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LETTERS

Production of an Alcohol-Based Hydrogen Storing Polymer

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Producing and storing hydrogen are important issues for the 21st century. In this paper, we report a method for instantaneous alcohol polymerization and hydrogen storage using hydrogen-rich 1-butanol as the starting material. Electron bombardment of 1-butanol produced a conductive liquid polymer that contained unstable hydrogen ions. Hydrogen was then extracted by the application of electricity. The reaction was quickly started and stopped at room temperature. The resulting alcohol polymers will be good candidates as fuel batteries for cell phones, motor vehicles, and spacecraft.

Introduction

Recently, there has been increasing interest in developing new methods for inexpensive[1,2] hydrogen generation.[3] Various approaches have been attempted in many different scientific fields, including chemistry[4] and biology.[5] The storage[6] and extraction of hydrogen are two of the issues that have delayed the development of new methods for hydrogen generation. Storage and extraction are opposite reactions, and researchers have encountered problems with the thermodynamic properties[6] of these processes. Hydrogen brittleness has also prevented the development of new methods, as have problems with safety and handling of hydrogen. Alcohol polymers are potentially good candidates for fuel batteries[7,8] because alcohols contain large quantities of hydrogen, they are easy to store, and they do not require specialized containers. In this study, we used 1-butanol as a hydrogen-rich material and applied plasma-induced polymerization[9−11] for storing hydrogen at room temperature in air. Electron bombardment of the surface of volatile 1-butanol produced a conductive liquid polymer containing unstable hydrogen ions. Electricity was subsequently applied to facilitate hydrogen extraction.

Experiments and Discussion

To produce and store hydrogen ions in 1-butanol, it is necessary to dissociate the C−H bonds of the 1-butanol molecules without causing evaporation or combustion. In this process, it is necessary to apply more energy than the bond strength of C−H bonds, which is known to be 4.27 eV. Electron bombardment at a kinetic energy level greater than 4.27 eV can be achieved by accelerating electrons toward the surface of 1-butanol in the form of electric potential. To bombard the 1-butanol surface with electrons, an atomic force microscope (AFM) tip was used as a negative electrode, and a tungsten rod (o.d. 1 mm) was used as a positive electrode (Figure 1a). One microliter of 1-butanol was supplied continuously to the tungsten rod with an injector to form a hemispherical, quasi-positive electrode (o.d. 1 mm). The AFM tip and tungsten electrode were mounted onto an XYZ-stage to accurately adjust the distance between the electrodes. An electric potential of 15 kHz−800 V was then applied between the electrodes. An Au-coated silicon

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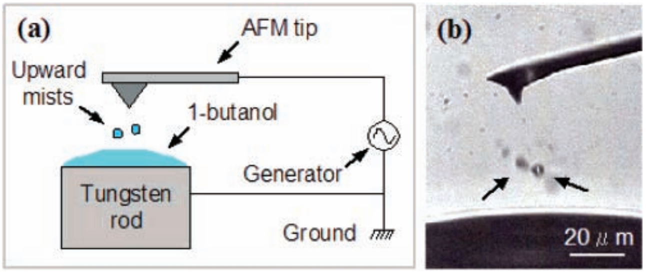

Figure 1. Strategy used to produce an alcohol polymer. (a) Apparatus used to produce the hydrogen-storing polymer. (b) Upward-moving mists (black arrows) induced by electron emission in an electric field. AFM tip, DF-20 (Au-coated silicon tip) SII. 1-butanol, Wako Pure Chemicals, 99.5%. Temperature, 26 °C. Humidity, 50%.

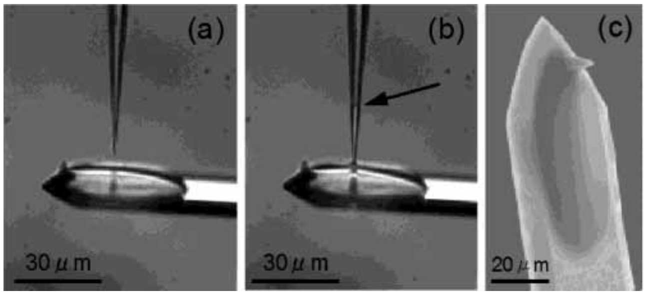

Figure 2. Images of the liquid 1-butanol polymer on the AFM tip. (a) Optical microscope image of the liquid 1-butanol polymer on the AFM tip. (b) Optical microscope image of the liquid 1-butanol polymer and its meniscus in the sharpened glass tube. (c) SEM image of the liquid 1-butanol polymer on the AFM tip. AFM tip, DF-20 (Au-coated silicon tip) SII.

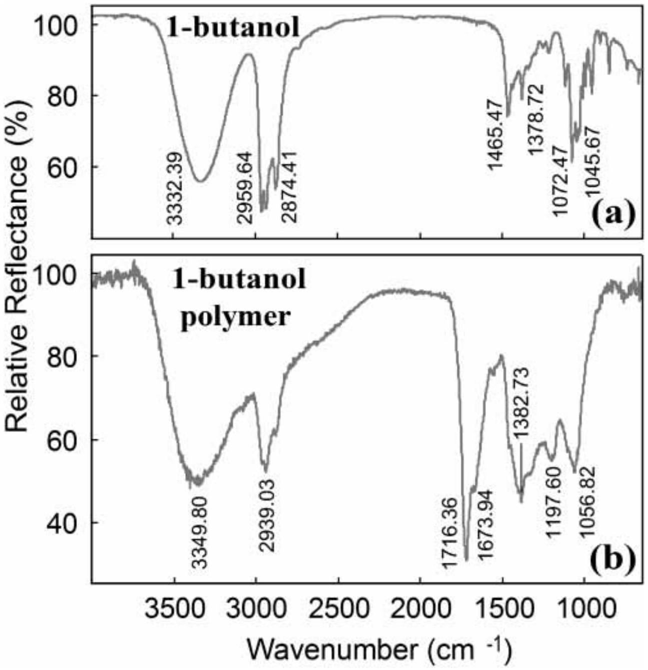

Figure 3. IR transitional spectrum of 1-butanol. (a) FTIR spectrum of 1-butanol. (b) FTIR spectrum of 1-butanol following electron emission in an electric field. Microscopic FTIR, Spectra-Tech, Inc., IRμs(II).

tip was used as the negative AFM tip. An optical microscope was used to observe the AFM tip and the 1-butanol surface. The 1-butanol was 99.5% pure. The experiments were conducted in the atmosphere at room temperature (26 °C) and a humidity of 50%.

Careful observation showed that nano- and microscale mists were produced from the 1-butanol surface. The mists moved in an upward direction toward the AFM tip (Figure 1a,b) and were found to adhere to the tip surface (Figure 2a−c). The mists were produced following the application of an electric potential difference of 800 V only when a maximum electron emission of 2 μA was applied, and as the distance between the electrodes approached 55 μm. The mists that adhered to the AFM tip were stable and did not disappear in air or vacuum. The mists on the AFM tip were observed with both optical and electron microscopes (Figure 2a−c). “Palpation” with a sharpened glass tube revealed that the liquid was viscous (Figure 2b, black arrow).

On the basis of these observations, we assumed that the volatile 1-butanol, with a permittivity on the tungsten electrode of 17.1, was attracted toward the more intense electric field at the negative AFM tip. The 1-butanol was found to collide with electrons emitted from the tip (Figure 1a,b). This collision could have resulted in the decomposition of 1-butanol molecules[12−15] and formation of the liquid 1-butanol polymer on the AFM tip (Figure 2a−c). During the decomposition−excitation process, both ions and radicals were produced.[12−15] However, the intense negative electric potential at the AFM tip would have repelled radicals and attracted positive ions in accordance with the Coulomb interaction. Therefore, the final product on the negative AFM tip should consist mainly of positive ions, such as hydrogen ions and partially ionized 1-butanol molecules. These positive ions would have been neutralized at the negative AFM tip and lead to the simultaneous formation of the 1-butanol liquid polymer to achieve a more energetically stable state on the AFM tip.

The polymerized 1-butanol and the hydrogen ions generated during this process were analyzed by the transitions of their FTIR spectra. Parts a and b of Figure 3 are the microscopic-FTIR spectra of 1-butanol and the liquid 1-butanol polymer on the AFM tip. The peak at 1674 (1 cm^{-1}) (Figure 3b) showed that C=C bonding was initiated by the polymerization of 1-butanol. The reduction in the size of peaks at 2874 and 2959 (1 cm^{-1}) (Figure 3a) showed that hydrogen atom bonds in the 1-butanaol molecules were forced to dissociate. The formations of the peaks between 1000 and 1500 (1 cm^{-1}) (Figure 3b) also suggested that the C−H bonds in the 1-butanol molecules were decomposed and started to form 3-D bridge structures following C−C or C=C bonding between partially decomposed 1-butanol molecules. Similar structures have been reported to occur during the polymerization processes in other studies.[14,15] In addition, Figure 3b suggests that 1-butanol was oxidized. During this process, electron emission caused the dissociation of oxygen molecules in air, induced plasma, and led to C=O bonding with unsaturated carbons from dissociated C−H bonds in the 1-butanol. The peak at 1716 (1 cm^{-1}) (Figure 3b) confirmed that 1-butanol was oxidized. This oxidation is known to occur commonly in the plasma polymerization process.[14]

The resistivity of the 1-butanol liquid polymer and the production of hydrogen from the polymer also promoted the decomposition of 1-butanol molecules and the generation of hydrogen ions. 1-Butanol is known to be a good insulator, with a resistivity of 10^{11} Ω cm. However, the resistivity of the liquid 1-butanol polymer measured in this study was much lower and was found to range from 0.8 to 480 Ω cm.

VCR analysis showed that the liquid 1-butanol polymer produced gas bubbles at a rate of 670 μm^3 s^{-1} when an electrode with a 6 V−50 Hz electric signal was attached to the liquid polymer on the AFM tip. The bubbles were analyzed by gas chromatography and were found to consist of 18.5% hydrogen,

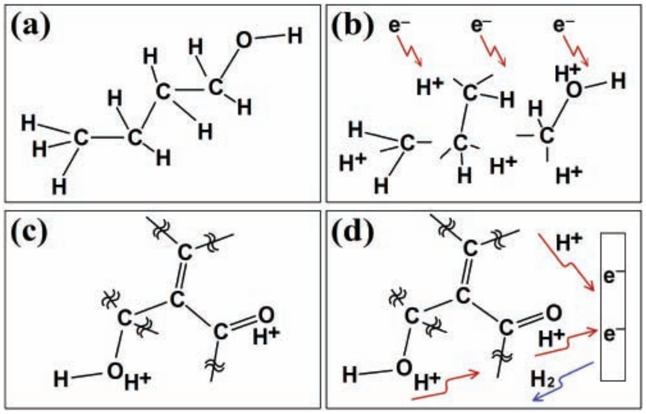

Figure 4. Model of the 1-butanol decomposition and hydrogen storage process. (a) 1-Butanol molecule. (b) Dissociation of a 1-butanol molecule by electron bombardment. (c) Probable structure of the 1-butanol polymer interacting with hydrogen ions. (d) Model showing the process of hydrogen production at the negative AFM tip.

32% carbon dioxide, and 1.5% nitrogen that may have been ingested from the atmosphere. However, we could not specify the remaining 48.5% of the components because of the broad peak of the chromatograph. On the basis of the inherent characteristics of plasma-induced reactions, the broad peak probably originates from both 1-butanol and plasma-induced molecules that were randomly composed of partially decomposed 1-butanol and dissociated radicals or ions, such as carbon, hydrogen, and oxygen. To obtain sufficient gas for analysis, the bubbles from 18 samples on the AFM tip were collected in a sharpened glass tube (see Supporting Information). Gas was collected for 5 s from each sample, during which time 1-butanol was not supplied (Figure 1b, black arrows).

The observed reduction in resistivity and production of hydrogen from the liquid 1-butanol polymer combined with the IR analysis showed that the C—H bonds in the 1-butanol molecules dissociated.[12−15] Hydrogen ions were then stored in the 1-butanol liquid polymer. The generation of hydrogen at a weak electric signal of 6 V−50 Hz suggested that the hydrogen ions had interacted with polar groups, such as O—H or C═O. These hydrogen ions contributed to generation of an electric current as carriers.

From these results, we propose that alcohol was polymerized and hydrogen was stored simultaneously in the plasma-induced polymerization process. Electrons emitted from the AFM tip caused the dissociation of C—H bonds in the 1-butanol molecules, producing hydrogen ions (Figure 4b) and inducing C—C and C═C bonding (Figure 4c) to form the liquid 1-butanol polymer. Electron emission also caused the dissociation of oxygen molecules in air and initiated C═O bonding with the unsaturated carbons from C—H bonds (Figure 4c). Hydrogen ions dissociated from C—H bonds were found to interact with either C═O or O—H groups (Figure 4c) and exhibited unstable resistivity. Hydrogen ions that interacted with the C═O or O—H groups migrated to the negative electrode and produced hydrogen when a 6 V−50 Hz voltage was applied (Figure 4d).

Conclusions

In this study, we demonstrated plasma-induced alcohol polymerization and simultaneous hydrogen storage using electron bombardment onto a surface coated with 1-butanol. Electron bombardment of 1-butanol produced a conductive liquid polymer that contained unstable hydrogen ions. Hydrogen was subsequently extracted after the application of electricity. In future work, we will investigate the reaction process and the mechanisms of hydrogen storage in greater detail, in an attempt to increase the ratio of hydrogen storage of the 1-butanol liquid polymer.

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Supporting Information Available: Production and ingestion of bubbles from the 1-butanol polymer on the AFM tip. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Barreto, L.; Makihira, A.; Riahi, K. *Int. J. Hydrogen Energy* **2003**, *28*, 267.
(2) Goltsov, V. A.; Veziroglu, T. N. *Int. J. Hydrogen Energy* **2001**, *26*, 909.
(3) Wild, P. J.; Verhaak, M. J. F. M. *Catal. Today* **2000**, *60*, 3.
(4) Joensen, F.; Nielsen, J. R. R. *J. Power Sources* **2002**, *105*, 195.
(5) Embley, T. M.; Martin, W. *Nature* **1998**, *396*, 517.
(6) Schlapbach, L.; Zuttel, A. *Nature* **2001**, *414*, 353.
(7) Lee, H. S.; Jeong, K. S.; Oh, B. S. J. *Hydrogen* **2003**, *28*, 215.
(8) Okumoto, M.; Mizuno, A. *Catal. Today* **2001**, *71*, 211.
(9) Wichson, B. M.; Brash, J. L. *Colloids Surf.* **1999**, *156*, 201.
(10) Zajickova, L.; et al. *Thin Solid Films* **2003**, *425*, 72.
(11) Kholdkov, I.; et al. *Vacuum* **2003**, *70*, 505.
(12) Levis, R. J.; Getahun, M, M.; Hershel, R. *Science* **2001**, *292*, 709.
(13) Levis, R. J. *J. Phys. Chem.* **1999**, *103*, 6493.
(14) Boenig, H. V., Eds. *Advances In Low-Temperature Plasma Chemistry, Technology, Applications*; Technomic Publishing: Lancaster, PA, 1984.
(15) Hollahan, J. R.; Bell, A. T. *Techniques and Applications of Plasma Chemistry*; John Wiley & Sons: New York, 1974.