Metal-Modified Niobium Carbides as Low-Cost and Impurity-Resistant Electrocatalysts for Hydrogen Evolution in Acidic and Alkaline Electrolytes

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Abstract

Low-cost and impurity-resistant electrocatalysts for the hydrogen evolution reaction (HER) are desired to replace expensive bulk Pt in membrane electrolysis cells. Monolayer (ML) Pt, Pd, and Ag on niobium carbide (NbC) thin films were synthesized for electrochemical testing as HER catalyst candidates. Density Functional Theory calculations predicted that ML Pt on NbC binds hydrogen similarly to bulk Pt, suggesting good HER activity. These results were confirmed through electrochemical measurements in both acidic and alkaline electrolytes. The Pt/NbC catalyst also maintained its activity in the presence of common impurity ions found in tap water. This makes ML Pt/NbC a promising replacement for Pt in water electrolysis cell cathodes. Future work on high surface area powders should be performed to further assess its suitability as a catalyst for membrane electrolyzers.

Key Words: *density functional theory, electrolysis, hydrogen evolution, impurity tolerance, niobium carbide*

1. Introduction

Water electrolysis as a hydrogen source for energy storage is attractive because it does not rely on the energy-intensive steam reforming of fossil fuels and is carbon- and pollution-free when powered by solar or wind energy. Polymer electrolyte membrane electrolyzers can achieve larger current densities and higher hydrogen purity than traditional alkaline electrolyzers, but they require large amounts of platinum-group metals to catalyze hydrogen evolution at the cell cathode [1–3]. Pt is the state-of-the-art catalyst, but its high cost and low abundance led to efforts to reduce Pt loading while maintaining high hydrogen evolution reaction (HER) activity [4]. Recent research in our group [5–7] focused on adding an atom-thick monolayer (ML) of precious metal onto transition metal carbide thin films – known to have bulk Pt-like electronic structures [8] – to minimize Pt-loading for the HER. These studies analyzed ML Pt on tungsten carbide (WC), titanium carbide (TiC), and molybdenum carbide (Mo_2C) in acidic electrolyte. The current work explores several novel aspects of utilizing niobium carbide (NbC) as an HER electrocatalyst: (1) determination of different metal modification effects of Pt, Pd, and Ag overlayers in an acidic environment; (2) direct comparison of the effect of acidic and alkaline electrolyte on the HER activity of Pt-modified NbC; and (3) investigation of ML Pt/NbC for the resistance of common impurity ions present in tap water.

NbC was selected as the substrate for several reasons. Similar to other early transition metals, Nb is orders of magnitude more abundant and less expensive than Pt [4]. NbC is stable at HER potentials at both high and low pH values [9]. And, unlike WC and TiC, NbC is easily synthesized from its oxide precursors at relatively low temperatures, leading to a high surface area catalyst with lower processing costs [10,11].

Electrocatalysts for alkaline HER are of interest because alkaline membrane electrolyzers are potentially less expensive than their acidic counterparts. Alkaline media are less corrosive and therefore require less noble and less expensive catalysts compared to acid media. This is especially important at the electrolyzer anode, where inexpensive metals are as active as the precious metals required in acidic cell [12]. It is well known, however, that hydrogen evolution and oxidation kinetics are slower in base than in acid, requiring greater than an order of magnitude increase in Pt loading to achieve similar cathode efficiency in alkaline electrolyzers compared to acid [13]. Thus, reducing the Pt loading to a single monolayer could have an even greater impact in alkaline than in acidic membrane electrolyzers.

The effect of impurities on the performance of electrocatalysts is also important to the large-scale use of water electrolyzers. Deionized water is currently required for membrane electrolyzers, but this is an inconvenience and an added cost [3]. It is desirable for electrocatalysts to at least be resistant to common impurities found in tap water. With this cost in mind, the current study also analyzes the performance of the electrocatalyst in the presence of impurity ions.

2. Experimental and Theoretical Methods

2.1 DFT Calculations

Spin polarized density functional theory (DFT) [14,15] calculations were performed using Vienna Ab-Initio Simulation Package (VASP) code [16,17]. A plane wave cut-off energy of 400 eV and $3 \times 3 \times 1$ Monkhorst-Pack grid were used for total energy calculations [18]. The interactions between electrons and nuclei were treated with all electron like projector augmented wave (PAW) potentials with the generalized gradient approximation (GGA) [19,20] using PW91

functionals [21]. Ionic positions were optimized until Hellman-Feynman force on each ion was smaller than 0.01 eV/Å.

The surfaces of NbC(111), both with and without monolayer (ML) Pt, Pd, or Ag, were modeled using a four layer 3×3 surface slab. The Pt, Pd, and Ag/TMC(111) surfaces were modeled by adding monolayer of Pt, Pd, and Ag on top of TMC(111) surfaces, respectively. A vacuum layer of ~ 12 Å thick was added in the slab cell along the direction perpendicular to the surface in order to minimize the artificial interactions between the surface and its periodic images. During geometry optimization, atoms in the top two layers were allowed to relax while the atoms in the bottom two layers were fixed. The binding energy of hydrogen (HBE) is calculated as

$$\text{HBE} = E_{\text{slab}+\text{H}} - E_{\text{slab}} - 1/2 E_{\text{H}_2} \quad (\text{Eq. 1})$$

where $E_{\text{slab}+\text{H}}$, E_{slab} , and E_{H_2} are the total energies of slab with adsorbed H, clean slab, and H_2 molecule in gas phase, respectively.

2.2 NbC Thin Film Synthesis:

Niobium foil (Alfa Aesar, 0.127mm thick, 99.97% excluding Ta) was cut to size, rinsed with acetone, soaked for several minutes in 0.3M NaOH, and then rinsed with DI water to remove impurities and oxides. Samples were heated in a quartz tube in a flowing CH_4 and H_2 environment, as described previously [9]. Pure H_2 was flown for 15 minutes at 1123K prior to furnace cooling to reduce surface carbon. Samples were passivated for one hour in 1% O_2 in N_2 before removal from the furnace. Resulting films were phase-pure face-centered cubic (FCC) NbC, as determined by XRD analysis in a previous study that used an identical synthesis [9].

2.3 Metal-modified NbC Physical Vapor Deposition and Characterization

NbC samples were loaded into an ultra-high vacuum (UHV) chamber equipped with x-ray photoelectron spectroscopy (XPS) and Pt, Pd, and Ag physical vapor deposition (PVD)

sources. XPS scans and PVD procedures are described in previous work [9], and the metal overlayer coverage was quantified by a peak ratio measurement [22].

2.4 Electrochemical Measurements

Electrochemical tests were conducted in a single, 5-port glass cell (Pine) at room temperature. 0.5M sulfuric acid (H_2SO_4) and 0.1M potassium hydroxide (KOH) electrolyte solutions were prepared from 93-98% assay H_2SO_4 (Fisher, trace metal grade) and KOH pellets (Sigma-Aldrich, 99.99% purity), respectively, with 18.2M Ω cm deionized water. Solutions were freshly prepared for each set of samples, and de-aerated continuously throughout the experiment with an Ar stream. A Pt wire was used as the counter electrode, and a $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode was used (all reported values in this work were corrected to the reversible hydrogen electrode (RHE)). Thin film samples were covered with electroplating tape so only 0.5cm² of the film was exposed to electrolyte. Samples were dipped in 0.3M NaOH in order to remove excess oxides and then rinsed in DI water before being loaded into the cell. Once in the cell, carbide samples were first equilibrated by cyclic voltammetry (CV) 20 times at 200mV/s between 0.05V and 0.4V vs. RHE. Then, cathodic linear sweep voltammetry (LSV) was performed at 2mV/s starting from 0.15V vs. RHE. Pt and Ag foils were tested in the same manner, but the equilibration cycled between 0.05V and 1.4V. Non-compensated solution resistance was accounted for using AC impedance spectroscopy. Each CV/LSV sequence was repeated two or three times per sample, totalling about 30 minutes of testing time. The last LSV curve for each sample was used for analysis. For the alkaline HER stability testing, a 10 minute HER test consisted of only one CV/LSV sequence, while a 60 minute test consisted of seven CV/LSV sequences. After electrochemical testing, thin film samples were rinsed with DI water, dried, and placed under vacuum for post-HER XPS scanning.

2.5 Synthetic Tap Water Composition and Testing

Synthetic tap water was prepared by adding ions found in drinking water (as described by Petrov et al.[23]) to deionized water. Sodium bicarbonate, calcium chloride, sodium sulfate anhydrous, and sodium nitrate from Fisher (all ACS certified), and magnesium chloride from Arcos (pure) were added to deionized water to achieve the ionic molarities in Table 1.

Table 1: Synthetic tap water composition

Ion	Concentration (mM)
Na ⁺	~3.5
Ca ²⁺	1.3
Mg ²⁺	0.3
Cl ⁻	2.9
HCO ₃ ⁻	2.5
SO ₄ ²⁻	0.5
NO ₃ ⁻	0.01

Sulfuric acid (0.5M) and potassium hydroxide (0.1M) were prepared the same as previously, but synthetic tap water was used instead of deionized water. It should be noted that in the basic solution, HCO₃⁻ is deprotonated and exists as the carbonate ion. Any pH change associated with the addition of the bicarbonate ion was accounted for by normalizing to an actual reversible hydrogen electrode (Pt wire in H₂ saturated electrolyte) inserted into the cell after each electrochemical test was completed. Electrochemical measurements were performed in the same manner as above.

3. Results and Discussion:

3.1 DFT Calculations of Hydrogen Binding Energy

A Pt-like hydrogen binding energy (HBE) is a useful predictor that a material will be an active HER catalyst like Pt. Literature shows that HBE correlates with the exchange current density (i_0), the experimental measure of HER and hydrogen oxidation reaction (HOR) activity, in both acidic [24,25] and alkaline environments [26]. The HBE values

calculated from density functional theory (DFT) are shown in Table 2, revealing that ML Pt/NbC and Pd/NbC have similar HBE values to that of bulk Pt(111). Table 2 also shows that Ag and Ag/NbC bind hydrogen too weakly to have sufficient hydrogen coverage and HER activity at low reducing potential. Based on DFT predictions, Pt/NbC and Pd/NbC were evaluated experimentally because of their favorable theoretical HBE values, and Ag/NbC was chosen as a negative control.

Table 2: DFT calculated hydrogen binding energies (HBE) on metal, transition metal carbide (TMC), and metal-modified carbide surfaces

Surfaces	HBE (eV)
NbC(111)	-1.14
Pt(111)	-0.47
Pd(111)	-0.64
Ag(111)	0.22
Pt _{ML} /NbC (111)	-0.47
Pd _{ML} /NbC (111)	-0.44
Ag _{ML} /NbC (111)	0.23

3.2 Deposition of Pt, Pd and Ag over NbC

XPS peak areas were measured as a function of metal deposition time on NbC to determine whether the metal growth occurred by ML (layer-by-layer) or by particulate (island) formation. Similar experiments were conducted previously to estimate the metal growth mechanism for Pd/Mo₂C, Pd/WC [7], and Pt/WC [5,27]. Figures 1a-1c show that the rates of growth for Pt, Pd, and Ag were linear and exhibited only slight changes in slope with the addition of each monolayer. This is characteristic of the layer-by-layer growth, as discussed by Humbert et al. for the Pt/WC system [27].

Figure 1: Metal growth experiments for physical vapor deposition of Pt (a), Pd (b), and Ag (c) on NbC thin films measured with a PHI 5600 XPS system with Al X-ray source.

3.3 HER Activity and Catalyst Stability in Acid Electrolyte

Figure 2a shows the HER polarization curves for Pt/NbC in 0.5M H₂SO₄. Bulk Pt-foil exhibited the highest activity, reaching -5mA/cm² within less than 50mV. The unmodified NbC showed low activity, requiring around 400mV to reach -5mA/cm². The polarization curves for various coverage of Pt on NbC fell much closer to bulk Pt. The exchange current densities for each sample were obtained by linearizing the cathodic Tafel equation (Eq. 2) and plotting the overpotential vs. the log₁₀ of the current density. The slope and intercept of the linear portions of the Tafel plots were used to calculate the log₁₀ of the exchange current density, as seen in Eq. 3.

$$\eta = m \log_{10} i + b \quad (\text{Eq. 2})$$

$$b = -m \log_{10} i_0 \quad (\text{Eq. 3})$$

The slope, y-intercept, current density, and overpotential are m, b, i, and η , respectively. For the HER, overpotential is equivalent to the measured potential vs. RHE.

The log₁₀(i₀) values are plotted as a function of Pt coverage on NbC in Figure 2b. Increasing Pt coverage on NbC increased activity, until the activity reached a plateau at 2.5ML, close to the measured value for bulk Pt. The Pt coverage trend was similar to that obtained in previous studies on carbides [5–7]. The log₁₀(i₀) of -3.2 for bulk Pt is also

in agreement with previous studies [5,28]. However, it should be noted that more recent work attributes this value to the activity derived from the diffusion limited current, and the HER i_0 values for Pt in high transport acidic environments are reported several orders of magnitude higher [29]. Thus, the trends depicted here should be viewed qualitatively.

Figure 2: Top -- Hydrogen evolution reaction (HER) polarization curves in Ar-saturated 0.5M H_2SO_4 for Pt/NbC (a), Pd/NbC (c), and Ag/NbC (e) thin films. Cathodic scans at 2mV/s. Metal coverage on NbC indicated in legend. Bottom -- Activity ($\log_{10}(i_0)$) vs. metal overlayer coverage plots for Pt/NbC in pure water (blue diamond) and synthetic tap water (red circle) (b), Pd/NbC (d), and Ag/NbC (f) obtained from Tafel analysis of acidic HER polarization curves.

The HER activity for Pd/NbC in acid (Figure 2c) was less active than HER on Pt/NbC in acid. Even high coverage Pd/NbC required greater than 100mV to reach $-5\text{mA}/\text{cm}^2$. Bulk Pd was not tested due to its strong affinity for hydrogen absorption at low reducing potentials in acidic environments, which convolutes the HER current [30]. A literature value for pure Pd HER exchange current density [31], derived from theoretical free energy calculations [32], was used for reference. The $\log_{10}(i_0)$ values for Pd/NbC (Figure 2d) showed a similar trend as Pt/NbC, with the HER activity increasing with Pd coverage. Here, however, the i_0 values reached a plateau about one order of

magnitude lower than Pt/NbC. Based on the HBE values for Pd/NbC in Table 2, the exchange current density was expected to be close to that of bulk Pt. One possibility for the lower activity of Pd/NbC may be explained by the formation of Pd hydride that could change the HER activity [29]. However, it should be pointed out that the Pd thin films in the current study were estimated to be no more than 2.5 monolayers. A previous study reported that Pd thin films of less than 3 monolayers should not have the ability to absorb hydrogen to form hydride [33]. Further studies are needed to understand the relatively low HER activity of Pd/NbC in acid.

Figure 2e shows the HER data for Ag/NbC in acid. All samples, including bulk Ag, required around 400mV to reach $-5\text{mA}/\text{cm}^2$. This low activity supported the DFT predictions that HBE values are too weak on Ag surfaces for active HER. Figure 2f shows that i_0 values for all Ag/NbC coverage were several orders of magnitude lower than medium and high coverage of Pt/NbC and Pd/NbC. The figure also shows that there was no correlation between Ag coverage and the HER activity, which can be explained by the HBE of the surfaces. The theoretical HBE for Ag, Ag/NbC, and NbC in Table 1 were all around 0.7eV from Pt (Ag and Ag/NbC on the weakly binding side, and NbC on the strongly binding side), which is near the peak of the HER volcano curve [25]. Thus, no matter what coverage of Ag on NbC is present, HER activity should remain the same, as seen in this experiment.

The XPS measurements of the stability of the Pt/NbC, Pd/NbC, and Ag/NbC samples for HER in acidic electrolyte are shown in Figure 3, which compares the XPS signals before and after HER experiments. Both Pt/NbC and Pd/NbC appeared to be stable under these conditions and maintained a similar coverage before and after the HER

experiment. Ag/NbC appeared to lose some coverage during the HER experiment, but this was not further investigated due to the low reactivity of all Ag/NbC samples. Although XPS results from the current study confirmed the stability of the Pt/NbC and Pd/NbC films before and after HER measurements, long term stability should be explored in future studies to determine the practical application of these electrocatalysts.

Figure 3: Metal overlayer stability from XPS peak area measurements before and after HER acid testing for Pt/NbC in pure water (solid blue) and synthetic tap water (striped red) (a), Pd/NbC (b), and Ag/NbC (c).

3.4 HER Activity and Catalyst Stability in Alkaline Electrolyte

The Pt/NbC film was the most suitable catalyst of the current study for HER in acid, based on high HER activity and overlayer stability. It was chosen to be further examined for HER suitability in alkaline conditions. The alkaline HER is known to be much slower than in acid, and that is confirmed for Pt/NbC in Figures 4a and 4b. It took over 100mV for bulk Pt to reach a current density of $-5\text{mA}/\text{cm}^2$, and the $\log_{10}(i_0)$ from the Tafel analysis (-3.68) was around half an order of magnitude lower than what was observed in acid. The alkaline i_0 value for platinum was slightly lower than the literature value, which was likely a result of evolved hydrogen bubbles reducing the available electrochemical surface area on the thin film [13]. Similar to that observed in acid, the

trend of increasing activity ($\log_{10}(i_0)$) with increasing Pt coverage on NbC was observed in alkaline electrolyte, with a plateau near the bulk Pt value (Figure 4b).

Figure 4: (a) HER polarization curves for Pt/NbC in Ar-saturated 0.1M KOH. Cathodic scans at 2mV/s. Pt coverage on NbC indicated in legend. (b) Activity ($\log_{10}(i_0)$) vs. Pt overlayer coverage plots for Pt/NbC obtained from Tafel analysis of alkaline HER polarization curves in pure water (blue diamond) and synthetic tap water (red circle).

The XPS measurements before and after HER tests (Figure 5a) showed that the Pt signal decreased after HER testing. This could be due to Pt either dissolving into electrolyte solution or agglomerating on the surface. If dissolution occurred, then Pt would have continued to dissolve with time; whereas if agglomeration occurred, then Pt coverage likely would have decreased until a critical agglomerate size was reached. To determine the coverage reduction mode, two separate HER tests on ~1ML Pt/NbC samples were performed for 10 and 60 minutes, respectively, in addition to the standard 30 minute HER.

Figure 5: Pt overlayer stability from XPS peak area measurements before and after alkaline HER testing for Pt/NbC in pure water (solid blue) and synthetic tap water (striped red) (a). Overlayer measurements from timed alkaline HER testing for Pt/NbC (b).

The results in Figure 5a show that only a 35% coverage reduction was observed after 10 minutes, while a ~50% reduction was observed at both 30 minutes and 60 minutes. This indicated that Pt agglomerates were likely forming on the surface, which decreased the Pt active area, but these agglomerates remained stable at least up to an hour. Longer time trials are needed to determine long-term stability. Surface characterization, possibly by atomic force microscopy, is needed to confirm the formation of Pt agglomerates. Overall, the HER activity and stability indicate that Pt/NbC may be a suitable replacement for Pt in alkaline membrane electrolyzers.

3.5 Pt/NbC Impurity Resistance

In order to extend HER studies from deionized to tap water, the HER performance of Pt/NbC in the presence of common impurity ions in tap water was measured in both acidic and alkaline electrolytes. The composition of the synthetic tap water used is in Table 1. Exchange current densities for 1ML Pt/NbC in acidic and alkaline synthetic tap water are shown as red circles in Figures 1b and 4b, respectively. In both cases, the

Pt/NbC catalyst maintained similar activity as in deionized water, exhibiting good resistance to tap water impurity ions. Additionally, the Pt/NbC overlayer stability in the presence of tap water ions before and after HER in acid and base, depicted in Figures 3a and 5a, resembled the corresponding pure water results. This indicates that overlayer stability is likely impacted more by solution pH than by tap water impurities.

The impurity resistance of the Pt/NbC surface is likely due to low binding energies of impurity ions on Pt/NbC. This means that protons would preferentially adsorb to the surface instead of impurities under relatively mild reducing conditions, allowing HER to proceed uninhibited. In the future, a DFT study of impurity ion binding energies could be used to support this hypothesis. Thus, DFT-calculated impurity binding energy may also be an important design parameter for development of new impurity resistant electrocatalysts.

Conclusions:

This work shows that HBE values calculated from DFT are good predictors of metal-modified carbide catalysts for the HER activity in both acidic and alkaline conditions. Pt/NbC shows high activity and stability for HER in acid. The HER on Pt/NbC in alkaline electrolyte is slower than in acid, but Pt-like activity for alkaline HER can also be achieved with monolayer loadings of Pt on NbC. The catalyst is also resistant to common impurity ions found in tap water. Overall, results from the current study suggest that Pt/NbC is a potential replacement for Pt in both acidic and alkaline environments. Future studies on high surface area Pt/NbC powder catalysts should be

performed to further assess its usability as a low-cost and impurity-resistant HER electrocatalyst.

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6. References:

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