In Situ Surface-enhanced Raman Analysis of Water Libration on Silver Electrode in Various Alkali Hydroxide Aqueous Solutions

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ABSTRACT

Water libration on a silver electrode in various alkali hydroxides (MOH, M = Li, Na, K or Cs) aqueous solutions was examined through simultaneous experiments using surface-enhanced Raman scattering (SERS) and electrochemical analysis. This technique, referred to as SERS spectroelectrochemistry, reveals the Raman spectral band between 200 and 750 cm⁻¹, assignable to water libration on the electrode surface, through electrode potential scanning. The Raman intensity in this spectral band changes with the electrode potential. The variation in Raman intensity of water libration observed when scanning the electrode potential is discussed in terms of water molecules at the electrode interface in various alkali hydroxide aqueous solutions.

1. Introduction

In electrochemistry, it is often necessary to conduct both experimental and theoretical investigations, including analysis of the standard electrode potential, the electric double layer, the diffusion layer, the diffusion coefficient of the ion, and thermodynamic parameters. The accumulation of this vast array of electrochemical data forms the basis of contemporary research on electrochemical devices such as batteries, capacitors and fuel cells. The electric double layer in aqueous solutions composes solvated ions and water molecules, additionally and occasionally composes specifically adsorbed atom and contact adsorbed atoms. Considering the electric double layer in aqueous solution, one of the fundamental issue is the dynamical motion of water molecules at the double layer region. In order to investigate this issue, focusing the vibration of water molecules at the double layer region is necessary. The vibration of water molecules includes several vibrating modes; translation, libration, bending vibration, stretching vibration and so on. Specially, the libration of water molecules may decide the water structure at the double layer.

Spectroscopy has progressed remarkably in the last three decades. Advances in spectroscopic analysis have been driven primarily by the need to clarify how surface physical chemistry, such as catalysis and corrosion, are involved in chemical reactions. Raman and FTIR spectroscopy provide high energy resolution, making these techniques a good choice for the measurement of vibrational spectra. The investigation of surface properties by spectroscopic analysis of electrochemical reactions emerged in the early 1990s as the fields of spectroelectrochemistry and electrochemical surface science. In situ Raman spectroelectrochemistry is a powerful tool for investigating electrochemical reactions. Our group has used this technique to identify electrochemical reactions on the anode and cathode of lithium-ion batteries, and near the interface between electrodes and electrolyte solution in fuel cells and molecular electronics devices. This combination of high-resolution Raman spectroscopy and electrochemical analysis has also proved to be advantageous for studying reactions in the interfacial reaction field between electrodes and electrolyte solution.

Surface-enhanced Raman scattering (SERS) has been widely used since 1974 to study the microscopic features of surfaces. In SERS, the Raman intensity of molecules adsorbed on the electrode surface increases by a factor of 10⁵ to 10⁶ compared with that for free molecules. A number of recent in situ SERS studies have examined features related to electrochemical reactions in redox reactions on electrodes, oxygen reduction reactions, and reactions of water and organic molecules adsorbed on Ag electrodes in aqueous solutions. Furthermore, we have reported a dynamical investigation of water molecules adsorbed on Ag electrodes in alkali hydroxide solutions with respect to the behavior of HOH bending vibration in the oxygen reduction reaction on Ag electrodes. Recently, Ambrosio et al. have investigated the characterization of water structure on Ag electrode by SERS. This report has revealed that the two-dimensional correlation spectra for water libration modes on Ag electrodes. The two-dimensional correlation spectra have suggested that water structure around alkaline ions depends on alkaline metal. Further analysis of the libration band for water molecules on Ag electrodes is required.

The present study investigates the behavior of water molecules on the surface of a Ag electrode by SERS spectroelectrochemistry and focuses on the dynamical changes in the Raman spectra of water libration at the interface between the electrode and the electrolyte solution at various electrode potentials in alkali hydroxide aqueous solutions.

2. Experimental

Details regarding the apparatus for in situ Raman spectroelectrochemistry used in the present analysis are provided elsewhere. An Ar ion laser beam (514.5 nm) was used to excite the Ag electrode. The laser beam was incident on the Ag working electrode surface at an angle of about 60° upon passing successively through several optics. The flat sapphire plate of the optical window of the electrochemical cell transmitted light scattered from the electrode.
surface, which was collected by an achromatic lens and focused on the entrance slit of a single-stage spectrometer (Jobin-Yvon) before pre-reduction of Rayleigh light by Raman notch filters (Kaiser Optical Systems). Raman spectra were obtained using a highly sensitive charge-coupled device (CCD) detector (Jobin-Yvon). This Raman system captured spectra over a typical range of several wavenumbers at each electrode potential. The dark current from the CCD detector was calculated by switching the scattered light on and off by a mechanical shutter, and the resulting value was subtracted from the measurement data. The data acquisition period for each spectrum during the in situ measurements was 6 s.

The electrochemical cell used in the present study was specially designed for in situ Raman spectroelectrochemistry. A polycrystalline Ag disk (99.999%, \( \varphi = 10 \times 2 \) mm), used as a working electrode, was mounted on a polychlorotrifluoroethylene rod. The effective area of the electrode in contact with the electrolyte was 0.21 cm\(^2\). A mirror surface on the electrode was obtained by acid etching in 10% HNO\(_3\) aqueous solution and ultrasonication in Milli-Q water. Air in the cell was purged using pure Ar gas before acquiring the cyclic voltammograms and ultrasonication in Milli-Q water. In the air cell was purged using pure Ar gas before acquiring the cyclic voltammograms and in situ Raman spectra. A Pt wire and a Ag/AgCl electrode were employed as the counter electrode and reference electrode, respectively. In this study, the electrode potential is given relative to the Ag/AgCl electrode in the aqueous system. In cyclic voltammetry, the potential of the Ag electrode was swept cyclically between \(-1.4\) and 0.8 V at a rate of 5 mV/s using a potentiostat (Solartron). No gas evolution from the Ag electrode was detected in this potential range. Alkali hydroxide aqueous solutions were prepared from high-purity reagents (99.95% LiOH, 99.99% NaOH, 99.99% KOH, 99.9% CsOH; Aldrich) and Milli-Q water. In the analysis using D\(_2\)O as a solvent, D\(_2\)O with purity of 99.75% was used to ensure that the isotope shifts in the Raman spectra could be resolved. The electrolyte concentration was set to 0.5 mol dm\(^{-3}\) throughout the experiments.

3. Results and Discussion

Before in situ experiments, we examined the Raman spectra of bulk water molecules in detail. Figure 1 shows Raman spectra for liquid (a) H\(_2\)O and (b) D\(_2\)O. In (a), the broad Raman band observed around 3300 cm\(^{-1}\) is included in the OH symmetric (3210 cm\(^{-1}\)) and asymmetric (3430 cm\(^{-1}\)) stretching vibrations.\(^{24}\) The medium Raman line observed at 3605 cm\(^{-1}\) shows concentration dependence. Thus, it was concluded that the Raman intensity for libration might increase with increasing alkali metal and OH\(^{-}\) concentrations.

Figure 2 shows cyclic voltammograms of the Ag electrode in 0.5 mol dm\(^{-3}\) LiOH aqueous solution measured over several oxidation and reduction cycles (ORCs). Qualitatively similar cyclic voltammograms were obtained for NaOH, KOH and CsOH aqueous solutions (data not shown). Additionally, we obtained similar cyclic voltammograms in all cases of alkali hydroxides dissolved in D\(_2\)O instead of in H\(_2\)O. The anodic current responses at (a) 0.45 V and (b) 0.68 V were followed by the cathodic current responses at (c) 0.35 V and (d) 0.02 V. The anodic current responses correspond to the oxidations (a) Ag \(\rightarrow\) Ag\(_2\)O and (b) Ag\(_2\)O \(\rightarrow\) AgO, while the reduction of silver oxides corresponds to (c) Ag\(_2\)O \(\rightarrow\) Ag\(_2\)O and (d) Ag\(_2\)O \(\rightarrow\) Ag.\(^{27-29}\) In this cyclic voltammogram, the current responses were found to increase gradually over successive ORCs, which is attributable to the increased roughness of the Ag electrode surface caused by repeated potential cycling.

Figure 4 represents the variation of the in situ Raman spectra of the Ag electrode in an aqueous solution with 0.5 mol dm\(^{-3}\) NaOH. Overlaying Raman lines of water molecules in Fig. 4, we note the characteristic feature of Raman lines in the frequency range of 2700–3000 cm\(^{-1}\) with potential scanning between \(-0.6\) and \(-1.0\) V. These Raman lines seem to be assignable for C-H stretching vibration of organic compounds in very low concentration. When organic compound adsorbed on Ag surface, SERS intensity from organic compounds is quite strong.\(^{30}\) SERS provides ultrasensitive
detection limits allowing detection and structural identification of single molecules. This means SERS can detect very low concentration impurity from the out of the experimental circumstances. In a series of experiments for the adsorption of water molecules on Ag in our previous reports, the observed electrode potential range is between $0.8$ and $1.4 \text{ V}$, also the observed electrode potential for adsorption oxygen molecules on Ag is between $-0.1$ and $-0.7 \text{ V}$, respectively.\(^2\) The adsorption of organic compounds with potential scanning between $0.6$ and $1.0 \text{ V}$ is not effective for the adsorption of water and oxygen molecules on Ag due to the difference of the electrochemical potential for the adsorption of molecules.

In Fig. 5, (a) and (b) present the variation in the in situ Raman spectra of the Ag electrode in a solution of LiOH in (a) H\(_2\)O and (b) D\(_2\)O in the frequency range of 200–1200 cm\(^{-1}\) with potential scanning between $-0.792$ and $-1.38 \text{ V}$ and between $-0.60$ and $-1.50 \text{ V}$ in cyclic voltammetry, respectively. Potentials outside these ranges resulted in roughening of the Ag electrode surface after several ORCs and were considered suitable for examination of the SERS effect. The intensity in the Raman band between 450 and 850 cm\(^{-1}\) gradually increased with decreasing potential [Fig. 5(a)]. In Fig. 5(b), which shows the results when using D\(_2\)O instead of H\(_2\)O, the intensity in the Raman band between 380 and 650 cm\(^{-1}\) increased gradually with decreasing potential. The Raman frequency in these two Raman bands was altered by the isotope effect due to the difference in mass between H and D.23 Considering the absence of detectable impurities in ion-exchange chromatography, flame atomic absorption spectrometry and inductively coupled plasma analysis, these Raman bands are almost identical to those for the libration of H\(_2\)O and D\(_2\)O molecules on the electrode surface.

Figures 6–8 show the variation in the Raman spectra acquired for solutions of NaOH, KOH and CsOH in H\(_2\)O and D\(_2\)O, respectively. The intensities of these in situ Raman spectra for libration at 450–850 cm\(^{-1}\) for H\(_2\)O and 375–650 cm\(^{-1}\) for D\(_2\)O in Figs. 5–8 gradually decrease together with the ionic radius of the alkali metal ion.

Next, we discuss the increase in Raman intensity with decreasing potential and the decrease in Raman intensity with decreasing ionic radius of the alkali metal ion, which indicates species dependence. According to a previous report, the Raman intensity for bending
vibration of HOH adsorbed on an electrode surface is dependent on electrode potential. It is interesting to see that the intensity of the Raman lines starts to increase at about $-0.8 \text{ V}$, which correspond to the potential zero charge, and becomes higher at more negative values of the electrode potential. This dependence of the Raman intensity is attributed to a difference in the number of water molecules sandwiched between the electrode and the outer Helmholtz plane and/or a difference in the hydration number of the cation. The hydration number decreases with increasing ionic radius for alkaline metal. With decreasing electrode potential, alkali metal ions are getting close to electrode surface with hydrated water molecules. Therefore, observed SERS intensity for water libration mode depends on alkali metal ions. Another possible explanation is the increase in concentration of alkali metal at the electrode/electrolyte interface with changing electrode potential, since the Raman intensity for libration increases with increasing alkali metal and OH$^-$ concentrations (Fig. 2). However, the absence of any appreciable increase in Raman intensity for CsOH solutions seems to indicate that Cs ions are not hydrated but rather contact-adsorbed onto the Ag surface.

4. Conclusion

We investigated the behavior of water molecules on a Ag electrode interface by SERS spectroelectrochemistry, focusing on the dynamical changes in the Raman spectra of water libration at the interface between the electrode and the electrolyte solution at various electrode potentials in alkali hydroxide aqueous solutions. The species dependence of the Raman intensities is attributed to a difference in the number of water molecules sandwiched between the electrode and the outer Helmholtz plane and/or a difference in the hydration number of the cation. In situ SERS spectroelectrochemistry proved useful for investigating the electrochemical behavior at the interface between electrode and electrolyte solution.

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