

Photocatalytic production of oxygen in a dual bed system using a reversible redox mediator on Ir-TiO₂ catalyst

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Abstract—Photocatalytic O₂ evolution by water splitting in an alkaline solution with a redox mediator was investigated in a dual bed system configuration: one bed was used for oxygen evolution and the other for hydrogen evolution. The employed photocatalyst was Ir-TiO₂ and the iodate ion, KIO₃, was used as a redox mediator. In order to find the optimum conditions for oxygen evolution, the effect of alkaline concentration, KIO₃ concentration and the amount of Ir loading on the photocatalytic reactivity was examined in an irradiation area of 0.055 m² reactor with a 400 W U.V. lamp. The experimentally obtained results showed that oxygen evolution depends on the concentration of the alkaline solution, the potassium iodate concentration and the amount of Ir loading.

Key words: Anatase, Iodate, Ir-TiO₂, Redox Mediator, Rutile

INTRODUCTION

Photocatalytic systems for the generation of H₂ and O₂ using semiconductors have received much attention, especially for their potential application to the direct production of H₂ from water [1-3]. The photoelectrochemical effect of a semiconductor originates from the creation of an electron and a hole following the absorption of light. Since the experimental findings of Fujishima and Honda on the splitting of water by photoelectrochemical cells [1], much effort has been made to construct efficient and practical systems based on this technique, and many semiconductor based systems have been built [2-4].

Generally, in semiconductor based systems, various novel metals are loaded on the oxide semiconductors as a co-catalyst in order to enhance the production of H₂ and O₂ from water by reducing the overpotential required for the water splitting reaction. Among these, the Ir co-catalyst is known to exhibit superior photocatalytic activity for oxygen evolution [5]. However, it is a known fact that Ir-loaded photocatalysts such as Ir-TiO₂ cannot split water into H₂ and O₂ in an aqueous suspension system, because of the existence of a significant backward reaction [6]. The dual bed configuration was first proposed by Linkous and Slattery [8]. In this approach, the photocatalytic system employs two modules, each consisting of a shallow, flat, sealed container, in which micron-sized photocatalytic particles are immobilized. An aqueous solution containing a redox mediator is pumped between the two chambers. Different photocatalysts are chosen for the respective modules, so as to bring about oxidative water splitting in one vessel, in order to evolve oxygen gas, and reductive water splitting in the other vessel, in order to evolve hydrogen.

We examined the possibility of using an Ir-TiO₂ photocatalyst with a redox mediator for the splitting of water to produce O₂ in a dual bed system where oxygen and hydrogen produced separate reactor under favorable condition. The photocatalytic activity of Pt-TiO₂ is much better than that of Ir-TiO₂ in case of water splitting using

sacrificial reactants [7]. However, as an oxidated redox mediator, Ir-TiO₂ showed better photocatalytic reduction ability than Pt-TiO₂.

In our previous work, the efficient evolution of hydrogen using a Pt-TiO₂ photocatalyst with an iodide/iodate (I⁻/IO₃⁻) redox mediator system was examined [9]. In this study, we selectively examined the photocatalytic activity of iridium-doped TiO₂ photocatalyst for oxygen evolution, using an iodide/iodate redox mediator system instead of sacrificial reagents in the tube type slurry reactor and also examined the effect of various parameters on the evolution of oxygen in a small module reactor in which the photocatalyst was precipitated on a quartz plate.

EXPERIMENTAL

1. Photocatalyst Preparation

Degussa P-25 titanium dioxide was used as the starting material for photocatalyst preparation. It was the mixed phase of TiO₂ powder with approximately 80 wt% anatase and 20 wt% rutile structure, consisting of spherical particles with an average diameter of 30 nm, and a measured BET surface area of 49±2 m²/g. The Ir-TiO₂ photocatalyst were prepared by impregnation of TiO₂ with an aqueous solution of IrCl₃ to give an Ir loading of 1.0 wt% by means of the reduction of the precursor. For instance, IrCl₃ (Aldrich, 0.78 g) was dissolved in 150 ml of distilled water and various TiO₂ powders (Degussa P-25, pure anatase or rutile powder, Aldrich 50 g) were dispersed in this solution, respectively. The solution mixture was stirred and 100 ml distilled water was slowly added. An equimolar sacrificial reagent (Merck, NaBH₄, 0.485 g in 10 ml D₂O) solution was added dropwise for the purpose of reducing the iridium. The resultant slurry, which was yellow color, was filtered and washed with distilled water. The precipitated catalyst was dried overnight in an oven at a temperature of 353 K.

2. Apparatus and Procedures

The oxygen evolution experiment was carried out in the pyrex glass reactor as shown in Fig. 1. The photocatalyst was immobilized on the quartz plate and placed at the bottom of the reactor. An aqueous solution of KOH (0.001 N-1.0 N) was employed as the elec-

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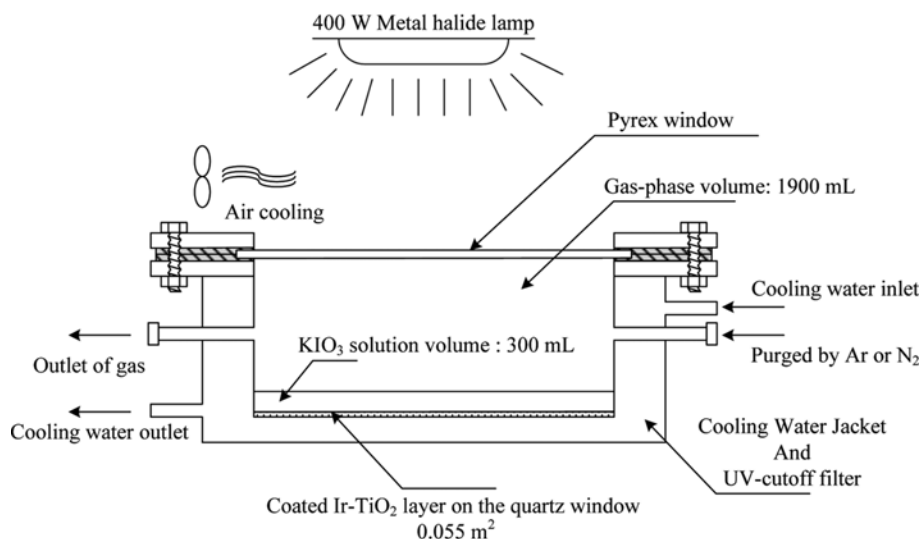


Fig. 1. Experimental set-up of employed photocatalytic reaction system.

trolyte and KIO_3 (1.0 mM-1.0 M) was used as the redox mediator. The reactor was purged with argon gas for more than 100 min and UV irradiation with a 400 W metal halide lamp was used to trigger the photocatalytic reaction. The evolved gas during the reaction was analyzed by gas chromatography every 30 minutes.

RESULTS AND DISCUSSION

1. Effect of Ir Loading on O_2 Evolution

Fig. 2 shows the effect of the Ir content on the oxygen evolution in the module reactor shown in Fig. 1. In case of the absence of Ir (only TiO_2), only a small amount of oxygen evolved during 10 hours. However, the oxygen evolution rate was sharply increased with in-

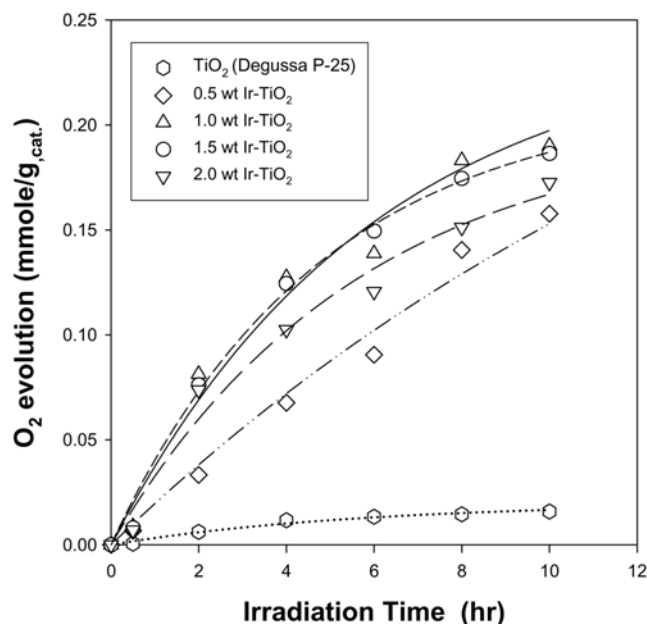


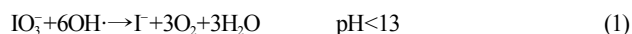
Fig. 2. Effect of Ir content on oxygen evolution. (Ir-doped TiO_2 1.0 g, 0.01 N KOH, 1.0 mM KIO_3)

creasing Ir content up to 1.5 wt% and then decreased thereafter. The reason for this trend is that the deposition of small amounts of Ir enhanced the removal of the photogenerated electrons from the TiO_2 , and enhanced the reduction of the IO_3^- ions. However, when the Ir content exceeded 1.5 wt%, a blockage of the photosensitive TiO_2 surface occurred, thereby decreasing the surface concentration of electrons and holes available for the reaction. Another possible reason for this result is that at higher metal loadings, the deposited metal particles may act as recombination centers for photogenerated electrons and holes [11].

2. Effect of KOH Concentration on O_2 Evolution

The effect of alkaline solution on the oxygen evolution rate was examined. In general, NaOH solutions have been used as the electrolyte for water splitting [6,10,12,13]. However, KOH solution is normally used in Ni- H_2 battery systems [14], because its high pH (e.g. over pH 10) facilitates the diffusion of hydroxyl ions and supports the reactions occurring at the photocatalyst. In addition, because the chosen redox mediator and electrolyte have the same cations (K^+), the effect of cations was removed. Therefore, KOH solution was chosen as the electrolyte for this study.

In this experiment, the effect of pH on the rate of oxygen evolution is shown in Fig. 3. It was observed that especially at pH 12 (KOH= 0.01 N), the oxygen evolution rates (Eq. (1)) was maximized. This indicated that there existed an optimum pH condition for oxygen evolution. The optimum pH seems to be determined by the competition between the influence of the concentration of OH^- and the backward reaction (Eq. (2)) that takes place over the oxidation sites of the photocatalyst [10,13,14].



3. Effect of KIO_3 Concentration on O_2 Evolution

Another important reaction parameter for oxygen evolution for the dual bed system was the redox mediator concentration, and the KIO_3 solution was employed as the redox mediator in this experiment. To evaluate the effect of KIO_3 concentration on the oxygen

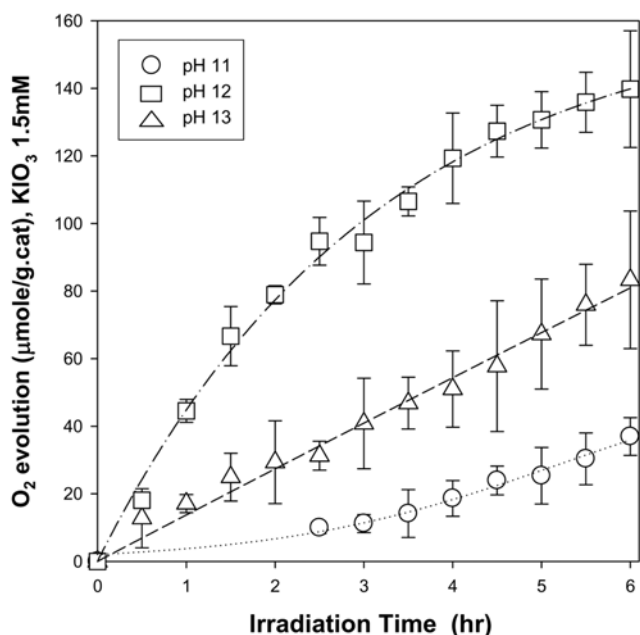


Fig. 3. Effect of the concentration of KOH on the oxygen evolution. (1.5 mM KIO₃ solution, 1.0 wt% Ir-doped TiO₂ 1.0 g)

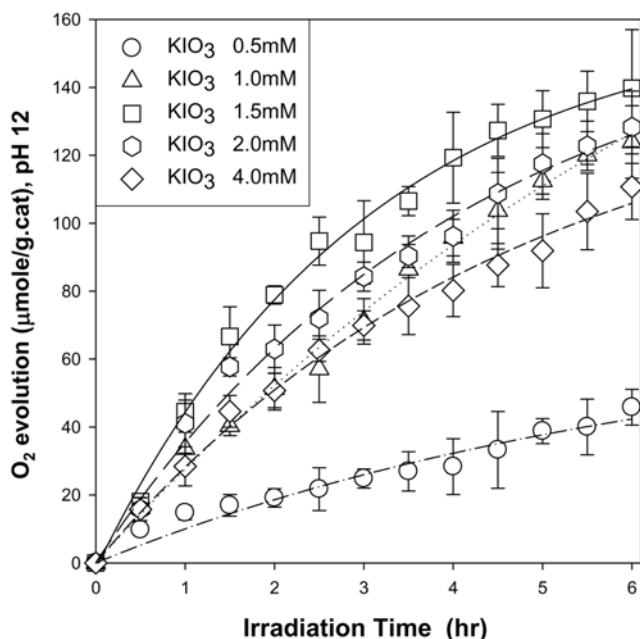


Fig. 4. Effect of the concentration of KIO₃ on the oxygen evolution. (0.01 N KOH solution, 1.0 wt% Ir-doped TiO₂ 1.0 g)

evolution, the concentration of KOH solution was fixed at pH 12. In this experiment, the KIO₃ concentration was varied from 0.5 mM to 4.0 mM. The effect of the KIO₃ concentration on the oxygen evolution is shown in Fig. 4, and it was found that 1.5 mM KIO₃ was the optimum concentration of KIO₃ for this experimental ranges.

As can be seen in Fig. 4, the oxygen evolution rate gradually decreased with the accumulation of the O₂ gases produced in the closed system due to the backward reaction. The IO₃⁻ anions, produced by the oxidation of I⁻, were reduced back to iodide ion (I⁻) by the

photocatalytically generated electrons at the oxidation sites of the photocatalyst. In general, the oxidation step of I⁻ ions is 10⁸ times faster than the reduction step of IO₃⁻ ions [16]. Therefore, the reduction of iodate ions (IO₃⁻) may be the rate-determining step in the water splitting reaction in this experiment.

In addition, the oxygen evolution over the anatase phase TiO₂ decreased with increasing concentration of the iodide (I⁻) ions produced by the reduction of the IO₃⁻ ions, as reported by Abe et al. [10,13]. As a result, the concentrations of the I⁻ and IO₃⁻ ions approached quasi-equilibrium in the electrolyte solution.

CONCLUSION

Photocatalytic oxygen evolution by water splitting in a dual bed system was investigated for the selective evolution of oxygen with Ir-TiO₂ catalyst. The photocatalytic evolution of oxygen in an alkaline solution with a redox mediator was carried out and the effects of various parameters on the oxygen evolution rate were determined. Within the operating ranges of this study, the effect of the concentration of KOH was examined and the optimum KOH concentration of 0.01 N was obtained. Secondly, the effect of KIO₃ concentration on the oxygen evolution rate was examined and the optimum concentration of KIO₃ for oxygen evolution was found to be 1.5 mM at the KOH concentration of 0.01 N. Finally, the optimum Ir-loading for oxygen evolution was found to be approximately 1.5 wt%.

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