In situ heterogeneous OER catalytic reaction study using Sum-frequency generation (SFG) spectroscopy

Donghwan Kim[1,2], Kyungwon Kwak[1,2] and Minhaeng Cho[1,2]

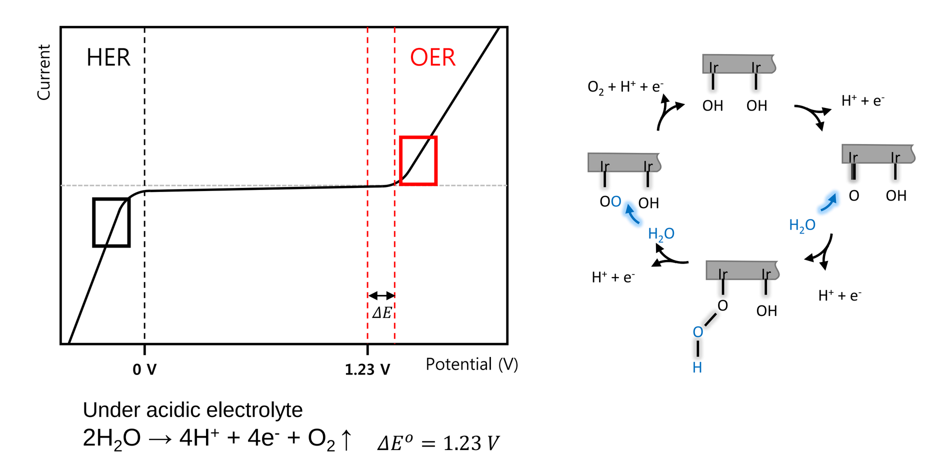
1. Center for Molecular Spectroscopy and Dynamics, Institute for Basic Science (IBS), Seoul 02841, Republic of Korea,

2. Department of Chemistry, Korea University, Seoul 02841, Republic of Korea

Abstract

Water oxidation is an essential reaction for energy storage such as forming of hydrogen or hydrocarbons without accumulation of by-product. Unfortunately, This reaction is consist of a complex multistep, which adds a considerably large overpotential to the actual process. Although many studies have been conducted on OER catalysts with low overpotential and high stability, the specific catalytic reaction mechanism has not yet been elucidated. To understand the nature of heterogeneous catalytic reaction mechanism in which the catalyst (Iridium) and water molecules participate in the reaction, it is important to use surface/interface selective spectroscopic method. Here, using vibrational sum-frequency generation (VSFG) spectroscopy, we selectively identified electrode-electrolyte interfacial molecules. We designed spectro-electrochemical (SEC) cell for in situ SFG experiment. In this work, using nonlinear spectroscopic method, we can observe that the hydrogen bonding network of the interfacial water molecules changes at each potential.

Water splitting reaction

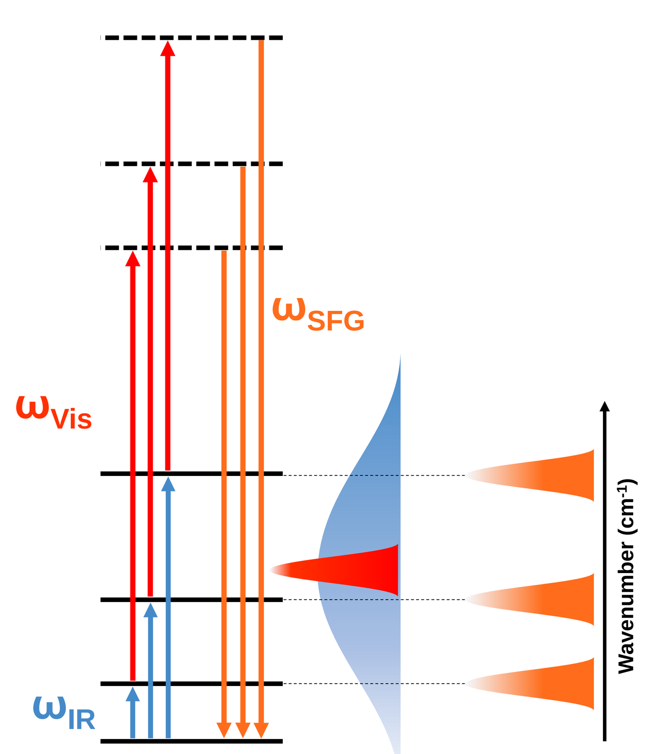


Under acidic electrolyte

$2H_2O \rightarrow 4H^+ + 4e^- + O_2\uparrow \quad \Delta E^0 = 1.23\ V$

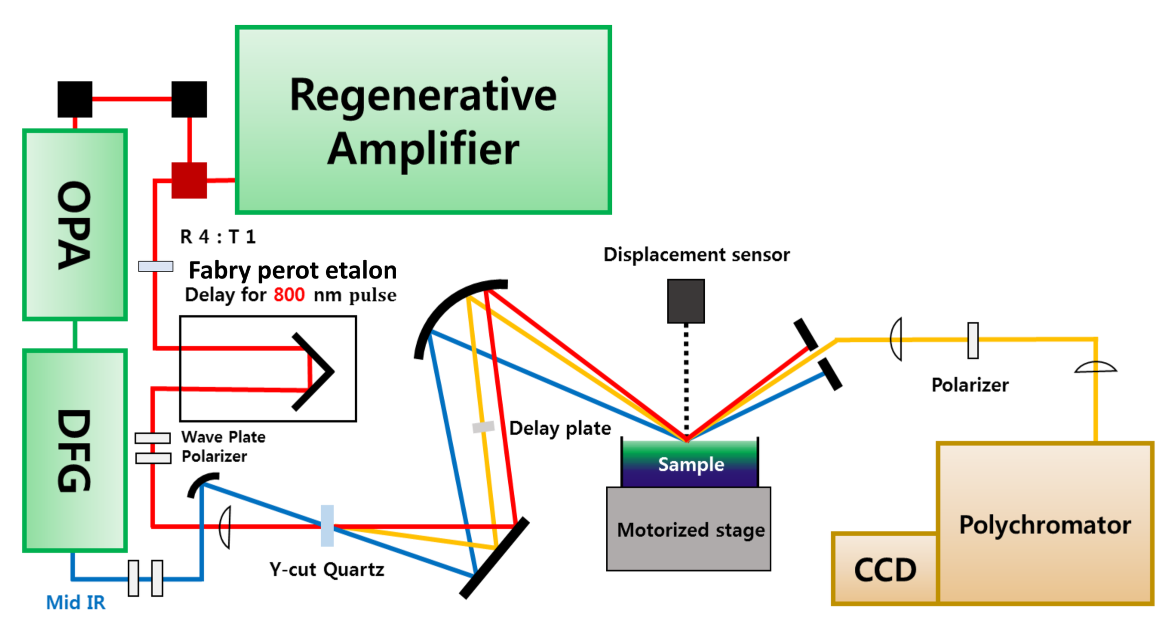
Experimental background

Concept of SFG



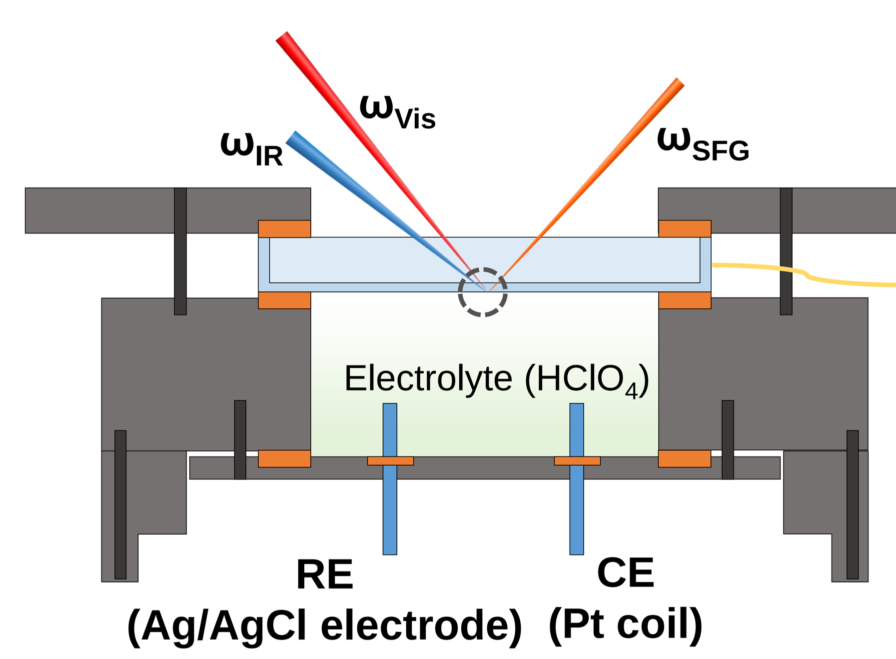
- ✓ The narrow band vis beam (800 nm) is just prerequisite for the second order nonlinear process.
- ✓ The broadband IR resonates with the vibrational mode of the sample.

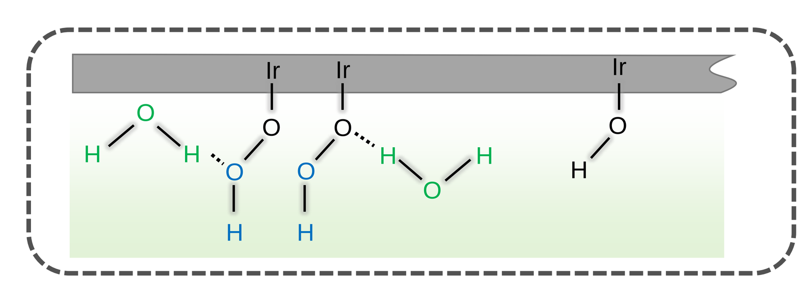
Experimental setup



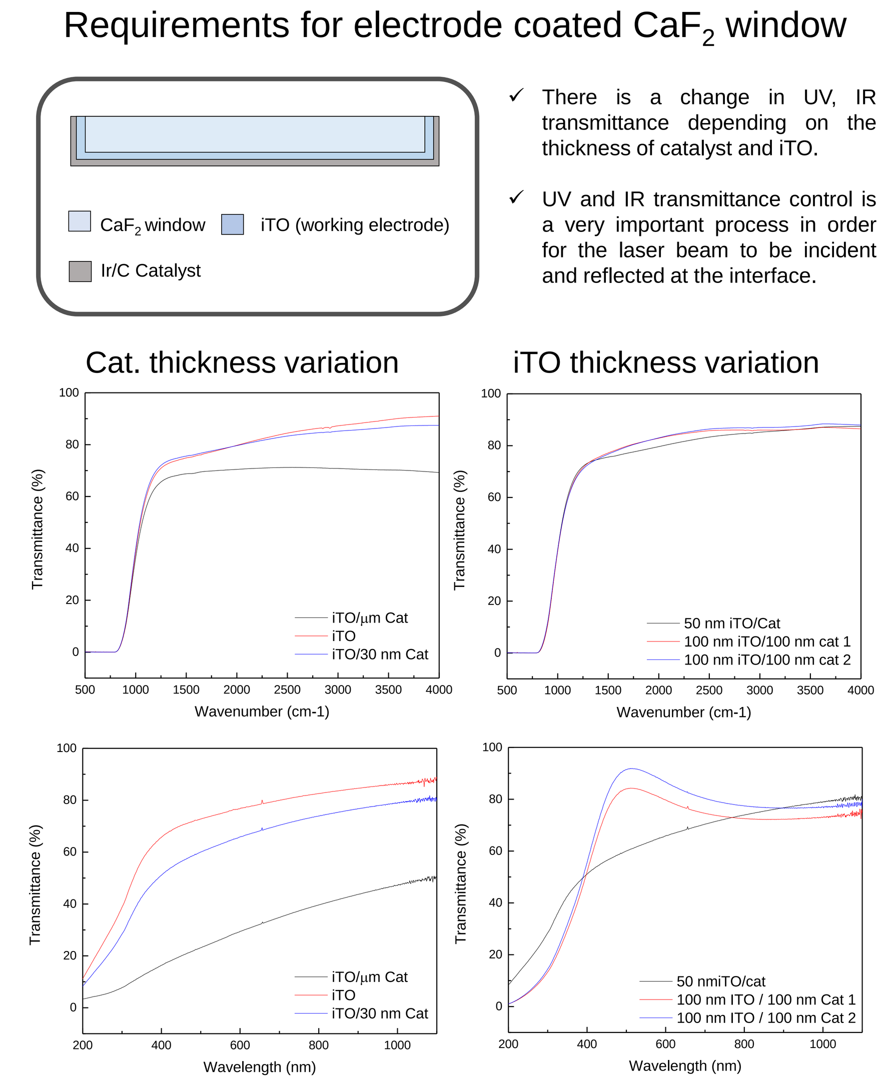
- ✓ 800 nm vis, tunable mid IR focused on sample stage and generate sum frequency signal.
- ✓ Using a displacement sensor, accurately measure the height of the sample stage to control the overlap between vis and IR.

In situ electrochemical cell





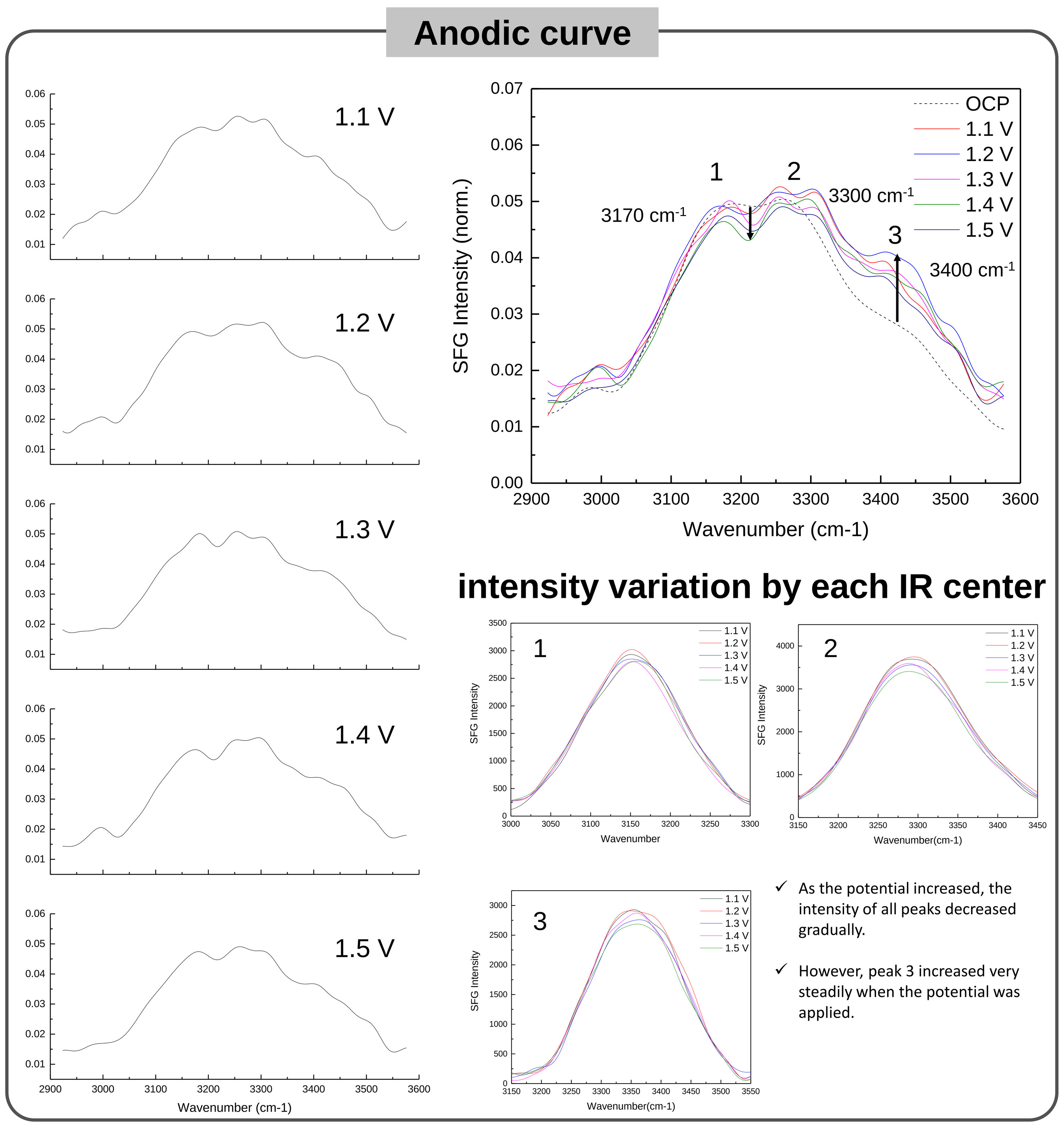
Requirements for electrode coated CaF_2 window



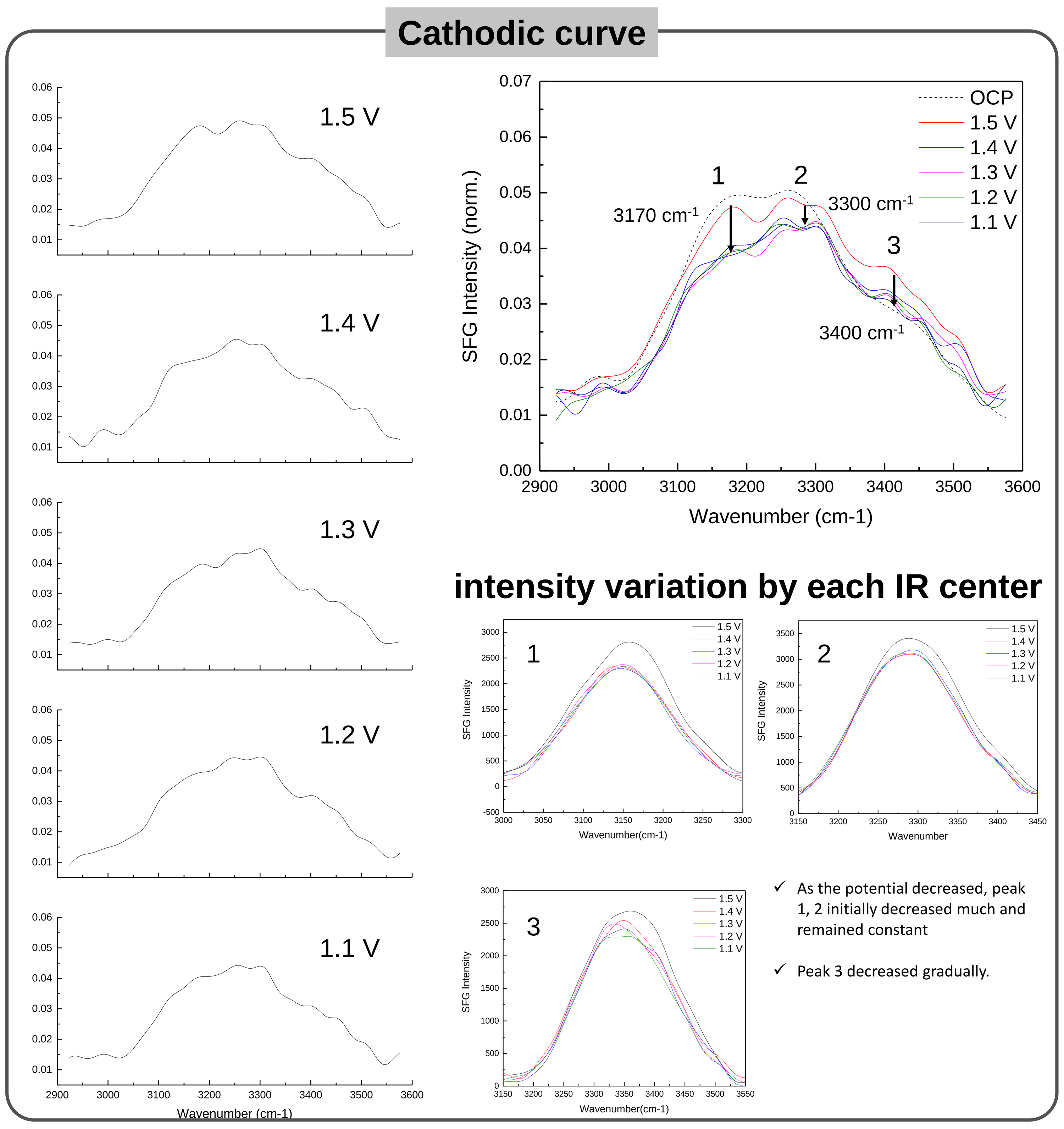
Experimental results

In situ heterogeneous catalysis experiment

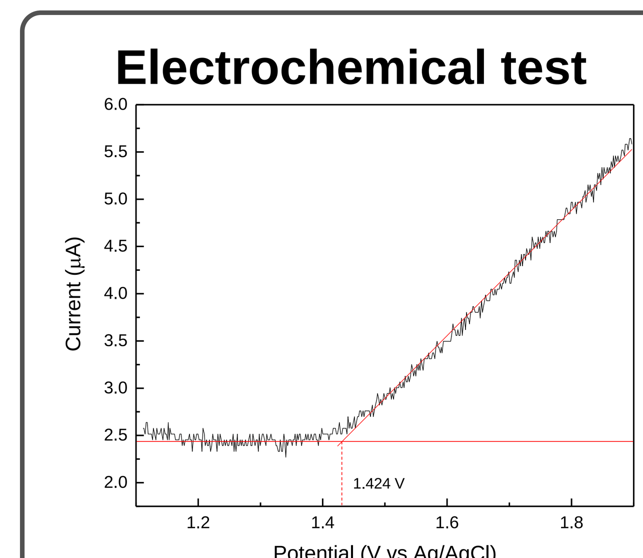
Anodic curve



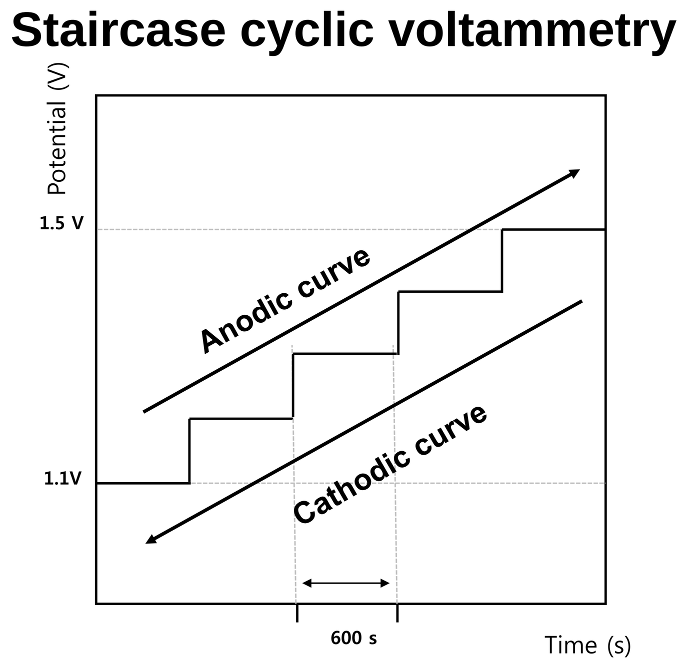
Cathodic curve



Electrochemical test



Staircase cyclic voltammetry



- ✓ Data acquisition time for each IR wavelength is 100 seconds.
- ✓ We used the SCV method to maintain a constant potential.

Summary

- ✓ As water is oxidized, the intensity of peak 1 and 2, which are strongly hydrogen bonded OH, decreased gradually and the intensity of peak 3, which is weakly hydrogen bonded OH, increased first and decreased.
- ✓ In cathodic curve, strongly hydrogen bonded OH component is reduced and remains constant and weakly hydrogen bonded OH component decreased.
- ✓ In the water oxidation reaction process, there is hydrogen bonding network variations.

Center for Molecular Spectroscopy and Dynamics, IBS-Korea University