

# Fixing Atmospheric Nitrogen in Alcohol during Plasma-Induced Alcohol Polymerization

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In this paper, we demonstrate plasma-induced fixing of atmospheric nitrogen during 1-butanol polymerization. Electrons emitted from the atomic force microscope (AFM) tip dissociate not only the C–H bonds in 1-butanol but also nitrogen and oxygen molecules in air. Those dissociated molecules become unstable ions or radicals (forming a plasma). The positive ions approach the more intense negative AFM tip in the unsymmetrical electric potential and compose 1-butanol polymer containing nitrogen on the tip during electrical neutralization. In the plasma-induced process, 13–47 wt % of nitrogen molecules were fixed to 1-butanol polymer. The reaction was quickly started and stopped at room temperature. This method could be applied to fix gases into a liquid at the molecular level to other sets of liquids and gases.

## Introduction

Fixing atmospheric nitrogen is an important issue in the fields of medicine, biology and agriculture.<sup>1–3</sup> We selected 1-butanol to fix atmospheric nitrogen without a catalyst at room temperature. The appropriate excitation energy must be applied to the target molecules and those molecules must be rearranged to induce a chemical reaction. Phonon, photon, and electron emissions can be applied to excite the target molecules.<sup>4–6</sup> In this paper, we apply an unsymmetrical electric potential to the 1-butanol surface to induce an upward 1-butanol current and simultaneous electron emission to the current.<sup>7</sup> The emitted electrons collide with the upward-flowing 1-butanol, nitrogen, and oxygen molecules and dissociate them simultaneously in air. The dissociated molecules become ions or radicals (forming a plasma).<sup>8,9</sup> The positive ions approach the more intense negative electrode in the unsymmetrical electric potential and form a 1-butanol polymer containing nitrogen and oxygen.

## Theoretical Basis

Two important factors are necessary for fixing atmospheric nitrogen to 1-butanol. First, a positive electrode covered with a dielectric 1-butanol and its upward current flowing toward a negative electrode in an electric potential provide the important route for discharging electrons. Second, electrons must be emitted with an appropriate kinetic energy toward the upward-flowing 1-butanol current in air to dissociate both 1-butanol and atmospheric nitrogen (forming a plasma).

Generating an unsymmetrical electric potential between a smaller negative electrode and a larger positive electrode covered with 1-butanol is a good strategy for satisfying these requirements. A smaller negative electrode simultaneously induces an upward-flowing 1-butanol current and generates electrons emitted into the current. Electrons emitted into the current dissociate both the C–H bonds in 1-butanol and nitrogen

molecules in air. Those dissociated molecules become unstable ions or radicals (forming a plasma). The positive ions approach the more intense negative electrode in the unsymmetrical electric potential, and 1-butanol polymer containing nitrogen is composed on the tip during the electrical neutralization.

The most important factor for fixing atmospheric nitrogen to 1-butanol is to simultaneously supply enough dissociation energy to 1-butanol and nitrogen molecules. When an electron emitted with sufficient kinetic energy collides with these molecules, the molecules are dissociated into ions or radicals. If the collision is conducted in an unsymmetrical electric potential, the positive ions will be electrically attracted to the negative electrode. They will then adhere to the electrode and compose 1-butanol polymer containing nitrogen. During the process, an electron avalanche will be induced and will dissociate a huge number of molecules in a chain reaction.

The dissociation energies of a C–H bond (4.27 eV) in 1-butanol, of a nitrogen molecule (9.78 eV), and of an oxygen molecule (5.13 eV) are less than 10 eV, so an electron with more than that energy can easily be accelerated in an electric potential. When an electron is accelerated in a 1.2 kV uniform static electric potential in a vacuum, it obtains 1.2 keV of kinetic energy. We assume in this paper for simplicity that an electron accelerated in 1.2 kV of unsymmetrical electric potential also has 1.2 keV of kinetic energy and ignore the work function of a tungsten electrode ( $\sim 5$  eV). An electron emitted in air initially has the same kinetic energy as in a vacuum but will gradually lose its kinetic energy during collisions with molecules in air. During the process, an electron avalanche<sup>10</sup> will be induced, and a huge number of molecules will be dissociated. When an electron is accelerated in a 1.2 kV unsymmetrical electric potential, the associated avalanche can dissociate 126 atmospheric nitrogen molecules (9.78 eV), 280 C–H bonds (4.27 eV) in 1-butanol, and 232 atmospheric oxygen molecules (5.13 eV).

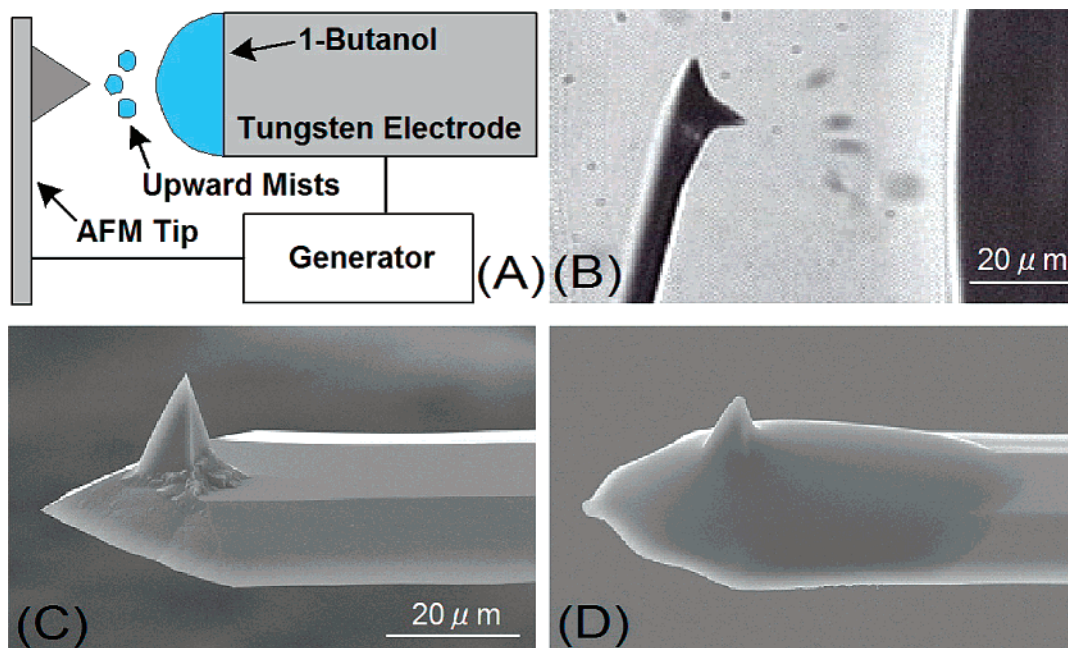
It is energetically possible to dissociate  $16 \times 10^{15}$  molecules per second during the electron avalanche when 1.2 keV/40  $\mu$ A electrons are emitted toward the nitrogen molecules since the dissociation energy of nitrogen molecules is 9.78 eV. Similarly,

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**Figure 1.** Strategy for fixing atmospheric nitrogen in alcohol. (A) Nitrogen fixing apparatus. (B) Upward mists induced by an unsymmetrical electric potential. (C) Blank AFM tip. (D) SEM image of 1-butanol polymer containing nitrogen on the AFM tip. AFM tip, DF-20 (Au-coated silicon tip) SII. 1-butanol, Wako Pure Chemicals, 99.5%. Temperature: 26 °C. Humidity: 50%.

$16 \times 10^{15}$  C–H and O=O bonds will be dissociated simultaneously per second under the same condition (1.2 keV/40 μA) through the chain reactions.

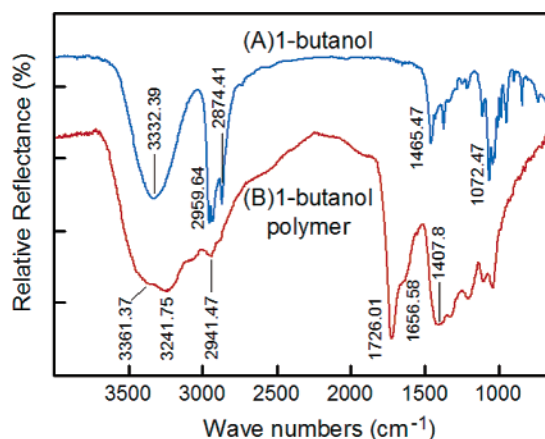
Practically, however, the emitted electrons will be used up before dissociating the expected number of nitrogen molecules through the electron avalanche. Some electrons will be scattered away after collisions and others will be used for decomposing oxygen molecules instead of nitrogen. For these reasons and some unknown factors, the actual number of nitrogen atoms fixed in the 1-butanol molecules will be lower than ideally estimated.

## Experiments and Discussion

Applying an unsymmetrical electric potential to the surface of 1-butanol generated a well-controlled electron emission. The atomic force microscope (AFM) tip was set as a negative electrode, and a tungsten rod ( $\phi = 1$  mm) was positioned as a positive electrode (Figure 1A). One microliter of 1-butanol was continuously supplied to the lateral side of the tungsten rod and formed a hemispherical liquid electrode ( $\phi = 1$  mm). A pulse electric potential of 1.2 kV and 15 kHz was applied between the electrodes.

A careful observation revealed an array of nano- or microscale mists that were directed toward the negative AFM tip from the 1-butanol surface (Figure 1B) and adhered to the tip (Figure 1D). The mists appeared when input electric current was 30 μA and as the distance between electrodes approached 45 μm, with a potential difference of 1.2 kV. The material that adhered to the AFM tip was stable and did not disappear in air or vacuum. Palpation confirmed the material to be a liquid with some viscosity, and the material was observed with SEM images (Figure 1D).

From these observations combined with theoretical considerations, we assumed that volatile 1-butanol with permittivity of 17.1 on the tungsten electrode was electrically attracted as an upward 1-butanol current toward the more intense electric potential at the negative AFM tip and collided with electrons emitted from the tip (Figure 1, parts A and B). The collision



**Figure 2.** IR spectrum transition of 1-butanol after electron emission. (A) FTIR spectrum of 1-butanol. (B) FTIR spectrum of 1-butanol polymer. Microscopic FTIR, Spectra-Tech, Inc., IRμs(II).

could result in the dissociation of not only 1-butanol but also nitrogen and oxygen molecules, and it formed 1-butanol polymer on the AFM tip (Figure 1D).

Electron probe microanalysis (EPMA) revealed that the 1-butanol polymer contained 13–47 wt % of nitrogen atoms (see Supporting Information). The dispersion of data probably resulted from inequality of samples, limitations of EPMA measurement, or inherent characteristics of plasma-induced chemical reactions. If we consider a 1-butanol polymer containing 25 wt % of nitrogen atoms, 67.8 wt % of carbon, and 7.2 wt % of oxygen, the ratio of the number of atoms per unit mass is 12:4:1 for carbon:nitrogen:oxygen. The data demonstrated that nitrogen molecules in air were fixed into the 1-butanol polymer.

The structure of 1-butanol polymer was analyzed through a transition of the FTIR spectrum. Parts A and B of Figure 2 are the microscopic FTIR spectra of 1-butanol and 1-butanol polymer on the AFM tip. IR peaks in Figure 2B were found to be broader than peaks in Figure 2A. Broad IR peaks can often be seen in polymer measurements. In particular, the appearance

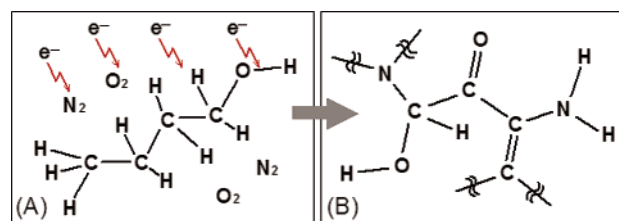
of 3241 (NH stretching), 1656 (NH<sub>2</sub> bending), and 1407 cm<sup>-1</sup> (CN bending) peaks suggests formations of similar structures of an amide group, and the signal is similar to that of formamide. Additionally, a 1726 cm<sup>-1</sup> (C=O stretching) peak in Figure 2B indicates that 1-butanol was oxidized. The oxidation process is often observed in plasma-induced reactions.<sup>11</sup>

The decomposition of 1-butanol molecules and successive formation of 3-D bridge structures can be estimated from the disappearance of the 2900 cm<sup>-1</sup> peaks and from the transition of the IR spectrum between 1000 and 1500 cm<sup>-1</sup> in Figure 2. The 2900 cm<sup>-1</sup> peaks correspond to C–H stretching, and the disappearance of the peaks clearly demonstrates that the C–H bonds in the 1-butanol molecules were dissociated due to electron emission. The IR peaks of 1-butanol between 1000 and 1500 cm<sup>-1</sup> are primarily due to C–H vibrations, such as scissoring vibration (1450 cm<sup>-1</sup>), symmetric bending vibration (1380 cm<sup>-1</sup>), and rocking vibration (900–1150 cm<sup>-1</sup>). The vanishing of these sharp peaks and the formation of broad peaks in this area also indicate the decomposition of C–H bonds in the molecules and subsequent formation of 3-D bridge structures with other decomposed molecules such as butanol, nitrogen, and oxygen. The C–C, C=C, and C–N bonds form among decomposed butanol, nitrogen, and oxygen to form 3-D structures of the polymer. The viscosity of the polymer increased as the percentage of the fixed nitrogen in the polymer increased. Therefore, the fixed nitrogen existing as C–N bonds in the polymer primarily contributed to the formation of 3-D bridge structures.

However, detecting the reaction processes and obtaining a uniform compound are difficult because the plasma-induced chemical reaction is inherently based on the probability of electrons colliding with molecules and successive shuffling of dissociated ions or radicals. The reaction speed also prevents detecting detailed reaction processes. All we can do at this stage is to estimate the energetically possible reactions and compare the product with the reactant materials using appropriate analyzers.

In the nitrogen-fixing process, electron emission decomposes both nitrogen molecules in air and C–H bonds in 1-butanol, induces plasma, and composes C–N and N–H bonds in 1-butanol polymer. It is energetically possible to dissociate nitrogen molecules (9.78 eV) and C–H bonds (4.27 eV) using electrons accelerated in a 1.2 kV field. Similarly, electron emission decomposes oxygen molecules (5.13 eV) in air, induces plasma, and composes C=O bonding with unsaturated carbons from C–H bonding in 1-butanol during the oxidation process. It is energetically possible to dissociate oxygen molecules (5.13 eV) and C–H bonds (4.27 eV), and subsequent formation of C=O bonds is much more stable (8.29 eV).

The EPMA and FTIR analyses revealed that atmospheric nitrogen molecules were fixed into 1-butanol molecules at the molecular level. Figure 3 represents a possible structure of the 1-butanol polymer based on the EPMA and FTIR analyses. However, as we stated previously, we could not expect to obtain a uniform molecular structure with a certain molecular weight through a plasma-induced reaction. Realistically, an amorphous polymer would be composed, and Figure 3 represents just some



**Figure 3.** Possible structure of 1-butanol polymer. (A) Electron emission toward the 1-butanol molecule. (B) Possible structures of 1-butanol polymer containing nitrogen after the electron emissions.

of the possible structures in the 1-butanol amorphous polymer; different atomic arrangements could appear randomly.

## Conclusions

We have demonstrated plasma-induced fixing of atmospheric nitrogen during 1-butanol polymerization. Electrons emitted from an AFM tip dissociate both C–H bonds in 1-butanol and nitrogen and oxygen molecules in air. Those dissociated molecules become unstable ions or radicals (forming a plasma). The positive ions approach the more intense negative AFM tip in the unsymmetrical electric potential and form 1-butanol polymer containing nitrogen on the tip during electrical neutralization. During the plasma-induced process, 13–47 wt % of nitrogen molecules were fixed to 1-butanol polymer. The reaction was quickly started and stopped at room temperature, and this method for fixing gases to a liquid at the molecular level could be applied to other sets of liquids and gases.

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**Supporting Information Available:** Figure showing the weight percent of the fixed atmospheric nitrogen in 1-butanol and other elements consisting of the 1-butanol polymer. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- (1) Hoshino, K. *J. Chem. Eur.* **2001**, 7, 2727.
- (2) Hoshino, K.; Inui, M.; Kitamura, T.; Kokado, H. *Angew. Chem. Int. Ed.* **2001**, 39, 2509.
- (3) Hoshino, K.; Kitamura, T. *Chem. Lett.* **2000**, 1120.
- (4) Levis, R. J.; Menkir, G. M.; Rabitz, H. *Science* **2001**, 292, 709.
- (5) Levis, R. J.; DeWitt, M. J. *J. Phys. Chem.* **1999**, 103, 6493.
- (6) Matsuura, H.; Tanikawa, T.; Takaba, H.; Fujiwara, Y. *J. Phys. Chem. A* **2004**, 108, 3235.
- (7) Imai, I., Eds. *DENJIKIGAKU O KANNGAERU*; Saiensu-sya: Tokyo, 1990. English translation. *A new approach to electromagnetic theory*; Bull. Soc. Fr.-Jpn. Sci. Pure Appl., Num. Spectrosc. **1990**, 4, 353.
- (8) Zajickova, L.; et al. *Thin Solid Films* **2003**, 425, 72.
- (9) Kholdkov, I.; et al. *Vacuum* **2003**, 70, 505.
- (10) *The Columbia Encyclopaedia*, 6th ed.; Columbia University Press: New York, 2002.
- (11) Boenig, H. V., Eds. *Advances In Low-Temperature Plasma Chemistry, Technology, Applications*; Technomic Publishing: Lancaster, PA, 1984.