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Study on the nanocomposites as cathodes for next-generation battery

2019 년 8 월

서울대학교 대학원

재료공학부

황 인 상
Abstract

Study on the nanocomposites as cathodes for next-generation battery

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Sodium and potassium ion batteries are the most promising candidate to the high price of current lithium-ion batteries. In general, the cathode material determines the performance of the entire battery. However, the electrode materials for sodium and potassium ion batteries reported so far have limited performance and require a search for new cathode materials. In this thesis, I present a new design strategy to develop cathode materials for sodium and potassium ion batteries using nanocomposite between alkali metal
compounds and transition metal compounds. Also, the study on the origin of the overpotential in nanocomposite electrodes is presented.

In chapter 2, the new type of sodium ion battery cathode materials is realized with NaF-FeF$_2$ nanocomposites. The new host structure for sodium ions is formed during battery operation. The origin of electrochemical activity is investigated with ex-situ X-ray diffraction (XRD) analysis and X-ray absorption near edge structure (XANES) analysis which reveals that the NaF decomposition during charge activates the nanocomposite electrode and Fe$^{2+}$/Fe$^{3+}$ redox couple is responsible for electrochemical activity. The host formation behavior during first charge is analyzed with the transmission electron microscopy (TEM) analysis which reveal that the transformation of FeF$_2$ into FeF$_3$ during charge occurs firstly at the surface of FeF$_2$ and propagates into the bulk.

In chapter 3, iron oxyfluoride with cubic symmetry, which is a new host structure for sodium ions, is realized with NaF-FeO nanocomposite. The Fe K-edge XANES reveal that the Fe$^{2+}$/Fe$^{3+}$ redox reaction occurs reversibly during charge/discharge. The ex-situ XRD and atomic resolution TEM analysis reveal that the host structure formed here is iron oxyfluoride with
cubic symmetry. Interestingly, the electrochemical profile is gradually changed as cycle proceeds. The F K-edge XANES analysis at various cycles reveal that the host structure is gradually formed as the cycle proceeds which coincident with the gradual changes in electrochemical profile.

In chapter 4, the high energy density cathode for potassium ion battery is realized with KF-MnO nanocomposite. The KF-MnO nanocomposite follows ‘surface conversion’ reaction which fluorine incorporation into MnO and oxidation of Mn mainly occur at the surface of MnO. The surface concentrated reaction is observed with TEM electron energy loss spectroscopy (EELS) and Mn L-edge XANES analysis. The high utilization of potassium ion per manganese results in high capacity and one of the highest energy density cathode in potassium ion battery ever reported.

In chapter 5, the origin of the overpotential in nanocomposite electrodes is studied with the MF$_x$-MnO (M=Li, Na, K, Rb, Cs, Mg, Ca, and Al) model system. As the MF$_x$ compounds varies, the activity of the nanocomposite electrode also varies. The origin of the overpotential is analyzed with various tools such as galvanostatic intermittent titration technique (GITT), X-ray photoelectron spectroscopy (XPS), and Rietveld refinement with Williamson-
Hall plot which indicate that the lattice energy of MF$_x$ is highly correlated with the activity of the nanocomposite electrodes. The lattice energy can be indicated as F 1s binding energy of MF$_x$ and the binding energy and electrochemical activity are successfully tuned by making solid-solution between LiF and CsF. The work presented in chapter 4 not only reveal the origin of overpotential but also shows expandability to other battery system such as Ca, Mg, Al battery.

**Keywords** : Energy storage, Nanocomposite, Sodium, Potassium, Batteries

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**Figure 5-1** (a) X-ray diffraction patterns of MF$_x$–MnO (M=Li, Na, K, Rb, Cs, Mg, Ca, Al) nanocomposites. Electrochemical profiles of (b) MF$_x$–MnO (M=Li, Na, K, Rb, Cs) and (c) MF$_x$–MnO (M=Mg, Ca, Al) nanocomposites
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**Figure 5-3** (a) First charge profile of the eight MFₓ–MnO nanocomposites in lithium hybrid cells. (b) Reversible capacities of the eight MFₓ–MnO nanocomposite electrodes. The blue bars represent the capacities delivered above 2.7 V, and the green bars represent the capacities delivered below 2.7 V.

**Figure 5-4** The first charge profile of (a) NaF-MnO and (b) AlF₃-MnO nanocomposites in 1 M LiPF₆ in EC/DMC and 1 M LiClO₄ in EC/DMC electrolytes.

**Figure 5-5** Initial profiles of the first charge for (a) MFₓ–MnO nanocomposites (M=Li, Na, K, Mg, and Ca; Group I) and (b) MFₓ–MnO
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Table 2-1 Data used to calculate average particle size of high energy ball milled (a) NaF and (b) FeF$_2$. Each particle size is estimated using Scherrer equation (K=0.9 is used).
Chapter 1. Introduction

1.1 Motivation and outline

Lithium-ion batteries (LIBs) are used in many fields, from small and portable electronic devices such as mobile phones and laptops, to large-scale devices such as energy storage system and electric vehicles in recent years. However, lithium prices continue to rise as global demand for batteries continues to increase and lithium is buried only in certain regions. To solve these problems, researches on battery system using sodium or potassium, which are relatively cheap and earth-abundant elements than lithium, are actively conducted.\(^1\text{--}^6\) Both sodium and potassium are monovalent cations such as lithium and exhibit similar chemical properties to lithium. In fact, materials such as layered or polyanion compounds, which exhibit electrochemical activity based on the reversible intercalation/deintercalation of lithium, also showed activity against sodium and potassium.\(^7\text{--}^{14}\) Although many materials have been reported as sodium or potassium battery cathodes, there is still a need to develop electrode materials with higher energy densities. In order to successfully function as new electrode materials, it is necessary to include 1) an alkali ion in the structure, 2) a transition metal capable of
changing the oxidation state during charge/discharge, and 3) a conduction path in which alkali ions can move freely within the structure. However, the cathode material satisfying the above three conditions is limited, and thus it was difficult to develop a new cathode material.

Recently, a new method of designing cathode material more freely without being restricted to the above three conditions has been reported. The new class of cathode material consists of a nanocomposite of an alkali ion compound and a transition metal compound. In the nanocomposite, the alkali ion compounds function as an alkali ion source and transition metal compounds function as redox host through reversible oxidation state change during battery operation. The nanocomposite cathodes are similar with ‘job sharing’ mechanisms in that two materials function as ion conduction and electron conduction path, respectively, but differs in that whole particle participate in the electrochemical reactions in nanocomposite cathodes.

Until now, nanocomposites such as LiF-FeF$_2$, LiF-MnO$_x$, LiF-FeO, and LiF-FeSO$_4$ are reported as LIBs cathode materials. However, since the research field is still in its early stages, relevant reports are limited and there is a lack of fundamental understanding of nanocomposites. Also, although most of the research is focused on the lithium system, the new design strategy
is believed to be applicable to other battery systems beyond lithium such as sodium and potassium.

In chapters 2 and 3, I present the studies to find new host structures for sodium ions through nanocomposites and reveal the underlying mechanisms. The NaF-FeF$_2$ (chapter 2) and NaF-FeO (chapter 3) nanocomposites were reported as new cathode materials for sodium-ion battery. The reversible oxidation state change of Fe during battery operation was analyzed with Fe K-edge X-ray absorption near edge structure (XANES) analysis. The structure change was tracked with Fe K-edge extended X-ray absorption fine structure (EXAFS) analysis and atomic resolution transmission electron microscopy (TEM) analysis to reveal the reaction mechanisms. The structure changes from FeF$_2$ to FeF$_3$-like and FeO to FeOF$_{\text{cubic}}$ during charge process were observed in NaF-FeF$_2$ and NaF-FeO nanocomposites, respectively. The FeF$_3$-like and FeOF$_{\text{cubic}}$ structures, which formed during battery operation, successfully functioned as a host structure for Na ions. The electrochemical responses were also changed as the formation of the host structure.

The nanocomposite cathodes provide new possibilities to find high-performance cathode materials. However, nanocomposite electrodes usually
show high overpotential during charge process, which is decomposition reaction of alkali fluorides such as LiF and NaF.\textsuperscript{15-17,23,25,26} In chapter 4, I presented the systematic studies which revealed the origin of overpotential in nanocomposite cathodes. The MF\textsubscript{x}-MnO (M= Li, Na, K, Rb, Cs, Mg, Ca, and Al) model system was introduced to reveal the origin of overpotential since the MnO is known to interact with fluorine only at the surface of MnO and the electrochemical reaction does not involve bulk diffusion of alkali ions. The systematic studies including galvanostatic intermittent titration technique (GITT) and X-ray photoelectron spectroscopy (XPS) analysis reveal that the lattice energy of fluoride compounds has a strong correlation with the overpotential and the activity of nanocomposite electrodes which indicated as F 1s binding energy of MF\textsubscript{x}.

The findings in MF\textsubscript{x}-MnO nanocomposite introduced in chapter 4 not only reveal the origin of the overpotential but also show expandability to other battery systems. In chapter 5, I presented the electrochemical activity and reaction mechanisms of KF-MnO nanocomposite operated in potassium system. The KF-MnO nanocomposite was successfully operated in the potassium cell. The oxidation state change of Mn during battery operation was analyzed with Mn K-edge XANES analysis and 2D electron energy loss
spectroscopy (EELS) mapping. The structure change during charge/discharge was observed with atomic resolution TEM.
1.2 References

(1) Kim, S. W.; Seo, D. H.; Ma, X.; Ceder, G.; Kang, K. Electrode materials for rechargeable sodium-ion batteries: potential alternatives to current lithium-ion batteries. *Advanced Energy Materials* **2012**, *2* (7), 710.


(7) Komaba, S.; Takei, C.; Nakayama, T.; Ogata, A.; Yabuuchi, N.
Electrochemical intercalation activity of layered NaCrO2 vs. LiCrO2.


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Chapter 2. New type of Na-ion battery cathode material: NaF-FeF₂ nanocomposite

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2.1 Introduction

Demands for green energy from renewable resources such as solar and wind power have got recently intensified to cope with the needs for the sustainable energy supply. Large-scale energy storage system would play an important role in the effective utilization of the energy generated from these renewable resources. Although Li-ion batteries (LIBs) are one of the leading candidates for these applications, the high cost and the possible safety problem remain as the critical issues to be resolved. Furthermore, there are growing concerns on the availability of lithium resources upon the widespread usages of LIBs for large scale applications such as electric vehicles ¹. On the other hand, Na-ion batteries (NIBs) hold merit for large energy storage devices particularly due to the use of the earth abundant sodium resources which can alleviate the concern on the scarcity of raw
materials and possibly reduce the cost $^{2-5}$. Moreover, one can take advantage of the well-established LIB technology because of the similar electrochemistry of NIBs with that of LIBs. Nevertheless, the energy density of NIBs is generally lower than that of the LIBs due to the NIB electrodes that typically show lower redox potential and contain heavier sodium element than those of lithium $^{6,7}$. In this respect, extensive research efforts have focused on developing new high-performance electrode materials for NIBs. Various materials have been proposed as positive electrode materials such as layered transition metal oxides $^{8-12}$, polyanion-based phosphates, $^{13-17}$ fluorophosphates $^{18-22}$ and sulfates $^{23-25}$, showing some promising electrochemical performance. However, the intercalation of large sodium ions typically induces a large volume change in the layered-type oxide electrodes, thus the full utilization of the high capacity of the layered electrodes is not trivial and often leads to a rapid capacity decay $^{8-10,12}$. The polyanion-based materials that contain the relatively large open framework for sodium ion intercalation are commonly heavier than layered oxides, which significantly reduces the specific/volumetric capacity $^{13-16}$. The exploration of new host structures for sodium ions, thus, is highly required, however, remains challenging.
Recently, our group reported that nano-scale mixture such as that of LiF and FeF$_2$ could exhibit the electrochemical activity in a lithium-ion cell (LiF-FeF$_2$ nanocomposite electrode) $^{26,27}$. In the electrode reaction of the nanocomposite, it was demonstrated that LiF component can serve as a lithium ion source in the cell, while the FeF$_2$ gets activated to provide the Fe$^{2+}$/Fe$^{3+}$ redox reaction via the eventual formation of FeF$_3$–like structure $^{26}$. The cell could deliver 190 mAh/g of reversible capacity even in the lithium-ion cell set-up, which was comparable to the performance of the state-of-the-art crystalline FeF$_3$ electrode in the lithium-metal half-cell set-up. More recently, the similar concept was also demonstrated for LiF-MnO$^{27}$ and LiF-MnO$_x$ (x=1, 1.33, 1.5, 2) $^{28}$ as LIB cathode materials, where the F$^-$ from the LiF decomposition could mediate the redox reaction of the electrode via the formation of MnOF-like phase. While this new concept of the electrode reaction was successfully demonstrated for LiBs, we believed that it could be generally applicable to the electrochemical storage of sodium ions as well due to the expected similarity between LiF and NaF. The validation of the composite redox reaction for sodium ion storage would further suggest new strategies to explore NIB electrodes beyond the intercalation concept. Here, we show that the electrochemical sodium ion storage is also possible for the
nanocomposite electrode using NaF-FeF$_2$ model system as a proof of the concept (Figure 2-1 (a)). Furthermore, the detailed mechanism occurring at the electrochemical process is carefully examined by probing the local structure of the materials in the electrode in comparison to the case of LIBs.


2.2 Experimental

NaF-FeF$_2$ nanocomposite was synthesized via a planetary ball miller (Fritsch, Pulverisette 5). As-received NaF (Alfa Aesar) and FeF$_2$ (98%, Aldrich) were ball milled at 560rpm for 48h (5-minute rest was conducted after every 25-minute cycling) separately with 20 wt% additional natural graphite. Each ball milling container was sealed in an Ar-filled glove box to minimize moisture exposure. After ball milling, the container was opened in an Ar-filled glove box. Stoichiometric NaF-C and FeF$_2$-C nanocomposite were mixed in conventional slurry making process.

The crystal structure of nanocomposite and precursors were analyzed using X-ray diffractometer (D2 phasor). The data was collected over a 2θ range of 10°~70°, with a step size of 0.01°, a step time of 0.6 s and Cu K$_\alpha$ was used as target material. The morphology of the sample was analyzed by field emission scanning electron microscope (MERLIN Compact, FE-SEM). Pt coating was done before SEM measurements.

The samples for TEM analysis were prepared by drying a drop of the NaF-FeF$_2$ suspension onto a carbon-coated copper grid. The structures and chemical composition were examined using a condenser lens aberration
corrected JEM ARM-200F (Cold FEG Type, JEOL) equipped with an EELS detector (965 GIF Quantum ER, GATAN) at 200 kV.

In HAADF STEM images, the point-to-point resolution was about 80 pm after the Cs correction, and the angular range of the annular detector used was 68-280 mrad. All images were acquired by a high-resolution CCD detector using a 2 k × 2 k pixel device (UltraScan 1000, GATAN). For STEM-EELS measurements, the energy dispersion was set as 0.25 eV/ch. The full width at half-maximum of the zero-loss peak in vacuum was 1.0 eV. The convergence and collection semi-angles were 19 and 26 mrad, respectively.

The NaF-FeF₂ nano-composite electrode was made as followed. NaF-C & FeF₂-C were synthesized using high energy ball miller as mentioned. Stoichiometric NaF-C & FeF₂-C were mixed in egg ball miller. NaF-FeF₂ active material (NaF: FeF₂ = 1.2: 1 molar ratio, total 70 wt%), Super P (20 wt%) and fluorine-free Polyacrylonitrile (PAN) binder (10 wt%) were mixed in N-methyl-1,2-pyrrolidone (NMP, 99.5%; Sigma-Aldrich, St. Louis, MO, USA) to make slurry. The slurry was then casted on aluminum foil with doctor-blade and dried in 30°C vacuum oven for 24 hours. The dried slurry was roll pressed using roll presser (Hohsen, Osaka, Japan). The disc shape
electrode was gained using 1/2 inch punching tool (Hohsen, Osaka, Japan).

The Na half-cell was assembled into a CR2032 coin cell using metallic Na (sodium cube 99%, Aldrich) as a counter electrode and a glass microfiber filter (grade GF/F; Whatman, US) as a separator. 1M NaPF$_6$ in EC/PC (1:1, v/v) electrolyte is used for all the electrochemical test which shows high stability at high voltage. Galvanostatic measurements of the NaF-FeF$_2$ nanocomposite electrode were performed with 20 mA/g and two types of cut-off voltages were applied (1.2-4.5 V and 1.2-4.8V) with a potentiogalvanostat (WBCS 3000; WonA Tech, Seoul Korea). The first charge process of 4.5 V charged sample was performed under constant current and constant voltage (CC/CV) mode under 20 mA/g of constant current and 4.5 V of constant voltage until current drops below 10 mA/g. All the gravimetric capacity shown was calculated using the weight of active material (NaF-FeF$_2$). Cyclic voltammetry test was performed after 2 cycles to stabilize cell. Two sets of the voltage range of 4.5-1.2 V and 4.8-1.2 V was applied and the scan rate was changed from 0.075 to 1 mV/s.

For ex-situ X-ray absorption spectroscopy (XAS) measurements at Fe K-edge region, each electrode which set at a certain state of charge was sealed
with Kapton film. Each ex-situ electrode was made as followed. Na half-cell was set at a certain state of charge using the same protocol and conditions used in the galvanostatic measurements except for the Fe free (0 %) Al foil was used for ex-situ XAS measurements. After the galvanostatic measurement is finished, the cell was disassembled in Ar-filled glove box and electrode was washed carefully with dimethyl carbonate (DMC) solvent. The electrode was dried in 30°C vacuum oven overnight. Ex-situ XAS was performed at the 7D XAFS, 8C nano-XAFS and 10C wide XAFS beamlines at the Pohang Light Source-Ⅱ (PLS-Ⅱ) using Si(111) double-crystal monochromator. The beam intensity was reduced by 20-30 % to minimize high-order harmonics. The Fe K-edge spectra of NaF-FeF$_2$ electrodes were recorded in transmission mode. Fe metal spectra was measured as reference data at the same time to calibrate energy. The storage ring was operated at 2.5 GeV with a ring current of 300 mA top-up mode. The measured XAS signal was transformed into R space after a proper background removal via the AUTOBK code (a part of IFEFFIT). The transformed R space data were fitted to EXAFS calculations with FEFF8.0 code 29 to study the quantitative structural properties around a Fe atom. The FeF$_2$ and FeF$_3$ reference powders were fitted with their general structure obtained from inorganic crystal
structure database (ICDS).

For the soft X-ray absorption spectroscopy (XAS) at Fe L-edge and F K-edge, each sample is prepared in the same manner except that the samples were directly attached to the holder without Kapton film. The XAS spectrum was measured at the 8A1 SPEM and 10D XAS KIST beamlines at the Pohang Light Source-Ⅱ (PLS-Ⅱ). The XAS spectrum was collected in total electron yield (TEY) mode.
2.3 Result and discussion

2.3.1 Synthesis and electrochemical properties

NaF powder was ball-milled with carbon and mixed with FeF₂ powder which was also ball-milled with carbon in a separate jar. The nanocomposite electrode was prepared using the mixture by a conventional slurry making process (The detailed method is provided in the experimental section). Figure 2-1 (b) shows the X-ray diffraction (XRD) patterns of the ball-milled NaF-C, FeF₂-C and the mixture of the two, respectively. In the XRD patterns, all the peak positions match well with those of the pristine NaF and FeF₂, and no other peak is observable, which indicates that neither decomposition nor phase transformation has occurred during the milling process of NaF and FeF₂. Particle sizes of the ball-milled NaF and FeF₂ were estimated from the XRD patterns by Scherrer equation ($\tau = \frac{K\lambda}{\beta \cos \theta}$), where $\tau$ is the crystalline size, $K$ is a shape factor (0.9 is used in this study), $\beta$ is a full width at half maximum and $\theta$ is a Bragg angle. The average crystalline size was determined to be approximately 13 nm for both cases, which is significantly smaller than the pristine state of particles (~several micrometers, see Table 2-1). The high-resolution transmission electron microscopy (HR-TEM) revealed that the
mixture is mainly composed of 5~10 nm sized particles with the characteristic inter-planar distance of FeF$_2$ crystal as shown in Figure 2-1 (c). The size reduction and the loss of the initial morphology after the high energy milling were also clearly seen in the scanning electron microscopy (SEM) images in Figure 2-2.

The electrochemical activity of the nanocomposite electrode was investigated in a half-cell using sodium metal anode. 1M NaPF$_6$ in ethylene carbonate/propylene carbonate (EC/PC, 1:1 volume ratio) was used as the electrolyte due to its high electrochemical stability over 5.0 V vs. Na/Na$^+$. Figure 2-1 (d) shows the typical charge/discharge profile of the NaF-FeF$_2$ nanocomposite electrode tested in a constant current mode (20 mA/g) after the first charging process. The first charging profile for the activation step is provided in Figure 2-3 (a). Cells were operated in two different voltage windows; one between 1.2 V and 4.5 V (NF45) and the other between 1.2 V and 4.8 V (NF48). The first discharge capacities of NF45 and NF48 were ~100 mAh/g and ~125 mAh/g, respectively. It should be noted that the nanocomposite electrode without the first charging process results in a negligible discharge capacity as shown in Figure 2-3 (b), indicating that the first charge process triggers the electrochemical activity of the electrode.
which was similarly observed in the case of LiF-FeF$_2$ in the previous report. Moreover, it is clear that a higher charge cut-off voltage increases the reversible capacity significantly, implying the voltage-dependent activation of the nanocomposite electrode in Figure 2-4. After the first charging activation, both the NF45 and NF48 electrode exhibited stable cycle performance with negligible capacity decay, moreover, the electrochemical profile remained unchanged during the cycles as shown in Figure 2-1 (e) and Figure 2-5. The NaF-FeF$_2$ electrode was also operated in the voltage range at 1.2~4.5 V after the first activation cycle to 4.8 V to see the activation effect in the first charge step (Figure 2-6). The cell once activated to 4.8 V showed a higher reversible capacity (~110 mAh/g) than NF45 (~100 mAh/g) in the same operating voltage range (1.2~4.5 V). This result implies that the initial high voltage charging of the cell (4.8 V) induces more electrochemical activation of the electrode, which is maintained even in the low voltage operation (4.5 V). Worthwhile to note is that the reversible capacity of NF45 slightly increases with cycling in Figure 2-1 (e) as well. It may indicate the gradual activation of the electrode occurs during the cycling even at the low voltage operation.
Figure 2-1 (a) Design concept of NaF-\(\text{FeF}_2\) nanocomposite electrode. (b) XRD (X-ray diffraction) patterns of ball milled NaF-C (red), ball milled FeF\(_2\)-C (blue) and NaF-\(\text{FeF}_2\) electrode (green). (c) HR-TEM image of as prepared NaF-\(\text{FeF}_2\) electrode. (d) Charge/discharge graph of NaF-\(\text{FeF}_2\) electrode after activation to different cut off voltage (4.5 V (red) and 4.8 V (blue)). (e) Cycle performance of NaF-\(\text{FeF}_2\) electrode which activated to 4.5 V (red) and 4.8 V (blue).
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**Table 1** Data used to calculate average particle size of high energy ball milled (a) NaF and (b) FeF$_2$. Each particle size is estimated using Scherrer equation (K=0.9 is used).
Figure 2-2 SEM images of (a) as prepared NaF, (b) as prepared FeF$_2$, (c) high energy ball milled NaF and (d) high energy ball milled FeF$_2$. It is clearly seen that the particle size was significantly reduced and the initial morphology was lost after high energy ball milling.
Figure 2-3 (a) Charge graph of initial activation step up to 4.5 V (orange) and 4.8 V (blue), (b) discharge graph of NaF-FeF$_2$ nanocomposite without activation charge process. When NaF-FeF$_2$ electrode discharged without activation, it shows negligible capacity (~40 mAh/g), which indicates NaF plays a crucial role in activating FeF$_2$. 
Figure 2-4 dQ/dV plots of NaF-FeF₂ which activated to (a) 4.5 V and (b) 4.8 V. dQ/dV graph is measured after activation step (following discharge and charge step). When NaF-FeF₂ electrode charge up to 4.8 V, clear dQ/dV peak around 3.3 V (highlighted as blue shade in Figure 2-4 (b)) appeared.
Figure 2-5 Charge/discharge profile of 2\textsuperscript{nd} (red) and 40\textsuperscript{th} (blue) cycle of (a) NF45 and (b) NF48. After the 40\textsuperscript{th} cycle, both samples show similar voltage profile with that of the 2\textsuperscript{nd} cycle.
Figure 2-6 Cycle performance of NaF-FeF$_2$ nanocomposite electrode operated between 1.2~4.5 V (NF45, red), 1.2~4.8 V (NF48, blue) and 1.2~4.8 V in the first cycle and 1.2~4.5 V in subsequent cycle (green).
2.3.2 Oxidation state and local structure analysis with X-ray absorption spectroscopy

The detailed electrode mechanism of NaF-FeF$_2$ nanocomposite electrode was investigated by \textit{ex situ} XRD and X-ray absorption spectroscopy (XAS). The \textit{ex situ} XRD in Figure 2-7 showed that the peaks corresponding to the crystalline NaF significantly reduce in the intensity during the first charge step, however, do not recover during the subsequent discharge. The \textit{ex situ} XAS in Figure 2-8 also indicated that the broad peak around $\sim$690 eV which is attributed to F K-edge signal from NaF$^{31-33}$ disappears during the charging process and do not reappear during the discharge. These observations are similar to the case of the LiF decomposition during the first charging process of the LiF-FeF$_2$ nanocomposite electrode $^{26}$, strongly suggesting the electrochemical decomposition of NaF during the first charging process. As in the case of the LiF-FeF$_2$ nanocomposite, it is expected that the electrochemical decomposition of NaF leads to the liberation of Na$^+$ ion and F$^-$ ion into the electrolyte.

The origin of the reversible capacity was examined by \textit{ex situ} X-ray absorption near edge structure (XANES) at Fe K-edge and XAS at Fe L-edge.
Fe K-edge XANES spectra of NF45 and NF48 are shown in Figure 2-9 (a) and (b). It is clear that Fe K-edge shifts to higher energy with charging, indicating that Fe$^{2+}$ is oxidized to Fe$^{3+}$ for both samples. The oxidation of the Fe in the FeF$_2$ during the charging is surprising and hard to comprehend in a conventional electrochemical reaction, however, consistent with the observation for the LiF-FeF$_2$ electrode, where the liberated F$^-$ ion mediates the redox reaction of Fe by being incorporated into the FeF$_2$ structure. It evidently proposes that the decomposition of NaF can successfully play the role of mediating the redox reaction of FeF$_2$ for NIB electrode as well. The F$^-$ ions from the electrochemical decomposition of NaF mediate the oxidation of Fe as previously observed in the LiF-FeF$_2$ electrode. When comparing the charged state of NF45 and NF48, Fe K-edge of the NF48 is located at a higher value than that of the NF45, which agrees with a higher capacity observed in the electrochemical measurement. It implies that as the cut-off voltage of the charging process increases, more F$^-$ is liberated and participates in the electrochemical reaction involving the FeF$_2$. The Fe K-edge shifts back to a lower value (almost identical to the as-prepared state) when discharged, which shows the reversibility of the charge/discharge reaction.

Fe L-edge XAS spectra of NF45 and NF48 provide more detailed redox
picture of the charge and discharge. Fe L-edge signal was collected in total electron yield (TEY) mode, which detects signals from the surface to 10 nm depth. Considering the particle size of NaF-FeF₂ nanocomposite (5~10 nm), it is expected that the XAS signals represent the whole information of the NaF-FeF₂ nanocomposite. When comparing the samples at various state of charging; as-prepared, half charged, fully charged (charged to either 4.5 V or 4.8 V), half discharged and fully discharged state (Figure 2-9 (c) and (d)), XAS spectra confirm that the Fe is the redox-active element of the nanocomposite electrode. However, the XAS analysis not only identifies the redox element, i.e. Fe, but also hints at the local structural information around the redox element. The two peaks in Figure 2-9 (c) and (d) marked as gray lines correspond to the characteristic Fe L-edge peaks around ~710 eV in iron fluorides 34. As the electrode charging proceeds, the second peak intensity gradually increases at the expense of the first peak in both NF45 and NF48. However, when the electrode is discharged, the relative intensity of the two peaks does not recover but remains the same as the end of the charged state. It indicates that an irreversible change of the Fe local environment has occurred during the charging process. In order to elucidate this finding, we took the same XAS spectra for pristine FeF₂, FeF₃, and NaFeF₃ as reference
samples in Figure 2-9 (e). Note that the relative intensities of the two peaks are distinct for FeF$_2$ and FeF$_3$, while the relative intensity is almost unchanged for the FeF$_3$ and NaFeF$_3$. For FeF$_2$, the first peak intensity is comparable to the second peak, on the other hand, it is much weaker than the second peak in the case of FeF$_3$ or NaFeF$_3$. The sodium insertion into FeF$_3$ structure, i.e. NaFeF$_3$, does not induce a significant change in the relative peak intensity indicating that it is a characteristic of FeF$_3$ structure. This comparison strongly suggests that NaF-FeF$_2$ nanocomposite electrode transforms to a structure containing the Fe local environment of FeF$_3$ during charging and the following discharge is accompanied with the sodium intercalation into the structure resembling NaFeF$_3$. Noteworthy is that at each fully charged states of NF45 and NF48 in Figure 2-9 (c) and (d), the second peak intensity appears higher for NF48 than NF45, indicating that the NF48 contains more Fe local environment of FeF$_3$ structure. This is in a good agreement with XANES results discussed earlier, which showed NF48 were more oxidized than NF45 at the fully charged state, thus delivered a higher capacity.
Figure 2-7 Ex-situ XRD graph of NaF-FeF$_2$ nanocomposite electrode. As prepared, half charged, 1$^{st}$ charged, and 1$^{st}$ discharged data is shown. Reference line of FeF$_2$, Al foil, and NaF is marked as dashed lines in the graph. It is clearly seen that the peak corresponding to NaF is decreased during charge and did not recovered in the discharge step.
Figure 2-8 Ex-situ XAS results in F K-edge region. When cell is charged to 4.8 V, broad shoulder peak around ~690 eV (marked as the gray line) disappears and does not recovered in discharge step. This implies first charge step is NaF decomposition reaction and irreversible.
Figure 2-9 Ex-situ XANES plot of (a) NF45 and (b) NF48. In both graph, as prepared (red), charged (blue) and discharged (green) state is plotted. Ex-situ XAS plot in the Fe L-edge region of (c) NF45, (d) NF48 at different state of charging and (e) reference powder.
2.3.3 Revealing host formation mechanism during initial charge

In order to confirm the proposed mechanism, the local structure around Fe at the charged state was further analyzed by extended X-ray absorption fine structure (EXAFS) analysis. Figure 2-10 (a) and (b) show the EXAFS spectra of NF45 and NF48, respectively, at as-prepared, fully charged and fully discharged states (The details on the data processing is provided in experimental section and supporting information). In addition, EXAFS spectra of FeF$_2$ and FeF$_3$ reference samples are provided in Figure 2-10 (c), which show two characteristic peaks at similar bonding lengths of ~1.7 Å and ~3.2 Å. The two peaks show clearly distinguishable relative intensity, which correspond to Fe-F shell (~1.7 Å), Fe-Fe shell (~3.2 Å) and multiple-scattering shells (~3.2 Å) in both FeF$_2$ and FeF$_3^{26,35,36}$. It is observed that the EXAFS spectra of as-prepared NF45 and NF48 samples are nearly identical to that of the FeF$_2$ reference powder, however, when NaF-FeF$_2$ nanocomposite is charged, the EXAFS spectra of the NF45 and NF48 are better fitted with the model of the two phase mixture of FeF$_2$ and FeF$_3$ (The detailed fitting procedure is provided in the supplementary text). Figure 2-10
(d) illustrates the estimated phase fraction of the FeF$_2$ and FeF$_3$ for as-prepared, charged NF5 and charged NF48. It shows, as the charge proceeds to 4.5 V, the fraction of FeF$_2$ decreases to 75 % and FeF$_3$ increases to 25 %. When the cell is further charged to 4.8 V, the fraction of FeF$_3$ reaches over 50 %. These results are in consistent with the observations from XAS in Figure 2-9, supporting the gradual transformation of FeF$_2$ to a new host structure, FeF$_3$, upon charging. The FeF$_3$ fraction tended to be underestimated because of our assumption of the well-crystalline FeF$_3$ as the reference sample in the fitting. The charged NF45 and NF48 would contain significant portion of the disorder induced by the F$^-$ incorporation in the room temperature electrochemical reaction. Similar underestimation could be found in the reconversion reaction of FeF$_3$, where the EXAFS peak remained similar with that of the FeF$_2$ even at the fully charged state due to the significant disorders in the structure $^{36,37}$. Considering EXAFS data along with Fe L-edge XAS analysis, it is proposed that the charged phase (after the activation charge step) is FeF$_3$-like phase, which subsequently forms NaFeF$_3$-like phase upon the sodiation during the discharge. The “-like” phase is denoted, since it is not the well-ordered FeF$_3$ and contains a significant amount of the disordered Fe-F bonding.
The FeF$_3$-like charged product could be directly visualized with Cs-corrected HAADF STEM (condenser lens spherical aberration-corrected high-angle annular dark-field scanning transmission electron microscopy). Since the charged phase of NF48 was unstable under a beam exposure (Figure 2-11), only the charged NF45 could be analyzed. The HAADF-STEM image of charged state of NF45 is shown in Figure 2-12 (a). Line electron energy loss spectroscopy (line EELS) was performed on a single particle as shown in Figure 2-12 (a) to reveal the spatial distribution of Fe$^{3+}$. The two line EELS spectra were collected every 1 nm distance along the two green lines shown in Figure 2-12 (a), and, in each line EELS spectrum, the maximum peak position is plotted versus distance (insets of Figure 2-12 (a)). Considering the characteristic Fe$^{2+}$ and Fe$^{3+}$ peaks at 708~709 eV and at 709.5~710.5 eV, respectively, (i.e. FeF$_2$ and FeF$_3$), it clearly indicates that the outer region of the particles are mostly oxidized to Fe$^{3+}$ as indicated with blue in the figures 38,39. The graphical representation in Figure 2-12 (b) estimated from the line EELS profiles and FFT (fast Fourier transformation) images (Figure 2-13) shows that Fe in the bottom right region of the particle (0~10 nm region in each line) is oxidized to Fe$^{3+}$, while the core region of the particle remains as Fe$^{2+}$ state, indicating the partial oxidation of Fe in NF45. Furthermore, it
clearly reveals that the Fe$^{3+}$ is mainly distributed along the particle surface, especially in the vicinity of the conductive carbon matrix where the NaF and FeF$_2$ nano-domain were mixed homogeneously. It is speculated that the NaF decomposition occurs efficiently when the electrical conduction is well provided by the carbon matrix. The FFT image in Figure 2-13 displayed that the crystalline is highly disordered around the surface region compared with the core region, strongly suggesting that the Fe oxidation and the F$^-$ ion incorporation primarily occurred on the surface and induced the significant distortion of the crystal. It is believed that the F$^-$ ion generated by the decomposition of NaF tends to be absorbed on the surface of FeF$_2$ near carbon matrix due to the shorter diffusion distance. This surface dominated reaction in NaF-FeF$_2$ nanocomposite was also confirmed with cyclic voltammetry (CV) for the scan rate of 0.075 mV/s to 1 mV/s in Figure 2-12 (c) and (d) for NF45 and NF48. The relationship between the scan rate and the redox peak current ($i \propto \nu^a$) in the inset of Figure 2-12 (c) and (d) displays that the slope was 0.88–0.97 for both oxidation and reduction reactions for NF45 and NF48, respectively, implying that the surface reaction is dominant in the NaF-FeF$_2$ nanocomposite electrode $^{40}$.

The expected reaction mechanism of NaF-FeF$_2$ nanocomposite is
schematically shown in Figure 2-14. When the NaF-FeF$_2$ electrode is charged, NaF is decomposed liberating F$^-$ ions. The F$^-$ ions absorb on the surface of FeF$_2$ and induce the gradual transformation of the FeF$_2$ into FeF$_3$-like structure from the surface to core, as the charge proceeds. When the cell is discharged, Na$^+$ ions diffuse into FeF$_3$-like structure and form NaFeF$_3$-like structure. The expected reaction mechanism is summarized below (equation (1) and (2)).

$$\text{NaF} + \text{FeF}_2 \xrightarrow{\text{charge}} \text{Na}^+ + \text{FeF}_3\text{-like} + e^- \text{ (first charge)}$$  

--- (1)

$$\text{Na}^+ + \text{FeF}_3\text{-like} + e^- \xleftarrow{\text{charge}} \xrightarrow{\text{discharge}} \text{NaFeF}_3\text{-like} \text{ (subsequent cycle)}$$  

--- (2)
Figure 2-10 Ex-situ EXAFS plot of (a) NF45 and (b) NF48. In both graph, as prepared (red), charged (blue) and discharged (green) state is plotted. (c) EXAFS plot of FeF$_2$ and FeF$_3$ reference powder. The fitting results of each reference powder is also plotted as dotted line. (d) EXAFS fitting results of as prepared, 4.5 V charged and 4.8 V charged sample.
Figure 2-11 Ex-situ Cs-STEM analysis on charged phase of NF48. (a) TEM images before beam alignments and (b) TEM images after alignments. FFT patterns is shown in right side of each images. As observed images shows clear dot pattern in FFT which indicates charged phase has crystallinity initially. The FFT images after beam alignments shows diffuse pattern and weak dot pattern which shows deformation of charged phase during beam alignments.
Figure 2-12 (a) A HAADF-STEM image of the charged NF45 single particle, the two green lines represent the points where the EELS data were collected. The line EELS data plotted as distance vs. peak position (peak in the 708~711 eV range) for line 1 and line 2 are shown in inset of Figure 2-12 (a). (b) Fe$^{3+}$ region speculated from line EELS and FFT results. Cyclic voltammetry test of (c) NF45 and (d) NF48. Relation between scan rates vs. peak current is shown in inset of each corresponding cyclic voltammetry graph (Figure 2-12 (c) and (d)).
Figure 2-13 Fast fourier transformation (FFT) images of charged state of NF45. The region 1 represents the core region and region 2 represents the surface region. Core region shows good crystallinity which corresponding to rutile structure. Surface region shows weaker signal than core region which indicate loss of ordering (disordered state).
Figure 2-14 Reaction mechanism of NaF-FeF₂ nanocomposite. FeF₂, FeF₃-like and NaFeF₃-like phase is colored as green, pale green and yellow. In first charge step, as charge proceeds FeF₂ particle gradually changed to FeF₃-like structure from the surface. Further reaction is occurred via insertion/deinsertion of Na⁺ ion into FeF₃-like structure.
2.4 Conclusion

In conclusion, we proposed a new type of positive electrode materials for NIBs based on the nanocomposite of alkali fluoride and metal fluoride using NaF-FeF\textsubscript{2} as a model system, and demonstrated that the nanocomposite can function as a high-performance cathode for NIBs due to the F\textsuperscript{-} redox mediation. The first charging process could activate the nanocomposite by liberating the F\textsuperscript{-} ions, which subsequently was adsorbed on the FeF\textsubscript{2} surface oxidizing the Fe redox element and gradually induced the formation of a new host structure for the sodium intercalation from the surface of FeF\textsubscript{2} particle. The electrode was capable of delivering ~125 mAh/g of reversible capacity when charged up to 4.8 V (NF48). This is the first successful demonstration that the electrochemical sodium ion storage is also possible for the nanocomposite electrode. We believe that this unique sodium ion storage phenomenon would open up a new avenue to design novel positive electrode materials for Na-ion batteries beyond the intercalation concept.
2.5 References


(2) Palomares, V.; Serras, P.; Villaluenga, I.; Hueso, K. B.; Carretero-González, J.; Rojo, T. Na-ion batteries, recent advances and present challenges to become low cost energy storage systems. Energy & Environmental Science 2012, 5 (3), 5884.

(3) Pan, H.; Hu, Y.-S.; Chen, L. Room-temperature stationary sodium-ion batteries for large-scale electric energy storage. Energy & Environmental Science 2013, 6 (8), 2338.


(5) Kim, S. W.; Seo, D. H.; Ma, X.; Ceder, G.; Kang, K. Electrode materials for rechargeable sodium-ion batteries: potential alternatives to current lithium-ion batteries. Advanced Energy Materials 2012, 2 (7), 710.

(7) Yabuuchi, N.; Kubota, K.; Dahbi, M.; Komaba, S. Research development on sodium-ion batteries. Chemical reviews 2014, 114 (23), 11636.


(14) Ha, K. H.; Woo, S. H.; Mok, D.; Choi, N. S.; Park, Y.; Oh, S. M.; Kim, Y.
Kim, J.; Lee, J.; Nazar, L. F. Na4-αM2+ α/2 (P2O7) 2 (2/3 ≤ α ≤ 7/8, M= Fe, Fe0. 5Mn0. 5, Mn): A Promising Sodium Ion Cathode for Na-ion Batteries. Advanced Energy Materials 2013, 3 (6), 770.


of High-Performance Cathode Materials for Na-ion Batteries, Na3 (VO1−
xPO4) 2 F1+ 2x (0 ≤ x ≤ 1): Combined First-Principles and Experimental

Yoo, H.-I.; Kang, K. A new high-energy cathode for a Na-ion battery with
ultrahigh stability. Journal of the American Chemical Society 2013, 135 (37),
13870.

(22) Recham, N.; Chotard, J.-N.; Dupont, L.; Djellab, K.; Armand, M.; Tarascon,
J.-M. Ionothermal synthesis of sodium-based fluorophosphate cathode

(23) Barpanda, P.; Chotard, J.-N.; Recham, N.; Delacourt, C.; Ati, M.; Dupont, L.;
Armand, M.; Tarascon, J.-M. Structural, transport, and electrochemical
investigation of novel AMSO4F (A= Na, Li; M= Fe, Co, Ni, Mn) metal
fluorosulphates prepared using low temperature synthesis routes. Inorganic
chemistry 2010, 49 (16), 7401.

Munichandraiah, N.; Ahuja, R.; Barpanda, P. Ionothermal Synthesis of High-
Voltage Alluaudite Na2+ 2xFe2-x (SO4) 3 Sodium Insertion Compound:
Structural, Electronic, and Magnetic Insights. ACS applied materials &
interfaces 2016, 8 (11), 6982.

(25) Wei, S.; Mortemard de Boisse, B.; Oyama, G.; Nishimura, S. i.; Yamada, A.


(36) Zhang, W.; Duchesne, P. N.; Gong, Z.-L.; Wu, S.-Q.; Ma, L.; Jiang, Z.; Zhang, S.; Zhang, P.; Mi, J.-X.; Yang, Y. In situ electrochemical XAFS studies on an iron fluoride high-capacity cathode material for rechargeable lithium batteries. The Journal of Physical Chemistry C 2013, 117 (22), 11498.

(38) Cosandey, F.; Al-Sharab, J. F.; Badway, F.; Amatucci, G. G.; Stadelmann, P. EELS spectroscopy of iron fluorides and FeF x/C nanocomposite electrodes used in Li-ion batteries. Microscopy and Microanalysis 2007, 13 (02), 87.


Chapter 3. In operando formation of new iron-oxyfluoride host structure for Na-ion storage from NaF-FeO nanocomposite

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3.1 Introduction

Na-ion batteries (NIBs) have attracted considerable attention as an alternative to Li-ion batteries (LIBs) because their components are more abundant in nature and more cost-effective than those of LIBs. The key to the success of NIBs lies in discovering new electrode materials that can provide high energy density. However, the search for new Na-ion host structures has been challenging because of the limited number of host crystalline materials in which Na de/intercalation can reversibly occur.\(^1\text{-}^4\) For the past decades, extensive research has led to the identification of important NIB cathode materials, including layered-type O3-NaTMO\(_2\) (TM = Co, Mn, Cr, Fe, and Ni),\(^5\text{-}^{10}\) P2-Na\(_x\)(Fe, Mn)O\(_2\) (0<\(x<1\)),\(^11\text{-}^{14}\) and polyanionic compounds such as Na\(_3\)(VO\(_x\))\(_2\)(PO\(_4\))\(_2\)F\(_{2-2x}\) (0<\(x<1\))\(^15\text{-}^{17}\) and NaFeSO\(_4\)F.\(^18\text{-}^{20}\) Although these
materials show promising electrochemical performance, the energy densities that they are capable of delivering do not yet reach those of state-of-the-art electrode materials in LIBs.

Recently, a new approach for cathode material design involving nanoscale mixing of alkali (Li or Na) metal compounds and transition metal compounds was reported. In nanocomposite electrodes, the initial electrochemical reaction occurs via the extraction of ions from the alkali metal compounds and electrons from the transition metal compounds. Thus, the two compounds in the nanocomposite serve as an ion host and an electron host, respectively. The concept is similar to the ‘job-sharing’ mechanism observed at the nanoscale interface proposed by Maier et al. in that two different hosts share the electrochemical reaction but differs in that the anion from the alkali metal compounds mediate the reaction; thus, the whole bulk structural materials can participate in the reaction. These types of nanocomposite electrode reactions are generally activated by the initial charge process, which is the decomposition reaction of alkali metal compounds such as LiF and NaF. During the charge process, the liberated \( \text{F}^- \) ion (the decomposition product of the alkali metal compounds) is absorbed on and/or diffuses into the transition metal compounds and activates the
nanocomposite electrodes.\textsuperscript{21-24,26,27} Although reports on nanocomposite electrodes are limited and further understanding is needed, the nanocomposite electrodes have been reported to follow one of two reaction mechanisms: ‘surface conversion’ or ‘host formation’. In the materials that follow the ‘surface conversion’ reaction, the reaction mainly occurs at the surface of the transition metal compounds, accompanying the phase transformation at the surface (\textit{e.g.}, LiF–MnO).\textsuperscript{21} For the ‘host formation’ reaction, new host structures for the respective alkali ions are formed during charge, and further reaction occurs via intercalation/deintercalation of alkali ions in the host structure. It has been reported that intercalation hosts could form, such as FeF\textsubscript{3} from LiF–FeF\textsubscript{2}\textsuperscript{23} and NaF–FeF\textsubscript{2}\textsuperscript{24} nanocomposite reactions, LiFeSO\textsubscript{4}F from LiF–FeSO\textsubscript{4}\textsuperscript{29} and Li\textsubscript{3}(VPO\textsubscript{4})\textsubscript{2}F\textsubscript{3} from 3LiF–2VPO\textsubscript{4}\textsuperscript{31} all of which were previously well-known host crystalline structures for either Li or Na. More recently, it was also observed that the host formation reaction can lead to the formation of new host structure, which has not been observed before. Jung \textit{et al.} showed that for the LiF–FeO nanocomposite, a cubic FeOF structure was unexpectedly formed with the same composition as the well-known rutile FeOF structure but with a different crystalline symmetry.\textsuperscript{22} This finding implies that the utilization of the host formation reaction can be an interesting
new approach to explore cathode materials with new intercalation host structures
3.2 Experimental

The NaF–FeO nanocomposite was synthesized using a planetary ball mill (Fritsch, Pulverisette 5). Stoichiometric amounts of NaF (Alfa Aesar) and FeO (Aldrich) were sealed in an Ar-filled glove box and ball milled at 560 rpm for 48 h to minimize moisture exposure. Both the NaF and FeO powders were used as received. To increase the electronic conductivity of the nanocomposite, an additional 20 wt% of conductive carbon (natural graphite, Bay carbon) was added at the same time. After ball milling, the NaF–FeO nanocomposite was collected in an Ar-filled glove box. The KF–FeO nanocomposite was synthesized in the same manner as the NaF–FeO nanocomposite except that KF (Aldrich) was dried in a 180°C vacuum oven before use.

The crystal structure of the NaF–FeO nanocomposite was analyzed using X-ray diffraction (XRD; D2 Phaser). Data were collected over the 2θ range of 10°–80° with a step size of 0.01° and step time of 0.6 s using Cu Kα radiation. Williamson–Hall plots were constructed using the FullProf software with Fm̅3m cubic FeO and NaF. For the ex situ XRD analysis, the cell was set to a certain state of charge. The cell was then disassembled in an
Ar-filled glove box. The collected electrode was washed with dimethyl carbonate (DMC) to remove the residual salt. The electrode was sealed with Kapton film to protect the electrode from moisture. The data were collected over the 2θ range of 30°–65° using a step size of 0.01° and a step time of 1.2 s to obtain reliable data. The morphology of the sample was analyzed using field-emission scanning electron microscopy (FE-SEM; MERLIN Compact). An approximately 10-nm Pt coating was applied before the scanning electron microscopy (SEM) measurement. For transmission electron microscopy (TEM) analysis, the ex situ electrode was prepared in the same way described previously. The powder was collected from the electrode and dispersed in DMC solvent. The suspension was then dropped onto a carbon-coated Cu grid. The grid was mounted in a TEM holder and analyzed using an analytical transmission electron microscope (JEOL, JEM-2100F).

The NaF–FeO and KF–FeO electrodes were prepared by mixing NaF–FeO or KF–FeO nanocomposite powder (70 wt%), fluorine-free polyacrylonitrile (PAN) binder (10 wt%), and conducting carbon (Super P) (10 wt%) with N-methyl-1,2-pyrrolidone (NMP, 99.5%; Aldrich) solvent. The slurry was cast onto Al foil with a doctor blade and dried in a vacuum chamber at 30°C for 24 h. Disc-shaped electrodes were prepared using a 3/8-
inch punch tool (Hohsen, Osaka, Japan).

The NaF–FeO nanocomposite electrode was tested in a Na half-cell using a CR2032 coin cell. Metallic Na (sodium cube 99%, Aldrich) was used as the counter electrode, a glass microfiber filter (grade GF/F; Whatman, US) was used as the separator, and 1 M NaPF$_6$ in ethylene carbonate/propylene carbonate (EC/PC, 1:1, v/v) was used as the electrolyte. The electrochemical tests were performed in an oven at 60°C at a constant current density of 50 mA/g using a potentiogalvanostat (WBCS 3000; WonA Tech, Seoul, Korea). The cut-off voltages for charge and discharge were 4.4 and 1.2 V vs. Na$^+$/Na, respectively. Cyclic voltammetry (CV) tests were performed over the voltage range of 1.2–4.4 V (vs. Na$^+$/Na), and the scan rate was varied from 0.075 to 1 mV/s. The average discharge voltage in each cycle was obtained by dividing the area under the discharge curve by discharge capacity in the capacity vs. voltage graph. The KF–FeO nanocomposite electrode was tested in a K half-cell using a CR2032 coin cell. Metallic K (Aldrich) was used as the counter electrode, and 1 M KPF$_6$ in EC/PC (1:1, v/v) was used as the electrolyte. The electrochemical tests were performed using the same procedure as that used for the NaF–FeO nanocomposite except that the voltage window was 1.5–4.2 V vs. K$^+$/K.
For the *ex situ* X-ray absorption spectroscopy (XAS) measurements in the Fe K-edge region, each electrode at a certain state of charge was sealed with Kapton film. Each *ex situ* electrode was prepared as follows. The Na half-cell was set at a certain state of charge using the same protocol and conditions used for the galvanostatic measurements except that Fe-free (0%) Al foil was used for the *ex situ* XAS measurements. After the galvanostatic measurement, the cell was disassembled in an Ar-filled glove box, and the electrode was washed carefully with DMC solvent. The electrode was then sealed with Kapton film. *Ex situ* XAS was performed at the 7D XAFS, 8C nano-XAFS, and 10C wide XAFS beamlines at the Pohang Light Source-II (PLS-II) using a Si(111) double-crystal monochromator. The beam intensity was reduced by 20%–30% to minimize high-order harmonics. Fe K-edge spectra of the NaF–FeO electrodes were recorded in transmission mode. Fe metal spectra were obtained as reference data at the same time to calibrate the energy. The storage ring was operated at 3.0 GeV with a ring current of 350 mA in top-up mode.

For the soft XAS analyses at the Fe L-edge and F K-edge, each sample was prepared in the same manner except that the samples were directly attached to the holder without Kapton film. The XAS spectra were measured
at the 8A1 SPEM and 10D XAS KIST beamlines at PLS-II. The XAS spectra were collected in total electron yield (TEY) mode and total fluorescence yield (TFY) mode at the same time.
3.3 Results and discussion

3.3.1 Synthesis and electrochemical properties of NaF-FeO

Here, we report a novel host structure for Na-ion storage, a cubic polymorph of the FeOF structure from a ‘host formation’ reaction, and reveal that this structure can serve as a promising new electrode material for NIBs with a respectable energy density and can outperform well-known rutile FeOF electrodes. The NaF–FeO nanocomposite was prepared by mixing NaF and FeO powder using high-energy ball milling. An X-ray diffraction (XRD) pattern of the as-synthesized NaF–FeO nanocomposite is presented in Figure 3-1 (a). Only peaks originating from NaF and FeO are observed in the XRD pattern, indicating that no side reactions or phase transformations occurred during the ball milling. The broad peaks in the XRD pattern suggest the size reduction of the NaF and FeO crystalline phases after the ball milling. The retention of each phase after ball milling was also confirmed by transmission electron microscopy (TEM) diffraction pattern (DP) analysis (Figure 3-2). The $d$-spacings in the DP image agree well with those of NaF and FeO, and the hollow-ring pattern with some bright spots indicates the random orientation of each crystalline phase in the nanocomposite. The scanning
electron microscopy (SEM) images in Figure 3-3 reveal that the pristine NaF and FeO particles with sizes of tens of micrometers were broken down into smaller pieces after the ball milling with average crystalline sizes of approximately 10 nm according to Williamson–Hall plots (Figure 3-4).

Figure 3-1 (b) presents the first charge and discharge profiles of the NaF–FeO nanocomposite electrode in a Na half-cell configuration with metallic Na as the anode and 1 M NaPF₆ in ethylene carbonate/propylene carbonate (EC/PC, 1/1, v/v) as the electrolyte in the voltage window of 1.2–4.4 V (vs. Na⁺/Na) using a current density of 50 mA/g at 60°C. The NaF–FeO nanocomposite electrode could deliver a discharge capacity of 150 mAh/g after the initial charging to 4.4 V, corresponding to the reaction of 0.6 Na ion per transition metal ion. The origin of the reversible capacity was probed using X-ray absorption near edge spectroscopy (XANES) at the Fe K-edge (Figure 3-1 (c)). In the XANES spectra, the Fe K-edge shifts to higher energy during charge and shifts back to lower energy during discharge, which indicates the reversible oxidation and reduction of Fe during the electrochemical reactions. The F K-edge X-ray absorption spectroscopy (XAS) spectra in Figure 3-1 (d) and (e) demonstrate that F⁻ anion incorporation to FeO occurs during charge process, which is consistent with
the previous observations of the F anion mediation in the nanocomposite electrochemical reaction.\textsuperscript{21-24} The F K-edge XAS spectra were simultaneously recorded in total fluorescence yield (TFY) and total electron yield (TEY) modes. Note that the surface-sensitive TEY mode collects signals from the near surface (~5–10 nm), whereas the TFY mode is more bulk sensitive. The NaF signals in the F K-edge region are broadly located from 688 to 700 eV with two characteristic peaks in the pristine NaF–FeO nanocomposite.\textsuperscript{34-36} During charge, these signals from NaF decreased with a notable reduction in the peak at ~700 eV, and a new peak at 684 eV arose in both the TFY and TEY modes. The signal at 684.3 eV is attributed to F–Fe bonding, which originates from hybridization between Fe 3$d$ and F 2$p$ orbitals, whereas the peak denoted by * is generated by energy absorption from F in both the Fe–F and NaF.\textsuperscript{34,37-39} These results suggest that decomposition of NaF occurred during charge and that the liberated F was absorbed on the FeO to form Fe–F bonding, similar to the behavior observed for a LiF–FeO nanocomposite electrode in a Li cell.\textsuperscript{22} Clear evidence of the NaF decomposition during charge was also observed in the \textit{ex situ} XRD analysis, as presented in Figure 3-5.

The electrochemical performance of the NaF–FeO nanocomposite
electrode was further investigated with cycles in Figure 3-6 (a). Notably, the charge/discharge profiles of the nanocomposite electrode gradually changed as cycling proceeded. For the initial discharge, a sloping profile was observed (Figure 3-1 (b)), whereas the discharge profile after 50 cycles increasingly displayed a plateau-like region at approximately 2.5 V. Quantitative examination of the average discharge voltage in Figure 3-6 (b) confirms the increase from 2.0 V in the 1st cycle to 2.25 V in the 50th cycle. The change in the redox potential was also evident in the cyclic voltammetry (CV) measurements (Figure 3-6 (c)) and dQ/dV analysis (Figure 3-7) for different cycles, which show that the peak at ~2.5 V progressively emerged as cycling progressed. With the emergence of the plateau region, the discharge capacity also increased from 150 mAh/g in the 1st cycle to 165 mAh/g in the 50th cycle (Figure 3-6 (d)). The evolution of the plateau-like region implies that substantial amounts of Na ions are stored in the local environments with equivalent Na chemical potentials, which is hardly observed for the surface or capacitive electrochemical reactions. In addition, the increase in the discharge voltage indicates the formation of energetically more stable storage sites for Na ions from the NaF–FeO nanocomposite electrode as cycling progresses. Both features strongly suggest the gradual formation of the host
structure for Na ions evolving from the NaF–FeO nanocomposite.
Figure 3-1 (a) XRD pattern of as-prepared NaF–FeO nanocomposite powder. (b) First charge/discharge profiles of NaF–FeO nanocomposite electrode at current density of 50 mA/g at 60°C. (c) Fe K-edge XANES spectra and F K-edge XAS spectra in (d) bulk-sensitive TFY mode and (e) surface-sensitive TEY mode in the first cycle. The red and blue dotted lines in Figure 3-1 (d) and (e) represent the characteristic F K-edge spectrum of Fe–F bonding and NaF. The peak marked with * is the main peak generated by energy absorption from F in both the Fe–F and NaF.
Figure 3-2 TEM DP image of as-prepared NaF–FeO nanocomposite powder. The hollow ring patterns are all matched with either FeO (blue) or NaF (green).
Figure 3-3 SEM images of (a) as-prepared NaF, (b) as-prepared FeO, and (c) NaF–FeO nanocomposite after high-energy ball milling.
Figure 3-4 Williamson–Hall plots of as-prepared NaF–FeO nanocomposite powder. The plots were constructed using the XRD results presented in Figure 3-1 (a).
Figure 3-5 Ex situ XRD patterns at first cycle. The peaks corresponding to NaF disappeared during charge (red to green) and reappeared during discharge (green to purple).
Figure 3-6 (a) Charge/discharge profiles of NaF–FeO nanocomposite for the first 50 cycles. (b) Average discharge voltage as a function of cycle number. (c) CV profiles at various cycles at scan rate of 0.5 mV/s. (d) Cycle life and coulombic efficiency of NaF–FeO nanocomposite at current density of 50 mA/g.
Figure 3-7 dQ/dV results for various cycles. Similar to the CV results in Figure 3-6 (c), a decrease in the 2.3 V redox reaction and an increase in the 2.8 V redox reaction were observed as cycling progressed.
3.3.2 Formation of cubic iron-oxyfluoride during battery operation

From the initial stoichiometry of the NaF–FeO nanocomposite and the fact that NaF decomposes and Fe–F bonding is formed during charging, the host structure formed is likely to be iron oxyfluoride (FeOF). However, it is noted that the discharge voltage of the iron oxyfluoride observed here is substantially higher than that of the well-known rutile FeO\textsubscript{x}F\textsubscript{2−x} \ ((0<\text{x}\leq1). In our case, almost half of the capacity was delivered above 2.5 V after the formation of the host structure, whereas, according to previous studies, negligible capacity could be delivered above 2.5 V for rutile FeO\textsubscript{x}F\textsubscript{2−x} \ ((0<\text{x}\leq1) electrodes.\textsuperscript{40-42} This difference suggests that the host structure formed during electrochemical charge/discharge of NaF–FeO may differ from the rutile FeO\textsubscript{x}F\textsubscript{2−x} \ ((0<\text{x}\leq1) structure. To gain further insight into the host structure, \textit{ex situ} XRD analysis was performed, as shown in Figure 3-8 (a). In this figure, the number corresponds to the cycle number, and C and D indicate the charged and discharged state, respectively. In the as-prepared state, the characteristic (111), (200), and (220) peaks of FeO were clearly observed at 36.4°, 42.3°, and 61.4°. However, after 5 electrochemical cycles, the peaks
from FeO decreased, and new peaks began to emerge at 35.2°, 43.0°, and 62.5°; after 20 cycles, these peaks were dominant over the pristine FeO peaks (Figure 3-9). The new peaks generally match with those of Fe₂O₃ with cubic P4₁32 symmetry, where the anion is richer than the cation, implying that the iron oxyfluoride that is likely to be formed resembles the crystal structure of cubic Fe₂O₃. The one of the possible reason why iron oxyfluoride formed in NaF-FeO shows an XRD pattern similar to that of cubic Fe₂O₃ is that the atomic arrangement iron oxyfluoride formed in NaF-FeO is similar to that of cubic Fe₂O₃, and the atomic numbers of F and O are similar, which makes it difficult to distinguish them on XRD.

We attempted to directly visualize the crystalline structure of the new host using Cs-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), as shown in Figure 3-8 (b). The atomic arrangement different from that of FeO was observed throughout the particle and the fast Fourier transform (FFT) image of the sample in the inset of Figure 3-8 (b) shows characteristic spots at 0.217 nm (blue), 0.261 nm (green), and 0.439 nm (yellow), which do not match with those of the pristine rocksalt FeO structure. The detailed structure was further probed in the area enclosed by the green box using atomic-resolution HAADF-STEM, as shown
in Figure 3-8 (c). The results consistently indicate that the new host differs from the pristine FeO. The atomic arrangement shown in Figure 3-8 (c) matched well with the characteristic Fe arrangement in the (110) plane of cubic Fe$_2$O$_3$, which agrees with the *ex situ* XRD analysis in Figure 3-8 (a). The line intensity profile alternates between a relatively dark spot (red) and a bright spot (green), and the dissimilar intensities of the red and green spots suggest the different number of atoms present in each column. It is noteworthy that the number of atoms in the green column is almost twice that in the red column in a typical cubic Fe$_2$O$_3$ structure, unlike in the rocksalt structure.

The HAADF-STEM and *ex situ* XRD analyses suggest that the host structure has cubic symmetry with Fe atomic arrangement similar to that of cubic Fe$_2$O$_3$. Given that the initial Fe:O stoichiometry is 1:1 and that the oxidation state of Fe increases close to +3, we suspect that the host structure formed in the NaF–FeO nanocomposite electrode is FeOF with cubic symmetry. The formation of cubic FeOF was also recently reported in the electrochemical cycling of a LiF–FeO nanocomposite electrode operated in a Li cell, which served as a Li intercalation host. The DFT calculation performed in LiF-FeO work showed that the formation energy of cubic FeOF
is 26.6 meV/f.u. higher than that of rutile FeOF which showed feasibility of forming cubic FeOF as metastable phase. The formation of cubic FeOF in both LiF–FeO and NaF–FeO systems implies that the formation of cubic FeOF might be a universal phenomenon if appropriate F-donating sources, such as LiF and NaF, are supplied. Moreover, the fact that cubic FeOF is formed instead of the thermodynamically stable rutile FeOF suggests that the initial crystalline symmetry of the pristine FeO has guided the formation of the cubic FeOF. The electrochemical reaction occurs at a relatively low temperature compared with the synthesis temperature of iron oxyfluorides, which is typically above 300°C. The low temperature during the phase transformation may lead to the sluggish atomic diffusion in the NaF–FeO nanocomposite, trapping it in the metastable cubic FeOF phase and retaining the pristine symmetry of FeO. After the formation of the host structure, the lattice parameter was 8.377 Å in the charged state and 8.440 Å in the discharged state within the cubic symmetry (Figure 3-10). Thus, the volume change during charge and discharge was 2.3%, which is slightly larger than the volume change of 1.5% for cubic FeOF operated in a Li cell system. The larger volume change in the Na system than in the Li system may be attributed to the larger radius of Na ions than Li ions in the intercalation.
To attain a better understanding of the formation mechanism of the host structure, \textit{ex situ} F K-edge XAS analysis was performed as cycling progressed (Figure 3-11). Figure 3-11 (a) and (b) show that, in the charged state, the signals from NaF were barely detected, whereas signals from Fe–F bonding were observed both in the bulk (TFY mode) and at the surface (TEY mode) for all the cycles. These findings indicate that F binds with Fe in FeO not only at the surface but also within the bulk in the charged states regardless of the cycle number. The Fe K-edge EXAFS spectra in the charged state also indicate that the changes in the EXAFS for different cycles were relatively small, suggesting that the local environment around Fe in the charged state was similar for all the cycles after the first charge process (Figure 3-11 (c)). However, in the discharged state, comparatively different XAS signals were observed for the bulk (Figure 3-11 (d)) and surface (Figure 3-11 (e)). For the initial few discharged cycle states (1D and 2D), the Fe–F bonding signal was only detectable in the bulk (\textit{i.e.}, TFY mode), whereas the NaF signal was detected for both modes. The XAS results suggest that most of the Na ions could not intercalate into the FeOF structure and underwent a surface conversion reaction to form NaF at the surface, similar to the findings in the LiF–MnO nanocomposite after the first discharge,\textsuperscript{21} whereas a fraction of
FeOF could be retained in the bulk, allowing Na-ion intercalation. As cycling proceeded, the Fe–F signal began to emerge in the surface-sensitive TEY mode and the NaF signals were gradually reduced in both the TFY and TEY modes in the discharged state. These results imply that the phase transition propagates from the bulk to the surface and that the NaF formation becomes difficult even at the surface, most likely because of the completion of the formation of the host structure. This gradual change in the discharged state was also confirmed by the Fe K-edge EXAFS results, as shown in Figure 3-11 (f). In this figure, the peak at 1.45 Å, which represents the Fe bonding to the anion (O and F) in the discharged states, increases as cycling proceeds, which supports the idea that the primary electrochemical reaction shifts from a ‘surface conversion’ to a ‘host formation’ reaction as cycling progresses. After cycling, the signals for the charged and discharged samples in both the TEY and TFY modes were almost identical, indicating that the host structure formation was completed and it is well maintained during charge and discharge (Figure 3-12).
Figure 3-8 (a) *Ex situ* XRD patterns of NaF–FeO nanocomposite electrodes. The red dotted lines indicate the peak positions of cubic FeO, and the purple dotted lines indicate the peak positions of cubic Fe$_2$O$_3$. (b) HAADF-STEM image of 20$^{th}$ discharged electrode (inset: FFT image). (c) Fe atomic arrangement of the area enclosed by the green box in (b). The Fe atomic arrangement of the (110) plane of cubic Fe$_2$O$_3$ is also shown. HAADF line intensity profile measured in the area enclosed by the red box. The red arrows indicate relatively dark spots, and the green arrows indicate relatively bright spots.
Figure 3-9 The ex-situ XRD results of NaF-FeO nanocomposite electrodes at as prepared and twentieth discharged state.
Figure 3-10 *Ex situ* XRD results of NaF–FeO nanocomposite electrodes at 20\textsuperscript{th} charged (green) and discharged (purple) states.
Figure 3-11  *Ex situ* F K-edge XAS spectra measured in charged state in (a) TFY mode and (b) TEY mode. The number represents the cycle number, and C and D indicates the charged and discharged state, respectively. (c) The Fe K-edge EXAFS spectra measured in the charged state. F K-edge XAS results measured in the discharged state in (d) TFY mode and (e) TEY mode. (f) The Fe K-edge EXAFS spectra measured in the discharged state.
Figure 3-12 F K-edge XAS spectrum measured in TEY mode in (a) the 50th charged and (b) 50th discharged states. F K-edge XAS spectrum measured in TFY mode in (c) the 50th charged and (d) 50th discharged states.
3.3.3 Electrochemical response change after host formation and investigation on potassium system

The electrochemical responses before and after host formation were examined using CV, as shown in Figure 3-13 (a) and (b). The CV tests were performed in the 2\textsuperscript{nd} and 20\textsuperscript{th} cycles at scan rates between 0.075 and 1 mV/s to distinctively investigate the behaviors before and after the host formation. Before the host formation (Figure 3-13 (a)), both the anodic and cathodic peaks increased with increasing scan rate without a change in the peak position, which is a typical characteristic of a surface capacitive reaction.\textsuperscript{21} However, as shown in Figure 3-13 (b), in the 20\textsuperscript{th} cycles (i.e., after the host formation), both the anodic and cathodic peaks shifted with increasing scan rate, indicative of a diffusion-limited process, which is often observed in electrode reactions involving an intercalation process.\textsuperscript{46} The rate capability results also clearly support the idea that the electrochemical responses of the electrodes changed as cycling progressed, as shown in Figure 3-13 (c) and (d). The rate tests were performed by increasing the discharge current density from 50 to 2000 mA/g. Figure 3-13 (c) shows that the capacity decrease and voltage drop at high current were relatively small before the host formation,
which is attributed to the surface electrochemical reaction. Approximately 70% of the low-rate capacity (the capacity at 50 mA/g) was retained at the current density of 2000 mA/g. However, relatively smaller capacity retention could be achieved after the host formation, where 55% of the low-rate capacity (capacity at 50 mA/g) was maintained at the current density of 2000 mA/g. This result indicates the comparatively sluggish reaction of intercalation compared with the surface conversion reaction.

Inspired by the finding that the cubic FeOF host can also be formed from FeO serving as a Na-ion host in the Na electrochemical system, similar to the Li electrochemical system, we attempted to verify whether this phenomenon is universal for other alkali metal systems. A KF–FeO nanocomposite was synthesized using high-energy ball milling and tested in a K half-cell configuration. Figure 3-14 shows that the KF–FeO nanocomposite electrode could deliver a first discharge capacity of 100 mAh/g with reversible Fe oxidation and reduction during the cycle. However, notably, the charge/discharge profile did not change, and capacity increase was not observed as cycling progressed (Figure 3-15). This finding differed from the results for the LiF–FeO and NaF–FeO nanocomposites, where a profile change was observed during cycling, accompanying the host formation.
reaction. The CV curves of KF–FeO in the 2\textsuperscript{nd} and 20\textsuperscript{th} cycles were typical profiles of surface electrochemical reactions, where the peak position does not change with scan rate (Figure 3-16). Both the charge/discharge profiles and CV results indicate that the host formation for K ions was not induced in the KF–FeO nanocomposite electrode during cell operation. In Figure 3-17, it was observed that in the discharged state after 20 cycles, the majority of the peaks from the \textit{ex situ} XRD analysis of the KF–FeO nanocomposite still corresponded to FeO while traces of cubic FeOF could be detected. These findings along with the results above suggest that the complete phase transformation from cubic FeO to cubic FeOF might be aided by an intercalation/deintercalation reaction of an alkali ion such as Li or Na. It is speculated that in the KF–FeO case, larger K ions may not be suitable for intercalation into the cubic FeOF structure, which would prohibit further transformation from FeO to cubic FeOF.
Figure 3-13 CV profiles of NaF–FeO nanocomposite electrode at various scan rates after (a) 1 cycle and (b) 19 cycles. Discharge profiles at various discharge current densities after (c) 1 cycle and (d) 19 cycles.
Figure 3-14 (a) Charge/discharge profile of KF–FeO nanocomposite at the first cycle at a current density of 50 mA/g and 60°C. (b) *Ex situ* Fe K-edge XANES spectra of KF–FeO nanocomposite in the first cycle.
Figure 3.15 (a) Charge/discharge profiles of KF–FeO nanocomposite at the 1st to 20th cycles. The cut-off voltages for charge and discharge were 4.2 and 1.5 V vs. K+/K, respectively. The cell was tested using 1 M KPF₆ in EC/PC as the electrolyte at a current density of 50 mA/g at 60°C. (b) Discharge capacity of KF–FeO nanocomposite as a function of cycle number.
Figure 3-17 CV profiles of KF–FeO nanocomposite at various scan rates after (a) 1 cycle and (b) 19 cycles.
Figure 3-17 Ex situ XRD patterns of KF–FeO nanocomposite in pristine (brown), 1\textsuperscript{st} discharged (green), and 20\textsuperscript{th} discharged (purple) states.
3.4 Conclusion

In summary, we investigated the Na storage behavior in a nanocomposite electrode of NaF and FeO in a Na electrochemical cell. *Ex situ* XRD and HAADF-STEM analysis revealed the formation of cubic FeOF, different from rutile FeOF, during cell operation of the NaF–FeO nanocomposite, which is analogous to previously reported results for a Li electrochemical cell. As the host structure is formed for Na-ion storage, the average voltage increases from 2.0 to 2.25 V, and the discharge capacity increases from 150 to 165 mAh/g. F K-edge XAS analysis and results for the KF–FeO nanocomposite suggest that the phase transformation of FeO to cubic FeOF occurs gradually as cycling progresses and that full transformation is only possible when the appropriate alkali ion sources are utilized. The work presented here broadens our understanding of the electrochemistry of nanocomposite electrodes and helps to open up new possibilities for finding promising electrode materials by screening polymorphs of pre-existing cathode materials.
3.5 References


(2) Kim, S. W.; Seo, D. H.; Ma, X.; Ceder, G.; Kang, K. Electrode materials for rechargeable sodium-ion batteries: potential alternatives to current lithium-ion batteries. *Advanced Energy Materials* **2012**, 2 (7), 710.


**Nature materials** 2012, 11 (6), 512.

(14) Yabuuchi, N.; Yoshida, H.; Komaba, S. Crystal structures and electrode performance of alpha-NaFeO2 for rechargeable sodium batteries. *Electrochemistry* 2012, 80 (10), 716.

(15) Bianchini, M.; Fauth, F.; Brisset, N.; Weill, F.; Suard, E.; Masquelier, C.; Croguennec, L. Comprehensive investigation of the Na3V2 (PO4) 2F3–NaV2 (PO4) 2F3 system by operando high resolution synchrotron X-ray diffraction. *Chemistry of Materials* 2015, 27 (8), 3009.


(19) Recham, N.; Chotard, J.-N.; Dupont, L.; Delacourt, C.; Walker, W.; Armand, W.


(26) Zhang, L.; Chen, G.; Berg, E. J.; Tarascon, J. M. Triggering the In Situ
Electrochemical Formation of High Capacity Cathode Material from MnO.  


(34) Nakai, S.-i.; Ohashi, M.; Mitsuishi, T.; Maezawa, H.; Oizumi, H.; Fujikawa, 100
Gong, Z.; Zhu, Z.; Yang, W. Synthesis and Reaction Mechanism of Novel
Fluorinated Carbon Fiber as a High-Voltage Cathode Material for

Shirley, D. Near-edge sodium and fluorine K-shell photoabsorption of alkali

(37) Cosandey, F.; Al-Sharab, J. F.; Badway, F.; Amatucci, G. G.; Stadelmann, P.
EELS spectroscopy of iron fluorides and FeF x/C nanocomposite electrodes
used in Li-ion batteries. *Microscopy and Microanalysis* **2007**, *13*(2), 87.

Maezawa, H. Core-exciton absorption in the F K absorption spectra of 3d

(39) Saifullah, M.; Botton, G.; Boothroyd, C.; Humphreys, C. Electron energy
loss spectroscopy studies of the amorphous to crystalline transition in FeF 3.

(40) Zhou, Y. N.; Sina, M.; Pereira, N.; Yu, X.; Amatucci, G. G.; Yang, X. Q.;
Cosandey, F.; Nam, K. W. FeO0. 7F1. 3/C Nanocomposite as a High-
Capacity Cathode Material for Sodium-Ion Batteries. *Advanced Functional
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Chapter 4. Investigation on reversible potassium storage behavior in KF-MnO nanocomposites

4.1 Introduction

Rechargeable batteries are expanding the area of application from small electronic devices such as smartphones and laptops to electric vehicles and large-scale energy storage system. The cost of the batteries is of immense concern in large-scale applications. Recently, Na- and K-ion batteries (NIBs and KIBs) have attracted immense interest towards large-scale application due to their lower cost than Li counterpart\textsuperscript{1-4}. Between them, KIBs have a higher potential in terms of the energy density, because the standard reduction potential of K\textsuperscript{+}/K (-2.92 V) is close to that of Li\textsuperscript{+}/Li (-3.04V)\textsuperscript{5,6}. Furthermore, while natural graphite is inaccessible for NIBs\textsuperscript{7,8}, it is frequently utilized as an anode material for KIBs\textsuperscript{6,9,10}. Overall, KIBs are promising candidates for high-energy-density future energy storage system.

Previously reported KIB cathode materials mostly adopt K\textsuperscript{+} intercalation/deintercalation reaction into a host structure, similar to classical Li-ion battery (LIB) and NIB cathode materials. For example, in layered
cathode materials such as $K_{0.6}CoO_2^{11,12}$ and $K_{0.5}MnO_2^{13,14}$, about 0.4 K$^+$ ion per transition metal (TM) reversibly takes part in the electrochemical reaction. Polyanionic materials such as $K_3V_2(PO_4)_3^{15}$, KVPO$_4$, and KVPO$_4$F$^{16}$, have also been reported to include the reversible intercalation/deintercalation of 0.6 to 0.7 K$^+$ ion per TM. However, the heavy polyanion framework limits its specific capacity below 100 mAh/g. In this regard, it is necessary to introduce a new design concept in order to find a new lightweight high energy density cathode material for KIBs that accommodates a large number of K ions per TM and yields high capacity.

Recently, a new cathode design strategy has been proposed in LIBs and NIBs, which utilizes the nano-scale mixture of alkali fluorides (LiF and NaF) and transition metal compounds such as FeF$_2^{17,18}$, MnO$^{19-22}$, FeO$^{19,23-25}$, VPO$_4^{26}$ and FeSO$_4^{27}$. All the nanocomposite electrode materials share a common feature; a first activation charge process$^{17,18}$. During the first charge, liberated fluorine ion from the decomposed alkali fluoride adsorbs on transition metal compounds to make a new structure. The detailed transformation mechanism can be classified into two categories; one is a host-formation reaction and the other is surface-conversion reaction. In host-formation reaction, new host structure (FeF$_3$-like phase$^{17,18}$ and cubic
FeOF\textsuperscript{23,25}) is gradually formed during cycling, followed by intercalation/deintercalation of alkali ions into the host structure. In surface-conversion reaction, fluorine ion incorporation and transition metal oxidation/reduction is mostly limited to the surface of transition metal compounds (LiF-MnO\textsuperscript{19}), resulting in a better rate capability due to the absence of bulk diffusion of alkali ions into the host structure\textsuperscript{19,23,28}. Between two transformation processes, the surface-conversion could be advantageous for KIBs since the intercalation of large K-ion into the host structure often induces large volume change during charge/discharge and shows sloping (stair-like) discharge profile which result in poor cycle performance and low average voltage\textsuperscript{12-14,29}. In this regard, we designed KF-MnO nanocomposite as a new cathode for KIB which follows the surface-conversion reaction due to it showed promising cell performance (0.8 e\textsuperscript{-}/Mn) in Li-hybrid cell by F incorporation into MnO\textsuperscript{28}. The KF-MnO nanocomposite electrode shows first discharge capacity of 160 mAh/g (0.8 K\textsuperscript{+}/Mn) with the average voltage of 2.4 V \textit{vs.} K\textsuperscript{+}/K. The energy density of KF-MnO nanocomposite is 390 Wh/kg, which is one of the highest reported among KIB cathode materials\textsuperscript{3,16,29,30}.
4.2 Experimental

The KF-MnO nanocomposite was synthesized via a planetary ball miller (Fritsch, Pulverisette 5). The KF (Aldrich) powder was dried overnight in a 180°C vacuum oven and the MnO (Aldrich) was used as received. The stoichiometric amounts of KF and MnO powder were mixed with additional 20 wt% of natural graphite (Bay carbon) and placed in a 250 ml bottle. The total amount of powder was 2.4 g, and 25 silicon nitride balls with 10 mm diameter were used. The composite powder was milled at 600 rpm for 48 hours and the 5 minutes of rest was applied after every 25 minutes of cycling. All processes were performed under an Ar-filled glove-box to minimize air exposure.

The crystal structure of the KF-MnO nanocomposite was analyzed using an X-ray diffractometer (D2 Phasor). The KF-MnO nanocomposite powder was placed in a holder and data were collected in the 2θ range from 10° to 80°. The step size was 0.01°, the step time of 1.2 s and Cu Kα was used as the target material. The Rietveld refinement and Williamson-Hall plot of KF-MnO nanocomposite powder were analyzed with FullProf program.

The morphological change of KF-MnO before and after ball milling was
analyzed by field emission scanning electron microscope (MERLIN Compact, FE-SEM). The powder samples were loaded on carbon tape and 10 nm Pt coating was performed before SEM measurement. For transmission electron microscope (TEM) measurements, the KF-MnO cell was set to a specific state of charge. The cell was then disassembled and the electrode was washed with dimethyl carbonate (DMC) solvent. The powder was collected from the electrode and dispersed in dimethyl ether (DME) solvent. The solvent was dropped onto the 200 mesh lacey carbon grids. The grid was dried overnight in 70°C vacuum oven then the grid was mounted in a TEM holder and analyzed with TEM (JEOL, JEM-2100F).

The KF-MnO nanocomposite electrode was prepared by mixing KF-MnO nanocomposite powder (70 wt %), fluorine-free polyacrylonitrile (PAN, Aldrich) binder (10 wt %) and conducting carbon (Super P, 10 wt %) with N-methyl-1,2-pyrrolidone (NMP, Aldrich) solvents. The slurry was cast into Al foil with a doctor blade and dried overnight in a vacuum chamber. The disc-shaped electrodes were obtained using 3/8 inch punching tool (Hohsen, Osaka, Japan) and the average loading was 1 mg/cm².

The KF-MnO nanocomposite electrode was tested in a K half-cell using
CR2032 coin cell. The metallic K (potassium cube 99 %, Aldrich) was used as a counter electrode and a glass microfiber filter (grade GF/F, Whatman, US) was used as a separator. The 1 M KPF$_6$ in ethylene carbonate/propylene carbonate (EC/PC, 1:1, v/v) was used as the electrolyte. The electrochemical tests were carried out in a 25ºC oven at a constant current of 20 mAh/g using potentiogalvanostat (WBCS 3000, WonA Tech, Seoul Korea). The cut-off voltages of charge and discharge were 4.4 V and 1.5 V, respectively.

For ex-situ X-ray absorption spectroscopy (XAS) measurements, each electrode was set at a certain state of charge. The cell was then disassembled and washed with DMC solvent. For the transition metal K-edge analysis, the electrodes were sealed with Kapton film. For the transition metal L-edge analysis, the washed electrodes were directly used. The ex-situ Mn K-edge analysis was performed at the 7D XAFS, 8C nano-XAFS, and 10C wide XAFS beamlines at the Pohang Light Source-Ⅱ (PLS-Ⅱ) using Si(111) double-crystal monochromator. The beam intensity was reduced by 30 % to minimize high-order harmonics. The Mn K-edge spectra were measured in transmission mode and the reference Mn metal signal was measured at the same time to calibrate energy. The Mn L-edge spectrum was measured at the 10D XAS-KIST beamline at the Pohang Light Source-Ⅱ (PLS-Ⅱ). The
XAS spectrum was collected in total electron yield (TEY) mode. The storage ring was operated at 3.0 GeV with a ring current of 350 mA top-up mode.

First-principles calculations were conducted using Vienna Ab initio Simulation Package (VASP) to gain insight on the feasibility of MnOF formation at the surface of MnO.\textsuperscript{31} We used projector-augmented wave pseudopotentials as implemented in VASP, and treated exchange-correlation energies with Perdew-Burke-Ernzerhof parameterization of generalized gradient approximation (GGA).\textsuperscript{32,33} In order to remedy the well-known delocalization error of $d$ electrons in GGA, GGA+$U$ approach was adopted with $U$ value of 3.9 eV for Mn.\textsuperscript{34,35} A kinetic cutoff energy of 500 eV was used for plane-wave basis sets, and all calculations were allowed to relax until the remaining force in the unit cell converges within 0.01 eV Å\textsuperscript{-1}.

The formation energy of MnOF ($\Delta G_f$) was calculated by a simple equation,

$$\Delta G_f = G_{MnOF} - G_{MnO} - \mu_F$$

where $G_{MnOF}$ and $G_{MnO}$ is Gibbs free energy of MnOF and MnO, respectively, and $\mu_F$ is a chemical potential of F in KF. The structure of MnOF was defined by following several processes. First, as HAADF results
implied, we removed tetrahedral Mn from Mn$_3$O$_4$ spinel, so that the composition became Mn$_2$O$_4$. Then, maintaining the lattice framework, half of O was replaced with F, since the anion lattice seems to remain intact (Figure S12). A lot of configurations in MnOF are generated during the O/F replacing process, so we selected the most thermodynamically stable configuration and used its energy for the calculation. $\mu_F$ was determined by using the experimental Gibbs free energy of formation of KF.
4.3 Result and discussion

4.3.1 Synthesis and electrochemical properties of KF-MnO nanocomposite

The KF-MnO nanocomposite was synthesized by mixing KF and MnO using a high energy ball miller (Figure 4-1 (a)). After the ball milling, the initial morphology of KF and MnO completely disappeared and large particles of over 100 μm were broken into small pieces (Figure 4-2). The phase analysis on as-prepared KF-MnO nanocomposites was conducted using X-ray diffraction (XRD) together with the Rietveld refinement (Figure 4-1 (b)). The Rietveld refinement was carried out using a two-phase model with KF and MnO both having a cubic Fm$\bar{3}$m structure and displayed the low $\chi^2$ value of 1.89. The lattice parameters of KF and MnO after ball milling were 5.333 Å and 4.442 Å, respectively, which are almost identical to those before ball milling (5.348 Å for KF and 4.445 Å for MnO). This result shows that all the peaks present in the XRD pattern agree well with KF and MnO, meaning that there was no side reaction or phase transformation during ball milling. The retention of each phase after high energy ball milling was also confirmed by transmission electron microscopy (TEM) diffraction.
pattern (DP) analysis (Figure 4-3).

The particle sizes of KF and MnO after ball milling were analyzed with XRD and TEM. The average crystallite sizes of KF and MnO analyzed by Williamson-Hall plot analysis were 8.6 nm and 13.8 nm, respectively (Figure 4-4). In high-resolution TEM (HRTEM), MnO of about 10~15 nm was also observed and showed a characteristic fast Fourier Transform (FFT) pattern of MnO (Figure 4-5). The spatial distribution of KF and MnO particle was observed via TEM energy dispersive spectroscopy (EDS) (Figure 4-1 (c) and Figure 4-6). In EDS 2D mapping, MnO particles of about 10 nm size could be identified. Interestingly, the spatial distribution of KF is rather uniform unlike MnO. The different physical properties such as density between KF (2.48 g/cm³) and MnO (5.43 g/cm³) may help dense MnO retain its particle shapes during ball milling as opposed to less dense KF that breaks more and distributes uniformly all over the region. The Williamson-Hall plot analysis performed on each KF and MnO particle before and after ball milling shows that the strain (slope in the Williamson-Hall plot) increase is greater in KF than in MnO (Figure 4-7). These results are agreeable since the intensity of KF both in the XRD pattern (Figure 4-1 (b)) and TEM DP (Figure 4-3) is lower than that of MnO.
The KF-MnO nanocomposite electrode was tested in K half-cell with K metal as an anode and 1 M KPF₆ in ethylene carbonate/propylene carbonate (EC/PC, 1/1, v/v) as an electrolyte. The voltage range of 1.5-4.4 V vs. K⁺/K with the current density of 20 mA/g at 25°C was used. In order to trigger an activation of the nanocomposite electrode, we charged the cell first. Note that KF-MnO nanocomposite electrode shows negligible capacity (below 1 mAh/g) when it discharged without the first activation charge step as shown in Figure 4-8. This result once again confirms the importance of first charge step in nanocomposite electrodes and the KF-MnO nanocomposite electrodes are activated by the aid of liberated fluorine ion which is the decomposition product of KF similar to the LiF-MnO and NaF-MnO nanocomposite electrode. The first charge and discharge profile is shown in Figure 4-9 (a). The first charge capacity was above 200 mAh/g and the subsequent discharge delivered 160 mAh/g, which corresponds to 0.8 K⁺ per one TM. The average discharge voltage of KF-MnO nanocomposite was 2.4 V, therefore the energy density of KF-MnO nanocomposite was 390 Wh/kg and this value is one of the highest energy densities ever reported for KIB cathode materials as shown in Figure 4-9 (b). We believe that the high utilization of K⁺ ion per TM together with its simple composition and light
weight is beneficial for realizing high energy density.

The KF-MnO nanocomposite electrode also exhibits noticeable rate performance (Figure 4-9 (c)). The KF-MnO nanocomposite electrodes were first charged at constant current density of 20 mA/g and discharged at various current density from 20 mA/g to 5000 mA/g. As shown in Figure 4-9 (c), the discharge capacity of 160 mAh/g, 133 mAh/g, 125 mAh/g, 100 mAh/g and 35 mAh/g was delivered at the current density of 20 mA/g, 100 mA/g, 500 mA/g, 2000 mA/g and 5000 mA/g, respectively. The KF-MnO electrode delivered over 60 % of low rate capacity (discharge capacity at 20 mA/g) at very high current density of 2000 mA/g. This performance is exceptional among cathodes for K-ion batteries, which suffer from slow K ion diffusion kinetics due to its large ionic size. This good rate capability originates from characteristic of the surface-conversion reaction of our nanocomposite electrode. The detailed analysis on reaction mechanism will be discussed in a later part of this paper. The KF-MnO nanocomposite electrode also exhibited stable cycle performance despite low coulombic efficiency. The low coulombic efficiency could be attributed to the instability of electrolyte at high voltage operation$^{14,16}$. 

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Figure 4-1 (a) Design concept of KF-MnO nanocomposite electrode. (b) The XRD pattern of as-prepared KF-MnO nanocomposite power and the Rietveld refinement result. The red dots are observed intensity and the black line is calculated intensity. The blue line is the difference between observed and calculated intensity. The green line is Bragg position of MnO and the purple line is Bragg position of KF. (c) The TEM 2D EDS mapping result on as-prepared KF-MnO nanocomposite. The green one corresponding to Mn and the red one corresponding to K. The scale bar corresponding to 100 nm.
Figure 4-2 Scanning electron microscopy (SEM) images of (a) MnO and (b) KF before ball milling. (c) SEM image of KF-MnO nanocomposite after ball milling.
Figure 4-3 (a) TEM DP image of as-prepared KF-MnO nanocomposite and (b) TEM image where DP measured.
Figure 4-4 Williamson-Hall plot result on KF-MnO nanocomposite powder. The refinement was done with two-phase model (a mixture of KF and MnO). The red circles are corresponding to KF and blue circles are corresponding to MnO.
**Figure 4-5** HRTEM image of as-prepared KF-MnO nanocomposite. The 10 nm MnO particles are observed in TEM image (inset: FFT image was taken on the red box)
Figure 4-6 (a) TEM image of as-prepared KF-MnO nanocomposite and 2D EDS mapping results of (b) Mn, (c) O, (d) K and (e) F. (f) The combined 2D EDS mapping of Mn, O, K and F with Figure 4-6 (a).
Figure 4-7 Williamson-Hall analysis performed on (a) KF and (b) MnO before (○) and after (●) ball milling.
Figure 4-8 Discharge profile of KF-MnO nanocomposite without activation charge step. Without the first activation charge, the nanocomposite shows negligible capacity.
Figure 4-9 (a) The first charge/discharge profile of KF-MnO nanocomposite electrode. The cell was operated between 1.5-4.4 V vs. K⁺/K. (b) The capacity vs. voltage plot of previously reported K-ion battery cathode materials (blue circle) and KF-MnO nanocomposite (red star). (c) The discharge capacity at a different current density (20, 100, 500, 2000 and 5000 mA/g) after charging at a same current density (20 mA/g). (d) The cycle performance of KF-MnO nanocomposite at a current density of 20 mA/g. The red circle is charge capacity and the blue circle is discharge capacity.
4.3.2 Surface concentrated reaction in MnO

To find the origin of electrochemical activity, oxidation state change of Mn during the cycle was tracked using several experimental tools. First, global oxidation state change of Mn was observed with Mn K-edge X-ray absorption near edge structure (XANES) analysis (Figure 4-10 (a)). During charge, the Mn K-edge shifts to higher energy, which indicates the global oxidation of Mn$^{2+}$ to higher oxidation state. The reduction of Mn was observed during discharge and the Mn K-edge shifted back to the initial position, indicating reversible oxidation/reduction of Mn during charge/discharge cycles. The oxidation state of Mn was also observed with line electron energy loss spectroscopy (EELS) at Mn L-edge. The high angle annular dark field scanning TEM (HAADF STEM) image of the charged KF-MnO nanocomposite is shown in Figure 4-10 (b). The line EELS profile of the charged KF-MnO nanocomposite was measured along the yellow line shown in Figure 4-10 (b). The charged KF-MnO nanocomposite showed different EELS spectrums at the core and the surface (Figure 4-10 (c)). The Mn L-edge shifted to the higher energy and peak shape changed at the surface of MnO which indicates that the surface of MnO was selectively oxidized during charge (Figure 4-10 (c) (right)). The oxidation state of Mn at the core
and surface of MnO determined with Mn L\textsubscript{3} peak position are 2+ and 3.1+ respectively (Figure 4-10 (d))\textsuperscript{37}. The oxidized Mn reduced to Mn\textsuperscript{2+} during discharge and showed uniform oxidation state throughout the MnO (Figure 4-10 (e) and (f)).

The oxidation state change of Mn during charge and discharge was also analyzed with Mn L-edge X-ray absorption spectroscopy (XAS) (Figure 4-11). Unlike Mn K-edge XANES where K-edge continuously shifts with oxidation and reduction of Mn, the Mn\textsuperscript{2+}, Mn\textsuperscript{3+} and Mn\textsuperscript{4+} shows individual characteristic peaks in Mn L-edge XAS (Figure 4-11 (a))\textsuperscript{19,38}, which can provide insight on the oxidation state of Mn. The Figure 4-11 (b) is the Mn L-edge XAS signal collected at as-prepared, charged, and discharged state. It is clearly shown that the Mn\textsuperscript{4+} signal at 643.1 eV is increased during charge and decrease during discharge. Together with our EELS observation, this indicates that the surface oxidation on MnO particle occurs universally in KF-MnO nanocomposite electrode.
Figure 4-10 (a) The ex-situ Mn K-edge XANES spectrum on as-prepared (red), charged (blue), and discharged (green) electrodes. (b) The HAADF-STEM image of charged KF-MnO and (c) line EELS spectrum measured along the line shown in Figure 4-10 (b). (d) The oxidation state of Mn at the core and the surface of MnO estimated with L₃ peak position. (e) The HAADF-STEM image of discharged KF-MnO and (f) line EELS spectrum measured along the line shown in Figure 4-10 (e).
Figure 4-11 The Mn L-edge XAS spectrum of (a) Mn$^{2+}$O, Mn$^{3+}$O$_3$, and Mn$^{4+}$O$_2$ reference powder. (b) The Mn L-edge XAS spectrum of KF-MnO nanocomposite electrode material at as-prepared, charged, and discharged state.
4.3.3 Reaction mechanism revealed with TEM analysis

To investigate the structure evolution of MnO during charge and discharge, we performed HAADF STEM imaging (Figure 4-12 and 4-13) at the same particles at which EELS line-scan was measured (Figure 4-10 (b) and (e)). Figure 4-12 (a) shows the HAADF image and the corresponding FFT pattern of MnO after charge. The surface and core region showed different atomic arrangement as clearly seen in the HAADF image and FFT patterns. The atomic arrangement in the core region deduced from the FFT image matches with Fm\(\bar{3}m\) MnO in \([\bar{1}10]\) zone axis. However, in the FFT image taken in the surface region, the additional peaks other than Fm\(\bar{3}m\) MnO were present as marked with red circles in Figure 4-12 (a). The transformed region has a thickness of 3 nm and matches well with the oxidized region observed in EELS line-scan data (Figure 4-10 (c)). The transformed region disappeared in the discharged particle and only the spot corresponding to Fm\(\bar{3}m\) MnO in \([\bar{1}10]\) zone axis was observed in FFT image in the whole region (Figure 4-12 (b)). This result shows that the oxidation/reduction of Mn and phase transformation at the surface occur simultaneously during charge/discharge. If we assume spherical MnO is 14 nm in diameter as deduced from
Williamson-Hall plot in Figure 4-1 (b) and Figure 4-4, and 3 nm from the surface is uniformly oxidized, the volume fraction of oxidized region is 82% \((100 \times \left(\frac{7^3-4^3}{7^3}\right))\). This calculation and the fact that part of the Mn is oxidized from Mn\(^{2+}\) to Mn\(^{4+}\) show the feasibility of high capacity expressed in KF-MnO nanocomposite electrode materials (0.8 e\(^{-}\)/Mn) even though manganese oxidation/reduction takes place only at the surface.

The information on the structure formed on the MnO surface after charge could be deduced through FFT (Figure 4-12 (a)) and HAADF line intensity profile (Figure 4-12 (c)) analysis. In Figure 4-12 (a), the d-spacing of the newly appeared peaks in the FFT is twice that of (111) of MnO which implies that the structure formed on the MnO surface after charging is superstructure of MnO. Similar result was also obtained from the HAADF line intensity profile in Figure 4-12 (c). It shows that the atoms locate at uniform distance of 0.257 nm (d-spacing of (111) of MnO) in core region. On the other hand, on the surface, atoms locate at a distance of 0.506 nm which is about double the d-spacing of the core region. The phase transformation process that takes place in KF-MnO nanocomposite with the introduction of F into MnO can be hinted in the process of layered to spinel transition in layered materials such
as LiMnO$_2$. In delithiated Li$_{1-x}$MnO$_2$, Mn in transition metal layer usually migrate to the Li layer through the tetrahedral site$^{39,40}$. Both in the MnO and LiMnO$_2$, the oxygen stacking sequence is cubic close packed ABCABC and Mn is located at octahedral site surrounded by six oxygen (Figure 4-13). This indicates that the Mn in MnO surface could also migrate to form new structure as F is introduced and Mn is oxidized during charge which leave vacant site inside to show superstructure peaks in FFT.

To find the origin of superstructure peaks in FFT shown in Figure 4-12 (a), FFT patterns of various manganese oxide with ABCABC oxygen stacking sequence were simulated (Figure 4-14). Figure 4-14 indicates that the superstructure peak, similar to that observed in Figure 4-12 (a), appears when the structure is composed of alternating Mn rich layer and Mn poor layer where Mn is evenly distributed in Mn poor layer (Figure 4-14 (d)). This result is coincident with the HAADF line intensity profile shown in Figure 4-12 (c). In Figure 4-12 (c), both the HAADF profiles of line 1 and line 2 show alternating Mn rich and Mn poor column at the surface of MnO. In addition, in both lines, the HAADF intensity is detected at the Mn poor column which indicates that the structure formed at the surface of MnO resembles Mn$_3$O$_4$ spinel structure. Indeed the MnO and Mn$_3$O$_4$ show structural similarity
Considering the initial ratio between Mn and O is 1 to 1 (MnO) and the Mn oxidation occurs with fluorine incorporation, the stoichiometry of new phase is likely MnOF\textsubscript{x} where x is larger than 1 because fluorine incorporation occurs only at the surface of MnO to have its environment locally rich with fluorine. The reaction mechanism is summarized below and is schematically shown in Figure 4-16.

**Reaction 1 (charge):**

\[
\text{KF} + \text{MnO} \xrightarrow{\text{charge}} \frac{1}{\chi}\text{MnOF\textsubscript{\chi} (surface)} + (1 - \frac{1}{\chi})\text{MnO (core)} + K^+ + e^- 
\]

**Reaction 2 (discharge):**

\[
\frac{1}{\chi}\text{MnOF\textsubscript{\chi} (surface)} + (1 - \frac{1}{\chi})\text{MnO (core)} + K^+ + e^- \xrightarrow{\text{discharge}} \text{KF} + \text{MnO}
\]

To verify the feasibility of the MnOF\textsubscript{x} phase formation at the surface, we modeled the possible MnOF structure formed at the MnO surface and calculated the formation energy of MnOF by performing density functional theory calculations. Based on the FFT simulation results (Figure 4-14) and the fact that oxidized Mn (3+ and 4+) is unstable at tetrahedral site\textsuperscript{41,42}, MnOF structure used in calculation was generated by removing Mn atoms at tetrahedral sites from spinel Mn\textsubscript{3}O\textsubscript{4} (Figure 4-17) and replacing half of the O
with F to describe the F incorporation at the surface. The formation energy of MnOF from KF and MnO was calculated to be $+0.195 \text{ eV}$, which implies that the MnOF phase could be reversibly generated as metastable phase during electrochemical reaction.
Figure 4-12 (a) The HAADF image of charged KF-MnO nanocomposite on [110] zone axis. The right of HAADF image is FFT images at the surface and the core region. (b) The HAADF image of discharged KF-MnO nanocomposite and its corresponding FFT pattern. (c) Magnified image of a surface region in Figure 4 (a) and the corresponding HAADF line intensity profiles.
Figure 4-13 The oxygen (red sphere) stacking sequence of (a) MnO at (111) and (b) layered LiTMO₂ at (001).
**Figure 4-14** Crystal structures and simulated FFT patterns of various manganese oxide with ABCABC oxygen stacking sequence. All the FFT patterns were simulated with the structure composed of only Mn and O. (a) LiMnO$_2$ (R-3m) and (b) Li$_2$MnO$_3$ (C2/m) which composed of alternating Mn layer and Li layer do not show superstructure peaks. (c) LiMnO$_2$ (I4$_1$/amd) which composed of alternating Mn rich layer and Mn poor layer do not show superstructure peaks. (d) Mn$_3$O$_4$ (P1) which composed of alternating Mn rich layer and Mn poor layer, but richer than that of LiMnO$_2$, shows superstructure peaks.
Figure 4-15 (a) The \( <010> \) projection in spinel \( \text{Mn}_3\text{O}_4 \) and (b) \( <110> \) projection in cubic \( \text{MnO} \) which show similar atomic arrangement.
Figure 4-16 Proposed reaction mechanism of KF-MnO nanocomposite.
Figure 4-17 The atomic arrangement of spinel Mn$_3$O$_4$ in <010> projection. (a) The stoichiometric spinel structure which two-thirds of Mn is located in octahedron (purple) and one-third of Mn is located in a tetrahedron (blue). (b) The structure which Mn in the tetrahedron is absent in spinel Mn$_3$O$_4$ structure.
4.4 Conclusion

In summary, we report a novel high energy density cathode material for K-ion battery by mixing KF and MnO at nano-scale. The KF-MnO electrode shows the highest energy density ever reported among K-ion battery cathode materials. The KF-MnO electrode shows high discharge capacity even at high current density owing to the surface-conversion reaction. The surface structure of MnO changes to MnOF_x during charge while core region remains as cubic MnO. The unique electrode design concept presented in this study can further be exploited via various combinations of compounds with K and transition metal compounds and, hence, pave its way for discovering high energy density electrode materials.
4.5 References


(4) Kim, S. W.; Seo, D. H.; Ma, X.; Ceder, G.; Kang, K. Electrode materials for rechargeable sodium-ion batteries: potential alternatives to current lithium-ion batteries. *Advanced Energy Materials* 2012, 2 (7), 710.

(5) Marcus, Y. Thermodynamic functions of transfer of single ions from water to nonaqueous and mixed solvents: Part 3-Standard potentials of selected electrodes. *Pure and applied chemistry* 1985, 57 (8), 1129.


(7) Dugas, R.; Zhang, B.; Rozier, P.; Tarascon, J. Optimization of Na-ion battery systems based on polyanionic or layered positive electrodes and carbon


(15) Han, J.; Li, G.-N.; Liu, F.; Wang, M.; Zhang, Y.; Hu, L.; Dai, C.; Xu, M. Investigation of K\textsubscript{3}V\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}/C nanocomposites as high-potential cathode materials for potassium-ion batteries. *Chemical Communications* **2017**, *53* (11), 1805.


(21) Zhang, L.; Batuk, D.; Chen, G.; Tarascon, J.-M. Electrochemically activated MnO as a cathode material for sodium-ion batteries. *Electrochemistry* 143


Chapter 5. Chemical origins of electrochemical overpotential in surface-conversion nanocomposite cathodes


5.1 Introduction

New cathode materials have been incessantly sought to overcome the energy and power density limitations of current lithium-ion batteries. Over the past several decades, various attempts have been made to replace the current LiCoO$_2$ chemistry$^1$ through simple substitutions with other transition metals such as Ni and Mn or by applying Li in a layered structure$^2$-$^5$ to develop new intercalation host structures.$^6$-$^7$ Although searching for new intercalation hosts has been one of the most important pathways in this effort, the discovery of an intercalation host that provides a high redox potential and large number of lithium sites, and can thus compete with state-of-the-art cathode materials, is challenging. Recently, the discovery of a new branch of cathodes based on
non-intercalation materials, a nanoscale mixture of LiF and transition metal compounds, was reported. In this branch of materials, the high redox potential of transition metal electrochemistry can be exploited without concerns about lithium intercalation,\textsuperscript{8-11} providing new opportunities to explore the potential of various transition metal compounds that were previously considered poor lithium hosts because of their incapability to intercalate. Materials such as FeF\textsubscript{2},\textsuperscript{12,13} MnO\textsubscript{x} (1 < x < 2),\textsuperscript{8-11} FeO,\textsuperscript{14} CoO,\textsuperscript{8} and NiO,\textsuperscript{15,16} which have traditionally been disregarded as cathode materials because of the absence of intrinsic lithium and low lithiation potential, are now receiving renewed interest.

The nanocomposite electrode reactions are generally activated by the initial charge process, which involves a dissociation reaction of the alkali metal compound (\textit{i.e.}, LiF). During the charge process, liberated F\textsuperscript{−} ion from the LiF dissociation is absorbed on and/or diffuses into the transition metal compound and triggers oxidation of the transition metal, activating the nanocomposite electrode. The incorporation of F\textsuperscript{−} ions is accompanied by a phase transformation mainly near the surface during the charge process (equation (1)); the transformed phase reverses back to the nano-mixture of LiF and the pristine transition-metal compound during discharge through a
surface-conversion reaction (equation (2)).

Charge reaction: \( \text{LiF} + Mn^{2+}O \rightarrow Li^{+} + Mn^{3+}O \cdots F^- \quad -----(1) \)

Discharge reaction: \( Li^{+} + Mn^{3+}O \cdots F^- \rightarrow \text{LiF} + Mn^{2+}O \quad -----(2) \)

Because the charge process involves the dissociation of LiF, which is electrically insulating with a strong ionic bond between Li\(^{+}\) and F\(^{-}\), a high overpotential is often required. Moreover, it is most severely observed during the first charge process, depending on the morphology and distribution of nanosized LiF particles after the synthesis of the nano-mixture. Thus, a high charging cut-off voltage of up to 4.8 V is generally required to induce fully oxidized state of the transition metal compounds and achieve a large capacity.\(^8\)\(^-\)\(^10\),\(^14\) These electrochemical features of the charging reaction with high charging voltage significantly reduce the energy efficiency and lead to long-term instability of the electrolyte systems.

Herein, we investigate the details of the chemical origin of the overpotential in the charging process of a nanocomposite cathode by systematically changing the fluorine source from LiF to MF\(_x\) (MF\(_x\)=NaF, KF, RbF, CsF, MgF\(_2\), CaF\(_2\), and AlF\(_3\)) using MnO as a model transition-metal compound. The F 1s binding energy of the MF\(_x\) compounds is shown to be
strongly correlated with the overpotential of the charge profile and the activity of the nanocomposite. In addition, we demonstrate that achieving high stability of the solvated cation in the electrolyte can also play a role in lowering the overpotential. Our investigation of the electrochemical activity using various metal fluorides not only provides a fundamental understanding of the surface-conversion reaction but also opens up an opportunity to extend the surface-conversion electrochemistry of nanocomposite electrodes to other rechargeable battery systems such as Na-, K-, Mg-, Ca-, and Al-ion batteries.
5.2 Experimental

To synthesize the MF$_x$–MnO (M= Li, Na, K, Rb, Cs, Mg, Ca, Al; x = 1–3) nanocomposites, as-received LiF (Acros-Organics), NaF (Acros-Organics), KF (Sigma-Aldrich), RbF (Alfa Aesar), CsF (Alfa Aesar), MgF$_2$ (Sigma-Aldrich), CaF$_2$ (Alfa Aesar), AlF$_3$ (Alfa Aesar), and MnO (Sigma-Aldrich) were used without any further treatment. Each nanocomposite was prepared using planetary ball milling (Pulverisette 5; Fritsch). Stoichiometric amounts of MF$_x$ and MnO (F/Mn = 1/1, m/m) and an additional 20 wt% of graphite (Bay carbon Inc.) were inserted into the container, which was sealed in an argon-filled glove box to minimize air exposure. The powders in the containers were mixed at 400 rpm for 48 h with 5 min of rest every 30 min using 20 silicon nitride balls (10 mm) to obtain nanosized composites. LiCsF$_2$ was mechanochemically synthesized by planetary ball milling of LiF and CsF (1:1, m/m). The procedure to synthesize the LiCsF$_2$–MnO nanocomposite was the same as that described above (F/Mn = 1/1, m/m).

Electrodes were fabricated using the following procedure. First, 70 wt% MF$_x$–MnO nanocomposite, 20 wt% conducting carbon (Super P; Timcal, Bodio, Switzerland), and 10 wt% polyacrylonitrile (PAN) binder were mixed
in N-methyl-1,2-pyrrolidone (NMP, 99.5%; Sigma-Aldrich) to make a slurry. The slurry was cast onto Al foil using a doctor blade in an argon-filled glove box. The NMP was evaporated overnight at 60 °C in an argon-filled glove box. The dried electrode was punched using a 1/2-inch punching tool. Coin cells (CR2032; Hohsen) were assembled in an argon-filled glove box using the MFₓ–MnO nanocomposite electrode, lithium metal counter electrode, a separator washed with acetone (GF/F filter, Whatman), and an electrolyte of 1 M LiPF₆ in ethyl carbonate/dimethyl carbonate (EC/DMC, 1:1, v/v). To determine the effect of the fluorine source in the electrolyte, a fluorine-free electrolyte of 1 M LiClO₄ in EC/DMC (1:1, v/v) was also used. To obtain statistically valid results, the galvanostatic charge/discharge profiles were measured 5 times for each MFₓ–MnO nanocomposite electrode and salt in the voltage range of 1.5–4.4 V vs. Li⁺/Li with a current density of 50 mAg⁻¹ at 60 °C using a potentiogalvanostat (WBCS 3000; WonA Tech, Seoul, Korea). For the GITT measurements, each of the eight MFₓ–MnO electrodes was charged at a rate of C/5 (a rate of C/N indicates full charge to the theoretical capacity in N hours). The overall overpotential was obtained from the total difference between the relaxed potential and the potential before the current was cut-offed. The IR drop was obtained from the instantaneous change in
the potential right after the current was cut-offed. The theoretical capacity was calculated based on the amount of one F per MnO reacted. Each nanocomposite was charged at a rate of C/5 for 30 min and rested for 6 h.

The prepared MF\textsubscript{x}–MnO nanocomposites and LiCsF\textsubscript{2} powder were characterized using XRD (D2 PHASER, Bruker) using Cu K\textalpha radiation (\(\lambda = 1.54178\ \text{Å}\)) at a scanning speed of 1.0\(^{\circ}\) min\(^{-1}\) in the 2\(\theta\) range of 20\(^{\circ}\)–80\(^{\circ}\) with a step size of 0.01\(^{\circ}\). Williamson–Hall plot analysis was performed to determine the average crystalline sizes of the eight MF\textsubscript{x}–MnO nanocomposites. The Williamson–Hall plot was constructed using the FullProf_Suite program, and the equipment factors (U, V, and W) were calibrated using LaB\textsubscript{6} powder to obtain precise data.

The chemical states and compositions of the MF\textsubscript{x}–MnO and LiCsF\textsubscript{2}–MnO nanocomposites were identified using XPS (Thermo VG Scientific). The spectra were calibrated using the carbon 1s peak position.

Density functional theory calculations were performed to determine the enthalpy of interaction \(H_{\text{int}}\) between the cations (Li\(^{+}\), Na\(^{+}\), K\(^{+}\), and Ca\(^{2+}\)) and salt anions (PF\textsubscript{6}\(^{-}\), ClO\textsubscript{4}\(^{-}\)), where \(H_{\text{int}}\) was defined as follows:

\[
H_{\text{int}} = H_{M\text{X}(\text{solv})} - H_{M(\text{solv})} - H_{X(\text{solv})}.
\]
Here, $H_{MX}$, $H_M$, and $H_X$ are the enthalpies of the cation–anion complex, isolated cation, and isolated anion, respectively, with consideration of implicit solvation. For all the geometric optimizations, we used the Gaussian 09 code$^{17}$ with the B3LYP/6-311G (3df) level of exchange-correlation functionals and basis sets.$^{18,19}$ To describe the electrolyte environment, the polarizable continuum model$^{20}$ as implemented in the Gaussian 09 code was included in all the calculations using the dielectric constant for an EC/DMC solvent.
5.3 Result and discussion

5.3.1 Electrochemical activities of MF$_x$-MnO nanocomposites and effects of metal fluoride selection

MF$_x$–MnO (MF$_x$=LiF, NaF, KF, RbF, CsF, MgF$_2$, CaF$_2$, and AlF$_3$) nanocomposites were prepared by high-energy ball milling with a fixed F:Mn ratio of 1:1 in the starting materials. All the nanocomposites were successfully prepared, with the characteristic peaks of the metal fluorides and MnO maintained in the X-ray diffraction (XRD) patterns without unintended chemical reactions producing impurity phases, as shown in Figure 5-1 (a). However, slight differences in the peak intensity and broadness of the MnO peaks for each nanocomposite were observed, which implies that the particle size or crystallinity of MnO may differ in each nanocomposite after the mixing process. These differences are attributed to the different hardness and/or physical properties of the metal fluoride in the starting materials. The effects of the particle size and crystallinity on the XRD peak broadness and intensity were separately analyzed in a Williamson–Hall plot, as shown in Figure 5-2 (a). The results indicate that the particle size of MnO in the MF$_x$–MnO nanocomposites ranged from 10 nm (LiF–MnO and NaF–MnO) to 80
nm (AlF$_3$–MnO). To exclude complications arising from the size difference in MnO in the comparison of their electrochemical activity, we separated the nanocomposites into two groups depending on their average particle sizes, as shown in Figure 5-2 (b). Group I includes the systems containing LiF, NaF, KF, MgF$_2$, and CaF$_2$ with MnO particle sizes of approximately 20 nm, and group II consists of the other systems containing RbF, CsF, and AlF$_3$ with MnO particle sizes larger than 45 nm.

First, we verified the feasibility of using the various metal fluorides as F$^-$ donors in the nanocomposite electrodes by investigating the electrochemical responses in the voltage range of 1.5–4.4 V vs. Li$^+/Li$ in a lithium half-cell configuration at 60 °C. Note that all the nanocomposite electrodes were evaluated in lithium hybrid cells using Li salts in the electrolyte and Li metal as the counter electrode. The concentration of M$^{x+}$ ions in the electrolyte is calculated to be about 0.1 M, much less than that of Li (1 M). Thus, except for during the first charging process, identical electrochemical reactions were expected in the subsequent cycles. Figure 5-1 (b) and (c) present the subsequent discharge/charge profiles of the nanocomposite electrodes after the first charge process up to 4.4 V vs. Li$^+/Li$ in lithium half-cells (comparisons of the first charge profiles of each electrode...
will be provided and discussed later). The profiles are similar to each other and to the typical profile of a LiF–MnO nanocomposite electrode except for slight differences in the specific capacity. The similar electrochemical activity in lithium hybrid cells for all the samples indicates that the surface-conversion reactions were successfully induced for all the electrodes regardless of the source of F⁻ ions in the starting compounds. Interestingly, not only monovalent alkali-metal fluorides but also multivalent-ion fluorides such as MgF₂, CaF₂, and AlF₃ could act as F⁻ ion sources in the nanocomposite electrode, which implies the potential feasibility of using nanocomposite electrode in rechargeable Mg-, Ca-, or Al-ion batteries. It is also noteworthy that when charged up to 4.4 V, the KF, RbF, and CsF systems could activate a first discharge capacity corresponding to ~0.8 electrons per MnO with characteristic redox reactions at 3.75 and 2.5 V, which is significantly greater than the capacity activated by LiF. Although LiF–MnO usually delivers a capacity of more than 0.9 e⁻, corresponding to ~240 mAh/g with a cutoff of 4.8 V, the 4.4 V cut-off voltage condition could not fully activate the MnO redox reactions in LiF–MnO, with a loss of the redox activity at 3.75 V. Figure 5-3 shows that the reversible capacities deliverable in the MFₓ–MnO nanocomposites is linked to the initial charging capability with respect to the
F⁻ ion supply. The first charging capacities with a 4.4 V cutoff were substantially larger with the KF, RbF, and CsF-based nanocomposite electrodes than with the other electrodes, such as the LiF-based ones. In the cases of NaF and AlF₃ in PF₆⁻ electrolyte, the charge profiles show slightly different behavior with other metal fluorides, which is speculated to be due to partial PF₆⁻ decomposition occurring in NaF and AlF₃ cases (Figure 5-4). Figure 5-1 (d) shows the correlation between the first charge capacity and reversible discharge capacity of each nanocomposite in the given voltage range. The reversible capacity increased as the first charge capacity increased, indicating the distinct dissociation properties of each metal fluoride and their importance in achieving a high capacity in a given voltage range.
Figure 5-1 (a) X-ray diffraction patterns of MF$_x$–MnO (M=Li, Na, K, Rb, Cs, Mg, Ca, Al) nanocomposites. Electrochemical profiles of (b) MF$_x$–MnO (M=Li, Na, K, Rb, Cs) and (c) MF$_x$–MnO (M=Mg, Ca, Al) nanocomposites after the first charge to 4.4 V vs. Li$^+/\text{Li}$ in 1 M LiPF$_6$ in EC/DMC (1:1, v/v) electrolyte. (d) Relation between the number of electrons transferred in the first charge and the reversible discharge capacity of MF$_x$–MnO nanocomposites.
Figure 5-2 (a) Williamson–Hall plot of MnO XRD peaks measured from MF$_x$–MnO nanocomposites (M=Li, Na, K, Rb, Cs, Mg, Ca, and Al). (b) Calculated mean sizes of MnO in each nanocomposite. The nanocomposites were classified into two groups according to the MnO particle size to avoid the MnO size effect on the electrochemical activity of the nanocomposites.
Figure 5-3 (a) First charge profile of the eight MF$_x$–MnO nanocomposites in lithium hybrid cells. (b) Reversible capacities of the eight MF$_x$–MnO nanocomposite electrodes. The blue bars represent the capacities delivered above 2.7 V, and the green bars represent the capacities delivered below 2.7 V.
Figure 5-4 The first charge profile of (a) NaF-MnO and (b) AlF₃-MnO nanocomposites in 1 M LiPF₆ in EC/DMC and 1 M LiClO₄ in EC/DMC electrolytes.
5.3.2 Overpotential in the first charge process

We analyzed and compared the first charge profiles of eight MF$_x$–MnO nanocomposite cathodes, as shown in Figure 5-5 (a) and (b) for group I and II, respectively. Particular attention was placed on the overpotential observed at the beginning of the first charge profiles (~0.2 electron) to avoid the complexity from the potentially different morphology and distribution of each MF$_x$ in the composite. MF$_x$ particles with minimum hindrance for dissociation in the electrodes in terms of morphology and connectivity would participate in the charging process during the early stage; thus, we could focus more on the intrinsic dissociation properties of MF$_x$ and less on the extrinsic effects. The figures clearly show that the initial charging voltage, which liberates F$^-$ ions, depends on the species of MF$_x$ compounds. For group I, the first charging voltage required to form 0.1F$^-$–MnO increases in the order of M= K<Na<Li≈Ca<Mg in MF$_x$ (Figure 5-5 (a)), which leads to the reversible capacity with the largest value for M=K in the order of M= K>Na>Li≈Ca>Mg in MF$_x$ (inset of Figure 5-5 (a)). The same trend was also observed for the group II compounds. The first charge voltage of the group II compounds forming 0.1F$^-$–MnO increased in the order of M= Cs<Rb<Al in
MF_x (Figure 5-5 (b)), whereas the reversible capacity was inversely correlated to the first charge voltage (inset of Figure 5-5 (b)).

To discuss the observed differences in the charging voltages, it is necessary to be reminded of the atomistic picture of the first charging process in nanocomposite electrodes. Equation (3) below, a detailed description of equation (1), illustrates the proposed reaction paths of the electrode during the charge, which can be divided into two individual processes: (i) MF_x dissociation (liberation of fluorine ions) and (ii) oxidation of manganese ions in MnO. These two reactions are expected to be correlated and to occur almost simultaneously. Because the dissociation of MF_x itself is not an electrochemical redox reaction, we suppose that the electrochemical bias applied to the electrode would first oxidize the MnO, producing manganese ions with higher oxidation states, which would then trigger the dissociation of MF_x. In addition, the liberated F^- ions would be immediately adsorbed on or diffuse into MnO, aiding in or stabilizing the oxidation of manganese ions in the MnO. Thus, the oxidation of Mn in the electrochemical reaction includes the additional energy required to dissociate the fluorine ions from MF_x, which adds up in the charging voltage. In this respect, it is not trivial to precisely distinguish the kinetic overpotential and thermodynamic
overpotential that is related to the MF$_x$ dissociation energy in the charging voltages.

\[
\frac{1}{x}MF_x + Mn^{2+}O \leftrightarrow \frac{1}{x}M^{x+} \cdots F^{-} \cdots Mn^{3+}O \leftrightarrow \frac{1}{x}M^{x+} + F^{-} \cdots Mn^{3+}O
\]

------ (3)

We performed galvanostatic intermittent titration technique (GITT) measurements to better understand the origin of the overpotential in the charging profile, as shown in Figure 5-5 (c). For all the MF$_x$–MnO electrodes, the hybrid cells were rested for 6 h after every 0.1 e$^-$/MnO charging at a rate of C/5 (inset of Figure 5-5 (c) and Figure 5-6). Figure 5-5 (c) summarizes the measured overpotentials and relaxed voltages from the GITT measurements for the 0.1F–MnO composition for each electrode. The overpotential originating from the ohmic (IR) drop (red colored bars) appears to be negligible, whereas the total reaction overpotentials excluding the IR drop (green colored bars) varied from 200 mV for KF–MnO to 1200 mV for AlF$_3$–MnO. The relaxed voltage was nearly the same as 3.08 V with a small variation of ~90 mV regardless of the type of metal fluoride because in the hybrid cell configuration, the voltage measured is simply the potential difference between Li metal and the final state of 0.1F–MnO. Thus, with the
GIT in the hybrid cell, it was not possible to decouple the kinetic overpotential and the thermodynamic overpotential that is related with respective MF$_x$ dissociation. The fabrication of cells composed of the respective M metal anode and MF$_x$–MnO cathode would provide further insight; however, the technical limitations of selecting an appropriate electrolyte, binder, and current collector compatible with each M metal chemistry remain unresolved. Nevertheless, the GITT results in Figure 5-5 (c) indicate that the total reaction overpotential is the lowest for KF and the highest for AlF$_3$, which correlates with the discharge capacities presented in Figure 5-5 (d). Regarding the overpotential, one may wonder if the low electrical conductivity of metal fluorides might be a major origin, as most fluoride compounds are well known to be electrical insulators.\textsuperscript{21} However, the effect of the electrical conductivity of MF$_x$ on the overpotential should be insignificant, considering that the oxidation and reduction occur not on the metal fluoride but on the MnO. Nevertheless, the low electrical conductivity of metal fluorides in the electrode could have partly increased the overall cell resistivity. The marginal effect of the electrical conductivity of MF$_x$ on the overpotential is consistent with the observation that the IR drop is relatively negligible in all cases.
Figure 5-5 Initial profiles of the first charge for (a) MF$_x$–MnO nanocomposites (M=Li, Na, K, Mg, and Ca; Group I) and (b) MF$_x$–MnO nanocomposites (M=Rb, Cs, and Al; Group II). The figures in the insets show the correlation between the reversible capacity and first charge potential at 0.1F–MnO. The first charging voltage on the right y-axis is the voltage required to form 0.1F–MnO. The voltage increases in the order of M=K<Na<Li≈Ca<Mg in MF$_x$ for group I and M=K>Na>Li≈Ca>Mg in MF$_x$ for group II. (c) Overpotential and relaxed voltage at 0.1F–MnO. The figure in the inset shows the GITT measurements for KF–MnO. (d) Overpotential at 0.1F–MnO vs. electrochemical activities.
Figure 5-6 GITT curves of MF$_x$–MnO nanocomposites at 60 ºC.
5.3.3 Core-electron binding energy of F\(^{-}\) ion as an indicator of overpotential and activity

The metal–fluorine bond strengths, which determine the dissociation energy in MF\(_x\), can be estimated from the electrostatic attraction force between the M ion and F\(^{-}\) ion in the ionic bond. In general, the bond strength in an ionic compound can be quantitatively assessed using the lattice energy, which is defined as the energy needed to separate the cation and anion completely as gaseous states from a solid crystal. Although the precise value of the lattice energy is difficult to determine experimentally for each MF\(_x\) because of the infeasible formation of gaseous ion states, we believe that simple comparisons of F 1s binding energies can provide relative measures of the lattice energy.\(^{22-25}\) The strong bonding between M and F, i.e., the large lattice energy, generally attracts electrons of F toward M, which reduces the electron shielding in F and results in a large F 1s electron binding energy. However, if the attraction force becomes smaller (i.e., small lattice energy), the electron shielding effect will increase, followed by a decreased F 1s electron binding energy. Thus, the binding energy of the F 1s core electron can be used as an experimental indicator to compare the level of difficulty of
dissociating a fluorine ion from MF$_x$.

Considering the F 1s core-electron level as an experimental indicator, we probed the F 1s region for the eight MF$_x$–MnO nanocomposites using X-ray photoemission spectroscopy (XPS) and determined the binding energy of the core electron, as shown in Figure 5-7 (a) (left). The peak values of the core-electron binding energies are comparatively plotted in Figure 5-7 (a) (right). Notably, a strong correlation was observed between the F 1s binding energies and the measured overpotentials of the corresponding MF$_x$–MnO nanocomposites, as shown in Figure 5-7 (b) (top). Moreover, the discharge capacity correlates with the F 1s binding energies of each MF$_x$ in the electrode, as observed in Figure 5-7 (b) (bottom). Linear regression analyses for the group I and group II indicate that each group shows a strong positive correlation according to the Pearson correlation coefficient. The linear relationship between binding energy and discharge capacity is also observed in 1 M LiClO$_4$ in EC/DMC electrolyte (Figure 5-8) except for the CaF$_2$-MnO due to the high stability of Ca$^{2+}$ ion in LiClO$_4$ electrolyte, which is discussed in a later part. Also, the first charge voltage of LiF-MnO nanocomposite in ether-based (TEGDME and DEGDME) electrolytes is similar with that in carbonate electrolyte (Figure 5-9), which implies that the linear relationship
between binding energy and discharge capacity of nanocomposite electrodes is also expected in ether-based electrolytes. The overall results show that the F 1s binding energy is a plausible indicator of discharge capacity of nanocomposite electrodes.

As the F 1s binding energy is an indicator of the lattice energy of MF$_x$, this finding implies that the dissociation energetics of MF$_x$ play an important role in determining the overpotential. It is noteworthy that the overpotentials for group II are higher (250–300 mV) than those for the group I at similar binding energies. The high overpotentials of group II are thought to originate from the slow kinetics induced by the small surface area of MnO resulting from the large particle size, which provides limited active sites for fluorine incorporation. This speculation is also consistent with the kinetics of the surface conversion reaction being dependent on the surface area of the active materials.$^8$

Inspired by the observation that the dissociation energy alters the electrochemical activity of MF$_x$–MnO nanocomposites, we further examined this effect by artificially regulating the F 1s binding energy by making a solid solution from LiF and CsF. LiCsF$_2$ was synthesized by ball milling LiF and
CsF powders. Figure 5-7 (c) shows that a LiCsF$_2$ phase was successfully obtained, with the XRD peak positions matching the reference peak positions (PDF# 22-1076). The XPS measurements in Figure 5-7 (d) indicate that the F 1s binding energy of LiCsF$_2$ was 684.3 eV, which lies between those for LiF (685.1 eV) and CsF (683.1 eV). Figure 5-7 (e) compares the electrochemical profile of the 0.5LiCsF$_2$–MnO nanocomposite electrode with that of LiF–MnO for reference. The capacity that could be retrieved at a cutoff voltage of 4.4 V increased by approximately 0.3 e$^-$/MnO for the 0.5LiCsF$_2$–MnO electrode with the clear 3.75 V redox activity reemerging, and the voltage profile of the first charge was markedly lower for LiCsF$_2$ than for LiF (Figure 5-10). This finding confirms that the lower binding energy in LiCsF$_2$ leads to a lower charging overpotential of the electrode and a higher practical capacity than those for LiF. Moreover, it should be noted that the use of LiCsF$_2$ can simultaneously provide lithium ions upon dissociation; thus, LiCsF$_2$ can potentially be used in a lithium-ion full cell with a lithium-free anode and serve as a lithium reservoir similar to LiF. Thus, the modification of the lattice energy of LiF by appropriate substitution by considering the trade-off between the binding energy and lithium composition is a plausible pathway to enhance the performance of nanocomposite electrodes for Li-ion
batteries.
Figure 5-7 (a) Binding energy of metal fluoride (MF₉)–MnO nanocomposites (M=Li, Na, K, Rb, Cs, Mg, Ca, and Al) from X–ray photoemission spectroscopy. (b) Dependence of first charge overpotential (top) and reversible capacity (bottom) on binding energy of F 1s in MF₉–MnO nanocomposites. (c) XRD patterns of LiCsF₂ after mechanochemical synthesis. (d) Binding energies of LiF–MnO, CsF–MnO, and 0.5LiCsF₂–MnO nanocomposites from X–ray photoemission spectroscopy. (e) Enhanced electrochemical activities of 0.5LiCsF₂–MnO nanocomposite.
Figure 5-8 The relation between F 1s binding energy of MF$_x$ compounds and discharge capacity in 1 M LiClO$_4$ in EC/DMC electrolyte.
Figure 5-9 The first charge profile of LiF-MnO nanocomposite in carbonate electrolyte and ether-based (TEGDME and DEGDME) electrolytes.
Figure 5-10 First charge profile of LiF–MnO and 0.5LiCsF$_2$–MnO nanocomposite electrodes.
5.3.4 Effect of stability of cation in electrolyte on electrochemical activity

Although we observed a clear correlation between the lattice energy of $MF_x$ and the electrochemical activity of the nanocomposite electrodes, more careful consideration was needed to elucidate this relationship because the final states of $MF_x$ dissociation are not in the gaseous state, as defined with the lattice energy, but in solvated-ion states in the electrochemical system. In this respect, we further examined the origin of the overpotential with respect to the resulting cation stability in the electrolyte. According to equation (1), the stability of the cation in the electrolyte can affect the $MF_x$ dissociation and subsequent fluorine donation to MnO. Hence, we attempted to regulate the stability of the cation in the electrolyte by changing the anion species from $PF_6^-$ to $ClO_4^-$. Figure 5-11 (a) shows that the reversible capacities of the nanocomposite electrodes are comparable for the $PF_6^-$ and $ClO_4^-$-based electrolytes within the error range except for the Al and Ca cases. For the Al case, a larger capacity was obtained using the LiPF$_6$ salt because of the electrolyte decomposition with unstable voltage profile during the first charging, with the $PF_6^-$ decomposition serving as an additional $F^-$ ion source.
(Figure 5-12).\textsuperscript{10,11} However, in the CaF\textsubscript{2}–MnO system, the reversible capacity was remarkably higher when the ClO\textsubscript{4}\textsuperscript{−}-based electrolyte was used rather than the PF\textsubscript{6}\textsuperscript{−}-based electrolyte. Moreover, the results were consistent for multiple experiments, with the same tendency observed beyond the experimental error ranges. This finding was rather unexpected, considering that PF\textsubscript{6}\textsuperscript{−} decomposition can often provide additional F\textsuperscript{−} ions; thus, more activations of the nanocomposite electrodes were previously observed.\textsuperscript{8,10,11} Although there is no plausible scenario that explains the higher fluorine incorporation in the less fluorine-rich electrolyte system, this finding simply indicates that CaF\textsubscript{2} donates fluorine ions to MnO more easily in the ClO\textsubscript{4}\textsuperscript{−} salt-based electrolyte than in the PF\textsubscript{6}\textsuperscript{−} salt-based electrolyte.

To understand this abnormal behavior in CaF\textsubscript{2}–MnO, first-principles calculations were performed to determine the relative stability of the cation with counter anions, as shown in Figure 5-11 (b) and Figure 5-13. The calculation results indicated that the binding of Ca\textsuperscript{2+} with 2ClO\textsubscript{4}\textsuperscript{−} is particularly preferable compared with that with 2PF\textsubscript{6}\textsuperscript{−} (by approximately 100 meV) under the same dielectric condition of an EC/DMC solvent, which contrasts with the cases of Li\textsuperscript{+} and Na\textsuperscript{+}. This finding indicates that the solvation of Ca\textsuperscript{2+} in ClO\textsubscript{4}\textsuperscript{−} medium would be energetically more favorable.
than that in PF$_6^-$ medium, prompting the more efficient dissociation of CaF$_2$. The promotion of the dissociation consequently results in a more feasible charging of the electrode and thus a higher reversible capacity in the ClO$_4^-$-based electrolyte than in the PF$_6^-$-based electrolyte. In contrast to the CaF$_2$ case, the binding enthalpies of LiF and NaF were in a similar range for both the ClO$_4^-$ and PF$_6^-$ cases. To further support this finding, the initial first charge profiles of the Li, Na, and Ca systems are compared in Figure 5-11 (c)–(e). The initial charge voltage of CaF$_2$–MnO in the ClO$_4^-$ salt system was approximately 95 mV lower than that in the PF$_6^-$ salt, whereas almost identical charge profiles were observed for the LiF–MnO and NaF–MnO systems in the PF$_6^-$ and ClO$_4^-$ salt-based electrolytes, which is consistent with our hypothesis.
**Figure 5-11** (a) Reversible capacities of eight MFₙ–MnO nanocomposites tested in 1 M LiPF₆ in EC/DMC (red) and 1 M LiClO₄ in EC/DMC (green). Each data set was tested 5 times, and the error bar is shown in the graph. (b) Interaction enthalpies of Ca²⁺, Li⁺, and Na⁺ with ClO₄⁻ (green) and PF₆⁻ (red) from first-principles calculations. (c) Initial profile of the first charge of 0.5CaF₂–MnO, (d) LiF–MnO, and (e) NaF–MnO nanocomposites as electrolyte salts.
Figure 5-12 Initial charge profile of 1/3AlF₃–MnO nanocomposite electrode tested in 1 M LiPF₆ in EC/DMC.
Figure 5-13 The calculation models of the Li and Na solvated with (a) ClO$_4^-$ and (b) PF$_6^-$ and (d) Ca solvated with (c) ClO$_4^-$ and (d) PF$_6^-$.
5.3.5 Comprehensive picture of origins of overpotential in first-charge activation

All the results above assist in elucidating the origin of the overpotential ($\eta$) in the first charge activation and the electrochemical activity of the MF$_x$–MnO nanocomposites, as summarized in Figure 5-14. We propose the following factors as those inducing the overpotential in the charging process, considering that a simultaneous process occurs that includes cation dissolution in the electrolyte and fluorine-ion incorporation into MnO. First, the energy required to separate the fluorine ion from MF$_x$ is dependent on the lattice energy, which can be experimentally probed using the core-electron energy of F as a facile indicator ($\eta_1$ in Figure 5-14 (a)). Second, the stability of the cation in the electrolyte can affect the overpotential, as verified for Ca ($\eta_2$ in Figure 5-14 (a)). Finally, the kinetic overpotential can be altered by changing the particle size of MnO, as observed in the comparison of the general overpotential ($\eta_3$ in Figure 5-14 (a)) between group I and II. The overall activation energy barrier ($E_A$) of the charging process is speculated to be governed by the energetics of the formation of the intermediate state of $M^{x+} \cdots F \cdots MnO$, which involves combined contributions from $\eta_1$, $\eta_2$, and
\( \eta_3 \) and determines the overall overpotential. Therefore, decreasing the ionic bond strength between the cation and anion in lithium or alkali-metal compounds is one way to lower the overpotential of the charging process. Moreover, regulating the stability of the cation in the electrolyte would also contribute to reducing the overpotential.
Figure 5-14 (a) The dissociation of the fluorine ion is affected by the lattice energy in MF$_x$, which can be estimated using the F 1s binding energy. The stability of the cation in the electrolyte determines the kinetics of cation dissolution into the electrolyte during the first charge. The particle size of MnO is another origin of the overpotential because the kinetics of the surface-conversion reaction is affected by the active surface area for fluorine incorporation. (b) Schematic diagram of Gibbs free energy versus reaction coordination of the first charge, which shows the overpotential required for the uphill reaction. The red and blue lines represent two cases where the system energy can be changed by the stability of the cation in the electrolyte.
5.4 Conclusion

We investigated the chemical origins of the charge overpotential in nanocomposite electrodes for rechargeable batteries. To understand the underlying mechanisms, various metal fluorides were introduced as fluorine sources to electrochemically activate MnO as a model system (MF$_x$–MnO; M=Li, Na, K, Rb, Cs, Mg, Ca, and Al). The lattice energy of the MF$_x$ compounds was shown to have a strong correlation with the overpotential of the charge profile and the activity of the nanocomposites, thus serving as the most critical factor in determining the overpotential. In addition, the stability of the cation in the electrolyte was shown to play a role in regulating the overpotential. Accordingly, it was successfully demonstrated that changing the lattice energy by introducing LiCsF$_2$ or changing the electrolyte composition could lead to a reduced overpotential. Our work helps improve our fundamental understanding of the surface-conversion reaction of nanocomposite electrodes, elucidating the origins of the charging overpotentials. Moreover, we believe that the new findings on the feasibility of using various metal fluorides as fluorine donors in nanocomposite electrodes may open up an opportunity to extend the surface-conversion electrochemistry of nanocomposite electrodes to other rechargeable battery
systems such as Na-, K-, Mg-, Ca-, and Al-ion batteries.
5.5 References


(2) Ohzuku, T.; Makimura, Y. Layered lithium insertion material of LiNi1/2Mn1/2O2: A possible alternative to LiCoO2 for advanced lithium-ion batteries. *Chemistry Letters* **2001**, *30* (8), 744.


Chapter 6. Summary

In this thesis, new design principle for rechargeable battery cathode materials were proposed and investigated with nanocomposite between alkali metal compounds and transition metal compounds. The contents include (i) the discovery of new intercalation host for sodium ions through host formation reaction demonstrated with NaF-FeF$_2$ and NaF-FeO nanocomposite, (ii) the fundamental understanding on the chemical origin of the overpotential in nanocomposite electrodes with MF$_x$-MnO model system, (iii) the discovery of the high energy density potassium ion battery cathode materials with KF-MnO nanocomposite.

In the part 2 and part 3, the new way to design rechargeable battery cathode materials was introduced. The new host structures for sodium ion were formed during operation of NaF-FeF$_2$ (part 2) and NaF-FeO (part 3) nanocomposite in sodium battery system. The FeF$_3$-like phase and cubic-FeOF phase were formed in NaF-FeF$_2$ and NaF-FeO nanocomposite, respectively. The liberated F$^-$ ion produced during the charge process, decomposition product of NaF, incorporate into the FeF$_2$ or FeO to trigger host formation. In both materials, the Fe$^{2+}$/Fe$^{3+}$ redox couple was responsible for reversible charge/discharge reaction. The host formation behavior during first charge was investigated in part 2 with NaF-FeF$_2$ nanocomposite. In NaF-FeF$_2$ nanocomposite, the fraction of FeF$_3$-like phase increased as the charge cut-off voltage increased which indicate the voltage dependent activation (host formation).
Also, the TEM EELS results showed that the phase transformation of FeF$_2$ to FeF$_3$ firstly occurs on the surface region of FeF$_2$ and propagate into bulk of FeF$_2$ as charged amount increased. The host formation behavior during multiple cycle was investigated in part 3 with NaF-FeO nanocomposite. In the case of NaF-FeO, the discharge profile gradually changed as the cycle progressed which indicate the change in reaction mechanism during cycling. The F K-edge XAS at various cycle indicated that at the initial cycle, host is not perfectly formed and surface conversion reaction was dominant. On the other hand, at the later cycle, the host is perfectly formed and most of the electrochemical activity was origin from reversible insertion/deinsertion of sodium ion into/from the host structure.

In chapter 4, the high energy density potassium ion battery cathode material realized by surface conversion reaction of KF-MnO nanocomposite was introduced. The KF-MnO nanocomposite shows high reversible capacity (0.8 e~/Mn) in potassium system. The EELS line-scans and Mn L-edge XAS results indicate that the oxidation/reduction of Mn mainly occurred at the surface of MnO which implies that KF-MnO follows surface conversion reaction. The structure change at the surface of MnO during charge/discharge was observed with atomic resolution TEM. The TEM result show that the surface of MnO changed into spinel-like structure as the F ion introduced into MnO while bulk of MnO still remained as pristine state.

In the part 5, the origin of the overpotential usually observed in the charge
process of nanocomposite electrode was investigated. The MF$_x$ compounds were systematically changed from LiF to AlF$_3$ (MF$_x$=LiF, NaF, KF, RbF, CsF, MgF$_2$, CaF$_2$, and AlF$_3$) where transition metal compound was fixed with MnO. As the MF$_x$ varied the electrochemical activity also varied. The GITT results indicate that the overpotential was highly correlated with the activity of nanocomposite and overpotential was mainly originated from different thermodynamic properties of MF$_x$ compounds. Given the charge process in nanocomposite electrode is decomposition reaction of MF$_x$, we investigate the relation between lattice energy and overpotential. The lattice energy highly correlated with overpotential of nanocomposite electrode since the definition of lattice energy is dissociate ionic compounds into gaseous ionic species. The lattice energy was easily indicated as the F 1s binding energy of MF$_x$ compounds. Also, the way of tuning the activity of the nanocomposite electrode by tuning the binding energy was demonstrated by making solid-solution.

I hope that the work presented here will provide guidelines in designing nanocomposite electrodes and open new opportunities in search for high energy density cathode materials beyond conventional cathode materials through numerous combination between alkali metal compounds and transition metal compounds. I also believe that the findings in this works could expanded to other areas such as F$^-$ ion battery or surface engineering where F containing compounds commonly used.
초록

소듐이온전지 및 포타슘이온전지는 높은 가격의 리튬이온전지를 대체할 수 있는 유망한 후보군이다. 일반적으로, 전체 전지의 성능은 양극재의 성능에 좌우된다. 하지만, 현재까지 보고된 소듐이온전지 및 포타슘이온전지의 보고는 제한적이고 새로운 양극재의 개발이 절실하다.

본 학위논문에서는 알칼리금속 화합물과 전이금속 화합물의 나노복합체를 이용한 소듐이온전지 및 포타슘이온전지 양극소재의 새로운 디자인 전략을 제시한다. 또한, 나노복합체 전극의 과전압 영향을 미치는 요인에 대한 분석도 소개한다.

제 2장에서는 NaF-FeF₂ 나노복합체를 통한 새로운 소듐이온전지 양극소재 개발에 대해 소개한다. 보터리 구동 중 소듐이온을 저장할 수 있는 새로운 호스트구조가 형성되었다. X-선 회전 및 가속기를 이용한 철의 산화수 분석 결과, 충전중의 NaF 분해가 나노복합체 전극을 활성화 시키고 Fe²⁺/Fe³⁺ 반응으로 전체 전기화학적 활성이 나타남을 확인했다. 첫 충전과정동안 호스트구조가 생기는 양상을 투과전자현미경을 통해 분석한 결과, FeF₂의 표면부터 FeF₃로 변해가고
점점 FeF₂ 내부까지 FeF₃로 변함을 확인하였다.

제 3장에서는 NaF-FeO 나노복합체로부터 합성된 큐빅대칭을 지니는 새로운 소듐이온전지 양극소재에 대해 소개한다. 방사선 가속기를 사용한 분석을 통하여 충전/방전 중 철의 산화수가 Fe²⁺/Fe³⁺로 가역적으로 변함을 확인하였다. X-선 회절 및 투과전자현미경 분석을 통하여 NaF-FeO로부터 생성된 호스트구조는 큐빅구조를 가지는 폴루오린이 포함된 산화철임을 확인했다. 또한 사이클이 지나면서 전기화학적 프로파일이 변함을 확인했다. 다양한 사이클에서 F K-edge XANES 분석을 진행한 결과, 소듐이온의 호스트구조는 사이클이 지나면서 점진적으로 형성됨을 확인하였고 이는 전기화학적 프로파일이 사이클에 따라 변하는 사실과 일치한다.

제 4장에서는 고에너지밀도를 가지는 KF-MnO 포타슘이온전지 양극소재를 소개한다. KF-MnO 나노복합체는 ‘표면 전환’반응을 따르는 물질로, 폴루오린이 MnO 표면에서만 집중적으로 반응하고 Mn의 산화수도 표면에서 주로 변함을 주사전자현미경 분석과 방사선 가속기를 통한 Mn L-edge 분석을 통해 밝혀내었다. 표면반응으로 인해 Mn가 하나당 많은 K를 이용할 수 있었고 이로 인해 지금까지 보고된 포타슘이온전지 양극소재 중 가장 높은 에너지 밀도를 가지는
양극소재를 개발할 수 있었다.

제 5장에서는 MF_x-MnO (M=Li, Na, K, Rb, Cs, Mg, Ca, and Al) 모델시스템을 통하여 나노복합체 전극에서 흔히 관찰되는 충전과
과전압에 영향을 미치는 요인에 대한 탐구를 진행했다. MF_x의 종류가
바뀌면 나노복합체의 활성 또한 달라짐을 확인했다. 다양한 전기화학적
분석법 및 리트벨트를 통한 구조분석을 통한 분석을 진행한 결과,
격자에너지가 나노복합체의 활성과 큰 관계가 있음을 확인했다. 또한
격자에너지는 F 1s 결합에너지로 표현될 수 있음을 확인했다.
결과적으로 F 1s 결합에너지를 알면 나노복합체의 활성을 예측할 수
있으며, LiF와 CsF의 고용체를 통한 결합에너지 조정으로 인해
나노복합체의 전기화학적 활성도 조정 할 수 있었다.

주요어 : 에너지 저장장치, 나노복합체, 소듐, 포타슘, 베타리
학번 : 2013-20636
Research Interests

Materials science for high-energy rechargeable batteries

New reaction chemistries in rechargeable batteries with nanocomposite materials

✓ Finding new advanced electrode materials for rechargeable batteries

✓ New host structure for sodium ion (NaF-FeF₂ and NaF-FeO nanocomposite)

✓ High rate electrode with ‘surface conversion’ reaction (KF-MnO nanocomposite)

Mechanism studies on battery electrochemistry

✓ Understanding the mechanism of electrochemical synthesis

✓ Factors affecting electrochemical activity in nanocomposite electrode materials

✓ Understanding the fluorine behavior during electrochemical reactions
Tracking transition metal valence state and local environment change during electrochemical reactions using X-ray absorption spectroscopy (XANES/EXAFS) analysis

Publications

† equal contribution
* corresponding authors


4. Sung-Kyun Jung†, **Insang Hwang†**, Il Rok Choi†, Gabin Yoon, 203

5. Sung-Kyun Jung†, Insang Hwang†, Sung Joo Kim†, Kyu-Young Park†, Donghee Chang, Kisuk Kang*, “Nanophenomena in Li-ion battery (Review article)”, Chemical Reviews, in preparation

6. Insang Hwang, Sung Joo Kim, Sung-Kyun Jung, Jaehoon Heo, “Realization of additional capacity from excess F-mediated full Fe⁰+/Fe⁴⁺ redox process”, in preparation


9. Kyu-Young Park, Inchul Park, Hyungsub Kim, Gabin Yoon,


Awards

1. **ICAE student award** (oral), 2017 International Conference on Advanced Electromaterials, “A new type of Na ion battery cathode material: NaF-FeF₂ nanocomposite”

2. **Best poster award** (poster), The 16th Korean-Japan Student Symposium, “A new type of cathode materials for sodium ion batteries: LiF-FeF₂ nanocomposite materials”

Patent

1. “All solid ion battery”, Kisuk Kang, Insang Hwang, Yeonsik Jung,
Jungkeun Yoo, Jaebeom Jeon, Kiung Jeon, Republic of Korea (2016), Registration number: 10-1688-367

2. “All solid ion battery”, Kisuk Kang, Insang Hwang, Yeonsik Jung, Jungkeun Yoo, Jaebeom Jeon, Kiung Jeon, United States of America (2019), Application number: 15/540,351


**Conference presentations**

**International**

1. “NaF-FeO nanocomposite for Na-ion battery cathode material”, 22nd International Conference on Solid State Ionics, PyeongChang, Korea, June 2019 *(Oral)*

2. “NaF-FeF\textsubscript{2} nanocomposite material for new type of sodium ion battery cathode material”, International Battery Association 2018, Jeju, Korea, March 2018 *(Poster)*

3. “A new type of Na ion battery cathode material: NaF-FeF\textsubscript{2}”
nanocomposite”, International Conference on Advanced Electromaterials 2017, Jeju, Korea, November 2017 (Oral)

4. “A new type of Na-ion battery cathode material: NaF-FeF$_2$ nanocomposite”, The 57th Battery Symposium in Japan, Chiba, Japan, November 2016 (Oral)

5. “NaF-FeF$_2$ nanocomposite: a new type of Na-ion battery cathode material”, International Conference on Electronic Materials and Nanotechnology for Green Environment, Jeju, Korea, November 2016 (Poster)

6. “A new type of cathode materials for sodium ion batteries: LiF-FeF$_2$ nanocomposite materials”, The 16th Korean-Japan Student Symposium, Sendai, Japan, October 2015 (Poster)

Domestic

1. “NaF-FeO 나노복합체의 전기화학적 구동을 통한 Na이온 호스트 구조 형성에 관한 연구”, 2019 Spring Meeting of the Korean Battery Society, Daejeon, Korea, May 2019 (Poster)

2. “In-operando formation of new iron-oxyfluoride host structure for
Na-ion storage: NaF-FeO nanocomposite”, 2019 Spring Meeting of the Korean Electrochemical Society, Jeju, Korea, April 2019 (Oral)

3. “A study on NaF-FeF₂ nanocomposite as a new type of sodium secondary battery cathode material”, 2017 Fall Meeting of the Korean Electrochemical Society, Daejeon, Korea, October 2017 (Poster)

4. “NaF-FeF₂ nanocomposite as a new type of Na-ion battery cathode material”, 2017 Fall Conference of the Korean Institute of Metals and Materials, Daegu, Korea, October 2017 (Poster)

5. “NaF-FeF₂ nanocomposite electrodes for Na-ion battery cathode material”, 2016 Fall Meeting of the Korean Ceramic Society, Seoul, Korea, November 2016, (Oral)