Direct Observation of Hydrogen Production from an Alcohol Polymer Stimulated by Surface Electron Current

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We report here on direct observation of hydrogen production from an alcohol polymer stimulated by surface electron current using an atomic-force microscope (AFM) tip. The initiation of the reaction and one location of hydrogen production were identified by direct microscale observations.

We used a plasma-induced method in recent research to compose an alcohol polymer.[1,2] The alcohol polymer stored hydrogen in the form of ions.[1,2] The application of different plasma conditions fixed the nitrogen in air and increased the viscosity of the alcohol polymer.[2] These reactions were achieved as airborne reactions[1,2] and could be directly observed between a pair of electrodes (Fig. 1). We report here on microscale observations of hydrogen production stimulated by surface electron current on an AFM tip.

Dynamics of the Reaction. Hydrogen production from alcohol molecules is initiated from the dissociation of hydrogen ions from the molecules. Dissociation of the hydrogen ions requires eigen dissociation energy on the order of the bonding energy.[3–6] One method for applying this eigen energy to the molecules uses collisions between the electrons and molecules in air (Fig. 1b).[3–6] Another method involves interaction between the surface electron current and molecules on the surface of the metal.[5–8] We directly observed the latter on a microscale for this paper. The observation supported hydrogen production from an alcohol polymer composed on the AFM tip being induced by interaction between the surface electron current and the alcohol polymer on the tip.

Apparatus. Figure 1a depicts the apparatus for observing the interaction between the surface electron current and the alcohol polymer at the border of the metal surface and the polymer. The core elements of this apparatus are a negative electrode consisting of an AFM tip, a positive tungsten electrode with a diameter of 1 mm, and 1-butanol placed on the positive tungsten electrode. The 1-butanol is supplied to the side of the tungsten electrode from a glass tube with an inner diameter of 10 μm. The distance between the AFM tip and the edge of the tungsten electrode is 0.4 mm; the surface of the 1-butanol was adjusted to 55 μm from the AFM tip. The AFM tip and the tungsten electrode were mounted on XYZ stages for fine adjustments of these placements. A generator was connected between the AFM tip and the tungsten electrode to apply a pulse electric potential. The experiments were conducted in air at a temperature of 26 °C and humidity of 50%.

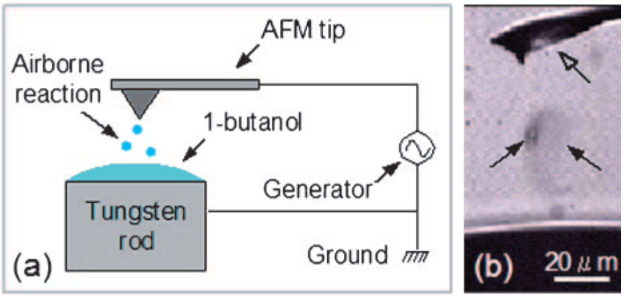

Fig. 1. Strategy for observing the interaction between the surface electron current and the alcohol polymer. The electron emission from the AFM tip induced an airborne reaction (Fig. 1a, black arrows) and formed an alcohol polymer on the tip (Fig. 1b, white arrow). The surface electron current induced hydrogen production from the polymer (Fig. 2b; AFM tip, DF-20 (Au-coated silicon tip), SII).

Airborne alcohol polymerization[1,2] was observed when a pulse electric potential of 0.8 kV–15 kHz was applied between the electrodes. Mist (Fig. 1b, right black arrow) and particles (Fig. 1b, left black arrow) were alternatively observed flowing from the surface of the 1-butanol on the positive electrode to the negative AFM tip. The mist and particles adhered to the AFM tip and formed a hemispherical shape (Figs. 2a, 2b). The adhered material was liquid and transparent with some viscosity. It was stable in both air and a vacuum.

Production of Bubbles Stimulated by the Surface Electron Current. The direct interaction between the surface electron current and alcohol polymer was analyzed from the production of bubbles inside the polymer that adhered on the AFM tip. Figures 2a and 2b represent the magnified images of Fig. 1b and illustrate the formation of bubbles from the inside of the alcohol polymer at the top of the AFM tip (Fig. 2b). These bubbles were produced when the distance between the AFM tip and the surface of the 1-butanol was reduced. Reducing the distance increases both the kinetic energy of electrons flowing along the AFM tip and the temperature of the polymer on the AFM tip as a result of an increase of Joule heating.

Figure 2b depicts the production of bubbles when the distance between the AFM tip and the surface of the 1-butanol was reduced by 15 μm from the original position (55 μm). The bubbles, with diameters of approximately 5 μm, were produced from the inside of the polymer located at the top of the

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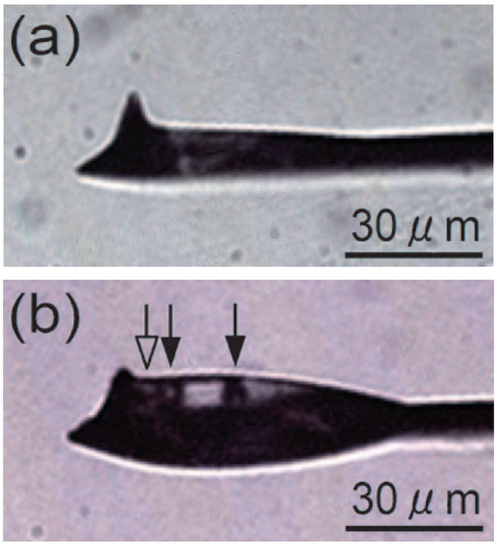

Fig. 2. Bubble production from the alcohol polymer (a) AFM tip covered with the alcohol polymer formed in Fig. 1b (white arrow). (b) Bubbles were generated inside the polymer around the AFM tip (white arrow) and migrated inside of the liquid polymer toward the bottom of the tip.

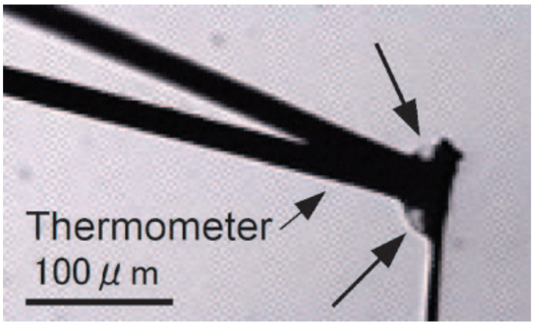

Fig. 3. Bubble production from the alcohol polymer. When a thermometer, to which is applied an electric potential of 50 Hz–6 V, contacted the polymer, bubbles were produced from the polymer between the AFM tip and the thermometer.

AFM tip (white arrow). These bubbles migrated into the liquid polymer, toward the base of the AFM tip (black arrows).

Discussion. The mechanisms of bubble production were analyzed from direct observations of the reaction combined with our previous research in which we directly measured the bubble temperature.[9] There are two possible causes of bubble production, a temperature increase due to Joule heating of the AFM tip or the interaction between the surface electron current and the alcohol polymer.

Figure 3 depicts the direct temperature measurement of the bubble produced from the alcohol polymer on the AFM tip. When a thermometer, to which is applied an electric potential of 50 Hz–6 V, contacted the polymer, bubbles were produced from the polymer between the AFM tip and the thermometer. Since the thermometer was originally at room temperature, contacting the polymer with the thermometer would not raise the temperature of the polymer. However, the temperature of the thermometer increased to 3 °C above room temperature. This clearly demonstrated that the bubble formation was not caused by the boiling of the polymer due to Joule heating but rather by the supplement of the electrons from the AFM tip and the resultant generation of enthalpy of gas formation.

In addition, the period of gas formation also supported the authors' hypothesis that the bubbles were produced when positive ions were neutralized by the supplement of electrons on the polymer. The bubble formation continued about 5 s after contact with the electrically energized thermometer. If the bubbles had been produced by the boiling of the polymer, the bubbles should continue to form as long as the electrically energized thermometer remained in contact with the polymer or until the polymer evaporated. In fact, however, the generation of bubbles ceased while there was still polymer on the AFM tip. This suggested that the polymer was sufficiently neutralized and stopped generating bubbles.

It would not be appropriate to apply the previous discussion for Fig. 3 to the explanation of Fig. 2b since the experimental procedures in the two figures differed. However, the facts that the 1-butanol was dissociated during the airborne plasma reaction (Fig. 1b, black arrow) and that hydrogen was detected by gas chromatography clearly demonstrated that the polymer should have been supplied electrons at a certain point for composing hydrogen molecules. The most probable site for supplying electrons is the negative AFM tip. Therefore, supplying electrons from the AFM tip is a requirement for initiating bubble formation and for the successive generation of gasses.

In contrast, the role of the temperature increase due to Joule heating would primarily be to accelerate the neutralization of the polymer and resultant formation of bubbles. Increasing the temperature of the polymer itself cannot dissociate 1-butanol molecules nor can it compose hydrogen from hydrogen ions.

In addition, bubbles produced due to a temperature increase would form from the border between the liquid polymer and the top of the AFM tip, where the temperature would be maximum near the outside of the polymer. Therefore, bubble production from the inside of the polymer indicates decomposition of the polymer as a result of interaction with the surface electron current.

Given the above, the reaction mechanisms can be assumed as follows. The electrons in the current flowing along the surface of the AFM tip interacted with the 1-butanol polymer at the point of the most intense electron current, the AFM tip. The interaction caused additional dissociation of the alcohol polymer and produced ions. The ions were then immediately neutralized at the tip, producing bubbles there. The temperature increase would have accelerated the neutralization of positive ions and generated the neutralized bubbles.

Summary. We analyzed the production of hydrogen from the inside of an alcohol polymer formed on an AFM tip. Direct observation of the reaction and the temperature measurement supported the reaction being induced by interaction between the surface electron current on the AFM tip and the alcohol polymer on the tip at their borders. This result indicates not only the existence of surface electron current but also its contribution to hydrogen production from the alcohol polymer.

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