



Ex-situ ^7Li MAS NMR Study of Olivine Structured Material for Cathode of Lithium Ion Battery

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Abstract ^7Li nuclear magnetic resonance (NMR) spectra have been observed for LiMPO_4 ($M = \text{Fe}, \text{Mn}$) samples, as a promising cathode material of lithium ion battery. Observed ^7Li shifts of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ($x = 0, 0.6, 0.8, \text{ and } 1$) synthesized with solid-state reaction are compared with calculated ^7Li shift ranges based on the supertransferred hyperfine interaction of Li-O-M . Ex situ ^7Li NMR study of $\text{LiFe}_{0.4}\text{Mn}_{0.6}\text{PO}_4$ in different cut-off voltage for the first charge process is also performed to understand the relationship between ^7Li chemical shift and oxidation state of metals affected by delithiation process. The increment of oxidation state for metals makes to downfield shift of ^7Li by influencing the supertransferred hyperfine interaction.

Keywords MAS NMR, ^7Li , Olivine, Lithium Ion Battery

Introduction

The olivine-type LiFePO_4 is an attractive cathode material and good alternative to the commercially used transition metal oxides LiMO_2 ($M = \text{Co}, \text{Ni}, \text{Mn}$) in lithium rechargeable batteries, due to its high theoretical capacity (170 mAh g^{-1}), excellent thermal

stability, low cost, and environmentally-friendly benefit.¹⁻⁴ LiFePO_4 cathodes provide an optimum reversible capacity of 162 mAh g^{-1} with a very flat charge/discharge potential of 3.4 V versus Li/Li^+ at a current of 0.1 mA/cm^2 , which has intrinsically lower energy density, in addition to its natural drawbacks such as low electronic and ionic conductivities compared to the currently used LiCoO_2 .⁴⁻⁶ The energy densities of other olivine-type cathode materials, such as LiMnPO_4 , LiCoPO_4 and LiNiPO_4 , have a similar theoretical capacity to LiFePO_4 and operating potentials of them are at 4.1, 4.9, 5.1 V versus Li/Li^+ , respectively. Even if the alternative cathode materials can provide high energy density, they cannot be used because the operating voltage of LiCoPO_4 and LiNiPO_4 is too high to decompose the organic electrolyte and LiMnPO_4 is electrochemically inactive.⁷ Also, their poor electronic conductivity makes impossible to achieve their theoretical capacity. There have been many attempts to improve electrochemical properties of LiFePO_4 by substitution of Fe ions with one or several metal ions, such as Mn, Co, and Ni.^{1, 7-10} The best substitution method on olivine materials is $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ due to appropriate operating voltages of 3.5 - 4.1 V.^{1, 4, 7}

As pioneering work, Padhi et al. have been showed

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that an increase in Mn content, x , in solid solutions of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ led to an apparent plateau at 4.1 V ($\text{Mn}^{2+}/\text{Mn}^{3+}$) and its increase in the width relative to that of the 3.4 V plateau ($\text{Fe}^{2+}/\text{Fe}^{3+}$) with a total capacity decrease.¹ Optimum charge/discharge performance of the solid solutions has been achieved with $x = 0.2, 0.4$ and 0.6 by Yamada et al.⁴ For these solutions, the total capacity has been close to the theoretical value and the width of the plateau at 4.1 V increased depending on the x value. An increase in Mn content up to 0.8 resulted in an abrupt decrease in capacity with much larger polarization. Instability of the $\text{Fe}_{0.2}\text{Mn}_{0.8}\text{PO}_4$ phase has been proposed due to the Jahn-Teller effect and accumulation of elastic energy under the constant lattice volume. Thus, $\text{LiFe}_{0.4}\text{Mn}_{0.6}\text{PO}_4$ appears to be the most promising cathode material with a capacity greater than 160 mAh g^{-1} generated at 3.5 - 4.1 V and with excellent reversibility.^{4, 11-14}

Solid-state NMR is powerful tool to study various materials.¹⁵⁻¹⁶ The ⁷Li and ³¹P magic angle spinning (MAS) nuclear magnetic resonance (NMR) in LiMPO_4 ($M = \text{Fe, Mn, Co, Ni}$) have been previously studied at various temperatures.¹⁷⁻¹⁸ The chemical shifts of them assigned to the supertransferred hyperfine of the ⁷Li and ³¹P nuclei with the unpaired electrons on the metal atom through the Li-O-M and P-O-M bonds, respectively. The prediction of ⁷Li NMR shifts in LiMPO_4 has been proposed, when high-spin configurations are assumed. The metal d-orbitals are split into three A' orbitals at higher energy than that of two A'' orbitals. The isotropic shifts of ⁷Li are determined following the equation:

$$\delta_{7\text{Li}} = \delta_{A'} \times \text{No. of unpaired electrons in } A' \text{ orbitals} + \delta_{A''} \times \text{No. of unpaired electrons in } A'' \text{ orbitals} \quad (1)$$

where $\delta_{7\text{Li}}$ is the observed chemical shift of ⁷Li NMR peak in ppm, $\delta_{A'}$ and $\delta_{A''}$ are contribution to the shifts of unpaired electrons in the A' and A'' orbitals, respectively. The contributions of an unpaired electron at 37 °C are determined that $\delta_{A'}$ is roughly -24 to -28 ppm, while $\delta_{A''}$ is roughly +70 to

+79 ppm. Herein, ⁷Li NMR shifts of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ in pristine are observed to prove that this calculation is useful for predicting ⁷Li shifts in these multimetal based olivine materials as previous report.¹⁸ Also, ex situ ⁷Li NMR has been studied to show that shifts of $\text{LiFe}_{0.4}\text{Mn}_{0.6}\text{PO}_4$ as a function of cut-off voltage are a particularly sensitive tool for understanding the oxidation state of metals during electrochemical process.

Experimental Methods

Sample preparation- $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ($x = 0, 0.6, 0.8,$ and 1) without additional carbon sources as a cathode material for lithium ion battery were synthesized by the solid-state reaction of a stoichiometric amount with $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$ (Junsei, $\geq 99\%$) Aldrich, $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Junsei, $\geq 99\%$), $\text{Mn}(\text{CH}_3\text{COO})_2$ (Aldrich, $\geq 98\%$), and $\text{NH}_4\text{H}_2\text{PO}_4$ (Aldrich, $\geq 99\%$). The obtained solid solution precursor was planetary milled with zirconia ball for 1 hr, dried in a 70 °C oven for about 12 hrs and ground by using pestle and mortar. The fine precursor powder was purged to prevent oxidation in a tube furnace under pure argon gas for 10 hrs, sintered at a rate of 5 °C/min to 700 °C for 5 hrs, and then cooled to room temperature.

Evaluation of electrochemical performance- The electrodes were prepared by slurry casting and pressing a mixture of 80 wt.% synthesized cathode material, 10 wt.% carbon black (Super P) and 10 wt.% poly (vinylidene fluoride) (PVDF, Aldrich, Mw = 534,000) on aluminum foil (thickness 15 μm) and dried in a vacuum oven at 110 °C for 12 hrs.

The amount of loaded on 15 mm diameter with $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ was about 6 mg. Lithium metal foil 15 mm in diameter and 0.30 mm thick was used as a counter electrode. The circular disk electrodes with Cellguard 2400 separator were assembled into 2016 coin cells in an argon-filled glove box. Non-aqueous 1.15 M LiPF_6 in ethylene carbonate/dimethyl carbonate/diethyl carbonate with 3:4:3 volume ratio

was used as electrolyte. Electrochemical cycle tests were performed at ambient temperature using a galvanostatic automatic battery cycler (WonATech WBCS3000) in the 2.0 - 4.6 V potential range at a constant current rate of 0.1 C, calculated based on the theoretical capacity. The specific capacity was calculated from the elapsed time, current and mass of the active material in the cathode by assuming that all the current passed was applied to lithium intercalation/deintercalation reaction. For ex situ NMR study, the cells were cut-off at 3.53, 4.03, and 4.19 V during charging process and then the cathode material was separated, washed, dried, and ground.

NMR experiments- All of ^7Li MAS NMR spectra were acquired at a Larmor frequency of 77.74 MHz on a Varian Unity INFINITY plus 200 spectrometer using a 1.8 mm MAS probe. The spectra were referenced to 1M LiCl, at 0 ppm. All spectra were acquired at 45 kHz (ν_r) with a rotor synchronized Hahn-echo pulse sequence ($90^\circ-\tau-180^\circ-\tau-\text{acq}$), where $\tau = 1/\nu_r$. A $\pi/2$ pulse width of 2.3 μs was used with a recycle delay of 0.3 s. For all samples, acquisitions of 10K transients at room temperature were obtained.

Results

^7Li NMR of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ - ^7Li magic angle spinning (MAS) NMR spectra of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ($x = 0, 0.6, 0.8, \text{ and } 1$) without additional carbon sources as a cathode material for lithium ion battery are shown in Figure 1. The ^7Li chemical shift measurements at room temperature are well agreed and slightly different within 10 ppm of those reported earlier.^{17,18} These differences can be attributed by difference in measuring temperature, sample degradation in the time between measurements, difference in sample spinning speeds resulting in differing sample temperature, and differences of measuring magnetic fields. In Figure 1(c), a ^7Li shift at 2.2 ppm is observed, which would be shown the existence of unreacted impurity. The isotropic ^7Li shifts for

$\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ are linearly proportional to Mn composition x . Table 1 shows the observed and calculated ^7Li shifts for $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$, which results are well agreed. Numbers of unpaired electrons in the A' and A'' orbitals for each metal are determined by the fraction of metals.

Ex situ ^7Li NMR of $\text{LiFe}_{0.4}\text{Mn}_{0.6}\text{PO}_4$ - The most promising cathode material with multi metal based olivine structure is $\text{LiFe}_{0.4}\text{Mn}_{0.6}\text{PO}_4$ due to having the best electrochemical properties, which is chosen to study ex situ ^7Li NMR.^{4, 11-14} Voltage profile of the Li/ $\text{LiFe}_{0.4}\text{Mn}_{0.6}\text{PO}_4$ cell during the first charge of the ex situ ^7Li NMR experiments performed at room

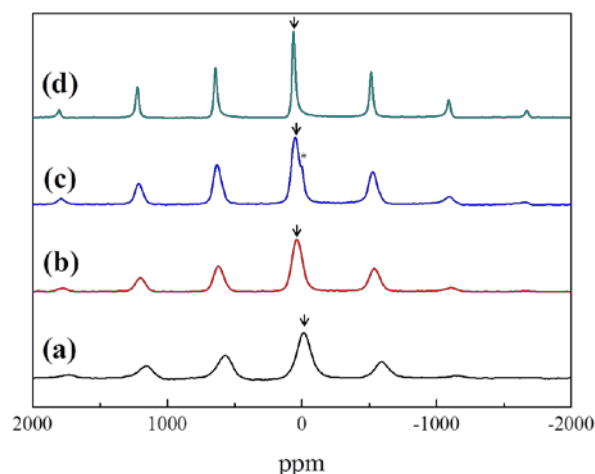


Figure 1. ^7Li MAS NMR spectra of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$: (a) $x = 0$, (b) 0.6, (c) 0.8, and (d) 1. Arrows indicate the isotropic peaks, while star for impurity peak.

Table 1. Chemical shifts of ^7Li NMR for $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ observed at room temperature while spinning rate at 45 kHz in a 4.70 T magnet and calculated shifts at 37 $^\circ\text{C}$ by equation 1.

Sample	Unpaired A' electrons	Unpaired A'' electrons	Observed ^7Li shift (ppm)	Calculated ^7Li shift range (ppm)
LiMnPO_4	3	2	60.9	56 ~ 86
$\text{LiFe}_{0.2}\text{Mn}_{0.8}\text{PO}_4$	3	1.8	51.5	42 ~ 70.2
$\text{LiFe}_{0.4}\text{Mn}_{0.6}\text{PO}_4$	3	1.6	39.0	28 ~ 54.4
LiFePO_4	3	1	-11.3	-14 ~ 7

temperature is presented in Figure 2. Two electrochemical processes at potential plateaus at

3.5 V and 4.1 V have been observed and corroborated earlier reports.¹¹⁻¹⁴ The vertical bars in Figure 2 indicate the cut-off voltage to be performed NMR experiments.

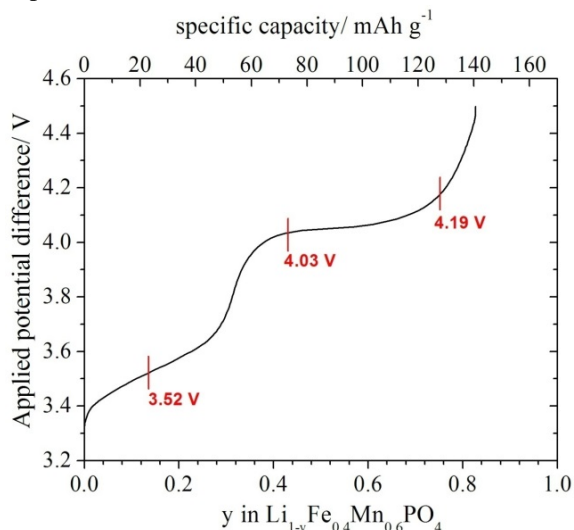


Figure 2. Voltage profile of the Li/LiFe_{0.4}Mn_{0.6}PO₄ cell during the first charge. The vertical bars indicate the cut-off voltage performed ex situ NMR experiments.

In Table 2, the oxidation states of metals by charging are estimated from the previous study by analyzing the X-ray absorption near edge structure (XANES) spectra of each metal in the material.¹³ The ^7Li NMR shifts as a function of cut-off potential are calculated by equation 1, while the numbers of unpaired electrons in the A' and A'' orbitals for metals are calculated from both the fraction of oxidation states and molar ratio for metals. As shown in Figure 3, ex situ ^7Li NMR shifts of LiFe_{0.4}Mn_{0.6}PO₄ in different

cut-off potential are observed within the range of shifts calculated by using previous reports. All NMR spectra in Figure 3 contain an additional peak around 0 ppm which would be originated from remaining electrolyte, unreacted reactant of lithium acetate dehydrate, and impurity. While ^7Li NMR shift of LiFe_{0.4}Mn_{0.6}PO₄ in cut-off potential of 3.52 V is not clarified due to overlapping with an additional peak as shown in Figure 3(a), it is fitted by DMFIT software and identified isotropic peak.¹⁹ Isotropic ^7Li peaks for LiFe_{0.4}Mn_{0.6}PO₄ in different cut-off potential are downfield shifted by increasing charge voltage.

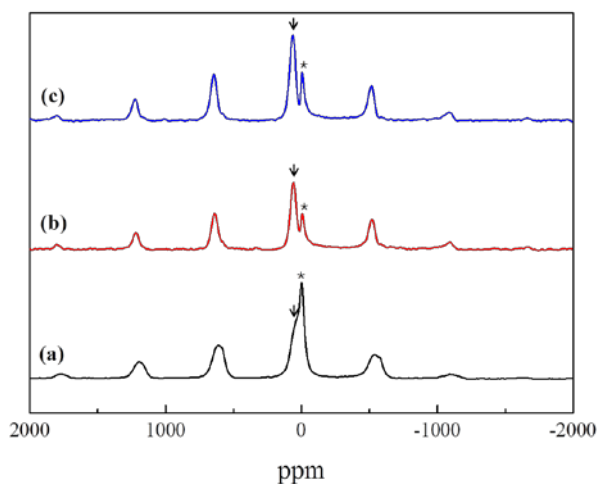


Figure 3. Ex situ ^7Li NMR spectra of LiFe_{0.4}Mn_{0.6}PO₄ in cut-off voltage of (a) 3.52, (b) 4.03, and (c) 4.29 V. Arrows indicate the isotropic peaks, while stars for impurity peaks.

Discussion

Table 2. Chemical shifts of ex situ ^7Li NMR for LiFe_{0.4}Mn_{0.6}PO₄ depending on oxidation states on metals by charging and compared with calculated shifts at 37 °C by equation 1.

Cut-off Potential (V)	Oxidation state of Fe	Oxidation state of Mn	Unpaired A' electrons	Unpaired A'' electrons	Observed ^7Li shift (ppm)	Calculated ^7Li shift range (ppm)
0	+2	+2	3	1.6	39.0	28 – 54.4
3.52	+2.2	+2	2.92	1.6	42.1	30.24 – 56.32
4.03	+3	+2	2.6	1.6	57.8	39.2 – 64
4.19	+3	+2.4	2.36	1.6	64.1	45.92 – 69.76

We have been measured ^7Li NMR spectra with $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$, which shifts are linearly proportional to Mn composition x due to increasing unpaired electrons in the A'' orbital for Mn. The NMR shifts are well agreed with previous report and shown to be a sensitive probe to the olivine structured cathode materials.¹⁸ The study of ex situ ^7Li NMR of $\text{LiFe}_{0.4}\text{Mn}_{0.6}\text{PO}_4$ is also performed to understand the relationship between ^7Li chemical shift and oxidation state of metals during charging process by delithiation. The increment of oxidation state for metals makes reducing the number of unpaired

electrons in A' orbital for both metals, which is reflected to downfield shift of ^7Li by influencing the supertransferred hyperfine interaction of Li-O-M . This ex situ ^7Li NMR study will provide the relationship between chemical shift and electrochemical performance for these promising cathode materials of lithium ion battery.

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