

Oxygen vacancy formation of perovskite type oxides at electrode / electrolyte interface for oxygen reduction catalysis studied by in-situ X-ray absorption spectroscopy

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Introduction

Due to growing concern about limited energy resources and global warming, fuel cells and metal-air batteries are of much interest in recent years because of its ultra-high energy density and environmental friendliness. In these batteries, sluggish kinetics of oxygen reduction reaction (ORR) at the cathode results in a large overpotential, hindering them viable. Thus, highly active ORR catalysts are strongly demanded.

Perovskite type oxides as ORR catalysts have attracted much attention due to their low cost and relatively high activity [1, 2]. Suntivich et al. have reported nearly unity occupancy of e_g orbital of transition metal ions is a descriptor of highly active ORR perovskite type oxides catalysts [3]. However, oxygen nonstoichiometry of perovskite type oxides has not been paid much attention. ORR proceeds under negative overpotential, which may cause oxygen vacancy formation in perovskite type oxides. The effect of oxygen vacancies under reductive condition should be taken into consideration to design highly active perovskite type oxide ORR catalysts. The oxygen vacancy is preferentially formed at electrode / electrolyte interface because of the potential difference at the interface. In this study, we construct model interface system of $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ thin film and alkali solution, and investigate oxygen vacancies at the interface of $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ with total-reflection fluorescence XAS (TRF-XAS) method [4]. This method is useful to observe electronic structure of electrode surface at the nanometer scale. Compared with the oxygen nonstoichiometry in $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ bulk, the oxygen vacancy formation mechanism is discussed.

Experimental

$\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ thin film electrode was prepared by pulsed laser deposition (PLD) method. (100)-oriented 0.5wt% Nb-doped SrTiO_3 was used as a substrate. For in-situ XAS measurements, a three electrode cell was constructed where counter and reference electrodes are Au rod and Ag/AgCl electrode, respectively. 0.1 M KOH under argon purged was used as electrolyte. XAS measurements were carried out at BL28XU, SPring-8, Japan. Fe K-edge XAS spectra at various potentials were measured in fluorescence mode by using 21-element solid state detector.

Results and Discussion

X-ray near edge structure (XANES) at Fe K-edge of the surface and bulk of $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ at various potentials are shown in Fig. 1. As the potential changes more negative, the absorption edge was shifted to lower energy, indicating the reduction of iron ions. According to Kroger-Vink notation, oxygen vacancies were introduced at negative potentials as follows:



The shift of absorption edge is clearly observed in

$\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ surface compared with $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ bulk. The result indicates that more oxygen vacancies were formed at the surface compared with bulk. At electrode / electrolyte interface, the potential drop is caused with in the space charge layer of electrode and the electrical double layer of electrolyte as shown in Fig. 2. The potential drop at the space charge layer creates more oxygen vacancy at the interface. When the applied potential is increased, the potential drop at the interface is increased. This results in the preferential oxygen vacancy formation at electrode / electrolyte interface.

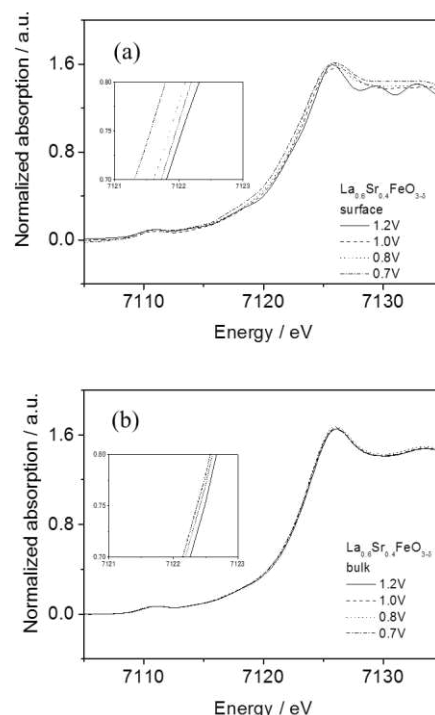


Fig. 1 Fe K-edge XANES spectra of $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ at (a) the surface and (b) bulk measured at various potentials.

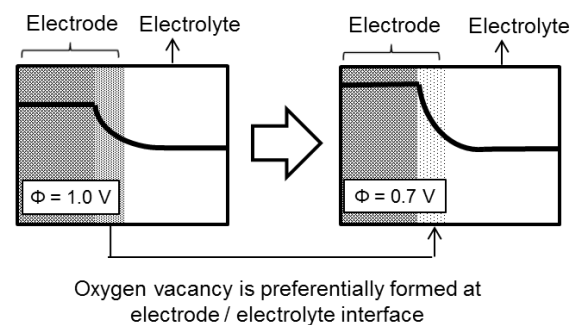


Fig. 2 Schematic picture of electrode / electrolyte interface.

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References

- [1] Jaka Sunarso, et al. J. Phys. Chem. C, **116**, 5827 (2012).
- [2] William G. Hardin, et al. J. Phys. Chem. Lett, **4**, 1254 (2013).
- [3] Jin Suntivich, et al. Nat. Chem., **3**, 546 (2011).
- [4] D. Takamatsu et al., Angew. Chemi. Int. Ed. **51**, 11597 (2012).