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In-Situ and Ex-Situ Fe K-Edge X-Ray Absorption Spectroscopic Studies for the Structural and Electronic Evolution of Strontium Ferrite upon Electrochemical Oxidation


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Abstract: A structural evolution from SrFeO$_2$ (brownmillerite) to SrFeO$_3$ (perovskite) upon electrochemical oxidation has been systematically studied by in-situ and ex-situ X-ray Diffraction (XRD) and X-ray absorption spectroscopy (XAS). According to the XRD analysis, the orthorhombic SrFeO$_2$ has been gradually converted to the cubic SrFeO$_3$ as the reaction proceeds. The mostly oxidized perovskite could be been obtained after 66 h. From the in-situ and ex-situ Fe K-edge XANES study, it has been found that the degree of oxidation goes to a maximum after 48 h and 30 h for the bulk and the surface, respectively. EXAFS results are also consistent with the above findings from the fact that no peak evolution could be observed after 48 h and 30 h for both ex-situ and in-situ studies, respectively.

1. INTRODUCTION

Thanks to its simple and optically-opened instrumentation, the electrochemical oxidation[1-3] can be combined with various spectroscopic methods. Among them, XAS measurement is known to be a powerful methodology to investigate the evolution of electronic and local structures of the material during the reaction[3-5]. Here, we report the in-situ XAS results of SrFeO$_3$, of which Fe$^{3+}$ ion converts completely to Fe$^{4+}$ one due to the electrochemical oxidation. Powder XRD and ex-situ XAS studies also have been performed to compare with the in-situ XAS results.

2. EXPERIMENTAL

Starting material, SrFeO$_3$ has been prepared by decomposing nitrate precursors at 1200°C in air, followed by annealing in N$_2$ atmosphere at 1000°C. Electrochemical oxidation has been performed by potentiostatic method, applying +400mV (vs. Hg/HgO) potential to a RDE type working electrode (SrFeO$_3$ pellet). Powder XRD patterns have been obtained from a Phillips PW1830 diffractometer using Ni-filtered Cu K$_\alpha$ radiation. XAS measurements have been carried out with synchrotron radiation by using the EXAFS facilities installed at beam line 7C of the Photon Factory, Tsukuba, operated at 2.5 GeV with
The structural transformation from brownmillerite ($\text{SrFeO}_2$) to perovskite ($\text{SrFeO}_3$) has been electrochemically made and its in-situ observation has been also performed XRD and XAS studies. According to the in-situ XAS results, it is understood that the sample surface is completely oxidized at 30 h, while the bulk needs at least 48 h to form perovskite with minor oxygen vacancy. The stabilization of $\text{Fe}^{4+}$ in the crystal lattice and the existence of distorted local symmetry have been confirmed by XANES study. Based upon the good consistency between in-situ XAS results and ex-situ one, it is found that XAS spectroscopic method is a powerful tool to elucidate the variation of the electronic and the local structure of the material during the electrochemical reaction.

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References