Spectroscopic Investigation of High Pressure Hydrogen Evolution Reaction

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The water molecules at the electrode interface play a crucial role in the electrochemical reactions. However, the relationship between the interfacial structure and the reaction efficiency is still under discussion.[1] Surface-enhanced Raman scattering (SERS) observations could be the powerful tool to get insight of interfacial water structure.[2,3] Recently, at the nanostructured surface, we have reported that the unique isotopic selectivity on the hydrogen evolution reactions (HER) could be observed.[4] In this study, we have conducted electrochemical SERS measurements at the nanostructure interface in the mixture solution of D_2O and H_2O to probe the HER process under static pressure control, enabling to reduce the bubble effects. Through attempts, we have obtained detail information about the electrode interface during HER.

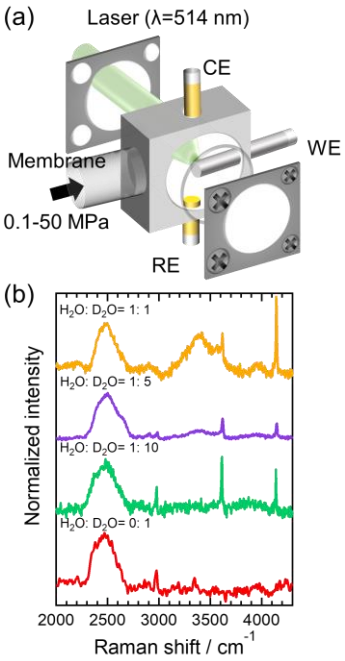

Fig. (a) Schematic picture for electrochemical SERS measurements under static pressure control. (b) Electrochemical SERS spectra of H_2, HD, and D_2 obtained in 0.5 M $NaClO_4$ aq. at 50 MPa. Each mixed ratio of H_2O and D_2O is indicated in the figure. The electrochemical potentials for each spectrum were (orange, green) −1.11 and (purple, red) −1.31 V vs. RHE.

SERS spectra were obtained at roughed Ag electrode in the three-electrode cell under static pressure at 50 MPa (Fig. a). Fig. b shows SERS spectra of the mixture solution of D_2O and H_2O with different mixed ration at HER potential region. The vibrational modes of H_2, HD, D_2 modes were observed at 4149, 3618, and 2964 cm^{-1}, respectively. Each band intensity ratio indicates the relative amounts of evolved gases at interface. The OH and OD stretching modes of interfacial molecules were also observed at 2500 and 3400 cm^{-1}, respectively. Interestingly, although the band intensity ratio of the stretching mode reflects the bulk components, each production ratio shows distinct values. This difference reflects the kinetic information about the isotopic selectivity of HER at the nanostructured interface. As the result, we have evaluated correlation between water and HER by static pressured electrochemical SERS.

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