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Analysis of the Production of Hydrogen from Alcohol from an Energy-Exchange Perspective

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This paper analyzes hydrogen production from alcohol with a pair of electrodes from an energy-exchange perspective. The electric energy between the electrodes was transformed into the kinetic energy of the emitted electrons and alcohol molecules for inducing their collisions. The collision caused the decomposition of alcohol molecules and the dissociation of hydrogen ions. The hydrogen ions were attracted to the negative electrode and produced hydrogen molecules during the electrode's electrical neutrality. Application of the classical electromagnetic theory was useful for understanding the series of reactions from an energy-exchange perspective.

Introduction

In this paper, we discuss the production of hydrogen, which is directly accomplished from liquid alcohol placed on a pair of electrodes. Three reaction steps are required for the production of hydrogen: (1) the dissociation of hydrogen ions from alcohol molecules, (2) the rapid electrical neutralization of the hydrogen ions at the negative electrode, and (3) the composition of hydrogen molecules from the ions. The reaction should be conducted in a restricted area for maximum effectiveness.

Analysis of the reactions between a pair of electrodes from an energy- and momentum-exchange perspective is useful for visualizing and understanding the core of plasma-induced reactions.[1−5] In particular, analysis of the roles of electrons in each reaction step reveals different features of plasma-induced reactions. Considering the energy exchange in the electric field, electrons and alcohol molecules between the electrodes elucidate the dissociation mechanism of hydrogen ions from alcohol molecules. Momentum exchange and conservation are important factors that should be considered for understanding the electric force acting on the surface of the alcohol placed on the electrode.

In this report, we assume that an electron is a particle with mass and charge, and the electrical interaction with other charged particles is expressed as a collision. In addition, we represent the electric field with electric lines of force for visualizing the field and the motion of the electrons moving along the field.

In the next three sections, we analyze the dynamics of the electric field, dielectric molecules, and liquid between the pair of electrodes.

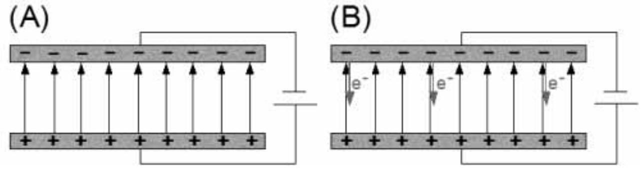

Figure 1. Electric field between a pair of electrodes in air. (A) Electrostatic field represented by the electric lines of force between the pair of parallel electrodes. (B) Random and violent electron emissions along the electric lines of force in air.

Dynamics between the Electrodes. The energy and momentum of the electric field, electrons, and molecules are exchanged between the electrodes.[1,2] Figure 1A represents a pair of parallel electrodes. When electrons are distributed between the electrodes, an electric field is generated. The field is represented by the electric lines of force. The lines of force are directed from the positive to negative charges. Since an electric line of force stores ${}^1/_2E$ (where E is the magnitude of the electric field) of electric energy per unit length, the density of electric energy between the electrodes is represented as[1,2]

$$U' = {}^1/_2\vec{E}\cdot\vec{D} \tag{1}$$

Here, U', $\vec{E}$, and $\vec{D}$ are the density of the electric energy (J/m^3), the electric field (V/m), and the electric flux density (1/m^2), respectively. Therefore, the total electric energy between the electrodes, U (J), is represented as

$$U = \frac{Q^2h}{2\epsilon S} \tag{2}$$

Here, Q is the total electric charge on the electrode (C), ϵ is the dielectric constant between the electrodes (C^2/N·m^2), h is the distance between the electrodes (m), and S is the area of the electrodes (m^2). In this analysis, electrons are assumed to be uniformly distributed on the electrodes.

Equation 2 shows that the total energy between the electrodes is a linear function of the square of the electric charge on the electrodes, Q^2, and the distance between the electrodes, h. The energy also linearly decreases as a function of the dielectric constant, ϵ, and the area of the electrode, S.

An electric line of force generates tension of E and pressure of ${}^1/_2E$ on the line. Therefore, the electric force acting along the electric line of force is represented by the Maxwell tensor below.[1,2] Here, T_n, T_{ik}, and n_k represent the n component of the

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$$T_n = T_{ik} n_k$$

$$T_{ik} = E_i D_k - U\delta_{ik} \tag{3}$$

Maxwell tensor, which is the electric force per unit area (N/m^2); the *ik* component of the Maxwell tensor (N/m^2); and the *k* component of the normal vector on the surface, respectively. D_k and δ_{ik} respectively represent the *k* component of the electric flux density and Kronecker's delta, which extracts a diagonal component of electrostatic energy, *U* (J), in eq 3. The electric force acting between the electrodes is then represented as

$$T_n = \frac{Q^2}{2\epsilon S} \tag{4}$$

Equation 4 shows that the electric force between the electrodes increases as the square of the electric charge on the electrodes, Q^2. The electric force decreases linearly with the dielectric constant, ϵ, and the area of the electrode, *S*.

According to eq 2, the electric energy between the electrodes is squared when the amount of electrons on the electrodes increases linearly. However, the electrodes can store only a certain amount of energy between them. Therefore, from the law of energy conservation, the extra energy must be transformed to other forms of energy. As we know, the energy is released as an electron emission from a negative electrode and flows to a positive electrode. In this case, the electric energy of the electric field is transformed to the kinetic energy of the electrons (Figure 1B).

The emitted electrons induce a magnetic field that generates an electric field. The continuous generation of such fields produces an electromagnetic wave. The wave propagates in space with an energy flow, which is represented by the pointing vector. Therefore, it is reasonable to assume that some kinetic energy of the emitted electrons propagates beyond the electrodes as the pointing vector. However, the electromagnetic energy does not propagate beyond the electrodes because the pointing vector, $\vec{S}$, is defined by the outer product of the electric field and the electric flux density, which is represented below.[1,2]

$$\vec{S} = \vec{E} \times \vec{D} \tag{5}$$

Equation 5 shows that the generated electromagnetic wave propagates toward the "electrons' current" itself. Therefore, the law of energy conservation is not violated when electrons are emitted between the electrodes.

However, if electrons are emitted in air, the electrons' kinetic energy is consumed during the collision between electrons and molecules. The molecules will be dissociated when the emitted electrons provide sufficient dissociation energy.[4−7]

The molecules between the electrodes significantly affect electron emission. When electron emission is generated in a vacuum, electrons are gently and uniformly emitted from the negative electrode. The required energy is just a work function of the electrode, which is an eigenvalue of the electrode. In contrast, electron emission in the air is achieved by a drastic and uncontrolled electric discharge. This originates from the electric insulation of the air. A large amount of energy is required to break down the insulation, and the energy is immediately released as the kinetic energy of the electrons once the insulation breaks down. This results in a violent electric discharge from specific points on the negative electrode, making it difficult to generate a gentle and uniform electron emission in air.

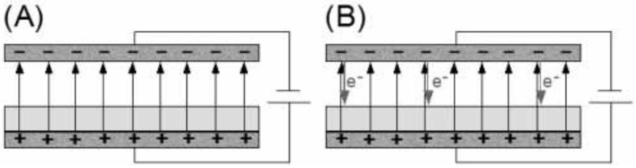

Figure 2. Quasi-positive electrode in air. (A) Electric field between the parallel electrodes with dielectric liquid applied to the positive electrode in air. (B) Random and violent electron emission onto the liquid placed on the positive electrode in air.

Application of a Liquid to the Electrode. Applying a dielectric or conductive liquid to the positive electrode causes the emitted electrons and the molecules composing the liquid to collide. Figure 2A represents a pair of electrodes with dielectric liquid applied to the positive electrode. If the electrons on the electrodes are distributed the same as in Figure 1A, then the same number of electric lines of force is generated. Therefore, the same electric flux density, $\vec{D}$ (1/m^2), is induced between the electrodes. However, the dielectric liquid affects the intensity of the electric field, $\vec{E}$ (V/m), and the field in the liquid area is represented as

$$\vec{D} = \epsilon_1 \vec{E} \tag{6}$$

Here, ϵ_1 represents the dielectric constant of the liquid (C^2/N·m^2). The electric field above the liquid (in air) is identical to that in Figure 1A.

The discontinuity of the electric field on the surface of the liquid is caused by the difference of the dielectric constants for the liquid and air. The difference generates the electric force on the liquid surface. The electric force is represented by the discontinuity of the Maxwell tensor on the liquid surface and is represented below.[2]

$$\{T_n\} = -\frac{1}{2}(\epsilon - \epsilon_1)\left\{\frac{{D_{\mathrm{n}}}^2}{\epsilon\epsilon_1} + {E_{\mathrm{t}}}^2\right\}\vec{n} \tag{7}$$

Here, $\{T_n\}$, D_{n}, and E_{t} represent the discontinuity of the Maxwell tensor (N/m^2), the normal component of the electric flux density (1/m^2), and the tangential component of the electric field (J/m^3) on the liquid surface, respectively.

Equation 7 indicates that if the dielectric constant of the liquid, ϵ_1, exceeds that of air, ϵ, the discontinuity of the Maxwell tensor becomes positive. This generates a tension on the liquid surface and the surface is electrically attracted to the negative electrode. In contrast, a pressure will act on the liquid surface if the dielectric constant of the liquid is less than that of the air.

In general, the dielectric constant of the liquid exceeds that of air, and the liquid surface is pulled toward the negative electrode (Figure 2A). Therefore, the surface density of the dielectric liquid decreases slightly in the electric field. This may release molecules composing the dielectric liquid. However, once the dielectric molecules are released from the liquid surface, the electric field will not attract molecules (not even the polarized ones). On the basis of eq 7, tension and pressure originate from the discontinuity of the dielectric constants at the border of the liquid and air. Therefore, once the dielectric molecules are released or evaporated from the liquid surface, the polarizability of the molecules equally interacts with positive and negative ideal parallel electrodes. Consequently, the molecules will not be attracted to the specific electrode but instead will hover around the liquid surface between the ideal parallel electrodes.

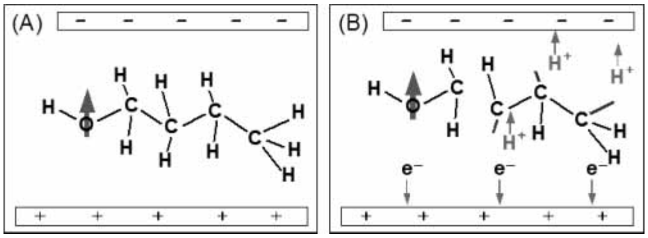

Figure 3. 1-Butanol molecule in a pair of electrodes. (A) Dielectric 1-butanol molecule arrayed parallel to the electric lines of force. (B) Dissociation of a 1-butanol molecule during the electron bombardment between a pair of parallel electrodes in air.

However, the molecules are subjected to the moment from the electric field, and the direction of the polarization of the molecules becomes parallel to the electric lines of force (Figure 3A, thick arrow). The driving force of this moment is the reduction of the polarization energy between the electric field and the polarization of the dielectric molecules as defined below.

$$U_{\mathrm{p}} = -\vec{p}\cdot\vec{E} \tag{8}$$

Here, U_{p} and $\vec{p}$ are the energy of the polarization interaction and the polarization of the dielectric molecules, respectively.

When the number of electrons exceeds the threshold of the electrode, electrons are emitted from the negative electrode to the surface of the liquid placed on the positive electrode (Figure 2B). However, the electron emission will continue to be random and uncontrollable as long as the electrons are emitted in air. Nevertheless, the condition illustrated in Figure 2B approaches the ideal. One requirement in plasma-induced reactions is to generate collisions with enough kinetic energy between the electrons and the molecules in air.

The pair of parallel electrodes begins to emit electrons at an electric field of around 10^6 V/m in air. The electrons emitted from such an intense electric field initially have 1 keV of kinetic energy. The kinetic energy of the electrons is consumed as the energy dissociates through molecule collisions. An electron with 1 keV of kinetic energy can dissociate 187 C−H bonds in the molecules.

Figure 3A illustrates the posture of the 1-butanol molecule in the electric field. The polarization vector of the molecule becomes parallel to the electric line of force in the electrodes. Figure 3B depicts the decomposition of the molecule through collisions between the emitted electrons and a 1-butanol molecule. If an appropriate dissociation energy is applied to the molecule through their collisions, hydrogen ions are dissociated[4−7] and attracted to the negative electrode (Figure 3B).

However, the efficiency of hydrogen production between the electrodes is low because the density of dielectric molecules and dissociated hydrogen ions from the molecules will not achieve sufficient levels for the continuous production of hydrogen at atmospheric pressure.

Application of the Tip on the Negative Electrode. Employing a tiny tip on the negative electrode is useful for attracting the dielectric molecules to the tip (Figure 4A). The attractive force between the tip and the dielectric molecules can be explained by eq 7. Although eq 7 is a macroscopic expression, the basic idea is applicable to the molecular scale. On the basis of eq 7, the important parameter for generating the electric force is the electric flux density, $\vec{D}$ (1/m^2), instead of the electric field, although they are related through eq 6. Since the Maxwell tensor is a linear function of the square of the electric flux density, the electric force drastically increases around the smaller electrode. Specifically, the electric force at the smaller electrode increases 100 times if the electrode is reduced to one-tenth and the other conditions are kept the same. Therefore, mounting a tiny tip on the negative electrode is the simplest and most effective method for increasing the electric force and attracting the dielectric molecules to the greater flux density at the tip on the electrode (Figure 4A). The evaporated molecules or electrically attracted molecules are directed toward the tip on the electrode, and the density of the molecules around the tip then becomes greater than that in other areas (Figure 4A). The high density of the molecules at the tip is beneficial for effectively bombarding electrons at the tip (Figure 4).

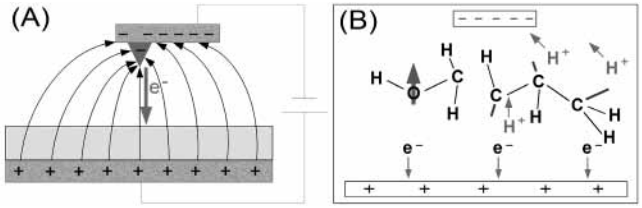

Figure 4. Electric field generated around a small electrode. (A) Generation of an asymmetrical electric field, electron emission, and molecular current toward the small negative electrode. (B) Decomposition of a 1-butanol molecule through electron bombardment at the small negative electrode.

Selective Electron Emission. Employing a tiny tip on the negative electrode is also useful for achieving controlled and selective electron emission from the tip (Figure 4A). The controlled electron emission from the tip can be explained by an analogy from fluid mechanics. In fluid mechanics, the stress concentration is observed at a defect in a container filled with water. If the water pressure is increased, the stress is concentrated at the defect. When the stress surpasses a certain threshold, the container breaks and water flows from the defect. The tip on the negative electrode plays a similar role for selectively emitting electrons when a certain electric potential threshold is exceeded, which corresponds to the pressure of the liquid.

The usefulness of the analogy between fluid mechanics and electrodynamics can be seen in comparing the momentum of the water and the electron. The momentum of the water that flows from the hole on the wall is represented by Torricelli's theorem as

$$P_m = \sqrt{2m\cdot mgh} \tag{9}$$

Here, P_m and m are the momentum of the water flow and the mass of the water, respectively, and g and h represent the gravitational acceleration and the distance between the liquid surface and the hole. Therefore, mgh represents the potential gravitational energy of the water. The potential energy is converted to liquid kinetic energy when the water flows from the hole.

The kinetic energy of an electron accelerated in the electric potential is

$$P_{\mathrm{e}} = \sqrt{2m_{\mathrm{e}}\cdot eV} \tag{10}$$

Here, P_{e} and m_{e} are the momentum and mass of the accelerated electron in the electric potential, respectively, and e and V are the electric charge of an electron and the electric potential of the field, respectively. Therefore, eV represents the kinetic energy of the electron accelerated in the potential.

A comparison of eqs 9 and 10 clearly demonstrates that their momentums are equally related to their potential energies. If the gravitational potential energy of water, mgh, in eq 9 is transformed to the kinetic energy of the water, the structure of the equations becomes identical. These identical equations come from the similarity between the perfect fluid and electric field. From the analogy of Torricelli's theorem, it is possible to estimate the dynamics of electrons emitted from the tip on the negative electrode (Figure 4A).

Although eq 10 is the expression for a uniform electric field and does not include the effect of the stress concentration at the tip on the electrode, the equation is useful for estimating the energy and momentum of the emitted electrons from the tip. The momentum of the electron can be evaluated by applying the electric potential to eq 10. The kinetic energy of the electron accelerated in the electric potential is also obtained from eV (J) in eq 10.

The important roles using a tip on the negative electrode are summarized in Figure 4. The negative tip generates a large electric flux density at the tip. The electrons are selectively emitted from the tip, and the alcohol molecules are simultaneously attracted to it through a polarization interaction. Large numbers of collisions between the electrons and molecules are achieved at the narrow area of the tiny tip. If the kinetic energy from their collision exceeds the dissociation energy of the molecules, the hydrogen ions are dissociated from the alcohol molecules around the tip. The dissociated hydrogen ions are attracted to the negative tip through the Coulomb interaction and achieve electrical neutrality at the negative electrode. The production of a high density of hydrogen ions in a narrow area is a significant advantage for immediately neutralizing the ions for the effective production of hydrogen molecules at the tip (Figure 4).

Experiments and Apparatus

The expected reactions described above were attempted in air using an atomic force microscope (AFM) tip as a negative electrode. Since air has an electric nonconductance, an electric field exceeding 10^6 V/m must be generated to induce electron emission in air. An electric potential of 0.8 kV must be applied between electrodes separated by 0.4 mm to generate a 10^6 V/m electric field and the resulting electron emission when using a pair of flat electrodes.

The application of an AFM tip as a negative electrode induces a stress concentration at the tip. This may make the electron emission from the tip easier than that from a flat electrode. However, we assume that the kinetic energies of the emitted electrons from the flat electrode and the tip are almost identical at the minimum electric potential (0.8 kV). The assumption is based on the fact that the electron emission from the flat electrode in air is also initiated from a spot. This indicates that the equipotential surface on the flat electrode is disrupted and the intensity of the electric potential is concentrated at the spot. The concentrated potential energy is released as electron emissions from the spot.

Since the stress concentration at a spot is a key factor for emitting electrons in air, the electrical states at the point of both flat and sharpened electrodes should be close to identical, at least at the moment of the emission. Therefore, the emitted electrons from both the flat and sharpened electrodes should have almost identical kinetic energies under the same electric potential. The essential quantity, such as the kinetic energy or moment of the emitted electrons, will be estimated on the basis of the apparatus described below.

The apparatus for producing hydrogen from alcohol is illustrated in Figure 5.[4] An AFM tip was used as a negative electrode and mounted on an *XYZ* stage for adjusting the relative position with respect to a positive electrode. The positive electrode consisted of a side of a tungsten rod with a 1 mm diameter. The side of the tungsten electrode was 0.4 mm from the AFM tip. 1-Butanol was introduced to the side of the tungsten electrode using a glass tube with an inner diameter of 10 μm. The 1-butanol placed on the tungsten rod comprised a quasi-positive electrode. A generator was connected between the AFM tip and the tungsten rod so that the tip formed a negative electrode and the tungsten rod became a positive electrode. The tungsten rod was also mounted on the *XYZ* stage to move the surface of the l-butanol 55 μm from the AFM tip. An electric pulse of 0.8 kV was applied at 30 kHz between the electrodes.

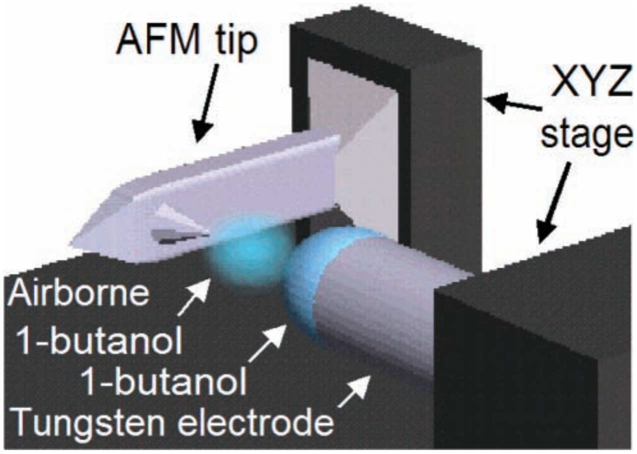

Figure 5. Strategy for producing hydrogen from 1-butanol. The components of the apparatus are a negative AFM tip, a positive electrode, and 1-butanol covering the positive electrode. AFM tip, OMCL-AC160TS-C2 (Au-coated silicon tip), Olympus.

On this apparatus, the kinetic energy of an emitted electron, K, can be estimated with eq 11.

$$K = eV \tag{11}$$

From this equation, the kinetic energy is calculated to be 0.8 keV. Although the equation is applicable in a vacuum and can only be applied right after the emission, the kinetic energy on an electron (0.8 keV) is sufficiently energetic to dissociate 187 C−H bonds. The momentum of an emitted electron can be estimated from eq 10 and can be represented as $P_e = \sqrt{1.6 m_e keV}$.

Production of Hydrogen. The production of hydrogen[8−11] from the tip of an AFM was observed with an optical microscope (Figure 6). On the basis of the estimation in Figure 4A, the formation of an asymmetrical electric field induced electron emission from an AFM tip and the simultaneous attraction of 1-butanol molecules toward the tip. The collision between the electrons and the attracted 1-butanol molecules was achieved around the tip (Figure 4A).

Figure 6A represents a negative AFM tip covered with the attracted 1-butanol. This was observed when the electron emission was stopped or the frequency of the pulse electric potential was <30 kHz. As soon as a pulse electric potential of 0.8 kV was applied to the AFM tip at a frequency of 30 kHz, several bubbles emerged (Figure 6B, right arrow). The bubbles increased in volume during the transfer from the point of the tip to the bottom of the tip (Figure 6B, left arrow). Expanded hemispherical bubbles with diameters of 10.5 μm burst each second at the left side of the AFM tip (Figure 6c, arrow). This produced 2400 μm^3/s of bubbles, and this production of bubbles continued as long as the experimental conditions were maintained.

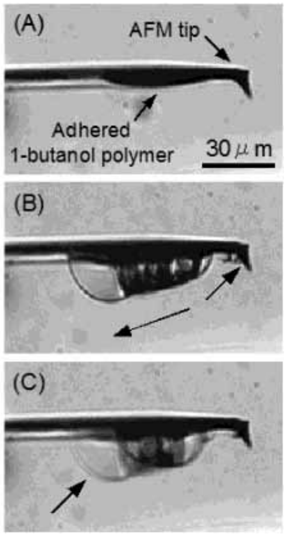

Figure 6. Hydrogen production from the AFM tip. (a) AFM tip covered with the attracted 1-butanol. (b) Hydrogen production from the tip of the AFM tip. (c) Hemispherical bubbles, including hydrogen, bursting at the base of the AFM tip (black arrow). AFM tip, OMCL-AC160TS-C2 (Au-coated silicon tip), Olympus.

The bubbles were ingested with a sharpened glass tube with a diameter of ~5 μm. The sharpened tube was fabricated from a 1 mm diameter glass tube and mounted on an *XYZ* stage to precisely insert the tip into the bubbles in Figure 6B (see the Supporting Information). The glass tube was connected to an air evacuated Tygon tube, and the produced bubbles were ingested into the Tygon tube for 7 s. The ingested gas was sampled with a 10 μL syringe and injected into the gas chromatographer. The gas chromatography detected 14.0% hydrogen, 31.4% carbon dioxide, and 1.3% nitrogen that may have been ingested with the bubbles from the atmosphere. The remaining 53.3% of the components could not be precisely detected with our instrument.

The reaction mechanisms of hydrogen production at the tip of the AFM tip can be explained from the estimations in Figures 4 and 6. The asymmetrical electric potential simultaneously induced electron emission from the tip and molecular flow toward the tip. This caused the electrons and 1-butanol molecules to collide. Hydrogen ions were dissociated from the molecules,[4−7] since the accelerated electrons in a 0.8 kV electric potential had enough kinetic energy (0.8 keV). The dissociated hydrogen ions were attracted to the negative AFM tip through the Coulomb interaction and achieved electrical neutrality at the tip. The neutralized hydrogen ions formed hydrogen molecules at the tip.

A direct temperature measurement of the bubbles during their production confirmed that the formation of the bubbles at the AFM tip did not require the boiling point of 1-butanol (117.3 °C). Supplying electrons to the adhered polymer in part A (left arrow) or B (right arrow) of Figure 6 easily caused the production of bubbles. The temperature was measured directly using a microscale almel−cromel thermometer (25 μm width). The micro-thermometer was attached to the adhered 1-butanol polymer in Figure 6A by applying a 6 V, 50 Hz sinusoidal signal between the thermometer and the AFM tip (see the Supporting Information). Attaching the micro-thermometer to the polymer with an electric signal enabled simultaneous production of bubbles from the polymer and temperature measurement. This direct temperature measurement during the production of bubbles revealed that the temperature increase was no more than 5 °C above room temperature (26 °C). This clearly shows that the bubble production does not involve boiling the 1-butanol polymer. In addition, bubbles were not produced when the electric signal (6V, 50 Hz) between the thermometer and the AFM tip was terminated. These results clearly demonstrate the bubble formation at the AFM tip in Figure 6 was primarily caused by supplying electrons to the adhered polymer, rather than by increasing the temperature. Since the almel−cromel thermometer was electrically insulated, the electrons were supplied from the AFM tip to the hydrogen ions when the thermometer became positive. The conductivity of the 1-butanol polymer, which is close to that of semiconductors,[4] should have also contributed to supplying electrons to the polymer.

However, this direct temperature measurement did not necessarily represent the real temperature of the bubbles in Figure 6. The measurement was difficult because of the intense electric potential (0.8 kV) at the AFM tip. The application of the almel−cromel thermometer to the AFM tip during the application of 0.8 kV of electric potential on the tip interferes with accurate temperature measurement as well as the plasma-induced reactions.

However, the temperature increase on the AFM tip might play an important role in the reaction in Figure 6. An experimental result suggests that a certain minimum temperature might be necessary for maintaining the massive production of bubbles shown in Figure 6B and C. Because the AFM tip was covered with the 1-butanol polymer, the production of bubbles in Figure 6 ceased when the frequency of the electric potential was decreased from 30 to 15 kHz. Since Joule heating is a linear function of the square of the electron current (electric current), the increase of the electron current induced by increasing the frequency from 15 to 30 kHz enhances heat loss by ~4 times. On the other hand, the efficiency of the reduction of hydrogen ions might double when the electric frequency is doubled. Therefore, the frequency increase mainly causes a temperature increase, particularly at the point of the AFM tip (Figure 6B, right arrow). This temperature increase might cause an evaporation or migration of the excess 1-butanol polymer from the point of the AFM tip, which is the most important area for the plasma-induced reactions, where the reactions are initiated (Figure 6B, right arrow).

Conclusion

We analyzed the mechanisms of hydrogen production from alcohol, based on classical electrodynamics and fluid dynamics. The similarity of these dynamics could be seen from the similar structures of eqs 9 and 10. Comparing these equations enabled us to estimate the behavior of the emitted electrons on a negative AFM tip. The formation of a narrow reaction area at the tip and the application of the minimum electric potential to the tip primarily contributed to the hydrogen production. The narrow reaction area was necessary for creating the highly efficient collisions between the emitted electrons and 1-butanol molecules. A reaction area nearer to the tip was also essential for the rapid electrical neutralization of the dissociated hydrogen ions. Therefore, the minimum electric potential had to be applied to the tip to emit electrons with enough dissociation energy. The application of a higher electric potential might be beneficial for dissociating larger numbers of molecules; however, the resulting violent emission might prevent the dissociated hydrogen ions from approaching the tip for electrical neutralization. The direct temperature measurement revealed that increasing temperature was not a requirement for producing hydrogen. However, supplying an appropriate number of electrons to the hydrogen ions was important. Nonetheless, a minimum temperature might be necessary for maintaining the condition of the AFM tip and the resulting continuous hydrogen production.

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Supporting Information Available: A discussion and figures on sampling gas bubbles on the AFM tip and direct temperature measurement. This material is available free of charge via the Internet at http://pubs.acs.org.

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