

# Microwave Non-thermal Effect on Water Electrolysis using Planer $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> Electrode; Acceleration of Electron Transfer by 2.45 GHz Oscillating Electric Field

**Masayuki Matsuhisa,<sup>a</sup> Fuminao Kishimoto,<sup>a</sup> Satoshi Fujii,<sup>b</sup> Shuntaro Tsubaki,<sup>a</sup> Masato M. Maitani,<sup>b</sup> Eiichi Suzuki<sup>a</sup> and Yuji Wada<sup>a,\*</sup>**

<sup>a</sup>*Tokyo Institute of Technology, Tokyo, 152-8552, Japan*

<sup>b</sup>*National Institute of Technology, Okinawa College, Okinawa, 905-2192, Japan*

<sup>c</sup>*The University of Tokyo, Tokyo, 153-8902, Japan*

\*Corresponding author: +81-3-5734-2879, yuji-w@apc.titech.ac.jp

**Abstract:** Various microwave effects on chemical reactions have been reported. These effects are classified into thermal effects and non-thermal effects. Thermal effects arise from the temperature alternation caused by microwaves, whereas the mechanism of non-thermal effects are unknown. In this work,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> electrodes with different morphologies were fabricated on TiO<sub>2</sub> substrates by electrodeposition or pulsed laser deposition (PLD). We demonstrated the enhancement of water oxidation of some  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> electrodes under pulsed microwave irradiation. This current enhancement correlated with the microwave electric field intensity. We conclude that the difference in morphology is a determinant of electron transfer enhancement by microwave electric field.

**Keywords:** microwave chemistry, electron transfer, electrochemical, non-thermal effect, hematite

## 1. Introduction

The enhancement of various chemical reactions under microwave irradiation has been reported. These are called as microwave effects. These effects are classified as thermal effects, and non-thermal effects. The thermal effects can be caused by the temperature rise of the reaction field realized by the characteristics of microwave heating such as, rapid heating, internal heating, and substance-selective heating [1]. On the other hand, the mechanisms of the non-thermal effects are still unknown [2]. The elucidation of the principle and clarification of control factors on the non-thermal effects is a key factor for the control of chemical reactions using microwaves.

Recently, we have succeeded in demonstrating the microwave effect on the electron transfer process in the photocatalytic reaction [3]. In this report, the rate constant of electron transfer from CdS quantum dots to bipyridine derivatives was calculated by their emission lifetimes measurements, and the acceleration of electron transfer reaction under microwave irradiation was demonstrated. However, this was one and only observation of the microwave non-thermal effects on electron transfer reaction. Therefore, we need to simply and directly observe the electron transfer process and discuss the microwave-enhanced electron transfer reaction in more detail.

In this report, we used an electrochemical method to demonstrate the microwave acceleration of electron transfer reaction on the solid surface. We have observed the electrochemical water oxidation reaction on an  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-deposited rutile TiO<sub>2</sub> substrate electrode under 2.45 GHz microwave irradiation. A rate-controlling step of the water oxidation reaction is the electron transfer from  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to water. Therefore, a change of the current density in water oxidation reaction can directly be attributed to the rate of the electron transfer. We discuss the physical mechanism of the microwave non-thermal effect based on the interaction between the solid surface and the microwave electric field.

## 2. Experimental

Various  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> electrodes on rutile TiO<sub>2</sub> (100) plane substrates were fabricated by using electrodeposition or PLD. In electrodeposition,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> electrodes were synthesized from an aqueous solution containing 0.02 M FeCl<sub>2</sub> · 4H<sub>2</sub>O. Electrodeposition was potentiostatically performed at 75 °C for 12 min by applying 1.2 V vs Ag/AgCl. After each deposition, to obtain crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> electrodes, as-deposited films were annealed in atmosphere at 520 °C for 2 h. The heating rate was 2 °C /min. In PLD,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> electrodes were fabricated on rutile TiO<sub>2</sub> (100) plane substrates in the PLD chamber. The pressure in the PLD chamber was adjusted to 1 mTorr with continuous flow of oxygen. The growth temperature was set 650 °C. The  $\alpha$ -

Fe<sub>2</sub>O<sub>3</sub> films on rutile TiO<sub>2</sub> substrates with single orientation were verified by X-ray diffraction.

The microwave irradiation was performed using a waveguide type 2.45 GHz microwave resonator. This apparatus can separate the electric field (E field) and the magnetic field (H field) distribution in a waveguide. Main cell was placed into the microwave resonator and another cell outside of the microwave resonator, and microwaves are irradiated to only the main cell containing  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> electrode as shown in Figure 1. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> electrodes, a fiber-optic thermometer and a salt bridge were placed into the main cell in contact with aqueous solutions of 0.1 M NaOH electrolyte (pH=13). The coiled platinum wire as a counter-electrode and an Ag/AgCl (in sat. KCl solution) electrode as a reference electrode were placed into the another cell. The current profiles of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> electrodes were investigated at the potential where water is oxidized under pulsed microwave irradiation (~20 W).

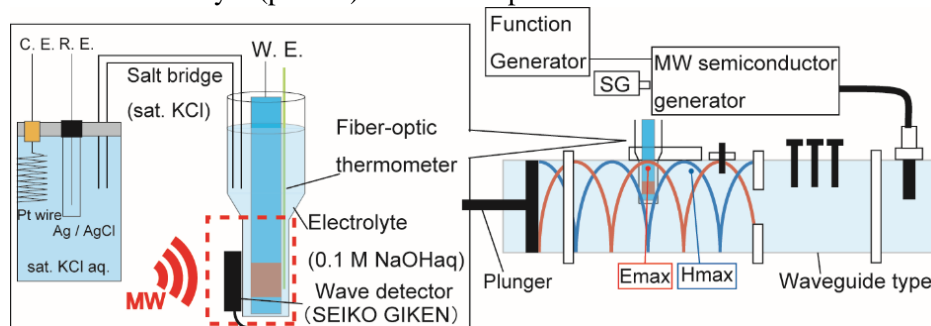


Figure 1. Schematic showing the details of the sample area

### 3. Results and discussion

Figure 2 shows the water oxidation current profile on each  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> electrodes under applied constant potential under microwave pulse irradiation. When inserting the main cell at the electric field maximum point in the waveguide and irradiating microwaves, the current value of water oxidation instantaneously increased. At this time, the rapid temperature rise of the bulk did not occur. Next, the difference of current increase shown in Figure 2 was plotted against the microwave E field intensity measured by optical E field sensor at the same time (Figure 3). The difference of current increase was linear to the microwave E field intensity.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> electrodes fabricated by electrodeposition or PLD were different in the difference of current increase. This phenomenon may be caused by the difference of crystal morphologies. From these results, we conclude that the microwave electric field non-thermally accelerates the electron transfer reaction.

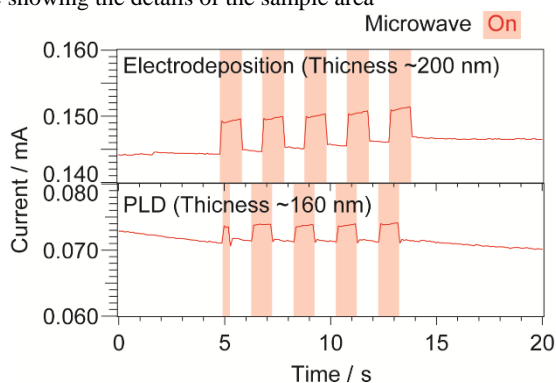


Figure 2. Water oxidation current profile under pulsed microwave irradiation

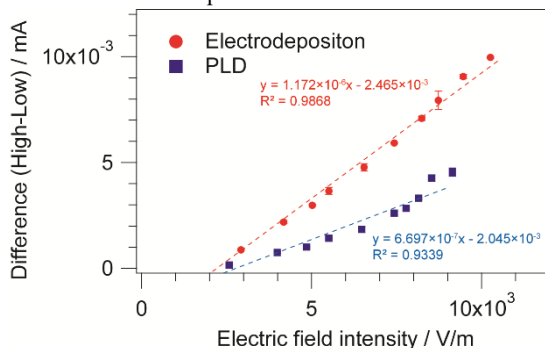


Figure 3. The electric field intensity dependence of the difference of current enhancement

### 4. Conclusions

We have successfully demonstrated enhancement of water oxidation current using  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> electrodes under pulsed microwave irradiation. The enhancement has a linear relationship with the microwave electric field intensity, showing a tendency of the different current increase depending on the deposition methods of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> electrodes. Therefore, changing the deposition state of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> crystals may be able to control the enhancement of electron transfer reaction by microwave oscillating electric field. This effect is understood as “non-thermal effects of microwaves”. This idea might be able to be extended to electron transfer reactions such as photocatalysis and organic reactions under microwave irradiation.

### References

1. D. Mochizuki, M. Shitara, M. Maitani and Y. Wada, Chem. Lett., 41, 1409–1411 (2012)
2. G. B. Dudley, R. Richert and A. E. Stigman, Chem. Sci., 6, 2144 (2015)
3. F. Kishimoto, T. Imai, S. Fujii, D. Mochizuki, M. M. Maitani, E. Suzuki and Y. Wada, Sci. Rep., 5, 11308 (2015)