and hexane (96%) were used as received without further purification. 1 g of iron powder was added to 15 ml of trifluoroacetic acid, and the mixture was refluxed at 100 °C for 24 h. The mixture was then dried at 100 °C to obtain iron trifluoroacetate powder. 1 mmol each of iron trifluoroacetate and sodium trifluoroacetate was added to 20 mmol each of 1-octadecene and a mixture of oleic acid and oleylamine in a three-neck flask at room temperature; the molar ratio of OA/OAm (mmol/mmol) was set at 20/0, 16/4, 15/5, 13.3/6.7, and 10/10, while the total amount of OA and OAm was fixed at 20 mmol. The mixture was heated to 120 °C at 10 °C min^{-1} under Ar flow on a rotary shaker, and kept at this temperature for 0.5 h. The mixture was then heated to 280 °C at 20 °C min^{-1}, and kept at this temperature for 0.5 h under an Ar atmosphere to obtain a dark ocher solution. After the resultant solution was allowed to cool to below 70 °C, it was poured into an excess amount of ethanol, and this mixture was centrifuged to give deposits. The deposits were washed more than three times in a mixture of ethanol and hexane. The products were characterized by X-ray diffraction (XRD, RINT2100, Rigaku). Typical working conditions were 50 kV and 300 mA with a scan rate of 1.0° min^{-1}. A sol of the resultant particles was dropped on carbon-coated copper grids so that their morphology and microstructure could be observed by transmission electron microscopy (TEM, JEM2100F, JEOL).

$NaFeF_3$ powder was also prepared by mechanochemical synthesis, and used as a reference in this study. The rotation speed and duration for planetary milling were set at 450 rpm and 130 min, respectively. The detailed procedures are described in our previous report [10].

Electrochemical properties were studied by charge and discharge measurements at 25 °C using a coin-type cell of R2032. A test electrode was prepared as follows; the resultant particles (70 wt.%) were mixed with acetylene black (25 wt.%) by ball milling at 350 rpm for 15 h. The mixture was added to a poly(vinylidenefluoride) binder (KF#7305, Kureha) (5 wt.%) dispersed in 1-methyl-2-pyrrolidinone. It was then homogenized by shaking with yttria-stabilized zirconia balls for 1 h. The slurry was applied to a current collector consisting of Al foil. After the sheet was dried at 80 °C for 0.5 h in a vacuum oven, it was extended by applying pressure. A Na-foil and a polypropylene film (Celgard 3501) were used as the counter electrode and separator, respectively. The electrolyte used was 1 mol dm^{-3} $NaClO_4$ dissolved in PC. Unless otherwise stated, the charge/discharge cycles were carried out at constant current rates of 1, 0.1, and 0.01 C, which correspond
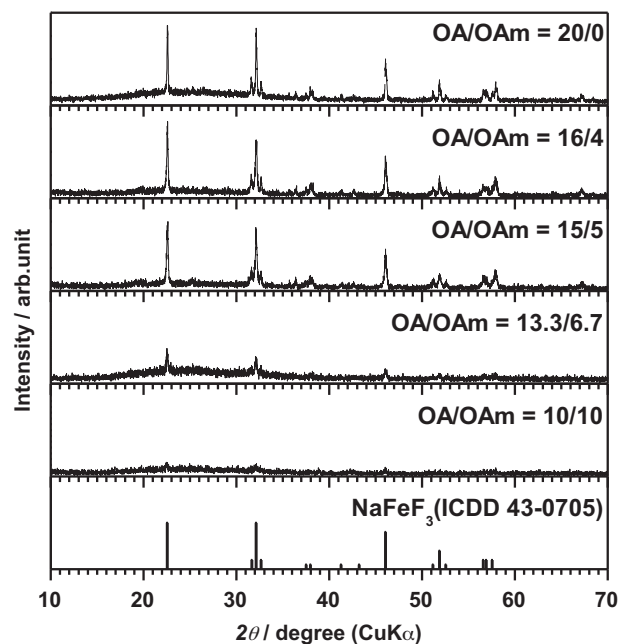

Fig. 1. XRD patterns of $NaFeF_3$ particles prepared at 280 °C by a liquid-phase synthesis.

to current densities of ca. 197, 19.7, and 1.97 mA g^{-1}, so that each charge and discharge process should theoretically be completed in 1, 10, and 100 h, respectively, with a relaxation period of 1 h at the end of each discharge/charge measurement. The charging and discharging processes ended at 4.5 V and 1.5 V, respectively. Cell assembly was conducted in an Ar-filled glove box.

3. Results and discussion

XRD patterns of the precursor particles prepared from iron powder and trifluoroacetic acid were very similar to those of manganese trifluoroacetate; to our knowledge, no diffraction data on iron trifluoroacetate are available for reference. In addition, no diffraction peak assigned to iron was observed in the XRD patterns. Therefore, the precursor should be iron trifluoroacetate. Fig. 1 shows XRD patterns of the resultant particles prepared by liquid-phase synthesis using the precursor particles. When no OAm was used, i.e. OA/OAm = 20/0, diffraction peaks appeared at 2θ angles of 22.6, 31.6, 32.1, 32.7, 37.5, 38.0, 46.1, 51.2, 51.9, 52.6, 56.9, and 57.6°, which were indexed as the (0 0 2), (0 2 0), (1 1 2), (2 0 0), (1 2 1), (1 0 3), (0 0 4), (1 3 0), (1 1 4), (1 3 1), (0 2 4), and (2 0 4) reflections of perovskite $NaFeF_3$, respectively. The diffraction peaks were observed at almost the same 2θ angles regardless of the molar ratio of OA/OAm in the range from 20/0 to 10/10, while the full width at half maximum (FWHM) of the diffraction peaks increased with an increase in the proportion of OAm. These results imply that the particle size should decrease with an increase in the proportion of OAm. In the present liquid-phase synthesis method, careful control of the synthetic atmosphere is required because cryolite Na_3FeF_6, instead of $NaFeF_3$, is easily formed upon exposure to air.

$NaFeF_3$ particles synthesized at OA/OAm ratios of 20/0, 13.3/6.7, and 10/10 were white, brown, and black, respectively. The $NaFeF_3$ particles were easily dispersed in hexane to form a transparent sol, which indicates that very small and highly dispersed particles were obtained. Fig. 2a and b shows typical TEM images of $NaFeF_3$ particles synthesized at an OA/OAm ratio of 20/0. The particles were highly dispersed with respect to each other, and their size was ca. 500–600 nm. Since a distinct crystal form, i.e. cuboid, was clearly observed, the $NaFeF_3$ particles were highly crystal-
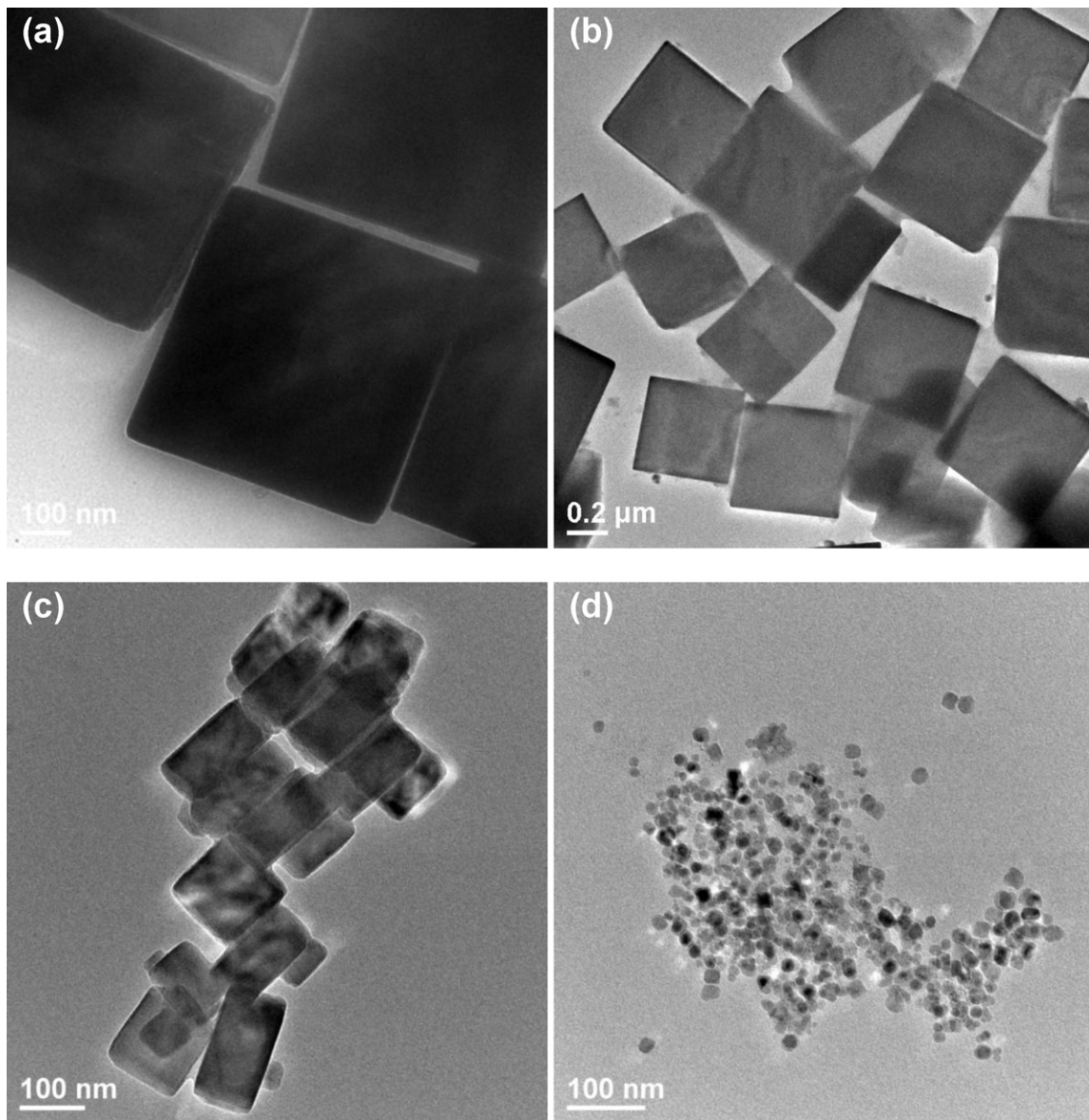
Fig. 2. TEM images of NaFeF$_3$ particles synthesized in organic solution with OA/OAm ratios of (a and b) 20/0, (c) 13.3/6.7, and (d) 10/10.

lized. The FT-IR spectrum of the NaFeF$_3$ particles (not shown) was very similar to that of oleic acid, in particular in a C–H stretching vibration region from 2800 to 3050 cm^{-1}. These results suggest that oleic acid molecules are attached to the NaFeF$_3$ particles. Hence, the NaFeF$_3$ particles could be dispersed due to the effect of steric hindrance between oleic acid molecules, which is in good agreement with the TEM observations, as shown in Fig. 2a and b. Typical TEM images of NaFeF$_3$ particles synthesized at molar ratios of OA/OAm = 13.3/6.7 and 10/10 are shown in Fig. 2c and d, respectively. Highly dispersed NaFeF$_3$ particles with a distinct crystal form were observed when synthesized at an OA/OAm ratio of 13.3/6.7, and their size was ca. 100–200 nm, as shown in Fig. 2c. The NaFeF$_3$ particles that were prepared at OA/OAm = 10/10 measured ca. 10–20 nm, and had irregular shapes. Thus, the particle size decreased in the order OA/OAm = 20/0 (ca. 500–600 nm) < 13.3/6.7 (ca. 100–200 nm) < 10/10 (ca. 10–20 nm). These results clearly indicate that the particle size decreased with an increase in the proportion of oleylamine, which is in good agreement with the order of the FWHM evaluated from the XRD patterns, i.e. the particle size of NaFeF$_3$ can be controlled by the ratio of OA/OAm.

Fig. 3a–c shows initial charge (extraction of Na$^+$ from NaFeF$_3$) and discharge (insertion of Na$^+$) curves of NaFeF$_3$ particles prepared by the present liquid-phase synthesis method, together with those of NaFeF$_3$ particles prepared by mechanochemical synthesis as a reference. The cell voltage gradually increased up to 4.5 V during charging at a rate of 0.01 C, as shown in Fig. 3a. NaFeF$_3$ particles synthesized at an OA/OAm ratio of 20/0 gave a charge capacity of 247 mAh g^{-1} at a rate of 0.01 C. This value was much higher than the theoretical specific capacity of NaFeF$_3$ (197 mAh g^{-1}). These results indicate that some side reactions, such as oxidative decomposition of an electrolyte, should also occur during charging. In the subsequent discharge process, the cell voltage gradually decreased to 1.5 V through an inflection part at around 2.9 V, and the discharge capacity was 170 mAh g^{-1}, which corresponds to 86.3% of the theoretical capacity of NaFeF$_3$. NaFeF$_3$ particles synthesized at OA/OAm = 13.3/6.7 and 10/10, as well as NaFeF$_3$ particles prepared by mechanochemical synthesis, showed charge and discharge behaviors similar to those for NaFeF$_3$ particles obtained at OA/OAm = 20/0, although their charge and discharge capacities were slightly higher. On the other hand, the charge and discharge
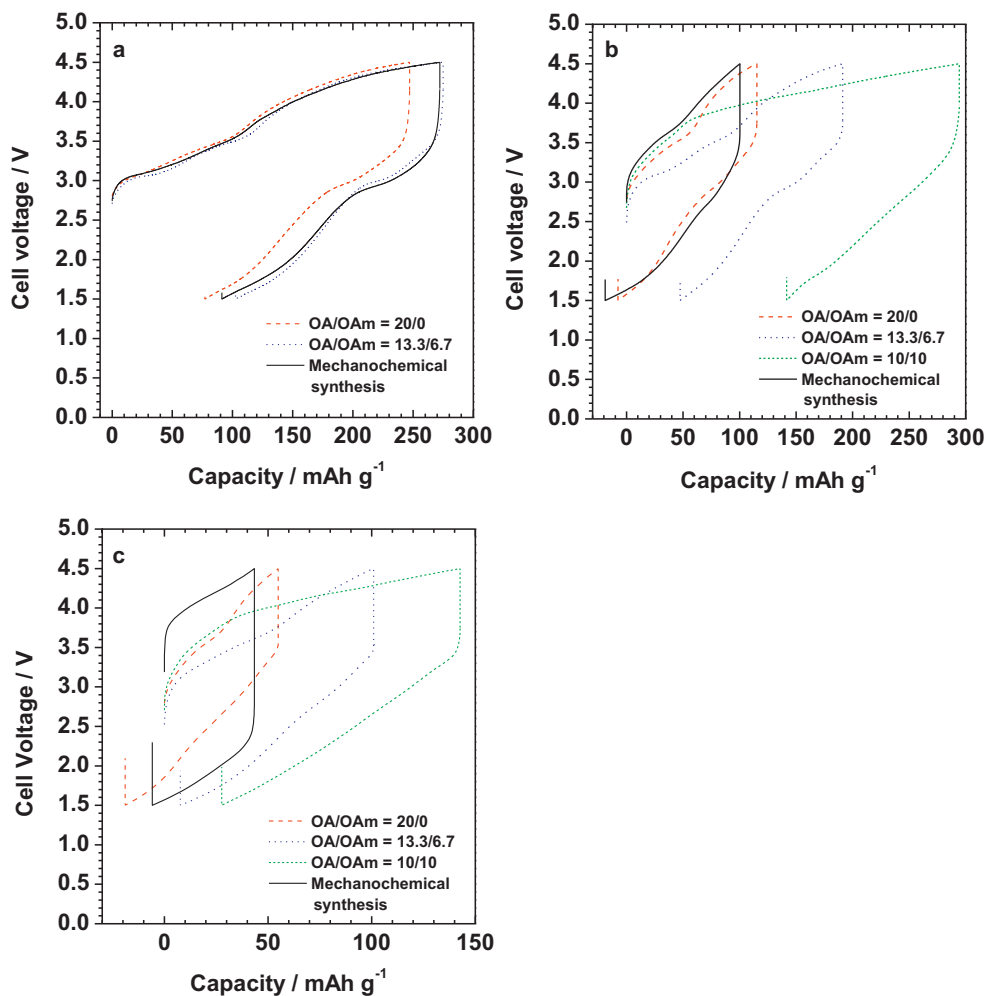
Fig. 3. Initial charge and discharge curves of NaFeF$_3$ particles at (a) 0.01, (b) 0.1, and (c) 1 C.

capacities clearly varied depending on the OA/OAm ratios at a rate of 0.1 C or higher; at 0.1 C, charge capacities were in the order mechanochemical synthesis < OA/OAm = 20/0 < 13.3/6.7 < 10/10, as shown in Fig. 3b. The corresponding discharge capacities were in the same order; 119, 123, 144, and 153 mAh g^{-1} for NaFeF$_3$ particles prepared by mechanochemical synthesis and liquid-phase synthesis at OA/OAm = 20/0, 13.3/6.7, and 10/10, respectively. When charge and discharge measurements were carried out at 1 C, the discharge capacities were in the same order as those obtained at 0.1 C; 49, 74, 93, and 115 mAh g^{-1} for NaFeF$_3$ particles prepared by mechanochemical synthesis and liquid-phase synthesis at OA/OAm = 20/0, 13.3/6.7, and 10/10, respectively, as shown in Fig. 3c. The dependence of the discharge capacity of NaFeF$_3$ particles on the discharge rate is summarized in Fig. 4. The discharge capacities decreased with an increase in the discharge rate. In addition, a difference in discharge capacity among the NaFeF$_3$ particles became obvious with an increase in the discharge rate. In particular, NaFeF$_3$ particles prepared by the present liquid-phase synthesis method gave very high capacities at 0.1 C or higher, compared to those obtained by mechanochemical synthesis. Our group previously reported that, while NaFeF$_3$ prepared by mechanochemical synthesis consisted of agglomerated particles (ca. 6 μm), the primary particles should be nano-sized [10]. NaFeF$_3$ particles prepared by mechanochemical synthesis in this work also consisted of primary particles of about ca. 20–50 nm, but they were strongly agglomerated to form micron-sized secondary particles. Thus, the size of the resultant NaFeF$_3$ particles was in the order
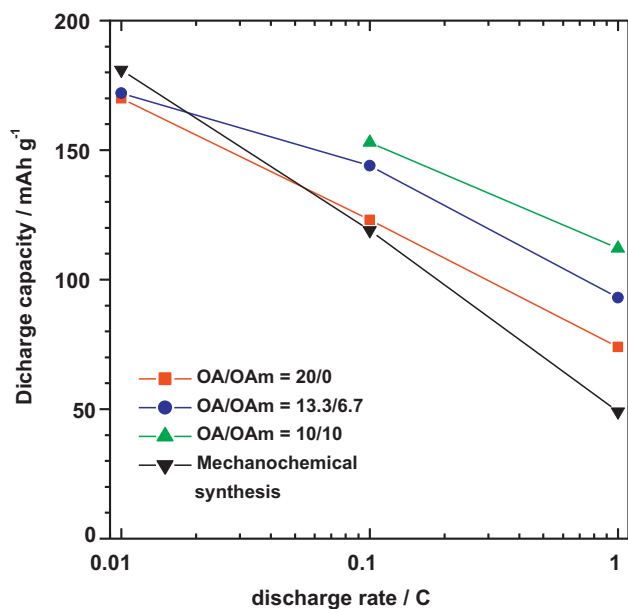

Fig. 4. Dependence of the discharge capacity of NaFeF$_3$ particles on the discharge rate.

mechanochemical synthesis (micron-size) > OA/OAm = 20/0 (ca. 500–600 nm) > 13.3/6.7 (ca. 100–200 nm) > 10/10 (ca. 10–20 nm). Based on these results, the discharge capacities were shown to increase with a decrease in the particle size of NaFeF$_3$. To enhance the charge and discharge reactions of Na-ion batteries, the rapid diffusion of Na-ion through the active materials as well as rapid Na-ion transfer across the interfaces between the electrolyte and active materials is essential. The use of nano-sized particles of active materials is very desirable for rapid charge and discharge reactions because the diffusion path for Na-ion within them can be shortened. In addition, nano-sized particles, which possess a large specific surface area, present a relatively large number of Na-ion insertion sites on their surface. Hence, the charge-transfer resistances at the interface between the electrolyte and active electrode materials are expected to be small. NaFeF$_3$ particles prepared by the present liquid-phase synthesis method were nano-sized and highly dispersed, and therefore large discharge capacities were obtained, particularly at high discharge rates, compared to the agglomerated nano-sized particles prepared by mechanochemical synthesis.

4. Conclusions

Highly dispersed nano-sized NaFeF$_3$ particles were prepared at 280 °C by liquid-phase synthesis using high-boiling-point organic solution. Their sizes ranged from ca. 10–20 nm to 500–600 nm depending on the ratio of OA/OAm in the synthesis solution. The NaFeF$_3$ particles were highly dispersed due to the effect of steric hindrance between attached oleic acid molecules. Charge and discharge curves of the fine NaFeF$_3$ particles showed a gradual increase and decrease in voltage, respectively, in the range 1.5–4.5 V. The discharge capacities obtained at 0.01 C were almost the same as those in the range 170–181 mAh g^{-1}, regardless of the particle size of NaFeF$_3$. However, a difference in discharge capacity among the NaFeF$_3$ particles became obvious with an increase in the discharge rate; smaller NaFeF$_3$ particles were associated with a higher discharge capacity, particularly at a rate of 0.1 C or higher. In addition, the highly dispersed NaFeF$_3$ particles prepared by the present liquid-phase synthesis method showed very high discharge capacities at 0.1 C or higher, compared to agglomerated nano-sized

particles prepared by mechanochemical synthesis. These results clearly indicate that the use of well-dispersed and nano-sized NaFeF$_3$ particles should effectively improve the rate performance of NaFeF$_3$. In addition, since the particle size of NaFeF$_3$ can be controlled by the composition of organic solvents in the present liquid-phase synthetic method, the present results may promote intensive studies on the particle-size effect in battery reactions with the use of highly dispersed nano-sized fluoride particles of active materials.

Acknowledgment

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