Comparison of STM Barrier Heights on HOPG in Air and Water

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Electron transfer between metal electrodes through water is an important process in electrochemistry. There have been theoretical predictions[1,2] that water molecules are ordered at a charged interface, which facilitates/impedes electron transfer in aqueous solutions. A study of surface X-ray scattering[3] shows that not only the extent of the ordering of water molecules but also the distance between the electrode and the first water layer depend on the polarity of the electrode potential.

Scanning tunneling microscopy (STM) enables us to directly investigate the electron transfer reaction near an electrode surface region. By measuring tunneling current (I_t) as a function of the distance between the tip of the probe and the electrode surface, tunneling barrier heights at the electrode can be determined. Various experimental results have shown that the apparent tunneling barrier height is significantly lowered in electrolyte solutions, compared with the height in UHV.[1,2,4-6] Recently, electron tunneling characteristics across an aqueous STM capacitor junction were studied[1,2] by measuring the tunneling current and local barrier height as a function of the junction distance and applied bias voltage for HOPG, Au, and TaTe$_2$ surfaces in air. The results show unusually low tunneling barrier heights. However, the experimental values of barrier heights measured in air and in electrolyte solutions suffer from wide scattering, ranging between 2 eV and a few meV.[4] Representative examples are shown in Table 1.

Although these barrier heights measured in electrolyte solutions and humid atmosphere can provide useful insights into the role of water molecules in tunneling processes, it is still necessary to examine the effect of water based on an experiment performed in pure water rather than on water in the atmosphere or solutions. To our best knowledge, there have been no experimental studies of tunneling barrier height on HOPG in water.

In the present work, we use a Pt/Ir tip both in air and water. The results of STM tunneling barrier heights for HOPG are compared with previously reported values.

Experimental Section

The experiments were performed using a Nanoscope E Scanning Probe Microscope (Digital Instruments, Santa Barbara, CA) in ambient atmosphere. The Pt$_{0.8}$/Ir$_{0.2}$ tip was coated with Apiezon wax. HOPG was used as a sample and fresh layers of HOPG were obtained by peeling off a few layers before each experiment. Prior to each tip-approach experiment, the surface was scanned in a constant height mode and atomic resolution was obtained with a tunneling resistance of *ca.* 4×10^8 Ω. Tunneling current (I$_t$)-displacement (z) measurements were performed by first setting the tip 2 nm away from the initial tunneling position, then approaching the tip toward the surface at a rate of 220 nm/s until the tip returned to the tunneling position. I$_t$ was monitored at 256 points within the 2 nm distance and each I$_t$-z plot was obtained by averaging 100 measurements.

Results and Discussion

When a square potential is assumed, the tunneling conductance, I_t/V_t, can be written as

$$I_t/V_t \propto \exp(-s\sqrt{\varphi}) \quad \text{(in eV and Å)} \tag{1}$$

where I_t and V_t are the tunneling current and voltage, respectively, φ is the local barrier height, and s is the tip-surface (gap) distance. Experimental barrier height $\varphi_{\exp}$ is described by Eq. (2),

$$\sqrt{\varphi}_{\exp} = -d\ln I_t/dz = -(d\ln I_t/ds)(ds/dz) = (ds/dz)\sqrt{\varphi} \tag{2}$$

where dz is the tip displacement. $\varphi_{\exp}$ can be calculated using Eq. (2) by measuring tunneling current as a function of tip displacement, z.

The current was measured in air while pushing the tip toward the sample surface until the tunneling position was reached, and the data were plotted for $\ln I_t$ versus z. The curve shown in Figure 1 was obtained by averaging 15 I_t-z plots. The experimental barrier height in tunneling range (equilibrium barrier height) was calculated by taking the slope near $z=0$, which corresponds to the initial tunneling position where the atomic STM image was obtained. The

Table 1. Tunneling barrier heights quoted by other authers along with present works' results

	tip	substrate	conditions	barrier height (eV)	reference
1	W, Pt-Ir	HOPG, Au, TaTe$_2$	in air	0.6-1.5	1, 2
2	Au	Au(111)	0.5 M NaClO$_4$	0.04	4
3	W	Ag	UHV	2	5
			heating in UHV to 100 °C	0.05	
4	Pt-Ir	Ag(111)	0.01 M HClO$_4$	0.1-0.6	6
5	Pt, W	Au	in water	0.5	7
6	Pt-Ir	Au(111)	0.4 M NaClO$_4$	1.07	8
			0.01 M HClO$_4$	1.00	
7	Pt-Ir	HOPG	in air	0.6	this work
			in water	0.1	

Notes

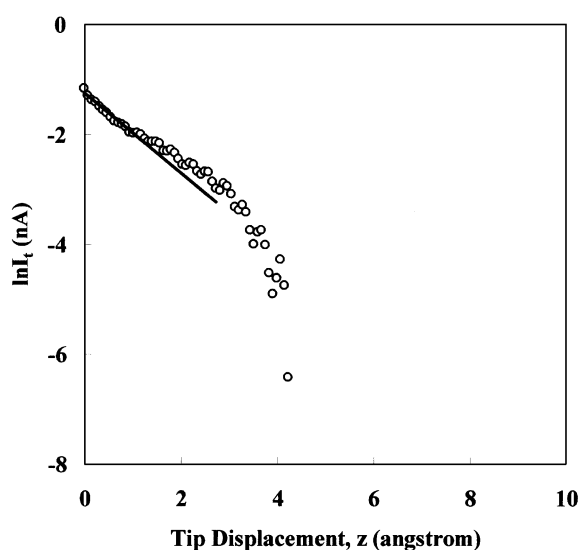*Bull. Korean Chem. Soc.* **2000**, Vol. 21, No. 6   645

Figure 1. Experimental tunneling current measured in air as a function of the tip displacement, z. The tunneling current is shown on a logarithmic scale. $z = 0$ corresponds to the equilibrium tunneling position where atomic STM image was obtained at sample bias voltage $V_s = 110$ mV and tunneling current $I_t = 293$ pA. The solid line was drawn for a visual guide and the slope was taken to calculate the equilibrium barrier height.

Figure 2. Experimental tunneling current measured in water as a function of the tip displacement, z. The tunneling current is shown on a logarithmic scale. $z = 0$ corresponds to the equilibrium tunneling position where atomic STM image was obtained at sample bias voltage $V_s = 115$ mV and tunneling current $I_t = 230$ pA. The solid line was drawn for a visual guide and the slope was taken to calculate the equilibrium barrier height.

calculated equilibrium barrier height is $\varphi_{air} = 0.6$ eV, which is similar to the value (0.6-1.5 eV) reported for W tip at a HOPG surface for large s in air.[1,2] The onset of the current increase occurs at around 4 Å away from the equilibrium tunneling position ($z=4$ Å).

Water was introduced to the electrochemical STM cell and an atomically resolved STM image was obtained. The tip-approach experiment was carried out in the same manner mentioned above. Figure 2 shows the plot for $\ln I_t$ versus z. The equilibrium barrier height calculated from the slope measured in the proximity of $z=0$ is 0.1 eV (φ_{water}) and the current increase commences at around $z=7$ Å.

There have been other studies on tunneling barrier height in electrolyte solutions. Linsay *et al.*[7,8] reported equilibrium barrier heights between ~1 eV and 1 meV on gold surface, which are independent of the medium or tip metal used. They attribute the anomalously low barrier height to the existence of insulating adsorbate layers on a dirty surface and mechanical distortions that finally lead to the reduction of tunneling barrier. Since the HOPG surface was freshly prepared before each experiment and the cleanness of the surface was ensured by taking atomically resolved STM topography images, the possibility of surface contamination can be excluded in the present study.

A plausible explanation for the reduced barrier height may be found in previous reports that suggest the role of water layers accumulated on the sample surface. There have been experimental and theoretical studies implying that the lowering of tunneling barrier heights in air can be attributed to the water layers condensed from atmospheric moisture between the tip and sample surface (STM junction).[1,2,9,10] As shown in Figures 1 and 2, the absolute value of the instant slope
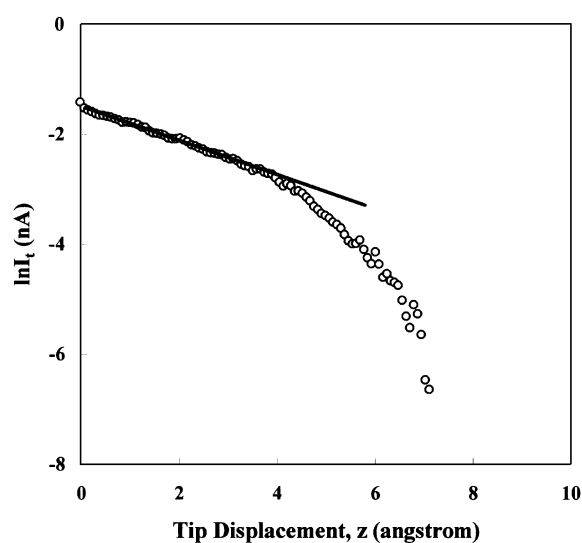
($|d\ln I_t/dz| = -d\ln I_t/dz$), which can be related to the instant barrier height as $\varphi = (-d\ln I_t/dz)^2$ using Eq. (2), decreases gradually as the tip approaches the sample surface and reaches its minimum value at $z=0$ (equilibrium barrier height). The barrier heights obtained in the present work are much lower than vacuum values. These low equilibrium barrier heights, φ_{air} and φ_{water}, are consistent with the experimental and theoretical results previously reported,[1,2,11] in which it is suggested that the three-dimensional nature of electron tunneling mediated by water molecules, *i.e.*, the existence of water facilitating electron tunneling in the applied electric field inside the STM junction, gives rise to the lowered barrier height in humid atmosphere, necessarily accompanying the increase in the tunneling distance.

Assuming the same resistance upon tip-surface contact as the one reported by Kang *et al.*[2] (W tip-HOPG in air), the equilibrium tunneling distance was estimated for the present experiment. The tunneling resistances both in air and water were calculated and used to estimate the equilibrium tunneling distances. The equilibrium tunneling distance was estimated to be *ca.* 9 Å in water, whereas an *ca.* 2 Å shorter distance was revealed in air. The equilibrium tunneling distances estimated in the present work are larger than those measured in UHV (3-5 Å) and it is consistent with the previously reported values (7-20 Å).[2] The electric field strengths inside the STM junction were calculated using the estimated tunneling distances and found to have similar values, 1.6×10^8 V/m and 1.3×10^8 V/m in air and water, respectively. The slightly different values appear to indicate the difference in the extent of polarization of water molecules near the surface. The degree of polarization of water molecules is expected to be larger near the surface than near the tip due to

646   *Bull. Korean Chem. Soc.* **2000**, Vol. 21, No. 6

Notes

the asymmetric nature of the STM junction. Under the positive sample bias, as in this experiment (see figure captions), more compact water layers are formed by higher electric fields, leading to the less efficient through-space electron tunneling. The difference in the equilibrium barrier height measured in this experiment can be ascribed partly to this polarization effect of water.

In atmospheric humidity, the condensation of water molecules should depend on the hydrophilicity of the surface. Heim *et al.*[9] have found that the adsorbed water layer can be pulled up to several hundred Å on the hydrophilic Pt/C surface, but no comparable effect is observed on Au surface, which is less hydrophilic. Note that the onset of the current increase in water, as shown in Figure 2 ($s = 16$ Å, $z = 7$ Å), is observed at the position farther from the surface than that measured in air, as shown in Figure 1 ($s = 11$ Å, $z = 4$ Å). Since HOPG is not very hydrophilic compared with other metals such as Au, TaTe$_2$, the thickness of the water layers condensed from the atmosphere would be limited in air. In water, on the other hand, thicker water layers can be formed on the HOPG surface. Therefore, the enhancement of tunneling probability by thicker water layers explains the different position of the onset of the current increase.

Summary

We examined experimental STM barrier heights for a Pt/Ir-HOPG system both in air and water to substantiate previous results. The electron tunneling in water commences at a longer distance from the sample surface than in air. The instant barrier height decreases gradually as the tip approaches the surface and reaches the minimum near $z = 0$, or the equilibrium tunneling position. The measured equilibrium barrier heights are 0.6 eV and 0.1 eV in air and water, respectively, which are an order of magnitude lower than vacuum values (3-5 eV). The lower barrier height and larger tunneling distance in water are ascribed to the formation of thicker water layers, resulting in the higher probability of three-dimensional electron tunneling between the tip and surface.

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