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Is Base-Inhibited Vapor Phase Polymerized PEDOT an Electrocatalyst for the Hydrogen Evolution Reaction? Exploring Substrate Effects, Including Pt Contaminated Au

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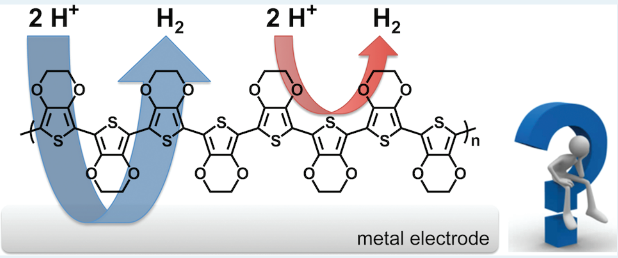

ABSTRACT: Studies of the hydrogen evolution reaction (HER) were carried out on base-inhibited vapor phase polymerized (BI-VPP) poly(3,4-ethylenedioxythiophene) (PEDOT)-poly(ethylene glycol) (PEG) thin films synthesized on several substrates, including gold, glassy carbon, and titanium, in an acidic electrolyte. The proton reduction overpotential became smaller and the current−potential (*i*-*E*) scans moved toward the thermodynamic potential with time. However, they did not move below the proton reduction potential of the substrate. Collectively, the results suggested to us that the polymer film was porous and that the porosity increased with time when the electrode was immersed in solution, with the hydrogen evolution catalysis taking place on the conducting substrate beneath the polymer rather than on our BI-VPP PEDOT-PEG thin films. Comparison of the HER on gold substrates with different impurities was also studied and traces of Pt and Pd at the ppm level significantly improved the HER activity of Au.

KEYWORDS: *base-inhibited vapor-phase polymerization (BI-VPP), PEDOT, PEDOT-PEG, conducting polymer, hydrogen evolution reaction*

INTRODUCTION

The hydrogen evolution reaction (HER) is a classical electrochemical reaction, and studies of it date back to the work of Tafel and many others in the early twentieth century.[1] Much has been written about the mechanism of this reaction, and the reason why some metals, like Pt, show very rapid electron transfer, and others, like mercury, show reaction rates that are many orders of magnitude lower. A two step mechanism[2,3] for the HER on platinum has been generally accepted. This consists of a fast initial step of proton discharge to give an adsorbed H atom (Volmer reaction), $H^+ + e^- \rightarrow H_{ads}$, followed by either a chemical recombination step (Tafel reaction), which is the rate determining step at low overpotentials, $H_{ads} + H_{ads} \rightarrow H_2$, or an electrochemical desorption step (Heyrovsky reaction), which is important at high overpotentials, $H_{ads} + H^+ + e^- \rightarrow H_2$. The HER on gold is proposed to occur by a similar mechanism.[4] The HER thus requires the adsorption of atomic hydrogen on the electrode surface promoting the one-electron reduction of proton (a reaction that occurs at much more negative potentials than the thermodynamic value for H^+/H_2). The relatively high rate of the reaction at Pt is the basis of the use of the normal (or standard) hydrogen electrode (N.H.E.), as first suggested by Nernst. For practical hydrogen generation via water electrolysis, Pt as a HER electrocatalyst, suffers from high cost, and the search for new, efficient, and inexpensive electrocatalysts continues.

Poly(3,4-ethylenedioxythiophene) (PEDOT), a conducting polymer used in antistatic coatings, photovoltaics, and other applications,[5] has recently been reported to show high electrocatalytic activities for the O_2 reduction[6] and proton reduction[7] reactions. The PEDOT-poly(ethylene glycol) (PEG) film used, which was synthesized by a novel base-inhibited vapor-phase polymerization (BI-VPP) route exhibited a small overpotential for the HER, approaching that of platinum. If BI-VPP PEDOT-PEG is indeed an electrocatalyst for these reactions, its low cost would make it an attractive cathode for water electrolysis. An interesting aspect of the reported behavior was that on continued use as a cathode or repeated cathodic current-potential scans, the behavior improved, that is, the overpotential decreased. However, explaining the high activity of this material is challenging and difficult to understand in terms of current models of the HER. We thus carried out experiments to test the activity of BI-VPP PEDOT-PEG for the HER, and found that the activity was related to the substrate material on which our polymer film was deposited. We found that the activity of substrate (i.e., gold), with or without the polymer film, was strongly dependent on trace amounts of Pt and Pd impurities.

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EXPERIMENTAL SECTION

Substrate Preparation. Titanium foil (0.25 mm thick, 150 × 150 mm^2) was purchased from Sigma-Aldrich (Milwaukee, WI) and cut into 15 × 15 mm^2 squares for use as electrodes. Prior to use, the Ti foils were immersed in acetone and ultrasonicated for 5 min. High-purity gold was evaporated onto the Ti surface to prepare the gold substrate using a DV-502A high-vacuum thermal evaporator (Denton Vacuum, Moorestown, NJ). Glassy carbon (GC) plates (1 mm thick, 50 × 50 mm^2) were purchased from Alfa Aesar (Ward Hill, MA). The GC plates were cut into 15 × 15 mm^2 squares and immersed into acetone or ethanol, ultrasonicated for 5 min, then immersed into DI water and ultrasonicated for 5 min. The cleaned GC plates were stored in DI water.

PEDOT-PEG Film Vapor Phase Polymerization. The PEDOT-PEG film was prepared following the reported procedures,[7] although it is possible that there are special conditions that affect film behavior. In more detail, iron(III) *p*-toluene-sulfonate (Fe(III)PTS) (Sigma-Aldrich, Milwaukee, WI) was dissolved in anhydrous 1-butanol (Fisher) containing <0.05% water to make a 40% solution. The base-inhibited PEDOT-PEG solution was prepared by adding 75 μL of pyridine (99+%, spectrophotometric grade, Sigma-Aldrich, Milwaukee, WI) and 220 μL of 50% PEG (20000 Da, Sigma-Aldrich, Milwaukee, WI) in water per 3.25 mL of 40% Fe(III)PTS solution. Then, 50 μL of the base-inhibited precursor solution was drop coated on one side of the substrate, dried at 75 °C in air for 5 min, and fixed in an environment saturated with 3,4-ethylenedioxythiophene (EDOT) (97%, Sigma-Aldrich, Milwaukee, WI) overnight. After the polymerization was complete, the sample was washed twice in ethanol.

Electrochemical Measurements. Linear scan voltammetry (LSV) was carried out using a CHI 630D electrochemical instrument (CH Instruments, Austin, TX) with a carbon rod as counter electrode and a homemade reversible hydrogen electrode (RHE) as reference electrode. Long-term constant current measurements were carried out using a PAR 173 potentiostat (Princeton Applied Research, Oak Ridge, TN) with a carbon rod as counter electrode (to avoid possible contamination of the solution by oxidation of the electrode material) and an Ag/AgCl (with a K_2SO_4 salt-bridge to avoid Cl^- contamination) as reference electrode. All potentials in this paper are reported vs the RHE.

RESULTS AND DISCUSSION

Effect of Soaking Time on the HER for a BI-VPP PEDOT-PEG Film on Gold. To test the effect of long-term soaking of the electrode on the electrochemical response, the electrode was immersed in 0.5 M H_2SO_4 for different times and transferred to an electrochemical cell containing 0.5 M H_2SO_4 where linear scan voltammograms (LSV) were recorded (Figure 1). Proton reduction scans at 5 mV/s of the BI-VPP PEDOT-PEG film on a gold substrate for immersion times of 0 to 160 h are shown. The volume of 0.5 M H_2SO_4 soaking solution did not change over the course of 160 h, so there was no significant concentration change. The onset potential of proton reduction was observed to shift to more positive potentials as the time the electrode was immersed in the electrolyte increased, which is similar to the previous results.[7] However, the proton reduction overpotential did not move to a position more positive than the HER potential of the gold substrate (dotted line), even after soaking in the electrolyte for more than 160 h, but ended up fairly close to the Au electrode behavior. Note that except for the time the electrode was in the cell for voltammetry, it was only soaked at open circuit.

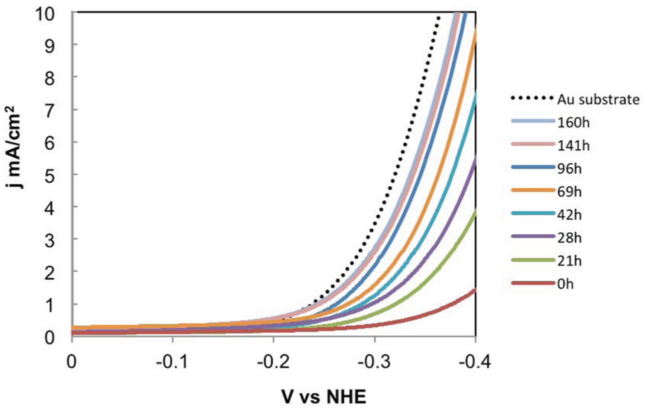

Figure 1. LSV of HER of BI-VPP PEDOT-PEG film on Au substrate with different times of soaking of the film. Scan rate 0.5 mV/s, in 0.5 M H_2SO_4 under N_2. The BI-VPP PEDOT-PEG film was kept in 0.5 M H_2SO_4 under a water vapor saturated atmosphere between each scan.

These results suggested to us that the BI-VPP PEDOT-PEG film itself is not electrocatalytic and that it is the increased access of the gold under layer that promotes the reaction. In essence, soaking assists in the transport of protons to the gold surface. The HER on metallic electrodes coated with polymer film has also been studied in the past, for example, by Schultze et al.,[8,9] Bard et al.,[10] and Li et al.[11] In these studies the polymer films were also said to be porous to solvent and proton, with hydrogen evolution taking place on the metallic substrate. Moreover, the results[12] of Aydin and Koleli revealed that conducting polymer coatings, including polyaniline (PAn), polypyrrole (PPy), and an aniline-pyrrole copolymer (PAn−PPy), on a Pt electrode showed a higher HER overpotential and higher activation energies than those on bare Pt. The penetration of the proton into a poly(N-methylpyrrole) (PNMP) film in acidic aqueous solution was reported to depend strongly on the counteranion originally doped into the PNMP during polymerization.[10] Even when the conjugation was destroyed by overoxidation, which changes the polymer from a conducting state to an insulating state, the HER can still take place if channels in the polymer exist. The polymers that interact by association with protons can also affect the HER process by modifying proton diffusion. Maksymiuk and Doblhofer[13] demonstrated that the presence of a polymer mixture coating of PNMP and poly(4-styrenesulfonate) (PSS) on gold can enhance the rate of electrochemical H^+ reduction when the concentration of proton in the electrolyte is small, because of a proton preconcentrating mechanism in the polymer. In contrast, the PNMP-PSS copolymer hindered the HER when the proton concentration was high by hindering the mass transfer of H^+ to the gold electrode. The fact that the HER potential shifted to more positive positions in Figure 1 can be attributed to enhanced proton diffusion in the BI-VPP PEDOT-PEG polymer because of enlarged ion channels and increased surface areas caused by the swollen polymer film as a result of the uptake of the electrolyte. The LSV data did not show a substantial change between times of 141 and 160 h, indicating that the BI-VPP PEDOT-PEG film became fully swollen at around 140 h immersion in 0.5 M H_2SO_4. The time required for our sample to reach saturation was longer than the time reported previously,[7] which may be attributed to differences in the film structure and thickness.

Long Duration Constant Current HER Electrolysis at a BI-VPP PEDOT-PEG Film on Gold. Long-term HER performance under continuous electrolysis of the BI-VPP PEDOT-PEG film on gold was also tested under constant current conditions (current density, 1.4 mA/cm^2) as shown in Figure 2. To avoid any experimental artifact from solvent evaporation and oxygen reduction, the long-term electrochemical test cell was maintained under continuous water vapor-saturated N_2 purging. For comparison, the potential obtained at that same current density is also presented (i.e., from Figure 1). There was no apparent difference between the results obtained from linear scan voltammetry, which sampled at different times after immersion in the sulfuric acid, and the potential readings from the electrochemical cell under continuous operation. These results indicate that the improvement of HER overpotential was mainly associated with the time of immersion in the 0.5 M H_2SO_4, rather than the electrochemical reaction itself. Note that under continuous electrochemical reaction the hydrogen evolution potential did not shift to a position more positive than that of the gold substrate, which agreed with results from the experiment in Figure 1, suggesting again that the active electrocatalyst for HER on the BI-VPP PEDOT-PEG film over gold substrate is indeed the Au foil beneath the polymer.

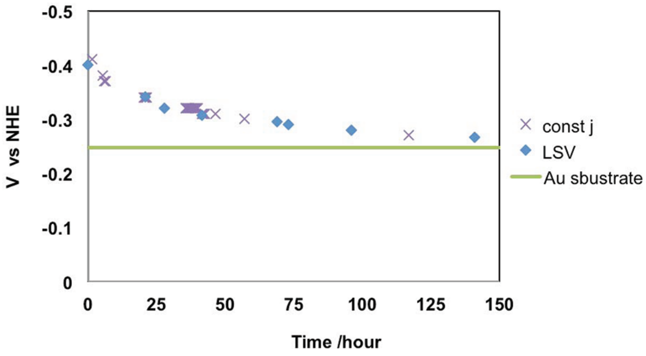

Figure 2. Long-term HER performance of BI-VPP PEDOT-PEG film on gold at constant current (1.4 mA/cm^2) under continuous water vapor saturated N_2 purging. For comparison, the potential at that same current density from wait and measure experiment and bare gold are also presented.

HER for a BI-VPP PEDOT-PEG Film on Different Substrates. To further investigate the substrate effect, we performed the same HER experiments on a BI-VPP PEDOT-PEG film on different substrates. LSV data with a fluoride doped tin oxide (FTO) substrate were irreproducible, probably because at the negative potentials for proton reduction changes in the FTO surface occur with a subsequent change in conductivity. However HER voltammograms with a PEDOT-PEG film could be obtained with glassy carbon (GC) plate and titanium foil, as shown in Figure 3. Similar results were observed as with a gold substrate, which is shown in the figure for comparison. In all cases, the initial potentials at 5.4 mA/cm^2 were more negative than the HER potential on the bare substrate at the same current density. They then shifted positively toward the bare substrate with the time the electrode was immersed in the electrolyte as seen with gold and in the reference electrodes.[7] Again, the proton reduction potential did not become more positive than the substrate. These results may be explained by the electrocatalytically active part of the surface being the substrate beneath the BI-VPP PEDOT-PEG film and not the PEDOT film itself. One can compare this behavior to that of electrodes with polymer-supported catalysts, which have been studied previously. The electrocatalytic properties of platinum microparticles supported by poly(vinylpyridine) films, were investigated for the HER in acidic media and the catalytic effects depended mainly on the size and amount of platinum particles dispersed in the polymer film.[14] Navarro-Flores and Omanovic[15] studied the HER on polypyrrole and polyaniline-supported Ni catalysts and found that the supported catalyst showed a significantly higher overall electrocatalytic activity in the HER compared to Ni electrodeposited on a flat two-dimensional substrate, because of the higher active surface area of the supported catalyst. Similar studies were reported for polypyrrole-supported nickel-phosphorus (Ni-P) by Abrantes and Correia.[16] The Ni-P from electroless deposition was said to improve the HER catalytic activity as the quantity of dispersed Ni-P increased, when compared to unmodified PPY. Makhloufi and co-workers[17] reported that copper-modified PPY showed noticeable enhancement for the rate of proton reduction that increased as the copper concentration increased. These findings agreed well with the conclusion that the electrochemically active electrocatalytic component is not the polymer film, but rather its metallic component.

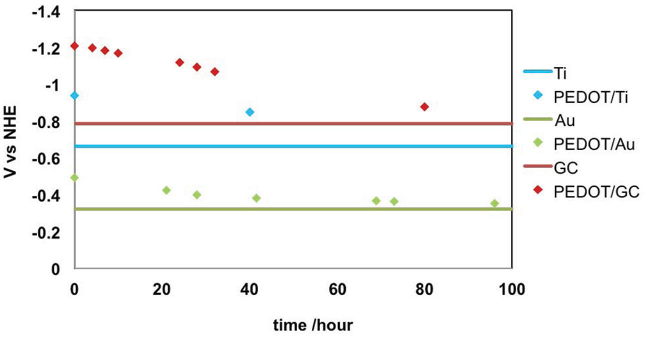

Figure 3. Comparison of long-term HER performance of BI-VPP PEDOT-PEG film on gold, titanium, and glassy carbon (GC) at constant current (5.4 mA/cm^2) under continuous water vapor saturated N_2 purging. The solid lines represent HER on bare substrates.

Effect of Noble Metal (Pt, Pd) Contamination of Au for the HER. Another factor that can be important in studies of polymers for cathodic reactions, involves situations when Pt is used as the counter electrode (anode). Pt anodes, especially in acidic media, are known to produce dissolved Pt ions in the solution as the reaction progresses.[18] Such dissolved Pt species can be reduced at the cathode, resulting in finely divided Pt particles on the film, often causing a large increase in activity with time. For example the high HER activity, comparable to metallic Pt reported for the BI-VPP PEDOT-PEG film[7] (the HER onset was ca. −0.19 V vs SCE after 72 h) might also be caused by such an effect (the counter electrode was not specified). A pure gold substrate is not expected to exhibit such a positive onset potential.[19−24] However, Au is often contaminated with Pt and Pd. For example, a recent report on presumed Au-catalyzed cross-coupling reactions[25] proposed that the catalytic cycles are, in fact, not catalyzed by Au but rather by trace amounts of Pd contamination. We thus examined the effect of the impurity content of HER active metals in our gold films. The Pt and Pd amounts in the gold source (sample 1) we used in our experiments (in Figures 1 to 3) were determined by inductively coupled plasma-mass spectroscopy (ICP-MS) and found to be 42 ppm (Pt) and 132 ppm (Pd). Such a high concentration of highly HER active metals can shift the proton reduction potential to more positive values compared to a pure gold film. To demonstrate this effect, LSV curves for the HER were taken under the same conditions with gold electrodes of higher purity: sample 2, (nominal purity 99.99%, Pt, 4.6 ppm and Pd 1.0 ppm), and ultrahigh purity gold, sample 3 (nominal purity 99.9995%, both Pt and Pd concentrations <0.2 ppm). The curves for all 3 samples, shown in Figure 4, strongly suggest that the overpotential for the HER is closely related to the amount of Pt and Pd in the gold film. As the content of highly HER active metals increased, the proton reduction potentials shifted positively with respect to the ultrapure Au sample. Pandelov and Stimming[22] studied electrochemical hydrogen evolution reactions on palladium nanoislands grown on Au, and demonstrated that an over 200 mV positive shift can be achieved even when the Pd coverage is only 0.034 of a monolayer. Schafer and Kibler[19] reported similar phenomena when they immersed a Au(111) single crystal into a Pd^{2+} containing solution. A shift of more than 100 mV was seen in their curves after the gold crystal was immersed for 10 min. In the same way, the overpotential of the HER in acidic electrolytes can be considerably reduced by a monolayer of Pt on a Ag(111) electrode.[26] Desic et al[23] studied platinum modification of a gold surface and gold modification of a platinum surface and their influence on hydrogen evolution. A platinum overlayer on the gold substrate significantly increased the activity for HER, making it comparable with pure platinum. Thus, we consider the shift of HER potential in Figure 4 may be attributed to Pt and Pd impurities in our gold films, and suspect that the gold used earlier might have also had substantial amounts of highly HER active metals.

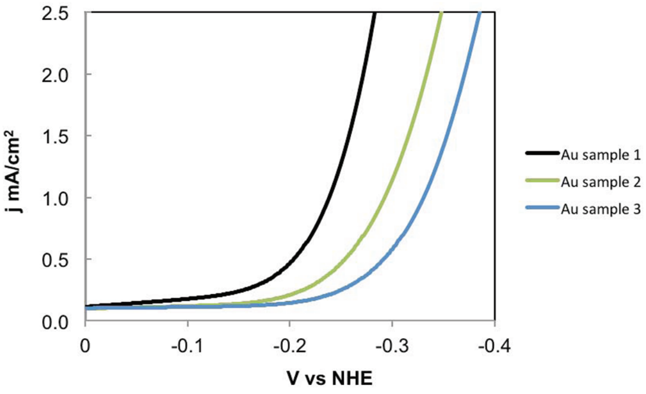

Figure 4. LSV of HER of bare Au substrate of different concentration of Pt and Pd impurities. Sample 1: Pt 42 ppm, Pd 132 ppm; Sample 2: Pt 4.6 ppm, Pd 1.0 ppm; Sample 3: Pt <0.2 ppm, Pd <0.2 ppm.

CONCLUSIONS

In summary, the reported low overpotential of hydrogen evolution reactions (HER) on BI-VPP PEDOT-PEG thin films was examined using polymer films on several substrates, including gold, glassy carbon, and titanium. The proton reduction potential showed improvement toward its thermodynamic potential over time as suggested earlier.[7] However, it was a function of the substrate material and did not move to a position more positive than the proton reduction potential of the substrate. The results suggested to us that the polymer film is porous, and the porosity increases with immersion time in solution, with the hydrogen evolution electrocatalysis was taking place on the substrate beneath the polymer rather than at the BI-VPP PEDOT-PEG thin film. Comparison of the HER on gold substrates with different impurities was also investigated. The results indicated that trace (ppm) amounts of Pt and Pd in Au can improve the HER activity significantly. The different behavior of our PEDOT films and the earlier ones may be due to some subtle differences in the preparation and experimental conditions between these two experiments.

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Notes

The authors declare no competing financial interest.

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