

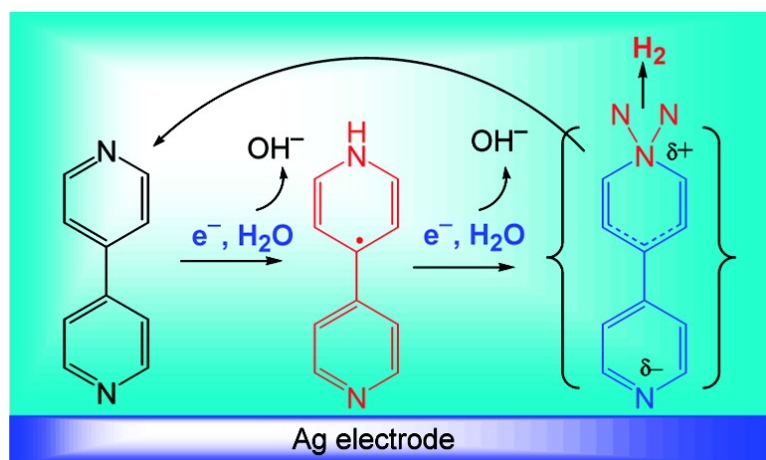
Communication

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## Hydrogen Evolution Reaction Catalyzed by Proton-Coupled Redox Cycle of 4,4'-Bipyridine Monolayer Adsorbed on Silver Electrodes

Taro Uchida, Hirokazu Mogami, Akira Yamakata, Yoichi Sasaki, and Masatoshi Osawa\*

Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan

Received May 8, 2008; E-mail: osawam@cat.hokudai.ac.jp

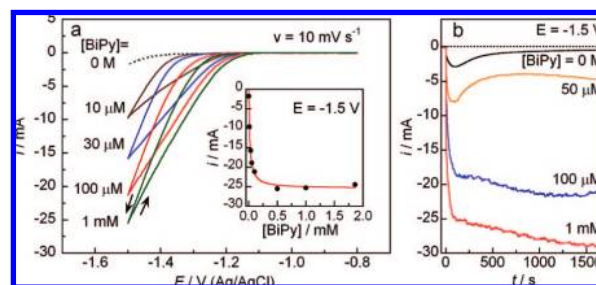
Hydrogen is becoming more important as an energy source for fuel cells. Electrolysis of water is one of the useful methods to produce H<sub>2</sub>. Among metallic electrocatalysts, Pt is the most active toward this reaction, while Ag, Cu, and Hg are several orders of magnitude less active.<sup>1</sup> However, hydrogen evolution reaction (HER) on such less-active metal electrodes is known to be enhanced by the addition of some organic molecules, such as thiourea,<sup>2–4</sup> pyridine,<sup>5</sup> thionine,<sup>6a</sup> NAD/NADH,<sup>6b</sup> methyl-viologen,<sup>6</sup> and vitamin K<sup>7</sup> into the solution. Reduction of adsorbed species is supposed to play a role in some cases,<sup>6,7</sup> but there is no clear interpretation for the origin of the enhanced HER. Here we report that 4,4'-bipyridine (BiPy) significantly enhances HER on Ag in neutral and basic solutions, and discuss its mechanism on the basis of in situ monitoring of the electrode surface by surface-enhanced infrared absorption spectroscopy in the ATR mode (ATR-SEIRAS).<sup>8</sup>

Cyclic voltammograms (CVs) for an Ag electrode (chemically deposited on a Ge ATR prism) in aqueous 0.1 M NaOH (Figure 1a) shows reduction current that increases with the increase in the BiPy concentration. The onset potential of the reduction current is positively shifted. At [BiPy] = 1 mM, the shift is ~0.2 V and the reduction current at -1.5 V (vs Ag/AgCl) is 14 times as large as that in the BiPy-free solution. The concentration dependence of the reduction current at -1.5 V can be fitted to the Langmuir isotherm (red curve in the inset), suggesting that BiPy adsorbed on the surface is responsible for the large reduction current.

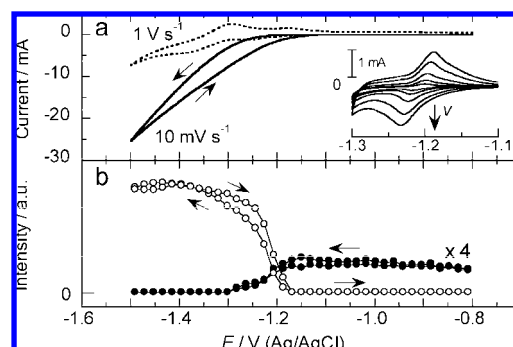
The enhancement factor reached to ~60 after 30 min polarization at -1.5 V (Figure 1b). The large current continued to flow for over 5 h accompanied by rigorous gas evolution. Gas chromatographic analysis showed that the evolved gas is pure H<sub>2</sub> (Faradaic yield of 97 ± 2%), which clearly shows that the reduction current is due to HER. Tafel plot of the reduction current under quasi-stationary conditions gave a straight line with a slope of 130 mV dec<sup>-1</sup> (Supporting Information Figure S1), indicating that HER is a one-electron (1e) process. The enhanced HER was also observed in neutral solution, but not at all in acidic solutions.

BiPy is known to be reduced to *N,N'*-dihydro BiPy (H-BiPy-H) via a single 2e-2H step in basic solutions at about -1.30 V.<sup>9,10</sup> The corresponding redox peaks were weakly observed at a fast sweep rate (dotted trace in Figure 2a). However, noticeable decrease of the BiPy concentration was not observed even after electrolysis at -1.5 V for 1 h as judged from UV-vis spectra of the solution, implying the suppression of the reduction to H-BiPy-H presumably due to the consumption of electrons by HER.

Careful inspection of the dotted CV in Figure 2a reveals an additional weak quasi-reversible redox couple around -1.2 V. The peak currents for the additional redox couple were directly proportional to the sweep rate  $\nu$  and the half-widths of the peaks were 70–90 mV (Figure 2a, inset). These features are characteristic of a 1e transfer process for a redox couple adsorbed on the electrode surface.<sup>11</sup> It is worth noting that the current for HER starts to flow around -1.2 V where the 1e reduction of adsorbed BiPy occurs.



**Figure 1.** (a) CVs for an Ag electrode in 0.1 M NaOH + (0–1 mM) BiPy at 10 mV s<sup>-1</sup>. Inset shows the current at -1.5 V plotted against BiPy concentration, which can be fitted to the Langmuir isotherm (red curve). (b) Chronoamperograms at -1.5 V under the same conditions as in panel a.

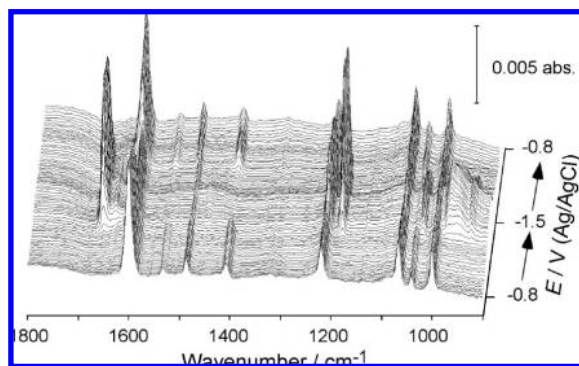


**Figure 2.** (a) CVs for an Ag electrode in 0.1 M NaOH + 1 mM BiPy at 10 mV s<sup>-1</sup> (solid) and 1 V s<sup>-1</sup> (dotted). Inset shows expanded CVs around -1.2 V at sweep rates  $\nu = 0.05, 0.1, 0.2, 0.4,$  and  $0.6$  V s<sup>-1</sup>. (b) Integrated intensities of IR bands at 1405 (●, BiPy) and 1663 cm<sup>-1</sup> (○, BiPy-H<sup>+</sup>) plotted against the applied potential.

The quasi-reversible redox wave and the onset potential of HER positively shifted with the decrease in pH of the solution by ~60 mV pH<sup>-1</sup> in a range of pH = 11–12 (Figure S2). At lower pH values, considerable increase of pH was observed during the electrolysis.<sup>12</sup> These results indicate that a proton from water is involved in the redox reaction of adsorbed BiPy and suggest that HER is initiated by its further reduction.

For further investigation of the reaction mechanism, the adsorbed state of BiPy on the electrode surface was examined by ATR-SEIRAS (Figure 3). Note that IR measurements are not disturbed by evolved H<sub>2</sub> bubbles in the ATR configuration.<sup>8b</sup> The spectrum at  $E > -1.2$  V was almost identical to that observed on Au electrodes in neutral solutions<sup>13</sup> and is ascribed to BiPy vertically adsorbed on the electrode surface via one N-end.

The spectrum reversibly changes when the potential is scanned across -1.2 V where the reversible redox reaction of adsorbed BiPy occurs. Time-resolved Raman studies on photolysis of BiPy revealed that monoanion radical (BiPy<sup>•-</sup>) is generated and the



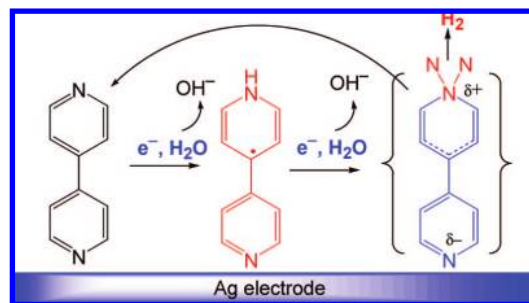
**Figure 3.** IR spectra of the Au electrode in 0.1 M NaOH + 1 mM BiPy acquired simultaneously with the CV in Figure 2 (at  $10 \text{ mV s}^{-1}$ ). A spectrum collected at  $-0.8 \text{ V}$  before adding BiPy into the solution was used as the reference.

radical withdraws a proton from solvents to yield *N*-monohydro radical (BiPy-H $^{\cdot}$ ).<sup>14</sup> Taking into account that the redox reaction at  $-1.2 \text{ V}$  is a  $1e-1H$  process, the same species is expected to be formed by the electrochemical reduction of adsorbed BiPy. In fact, the spectrum at  $E < -1.2 \text{ V}$  was in reasonable agreement with the calculated IR spectrum of BiPy-H $^{\cdot}$  (Table S1). The observed bands are assigned to  $a_1$  modes (in  $C_{2v}$  symmetry) having transition dipole moments along the long axis of the molecule. By applying the surface-selection rule in SEIRAS,<sup>8</sup> it is concluded that BiPy-H $^{\cdot}$  also is vertically oriented. The spectrum of BiPy-H $^{\cdot}$  is stably observed down to  $-1.5 \text{ V}$ . On the other hand, spectral changes corresponding to the  $2e-2H$  reduction of BiPy to H-BiPy-H around  $-1.3 \text{ V}$  are not found reflecting the suppression of this reaction.

Heyrovsky<sup>15</sup> observed  $\text{H}_2$  evolution on Hg electrodes in BiPy-containing basic solutions under light illumination and proposed a photocatalytic mechanism. The HER observed in the present study occurred even in the dark, and hence its mechanism is apparently different. As noted before, the coincidence of the onset potential of the enhanced HER and the  $1e-1H$  redox potential of vertically adsorbed BiPy strongly suggests that the reduction of adsorbed BiPy is a key step in the enhanced HER. The Tafel slope of  $130 \text{ mV dec}^{-1}$  for HER excludes nonelectrochemical mechanisms such as catalytic splitting of water by BiPyH $^{\cdot}$  and combination of H(-N) atoms of two neighboring BiPyH $^{\cdot}$ . Since BiPyH $^{\cdot}$  can be further reduced,<sup>9,10,14</sup> it is reasonable to propose that further  $1e-1H$  reduction of adsorbed BiPyH $^{\cdot}$  results in HER. This proposal appears to conflict with the IR observation that the band intensity of BiPyH $^{\cdot}$  was nearly constant during HER (Figure 2b), but it should be noted that the product should not be H-BiPy-H because one N-end of BiPyH $^{\cdot}$  is blocked by the adsorption. If the product is assumed to be unstable and immediately decomposed to  $\text{H}_2$  and BiPy, BiPyH $^{\cdot}$  can be reproduced by reduction and the processes can be catalytically cycled as illustrated in Scheme 1.<sup>16</sup> DFT calculations in which one N-end of the molecule is protected from protonation to model the adsorbed state suggested that a very likely product is semiquinone-like *N,N*-dihydro BiPy, and that it is stabilized by the decomposition to  $\text{H}_2$  and BiPy. Although such a process could not be confirmed spectroscopically, the experimental data given above are reasonably explained by this catalytic mechanism.

Finally, we wish to comment on the behavior of BiPy in acid, where the enhanced HER was not observed. A combined ATR-SEIRAS and STM study in acid revealed that diprotonated BiPy

**Scheme 1.** Proposed Mechanism for HER Catalyzed by Adsorbed BiPy



([H-BiPy-H] $^{2+}$ ) is adsorbed flat on Cu electrodes via  $\pi$  electrons and that its  $1e$  reduced species, semiquinone radical ([H-BiPy-H] $^{\cdot}$ ), are piled up to form one-dimensional columns extending parallel to the surface.<sup>17</sup> The IR spectra of BiPy adsorbed on the Ag electrode in acid (Figure S3) were essentially identical to those observed on Cu and the vertically oriented BiPyH $^{\cdot}$  was not detected. This fact reinforces the importance of the specific adsorption of the molecule via one N-end for the catalytic HER.

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**Supporting Information Available:** Experimental details, Tafel plot, calculated vibrational frequencies of BiPy-H $^{\cdot}$ , and SEIRA spectra of BiPy adsorbed on Ag in acid. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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