

SFG study on potential-dependent structure of water at Pt electrode/electrolyte solution interface

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ABSTRACT

Structure of water at Pt/electrolyte solution interface was investigated by sum frequency generation (SFG) spectroscopy. Two broad peaks were observed in OH stretching region at ca. 3200 cm^{-1} and ca. 3400 cm^{-1} , which are known to be due to the symmetric OH stretching (ν_1) of tetrahedrally coordinated, i.e., strongly hydrogen bonded “ice-like” water, and the asymmetric OH stretching (ν_3) of water molecules in a more random arrangement, i.e., weakly hydrogen bonded “liquid-like” water, respectively. The SFG intensity strongly depended on electrode potential. Several possibilities are suggested for the potential dependence of the SFG intensity.

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1. Introduction

Interfacial water molecules play an important role in many physical, chemical and biological processes. Molecular-level understanding of the structural arrangement of water molecules at an electrode/electrolyte solution interface is one of the most important issues in electrochemistry. The presence of oriented water molecules, caused by an interaction between water dipoles and the strong electric field in the double layer, has been proposed [1–3]. It has been also proposed that water molecules are present at the electrode surface in the form of clusters [4,5]. Despite the numerous studies on the structure of water at metal electrode surfaces using various techniques such as surface enhanced Raman spectroscopy (SERS) [6,7], surface infrared spectroscopy [8,9], surface enhanced infrared spectroscopy (SEIRAS) [10] and X-ray diffraction [11,12], the exact nature of the structure of water at electrode/solution interface is still not fully understood.

Sum frequency generation (SFG) is a second-order nonlinear optical process, in which two photons of frequencies ω_1 and ω_2 generate one photon of sum frequency ($\omega_3 = \omega_1 + \omega_2$). The second-order nonlinear processes including SFG are inhibited in media with inversion symmetry under the electric dipole approximation and take place only at the interface between these media where the inversion symmetry is necessarily broken. By using visible light of fixed wavelength and tunable IR light as two input light source, SFG spectroscopy can be surface sensitive vibrational spectroscopy as

proved by Shen and co-workers [13,14]. SFG spectroscopy is particularly useful to study the structure of water molecules at various interfaces where presence of much larger amount of bulk water than interfacial water makes the measurement of interfacial water by other vibrational techniques very difficult [15–20]. Furthermore, SFG is free from the ambiguity associated to the choice of reference spectrum and can avoid the necessity of working with a rough electrode as required for SEIRAS and SERS. Thus, SFG spectroscopy is an ideal technique to investigate the structure of the water at metal electrode/electrolyte solution interfaces [21–26].

Tadjeddine and co-workers applied SFG spectroscopy to investigate Pt single and poly crystalline electrode/electrolyte solution interfaces in external reflection mode with thin electrolyte solution layer. They reported that SFG peaks corresponding to water dimers bonded to three hydrogen terminals on Pt (Pt-H) by hydrogen bonding at Pt/H₂SO₄ solution interfaces [21]. They also mentioned that SFG signal in OH stretching was quite weak in perchlorate solution and proposed that water in hydration shell predominates the interfacial water [23,24].

We examined the structure of water at Au/10 mM H₂SO₄ solution interface under potential control in internal reflection mode using a thin gold film electrode [25]. A broad band centered around 3500 cm^{-1} with a shoulder around 3250 cm^{-1} was observed, indicating that water molecules at Au electrode are rather weakly hydrogen bonded, i.e., disordered. It was also found that the SFG intensity of the OH stretching becomes minimum at the pzc and increases as the potential becomes more negative or positive than the pzc but the orientation of the water molecules at Au electrode does not flip when the charge of the electrode changes its sign because sulfate anion is adsorbed on the Au electrode when the

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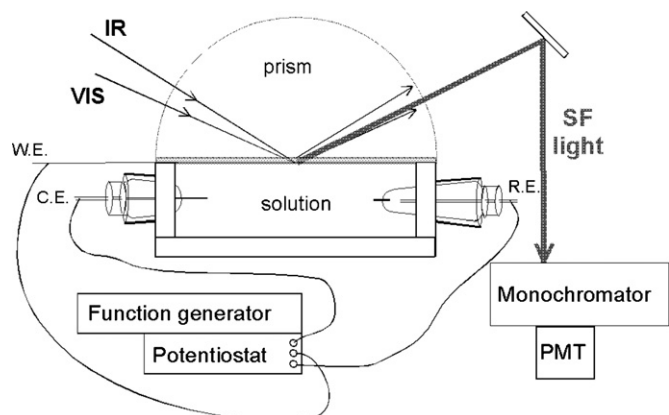


Fig. 1. Schematic diagram of a spectroelectrochemical cell and measuring arrangement used in the present study to detect SFG signal at metal/electrolyte solution interface.

potential of the electrode is more positive than the potential of zero charge (pzc), resulting in the net surface charge to be negative.

Gewirth and co-workers observed four different OH stretching mode in SFG spectra at Ag(100)/0.1 M NaF solution interface under potential control measured in external reflection mode and assigned them to (1) weakly hydrogen bonded water, (2) strongly hydrogen bonded water, (3) water specifically adsorbed on the Ag surface, and (4) hydronium cation, H_3O^+ , which was observed only at potential near the pzc [26].

Here, we measured the potential-dependent SFG spectra at a Pt thin film electrode/0.1 M HClO_4 solution interface in internal reflection mode. In contrast to the spectra at the gold electrode, two broad peaks were observed in OH stretching region at ca. 3200 cm^{-1} and ca. 3400 cm^{-1} , which are known to be due to the strongly hydrogen bonded, i.e., “ice-like”, water and the weakly hydrogen bonded, i.e., “liquid-like” water, respectively, suggesting that water is more highly oriented at the Pt electrode than at the Au electrode. Parabolic behavior of SFG intensity was observed between -200 and 600 mV with a minimum around 200 mV , which is close to the pzc of the Pt electrode in HClO_4 solution. The SFG intensity of OH stretching decreased as potential became more positive in a Pt oxide formation region ($>600\text{ mV}$).

2. Experimental

The SFG system used in the present study was described in detail elsewhere [18]. Briefly, a picosecond Nd:YAG laser (EKSPLA, PL2143B) with a 25-ps pulse width and repetition rate of 10 Hz was employed to pump an OPG/OPA/DFG (EKSPLA, PG401VIR/DFG) system, which generates tunable infrared pulses. The loosely focused visible (532 nm , $100\text{ }\mu\text{J/pulse}$) and IR ($2800\text{--}3800\text{ nm}$, $100\text{ }\mu\text{J/pulse}$ at 3000 nm) beams were overlapped at the sample surface. The incident angles of the visible and IR beams were about 70° and 50° , respectively. The SFG signal was separated from the reflected visible and IR pulses by passing through irises and a monochromator (Oriel instruments, MS257) and was detected by a photomultiplier tube (Hamamatsu, R3896) and normalized to the intensities of the IR and visible pulses. Temporal and spatial overlaps were adjusted by monitoring the SFG signal from a quartz plate. The polarization of SFG, visible and IR beams are all p.

Electrochemical measurements were carried out using an internal reflection type spectroelectrochemical cell made of Kel-F as shown in Fig. 1. Before use, cell was cleaned in H_2SO_4 bath in order to minimize organic contaminants, followed by rinsing with Milli-Q. An Ag/AgCl (saturated NaCl) and a Pt wire were employed

as a reference electrode and a counter electrode, respectively. Ten nanometer thick Pt films evaporated on IR-grade fused quartz hemi cylindrical shaped prism (Daico MFG Co., Ltd.) with a 5 nm Ti buffer layer was used as a working electrode. XPS measurements clearly showed that there was no Ti or Ti oxide at the surface. The electrolyte solutions were prepared using reagent grade HClO_4 (Wako Pure Chemicals) and purified water provided by a Milli-Q system (Millipore Inc.) and deaerated by bubbling high-purity Ar gas (99.999%) for at least 30 min prior to the spectroelectrochemical measurements. The electrode potential was controlled with a potentiostat/function generator (Toho Technical Research, PS-07).

The electrode potential, current, and SFG signal were recorded by using a personal computer (DELL, Dimension 3000) through a 13-bit AD converter (Stanford Research System, SR245). All the measurements were carried out at room temperature (ca. 22°C).

3. Results and discussions

Fig. 2 shows a typical cyclic voltammogram of a thin Pt film electrode in a 0.1 M HClO_4 solution. The hydrogen waves in the potential range between -250 and ca. 50 mV were observed and surface oxidation and reduction peaks were observed in positive potential region ($>600\text{ mV}$). This result confirmed that the conductivity of the Pt thin film was good enough to be used as an electrode.

Fig. 3 shows SFG spectra in OH stretching region ($2800\text{--}3800\text{ cm}^{-1}$) obtained at the Pt electrode in a 0.1 M HClO_4 solution at various potentials. Two broad peaks were observed in contrast to the report by Tadjeddine and co-workers. This maybe due to the difference in the experimental configuration as strong IR absorption by water layer, although it was very thin, made the SFG measurements in OH stretching region very difficult in external reflection mode employed by Tadjeddine's group. Two broad peaks were observed at ca. 3200 cm^{-1} and ca. 3400 cm^{-1} . This is in contrast to the result obtained at the Au electrode in HClO_4 solution where only one broad band centered around 3500 cm^{-1} was observed [27]. The peaks at around 3200 and 3400 cm^{-1} have been assigned to the vibration of OH oscillators of three coordinated hydrogen bonded water i.e., less ordered “liquid-like” water, molecules and that of the four coordinated hydrogen bonded water, i.e., highly ordered “ice-like” water molecules, respectively, based on the IR study of water clusters [28]. Thus, the intensity ratio between these two peaks can be considered as an index of the order of the interfacial water [29]. These results suggest that water molecules at Au surface are less ordered than those at Pt surface. Although there is no spectroscopic evidence to show

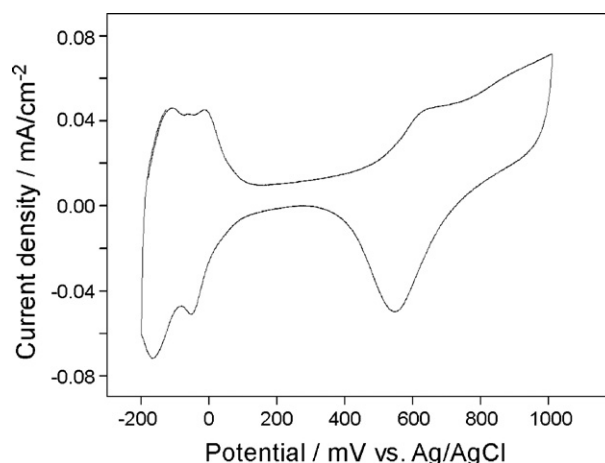


Fig. 2. Cyclic voltammogram of a Pt thin film electrode in 0.1 M HClO_4 solution. Sweep rate: 50 mV/s .

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