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# Nanomanufacturing of Non-Noble Amorphous Alloys for Electrocatalysis

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storage devices due to their high energy density compared to that for batteries and super-capacitors. However, the critical bottleneck in the widespread adoption of fuel cell technology is the high cost of electrocatalysts used in these devices, which may be lowered by minimizing the noble-metal loading and improving their performance. To that end, alloy catalysts have been developed, which incorporate a broad range of nonprecious transition metals and nonmetals. However, such alloys are limited by their phase stability range and are susceptible to poisoning and performance degradation over time. A potential escape from such limitations is provided by amorphous alloys, which can give access to a much



broader composition range of favorable chemistry while exhibiting exceptional chemical stability and durability. This potential of broad chemistry is, however, often limited when the amorphous alloy is fabricated by melt quenching. To overcome this limitation, we introduce a facile pulsed electrodeposition approach to synthesize metallic glass nanowire arrays for two-model alloy systems. This highly practical nanomanufacturing route allows the synthesis of fully amorphous nanowires for alloys with little or no noblemetal content, which exhibit excellent performance in terms of electrocatalytic activity and stability toward electro-oxidation of methanol. Density of states calculated using first-principles show strong d-orbital contributions to the states at the Fermi level and electron localization on the surface of the amorphous alloys accounting for their high catalytic activity.

KEYWORDS: metallic glass, catalysts, fuel cell, pulse electrodeposition, nanowires, electronic structure

## INTRODUCTION

Direct alcohol fuel cells have attracted widespread interest recently because of less corrosive fuels, better water management, resistance to poisoning, and decreased fuel crossover rates.<sup>1-3</sup> Carbon-supported noble-metal nanoparticles represent state-of-the-art catalyst architecture in direct alcohol and hydrogen fuel cells due to their high catalytic activity, while metal-free catalysts do not meet the requirements for practical use.<sup>2,4</sup> However, agglomeration and dissolution of metalnanoparticle catalysts in these devices as well as numerous interfaces with the support material hinder mass diffusion and charge transfer leading to poor efficiency and limited durability.<sup>3</sup> To overcome this limitation, one-dimensional nanostructures including rods, tubes, and wire geometries have been utilized as novel strategies for fuel cell electrocatalysts that provide facile pathways for electron transfer while offering large surface area for catalytic reactions lasting over many cycles.<sup>5,6</sup> In particular, amorphous metallic nanowires have attracted increasing attention in recent years because of their high catalytic activity from the atomic-scale disordered

structure, resistance to poisoning, and excellent durability under fuel cell operating conditions.<sup>7–9</sup> These nanowires were synthesized by thermoplastic forming of metallic glasses in their supercooled liquid region.<sup>10–12</sup> However, only a few and narrow composition ranges, often with high noble-metal content, are amenable to this thermomechanical processing route. To overcome the limitations set by the requirements of thermoplastic forming and to realize the potential functionality of amorphous metal nanostructures, here we demonstrate template-assisted pulsed electrodeposition as a facile and scalable nanomanufacturing approach for obtaining metallic glass nanowires with high electrocatalytic activity. Amorphous alloys are obtained in simple chemistries that are extremely

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**Figure 1.** Synthesis of the amorphous alloy nanowires: (a) schematic showing concurrent electrodeposition of Ni, Pd, and P in anodic aluminum oxide (AAO) templates in a solution containing the corresponding ions and scanning electron microscope (SEM) top view of the AAO nanomold with pores in an ordered columnar arrangement; (b) potential transient vs electrodeposition time during the deposition of Ni–P and Ni–Pd–P nanowires; SEM images of freestanding Ni–P nanowires with (c) an average length of ~3  $\mu$ m and an aspect ratio ( $\theta$ ) of 25, (d) an average length of ~15  $\mu$ m and an aspect ratio ( $\theta$ ) of 120.



**Figure 2.** Structure and composition of the amorphous alloy nanowires: (a) TEM bright-field image of  $Ni_{80}P_{20}$  nanowires with the insets showing (a1) diffused ring in selected area diffraction pattern indicating amorphous structure, (a2) corresponding elemental peaks from EDS, and (a3) high-resolution TEM image of the selected region of the nanowire; (b) TEM bright-field image of  $Ni_{75}Pd_{10}P_{15}$  nanowire with the insets showing (b1) diffused ring in the selected area diffraction pattern, (b2) corresponding elemental peaks of Ni, Pd, and P seen in EDS, and (b3) high-resolution TEM image of the selected region of the nanowire; (c) STEM-EDS elemental area map of Ni–P nanowires with composition determined to be  $Ni_{80}P_{20}$ ; and (d) STEM-EDS elemental area map of a Ni–Pd–P nanowire with composition determined to be  $Ni_{75}Pd_{10}P_{15}$ . The elemental maps show a homogeneous distribution of the constituent elements in the nanowire with no segregation.

difficult (if not impossible) to obtain by the traditional route of

In pursuit of metallic glass electrocatalysts for fuel cells that are free from platinum-group metals, the Ni–P binary system was selected because it shows high activity in heterogeneous

rapid melt quenching.



**Figure 3.** Amorphous structure and surface characterization of the electrodeposited alloys: (a) X-ray diffraction (XRD) pattern of pulsed electrodeposited flat  $Ni_{80}P_{20}$  and  $Ni_{75}Pd_{10}P_{15}$  alloys showing broad diffraction peak indicating amorphous structure. (b) Differential scanning calorimetry (DSC) curves of as-deposited  $Ni_{80}P_{20}$  and  $Ni_{75}Pd_{10}P_{15}$  alloys showing distinct glass-transition ( $T_g$ ) and crystallization temperature ( $T_x$ ). X-ray photoelectron spectroscopy (XPS) spectra for (c) Ni 2p and (d) P 2p in  $Ni_{80}P_{20}$  nanowires, showing no oxidation of Ni and P on the surface of nanowires. XPS spectra for (e) Ni 2p, (f) Pd 3d, and (g) P 2p in  $Ni_{75}Pd_{10}P_{15}$  nanowires showing three oxidation states for Ni and no oxidation for Pd and P on the surface of nanowires.

catalysis.<sup>13,14</sup> Specifically, the Ni<sub>80</sub>P<sub>20</sub> alloy was chosen because it is close to eutectic composition in the Ni–P phase diagram and favors multiscale amorphous alloy formation in simple as well as complex geometries. Effect of small addition of Pd on amorphous structure stability and catalytic activity enhancement was studied with an alloy of composition Ni<sub>75</sub>Pd<sub>10</sub>P<sub>15</sub>. The catalytic behavior of transition-metal phosphides (including nickel phosphide), which are crystalline stoichiometric compounds, has been widely studied and reported.<sup>15</sup> In contrast, there are few reports and very limited understanding of the catalysis mechanisms in amorphous metallic alloys or metallic glasses.<sup>16</sup>

## RESULTS AND DISCUSSION

Metallic Glass Nanowire Synthesis and Characterization. Synthesis of  $Ni_{80}P_{20}$  and  $Ni_{75}Pd_{10}P_{15}$  amorphous nanowires using commercially available anodic aluminum oxide (AAO) nanomolds is shown in Figure 1. The nanowires were synthesized from a solution containing Ni-, Pd-, and Psolvated ions, as shown schematically in Figure 1a. Freestanding nanowires are obtained by dissolving the templates in an alkaline solution. Nanowire growth initiates at sufficient overpotential on the substrate by concurrent deposition of Ni, Pd, and P. Chemical composition of the nanowires is controlled through the variation in pulse current and potential during the co-electrodeposition of dissolved ions. To quantify the nucleation and growth mechanism, the deposition potential is monitored as a function of process time for both Ni-P and Ni-Pd-P nanowires at a fixed deposition current density (Figure 1b). The potential-time transient shows a sharp increase initially for both Ni-P and Ni-Pd-P due to the charging of the double layer,<sup>17</sup> which is followed by a nonlinear decrease with electrodeposition time. The formation and subsequent charging of the double layer occurred after  $\sim 60$  s, which may be due to diffusion-controlled kinetics of the process during the deposition in nanopores. Discharging of the ionic species leads to the formation of nuclei on the Au substrate at the bottom of the AAO template. With the application of a continuous overpotential, nuclei growth proceeds vertically in the nanopores. During the growth stage, the potential reduces continuously and reaches steady state with the increase in nanowire length. The homogeneous distribution of pores resulted in uniform growth of the nanowires with an aspect ratio ( $\theta$ ) from 25 to 120, as shown in Figure 1c-e.

The structure and chemical composition of the nanowires were evaluated by transmission electron microscopy (TEM). Figure 2a shows a number of Ni–P nanowires with selected area diffraction (SAD) pattern in the form of a diffused ring supporting their amorphous structure (Figure 2a1). The composition of these nanowires was confirmed to be  $Ni_{80}P_{20}$ using scanning transmission electron microscopy energydispersive X-ray spectrometer (STEM-EDS; Figure 2a2). High-resolution TEM (HRTEM) image of the nanowires



**Figure 4.** Catalytic performance of the amorphous alloy nanowires: (a) cyclic voltammograms of pulsed electrodeposited amorphous Ni<sub>80</sub>P<sub>20</sub> and Ni<sub>75</sub>Pd<sub>10</sub>P<sub>15</sub> nanowires (NWs) and flat specimen of identical composition in 0.1 KOH + 0.5 M methanol at a scan rate of 100 mV/s; (b) magnified view of the colored rectangle in part (a) showing the onset potentials for both the nanowires in comparison with commercial Pt/C; (c) chronoamperometry response of Ni<sub>80</sub>P<sub>20</sub> and Ni<sub>75</sub>Pd<sub>10</sub>P<sub>15</sub> nanowires at potentials of -680 and -800 mV (vs SCE), respectively, in 0.1 KOH + 0.5 M methanol with steady-state current density obtained after ~2000 s. The amorphous nanowires of both compositions exhibit good durability and retain a relative current density of 70% after 1.5 h that was comparable or better than commercial Pt/C catalyst; (d) EIS Nyquist plots for Ni<sub>80</sub>P<sub>20</sub> and Ni<sub>75</sub>Pd<sub>10</sub>P<sub>15</sub> alloys in 0.1 KOH + 0.5 M methanol at open-circuit potential (OCP). The inset shows the equivalent electrical circuit used for fitting the EIS data in which *R*<sub>s</sub> is the solution resistance, CPE describes the double-layer capacitance at the interface of catalyst/solution, *R*<sub>ct</sub> represents the charge-transfer resistance, and *W* is related to a Warburg's diffusion element. The charge-transfer resistance (*R*<sub>ct</sub>) was relatively low for both the alloys, with a value of 1610 Ω for Ni<sub>75</sub>Pd<sub>10</sub>P<sub>15</sub> and 1940 Ω for Ni<sub>80</sub>P<sub>20</sub>.

shows disordered atomic arrangement without any lattice fringes (Figure 2a3). The TEM image of a nanowire for the Ni-Pd-P system is shown in Figure 2b with the composition determined to be Ni75Pd10P15. The Ni-P and Ni-Pd-P nanowires were dispersed in deionized (DI) water with a concentration of 0.5 mg/mL, and inductively coupled plasmaoptical emission spectrometry (ICP-OES) technique also demonstrated that the composition was very close to  $Ni_{75}Pd_{10}P_{15}$  and  $Ni_{80}P_{20}$ , with an error of less than  $\pm 0.5$ atom %. Diffused electron diffraction pattern and disordered atomic arrangement in HRTEM support its amorphous structure (insets of Figure 2b). EDS mapping of the Ni<sub>80</sub>P<sub>20</sub> nanowires in Figure 2c demonstrates a large-scale chemical homogeneity of Ni and P with no detectable elemental segregation. Similar uniform elemental distribution is also seen for the  $Ni_{75}Pd_{10}P_{15}$  nanowires (Figure 2d). This composition is very different from  $Ni_{40}Pd_{40}P_{20}$ , which has been reported to be a bulk glass former.<sup>18</sup> Here, we demonstrate a fully amorphous structure for a previously unknown composition in the Ni-Pd-P system with much lower Pd content using pulsed electrodeposition. The formation of an amorphous structure for Ni<sub>75</sub>Pd<sub>10</sub>P<sub>15</sub> and Ni<sub>80</sub>P<sub>20</sub> by pulsed electrodeposition may be attributed to the large overpotential as well as the high pulse frequency. Large overpotential leads to instantaneous discharging of metal atoms reaching the substrate.<sup>14</sup> In addition, the high pulse frequency forces the depositing atoms to grow in a disordered fashion because of insufficient time to assume their thermodynamically stable crystalline form. The precise control over nanowire chemistry through processing conditions opens

up a wide composition range since amorphous alloy formation is not limited by the equilibrium phase diagram.

Pulsed electrodeposition was used for synthesizing flat amorphous deposits with composition identical to the nanowires as confirmed by X-ray diffraction and differential scanning calorimetry. X-ray diffraction (XRD) of 30  $\mu$ m thick flat specimens of Ni80P20 and Ni75Pd10P15 indicated a fully amorphous structure, as shown in Figure 3a. DSC analysis was performed to determine the thermal stability and crystallization behavior of the as-deposited flat specimens of Ni<sub>80</sub>P<sub>20</sub> and  $Ni_{75}Pd_{10}P_{15}$  in the temperature range of 150–500 °C, as shown in Figure 3b. Both compositions showed a distinct glass transition  $(T_g)$  followed by a supercooled liquid region and then exothermic peak corresponding to crystallization  $(T_x)$ . The surface chemistry and oxidation state of the constituent elements in synthesized nanowires were analyzed using X-ray photoelectron spectroscopy (XPS) and are shown in Figure 3c-g. Deconvolution of the oxidation states for Ni and P in Ni<sub>80</sub>P<sub>20</sub> nanowires is shown in Figure 3c,d, respectively. The  $2p_{3/2}$  and  $2p_{1/2}$  peaks of Ni suggest that it was in its zero-valent state (Ni<sup>0</sup>). The peak positions did not show any shift as compared to that of pure Ni,<sup>19</sup> indicating no significant change in core level of Ni with respect to the Fermi level after alloying with P. Ni or Ni(hydroxides) act as a promoter in methanol oxidation.<sup>14,20,21</sup> On the other hand, as compared to red phosphorus,<sup>22</sup> there was a 0.3 eV negative shift in the binding energy of P in Ni-P nanowires due to its higher electronegativity as compared with that of Ni. For Ni<sub>75</sub>Pd<sub>10</sub>P<sub>15</sub> nanowires, the Ni 2p peaks were deconvoluted to three different surface chemical states of Ni<sup>0</sup>, Ni(OH), and NiO (Figure 3e). Oxygen-containing species readily form on surface Ni sites at lower potentials in alkaline media as shown for ethanol oxidation reaction (EOR).<sup>23</sup> The metallic and oxidized states of Ni in Ni75Pd10P15 nanowires served as oxophilic sites for the source of oxygen required for removal of surface CO and promoted methanol electro-oxidation via a surface redox process.<sup>24,25</sup> Palladium was mainly present in a zero-valent state  $(Pd^{0})$ , as shown in Figure 3f, with no trace of oxide. This facilitated the adsorption and desorption of chemical species during methanol electro-oxidation and provided a large number of active sites.<sup>26</sup> The 3d<sub>3/2</sub> peak of Pd<sup>0</sup> was located at 335.7 eV, a 0.6 eV positive shift compared to that of pure Pd due to its higher electronegativity compared with that of Ni.<sup>27</sup> This indicated a downward shift in the core level of Pd with respect to the Fermi level when codeposited with Ni and P.<sup>28</sup> A negative shift in the Pt d-band center as a result of alloying with a second metal having a lower work function has been recently reported for Pt-Co and Pt-Ru alloys.<sup>29</sup> The adsorption of both reactants and intermediates is weakened with a suitable downshift of the d-band center, which leads to the promotion of electro-oxidation.<sup>30</sup> The binding energy of P in  $Ni_{75}Pd_{10}P_{15}$  ternary nanowires showed a 0.4 eV negative shift as compared with that of red phosphorus (Figure 3g). The P<sup>0</sup> atoms accepted partial electrons from the surrounding metals (Ni and Pd) and the binding energy for  $2p_{3/2}$  decreased with the excess electrons in the valence band, similar to negative binding energy shifts observed for Pd-P<sup>31</sup> and Cr-To summarize, the XPS results suggest that the P.<sup>3</sup> amorphous structure of nanowires would favor efficient electrocatalysis due to the modification of surface electronic states of the active Pd and Ni sites.<sup>33</sup> Thus, pulsed electrodeposition represents a tunable and scalable approach to synthesize "the best" catalyst chemistry for fuel cell reactions.

Electrocatalytic Performance of the Metallic Glass Nanowires. Cyclic voltammetry (CV) was performed for methanol oxidation reaction (MOR) in an alkaline medium at a sweep rate of 50 mV/s in a solution containing 0.5 M  $\,$ methanol, as shown in Figure 4a. We chose commercial Pt/C as a benchmark for comparing the performance of our Ni-P and Ni-Pd-P catalysts, as shown in Figure 4. The NiP catalysts form a redox couple, Ni(OH)<sub>2</sub>/NiOOH, during a potential sweep in an alkaline electrolyte.<sup>14</sup> Ni(OH)<sub>2</sub>/NiOOH transformation increases the anodic peak current density in the forward direction in the presence of methanol, and NiOOH acts as an electron-transfer mediator for the oxidation of methanol. The decrease in cathodic peak current density in the reverse direction indicates the consumption of the majority of NiOOH species during methanol oxidation. The second oxidation peak is attributed to incomplete oxidation of methanol in the forward direction when Ni(OH)<sub>2</sub>/NiOOH transformation partially covers the active sites available for methanol adsorption.<sup>34</sup> A slightly different behavior was observed for Ni75Pd10P15. Two discrete anodic current peaks were observed for this catalyst, centered at ~0.670 mV (vs SCE) during the anodic sweep and ~0.490 mV during the cathodic sweep. The peak in the anodic direction is attributed to the oxidation of freshly chemisorbed species from methanol adsorption.<sup>35</sup> The oxidation peak in the reverse sweep direction is associated with the removal of carbonaceous species not completely oxidized during the forward scan.<sup>36,37</sup> There is another peak at the end of the anodic potential sweep,

which is related to the oxidation of  $Ni(OH)_2$  to NiOOH. Both the Ni<sub>80</sub>P<sub>20</sub> and Ni<sub>75</sub>Pd<sub>10</sub>P<sub>15</sub> nanowires demonstrate high electrocatalytic activity toward methanol oxidation reaction (MOR), as shown in Figure 4. Surface characterization and oxidation state of the nanowires (Figure 3) suggest that their amorphous structure would favor efficient electrocatalysis due to the modification of electronic states of the active Pd and Ni sites.<sup>33</sup> For the Ni<sub>80</sub>P<sub>20</sub> nanowires, two oxidation peaks at ~800 and ~810 mV (vs SCE) are present (Figure 4a). The oxidation peak current density for Ni75Pd10P15 nanowires (33.1 mA/ cm<sup>2</sup>) is ~1.5 times higher than that for  $Ni_{80}P_{20}$  nanowires  $(22.4 \text{ mA/cm}^2)$  with the same dimensions and aspect ratio. The peak current density for commercial Pt/C in methanol electro-oxidation was lower than that of Ni<sub>75</sub>Pd<sub>10</sub>P<sub>15</sub> nanowires but higher than that of  $Ni_{80}P_{20}$ . Such increased density in Ni75Pd10P15 nanowires indicates that Pd, even in a small fraction, facilitates the oxidation of CO<sub>ads</sub> to CO<sub>2</sub> (or HCO<sub>3</sub><sup>-</sup> and  $CO_3^{2-}$  in alkaline media).<sup>38</sup> The anodic peak potential for Ni<sub>75</sub>Pd<sub>10</sub>P<sub>15</sub> nanowires is ~150 mV more negative than Ni80P20, indicating higher catalyst efficiency for the alloy with a small fraction of Pd. Methanol electro-oxidation was performed on the flat amorphous deposits with identical composition as the nanowires for comparison. The nanowires exhibit up to a 20-fold increase in peak oxidation current density compared to the flat counterpart indicating an order of magnitude enhancement in electrochemical surface area. The onset potential is ~0.370 mV (vs SCE) for Ni<sub>75</sub>Pd<sub>10</sub>P<sub>15</sub> nanowires, which is ~120 mV lower than  $Ni_{80}P_{20}$  nanowires indicating that the incorporation of Pd in Ni-P reduces the overpotential, as shown in Figure 4b. Both the Ni<sub>75</sub>Pd<sub>10</sub>P<sub>15</sub> and Ni<sub>80</sub>P<sub>20</sub> nanowires show lower onset potential compared with commercial Pt/C, indicating higher efficiency for the amorphous catalysts. To evaluate the stability of the nanowires toward methanol oxidation reaction (MOR), the current density was measured as a function of time with Ni<sub>80</sub>P<sub>20</sub> and Ni<sub>75</sub>Pd<sub>10</sub>P<sub>15</sub> nanowires polarized at +810 and +670 mV (vs SCE), respectively (Figure 4c). The  $Ni_{80}P_{20}$  and  $Ni_{75}Pd_{10}P_{15}$ nanowires show a relatively small drop in current density at the applied constant potentials for a long duration (4800 s), which indicates good stability and durability that is comparable or better than commercial Pt/C. Electrical conductivity of the catalysts was measured in terms of their charge-transfer resistance using electrochemical impedance spectroscopy (EIS) in methanol. The Nyquist plot in Figure 4d shows linear diffusion behavior for both Ni<sub>80</sub>P<sub>20</sub> and Ni<sub>75</sub>Pd<sub>10</sub>P<sub>15</sub>. A Warburg's diffusion element was used for fitting the EIS data using an electrical equivalent circuit shown as an inset in Figure 4d. The charge-transfer resistance  $(R_{ct})$  was relatively low for both the alloys, with a value of 1610  $\Omega$  for Ni<sub>75</sub>Pd<sub>10</sub>P<sub>15</sub> and 1940  $\Omega$  for  $Ni_{80}P_{20}.$  The higher catalytic performance of  $Ni_{75}Pd_{10}P_{15}$  nanowires compared to that of binary  $Ni_{80}P_{20}$  may be attributed to the synergistic effect between Pd and Ni.<sup>39</sup> Higher catalytic reactivity of bimetallic Ni-Pd nanowires toward hydrogenation of *p*-nitrophenol as compared with that of Pd nanowires, Pd nanoparticles, and Pd-Ni nanoparticles has been recently reported.<sup>40</sup> The ratio of bridge-bonded CO  $(CO_B)$  on neighboring Ni sites to linearly bonded CO  $(CO_L)$ on Ni sites would be reduced for amorphous Ni-P due to a "structural effect",41 in which the perturbed atomic arrangement in Ni-P and Ni-Pd-P amorphous catalysts results in a change in the adsorption behavior of chemical species. CO<sub>B</sub> adsorption on Pd sites is stronger than CO<sub>L</sub>, which has been shown to be effective in the removal of CO<sub>ads</sub> intermediates in



**Figure 5.** Electronic structure and charge redistribution on the surface of amorphous alloys: atomic structure models of amorphous alloys generated by heating to high temperature followed by quenching and relaxation for the compositions: (a)  $Ni_{80}P_{20}$  and (b)  $Ni_{75}Pd_{10}P_{15}$ ; density of states (DOS) for (c)  $Ni_{80}P_{20}$  and (d)  $Ni_{75}Pd_{10}P_{15}$ ; electron localization function (ELF) distribution on the surface of (e)  $Ni_{80}P_{20}$  and (f)  $Ni_{75}Pd_{10}P_{15}$ . Both nanowires are metallic with finite DOS at the Fermi energy.

the ethanol oxidation reaction and subsequent catalytic performance promotion. Overall, the homogeneous dispersion of active species and the high concentration of unsaturated surface sites in the amorphous nanowires likely lead to their superior catalytic performance.

Theoretical Investigations to Determine Local Atomic Environment and Catalysis Mechanism. Catalytic activity is primarily determined by the local atomic environment on the surface of a catalyst and corresponding electronic structure.<sup>42</sup> To that end, first-principles calculations were performed for amorphous Ni75Pd10P15 and Ni80P20 nanowires to determine the mechanism for high catalytic activity in methanol oxidation reaction (MOR). Several atomic structures of the amorphous  $\mathrm{Ni}_{80}\mathrm{P}_{20}$  and  $\mathrm{Ni}_{75}\mathrm{Pd}_{10}\mathrm{P}_{15}$  nanowires with various possible topological structures were modeled (Figure 5a,b). The *d* states of transition metals play a critical role in determining their catalytic properties.<sup>43,44</sup> The calculated density of states (DOS) of Ni and Pd were found to have strong d-orbital contributions to the states at the Fermi level (Figure 5c,d), which may account for the high MOR activity for amorphous Ni<sub>80</sub>P<sub>20</sub> and Ni<sub>75</sub>Pd<sub>10</sub>P<sub>15</sub>. The surface electronic structure and the interactions between Ni, Pd, and P through active sites strongly affect CH<sub>3</sub>OH adsorption and catalytic activity of the two metallic glasses. As shown in the electron localization function (ELF) plots (Figure 5e,f), the charges redistribute among the sites due to higher electronegativity of P. Electron localization was seen on the surface of the nanowires in contrast to the highly delocalized states for the subsurface layers. In addition, as shown in Figure 5d,f, Pd preferentially redistributed on the surface of the Ni75Pd10P15 nanowires. This may provide an even higher density of active sites for MOR, which explains the better catalytic activity seen experimentally for Ni75Pd10P15 compared to that for Ni80P20 nanowires.

## CONCLUSIONS

In summary, pulsed electrodeposition was demonstrated to be a facile and scalable approach to fabricate amorphous nanowire arrays. These metallic glass nanowires with little to no noblemetal content showed high catalytic activity and excellent stability in methanol oxidation reaction. Pulsed electrodeposition allows composition optimization for specific reactions to overcome today's challenges in fuel cells of performance, durability, and cost. This work may stimulate further investigations and extensive use of non-noble amorphous alloys in fuel cells, batteries, and other electrochemical energy conversion and storage devices.

#### EXPERIMENTAL SECTION

Synthesis of Metallic Glass Nanowires. The Ni-P nanowires were synthesized using pulsed electrodeposition in an electrolyte containing 30 g/L NiCl<sub>2</sub>, 15 g/L H<sub>3</sub>BO<sub>3</sub>, and 16 g/L H<sub>3</sub>PO<sub>3</sub>. Nanowires were deposited in a commercially obtained porous anodic aluminum oxide (AAO) template (InRedox) vertically aligned with a pore length of ~50  $\mu$ m and a diameter ranging from 20 to 120 nm. A thin layer of Au (150 nm) was sputtered on the backside of the AAO template to serve as a conductive substrate. The AAO template with the Au backing plate was fixed in a Teflon holder with a conductive path and connected as cathode during the deposition. The electrolyte was magnetically stirred at 250 rpm during the deposition to maintain laminar flow. A pure nickel plate kept horizontally at a 2 cm distance from the substrate was used as the anode. A pulse power supplier (Dynatronix-MicroStar) was used to generate equal current/potential pulses with varying amplitude and frequency. The nanowires were grown under galvanostatic conditions, where a pulsed peak current density of 5 A/dm<sup>2</sup> was used with a frequency of 100 Hz for various times ranging from 10 to 30 min. A fixed duty cycle of 50% was used for the deposition (d.c.  $=\frac{t_{on}}{t_{on}+t_{off}}$ , in which  $t_{on}$  is the time of pulsing and  $t_{\rm off}$  is the relaxation off-time). The nanowires in AAO were then washed with DI water and dipped in a 2 M NaOH solution for 2 h to remove the AAO template and obtain them in freestanding form.

The maximum current density for the  $Ni_{75}Pd_{10}P_{15}$  amorphous nanowires was chosen to be 5 mA/cm<sup>2</sup> in this study to obtain a higher



Figure 6. Electrochemical reactions during the concurrent electrodeposition process for obtaining (a) Ni-P and (b) Ni-Pd-P alloys.

fraction of Ni and P while keeping the Pd content low. Other parameters such as the solution pH, temperature, and concentration of metal ions were kept constant during the synthesis. The template pores were subjected to pore wetting and de-aeration by soaking in an ultrasonic bath with double-distilled water for 15 min prior to deposition to prevent capillary effects during nanowire growth. The area of the AAO template exposed to the electrolyte was limited to  $0.827 \text{ cm}^2$ .

For deposition of the Ni–Pd–P nanowires, 5 g/L PdCl<sub>2</sub> was initially dissolved in 0.5 M HCl for 4 h, and the homogenized solution was added to the mixture of NiCl<sub>2</sub> and H<sub>3</sub>PO<sub>3</sub>. The pH of the solution was adjusted to 1.5 with 0.1 M NaOH. The electrolyte was stirred at 350 rpm for 24 h before deposition at room temperature. Prior to electrodeposition, palladium forms  $[PdCl_4]^{2-}$  when dissolved in HCl.<sup>45</sup> In the mixed solution for Ni–Pd–P nanowire synthesis, deposition proceeds with the formation and charging of the double layer of hydronium ions  $(H_3O)^+$ ,  $[PdCl_4]^{2-}$ , and Ni<sup>2+</sup> on the bottom of the AAO nanomolds. During charging,  $[PdCl_4]^{2-}$  and Ni<sup>2+</sup> are reduced by accepting electrons from the electrolyte through H<sub>3</sub>O<sup>+</sup> ions<sup>46</sup> and deposited in the nanomold. P is concurrently deposited through an indirect mechanism by the formation of intermediate phosphine.<sup>47</sup>

The electrochemical reactions and reduction of chemical species in the electrolyte for Ni–P and Ni–Pd–P electrodeposition are summarized in Figure 6.

Characterization of Metallic Glass Nanowires. The surface morphology of the nanowires was characterized using an FEI Nova NanoSEM 230 scanning electron microscope (SEM). The structure and elemental composition of the nanowires were analyzed using transmission electron microscopy (TEM) (FEI Tecnai G2 TF20 operating at 200 kV) equipped with an EDAX energy-dispersive X-ray spectrometer (EDS). To analyze the surface chemical state of the nanowires, X-ray photoelectron spectroscopy (XPS-PHI 5000 Versaprobe) was used. Differential scanning calorimetry (DSC-Netzsch) was employed to obtain the glass transition  $(T_{\alpha})$  and crystallization  $(T_x)$  temperatures of the metallic glasses with a heating rate of 20 K/min. Cyclic voltammetry (CV) and chronoamperometry techniques were used for electrochemical measurements in a standard three-electrode cell with Pt wire as auxiliary, saturated calomel electrode (SCE) as a reference, and the nanowires as the working electrode. The cyclic voltammetry was done at room temperature with a scan rate of 50 mV/s, while chronoamperometry was done at a scan rate of 10 mV/s for 80 min. Electrochemical impedance spectroscopy (EIS) measurements were done at open-circuit potential (OCP) from 1000 kHz to 10 mHz to analyze the electrochemical behavior of catalysts in 0.1 KOH + 0.5 M methanol.

**Computational Methodology.** Amorphous  $Ni_{75}Pd_{10}P_{15}$  and  $Ni_{80}P_{20}$  alloys were generated by heating to high temperature followed by quenching and relaxation. The electronic structure of the two amorphous alloys was calculated using the density functional theory (DFT) via VASP (Vienna ab initio simulation package) with the Hubbard U (DFT + U) corrections.<sup>42,48</sup> The DFT calculations were made by employing project-augmented wave (PAW) pseudopotentials and Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional with spin polarization.<sup>49</sup> The wave functions were

expanded using a plane-wave basis set with a kinetic energy cutoff of 550 eV, and the geometries were fully relaxed until the residual force convergence value on each atom was less than 0.02 eV/Å. The Brillouin zone was sampled by a  $3 \times 3 \times 3$  gamma *k*-point mesh and a vacuum spacing of at least 20 Å in the *z*-direction perpendicular to the surface. The density of states (DOS) and electron localization function (ELF) were also calculated using VASP. The cutoff energies for DOS and ELF were both 550 eV, and the *k*-point meshes were  $3 \times 3 \times 3$  and  $6 \times 6 \times 6$  for ELF and DOS, respectively.

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#### **Author Contributions**

V.H. performed the synthesis and characterization and wrote the paper. X.W. performed computational modeling of the amorphous alloys. R.S. performed the TEM characterization. Z.X. designed and supervised the computational modeling. J.S. performed data analysis and revised the paper. S.M. designed and supervised the overall research work and wrote the paper.

#### Notes

The authors declare no competing financial interest. The data supporting the findings of this study are available from the corresponding author upon request.

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