

XAFS analysis of 2-line ferrihydrite electrode for studying charging and discharging mechanism of Li-ion battery

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1. Introduction

Biogenous iron oxide (*L*-BIOX) is the structure created by the iron-oxidizing bacteria, that has become an inner diameter of about 1 μ m tube. The tube of *L*-BIOX consists of about 3 nm sized amorphous iron oxide. It has been found that *L*-BIOX has good charge and discharge characteristics as Li-ion battery (LIB) anode material ^[1]. Discharge mechanism of the *L*-BIOX electrode is reduced to iron metal state by Li insertion into *L*-BIOX, returns to the oxide by Li desorption, it has been shown to be a so-called conversion reaction ^[1]. In addition, in the Si-K edge and P-K edge XAFS experiment, it has been orphaned SiO₄ tetrahedral, Li that is Li₄SiO₄ similar in that invade been elucidated. As shown in this example, it is progressing elucidation of charging and discharging mechanism by analyzing the local structure ^[2].

We learn the life activity of the naturally occurring bacteria in the above BIOX, and we are aiming for a new material creation. 2-line ferrihydrite (2L-Fh), that is a low-crystalline iron oxide as well as *L*-BIOX, is considered a suitable material for LIB negative electrode, by combining the element-added 2L-Fh, has promoted the evaluation of the current charge and discharge characteristics.

In this paper, we report the results of the oxygen coordination number of Al in a 2L-Fh with the addition of Al was evaluated by Al-K edge XAFS analyzing.

2. Experimental

Al-doped 2L-Fh was synthesized by the following procedure.

- (1) It were weighed the powders of Fe(NO₃)₃ · 9H₂O and Al(NO₃)₃ · 9H₂O, the value of Al/(Al+Fe) is set to be to 0.1, 0.2, 0.3, 0.4, 0.5. Later, they were mixed in a mortar.
- (2) The 12-fold molar amount of NH₄HNO₃ of Fe(NO₃)₃ · 9H₂O in addition to the above mixed powder was kneaded until a paste in a mortar.
- (3) The above paste was allowed to stand for about 12 hours.

(4) Suspending the standing paste in distilled water, the powder was collected by suction filtration and dried under reduced pressure for 2 days.

(5) The above powder was dried for about 12 hours in a vacuum atmosphere at 120° C.

Al-K edge XAFS measurements were carried out at Ritsumeikan University SR Center BL-13. To prepare a sample mixed with conductive carbon was applied on a copper foil was solved charge up problems in XAFS measurements. Analyzing crystal was used KTP (011). Measurement mode was conducted in all electron yield method, in that the photoelectron and the Auger electron currents are measured which is generated with the X-ray absorption.

As a reference material, Al-metal foil, α - alumina, $40\text{Li}_2\text{O} \cdot 15\text{Al}_2\text{O}_3 \cdot 45\text{SiO}_2$ glass (LAS-glass), $47\text{Li}_2\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot 51\text{P}_2\text{O}_5$ glass (LAP-glass) was used. Oxygen coordination number of Al in the glass was determined by ^{27}Al nuclear magnetic resonance (NMR) spectrum.

3. Results and Discussion

Al-K edge XANES spectra of the reference materials are shown in figure 1. The absorption edge energy of the Al-metal and the α -alumina, which is a typical oxide, are each about 1558eV and 1565eV. Because each peak shapes are very different, the difference in chemical states of the Al metal and the α -alumina can be clearly distinguished.

They were confirmed by ^{27}Al MAS-NMR measurement, that the oxygen coordination number of Al in LAS-glass is a 4-coordinate at the rate of 97%, and that the oxygen coordination number of Al in LAP-glass is a 6-coordinate at the rate of 90%, respectively.

Al of α -alumina and Al of the LAP-glass are both present in oxygen 6-coordination. Therefore, the value of both samples of the absorption edge energy (E_0) is near, and approximate shape of the peaks were similar.

On the other hand, Al in LAS-glass is oxygen 4-coordination. E_0 value of LAS-glass is shifted to the low-energy side compared with α - alumina. And the second peak as counted from the absorption edge in the signal LAS-glass is small. Thus, XANES-signal of LAS-glass and one of α - alumina were clearly different.

From the above results, we have determined that E_0 of the oxide glass is correlated to the oxygen coordination number of Al. In other words, E_0 can be an indicator of the oxygen coordination number of Al. 2L-Fh, which is in the present study of the subject, is the iron oxide amorphous. Therefore, Al in the 2L-Fh may be considered to be a chemical state similar to the

glasses described above.

The relationship of E_0 and Al_2O_3 content of Al-doped 2L-Fh is shown in figure 2. They are shown that E_0 is the energy value at which the peak strength when normalized indicates 0.5, and that Al_2O_3 -content is an analytical value of $\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3+\text{Fe}_2\text{O}_3)$ (mol %), respectively.

All E_0 -value of Al-doped 2L-Fh is between LAS-glass and LAP-glass, and the chemical state of Al had mixed the oxygen 4-coordination and 6-coordination.

Increasing Al_2O_3 content, E_0 -value is close to the value of the LAS-glass. Therefore, as the amount of Al_2O_3 is larger, the proportion of the oxygen 4-coordination of Al increases.

It was confirmed that aluminum ions of 2L-Fh are mixed in the state of oxygen 4-coordination of state and 6-coordination by XAFS analysis. In addition, the proportion of 4-coordinate Al increases as the ratio of Al_2O_3 increases.

References

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- [2] R. Sakuma, H Hashimoto, G. Kobayashi, T. Fujii, M. Nakanishi, R.Kanno, M.Takano, J. Takada, *Materials Lett.* **139** (2015) 414.

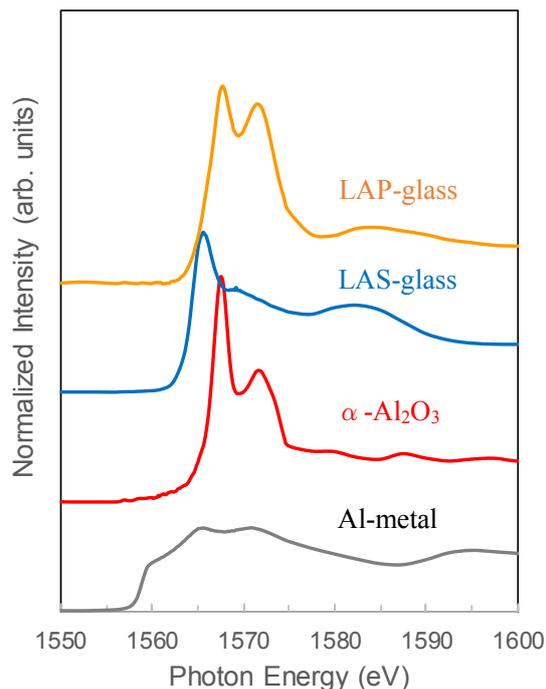


Fig. 1. Observed Al K-edge XANES spectra of Al-reference samples.

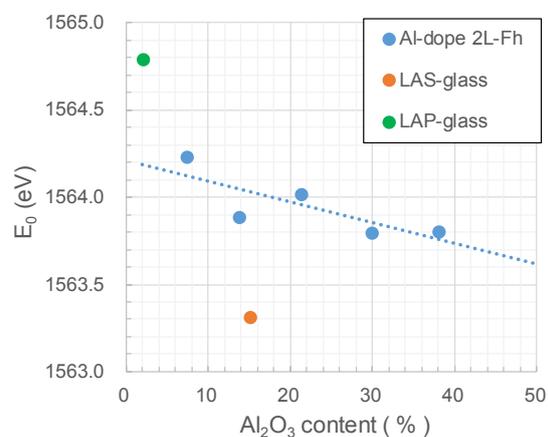


Fig. 2. Correlation of E_0 value and Al_2O_3 amount.