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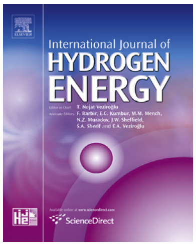

Metal-modified niobium carbides as low-cost and impurity-resistant electrocatalysts for hydrogen evolution in acidic and alkaline electrolytes

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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.

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 (TMC) 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 environement; (2) direct comparison of the effect of acidic and alkaline electrolyte on the HER activity of Pt-modified NbC; and (3)

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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 electocatalysts 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.

Experimental and theoretical methods

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 × 3 × 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

$$\mathrm{HBE} = E_{\mathrm{slab+H}} - E_{\mathrm{slab}} - \frac{1}{2}E_{\mathrm{H_2}} \quad (1)$$

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

NbC thin film synthesis

Niobium foil (Alfa Aesar, 0.127 mm thick, 99.97% excluding Ta) was cut to size, rinsed with acetone, soaked for several minutes in 0.3 M 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 min at 1123 K prior to furnace cooling to reduce surface carbon. Samples were passivated for 1 h 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].

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].

Electrochemical measurements

Electrochemical tests were conducted in a single, 5-port glass cell (Pine) at room temperature. 0.5 M sulfuric acid (H_2SO_4) and 0.1 M potassium hydroxide (KOH) electrolyte solutions were prepared from 93 to 98% assay H_2SO_4 (Fisher, trace metal grade) and KOH pellets (Sigma–Aldrich, 99.99% purity), respectively, with 18.2 M 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 Hg/Hg_2SO_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 0.5 cm^2 of the film was exposed to electrolyte. Samples were dipped in 0.3 M 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 200 mV/s between 0.05 V and 0.4 V vs. RHE. Then, cathodic linear sweep voltammetry (LSV) was performed at 2 mV/s starting from 0.15 V vs. RHE. Pt and Ag foils were tested in the same manner, but the equilibration cycled between 0.05 V and 1.4 V. Non-compensated solution resistance was accounted for using AC impedance spectroscopy. Each CV/LSV sequence was repeated two or three times per sample, totaling about 30 min of testing time. The last LSV curve for each sample was used for analysis. For the alkaline HER stability testing, a 10 min HER test consisted