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XANES analysis for cation-vacancy distribution induced by doping Al ions in transition-metal-oxide anodes of lithium battery

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Abstract

We measured an Al K-edge x-ray absorption near edge structure (XANES) spectrum of Al doped NiO for anode materials of lithium ion batteries. We found that the spectrum of the Al doped NiO is similar to that of γ -Al₂O₃. Calculated **site-specific** XANES spectra strongly correspond to the coordination nature around the absorbing Al ion, indicating aggregation of cation vacancies surrounded by Al ions in the Al doped NiO. These findings could be useful to understand how Li ions migrate in the anode.

Keywords: XANES, vacancy, lithium battery, transition metal oxide, aluminium, first-principle calculation

1. Introduction

Lithium-ion secondary batteries have been one of the essential staffs for our ubiquitous society with mobile electronic devices. The metal oxide nanoparticle is one of the candidates to provide high capacity and good rate property to the battery with low cost. In particular, 3d transition metal oxide nanoparticles can reversibly react with lithium, so called conversion reaction ($\text{MO} + 2\text{Li}^+ + 2\text{e}^- \rightleftharpoons \text{Li}_2\text{O} + \text{M}$) [1], to achieve higher capacities of 700 mAhg⁻¹ [1] than that of the graphite one of 370 mAhg⁻¹ which is currently used [2]. Although the nanoparticles also have good cycle performances as well as high reversible capacities, their capacity in the lower voltage region is very limited [3]. Hence, the improvement of the performance in the low voltage region is of great importance.

Quan et al. reported that a Ni-V oxide exhibits better electrochemical properties than Ni-Fe and Mg-Fe oxides: its charge capacity achieved more than 820 mAhg⁻¹ under 1.5 V after 20th charge-discharge cycle [2, 4]. One of the key factors is **vacancies** to compensate the excess charge of the higher valent vanadium ions and to keep the charge neutrality. They also confirmed Li⁺ ions are inserted into cation vacancies in the Ni-V oxide by using XRD patterns and EXAFS analyses [3]. Moreover, Koo et al. showed that a high concentration of cation vacancies in iron-oxide nanoparticles leads a high capacity of about 132 mAhg⁻¹ at a high voltage of 2.5 V without fading during more than 500 charge-discharge cycles [5]. By combining these results, the doping Al ion in divalent metal oxide nanoparticles should be reasonable to improve anode characters because the Al ion could accept three electrons, induce host-cation vacancies in matrices to compensate the ex-

cess charge, and has its low reduction potential as a light element. Furthermore, for the high cost-performance and lower toxicity of Al, its application to devices has few problems in terms of the resources. However, the local environment around Al including cation vacancies has not been investigated **to the best of our knowledge**. The information of the local structure is essential to understand roles of the doping ions and vacancies during the charge-discharge operation. X-ray absorption near edge structure (XANES) is a powerful method to investigate a local structure around a specific element selected by tuning incident x-ray photon energy. Moreover, the first principle calculations can provide each **site-specific** spectrum separately, which never be obtained only from the observed spectra. By combining with these, we can investigate the local structure around doped ions surrounding by each different local coordination of vacancies.

In this paper, we measured an Al K-edge XANES spectrum of a Ni_{1-3x/2}Al_x□_{x/2}O (□ : Ni²⁺ vacancy) anode material and compared it with the spectrum of γ -Al₂O₃ as a reference of Al materials. We found that the spectrum of Ni_{1-3x/2}Al_x□_{x/2}O is similar to that of γ -Al₂O₃ which mainly has a defect spinel structure. We calculated Al K-edge XANES spectra of γ -Al₂O₃ and Ni_{1-3x/2}Al_x□_{x/2}O to understand the relationship between the local structure around Al ions and its corresponding **site-specific** spectra. In γ -Al₂O₃, cation vacancies are homogeneously **distributed**, in other words, an interaction between the vacancies is repulsive. On the other **hand**, we found that cation vacancies aggregate and are surrounded by Al ions in the Al doped NiO. These findings could be useful to understand how Li ions migrate in the anode. [3, 5]

2. Experimental

All the chemicals used in this study were purchased from Kishida chemical (GR grade). A precursor of NiAl-layer double hydroxides (LDHs) was synthesized by a co-precipitation method using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3$ as starting materials [3]. An aqueous solution containing 1M NaOH and 0.1 M Na_2CO_3 was added dropwise into the aqueous solution containing Ni:Al with a ratio of 2:1. The obtained gel was stirred **vigorously** for 12 h. After precipitating and washing with copious amounts of water, the obtained LDHs were dried at 120 °C for overnight. Then the LDHs were calcined at 400 °C for 12 h to obtain $\text{Ni}_{1-3x/2}\text{Al}_x\text{O}$ ($x = 1/3$). The stoichiometry was determined by an inductively coupled plasma method for a melted sample.

Al K-edge XANES spectra were measured at BL-10 of Ritsumeikan University synchrotron radiation center by a fluorescence mode.

3. Calculation

The *ab-initio* calculations are performed by using the WIEN2k code [6], which is based on a full-potential linear augmented plane wave + local orbital method [7, 8]. The PBE functional [9] is employed as the effective exchange-correlation functional. The muffin-tin radii R of Ni, O and Al ions are 1.11, 0.96 and 1.03 Å, respectively. The cut off parameter K_{max} is set to satisfy $R_{max}K_{max} = 7.0$. The number of k points is $2 \times 2 \times 2$. The core orbitals are set to 1s, 2s and 2p for Ni and 1s for O and Al atoms. Each calculated spectrum is broadened by the Gaussian and Lorentzian broadening of 1.0 eV and 2.0 eV full width at half maximum, respectively.

Figure 1(a) shows a rather classical structural model for $\gamma\text{-Al}_2\text{O}_3$, based on MgAl_2O_4 structure and introduced Al defects. There are 8 tetrahedral (Td) and 16 octahedral (Oh) sites in the unit cell. We randomly introduce three Al defects in position at Td or Oh sites. Figure 1(b) shows a structural model for $\text{Ni}_{1-3x/2}\text{Al}_x\text{O}$ based on the rock-salt NiO. To reproduce the experimental stoichiometric ratio ($x = 1/3 = 0.3333$), 10 Al ions and 5 cation vacancies randomly occupy at the Ni sites in $2 \times 2 \times 2$ supercells of NiO, where 32 oxygen atoms are included. As a result, the stoichiometric ratio in the structural model is $x = 10/32 = 0.3215$, which is close to the experimental ratio. Hereafter, we will call NiO:Al instead of $\text{Ni}_{1-3x/2}\text{Al}_x\text{O}$.

4. Results and Discussion

Figure 2 shows the observed Al K-edge XANES spectra of $\gamma\text{-Al}_2\text{O}_3$ and NiO:Al. The NiO:Al spectrum has similar structure to the $\gamma\text{-Al}_2\text{O}_3$ one, which implies that a local environment around an Al ion in NiO:Al could be close to that in $\gamma\text{-Al}_2\text{O}_3$. It should be noted that the shapes and threshold energies of these spectra are significantly different from those of metal Al and $\alpha\text{-Al}_2\text{O}_3$ [10, 11].

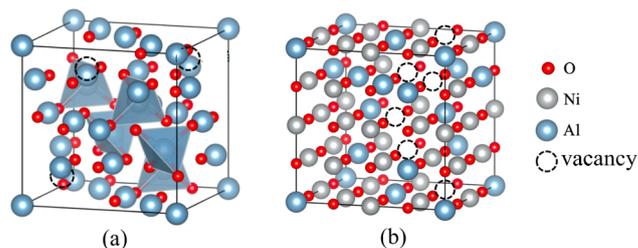


Figure 1: Structural models of (a) $\gamma\text{-Al}_2\text{O}_3$ and (b) $\text{Ni}_{1-3x/2}\text{Al}_x\text{O}$.

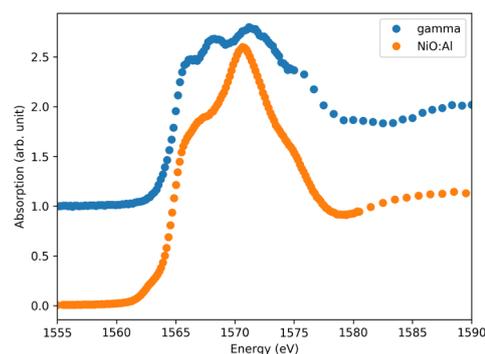


Figure 2: The observed Al K-edge spectra of $\gamma\text{-Al}_2\text{O}_3$ (gamma) and $\text{Ni}_{1-3x/2}\text{Al}_x\text{O}$ (NiO:Al).

As **previously**, $\gamma\text{-Al}_2\text{O}_3$ has Oh coordination around an Al site. Similarly, when an Al ion substitute a Ni site in NiO:Al, the Al ion has a local Oh coordinate. Hence, a question is **whether** Al K-edge XANES spectra for these Oh Al sites are similar or not. Furthermore, since $\gamma\text{-Al}_2\text{O}_3$ also has the Td Al sites, a Td Al site in NiO:Al could be one possibility of an ionic position to put the Al ion in NiO although it is **unlikely** in the rock salt structure. **Additionally**, cation vacancies to maintain the charge neutrality **have an influence** to the local environment around neighboring Al ions. Thus, in order to understand **correspondence** between the XANES spectra and the local geometry, we calculate each Al site contribution to XANES spectra for $\gamma\text{-Al}_2\text{O}_3$ and NiO:Al under a random cation vacancy occupation and compare each spectrum.

Figure 3 shows the total and **site-specific** calculated spectra for $\gamma\text{-Al}_2\text{O}_3$ with two different cation vacancy configurations, as mentioned in Fig. 1(b). The cation vacancies are only located at the Td (Fig. 3(a)) and Oh (Fig. 3(b)) Al sites, respectively. The **site-specific** spectra show significant difference between the local Td and Oh Al sites. The Td spectra show a relatively sharp peak at near-threshold energy, while the Oh ones have a broadened peak at higher energy. This indicates that the Al ions at the Td and Oh sites have different electronic structures, suggesting an idea to interpret Al K-edge XANES spectra by each site contribution and a local coordination around the absorbing Al ion. By comparison of the calculated

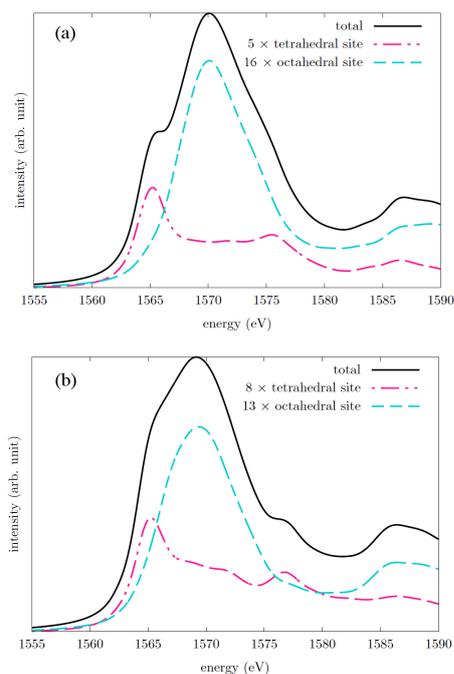


Figure 3: The calculated Al K-edge XANES spectra for the spinel structural models of γ -Al₂O₃. The cation vacancies are only located at (a) Td and (b) Oh Al sites, respectively.

spectra with the observed spectrum, the total spectrum only with the Oh cation vacancies in Fig. 3(b) shows better agreement than that with the Td vacancy sites. This is consistent with total energy calculations for a spinel-structure based γ -Al₂O₃ [12], which showed that distant Oh cation vacancies are the most stable. Therefore, the analysis of Al K-edge XANES spectra can give the information of a local environment of Al ions and cation vacancies. It should be mentioned that the calculated spectra miss the peak located at 1568 eV in the observed spectrum. This peak has not been reproduced in a literature showing calculated XANES spectra with an optimized γ -Al₂O₃ structure [13]. It is expected that the results are possibly improved by taking the effects of non-spinel sites and a glass-like random network structure into account [13]; however, this is far beyond our present research scope.

We apply the same approach to NiO:Al to investigate the correspondence between a local geometry and a site-specific XANES spectrum. Figure 4(a) shows the compared calculated Al K-edge XANES spectrum of NiO:Al with the observed spectrum. The calculated spectrum exhibits a similar broadened feature to the Oh Al XANES in γ -Al₂O₃. We verified the effects of the Hubbard U parameter to the Al K-edge XANES spectrum in NiO:Al with an assumed antiferromagnetic order (not shown); however, there was almost no effect of the U parameter. This is consistent with a more detailed calculation of Ni K-edge XANES spectra in NiO, which concluded that the Hubbard U has an influence only at the very near edge, in other words, pre-edge peaks [14]. Figures 4(b) and (c) also show

the contribution from each absorbing Al site to total calculated XANES. We roughly classify the spectra of Al 5, 6, 9 and 10 sites in the same group by the spectral shape, which shows poor agreement with the observed spectrum. On the other hand, the spectra of Al 7 and 8 sites agree with the observed spectrum of the peak at 1571 eV in particular. Surprisingly, the spectral tendency corresponds well to the coordinative nature around the absorbing Al ion, as shown in Figure 5. The group of Al 5, 6, 9 and 10 sites has a larger Ni coordination number and smaller vacancy and Al coordination number, whereas the group of Al 7 and 8 sites has the opposite tendency from the former group. Therefore, to get good agreement with the observed spectrum within the present models, we should increase the Al site surrounded by as many Al ions and vacancies as possible. This indicates that Al ions prefer to aggregate and attract cation vacancies in NiO:Al. This behavior of the cation vacancy is opposite from the case of γ -Al₂O₃ [12]. The vacancy aggregation could be related to the migration path of Li ions in the anode electrode, which provides a high capacity and excellent stability [3, 5].

In this discussion, since we mainly focused on the peak at 1571 eV, the peak at 1566 eV had not been discussed yet. In analogy to the case of γ -Al₂O₃, the discrepancy including the peak could be attributed to a distorted Al site like a local tetrahedral site in γ -Al₂O₃ at most. One possible scenario may be that an Al site adjacent to cation vacancies distorts and become close to the tetrahedral site. In addition, the peak observed for γ -Al₂O₃ at 1568 eV does not appear in the observed spectrum of NiO:Al. This could be explained by the absence of the fluctuated site-position effects of γ -Al₂O₃ in NiO:Al [13]. In another aspect, the peak absence indicates no dominant contribution of various Al₂O₃ compounds to the NiO:Al spectrum [10]. Nevertheless, there is still a possibility of existence of particular Al compounds which give better agreement of their XANES spectra with the observed NiO:Al one. The determination of the detailed local structure are left for our future work to get full understanding of the potential lithium battery anode.

5. Conclusion

We have investigated the local structure around an Al ion in γ -Al₂O₃ and NiO:Al by using Al K-edge XANES spectra. From the view point of the similarity of the observed XANES spectra between γ -Al₂O₃ and NiO:Al, we focused on the contribution of octahedral Al sites to the calculated XANES spectra. The site contributions to the calculated XANES spectra are different between the local Td and Oh Al sites in γ -Al₂O₃. We found the well correspondence between the shape of the site-specific spectra and the coordination number around the absorbing Al ion. This result indicates that the Al ions and cation vacancies aggregate in NiO:Al. In future we study the geometrical relationship between Al ions and cation vacancies in more

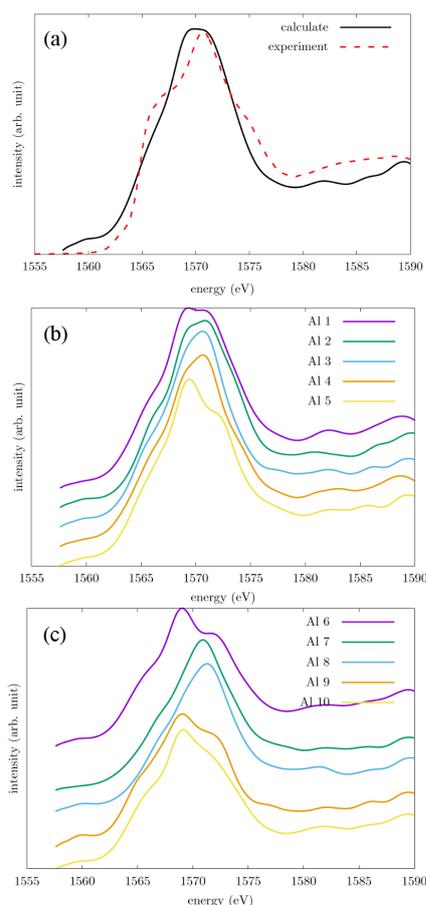


Figure 4: Calculated Al K-edge XANES spectra for $\text{Ni}_{1-3x/2}\text{Al}_x\text{O}_{x/2}$.

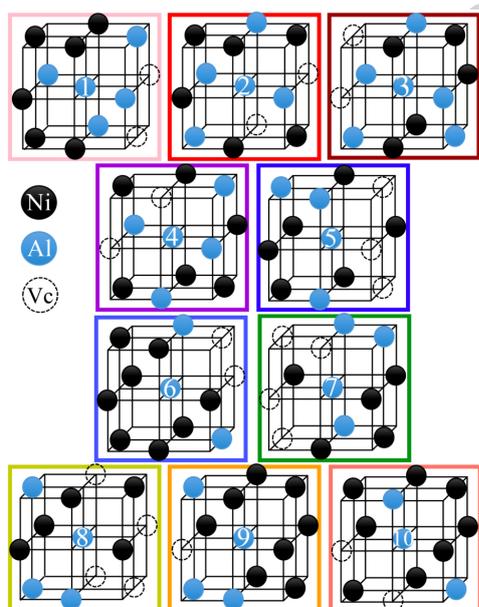


Figure 5: Local coordination around Al ions. The cation vacancy is indicated by V_c .

230 detail, as well as the effects of the aggregation to practical electrochemical properties of the electrode.

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