

The New Distributions of Water Molecules at Ni(111)-2x2-O and Cu(111) Electrode Interfaces

Masatoki Ito^a, Masashi Nakamura^b, ^a*Department of Chemistry, Keio University,* ^b*Chiba University, Japan.* E-mail: masatoki@chem.keio.ac.jp

[I] The structures of a monomeric water molecule adsorbed on $p(2\times 2)$ -Ni(111)-O surface were determined by difference Fourier calculations (unique reflection intensities observed are 120(140K) and 80(25K)). At temperatures of 25 K, water molecules chemisorb predominantly at 2×2 oxygen atom sites, forming an OH---O_{ad} (2×2) hydrogen bond. A 2×2 oxygen atom (O_{ad}) is surrounded by one to three monomeric water molecules, which take statistically disordered positions with threefold symmetry. At temperatures of 140 K, monomeric water molecules occupy a top site of Ni atoms via an oxygen lone pair and are stabilized as a singleton molecule on the surface with a distance of 0.2241(22)nm.

[II] Further, we report surface X-ray scattering measurements result of the water distribution perpendicular to a Cu(111) electrode in 0.05M H₂SO₄ solution at -0.40V(vs, NHE). The new water phase on Cu(111) was found with a space group, P3m1, a=b=0.31nm, c=0.63nm, Z=3, $\rho=1.62(\text{g}/\text{cm}^3)$. The important features of the water distribution are (1) the network structure is a simple closest pack type and not a honeycomb or a diamond-like structure, (2) oxygen positions of water molecules show continuous disordering in time and space (fluctuating), (3) configuration around oxygen is not a tetrahedral but a three (or six) coordination. Proton (electron) transfer across water double layer could be facilitated by flipping of water molecule toward the electrode surface.

Keywords: water adsorption, water double layers, new water structure