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First-principles study of the change in the electronic properties of NiF₂ by the introduction of oxygen

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HIGHLIGHTS
• Effect of O-doping on electronic state of NiF₂ is studied with first-principle method.
• Introduction of O increases covalent nature of NiF₂.
• New energy levels are formed in band gap region by interaction of Ni3d–O2p orbitals.
• The results support O-doping increases electrical conductivity of metal fluorides.

Abstract
NiF₂ is investigated as a conversion-reaction-based positive electrode material in applications to lithium ion batteries. Despite high discharge capacity, slow reaction kinetics due to poor electrical conductivity is a general drawback of the conversion reaction. The electronic features of NiF₂ were investigated using the DV-Xα molecular orbital method in this study. The effects of oxygen doping on the bonding characteristics and electrical conductivity were examined in particular. An analysis of the bond overlap population and spatial distribution of electrons showed that the Ni–O bond has a more covalent nature than the Ni–F bond, and doping of oxygen increases the covalent characteristics of Ni–F bond. New energy levels were generated in the band gap region through an interaction between the Ni3d and O2p orbitals with the introduction of oxygen. The electrical conductivity of NiF₂ is expected to be increased by the substitution of fluorine by oxygen owing to the higher covalent character and the formation of new energy levels.

1. Introduction
Lithium ion batteries (LIBs) are currently the main power source of mobile electronic devices owing to their high density of energy storage [1,2]. Rapid progress of mobile devices and the expansion of applications of LIBs to electric vehicles or power storage systems require a persistent increase in the energy storage capacity of LIBs. Thus, the development of high capacity active materials is essential, but this appears to be difficult because the limit for increasing the capacity of conventional materials, whose electrochemical performance is based on intercalation/deintercalation of Li ions, has being reached. The number of available electrons is determined by the number of Li sites in the crystal for the intercalation-based materials. For example, LiCoO₂, which is the positive electrode material used most widely, can accommodate only one Li ion, therefore, only one electron per a formula unit is possible by making use of only two oxidation states of Co³⁺ and Co⁴⁺.

New active materials of a conversion reaction have attracted considerable attention as an alternative [3–5]. NiF₂ is one of the candidate materials for positive electrode owing to its relatively high operating voltage [5–7]. Nevertheless, the slow kinetics of the conversion reaction causes a decrease in the discharge voltage and a difficulty of achieving high rate or room temperature operation. The reaction rate is closely related to the electrical conductivity and ionic diffusivity [6,8–10]. Therefore, improving them would be a key factor for the application of these materials to LIBs. Compositing metal fluoride with carbon, CNT, and graphene has been reported to be effective increasing the electrical conductivity and achieving stable electrochemical operation [6,7,11–13].

The partial oxidation of fluoride materials has been evaluated as a way of improving the intrinsic conductivity [10,14–16]. Metal oxyfluorides, such as FeOF or Fe₂OF₄, or partially oxidized NiF₂ can show better electrochemical properties than pure fluorides. Researchers have attributed this improvement to the increased conductivity by the introduction of covalent M–O bonds into highly insulating M–F ionic bonds [6,10,14,15], but this interpretation is not based on precise analysis or supporting information. Therefore, in this study, the electronic states of NiF₂ were...
examine by a first principle method, focusing on the change in the electronic states and the bonding nature with the partial substitution of F by O in particular. The effect of the introduction of O on the electrical conductivity of NiF₂ is discussed based on the calculation results.

2. Methods and theory

The electronic properties, such as the density of states (DOSs), bond overlap population (BOP), and spatial charge distribution were analyzed using a first-principles discrete variational Xα (DV-Xα) molecular orbital method [17]. This method solves numerically the Schrödinger equation for a many-body system based on a linear combination of atomic orbitals (LCAOs) approximation and the Xα potential using the Hartree–Fock–Slater method [18,19]. The molecular orbitals based on the LCAO approximation and the exchange interaction term of the Xα potential are expressed as follows:

\[ \varphi_j(r) = \sum_i c_i \chi_i(r), \quad V_{xc}(r) = -3\alpha \left( \frac{3\rho(r)}{4\pi} \right)^2 \]

where \( \varphi_j \) is the molecular orbital wave function, \( c_i \) is a weighting coefficient, \( \chi_i \) is the atomic orbital wave function, and \( \rho \) is the electron density. The \( \alpha \) parameter varies in value depending on the atomic species and approaches 2/3 with increasing atomic number [20].

The DV-Xα molecular orbital method requires no restrictions imposed in the form of the basis functions because the calculation is conducted numerically. Consequently, atomic orbital can be used as a basis function, i.e., there is no need to consider whether the basis function is integrable or not. In addition, this method does not use the pseudopotential approximation. All the atomic orbitals of the model cluster are included in the calculation, which can provide reliable information on the molecular orbitals and electron distributions [21–24].

[Ni₁₁F₂₂] and [Ni₁₁F₂₁O₁] cluster models (Fig. 1) were prepared for the calculation of this study. A Ni atom was centered in both clusters, and one of the six neighboring F atoms was substituted by O in the [Ni₁₁F₂₁O₁] cluster. Atoms beyond a certain distance from the central Ni atom were removed, and the clusters were modified so that the surface would be terminated with F atoms. Although the Ni/F ratio of the clusters was deviated from the stoichiometric value for the preparation method, this does not cause any significant error because an analysis of the electronic properties was performed only for atoms of the inner position in the cluster. Rather, this technique appears to be very useful in that the surface F atoms provide a bulk-like environment for the target atoms inside by ensuring they contain no broken bonds [21]. Any changes in the lattice structure with substitution of O for F is not reflected, which might be justified considering that the introduction of O was reported to make only a very slight change to the lattice parameter for NiF₂ because of the similar ionic radii of O and F [14]. In addition, a distortion of the structure is expected to be negligible because only one F atom out of 22 was substituted.

Fig. 1 shows a diagram of the clusters, and Table 1 provides the structural information, in which opposite magnetic moments were applied to Ni1, Ni2, and Ni3, considering that NiF₂ is an antiferromagnetic material under the Néel temperature [6]. The electronic states and bonding characteristics were calculated using the SCAT program of the DV-Xα software package [17]. The distribution of charge was calculated by Mulliken population analysis. All the DOS diagrams were constructed assuming that each energy level shows a Gaussian distribution of which the full width half maximum (FWHM) is 0.1 eV. The clusters were located in a uniform Madelung potential field to reflect the electrostatic interaction with the surrounding atoms because the DV-Xα method does not use periodic boundary conditions. The Madelung potential field was composed of positioning point charges at the atomic sites and translating nine unit cells for each direction.

3. Results and discussion

Fig. 2 shows the DOS diagrams calculated using the DV-Xα molecular orbital method. The energy level of the highest occupied molecular orbital (HOMO) was positioned at 0 eV in the figures. Fig 2(a) shows the total DOS of NiF₂ calculated by the DV-Xα molecular orbital method. The HOMO and LUMO (lowest unoccupied molecular orbital) levels were almost connected in the diagram, which indicates the DV-Xα molecular orbital method underestimated the band gap of NiF₂. For a comparison, the DOS diagrams obtained from a density functional theory (DFT) calculation are presented in Fig. 2(b) and (c). The generalized gradient approximation (GGA) provided similar result to the DV-Xα method, whereas GGA + U method \((U = 5.0\) eV) broadened the gap between the HOMO and the LUMO levels by taking into account the strong correlated character of the Ni d-electrons.

The DOS diagrams of NiF₂ calculated with introduction of O (O-doped NiF₂) by the DV-Xα, GGA, and GGA + U methods are presented in Fig. 2(d)–(f), respectively. Comparing with the DOS of pure NiF₂ presented in Fig. 2(a)–(c), it can be noticed that new levels are formed near the 0 eV region. Fig. 2(f) shows that the new energy level is located in the band gap. Although the DV-Xα and simple GGA method could not show the position of new levels clearly due to the underestimated band gap, it seems that they still reflect the overall characteristics, i.e., formation of new energy levels near the band gap region, thus the DV-Xα molecular orbital method appeared to be acceptable for providing a reasonable discussion on the change in the electronic states with the introduction of O. Thus, the DV-Xα molecular orbital method was used as the main calculation tool in this study, considering that the method

<table>
<thead>
<tr>
<th>Distance from the center (Å)</th>
<th>Number of atoms</th>
<th>Spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (centered atom) 0</td>
<td>1</td>
<td>High (up)</td>
</tr>
<tr>
<td>F (O)</td>
<td>1.986–2.018</td>
<td>6</td>
</tr>
<tr>
<td>Ni</td>
<td>3.084</td>
<td>2</td>
</tr>
<tr>
<td>F</td>
<td>3.537</td>
<td>4</td>
</tr>
<tr>
<td>Ni</td>
<td>3.632</td>
<td>8</td>
</tr>
<tr>
<td>F</td>
<td>3.668–4.140</td>
<td>12</td>
</tr>
</tbody>
</table>
is especially useful in analysis of population and nature of each molecular orbital.

One of the spin directions was fully filled with electrons (i.e. the levels are all below the HOMO level which is positioned at 0 eV in the figures) and the other was only partially filled for pure NiF$_2$, indicating that Ni is in a high spin state. The magnetic moment of Ni calculated by the DV-X$^a$ method was 1.7 $\mu$B. The new energy levels appeared to be generated by interaction between Ni3d and O2p orbitals from the examination of the contribution of each atomic orbital to the new levels.

The change in the bonding nature of NiF$_2$ was investigated by examining the effective charge of the atoms and the BOP of the bonds among them. Table 2 lists the effective charge of each atom obtained from a calculation of the molecular orbitals. The introduction of O decreased the effective charge of Ni and F. This suggests that the substitution of O for F alleviates the ionic characteristics of NiF$_2$. Fig. 3 presents the overlap population (OP) diagrams. The left and the right parts of each diagram in Fig. 3 denotes the overlap population of antibonding and bonding orbitals, respectively. The integrated value of the overlap population below the HOMO level, i.e. the BOP is a measure of the covalent nature of the bonds [18].

<table>
<thead>
<tr>
<th></th>
<th>NiF$_2$</th>
<th>O-doped NiF$_2$</th>
<th>Change of charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>+1.140</td>
<td>+1.106</td>
<td>3.0%</td>
</tr>
<tr>
<td>F</td>
<td>−0.595</td>
<td>−0.586</td>
<td>1.5%</td>
</tr>
<tr>
<td>O</td>
<td>−0.797</td>
<td>−</td>
<td>−</td>
</tr>
</tbody>
</table>

Fig. 2. Density of states (DOSs) diagrams calculated: (a)–(c) total DOS of pure NiF$_2$ obtained by the DV-X$^a$ molecular orbital method, DFT calculation based on GGA, and on GGA + U, (d)–(f) total DOS of oxygen-doped NiF$_2$ by the DV-X$^a$, GGA, and GGA + U method, respectively.

Fig. 3. Overlap population (OP) diagrams calculated using the DV-X$^a$ molecular orbital method: (a)–(c) OP diagrams of Ni–F, Ni–Ni, and F–F of pure NiF$_2$, (d)–(f) OP diagrams of Ni–F, Ni–O, and F–O of oxygen-doped NiF$_2$. 
Table 3
Bond overlap population of bonds calculated by DV-Xα molecular orbital method.

<table>
<thead>
<tr>
<th>Bond</th>
<th>NiF₂</th>
<th>O-doped NiF₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Antibonding</td>
<td>Bonding</td>
</tr>
<tr>
<td>Ni–F</td>
<td>0.078</td>
<td>0.196</td>
</tr>
<tr>
<td>Ni–O</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ni–Ni</td>
<td>0.009</td>
<td>0.011</td>
</tr>
<tr>
<td>F–F</td>
<td>0.004</td>
<td>0.004</td>
</tr>
<tr>
<td>F–O</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond</th>
<th>Ni–Ni</th>
<th>F–F</th>
<th>F–O</th>
<th>Ni–O</th>
<th>Ni–F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antibonding</td>
<td>0.009</td>
<td>0.004</td>
<td>0.004</td>
<td>0.080</td>
<td>0.078</td>
</tr>
<tr>
<td>Bonding</td>
<td>0.011</td>
<td>0.004</td>
<td>0.004</td>
<td>0.338</td>
<td>0.197</td>
</tr>
</tbody>
</table>

4. Conclusions

The electronic states of NiF₂, which is investigated as a conversion-reaction based positive electrode material in lithium ion batteries, was studied by a molecular orbital method using the DV-Xα simulation method. The effect of oxygen doping on the bonding characteristics and electrical conductivity was discussed in particular. From an analysis of the bond overlap population and distribution of electrons, it appears that the Ni–O bond has more covalent features than the Ni–F bond and oxygen doping increases covalent characteristics of the Ni–F bond. New energy levels, which were composed mainly of an interaction of Ni3d and O2p orbitals, formed in the band gap region after the substitution of oxygen for some of the fluorine ions. The changes with the introduction of oxygen are expected to increase the electrical conduction of NiF₂.

Acknowledgement

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References