Enhanced Rate Capability and Cycle Performance of Titanium-Substituted P2-Type Na$_{0.67}$Fe$_{0.5}$Mn$_{0.5}$O$_2$ as a Cathode for Sodium-Ion Batteries

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ABSTRACT: In this study, we developed a doping technology capable of improving the electrochemical performance, including the rate capability and cycling stability, of P2-type Na$_{0.67}$Fe$_{0.5}$Mn$_{0.5}$O$_2$ as a cathode material for sodium-ion batteries. Our approach involved using titanium as a doping element to partly substitute either Fe or Mn in Na$_{0.67}$Fe$_{x}$Mn$_{1-x}$O$_2$. The Ti-substituted Na$_{0.67}$Fe$_{0.5}$Mn$_{0.5}$O$_2$ shows superior electrochemical properties compared to the pristine sample. We investigated the changes in the crystal structure, surface chemistry, and particle morphology caused by Ti doping and correlated these changes to the improved performance. The enhanced rate capability and cycling stability were attributed to the enlargement of the NaO$_2$ slab in the crystal structure because of Ti doping. This promoted Na-ion diffusion and prevented the phase transition from the P2 to the OP4/"Z" structure.

1. INTRODUCTION

Sodium-ion batteries (SIBs) have been drawing much attention as candidates to replace lithium-ion batteries (LIBs) because sodium is a much more abundant and affordable alkali metal than lithium.\textsuperscript{1–4} Lately, various cathode materials for SIBs have been developed. In particular, layer-structured materials such as Na$_{2/3}$Co$_{2/3}$Mn$_{1/3}$O$_2$, Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$, and Na$_{2/3}$Ni$_{1/3}$Fe$_{1/3}$Mn$_{1/3}$O$_2$ have been attracting considerable attention.\textsuperscript{5–18} NaMeO compounds with a layered structure can be classified as being either of the prismatic (P2) or octahedral (O3) type.\textsuperscript{16,17} In these materials, the sodium ions are intercalated between the MeO$_2$ slabs. O3-type materials including NaFe$_{1/2}$Co$_{1/2}$O$_2$, NaNi$_{1/2}$Fe$_{1/2}$Mn$_{1/2}$O$_2$, and NaFe$_{1/2}$Mn$_{1/2}$O$_2$ have lower reversible discharge capacities than P2-type materials because of their complicated phase transition and alignment of sodium ions. Thus, P2-type materials such as Na$_{2/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$, Na$_{2/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$, and Na$_{2/3}$Ni$_{1/3}$Ti$_{1/3}$O$_2$ have been extensively investigated. Although P2-type Na$_{2/3}$Fe$_{x}$O$_2$ has been considered a promising cathode material based on previous experimental evidence and cost, this material is extremely difficult to synthesize because of the instability of the Fe$^{4+}$ ions in the oxide-ion framework in air. Therefore, in an attempt to stabilize the P2 phase, Na$_{0.67}$Fe$_{0.5}$Mn$_{0.5}$O$_2$ was synthesized by partly substituting Fe with Mn.\textsuperscript{19,20}

P2-type Na$_{0.67}$Fe$_{0.5}$Mn$_{0.5}$O$_2$ (NFMO)\textsuperscript{17,25,26} is one of the most promising cathode materials for SIBs. All of the constituent elements (Na, Fe, and Mn) are abundantly available, and NFMO has a high energy density of 520 W h/ kg and high capacity of 190 mA h g$^{-1}$, which enhances the attractiveness of this material as a cathode material for SIBs. However, the complicated intercalation and de-intercalation processes of sodium ions deteriorate the electrochemical properties including the rate capability and cycling stability of NFMO.\textsuperscript{12,13,15,17} It has been reported that similar problems presented by the active materials for LIBs could be overcome by doping the crystal structure with inert alien elements.\textsuperscript{27–32} Some of these elements could improve the electrochemical properties by stabilizing the phase transition and raising the electronic conductivity without participating in the electro-chemical reaction. Fortunately, the doping technology has also been reported to be effective for producing cathode materials for SIBs.\textsuperscript{33–40} On the basis of these studies, we aimed to solve the problems associated with NFMO in terms of its rate capability and cycling stability by partly substituting Fe with Ti or Mn in NFMO. We expected that the higher bonding energy of Ti–O ($\Delta H^\text{f}$=402 kJ/mol) would be able to stabilize the crystal structure of NFMO when it is doped with Ti.\textsuperscript{41}

Received: October 4, 2017
Accepted: January 3, 2018
Published: January 11, 2018
2. RESULTS AND DISCUSSION

2.1. Physical Properties. All samples have a P2-type structure with a $P6_3/mmc$ symmetry, as confirmed by powder X-ray Rietveld refinement. The final refinement profiles are shown in Figure 1a–e for NFMO, Mn–Ti05, Mn–Ti10, Fe–Ti05, and Fe–Ti10, respectively, and the lattice parameters are summarized in Table 1. Although each sample contains a small quantity of unidentified impurities, they do not affect the refinement because the observed peaks for the impurity phase are relatively weak. The lattice parameters of each sample are compared in Figure 1f. The refined atomic parameters are summarized in Tables S1–S5 in the Supporting Information.

The increase in the titanium content causes the $a$ parameter to increase, whereas the $c$ parameter decreases, which seems to be due to the smaller ionic size of Ti$^{4+}$ (0.605 Å) than Fe$^{3+}$ (0.645 Å) or Mn$^{3+}$ (0.645 Å). In the P2-type structure, the sodium ions are situated in trigonal prismatic sites located between the transition metal oxide (MO$_2$) sheets of the layered structure. There are two sodium sites, Na1 and Na2, which share faces or edges with the MO$_2$ octahedra. As shown in Tables S1–S5 in terms of occupancy, the Na2 site is preferred to the Na1 site for all samples. This observation, which is consistent with that of previous structural studies on a similar compound, P2-Na$_{2/3}$Co$_{2/3}$Mn$_{1/3}$O$_2$, is attributed to the Na1 site being less favorable owing to the face-sharing characteristics of Na1 compared to the edge-sharing Na2 site; thus, a stronger repulsion exists between Na1 and the transition metal ion.

The effect of substituting Ti for Fe or Mn was examined by calculating the thicknesses of the MO$_2$ slab and the Na layer of each sample by employing Rietveld analysis. The results are summarized in Figure 2 and Table 2. Substitution by Ti$^{4+}$ decreases the MO$_2$ slab thickness but increases the thickness of the Na layer. The decrease in the MO$_2$ slab is attributed to the greater bonding energy of Ti–O than that of Fe–O or Mn–O. The enlarged Na slab thickness is beneficial for Na-ion diffusion in the crystal structure during the charging and discharging processes. However, the Na slab thickness of the sample decreased with increasing Ti substitution amount from 5 to 10%, contrary to the expectation that increasing Ti substitution would lead to the increase in the Na slab thickness. The reason may be the change in the valence state and ionic radius of Fe and Mn ions caused by Ti substitution. Ti substitution to Fe or Mn would lower the valence state of Fe or Mn and thus increase the ionic radius of Fe or Mn, which would enlarge the MO$_2$ slab thickness and decrease the Na slab size. The atomic compositions of the samples were measured by plasma–optical emission spectroscopy (ICP–OES), and the results are listed in Table 3. The measurements were almost identical to the estimated value by the amount of the precursor reagents.

Table 1. Crystallographic Lattice Parameters Refined by the Rietveld Method of the As-Prepared Materials

<table>
<thead>
<tr>
<th>samples</th>
<th>$a$/Å</th>
<th>$c$/Å</th>
<th>cell volume/Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>NFMO</td>
<td>2.9270(1)</td>
<td>11.2493(3)</td>
<td>83.47(1)</td>
</tr>
<tr>
<td>Mn–Ti05</td>
<td>2.9325(1)</td>
<td>11.2359(3)</td>
<td>83.68(1)</td>
</tr>
<tr>
<td>Mn–Ti10</td>
<td>2.9367(1)</td>
<td>11.2279(3)</td>
<td>83.86(1)</td>
</tr>
<tr>
<td>Fe–Ti05</td>
<td>2.9292(1)</td>
<td>11.2374(3)</td>
<td>83.50(1)</td>
</tr>
<tr>
<td>Fe–Ti10</td>
<td>2.9293(1)</td>
<td>11.2328(3)</td>
<td>83.47(1)</td>
</tr>
</tbody>
</table>

Figure 1. Observed and calculated XRD profiles for the materials: (a) NFMO, (b) Mn–Ti05, (c) Mn–Ti10, (d) Fe–Ti05, (e) Fe–Ti10, and (f) linear relationship of lattice parameters for each material.
Figure 2. Refined crystal structure of each material: (a) NFMO, (b) Mn–Ti05, (c) Mn–Ti10, (d) Fe–Ti05, (e) Fe–Ti10, and (f) linear relationship of d-spacing for each material.

Figure 3a–c shows the particle size and morphology of the samples. The particles have irregular sizes and platelet shapes. We can see that Ti substitution does not cause any significant change in the particle size and shape.

Table 2. Interatomic Distances, Slab Thickness (MO$_2$), and d-Spacing of Na Layer for the As-Prepared Materials

<table>
<thead>
<tr>
<th>specimen</th>
<th>MO$_2$</th>
<th>Mn–Ti05</th>
<th>Mn–Ti10</th>
<th>Fe–Ti05</th>
<th>Fe–Ti10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$<em>{0.67}$Fe$</em>{0.5}$Mn$_{0.5}$O$_2$</td>
<td>2.097</td>
<td>2.072</td>
<td>2.083</td>
<td>2.048</td>
<td>2.080</td>
</tr>
<tr>
<td>Na$<em>{0.67}$Fe$</em>{0.45}$Mn$<em>{0.5}$Ti$</em>{0.05}$O$_2$</td>
<td>3.528</td>
<td>3.546</td>
<td>3.532</td>
<td>3.571</td>
<td>3.536</td>
</tr>
</tbody>
</table>

Table 3. ICP–OES Results of the Samples

<table>
<thead>
<tr>
<th>theoretical chemical formula</th>
<th>Na</th>
<th>Fe</th>
<th>Mn</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$<em>{0.67}$Fe$</em>{0.5}$Mn$_{0.5}$O$_2$</td>
<td>0.647</td>
<td>0.501</td>
<td>0.521</td>
<td></td>
</tr>
<tr>
<td>Na$<em>{0.67}$Fe$</em>{0.45}$Mn$<em>{0.5}$Ti$</em>{0.05}$O$_2$</td>
<td>0.650</td>
<td>0.511</td>
<td>0.405</td>
<td>0.092</td>
</tr>
<tr>
<td>Na$<em>{0.67}$Fe$</em>{0.4}$Mn$<em>{0.5}$Ti$</em>{0.1}$O$_2$</td>
<td>0.656</td>
<td>0.464</td>
<td>0.501</td>
<td>0.047</td>
</tr>
</tbody>
</table>

2.2. Electrochemical Properties. The samples were analyzed by X-ray photoelectron spectroscopy (XPS) to investigate the change in the oxidation state of the transition metal elements in NFMO and Fe- or Mn-doped samples (Figure 4). The spectrum for Fe 2p$_{3/2}$ (Figure 4a) is composed of Fe$^{2+}$ and Fe$^{3+}$ of which the binding energies are observed at 708.9 and 710.4 eV, respectively.$^{38,43,44}$ In NFMO, Mn–Ti10, and Fe–Ti10, the ratio between Fe$^{2+}$ and Fe$^{3+}$ is almost identical. The spectrum for Mn 2p$_{3/2}$ (Figure 4b) contains Mn$^{3+}$ and Mn$^{4+}$ of which the binding energies are observed at 641.2 and 644.1 eV, respectively.$^{36,38,40}$. When we compare the spectrum for Mn 2p$_{3/2}$ of NFMO, Mn–Ti10, and Fe–Ti10, the peak intensity of Mn$^{3+}$ was found to increase with Ti substitution and reached a maximum for Fe–Ti10.

Figure 3. SEM images of as-prepared (a) NFMO, (b) Mn–Ti10, and (c) Fe–Ti10.
The XPS spectrum of Ti 2p 3/2 (Figure 4c) shows the existence of Ti⁴⁺, the binding energy of which is observed at 457.0 eV.⁴⁷,⁴⁸ However, Ti⁴⁺ is electrochemically inert in the potential range of 1.5−4.2 V versus Na⁺/Na, and it does not contribute to the capacity during cycling. The XPS result shows that the presence of Ti⁴⁺ has a greater effect on the valence state of Mn than on that of Fe, and this is closely related to the discharge capacity of the samples.

Figure 5 represents the cyclic voltammetry (CV) curve measured at 0.1 mV s⁻¹ from 1.5 to 4.2 V for the electrodes. All electrodes exhibited two identical redox pairs: one at low potential for Mn⁵⁺/⁴⁺ and the other at high potential for Fe⁵⁺/⁴⁺.¹⁷,²⁶,³⁸ As mentioned above, Ti⁴⁺ does not participate in the redox reaction over the potential range considered in this analysis.²⁰,³⁹ The potential gap between the peaks of a redox reaction implies the reversibility of the electrochemical reaction.⁴⁹ The reversibility is closely related with the structural stability of the layered cathode materials.⁵⁰ The potential gap corresponding to the Mn⁵⁺/⁴⁺ redox pair is denoted as E_a and that for Fe⁵⁺/⁴⁺ is denoted as E_b. The value of E_a of NFMO, Mn−Ti10, and Fe−Ti10 was 0.47, 0.67, and 0.64 V for the first scan and it changed to 0.50, 0.47, and 0.47 V at the fourth cycle, respectively. This means that the reversibility of the electrochemical reaction (Mn⁵⁺/⁴⁺) of NFMO reduced, whereas those of the other samples enhanced during the four scans. Similarly, the values of E_b of NFMO, Mn−Ti10, and Fe−Ti10 are 0.89, 0.98, and 0.85 V for the first scan and they changed to 0.87, 0.95, and 0.84 V at the fourth cycle, respectively. This means that the reversibility of the electrochemical reaction (Fe⁵⁺/⁴⁺) of all samples was enhanced during the four scans. In addition, the shapes of the respective CV curves appear different: NFMO exhibited sharp redox peaks, whereas the other two samples showed broad peaks, which indicates that NFMO would have a more distinct voltage plateau during cycling.

Figure 6 shows the initial charge and discharge profiles of the samples measured at 13 mA g⁻¹ (0.05 C) in the potential range of 1.5−4.2 V. Generally, NaMeO₂ with a layered structure has a profile with multiple plateaus during sodiation/desodiation due to phase transitions. These plateaus related with the phase transition can negatively affect the rate capability and cycling stability.¹¹−¹⁵,²⁰,³⁶,⁴⁰ NFMO shows a phase transition from P2 to OP4/”Z” above 4.0 V during the charging process, which badly affects the cycling stability.¹⁵,¹⁷ In particular, above 4.0 V, the charge profiles of both Fe−Ti05 and Fe−Ti10 are smoother or more sloped than those of NFMO, Mn−Ti05, and Mn−Ti10. This means that the substitution of Fe by Ti in NFMO can improve the structural stability by preventing the phase transition from P2 to OP4/”Z”.⁵⁷,⁴⁰ The initial discharge capacity of NFMO, Mn−Ti05, Mn−Ti10, Fe−Ti05, and Fe−Ti10 was 190, 187, 182, 181, and 170 mA h g⁻¹, respectively.

Figure 4. XPS spectra of the transition metal element in powder samples: (a) Fe, (b) Mn, and (c) Ti.

Figure 5. CV profiles of (a) NFMO, (b) Mn−Ti10, and (c) Fe−Ti10 at a scan rate of 0.1 mV s⁻¹ in the voltage range of 1.5−4.2 V.

Figure 6. Initial charge/discharge curves of as-prepared NFMO, Mn−Ti05, Mn−Ti10, Fe−Ti05, and Fe−Ti10.
Because of the electrochemical inactivity of the Ti ion, Ti substitution lowered the reversible capacity relative to NFMO. We could observe the difference in the capacity decrease caused by Ti substitution among the samples, depending on which the element was replaced by Ti (Mn or Fe). As could be seen in the XPS result represented in Figure 5, the ratio of Mn$^{3+}$ in Mn–Ti10 increased, whereas the total amount of Mn reduced, which resulted in a smaller capacity decrease than Fe–Ti10. Fe–Ti10, which contains the lowest amount of Mn$^{3+}$, exhibited the lowest discharge capacity among the samples. This was attributed to the decrease in the amount of Fe$^{3+}$ and total Fe, which has a greater impact on the capacity than Mn$^{3+}$. However, caution should be exercised when interpreting the difference in capacity among the samples only by the XPS result as it only reflects the information on the surface chemistry. The difference in capacity may be related with the phase transition to OP4/Z$^\prime$ to a greater extent. The phase transition adversely affects the structural stability but positively contributes to the capacity, exhibiting a long plateau in the capacity–voltage profile during discharge. Thus, NFMO shows the largest capacity, and the samples in which Ti is substituted for Fe exhibit reduced discharge capacity, thereby preventing the phase transition to OP4/Z$^\prime$. The black, blue, and green arrows in the cyclic voltammograms (Figure 5) present the potential at which the reduction of Fe$^{4+}$ to Fe$^{3+}$ is complete for the NFMO, Mn–Ti10, and Fe–Ti10 samples, respectively. The black, blue, and green points in Figure 6 correspond to the potential indicated by the black, blue, and green arrows, respectively. Combining these figures, we could see that the contribution of Fe$^{3+}$/Fe$^{2+}$ to the overall discharge capacity of Fe–Ti10 was greatly reduced, and this reduction was caused by the prevention of the phase transition. The ex situ X-ray diffraction (XRD) analysis was carried out for the electrodes charged up to 4.0 and 4.2 V to confirm the effect of Ti substitution on phase transition. As shown in Figure S1a,b, all of the electrodes exhibited the P2 phase at 4.0 V, but NFMO and Mn–Ti10 showed significant phase transition to OP4 at 4.2 V, whereas Fe–Ti10 almost maintained P2 phase. We could confirm that Ti substitution for Fe could prevent the phase transition to OP4 from this result.

Figure 7 shows the rate capability of the samples tested at various current densities. All samples showed reduced discharge capacities when the current density was increased from 13 to 1040 mA g$^{-1}$. As shown in the figures, the rate capabilities of the Ti-substituted samples were enhanced, with the capacity retention rates of the 5% Ti-substituted samples being enhanced the most at high current densities. At the same time, the rate capabilities of the samples in which Fe was substituted by Ti were higher than those of the Mn samples doped with Ti. The rate capability has been reported to be closely related to the NaO$_2$ slab size that supports diffusion of the Na ion, and in our study, this was also confirmed by the correlation between the rate capability and the layer structure illustrated in Figure 2.$^{36,40}$

Figure 8 shows the cycling stabilities and discharge/charge efficiencies measured at 0.05 C (13 mA g$^{-1}$) and 0.5 C (130 mA g$^{-1}$) for each material. As shown in Figure 7a, the charge and discharge efficiencies of each material were close to 100% at 0.05 C. After 45 cycles, the capacity retention rates of NFMO, Mn–Ti05, Mn–Ti10, Fe–Ti05, and Fe–Ti10 were approximately 77, 74, 76, 81, and 84%, respectively. In the case of the sample in which Ti was substituted for Mn, the capacity retention rate was lower than that of NFMO at 0.05 C, whereas the capacity retention rate of the sample in which Fe is substituted by Ti was significantly increased. This is closely related to the reversibility in the electrochemical reaction shown in Figure 5.

As shown in Figure 8b, at 0.5 C (130 mA g$^{-1}$), the capacity of NFMO stabilized after rapidly decreasing up to ~20 cycles. This rapid capacity fading at an early stage is associated with the low discharge/charge efficiency. In spite of the capacity stabilization after ~20 cycles, the capacity retention rate after 45 cycles was only approximately 37%. The capacity retention rates of Mn–Ti05, Mn–Ti10, Fe–Ti05, and Fe–Ti10 after 45 cycles were approximately 42, 43, 48, and 64%, respectively. All
of the Ti-substituted materials had higher capacity retention rates than NFMO at 0.5 C. This means that the capacity retention rate at high current density can to a larger extent be attributed to Ti substitution, and this is believed to be related with the bonding energy. In other words, the higher bonding energy of the Ti–O bond (ΔH$_{f298K}$ = 662 kJ/mol) than those of Fe–O (ΔH$_{f298K}$ = 409 kJ/mol) and Mn–O (ΔH$_{f298K}$ = 402 kJ/mol) would improve both the structural and cycling stabilities. Specifically, when Ti is substituted for Fe, the structural stability could be further improved by controlling the phase transition to OP4/″Z″, thereby greatly improving the capacity retention rate compared to when Ti is substituted for Mn.

Figure 9 presents the results of the electrochemical impedance spectroscopy measurement for NFMO, Mn–Ti10, and Fe–Ti10 after the 1st and 30th cycles. All of the Nyquist plots have two semicircles, with that appearing at high Mn.

Figure 9. Impedance spectroscopy of NFMO, Mn–Ti10, and Fe–Ti10 after (a) 1 cycle and (b) 30 cycles at 0.5 C (130 mA g$^{-1}$).

3. CONCLUSIONS

We proposed Ti substitution for Fe or Mn in NFMO to improve the electrochemical properties of NFMO. The Ti-substituted samples delivered lower discharge capacities than that of NFMO. In particular, the discharge capacity lowered more when Fe was replaced by Ti. This difference in the discharge capacity is believed to be associated with the change in the lattice constant along the c-axis involved in phase transition at above 4.0 V. Furthermore, the rate capability and the cycling stability were greatly improved by Ti substitution. The improved rate capability is attributed to the enlarged space for the Na-ion transport in the NaO$_2$ slab sandwiched between the MeO$_2$ (M = Fe, Mn) slabs. The cycling stability of different samples depended on the current density. Although the cycling stability of all samples was similar at a low current density (0.05 C), the Ti-substituted samples exhibited superior cycling stability to NFMO at a high current density (0.5 C). The higher cycling stability was attributed to high charge/discharge efficiency. From these results, we concluded that Ti substitution, especially of Fe, is an effective approach to enhance the electrochemical properties of P2-type NFMO.

4. EXPERIMENTAL SECTION

4.1. Synthesis. P2-type sodium iron manganese oxides—Na$_{0.67}$Fe$_{0.5}$Mn$_{0.5}$O$_2$, Na$_{0.67}$Fe$_{0.50}$Mn$_{0.45}$Ti$_{0.05}$O$_2$, Na$_{0.60}$Fe$_{0.50}$Mn$_{0.40}$Ti$_{0.10}$O$_2$, Na$_{0.60}$Fe$_{0.45}$Mn$_{0.55}$Ti$_{0.05}$O$_2$, and Na$_{0.67}$Fe$_{0.40}$Mn$_{0.50}$Ti$_{0.05}$O$_2$—were synthesized by a solid-state reaction and are denoted as NFMO, Mn–Ti05, Mn–Ti10, Fe–Ti05, and Fe–Ti10, respectively. Na$_2$CO$_3$ (Samchun), Fe$_2$O$_3$ (Samchun), Mn$_2$O$_3$ (Sigma-Aldrich), and TiO$_2$ (Daejong) were homogeneously mixed together and precalcined at 450 °C for 6 h in air. Then, the precalcined material was pelletized, and the pellet was calcined at 900 °C for 15 h in air.

4.2. Characterization. XRD analyses were carried out using an X-ray diffractometer (Rigaku, Ultima VI) over the 20 range of 10°–80° with monochromatized Cu Kα radiation. Crystal structures were refined using the powder profile refinement program GSAS, for which the initial structural model of Na$_{0.67}$Mn$_{0.5}$Fe$_{0.5}$O$_2$ was adopted from the literature. The refinement parameters were the scale factors, background, unit-cell parameters, peak-profile coefficients, atomic coordinates of the oxygen atoms, occupancies of the sodium atoms, and isotropic thermal parameters. The total amount of sodium...
in each sample was restrained to conform to the nominal chemical composition.

The atomic compositions of the samples were analyzed by inductively coupled ICP—OES (Optima 8300, PerkinElmer). The morphology of the powder was observed using high-resolution field emission scanning electron microscopy (FESEM, Sigma 500, ZEISS). The surface chemistry of the samples was analyzed by XPS using an X-ray photoelectron spectrometer (MultiLab 2000, Thermo Fisher Scientific) equipped with a Mg Kα X-ray source.

4.3. Electrochemical Properties. The electrochemical properties of the samples were measured with CR2032 coin-type cells. The cathode was prepared by casting a slurry on an aluminum foil with a doctor blade. The slurry was composed of an active material, a conductive agent (Super P, TIMCAL), and poly(vinylidene difluoride) (KF1300, Kureha) with a mass ratio of 80:10:10. Then, the cathode was vacuum dried in an oven at 120 °C for 12 h. The sodium metal was used as a counter electrode. A 1.0 M solution of NaClO4 in EC/PC (volume 1:1) was prepared and used as an electrolyte. A glass fiber membrane was employed as a separator. All of the coin-type cells were assembled in an Ar-filled glovebox. The coin-type cells were subject to galvanostatic cycling using a cycler (PNE Solution) at various current densities in a voltage range of 1.5–4.2 V. CV analysis was also conducted for the cells at a scan rate of 0.1 mV s⁻¹, and electrochemical impedance spectroscopic data were collected from 0.5 mHz to 1 MHz for the cells using an electrochemical workstation (Biologic VSP).

## ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01481.

Ex situ XRD patterns of the electrodes at 4.0 and 4.2 V, refined crystal sites, and atom occupancies of the samples by the Rietveld method (PDF)

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Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This research was supported by The Leading Human Resource Training Program of Regional Neo industry through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (NRF-2016H1D5A19150545) and the Ministry of Trade, Industry and Energy (MOTIE), Korea Institute for Advancement of Technology (KIAT) through the Encouragement Program for The Industries of Economic Cooperation Region (R0004911).

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