Investigation of catalytic effect of Cr^{3+} substitution for Fe_2O_3 toward photochemical and electrochemical water oxidation

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Abstract: Catalytic property of $Fe_{2-x}Cr_xO_3$ for water oxidation was investigated by photochemical and electrochemical measurements. Surface water oxidation activity of $Fe_{2-x}Cr_xO_3$ with Ru(II) photosensitizer was reduced by an increase of the Cr concentration in $Fe_{2-x}Cr_xO_3$. On the other hand, the Cr-substitution improved electrochemical water oxidation activity to form oxygen by five-fold. Electrochemical impedance measurements indicated that the Cr-substitution decreased the resistance of charge transfer inside the oxide bulk, thereby contributing to improved performance for the electrochemical water oxidation.

Keywords: Water splitting, Cocatalyst, Semiconductor photocatalyst.

1. Introduction

Water splitting into H_2 and O_2 has attracted attention as one of the possible forms of hydrogen evolution. This reaction consists of two redox reactions; proton reduction and water oxidation. Especially, water oxidation has been usually regarded as more difficult step because 4 electrons are required to accomplish the reaction. Under these backgrounds, many kinds of catalysts for water oxidation have been developed. Especially, metal oxides are well known as stable catalysts under photochemical and electrochemical water oxidation reactions. In addition, metal oxides that work as catalysts for water oxidation would be good candidates as nanoparticle cocatalysts in combination with a semiconductor photocatalyst.[1] Recently, multi-component materials that have more than two metal species have been reported as more efficient catalysts for water oxidation than single component ones.[2]

Recently, our group has reported that Fe-Cr mixed oxide nanoparticles deposited on the $SrTiO_3$ surface worked as better cocatalysts for photocatalytic water oxidation than Fe or Cr single oxide.[3] However, the detailed working mechanism of Fe-Cr mixed oxide has been still uncovered. In order to investigate the mechanism, we focused on bulk Fe-Cr mixed oxide ($Fe_{2-x}Cr_xO_3$) as a model catalyst. Because different from nanoparticulate systems, it is easy to apply such as bulk oxide material for a series of mechanistic investigations. In this work, we investigated the catalytic performance of $Fe_{2-x}Cr_xO_3$ for photochemical and electrochemical water oxidation aiming to clarify the promotional effect of Cr^{3+} substitution for Fe_2O_3.

2. Experimental

$Fe_{2-x}Cr_xO_3$ preparation: Particulate $Fe_{2-x}Cr_xO_3$ was prepared by a coprecipitation method. Appropriate amounts of $Fe(NO_3)_3\cdot 9H_2O$ and $Cr(NO_3)_3\cdot 9H_2O$ were dissolved in pure water. After addition of ammonia solution, the formed precipitate was collected, and dried at 343 K for 1 day. After grinding the dried powder, it was calcined at 573 K for 2 h, and then 873 K for 2 h in air.

Photochemical water oxidation: $Fe_{2-x}Cr_xO_3$ was dispersed in a phosphate buffered solution (100 mL, 50 mM, pH 7.5) containing 5 mM $Na_2S_2O_8$ and 0.25 mM $[Ru(bpy)_3]SO_4$ (bpy = 2,2'-bipyridine). The solution was irradiated by a 300 W xenon lamp ($480 < \lambda < 500$ nm) under a degassed atmosphere. The evolved oxygen was analysed by an on-line gas chromatograph (GC 3200, GL science).

Electrochemical water oxidation: $Fe_{2-x}Cr_xO_3$ was loaded on a FTO conductive glass electrode by a squeegee method, followed by annealing under air at 673 K for 1 h. Electrochemical reaction was conducted using potentiostat control under dark condition with three electrodes, which are $Fe_{2-x}Cr_xO_3$/FTO working electrode, a Pt wire counter and Ag/AgCl reference. Cyclic voltammetry and potential controlled electrolysis measurements were carried out in 100 mM aqueous phosphate buffered solution (pH 7.5) after purging the solution with Ar gas. The evolved oxygen during the electrolysis was analysed by gas chromatography (MGC3000A, Inficon). Electrochemical impedance spectroscopy was measured using a bipotentiostat (HZ-7000 and HZA-PGS1, Hokuto Denko) with an alternate current signal of 10 mV of amplitude superposed on the direct current component. Phosphate buffered solution (100 mM, pH 7.5) that used in the measurement contained 3–3.5 wt% of H_2O_2 as a sacrificial electron donor.

3. Results and discussion

Figure 1 shows the time courses of O_2 evolution using $Fe_{2-x}Cr_xO_3$ having different compositions under the photochemical water oxidation condition. Note that no O_2 evolution was observed without $[Ru(bpy)_3]SO_4$ photosensitizer. Comparing to pure Fe oxide, the O_2 evolution activity was degraded with an increase of the Cr concentration in $Fe_{2-x}Cr_xO_3$, and Cr_2O_3 was completely inactive. This result suggests that water oxidation activity on the surface of $Fe_{2-x}Cr_xO_3$ is dropped with increasing the Cr ratio in the oxide.

Figure 2 shows the current-time curves for $Fe_{2-x}Cr_xO_3$/FTO electrodes recorded at +1.80 V (vs. RHE). In the case of Cr_2O_3, the anodic current density was finally decreased to approximately 5 µA cm^{-2}. O_2 was not evolved, while oxidative dissolution of Cr^{3+} to Cr^{6+} was observed. By contrast, the Fe_2O_3 electrode showed stable current density around 0.01 mA cm^{-2} for 50 min electrolysis with nearly 100% faradaic efficiency of water oxidation. In the cases of Fe and Cr mixed oxide, not only current density but also O_2 evolution was improved than Fe_2O_3/FTO, although there were certain contributions of Cr^{3+} oxidation, with 10–30% faradaic efficiencies. It was also revealed by means of electrochemical impedance spectroscopy that charge transfer resistance in $Fe_{2-x}Cr_xO_3$ was lower than that in Fe_2O_3. From these results, it is concluded that the electrocatalytic activity of Fe_2O_3 for water oxidation is enhanced by Cr substitution that reduces the charge transfer resistance in the oxide bulk.

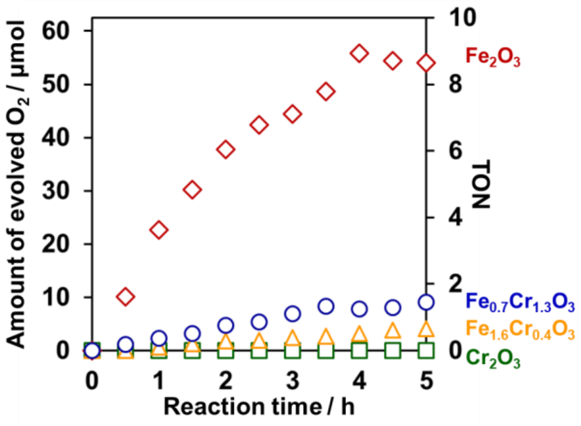

Figure 1. The time course of photochemical water oxidation using $Fe_{2-x}Cr_xO_3$ with Ru(II) photosensitizer.

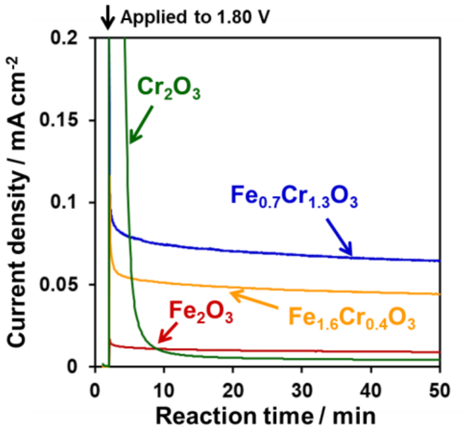

Figure 2. Current-time curves during potential controlled electrolysis under + 1.80 V RHE using $Fe_{2-x}Cr_xO_3$/FTO.

4. Conclusions[4]

The catalytic property of $Fe_{2-x}Cr_xO_3$ for water oxidation was investigated. From photochemical water oxidation, catalytic activity for water oxidation on the $Fe_{2-x}Cr_xO_3$ surface was decreased by Cr^{3+} substitution for Fe^{3+} in Fe_2O_3. On the other hand, in the electrochemical condition, water oxidation activity was enhanced with the substitution, because of the enhancement of charge transfer in oxide particles. Therefore, in the case of the Fe-Cr mixed oxide cocatalyst, the enhanced activity for water oxidation would result from improvement of charge transfer from the mixed oxide nanoparticle to water.

References

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