Engineering Palladium Surfaces to Enhance the Electrochemical Storage of Hydrogen

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Materials can be engineered to have enhanced hydrogen storage capabilities during electrolysis by modifying the composition of the first few atomic layers. The changes in composition of the near surface can radically affect the electrochemical insertion of hydrogen. The hydrogen stored under galvanostatic conditions was investigated after altering the composition of the Pd surface with various combinations of Pb, Bi, and Pt. It was found that the addition of a underpotential deposition of Bi on the Pd cathode increases the hydrogen content from PdH$_{0.77}$ to PdH$_{0.81}$ at $-10.9$ mA cm$^{-2}$, and the addition of Pt to the Bi further increased the hydrogen content to PdH$_{0.87}$. This work provides a fundamental basis for the future design of surface alloys yielding enhanced electrochemical hydrogen storage in Pd and other hydrogen absorbing materials.

Introduction

Hydrogen (H) is currently used as an alternative energy source, yet obtaining a method to increase the storage remains a challenge. One method of storage that can be investigated is the electrochemical storage of H. This method generates and stores hydrogen that is absorbed into the cathode during water electrolysis. Hydrogen evolution and absorption from alkaline solutions proceeds through the following four reaction steps:

\[
H_2O + M + e^- \rightleftharpoons MH_{surf} + OH^- \quad [1]
\]

\[
2MH_{surf} \rightleftharpoons 2M + H_2 \quad [2]
\]

\[
H_2O + MH_{surf} + e^- \rightleftharpoons H_2 + OH^- + M \quad [3]
\]

\[
MH_{surf} \rightleftharpoons M_bH_{bulk} \quad [4]
\]

where the reactions are Volmer [1], Tafel [2], Heyrovsky [3], and Penetration [4], respectively. $M$, $M_b$, $H_{surf}$, and $H_{bulk}$ represent the adsorption site on the surface metal, absorption site in the bulk metal, adsorbed hydrogen, and absorbed H, respectively. An understanding of how to increase the electrochemical insertion efficiency of H by modifying the composition of the surface would be beneficial to the electrochemical H storage, studying superconductivity and H embrittlement, and may provide further insight into electro-reductions involving H.

Pd is an excellent substrate material to study the H insertion because it has a well characterized relationship between electrical resistance and quantity of absorbed H. Therefore, the H content can be measured in situ. Our previous work demonstrated that there is an optimal Pb surface coverage to achieve the maximum amount of inserted H in
0.1 M LiOH electrolyte at −0.5 V vs RHE (1). The analysis of the bulk H content, a proxy for the H surface chemical potential ($\eta_2$), with respect to applied current density and measured overpotential suggested a delicate balance between the Volmer, Heyrovsky, and Tafel reaction rates. It is this balance that permits enhanced H insertion. Specifically, the results showed decreased Tafel rates were correlated with increased storage at the selected potential of approximately −0.5 V vs RHE. The addition of Pb decreased the Tafel rate up to a certain amount before the overpotentials necessary to drive the currents were large enough that the Heyrovsky mechanism was enhanced. Overall, the results suggested that sub monolayer additions to the surface of a substrate can enhance H storage and that the surface can be engineered to achieve higher loadings.

This work sets out to provide further engineering insight to assist the future optimization of surface alloys for the maximization of electrochemically stored H. Previously published mathematical relationships show a connection between the exchange current densities for the reactions and the chemical potential of H (2–6). Since exchange current densities are material properties, one can study different combinations of surface additions to fine tune these properties and maximize the stored H. Density functional theory (DFT) calculations were used as a first step in screening materials for further study. Then, the amount of stored H obtained in Pd after the addition of different surfaces consisting of Bi, Pt, and Pb were studied. Further studies on the chemical potential of adsorbed H provided insight into how each of these surfaces is affecting the individual exchange current densities of the Volmer and Tafel reactions.

**Experimental**

**Cathode Assembly**

The Pd cathodes were configured to allow simultaneous four-point resistance measurements during the electrochemical experiments. Pd foils (ESPI, 99.95%) were cold-rolled in-house to a mirror finish, a thickness of 40-50 µm, and cut to dimensions of 7 mm × 40 mm. Five Pt wires were spot welded directly to the Pd foils using a Tungsten tip. The Pt wires were encapsulated using PTFE/FEP shrink tubing (Zeus). The contacts to the foil were entombed with polydimethylsiloxane (PDMS, Sylgard 184) inside PTFE/FEP shrink wrap tubes. The assembly was placed in an oven at 100 °C for at least 1 h to cure the PDMS. A photograph of the cathode assembly for the experiments is shown in Figure 1. The average geometric surface area of the cathodes exposed to the electrolyte was 4.6 ± 0.1 cm$^2$. All reported current densities ($j$) will be referred to the geometric area.

**Configuration of the electrochemical cell**

The cell configuration is the same as that reported previously (1). Briefly, a borosilicate glass split cell was used where a Nafion 1110 proton exchange membrane separated the cathode and anode compartments to prevent deposition of the Pt anode onto the cathode. Ar purging was performed in both compartments throughout the experiments to mitigate the effects of O$_2$ on the measurements. The Pd cathode and a Gaskotel® reversible hydrogen electrode (RHE) reference electrode were placed in 0.1 M LiOH, and a Pt foil anode was placed in 0.1 M H$_2$SO$_4$. 
Energy Dispersive X-Ray Spectroscopy (EDS) Measurements

EDS measurements were taken using a scanning electron microscope equipped with a Bruker XFlash 410-M X-ray detector. The electron energy was 5 keV and the beam intensity was set to 19.

Electrochemical measurement procedure.

The electrochemical measurements were performed under computer control using a Bio-Logic VSP potentiostat/galvanostat in galvanostatic mode. A galvanostatic step cycle consisted of 11 steps from −0.5 mA to −50.5 mA in −5 mA increments. The current was held for 2 h at each current setting to allow time for the H content in the cathode to reach its quasi-steady state value. The stability of the surface layers was studied by observing the changes in the stored H by running through at least three galvanostatic step cycles. The second cycle was used for the other analysis. Additional information on the procedure can be found in Ref (1).

Deposition procedures.

The effects of Bi, Pt, Pb, and Bi+Pt surfaces on the occlusion of H by Pd foils were investigated. The electrochemical measurement procedure was first performed on all the Pd cathodes in their pristine state without a coating to serve as controls. This also solution hardens and deforms the cathodes so that these effects are separated from the surface treatments. Before performing a deposition, the samples were run anodically in 1% tr. metal grade HNO₃ up to 0.3 V vs Pd until the resistance was within 1% of the original resistance, indicating that there was <1% H left in the Pd. The underpotential deposition of the materials was selected as the primary deposition method, as it is expected to deposit the most uniformly and to 1 monolayer (ML).

Bi deposition. Two Bi surface thicknesses were investigated. The first thickness was deposited by underpotential deposition (UPD). The UPD Bi was deposited in a Bi₂(SO₄)₃
solution prepared by dissolving Bi (99.998% MetalShipper) in hot concentrated H$_2$SO$_4$ (trace metal grade, Fischer Scientific). The concentrated H$_2$SO$_4$ solution was diluted to 1 mM Bi in 0.5 M H$_2$SO$_4$. The UPD was performed by first holding the sample at 0.9 V vs Ag/AgCl for 1 min prior to stepping the potential down to 0.1 V vs Ag/AgCl for 5 min. The UPD potential of 0.1 V vs Ag/AgCl was chosen because cyclic voltammetry measurements showed bulk Bi deposition occurred at roughly 0.04 V vs Ag/AgCl. EDS analysis for this sample showed 1.8 ± 0.5 at% Bi at 5 kV.

The second investigated thickness was performed by bulk deposition of Bi at −0.5 V vs Ag/AgCl for 3 min. This potential is below that required for electrolysis, so it is likely that the coating does not have the same uniformity as that of the UPD Bi sample. EDS showed 4.9 ± 0.9 at% Bi, roughly three times the amount of Bi obtained by the UPD of Bi.

Pb deposition. UPD of Pb was performed using a solution of 0.1 M NaClO$_4$, 1.0 mM HClO$_4$, and 1.5 mM Pb(ClO$_4$)$_2$ at a potential of -0.425 V vs Ag/AgCl held for 4 min (1).

Bi(UPD)+Pt deposition. Pt was deposited via a galvanic exchange reaction between Pt and Bi. After Bi UPD, the sample was rinsed in DI water and placed in a solution of 0.1 M NaClO$_4$, 5 mM HClO$_4$, and 5 mM K$_2$PtCl$_4$ for 20 min. EDS measurements showed a final Pt/Bi atomic ratio of 0.13 ± 0.01 after the Bi/Pt exchange.

Pt deposition. The Pt deposition was performed by galvanic exchange between Pt and H. Therefore, the potentiostatic H stripping was not performed for this sample to allow H to remain on the surface to be available for the Pt/H exchange. This resulted in significant Pt deposition during the 12 min exposure to the Pt solution. EDS analysis showed 40-50 at% Pt at 5 kV. In contrast, soaking a piece of unrun Pd overnight in the Pt solution resulting in an EDS measured Pt amount of <0.1 at% at 5 kV, suggesting the rate of exchange between Pt and Pd is insignificant.

Procedure to determine H content.

The four-point resistance measurement was used to infer the H content in PdH$_x$ (1, 7, 8). This technique uses the empirical relationship between the atomic H/Pd ratio ($x$) and the ratio of the measured resistance ($R$) to the initial resistance ($R_o$) determined by Zhang et al. by fitting experimental data to the fourth order polynomial equation (7):

$$\frac{R}{R_o} = 1 + 1.69731x - 5.34162x^2 + 13.4472x^3 - 9.87644x^4$$

[5]

The resistance was measured using an HP4263B LCR meter with 1 V$_{rms}$ and 10 kHz signal. The LCR meter was isolated from the galvanostat via a transformer circuit.

DFT modelling setup.

All DFT calculations were performed by using ATK QuantumWise package with numerical atomic basis sets (9–11). The exchange-correlation functional used in the calculations was at the generalized gradient approximation level, known as GGA-PBE.
and is proved to show high precision calculation outcomes for transition group metals (12, 13). The optimized double-zeta polarization basis set was employed. The accuracy of the model was tested against known experimental values of crystal lattice constants, and H adsorption energies on given metal surfaces. The accuracy was found to be within 3% of experimentally accepted values. For the (111) surface we used \( p(2\times2 \sqrt{3}) \) eight-layer slab with adsorbate on one side and 15 Å / 5Å of free space above/below.

### Results and Discussion

#### Surface design considerations

To design a surface to enhance H storage, it is first necessary to understand how the addition of materials to the surface can affect the chemical potential of adsorbed H (the driving force for H insertion). It has been shown that the measured overpotential (\( \eta \)) can be separated into two components (\( \eta = \eta_1 + \eta_2 \)). \( \eta_1 \) is the overpotential required to drive the Volmer reaction and \( \eta_2 \) is the chemical potential of the adsorbed H. The chemical potential of absorbed H is a function of bulk H content (\( x \)). At steady state, the chemical potentials of the adsorbed and absorbed H are equivalent, so \( x \) can be used to approximate \( \eta_2 \). As such, Zhang et al. developed the following empirical equation (2):

\[
-f\eta_2 = 6.44 - \frac{a}{T} + x \frac{b}{T} + \ln \left( \frac{x}{1-x} \right) - 0.5\ln(f_{H_2,0})
\]

[6]

when \( x \geq 0.71, f = F/RT \), \( a \) is equal to 6031.13 K, and \( b \) is equal to 5409.65 K, and \( f_{H_2,0} \) is 1 atm.

To simplify the analysis of \( \eta_2 \), the reaction pathway is assumed to be dominated by either Volmer-Tafel or Volmer-Heyrovsky, instead of a mixed Volmer-Heyrovsky-Tafel pathway. If Volmer-Tafel route is dominate, the relationship between \( \eta_2 \) and \( \eta \) is (3):

\[
\eta_2 = \frac{1}{2f} \left( \ln \left( \frac{j_{OV}}{j_{oT}} \right) - (1 - \alpha_V)f\eta \right)
\]

[7]

assuming the H surface coverage (\( \theta \)) and equilibrium H surface coverage (\( \theta_o \)) are both \( << 1 \) (6).

The relationship between \( \eta_2 \) and \( \eta \) for a Volmer-Heyrovsky route is approximated to (4):

\[
\eta_2 = \frac{1}{f} \ln \left( \frac{1 + \left( \frac{j_{oV}}{j_{oH}} + \frac{j_{oH}}{j_{oV}} \right)}{2} \exp(-f\eta) \right)
\]

\[
\left( \frac{j_{oV}}{j_{oH}} + \frac{j_{oH}}{j_{oV}} \right) + \exp(-f\eta)
\]

[8]

where \( j_{oV}, j_{oT}, \) and \( j_{oH} \) are the exchange current densities for the Volmer, Tafel, and Heyrovsky reactions, respectively, and \( \alpha_V \) is the symmetry coefficient for the Volmer reaction.
Equations [7] and [8] show that $\eta_2$, and therefore $x$, is modified by changing the exchange current densities of the three reactions. Thus, an optimum surface composition can be designed because the exchange current densities are a result of material properties. More specifically, $\eta_2$ at a given $\eta$ will be larger for a surface with increased equilibrium rate of adsorption ($j_{oV}$) and/or decreased equilibrium rate of desorption ($j_{oT}$ or $j_{oH}$). The equations also show that $\eta_2$ for a Volmer-Tafel route is linear with $\eta$, and it is asymptotic with $\eta$ for the Volmer-Heyrovsky route.

Selection of surface materials

DFT is a beneficial tool widely used to model various material properties and their interactions with H. In addition, DFT can be used as a first step in screening potential materials for further study (14–17). As such, DFT can be used to calculate the Gibbs free energy of H adsorption as a function of H coverage as a first approximation for finding trends for $j_{oV}$ and $j_{oT}$. $j_{oV}$ is proportional to $\theta^\alpha (1-\theta)^{1-\alpha}$, where $\theta$ is the ratio of the sites occupied by H to maximum available sites (18). Therefore, as a first approximation, materials with a low equilibrium $\theta$ will have a lower $j_{oV}$, as long as $\theta<0.5$ and assuming $\alpha_V=0.5$.

The $j_{oT}$ of the surface can be decreased by the addition of what are commonly referred to as Tafel poisons to the surface. Tafel poisons are materials with a higher Gibbs free energy of H adsorption than that of the pristine surface. Therefore, the number of available adsorption sites for H on a Tafel poisoned surface is limited. The presence of a Tafel poison on the Pd surface would push H towards energetically preferable exposed Pd sites where the Gibbs energy of adsorption is lower. This is similar to the effect described in Lindlar catalysts (19). Also, the Tafel reaction is a two-species reaction. Therefore, to escape from the surface as H$_2$, the adsorbed H atom needs to traverse over the energetically unfavorable sites occupied by Tafel poisons to recombine with a distant neighbor. This property limits the number of recombination sites and will therefore decrease the Tafel reaction rate. Figure 2 shows the top view of a Pd surface, where top Pd atoms have been partially displaced with Bi as a substitutional dopant. Here, the electron density is used as a proxy for adsorption energy. The darker areas around Pd atoms indicates preferential adsorption. This also demonstrates the concept of “exclusion” zones around Bi atoms, where H adsorption is limited. The combination of these two mechanisms results in a decrease in $j_{oT}$, i.e. the Tafel reaction is poisoned. In addition, the former mechanism poses another problem in that the poison causes a decrease in the concentration of preferable adsorption sites, which should also decrease $j_{oV}$.

Figure 3 shows the calculated Gibbs free energy of adsorption vs H surface coverage for Pd, Pt, Bi, and Pb, modeled in a similar fashion as that reported in Ref (20). These results show that Pt has a higher H surface coverage at equilibrium than Pd, suggesting that Pt should have a higher $j_{oT}$ than Pd. Indeed, experimental studies of the H evolution reaction (HER) rate on Pt is higher than that of Pd in alkaline solutions (21). Therefore, Pt is a good candidate to increase the $j_{oV}$ of the surface. Note: equilibrium is taken at a Gibbs free energy of adsorption of 0 eV.
Figure 2. Electron density contour map of a Pd surface where the top layer is partially displaced by Bi atoms acting as Tafel poisons. H will preferentially adsorb around Pd atoms, avoiding higher energy exclusion zones around Bi.

The DFT modeling also shows Pb and Bi are good candidates to decrease $j_{oT}$ of the surface. Both elements are considered Tafel poisons, as they require more energy to adsorb H than the Pd and Pt at all tested coverages. The competing effect, a reduction in $j_{oV}$ is also observed by the projected very low equilibrium H surface coverage. However, computational limitations prevented the extension of the study to an equilibrium surface coverage is lower than 0.125 ML. Finally, modeling suggests Bi is a better Tafel poison than Pb since the Gibbs free energy of adsorption is 0.56 eV vs 0.27 eV for Bi and Pb respectively, at a H coverage of 0.125 ML.

Figure 3. DFT calculated free energy of adsorption vs H surface coverage for Pd, Pt, Pb, and Bi.

Also, the down selection of candidate materials with properties relevant to the enhancement of electrochemical occlusion of H can be found by a looking at published volcano plots (overall HER exchange currents vs Gibbs free energy of adsorption) (21, 22). The exchange current rates can be used to approximate the trends in $j_{oV}$; since the
Volmer reaction is the only reaction that brings H to the surface. In addition, one would find a material with a high Gibbs free energy of adsorption would tend to have a reduce $j_\text{ov}$. Using such trends, one might find that Ir might be an alternate material to enhance $j_\text{ov}$, and Hg and Cd might be other materials to diminish $j_\text{ov}$, for example. Finding a similar predictor for $j_\text{oH}$ for various materials appears to be more complex, requiring additional DFT modelling of the Heyrovsky reaction on different surfaces or taking measurements and fitting the data with kinetic models to elucidate the rates of the reactions (2). The DFT modelling shown in Figure 3, suggest experimenting with different surfaces consisting of Pt (to enhance $j_\text{ov}$), Bi, and Pb (to decrease $j_\text{oT}$) on the Pd could further enhance the electrochemical insertion of H.

Surface studies

The effects of changing the elemental composition of the Pd surface to consist of Pt, Bi, Bi+Pt, and Pb were investigated by analyzing the traditional Tafel plot, $x$ vs Log($|j|$), $x$ vs $\eta$, and corresponding $\eta_2$ vs $\eta$ plots. The plots for a Pd control, Bi(UPD), Pt, and Bi(UPD)+Pt samples are displayed in Figure 4(a-d).

Figure 4(a) shows that the addition of Pt did not have a significant impact on $x$ for the investigated currents. By analyzing the Tafel plot in Figure 4(b), the addition of Pt required even lower overpotentials than the Pd sample. This result corroborates previous reports showing Pt to have enhanced HER activity over Pd in alkaline solutions (21). Interestingly, the Pt overlayer improved the $x$ obtained at equivalent $\eta$ (Figure 4(c)). According to Eq. [7], shifts in the $\eta_2$ vs $\eta$ plot (Figure 4(d)) to smaller cathodic overpotentials is a result of larger $j_\text{ov}/j_\text{oT}$. This means that at any selected overpotential, the Pt overlayer would result in the maximum $x$ as compared to all investigated surfaces assuming it stays on a linear trajectory. However, Pt is such a good catalyst that extraordinary currents are required to obtain high enough $\eta$ to obtain the higher $x$.

Next, the addition of Bi(UPD) to the Pd surface only showed a moderate increase in $x$ of up to 7% of the Pd control at the investigated currents (Figure 4(a)). In addition, the poor HER activity of Bi caused an increase in the cathodic overpotentials necessary to drive the investigated currents (Figure 4(b)). At larger cathodic overpotentials of $-\eta>0.7$ V, a curve in the $x$ vs $\eta$ and $x$ vs Log($|j|$) plots is observed and is indicative of the Heyrovsky reaction rate overtaking the Tafel reaction rate. Finally, the addition of Bi required larger cathodic overpotentials than the other investigated samples to achieve an equivalent $x$, resulting in a shift in the linear portion of the $\eta_2$ vs $\eta$ curve to larger cathodic overpotentials. This shift is indicating that the addition of Bi lowers the $j_\text{ov}/j_\text{oT}$ ratio according to Eq. [7].

Finally, the addition of Pt to the Bi(UPD) surface showed the most improvement in the amount of electrochemically stored H, with up to 13% greater $x$ than the Pd control for the investigated currents (Figure 4(a)). For comparison, a H$_2$ fugacity exceeding 1400 atm is required to obtain the equivalent PdH$_{0.87}$ by H$_2$ gas loading (2, 23). The addition of a small amount of Pt to the Bi layer reduced the cathodic overpotentials compared to the Bi layer alone, but still required larger cathodic overpotentials than the Pd control. The $\eta_2$ vs $\eta$ curve shifted towards lower cathodic overpotentials, again indicating an increase in $j_\text{ov}/j_\text{oT}$, yet not as high as the Pt layer. This sample outperformed the maximum $x$ for all samples, indicating a successful engineering of a surface to enhance H storage by the combination of a Tafel poison and Volmer promoter.
Up to this point, only surfaces where the Volmer-Tafel reaction appeared to dominate in the investigated region have been discussed. However, the $j_{oH}$ is also a material property and is therefore important in the design process. The Heyrovsky rate is also dependent on overpotential and H surface chemical potential. Thus, it is expected, that the Volmer-Heyrovsky mechanism would be dominant at higher cathodic overpotentials, thereby limiting the maximum obtainable $x$. Therefore, it is important to study the Heyrovsky reaction to gain a better understanding how material properties affect it. In so doing, a more complete methodology to optimize the design of the surface composition can be accomplished.

The addition of UPD Pb, and a bulk Bi deposition to the surface of Pd are examples that appear to show evidence of the Volmer-Heyrovsky route dominating in the investigated region, as indicated by the limiting $x$ obtained in Figure 5(a). The addition of these materials to the surface significantly increased the overpotentials necessary to drive the currents (Figure 4(b)), as expected. Thus, the Heyrovsky played a more significant role in the investigated region, specifically when $-\eta > 0.7$ V. The limiting $x$ increases in the order Bi(UPD) < Pb(UPD) < Bi(Bulk). According to Eq. [8], the $j_{oV}/j_{oH}$ ratio follows the same trend, indicating the possibility of the surface affecting the $j_{oH}$. $x$ was also observed to decrease as overpotentials became even more negative, which indicates the symmetry coefficients for the Volmer and Heyrovsky reactions are not equivalent (2). The combination of these effects indicates the importance of fitting the data with a complete set of kinetic equations describing all three reactions (Volmer, Heyrovsky, and Tafel), which is work currently underway. Modelling the Heyrovsky rate will provide insight into how different materials affect the $j_{oH}$ to further the optimization of the surface composition. It should be noted, that it is believed that other materials and combinations
of materials may promote the Heyrovsky mechanism at lower overpotentials than those investigated here.

Figure 5. (a) $x$ vs Log($|j|$), (b) $\eta$ vs Log($|j|$), (c) $x$ vs $\eta$ and (d) $\eta_2$ vs $\eta$ for Pd control, Bi(UPD), Pb(UPD), and Bi(Bulk) samples.

Despite the predictions based on the DFT analysis (Figure 3), the Pb(UPD) sample proved to be a worse HER catalyst than Bi(UPD), as indicated by the larger cathodic overpotentials (Figure 5(b)). This observation does, however, corroborate other experimental observations that Bi is slightly more active for the HER than Pb (24). The addition of the thicker Bi(Bulk) layer to the surface further increased the observed cathodic overpotentials above that observed for the Pb(UPD). The change in overpotentials between Bi(UPD) and Bi(Bulk) could be a result of voids in the surface layer, which exposes Pd. As more Bi is added, the concentration of voids decreases, resulting in an increase in cathodic overpotentials as the surface behaves more like bulk Bi.

Isolating $j_{oV}$ and $j_{oT}$

For surfaces where the HER is following predominately Volmer-Tafel reaction route throughout the investigated current density region, it is possible to ascertain the impact of the surface composition on $j_{oV}$ and $j_{oT}$ individually. Recall that under this condition, there is a linear relationship in the $\eta_2$ vs $\eta$ plots. Such a separation of $j_{oV}$ and $j_{oT}$ could prove beneficial to understand the effects of each material in the surface layer, and is advantageous over fitting the data to the Eq. [7], which would only result in the ratio of $j_{oV}/j_{oT}$. The procedure to isolate the roles of $j_{oV}$ and $j_{oT}$ involve making Tafel-like plots of $\eta_1$ and $\eta_2$ vs Log($|j|$). Taking a linear fit of the $\eta_1$ vs Log($|j|$) provides information about
the Volmer reaction, and the linear fit of $\eta_2$ vs Log($|j|$) does the same for the Tafel reaction (4, 25, 26). The $j_oV$ (from $\eta_1$ vs Log($|j|$)) and $j_oT$ (from $\eta_2$ vs Log($|j|$)) are found by taking the intercepts of the linear fits of the plots. Figure 6(a) shows the procedure performed on the Bi(UPD)+Pt sample.

Figure 6. (a) $\eta$, $\eta_1$, $\eta_2$, vs Log($|j|$) for the Bi(UPD)+Pt sample, and (b) the $j_oV$ and $j_oT$ obtained for the samples from Figure 4.

By performing this Tafel-plot analysis, one can separate the effects of the added materials on $j_oT$ and $j_oV$ and compare the values to that obtained by the Pd control. The values obtained using the described method are displayed in Figure 6(b). The addition of the Tafel poison Bi did decrease $j_oT$ from that of the Pd substrate. However, it more significantly decreased $j_oV$, which decreased the $j_oV$/$j_oT$ ratio resulting in the shift of $\eta_2$ towards larger cathodic overpotentials observed in Figure 4(d). Again, this is a result of the competing effect of adding a Tafel poison – the Volmer reaction is also reduced because Bi reduces the number of available H adsorption sites at a given energy. The addition of Pt to the surface had little effect on $j_oT$, but increased $j_oV$ as desired, therefore resulting in the increase in $j_oV$/$j_oT$. Finally, the addition of Pt to the Bi surface married the two properties, i.e. $j_oV$ was enhanced, and $j_oT$ was diminished. The result was a higher $j_oV$/$j_oT$ ratio than the Pd. The surface properties were modified such that larger cathodic overpotentials were required than that of pristine Pd in a way to promote larger quantities of stored H at the investigated currents. The presented analysis demonstrates that materials can be selected based on known properties, and that modelling can predict their effects on the exchange current densities for the Volmer and Tafel reactions.

It may be interesting to also view the $x$ vs half-cell power (Figure 7). Here, it is observed that despite the Pt surface having the greatest $j_oV$/$j_oT$ ratio, it is such a good HER catalyst that much larger half-cell powers must be applied to achieve any significant enhancement in $x$. The Bi(UPD)+Pt sample, on the other hand, still had a higher $j_oV$/$j_oT$ than the Pd substrate, but it also showed the highest amount of stored H at an equivalent half-cell power.

Coating Stability

Another factor to consider in designing catalytic surfaces is the stability of the surface. The reproducibility of $x$ between consecutive galvanostatic step cycles was used as a measure of the stability of the surface. The Bi(UPD) and Bi(bulk) coatings showed particularly poor stability. This instability may indicate that the deposited surface is restructuring during the experiment. Despite Pb being more soluble than Bi in the
alkaline solutions, the results presented in Figure 8 suggest the Pb to be more stable than Bi on the Pd surface. The preferred crystal structure for Pd and Pb is FCC, while Bi is rhombohedral. This difference in preferred crystal structure could play a role in instability of the Bi surface. Furthermore, the incorporation of Pt to the Bi UPD layer appeared to improve the stability, suggesting the instability is facilitated by the incompatibility of H on the Bi. Regardless, the results of this work suggest more time should be devoted toward stabilizing surfaces and understanding the mechanisms for the instability for further study.

Figure 7. $x$ vs half-cell power (applied current $\times \eta$) for the Bi(UPD), Pt, and Bi(UPD)+Pt samples.

Figure 8. $x$ vs $\log(|j|)$ obtained for the first three galvanostatic step cycles for the Pb(UPD) (blue) and Bi(UPD) (gold) samples.
Penetration rate

Finally, predicting how changing the surface composition affects the rates of insertion and desertion is another property of interest for H storage applications. To this end, the energy profile of a H atom penetrating into the Pd bulk through an FCC site was modelled by DFT to gain an understanding of the energy barriers associated with H penetration. The topmost layer of the Pd was substituted (maintaining the FCC structure) with Pb, Bi, and Pt. As shown in Figure 9, the energy barrier for H to penetrate through one layer of either Pb or Bi is substantial, meaning that H atom does not want to penetrate where the Tafel poisons are present. In contrast, the addition of one layer of Pt does not significantly affect the energy barriers associated with penetration. The modelling suggests that the H that absorbs into the Pd goes in through defects in the surface layer or regions occupied by Pd or Pt. Therefore, the surface layer needs to be thin so that enough exposed Pd or Pt sites are available to allow adequate H insertion rates. In fact, the previous report showed an exponential trend in the amount of Pb deposited on the surface and the amount of time required to reach a steady-state \( x \) (1). Furthermore, this effect has been used to “seal” H in the cathode by depositing a thick layer of the Tafel poison Hg onto the surface (27).

![Figure 9. The variation of Gibbs free energy of a H atom as it penetrates into the substrate material (Pd). The four cases represent different top layers (Bi, Pb, Pt and Pd). DFT calculations are done at a H surface coverage of 0.125 ML.](image)
Conclusions

The engineering of a surface composition specifically designed to enhance the amount of electrochemically stored hydrogen has been successfully demonstrated. The methodology on the selection of appropriate surface materials hinges on the inherent material properties that affect the exchange current densities for the Volmer ($i_{oV}$), Tafel ($i_{oT}$), and Heyrovsky ($i_{oH}$) reactions. Specifically, the combination of a material known for high $i_{oV}$ (Pt) with a material known for low $i_{oT}$ (Bi) permitted the maximum amount of stored hydrogen for the investigated surfaces. Overall, this work provides a critical step towards the future optimization of surface composition to maximize the electrochemical hydrogen storage capability.

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References