

Electronic Structure Analysis on Fluorine Induced LaNiO₃ Perovskite Oxides

Ayane Sugimura¹, Daisuke Shibata², Mayu Morimoto², Yasuhiro Inada¹,
Chengchao Zhong¹, Keiji Shimoda^{2,3}, Ken-ichi Okazaki^{1,2}, Yuki Orikasa¹

- 1) Department of Applied Chemistry, Graduate School of Life Sciences, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu 525-8577, Japan
- 2) Research Organization of Science & Engineering, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu, 525-8577, Japan
- 3) Ritsumeikan Global Innovation Research Organization, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu, 525-8577, Japan

Perovskite-type oxides, LaNiO₃, have been used as electrocatalysts for the oxygen evolution reaction (OER) in alkaline water electrolyzers. For further development of high OER activity, the tailoring of defect chemistry is important. This study attempts to introduce fluoride ions into the crystal structure of LaNiO₃ by chemical fluorination. Mixtures of LaNiO₃ and polyvinylidene difluoride (PVDF) are annealed at 350°C. The products are characterized by X-ray diffraction and Ni, F and O *K*-edge X-ray absorption spectroscopy. Decomposition of PVDF results in fluorination of LaNiO₃ with decreasing Ni valence state. The highly ionic nature of the fluoride ion reduces the hybridization state between O *2p* and Ni *3d* orbitals.

1. Introduction

Perovskite-type oxides have been used as electrocatalysts for oxygen evolution reaction (OER) in alkaline water electrolyzers. In the research of highly active perovskite-type oxides, the descriptor for OER has been studied. In simple perovskite oxides composed of lanthanides and *3d* transition metals, the electrons in the *e_g* orbitals in the transition metals affect the *2p* orbitals formed by oxygen-derived intermediates under OER [1]. Therefore, the number of electrons in the *e_g* orbitals can be used as a descriptor for OER, and it has been found that the activity is maximum when the number of *e_g* electrons is 1.2 [1]. It has been reported that LaNiO₃ has an *e_g* electron number of 1.0 and exhibits relatively high OER activity. Under conditions of high temperature reducing atmosphere, approximately 1% of oxygen deficiency is introduced into the LaNiO₃ crystal structure [2]. However, under strong reducing conditions, the perovskite-type structure is not stable [3], which makes it difficult to control the number of *e_g* electrons. In this study, we have attempted to suppress the structural instability caused by oxygen vacancies by partially substituting fluorine for oxygen sites in LaNiO₃. The chemical fluorination reactions of Sr₃Fe₂O_{6.28} [4], BaFeO_{2.5} [5], and La₂CuO₄ [6], by using PTFE (polytetrafluoroethylene), PVDF (polyvinylidene difluoride), and NH₄F, respectively, have been reported. Here, we investigate the topotactic fluorination reaction in LaNiO₃ by annealing a mixture between LaNiO₃ and PVDF in a sealed stainless-steel tube, where the reaction gas is released by thermal decomposition of PVDF. The

synthesized materials are characterized for crystal structure by X-ray diffraction (XRD), and then electronic structure analysis by Ni, F and O *K*-edges X-ray absorption spectroscopy (XAS) is performed.

2. Experimental

LaNiO₃ (Kojundo Chemical Laboratory Co., Ltd.) and PVDF powder (Sigma-Aldrich) were each weighed and mixed in a mortar. The weight ratio of LaNiO₃ to PVDF was LaNiO₃:PVDF=1:0.1 (hereafter denoted PVDF 10%) and 1:0.2 (PVDF 20%). The mixed samples were pelletized and sealed in a stainless-steel container. The sealed containers were annealed at 350°C for 12 hours. XRD experiment was performed using an Ultima-IV diffractometer (Rigaku) with Cu K α radiation as the X-ray source and a tube voltage and current of 40 kV and 40 mA, respectively. Ni *K*-edge XAS measurements were performed at the beamline BL-4 in the Ritsumeikan University SR Center. The samples were mixed with BN and measured in transmission mode. F and O *K*-edge XAS measurements were carried out at the beamline BL-11 in the Ritsumeikan University SR Center. The powder samples were mounted on carbon tape, and the spectra were taken with the partial electron yield (PEY) and partial fluorescence yield (PFY) modes under vacuum.

3. Results and discussion

XRD patterns of LaNiO₃, PVDF 10% and PVDF 20% are shown in Fig. 1. The PVDF-treated samples show a lower angle shift of the diffraction peaks, especially at higher angles, compared to LaNiO₃. In addition, the peaks are broadened, indicating less

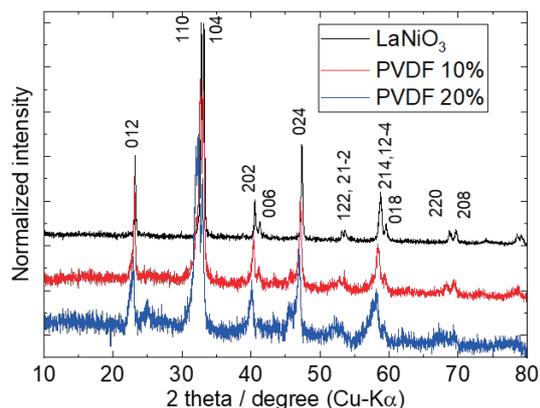


Fig. 1 XRD patterns of LaNiO₃ and annealed mixtures of LaNiO₃ containing PVDF 10% and 20%.

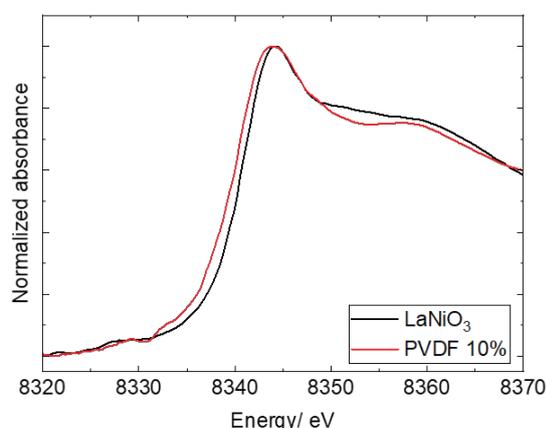


Fig. 2 Ni K-edge XANES of LaNiO₃ and PVDF 10%.

crystallinity in the PVDF-treated samples. Although most of the peaks are assigned to the reported LaNiO₃ phase with space group *R3/C* [7], unidentified peaks are observed for PVDF 20%, particularly around 25 degrees. This peak and the broadening around 32 degrees may be due to the formation of a LaNiO_{2.5} defect perovskite phase [8], although sufficient crystal structure analysis has not been performed. The lattice parameter of PVDF 10% and PVDF 20% is larger than that of LaNiO₃. The lattice expansion is due to the formation of Ni²⁺ with large ionic radius than Ni³⁺ by the nickel reduction reaction. The nickel reduction reaction is probably due to the introduction of oxygen defects and the progressive exchange reaction between oxide and fluoride ions. Therefore, the defect structure is discussed in terms of the electronic structure change from the results of XAS. In the following discussion, we will compare LaNiO₃ and PVDF 10% to avoid ambiguity due to the impurity formation in PVDF 20%.

Figure 2 shows X-ray absorption near edge

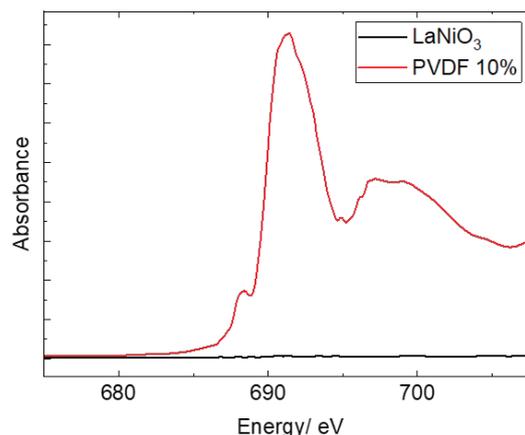


Fig. 3 F K-edge XANES of LaNiO₃ and PVDF 10% obtained in PFY mode.

structures (XANES) at Ni K-edge of LaNiO₃ and PVDF 10%, where the absorption edge appears at about 8340 eV. The Ni K-edge absorption is usually interpreted from the transition of core electrons to the Ni 4*p* empty states. Compared to LaNiO₃, the spectrum of PVDF 10% is shifted towards lower energy. This is a direct result of the Ni reduction and is in good agreement with the crystal lattice expansion shown by XRD. Taking the position of the Ni K-edge from the energy at the half-maximum of the absorption, the observed energy shift is about 0.9 eV. This shift is consistent with the reported absorption edge difference between La₂NiO_{4+δ} and La₄Ni₃O_{10-δ}, where the valence shift was estimated to be 0.34 [9]. The synthesized PVDF 10% in this study is expected to have a similar nickel valence reduction compared to LaNiO₃.

Figure 3 shows F K-edge XANES spectra of LaNiO₃ and PVDF 10% obtained in fluorescence mode without normalization. The absorption intensity at F K-edge of PVDF 10% is clearly observed. The XRD results have shown no clear phase-separation behavior in PVDF 10%, but F K-edge XANES spectra indicated that the heat treatment with PVDF introduces fluoride ions into the LaNiO₃ crystal structure without secondary phase formation. In this fluorination reaction, the Ni valence decreases at the same time. The reaction scheme of LaNiO₃ with PVDF treatment is shown below:



It is shown that fluoride ions are incorporated into the oxygen defect sites, resulting in a decrease in the Ni valence.

The substitution of oxide ions by fluoride ions may cause the electronic structure change in the oxygen orbital. Figures 4 (a) and (b) show the O K-edge XANES of LaNiO₃ and PVDF 10% obtained in PEY and PFY modes, respectively. The spectra

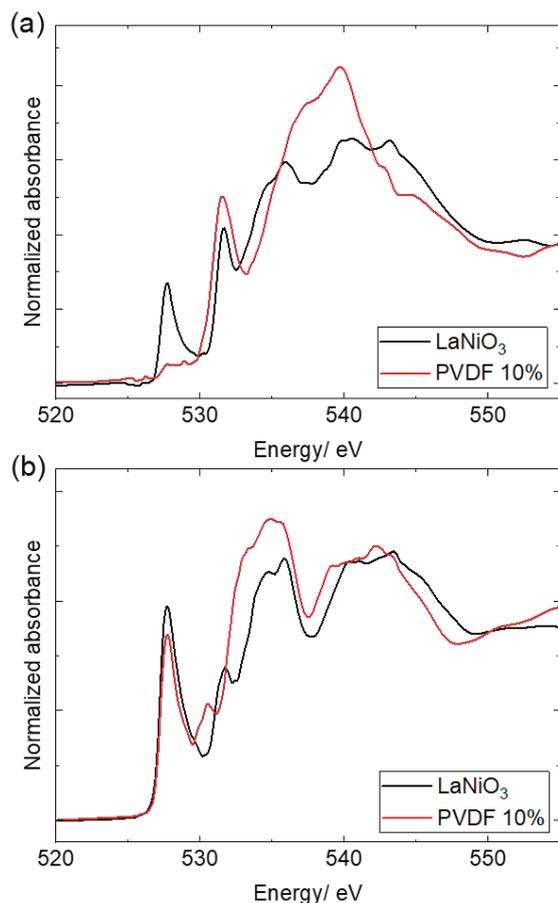


Fig. 4 O *K*-edge XANES of LaNiO₃ and PVDF 10% obtained in (a) PEY and (b) PFY modes.

correspond to the electron transition from the O 1s core level to the unoccupied states. The first peak at 528 eV is attributed to the hybridization state, which is related to the character of the O 2*p*-Ni 3*d* states [10]. The second peaks at 532 eV correspond to the band of La 5*d* characters. The broad peak centered at 540 eV is due to the Ni 4*sp* character. The first peak at 528 eV disappears for PVDF 10% especially in the XANES measured in PEY mode. This indicates that the hybridization between O 2*p* and Ni 3*d* is weakened by the introduction of fluoride ions into the oxide ion site on the surface of LaNiO₃ due to the highly ionic nature of fluoride ions in LaNiO₃. The decrease of hybridization state was reported in the introduction of oxygen deficiency in La_{0.6}Sr_{0.4}CoO_{3-δ} [11]. The observed electronic structure change in fluorine induced LaNiO₃ might influence OER activity.

4. Conclusions

This study has examined the fluorination reaction to LaNiO₃ by annealing of a mixture of LaNiO₃ and PVDF. Calcination of the PVDF mixture introduces fluoride ions into LaNiO₃, but the high ratio of PDVF causes phase separation. Ni *K*-edge XANES analysis

has revealed the decreasing of Ni valence by the calcination of PVDF mixture. The observed Ni reduction is due to oxygen defect formation and/or fluoride ion substitution on oxide ion site. O *K*-edge XANES shows that the introduction of highly ionic fluoride ions weakens the hybridization between O 2*p* and Ni 3*d* states.

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References

- [1] J. Suntivich, K. J. May, H. A. Gasteiger, J. B. Goodenough and Y. Shao-Horn, *Science*, **2011**, 334, 1383.
- [2] S. Rakshit and P. S. Gopalakrishnan, *J. Solid State Chem.*, **1994**, 110, 28.
- [3] R. A. Budiman, S.-i. Hashimoto, T. Nakamura, K. Yashiro, K. Amezawa and T. Kawada, *ECS Trans.*, **2015**, 66, 177.
- [4] Y. Tsujimoto, K. Yamaura, N. Hayashi, K. Kodama, N. Igawa, Y. Matsushita, Y. Katsuya, Y. Shirako, M. Akaogi and E. Takayama-Muromachi, *Chem. Mater.*, **2011**, 23, 3652.
- [5] O. Clemens, C. Rongeat, M. A. Reddy, A. Giehr, M. Fichtner and H. Hahn, *Dalton Trans.*, **2014**, 43, 15771.
- [6] S. Adachi, X. J. Wu, T. Tamura, T. Tatsuki, A. Tokiwa-Yamamoto and K. Tanabe, *Physica C*, **1997**, 291, 59.
- [7] J. L. García-Muñoz, J. Rodríguez-Carvajal, P. Lacorre and J. B. Torrance, *Phys. Rev. B*, **1992**, 46, 4414.
- [8] M. Toshihiro, U. Osamu, I. Tomomi, N. Ichiro, M. Ichiro, K. Tsuneo, K. Shinichi and K. Fumikazu, *Bull. Chem. Soc. Jpn.*, **1994**, 67, 687.
- [9] R. J. Woolley, B. N. Illy, M. P. Ryan and S. J. Skinner, *J. Mater. Chem.*, **2011**, 21, 18592.
- [10] J. Suntivich, W. T. Hong, Y.-L. Lee, J. M. Rondinelli, W. Yang, J. B. Goodenough, B. Dabrowski, J. W. Freeland and Y. Shao-Horn, *The J. Phys. Chem. C*, **2014**, 118, 1856.
- [11] Y. Orikasa, T. Ina, T. Nakao, A. Mineshige, K. Amezawa, M. Oishi, H. Arai, Z. Ogumi and Y. Uchimoto, *J. Phys. Chem. C*, **2011**, 115, 16433.