Enhanced water oxidation over Ru-polyoxometalate by radio-frequency irradiation

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Abstract: Electromagnetic wave was used to enhance water oxidation over Ru-polyoxometalate. Radio frequency (RF) reaction system was first developed by connecting signal generator and GaN RF amplifier since Ru-polyoxometalate exhibit higher dielectric loss at lower frequency than conventional microwaves. The pulsed RF at 200 MHz was applied to anodic cell containing aqueous Ru-polyoxometalate which was connected to cathodic cell by salt bridge. The pulsed RF exhibited instantaneous increase in oxidation current while microwaves did not show clear enhancement. Higher oxidation current was obtained by replacing cation (Rb^+ and K^+) to H^+ due to high dielectric loss of H^+ at radio frequency.

Keywords: water oxidation, Ru-polyoxometalate, electromagnetic waves, radio frequency

1. Introduction

Water oxidation is a key process in efficient hydrogen production by water splitting. Electromagnetic waves can enhance chemical reactions by directly interacting with dipolar molecules and ions. Microwaves (MW; 2.45 GHz) has been widely investigated for enhancing various chemical reactions. Recently, we reported that pulsed microwaves at 2.45 GHz exhibit enhanced water oxidation over an α-Fe_2O_3 deposited electrode [1]. However, the dielectric property of materials are widely dependent on frequency of electromagnetic waves. For instance, water exhibit the highest dielectric loss at around 15 - 20 GHz while electrolytes exhibit elevated dielectric loss at relatively lower frequency below 1 GHz due to ionic conduction mechanism.

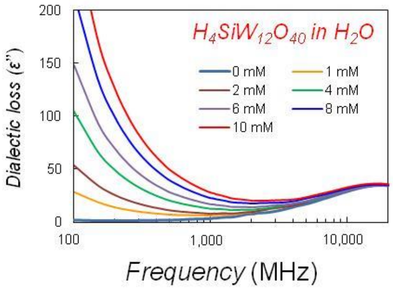

Figure 1. The dielectric loss of aqueous solutions of silicotungstic acid ($H_4SiW_{12}O_{40}$) in a frequency range between 100 MHz and 20 GHz.

Since polyoxometalates exhibit elevated dielectric loss at radio frequency (RF) band (Fig. 1), we developed RF reaction system to obtain more selective propagation of electromagnetic waves to the polyoxometalate catalysts than conventional microwaves. In this paper, we report enhanced water oxidation reaction over Ru-polyoxometalate by an applied RF at 200 MHz.

2. Experimental

2.1. RF reaction system: The RF irradiation system (Fig. 2A) was prepared by connecting signal generator (Keysight; 8648C) and GaN power amplifier (Mini Circuits; ZHL-100W-GAN+, frequency; 20-500 MHz, max output; 100 W). The parallel plate type applicator was constituted with two electrodes and impedance matching system using variable condenser. The RF power was continuously monitored by power monitor (Anritsu; ML2438A) and power sensor (Anritsu; MA2481A) connected to directional coupler.

2.2. Water oxidation over Ru-polyoxometalate under RF irradiation: Ru-polyoxometalate was prepared according to the previous report [2]. The cation of Ru-polyoxometalate was further exchanged from Rb^+ and K^+ to H^+ by proton exchange resin. Degree of cation exchange was measured by ICP-OES. Dielectric properties of Ru-polyoxometalates between 200 MHz and 8.5 GHz were determined by using the coaxial probe method. The anodic cell was placed inside the RF applicator and connected to cathodic cell by a salt bridge. Working electrode (ITO) was placed in between the RF parallel plates. The pulsed RF (5 sec, 5 – 20 W) was applied to anodic cell. The oxidation current at a given potential vs Ag/AgCl was monitored by potentio/galvanostat (Biologic, SP-200).

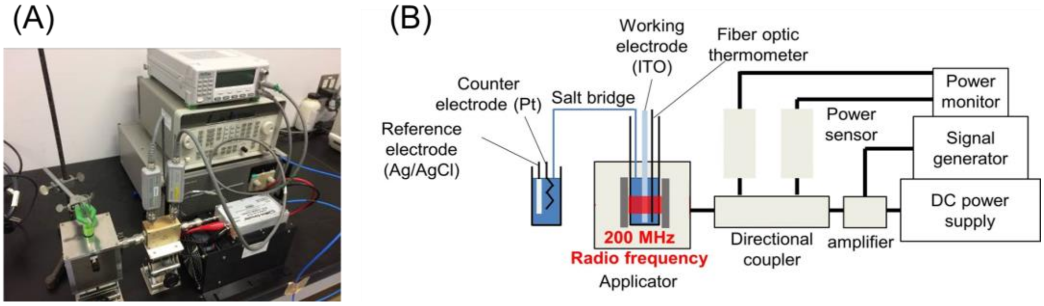

Figure 2. (A) RF reaction system (200 MHz) and (B) schematic diagram of electrochemical reaction under RF irradiation

3. Results and discussion

Ru-polyoxometalate gave increased microwave absorption (dielectric loss) below 1 GHz and cation exchange to H^+ further increased dielectric loss depending on the degree of cation exchange (Fig. 3A). For instance, Ru-polyoxometalate (9 H^+ type) gave 4.65-fold higher dielectric loss at 200 MHz (RF) than 2.45 GHz (MW). The RF absorption of Ru-polyoxometalate were strongly controlled by the cation of polyoxometalate. The pulsed RF at 200 MHz gave instantaneous increase in oxidation current which indicated the RF irradiation enhances the water oxidation reaction over Ru-polyoxometalate (Fig. 3B). The increment of oxidation current (Δj) exhibited linear correlation with the number of H^+ (Fig. 3C). In addition, the increment of oxidation current increased in correlation with applied RF power (Fig. 3D). The results indicated that enhancement of water oxidation activity could be controlled by the frequency of applied electromagnetic waves, the dielectric property of the Ru-polyoxometalate, as well as applied RF power.

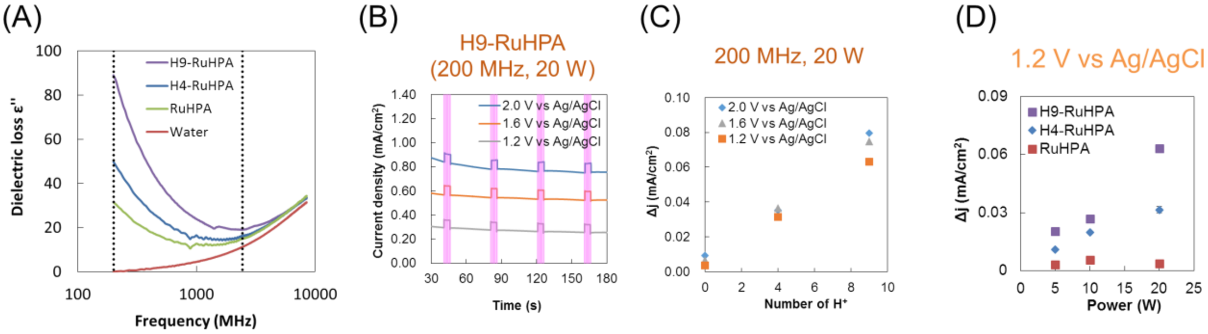

Figure 3. Dielectric property and water oxidation activities of Ru-polyoxometalates under RF. (A) Cation-dependent dielectric property of Ru-polyoxometalate. (B) Current density during pulsed RF irradiation. (C) Increment in water oxidation current during RF irradiation as a function of number of H^+ in Ru-polyoxometalate. (D) Increment in water oxidation current as a function of applied RF power.

4. Conclusions

This paper demonstrated the improvement of water oxidation activity of Ru-polyoxometalate by applied electromagnetic waves. RF at 200 MHz were found selectively propagates to Ru-polyoxometalate due to ionic conduction mechanism and exhibited enhanced water oxidation during pulsed RF irradiation. In addition, the dielectric property of Ru-polyoxometalate were found key parameters to control the water oxidation activity of Ru-polyoxometalate under RF irradiation.

References

1. Kishimoto et al., Sci Rep, 6, (2016), 35554.
2. Y. V. Geletii, et al., Angew. Chem., 120, (2008), 3960.