Optimal Surface Doping of Lead for Increased Electrochemical Insertion of Hydrogen into Palladium

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ABSTRACT

Increasing the amount of hydrogen that is electrochemically inserted into materials is important for studying superconductivity and hydrogen embrittlement, and improving hydrogen storage capabilities. Surfaces can be engineered to accomplish this task with better insight into how the composition of a material's first few atomic layers affects the electrochemical insertion of hydrogen. To this end, different amounts of Pb were added to the 0.1 M LiOH electrolyte to be deposited onto Pd cathodes during galvanostatic experiments. The investigated amount of added Pb was between $1\,\mu g\,cm^{-2}$ and $23\,\mu g\,cm^{-2}$ with respect to the geometric area of the Pd cathode. The optimum surface doping level $2.9\,\mu g\,cm^{-2}$ of Pb ($\sim$1.4 mass equivalent monolayers) was found to achieve the highest quantity of inserted hydrogen at approximately $-0.5\,V$ vs RHE. Additionally, the hydrogen content increased from $PdH_{0.75}$ to $PdH_{0.86}$ with increasing Pb amounts up to $2.9\,\mu g\,cm^{-2}$ at a constant current of $-14.5\,mA\,cm^{-2}$. For comparison, the same change in hydrogen content from pressurized gas loading experiments would require an increase in hydrogen fugacity from about 6 to 1420 atm. Preliminary analysis concerning the adsorbed hydrogen chemical potential suggests the Pb is affecting the balance between the Volmer, Heyrovsky, and Tafel reaction rates, which changes the hydrogen surface chemical potential, and ultimately controls the hydrogen insertion. Furthermore, the addition of Pb was found to decrease the rate of hydrogen insertion. This work provides a fundamental basis for the future design of metal surfaces yielding enhanced electrochemical hydrogen insertion in Pd and other hydrogen absorbing materials.

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1. Introduction

Electrochemical insertion of hydrogen in materials is of interest for superconductivity studies [1], hydrogen embrittlement studies [2], and hydrogen storage applications [3,4]. Modifying the surface of metals with known hydrogen insertion promoters (e.g. Pb, As, thiourea, *etc.*) can increase the adsorbed hydrogen chemical potential obtained during aqueous electrolysis [5,6]. Diffusion of the hydrogen into the bulk ensues due to the chemical potential gradient, resulting in an elevated hydrogen content in the bulk of the electrode material. Quantities as small as nanomolar of insertion promoters in the electrolyte have resulted in such effects [5]. Hydrogen insertion promoters are commonly used to study hydrogen embrittlement [2], and have also garnered interest in

enhancing the hydrogen storage capability of materials [3,7]. Although a number of explanations for the insertion enhancement obtained by non-metallic insertion promoters (e.g. thiourea [3,8,9], As [10], H_2S [11]) have been presented, explanations as to how the addition of surface metals behave as insertion promoters is still lacking.

A better understanding of how the addition of surface metals affect hydrogen insertion could lead to the engineering of surfaces to maximize such an effect. Pd was chosen as the cathode material to study the effects of the surface promoter Pb on hydrogen insertion. Pd is a material known to absorb large quantities of hydrogen, reaching $PdH_{0.69}$ at 1 atm H_2 [12]. The hydrogen content in palladium hydrides can be determined by the measurement of electrical resistance as there is a well-studied relationship between electrical resistance and hydrogen content up to $PdH_{1.0}$ [12–14]. Galvanostatic measurements were performed to observe the changes in electrode potential and hydrogen content under different effective Pb surface coverages. The results show that

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there is an optimum Pb coverage $\sim 3\,\mu g\,cm^{-2}$ to achieve the maximum hydrogen content at $\sim -0.5\,V$ vs RHE. At this coverage, the reaction route is likely a mixture between Volmer-Tafel and Volmer-Heyrovsky routes. The Pb is likely acting to suppress the Tafel reaction, making it possible to get a higher chemical potential for hydrogen on the surface without fully enabling the Heyrovsky mechanism. Above this coverage, the reaction route begins to change to primarily Volmer-Heyrovsky. This finding suggests that surfaces can be engineered to maximize hydrogen insertion under given working conditions.

2. Experimental section

2.1. Cathode Assembly for Simultaneous Resistance Measurements

The Pd cathode was placed in a configuration to allow simultaneous four-point resistance measurements during the electrochemical experiments. An illustration of the cathode assembly can be found in Fig. S1(a) in the supplementary material. Pd cathodes were fabricated in-house by cold rolling sections of a Pd sputter target (ESPI, 99.95%) to a thickness of 40-50 μm. The final passes through the mill were made with polished rollers to produce a mirror finish on the cathodes. The Pd cathodes were cut to dimensions of 7 mm $\times$ 40 mm. Two 4.1 mm diameter holes were punched in the ends of the foils so that polyether ether ketone (PEEK) screws could thread through to immobilize the cathode and provide mechanical compression for the electrical connections with 50 μm thick Pt flags. One of the Pt flags was 10 mm $\times$ 10 mm and had two Pt wires for four-point resistance measurements and one Pt wire for power. Another Pt flag was 10 mm $\times$ 7.5 mm and had the other two Pt wires for four-point resistance measurements. All Pt wires were spot-welded to the Pt flags using high-melting point tungsten welding tips to reduce the possibility of contamination. The Pt flags also had 4.1 mm diameter holes punched out. The cathode was placed on a polytetrafluoroethylene (PTFE) support between two PEEK spacer blocks, followed by the Pt foils, the Pd cathode, and another PEEK spacer block. The assembly was fastened to the PTFE support with PEEK screws and nuts. As assembled, the total exposed Pd (including front and back geometric areas) in contact with electrolyte was 2.8 cm^2. All Pt wires were encapsulated with PTFE/FEP dual shrink tubing (Zeus) and the PEEK blocks were sized to minimize the effect of Pt on the electrochemical measurements.

2.2. Cathode Cleaning

The Pd foils and cathode assembly were cleaned of impurities so that only the effects of Pd and Pb were observed. The as-rolled and sized Pd foils were first cleaned by sonicating at room temperature in isopropyl alcohol (IPA) followed by sonication in acetone for 5 min each. The foils were then rinsed in IPA and deionized (DI) water. The foils were placed in a vial that contained concentrated HNO_3 (trace metal grade, Fisher Chemical) and kept at 90 $^\circ C$ for 40 min. Finally, the foils were rinsed in DI water and blow dried by compressed difluoroethane gas (Falcon Dust-Off). A foil was then placed in the cathode assembly, which was subsequently soaked in 5% HNO_3 and rinsed in DI water prior to placing into the electrolyte. The cell preparation and experiments were performed under a NuAire horizontal laminar flow hood (NU-301-630) to prevent environmental contamination.

2.3. Configuration of Electrochemical Cell

A borosilicate glass split-cell was used to prevent the deposition of Pt on the cathode and remove the effects of O_2 on the electrochemical experiments. An illustration of the cell can be found in Fig. S1(b) in the supplementary material. The cell had a water jacket to maintain the cell at 25 $^\circ C$ via a water chiller. The two sides of the cell were separated by a Nafion^{TM} 1110 proton exchange membrane. A batch of membranes were cleaned by soaking in 5% HNO_3 at 60 $^\circ C$ for at least two hours, and subsequently stored in a fresh 5% HNO_3 solution at room temperature until use. A new membrane was used for each experiment after rinsing in DI water. The electrolyte on the cathode side of the cell was 0.1 M LiOH, which was prepared in-house in a glove bag under an Ar environment by dissolving Li metal (Sigma-Aldrich, ribbons or granular > 99% trace metals basis) in DI water. A reversible hydrogen electrode (RHE; Gaskatel Hydroflex® RHE) was also placed in the 0.1 M LiOH compartment. The electrolyte on the anode side of the cell was 0.1 M H_2SO_4 (Fisher Scientific, trace metal grade). Fresh electrolytes were prepared for every experiment. The anode for all experiments was a Pt foil of dimension 10 mm $\times$ 40 mm, also with two holes punched, and a spot-welded Pt wire lead. Heavy Ar purging (>100 bubble s^{-1}) was performed for at least 10 min prior to starting all experiments and slow Ar bubbling (1-2 bubble s^{-1}) was maintained on both sides of the cell throughout the experiments to purge of O_2 and CO_2 in the cathode compartment. A thermocouple for cell temperature measurements was placed in the solution through a PTFE sleeve which was pinned near the bottom of the cathode. The cell was thermally stabilized for at least 10 min before running the experiments.

2.4. Pb Doping Solution

Pb was deposited on the cathode by adding a solution containing Pb directly into the electrolyte during electrolysis. The Pb doping solution was prepared by dissolving Pb in 0.1 M LiOH in a water bath at 90 $^\circ C$ for 4.5 h. The Pb concentration was measured by inductively coupled plasma mass spectroscopy (ICP-MS). This solution was then diluted to a concentration of 10 ppm Pb in 0.1 M LiOH. The amount of Pb added to the electrolyte is reported as μg per cathode geometric area (i.e. $\mu g\,cm^{-2}$). It is assumed that the cathode-to-cathode difference in electrochemical surface area is small, considering they were all prepared the same way. The Ar flow was increased to >100 bubbles s^{-1} for about 10-15 min after doping the electrolyte to mix the solution.

2.5. Electrochemical Measurement Procedure

The electrochemical measurement protocol was designed to provide the necessary data to observe changes in hydrogen insertion as a function of current density (j), and calculate the Tafel slopes and exchange current densities obtained from Tafel plots. Electrochemical measurements were performed using a Bio-Logic potentiostat/galvanostat module. All applied current densities throughout the experiment were cathodic and are reported here with respect to the Pd geometric surface area of 2.8 cm^2. A constant current of $-3.6\,mA\,cm^{-2}$ was applied to the Pd electrode for about 15.5 h to reach a steady state hydrogen content. Afterward, the electrolyte was spiked with Pb without disrupting the current, which was maintained for another 4 h. Next, galvanostatic stepping was performed from $-0.18\,mA\,cm^{-2}$ to $-18\,mA\,cm^{-2}$ in $-1.8\,mA\,cm^{-2}$ increments holding for about 1 h at each current density. The first iteration of the stepping protocol will be referred to as galvanostatic step (GS) cycle 1. Subsequently, the cathode was held at $-3.6\,mA\,cm^{-2}$ again for about 4 h and the stepping protocol was repeated (referred to as GS cycle 2, and so on). Fig. S2 in the supplementary material shows the protocol in detail. All the data presented in this work was obtained from GS cycle 2 so that adequate time was allowed for Pb deposition. The hydrogen content reported herein was obtained at the end of each