Electrochemical performance of composites of spinel-type LiFe$_{1-x}$Mn$_x$SiO$_4$ nanocrystals and glassy phase synthesized by quenching of melts

Takuya TOGASHI, Tsuyoshi HONMA and Takayuki KOMATSU

Department of Materials Science and Technology, Nagaoka University of Technology, 1603-1 Kamitomioka-cho, Nagaoka 940–2188, Japan

New composite ceramics consisting of spinel-type LiFe$_{1-x}$Mn$_x$SiO$_4$ nanocrystals and glassy phase were synthesized by a quenching of melts with the compositions of 25Li$_2$O–(25−y)Fe$_2$O$_3$–2yMnO$_{1.5}$–SiO$_2$ (y = 0–25, mol %) and their electrochemical performance as cathode materials for Li$^+$ ion secondary batteries (LIBs) was examined. In the melt-quenched samples with y = 0–7.5, the formation of LiFe$_{1-x}$Mn$_x$SiO$_4$ nanocrystals with a diameter of ~30 nm was confirmed together with the presence of the glassy phase from XRD, STEM-EDX, and HRTEM measurements. The electrical conductivity (σ) of the melt-quenched samples (composites) at room temperature decreased rapidly with increasing MnO$_2$ content, i.e., σ = 2.0 × 10$^{-3}$ S cm$^{-1}$ for the sample with y = 0 and σ = 5.7 × 10$^{-4}$ S cm$^{-1}$ for the sample with y = 7.5, and the activation energy (E$_a$) of σ was 0.2–0.3 eV. From the electrochemical charge and discharge curves, it was clarified that the melt-quenched samples work as cathode materials for LIBs. The sample with LiFe$_{0.7}$Mn$_{0.3}$SiO$_4$ nanocrystals showed a large discharge capacity of 361 mAh g$^{-1}$ at the first cycle, although a large decrease in the discharge capacity with cycling was observed. The melt-quenched samples with y = 10–25 were glasses with no crystals, but they also showed Li$^+$ ion battery performance.

©2015 The Ceramic Society of Japan. All rights reserved.

Key-words : Composite, Spinel-type LiFe$_{1-x}$Mn$_x$SiO$_4$, Nanocrystal, Melt-quenching, Lithium ion battery

1. Introduction

Lithium ion battery (LIB) has been used as energy source for many portable devices such as mobile computer because of its high-energy density and good cycle performance. LiCoO$_2$ is a well-known cathode material and has been widely used in LIBs. However, because LiCoO$_2$ is composed of cobalt being a rare element and delithiated LiCoO$_2$ crystals release O$_2$ gas due to their decomposition easily at high temperatures,\(^\text{1})\) it is of importance to develop new cathode materials without rare elements and with high thermal stability. As one of the alternative materials for LiCoO$_2$, an olivine-type LiFePO$_4$ has received much attention because of its good thermal stability, an abundance of Fe element, and the high theoretical capacity of 170 mAh g$^{-1}$.\(^\text{2–9})\) The electrical conductivity of LiFePO$_4$ at room temperature is, however, very low, i.e., ~10$^{-9}$ S cm$^{-1}$, and it is necessary to design carbon coating on the surface of LiFePO$_4$ particles.\(^\text{10})\)

Recently, our research group\(^\text{10)}\) succeeded in synthesizing new spinel-type lithium iron silicate crystals (designated as LiFeSiO$_4$) using a conventional melt-quenching method and found that LiFeSiO$_4$ crystals exhibit a high electrical conductivity of 2.5 × 10$^{-4}$ S cm$^{-1}$ at room temperature. We demonstrated that new spinel-type LiFeSiO$_4$ crystals synthesized work as cathode materials in LIBs.\(^\text{10)}\) Furthermore, our research group\(^\text{11)}\) examined the crystalline phases and electrical conductivity of melt-quenched samples in the Li$_2$O–Fe$_2$O$_3$–SiO$_2$ system more in detail and clarified that the formation behavior of LiFeSiO$_4$ crystals is sensitive for the chemical composition of melts and cooling rate.

We also proposed that the chemical composition of LiFeSiO$_4$ would be spinel-type Li$_{1+x}$Fe$^{3+}$$_{1-x}$+ $\delta$SiO$_4$ and both of Li$^+$ ion conductivity and electron hopping conductivity between Fe$^{3+}$ and Fe$^{2+}$ are present.\(^\text{13})\) It is noted that LiFeSiO$_4$ crystals can be formed only by a rapid quenching of melts with the compositions of around LiFeSiO$_4$ and cannot be synthesized by a conventional solid state reaction, meaning that LiFeSiO$_4$ is a metastable crystalline phase. It should be pointed out that there has been no report on the fabrication and characterization of spinel-type LiFeSiO$_4$ crystals by other research groups.

The melt-quenching and the crystallization of glasses are very unique methods for the synthesis of materials. For instance, these methods often provide metastable phases, i.e., new crystalline phases\(^\text{12,13})\) and have an advantage in the design and control of crystal morphologies, i.e., more simple and shorter fabrication time compared with other methods. Indeed, besides of LiFeSiO$_4$ crystals,\(^\text{10,11})\) other cathode materials for LIBs such as LiFePO$_4$, Li$_3$V$_2$(PO$_4$)$_3$, and $\beta$-LiVOPO$_4$ have been synthesized through the crystallization of glasses (i.e., the glass-ceramic route).\(^\text{14–18})\) The direct melt casting process to make electrochemically active LiFePO$_4$ cathode materials has been proposed by Gauthier et al.\(^\text{19,20})\) Recently, Homma et al.\(^\text{21})\) developed glass-ceramics consisting of Na$_3$Fe$_2$O$_5$ crystals through the crystallization of 40Na$_2$O–20Fe$_2$O$_3$–40P$_2$O$_5$ glass and demonstrated that those glass-ceramics work as cathode materials for rechargeable Na$^+$ ion secondary battery.

The purpose of this study is to synthesize spinel-type LiFe$_{1-x}$Mn$_x$SiO$_4$ crystals by using the melt-quenching method in the Li$_2$O–Fe$_2$O$_3$–MnO$_2$–SiO$_2$ system and to clarify their electrochemical performance as cathode materials for LIBs. There has been no report on the synthesis of spinel-type LiFe$_{1-x}$Mn$_x$SiO$_4$ crystals

\(^1\) Corresponding author: T. Komatsu; E-mail: komatsu@nms.nagaokaut.ac.jp
so far. Because Mn ion is one of the most important transition metal ions in LIBs, it is of particular interest to synthesize new LiFe1–yMnSiO4 crystals and characterize their battery performance. Honma et al.22) have reported the fabrication of LiFe1–yMnPO4 crystals by using the crystallization of glasses in Li2O–Fe2O3–MnO2–P2O5 system and found that the substitution of Mn ions for Fe ions has a strong effect on the glass-forming tendency and also Li+ ion battery performance.

2. Experimental

Samples with the compositions of 25Li2O–(25 − y)Fe2O3–2yMnO2–50SiO2 (y = 0–25) (mol%), i.e., the nominal composition of LiFe1–xMnSiO4 (x = 0–1.0), were prepared by a melt quenching method. Commercial reagents of Li2CO3 (99.9%, Kojundo Chem.), Fe2O3 (99.9%, Kojundo Chem.), MnO2 (85.0%, Kanto Chem.), and SiO2 (Guaranteed Reagent, Nacalai Tesque) were used as raw materials and were mixed. The mixtures were melted using a platinum crucible at 1400°C for 25 min in an electric furnace in air. The melts were poured onto an iron plate and were pressed by the other iron plate to a thickness of 0.5 mm. The quenching rate of melts is around 10⁴K/min.11)

Differential thermal analyses (DTA) (Rigaku TG-8120) were carried out for the melt-quenched powder samples (pulverized after melt-quenching) in order to check the presence of glassy phase. Crystalline phases in the melt-quenched samples were identified using X-ray diffraction (XRD) analysis at room temperature (RT). Electrical conductivities of melt-quenched samples were measured using an alternative current (AC) impedance method (HIOKI 3522-50 LCR HiTESTER) in the temperature range of RT to 250°C. Metal gold sputtered was used as electrodes. The composition of the crystals formed in the melt-quenched samples was analyzed by scanning transmission electron microscope-energy dispersive X-ray spectroscopy (JEOL: STEM-EDX, JEM-2100F).

The charge/discharge tests for the melt-quenched samples were measured by following procedures. First, plate-shaped quenched samples were pulverized by milling and were mixed with carbon by planetary ball milling (Premium line P-7, Fritsh Co.). Second, Poly-vinylidene-di-fluoride (PVDF #1100, Kishida Chemical Corp.) and N-methyl-2-pyrrolidone were added to the mixtures, and the slurries obtained were spread on aluminum foils by a bar coater. The weight ratio of the mixtures was 83.3 wt % for the samples, 8.3 wt % for carbon, and 8.3 wt % for PVDF. The sheets were dried at 80°C for 1 h, and circular disks as cathodes were prepared by cutting the sheets. Test cells were assembled using the disk as a cathode, a lithium metal as an anode, and a solution of 1 mol/L LiPF6 EC/DEC as an electrolyte in Ar atmosphere (RH% < 2.0 × 10⁻³). The charge/discharge performance tests were carried out by using charge/discharge measurements (HJ-1001, Hokuto densko) at 25°C. The cell potential was swept in the 1.0–4.5 V, and the charge/discharge rate was 0.1 C.

3. Results and discussion

3.1 Crystalline phase in melt-quenched samples

The powdered XRD patterns at RT for the melt-quenched samples in 25Li2O–(25 − y)Fe2O3–2yMnO2–50SiO2 (y = 0–25) (mol%) are shown in Fig. 1. The samples with y = 0 and y = 25 correspond to the nominal compositions of LiFeSiO4 and LiMnSiO4, respectively. As seen in Fig. 1, the samples with y = 0–7.5 show some peaks, indicating the presence of crystalline phases, and the samples with y = 10–25 have only halo patterns, indicating the formation of glasses. These results indicate that the melt-quenched samples with y = 0–7.5 are considered to be composite materials consisting of crystalline and glassy phases. In the DTA patterns (not shown here), endothermic dips corresponding to the glass transition were observed for all melt-quenched samples, and the glass transition temperature was 372–524°C.

The XRD peaks observed in the sample with y = 0 are assigned to the spinel-type LiFeSiO4 with a space group ofFd3m (227) of a normal spinel structure, as reported in the previous papers.10,11) Similar XRD patterns were also observed in the samples with y = 2.5, 5.0 and 7.5. The position of XRD peaks shifted to the lower 2θ angle with the substitution of Mn for Fe. The lattice constants of crystals formed in the quenched samples with y = 0–7.5 were estimated using the least squares method in the assumption of spinel-type cubic structure, and the XRD peaks were fitted well with Ref. 10) We tried to clarify the structure of crystals formed by using a Rietveld analysis more in detail. However, at this moment, it is difficult to get a good fitting, because there are many factors such as the selection of sites in each element.

The results on the lattice parameters are shown in Fig. 2, indicating that the value of the a-axis of spinel-type crystals formed increases with increasing MnO2 content, e.g., a = 0.8331 nm for the sample with y = 0 and a = 0.8380 nm for the sample with y = 7.5. According to Shannon,23) the ionic radii of Fe and Mn ions with oxygen octahedral coordination are as follows: 0.61 nm for Fe²⁺, 0.55 nm for Fe³⁺, 0.67 nm for Mn²⁺, and 0.58 nm for Mn³⁺. The increase in the a-axis shown in Fig. 2, therefore, suggests the gradual substitution of Mn ions for Fe ions in spinel-type crystals. Honma et al.22) found that the lattice constants of olivine-type LiFe1–xMnPO4 crystals formed through the crystallization of Li2O–Fe2O3–MnO2–P2O5 glasses increase with the substitution of Mn ions for Fe ions. As seen in Fig. 1, the XRD peaks are broad, and thus the average size of LiFe1–xMnPO4 crystals was estimated from the peak width of XRD patterns using the Scherrer’s equation. The results on the average size are shown in Fig. 2, and it is found that the crystal size is around 14–32 nm. From the results shown in Figs. 1 and 2, it is considered that spinel-type LiFe1–xMnPO4 nano-scale crystals are formed during the quenching of 25Li2O–(25 − y)Fe2O3–2yMnO2–50SiO2 melts with y = 0–7.5.

The micro-structure of melt quenched samples was examined from high resolution transmission electron microscope (HRTEM:
3.2 Electrical conductivity of melt-quenched samples

The temperature dependence of electrical conductivities ($\sigma$) for the melt-quenched samples in the temperature range of RT to 250°C is shown in Fig. 3. The electrical conductivity increased with increasing temperature for all melt-quenched samples. In particular, the sample with $y = 0$, i.e., LiFeSiO$_4$ sample, shows a very high electrical conductivity of $\sigma = 2.0 \times 10^{-13}$ S/cm at RT and a very low activation energy ($E_a$) for the electrical conductivity of $E_a = 0.3$ eV. Here, the activation energy of $\sigma$ was evaluated from the data shown in Fig. 3 using the Arrhenius relation, i.e., $\sigma = \sigma_0 \exp(-E_a/kT)$, where $\sigma_0$ is the pre-exponential factor, $k$ is the Boltzmann constant, and $T$ is the temperature.

For the melt-quenched samples with $y = 2.5$, 5.0, and 7.5, it is found that the electrical conductivity at RT decreases steeply with the substitution of MnO$_2$ for Fe$_2$O$_3$, i.e., $\sigma = 1.2 \times 10^{-8}$ S/cm for $y = 2.5$, $\sigma = 6.0 \times 10^{-8}$ S/cm for $y = 5.0$, and $\sigma = 5.7 \times 10^{-8}$ S/cm for $y = 7.5$. Because the melt-quenched samples with $y = 0$–7.5 are composite materials consisting of spinel-type LiFe$_{1-x}$Mn$_x$SiO$_4$ nanocrystals and glassy phase, the electrical conductivity of the melt-quenched samples depends largely on the amount of spinel-type LiFe$_{1-x}$Mn$_x$SiO$_4$ nanocrystals. It is expected that the amount of spinel-type LiFe$_{1-x}$Mn$_x$SiO$_4$ nanocrystals in the melt-quenched samples with $y = 5.0$ and 7.5 would be small, because the intensity of XRD peaks is weak, as shown in Fig. 1, consequently providing an extremely low electrical conductivity at RT. The glassy samples with $y = 10$, 12.5, and 25, which contain no spinel-type LiFe$_{1-x}$Mn$_x$SiO$_4$ crystals, show very low electrical conductivities of the order of $10^{-11}$–$10^{-13}$ S/cm at RT.

As seen in Fig. 3, the samples with $y = 2.5$, 5.0, and 7.5 show a unique temperature dependence of electrical conductivity. That is, the temperature dependence of $\sigma$ in the low temperature side is different from that in the high temperature side. For instance, the sample with $y = 2.5$ has the values of $E_a = 0.20$ eV in the temperature range of RT to 120°C and of $E_a = 0.51$ eV in the temperature range of 120 to 250°C. These results suggest that the main electrical conduction mechanism changes from the electronic conduction to the ionic conduction depending on the temperature. Because the glass transition temperature for the melt-quenched samples, i.e., for the glassy phase, is 372–524°C, the phase transformation such as crystallization is not expected in the temperature range of RT to 250°C. As seen in Fig. 3, the melt-quenched sample with no Mn ions exhibits only one activation energy in the temperature range of RT to 250°C. In the Cole-Cole plots obtained from the impedance measurements in the frequency range of 0.4 Hz to 100 kHz for the melt-quenched samples, one semicircle was observed in each plot, and the capacitance of the resistance component was estimated to be the order of pF. These results suggest that the main resistance component in the melt-quenched samples is a bulk resistance. From the Cole-Cole plots, the constant phase element (CPE) index number $p$ was estimated by using the equation of $Z = R/\{1 + (\omega RC)^p\}$ based on the assumption of RC parallel circuit, where $R$ is resistance of bulk, $\omega$ is angular frequency, and $C$ is capacitance. As a result, the values of $p$ ~0.7 were obtained, indicating that the semicircles are slightly distorted. As discussed in the previous paper, in spinel-type Li$_{1+y}$Fe$_{1+y}$Mn$_x$SiO$_4$ crystals with no Mn ions, both of Li$^+$ ion conductivity and electron hopping conductivity between Fe$^{3+}$ and Fe$^{2+}$ are present. In particular, the electron hopping conductivity between Fe$^{3+}$ and Fe$^{2+}$ ions provides very low activation energies of $E_a = 0.1$–0.3 eV. In addition, it is considered that generally the activation energy for lithium ion conduction is larger than that for electronic hopping conduction. Indeed, as seen in Fig. 3, the activation energies of the samples with $y = 10$–25 consisting of only the glassy phase (Fig. 1) are large compared with the sample with $y = 0$ consisting of both the crystalline phase and residual glass phase. It is considered that the appearance of two activation energies for the electrical conductivity in the melt-quenched samples with $y = 2.5$, 5.0, and 7.5 might be related to the presence of both Fe and Mn ions, because the amount and quality of crystals change depending on the Fe/Mn ratio as seen in Fig. 1.

The values of $\sigma$ at RT and $E_a$ in the low temperature side evaluated from Fig. 3 are summarized in Fig. 4 as a function of MnO$_2$ content. For the glassy samples with $y = 10$, 12.5, and 25,
the values of $E_a$ were evaluated from the data in the high temperature side, and the values of $\sigma$ at RT were deduced from the Arrhenius relation (i.e., extending to the low temperature side). The data evaluated for the glassy samples are also summarized in Fig. 4. It is obvious that the melt-quenched samples with spinel-type LiFe$_{1-y}$Mn$_y$SiO$_4$ nanocrystals exhibit extremely different electrical conductivity behavior compared with the glassy samples with no crystals. The glassy samples show a large activation energy of $E_a = 0.7$–1.0 eV. Okada et al.\textsuperscript{24} examined the Li$^+$ ion conductivity in Li$_2$O–Nb$_2$O$_5$–P$_2$O$_5$ glasses and reported the following values, e.g., $\sigma = 1.27 \times 10^{-7}$ S/cm at RT and $E_a = 0.49$ eV in the temperature range of RT to $200^\circ$C. It is, therefore, considered that 25Li$_2$O–(25–$y$)Fe$_2$O$_3$–$2y$MnO$_2$–50SiO$_2$ glasses with $y = 10, 12.5,$ and 25 prepared in this study might have glass structures having high barriers for Li$^+$ mobility.

### 3.3 Li$^+$ ion battery performance in melt-quenched samples

The electrochemical charge and discharge curves for the melt-quenched samples ($y = 0, 2.5, 5.0,$ and 7.5) with spinel-type LiFe$_{1-y}$Mn$_y$SiO$_4$ nanocrystals are shown in Fig. 5. In these experiments, the charge and discharge operations were swept in the range of 1.0–4.5 V at the rate of 0.1C, and the cycling was carried out five times. It is seen that the capacities for the first charging are smaller than those in the following charging cycles from the second to the fifth. In the charging for LIBs, i.e., the deintercalation of lithium ions, the oxidation of transition metal (TM) ions is usually occurred to keep the charge neutrality of cathode materials. In other words, the presence of TM ions having low valences in cathode materials is important for an effective charging. In the present study, the samples of 25Li$_2$O–(25–$y$)Fe$_2$O$_3$–$2y$MnO$_2$–50SiO$_2$ ($y = 0$–25) (mol %) were prepared by a melt-quenching method without using any special reducing processing, and thus, it is expected that a large amount of Fe and Mn ions with the high valence states such as Fe$^{3+}$ and Mn$^{4+}$ is present in the melt-quenched samples. This would be one of the reasons for the small capacities in the first charging.

It is seen that the first discharge capacity increases with increase MnO$_2$ content. That is, the sample with $y = 0$ shows the capacity of 180 mAhg$^{-1}$ in the first discharge, and a large capacity of 361 mAhg$^{-1}$ was observed for the sample with $y = 7.5$. Here, the experimental capacity was estimated by a value in the cut-off voltage. Generally, it is expected that the number of
electron which is possible to react in electrochemical reaction, namely the theoretical capacity, increases with the substitution of Mn ions for Fe ions, because Mn ions can take various valences of Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$. In the present experiments, the actual capacity for the sample with $y = 7.5$ in the first discharge was particularly larger than the theoretical capacity. If the discharge capacity of 361 mAh g$^{-1}$ is caused by the discharge mechanism, it is considered that around two molar Li$^{+}$ ions and two molar electrons are reacted during the discharging in the first cycle for the crystals formed in the sample with $y = 7.5$. However, in the case for the sample with $y = 7.5$, the size of crystallinity in the sample was smaller than other samples in $y = 0$–5.0 because the intensity of XRD peak was small. It is, therefore, considered that the larger capacity observed in the unstable glass with $y = 7.5$ might be mainly due to the residual glass, although the details are not clear at this moment. It is also seen that the change in the discharge capacity with cycling depends largely on the content of MnO$_2$ (Fig. 5). That is, the sample with $y = 7.5$ exhibits a large decrease in the capacity with cycling, but in the sample with $y = 0$, the decrease in the capacity with cycling is small. It is concluded from Fig. 5 that the melt-quenched samples containing spinel-type LiFe$_{1-y}$Mn$_y$SiO$_4$ nanocrystals in the system of 25Li$_2$O–(25–$y$)Fe$_2$O$_3$–2yMnO$_2$–50SiO$_2$ with $y = 0$–7.5 work as cathode materials for Li$^+$ ion secondary battery. The charge and discharge potentials in the second cycle for the melt-quenched samples with $y = 0$–7.5 were $\sim$2.0 and $\sim$1.3 V, respectively, being almost irrespective of the chemical composition of samples (i.e., the ratio of Fe$_2$O$_3$/MnO$_2$). In the present study, unfortunately, the improvement of charge and discharge potentials by the substitutions of MnO$_2$ for Fe$_2$O$_3$ was not observed, although in the case of Li$_2$O–Fe$_2$O$_3$–MnO$_2$–P$_2$O$_5$ system the substitution of Mn ions for Fe ions improves Li$^+$ ion battery performance.\(^{22}\) As found in this study, the melt-quenched samples of 25Li$_2$O–(25–$y$)Fe$_2$O$_3$–2yMnO$_2$–50SiO$_2$ ($y = 0$–25, mol %) are composite materials with both spinel-type LiFe$_{1-y}$Mn$_y$SiO$_4$ nanocrystals and glassy phase, and the amount of LiFe$_{1-y}$Mn$_y$SiO$_4$ nano-crystals decreases largely with the substitutions of MnO$_2$ for Fe$_2$O$_3$. The problems of small charge and discharge potentials and large hysteresis observed in the present study might be improved through the optimization of chemical composition and the increase in the amount of spinel-type LiFe$_{1-y}$Mn$_y$SiO$_4$ nanocrystals in the Li$_2$O–Fe$_2$O$_3$–MnO$_2$–SiO$_2$ system.

After the charge and discharge experiments (i.e., after five times cycling), the micro-structure of the sample with $y = 7.5$ used as cathode materials was examined from STEM and HRTEM observations, and the results are shown in Fig. 6. Crystalline particles with a diameter of $\sim$30 nm are observed clearly. This value of $\sim$30 nm is well consistent with the values of 14–32 nm estimated from XRD patterns (Fig. 2). The EDX spectra of a crystal and the other part (the points of A and B marked in the TEM image) are shown in Fig. 7. It is found that the crystal contains the elements of Fe, Mn, Si, and O with the atomic ratio of 0.37:0.17:1.0:2.7. Similar EDX results were obtained in other crystalline particles, indicating that the average ratio of Fe and Mn elements in the crystalline particles is Fe/Mn = 0.69/0.31. It should be pointed out that the chemical composition of 25Li$_2$O–(25–$y$)Fe$_2$O$_3$–2yMnO$_2$–50SiO$_2$ with $y = 7.5$ provides the ratio of Fe/Mn = 0.7/0.3. In other words, the present study strongly suggests that spinel-type LiFe$_{1-y}$Mn$_y$SiO$_4$ nanocrystals being present in the melt-quenched sample of 25Li$_2$O–(25–$y$)Fe$_2$O$_3$–2yMnO$_2$–50SiO$_2$ with $y = 7.5$ would be close to LiFe$_{1-y}$Mn$_y$SiO$_4$. Unfortunately, Li element is not measured in STEM-EDX measurements used in this study. Furthermore, at this moment, the valences of Fe and Mn in spinel-type LiFe$_{0.7}$Mn$_{0.3}$SiO$_4$ nanocrystals have not been determined. The content of Li in spinel-type LiFe$_{0.7}$Mn$_{0.3}$SiO$_4$ nanocrystals would vary depending on the valences of Fe and Mn ions. In this paper, we use the notation of LiFe$_{1-y}$Mn$_y$SiO$_4$ for the spinel-type crystals being present in the melt-quenched samples. As shown in Fig. 7, the presence of Fe, Mn, Si, and O is clearly detected in the point B, and the atomic ratio of Fe:Mn:Si:O = 0.58:0.13:1.0:3.4 was obtained. In addition, we measured ex-situ XRD patterns for the discharged cathodes after the cell tests and examined whether the structural change in crystals is taking place during the battery performance tests or not. As a result, any change was not observed.
in the diffraction positions of crystals in the samples with \( y = 0 - 7.5 \), and also any formation of crystals was not confirmed in the samples with \( y = 10 - 25 \). It is, therefore, concluded that spinel-type LiFe\(_{1-x}\)Mn\(_x\)SiO\(_4\) nanocrystals are stable even in electrochemical reactions and any destruction of the crystal structure does not occur during the charge and discharge processing. Furthermore, it is also concluded that the glassy samples with \( y = 10 - 25 \) still keep the glassy state without causing any crystallization during the cell tests.

The electrochemical charge and discharge curves for the melt-quenched glassy samples with \( y = 10, 12.5, \) and 25, which contain no crystals, are shown in Fig. 8. It is seen that these glasses also show Li\(^+\) ion secondary battery performance, although the values of the discharge capacity are not so large and the discharge capacity decreases rapidly with cycling. At this moment, the electrochemical reaction as cathode materials in these glasses is unclear. There has been no report on the glass formation in the quaternary system of Li\(_2\)O-Fe\(_2\)O\(_3\)-Mn\(_2\)O\(_3\)-SiO\(_2\). It is required to clarify the nano-scaled glass structure and valences of Fe and Mn ions in the glasses obtained in this study.

As clarified in this study, spinel-type LiFe\(_{1-x}\)Mn\(_x\)SiO\(_4\) nanocrystals are formed during the quenching of 25Li\(_2\)O-(25-y)Fe\(_2\)O\(_3\)-yFe\(_2\)O\(_3\)-50SiO\(_2\) melts with \( y = 0 - 7.5 \). It is considered that the electrical conductivity and Li\(^+\) ion battery performance (charge and discharge behaviors) depend on the amount of LiFe\(_{1-x}\)Mn\(_x\)SiO\(_4\) nanocrystals. In order to enhance the battery performance, it would be necessary to increase the amount of LiFe\(_{1-x}\)Mn\(_x\)SiO\(_4\) nanocrystals being present in the samples. All the melt-quenched samples obtained in this study were heat-treated at various temperatures in air and reducing atmosphere (5%H\(_2\)), and the possibility of the evolution of spinel-type LiFe\(_{1-x}\)Mn\(_x\)SiO\(_4\) nanocrystals was examined from XRD analyses. But, any indication on the increase in the amount of LiFe\(_{1-x}\)Mn\(_x\)SiO\(_4\) nanocrystals has not been observed (the data are not shown here). Furthermore, even in the 25Li\(_2\)O-(25-y)Fe\(_2\)O\(_3\)-2yMn\(_2\)O\(_3\)-50SiO\(_2\) glasses with \( y = 10.0 - 25.0 \) (Fig. 1), the crystallization of spinel-type LiFe\(_{1-x}\)Mn\(_x\)SiO\(_4\) nanocrystals has not been observed. At this moment, therefore, we can say that spinel-type LiFe\(_{1-x}\)Mn\(_x\)SiO\(_4\) nanocrystals can be formed only by the rapid quenching of the corresponding melts.

4. Conclusion

We synthesized new composite ceramics consisting of spinel-type LiFe\(_{1-x}\)Mn\(_x\)SiO\(_4\) nanocrystals and glassy phase by using a quenching of melts with the compositions of 25Li\(_2\)O-(25 - y)-Fe\(_2\)O\(_3\)-2yMn\(_2\)O\(_3\)-50SiO\(_2\) (\( y = 0 - 25 \), mol %) and examined their electrochemical performance as cathode materials for Li\(^+\) ion secondary batteries (LIBs). The formation of LiFe\(_{1-x}\)Mn\(_x\)SiO\(_4\) (\( x = 0 - 0.3 \)) nanocrystals (~30 nm) was confirmed from XRD and STEM-EDX measurements in the melt-quenched samples with \( y = 0 - 7.5 \). The melt-quenched samples with \( y = 10 - 25 \) were glasses with no crystals. The electrical conductivity (\( \sigma \)) of the melt-quenched samples at RT decreased rapidly with increasing MnO\(_2\) content, i.e., \( \sigma = 2.0 \times 10^{-3} \text{Scm}^{-1} \) for the sample with \( y = 0 \) and \( \sigma = 5.7 \times 10^{-4} \text{Scm}^{-1} \) for the sample with \( y = 7.5 \), and the activation energy (\( E_a \)) of \( \sigma \) was 0.2 - 0.3 eV. The sample with LiFe\(_2\)Mn\(_{0.5}\)SiO\(_4\) nanocrystals showed a large discharge capacity of 361 mAhg\(^{-1}\) at the first cycle, although a large decrease in the discharge capacity with cycling was observed. The present study proposes that the melt-quenched samples work as cathode materials for LIBs.

Acknowledgments This work was supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sport, Culture, and Technology, Japan (No. 23655194) and the Program for High Reliable Materials Design and Manufacturing in Nagoya University of technology.

References

1) J. R. Dahn and E. W. Fuller, *Solid State Ionics*, 69, 265–270 (1994).
2) A. K. Padhi, K. S. Nanjundaswamy and J. B. Goodenough, *J. Electrochem. Soc.*, 144, 1188–1194 (1997).
3) H. Huang, S. C. Yin and L. F. Nazar, *Solid State Lett.*, 4, A170–A172 (2001).
4) A. Yamada, S. C. Chung and K. Hinokuma, *J. Electrochem. Soc.*, 148, A224–A229 (2001).
5) N. Ravet, Y. Chouinard, J. F. Magnan, S. Besner, M. Gauthier and M. Armand, *J. Power Sources*, 97–98, 503–507 (2001).
6) P. P. Prosini, D. Zanet and M. Pasquali, *Electrochim. Acta*, 46, 3517–3523 (2001).
7) S. Y. Chung, J. T. Bloking and Y. M. Chiang, *Nat. Mater.*, 1, 123–128 (2002).
8) Z. Chen and J. R. Dahn, *J. Electrochem. Soc.*, 149, A1184–A1189 (2002).
9) F. Croce, A. D. Epifanio, J. Hassoun, A. Deptula, T. Olszczak and B. Scrosati, *Electrochem. Solid-State Lett.*, 5, A47–A50 (2002).
10) T. Honma, T. Tagashi and T. Komatsu, *J. Ceram. Soc. Japan*, 120, 93–97 (2012).
11) T. Tagashi, T. Honma and T. Komatsu, *J. Am. Ceram. Soc.*, 97, 835–842 (2014).
12) K. Shiota, T. Komatsu, H. G. Kim, R. Sato and K. Matusita, *J. Non-Cryst. Solids*, 189, 16–24 (1995).
13) T. Honma, Y. Benino, T. Fujiwara, R. Sato and T. Komatsu, *Opt. Mater.*, 20, 27–33 (2002).
14) K. Hirose, T. Honma, Y. Benino and T. Komatsu, *Solid State Ionics*, 178, 801–807 (2007).
15) K. Nagamine, K. Hirose, T. Honma and T. Komatsu, *Solid State Ionics*, 178, 508–515 (2008).
16) K. Nagamine, T. Honma and T. Komatsu, *J. Am. Ceram. Soc.*, 2015.
17) K. Nagamine, T. Honma and T. Komatsu, J. Power Sources, 196, 9618–9624 (2011).
18) T. Nagakane, H. Yamauchi, K. Yuki, M. Ohji, A. Sakamoto, T. Komatsu, T. Honma, M. Zou, G. Park and T. Sakai, Solid State Ionics, 206, 78–83 (2012).
19) M. Gauthier, C. Michot, N. Ravet, M. Duchesneau, J. Dufour, G. Liang, J. Wontcheu, L. Gauthier and D. D. MacNeil, J. Electrochem. Soc., 157, A453–A462 (2010).
20) D. D. MacNeil, L. Devigne, C. Michot, L. Rodrigues, G. Liang and M. Gauthier, J. Electrochem. Soc., 157, A463–A468 (2010).
21) T. Honma, T. Togashi, N. Ito and T. Komatsu, J. Ceram. Soc. Japan, 120, 344–346 (2012).
22) T. Honma, K. Nagamine and T. Komatsu, Ceram. Int., 36, 1137–1141 (2010).
23) R. D. Shannon, Acta Crystallogr., A32, 751–767 (1976).
24) T. Okada, T. Honma and T. Komatsu, Mater. Res. Bull., 45, 1443–1448 (2010).