Palladium Coated Copper Nanowires as a Hydrogen Oxidation Electrocatalyst in Base

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Palladium (Pd) nanotubes are synthesized by the spontaneous galvanic displacement of copper (Cu) nanowires, forming extended surface nanostructures highly active for the hydrogen oxidation reaction (HOR) in base. The synthesized catalysts produce specific activities in rotating disk electrode half-cells 20 times greater than Pd nanoparticles and about 80% higher than polycrystalline Pd. Although the surface area of the Pd nanotubes was low compared to conventional catalysts, partial galvanic displacement thinned the noble metal layer and increased the Pd surface area. The use of Pd coated Cu nanowires resulted in a HOR mass exchange current density 7 times greater than the Pd nanoparticles. The activity of the Pd coated Cu nanowires further nears Pt/C, producing 95% of the mass activity.

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The commercial deployment of proton exchange membrane fuel cells (PEMFCs) is primarily limited by the cost of platinum (Pt) catalysts. Hydroxide exchange membrane fuel cells (HEMFCs) were recently developed as a potential alternative to PEMFCs as they can avoid the use of Pt group metal (PGM) catalysts, particularly at the cathode in the oxygen reduction reaction (ORR).^{1–5} In both PEMFCs and HEMFCs, kinetic losses are primarily attributed to the cathode, where ORR on Pt requires an overpotential of approximately 0.3 V. In base, however, the hydrogen oxidation reaction (HOR) on Pt is two orders of magnitude slower than in acid.^{6,7} A reduction in HOR catalyst cost can significantly improve the commercial prospect of HEMFCs.

Pd has previously been studied as a HOR catalyst and alternative to Pt in membrane electrode assemblies for PEMFCs and alkaline (liquid electrolyte) fuel cells.^{8–12} Pd-based catalysts, including Pd-gold (Au) alloys, Pd-Pt alloys, and Pd modified polythiophene, have also been studied for catalyzing HORs in acid or gaseous environments.^{13–15} Although fundamental studies of the kinetics of HOR on Pd in base are largely unavailable, recent rotating disk electrode (RDE) results provide insight, allowing for the design and electrochemical characterization of HOR catalysts in base. Shao-Horn et al. determined the HOR/hydrogen evolution reaction (HER) exchange current densities of carbon supported Pt (Pt/C) and bulk polycrystalline Pt (BPt).⁷ Sheng et al. further correlated hydrogen binding energy (HBE) with HER/HOR activity in a volcano relationship for a variety of metals, including Pd.¹⁶

Galvanic displacement has recently been used in the development of extended surface fuel cell catalysts.¹⁷ Although most of the work into developing advanced geometry catalysts has focused on ORR in PEMFCs, Pt coated copper (Cu) nanowires (Pt/CuNWs) were recently studied as catalysts for HOR in base in RDE half-cells.¹⁸ Pt/CuNWs significantly exceeded the HOR mass and area exchange current densities of Pt/C, potentially benefitting from compressive strain and Cu surface impurities facilitating hydroxyl adsorption.^{19,20} In this study, we galvanically displaced CuNWs with Pd, forming Pd coated CuNWs (Pd/CuNWs) and Cu templated Pd nanotubes (PdNTs (Cu)). These materials were investigated for HOR in base to: improve the HOR mass and area activities of Pd catalysts; and to provide the HOR activity of Pt/C at a significantly reduced cost.

Experimental

CuNWs were synthesized by the hydrazine reduction of Cu nitrate in sodium hydroxide, with ethylene diamine provided for shape

control.²¹ An aqueous 15 M sodium hydroxide (Fisher) solution (200 ml) was first prepared in a 500 ml round bottom flask and cooled to 10°C. Cu nitrate (Sigma Aldrich, 188 mg in 10 ml water), ethylene diamine (Sigma Aldrich, 1.5 ml), and hydrazine (Sigma Aldrich, 0.25 ml, 35 wt%) were added in sequence to the sodium hydroxide solution. Reactants were added slowly and thoroughly dispersed. Upon incorporation of the hydrazine, the flask was capped and placed in an oil bath at 60°C for 1 h without stirring. Following synthesis, the flask contents were cooled in an ice bath. The CuNWs were collected by filtration, washed in water, and stored in an argon glove box. This method is similar to that published by Zeng et al.; the synthesis procedure used here differs in the methods for washing (filtration was used to increase yield) and storage in a glove box to avoid storage in hydrazine.²¹

PdNTs (Cu) were synthesized by the galvanic displacement of CuNWs.²² CuNWs (16.8 mg) were dispersed in 400 ml of water and stirred at room temperature in a 1 L round bottom flask. Following 15 min of flowing argon, potassium tetrachloropalladate (72.0 mg in 200 ml water) was added dropwise to the flask over 15 min. The synthesis continued at room temperature for 1 h and was subsequently heated to 40°C for 30 min to promote the full displacement of Cu. After being cooled to room temperature, the PdNTs (Cu) were washed in 1 M hydrochloric acid, water, and 2-propanol. This method is similar to that published by Xia et al.²³ Slight variations were used in this method for concentration and drop time; these modifications matched our synthesis protocols and potentially allowed for a more complete templating of CuNW growth directions.²² The temperature was also increased to promote the complete deposition of available Pd precursor.

Pd/CuNWs were synthesized by the partial galvanic displacement of CuNWs.²² All synthesis methods were identical to the synthesis of PdNTs (Cu), except the Pd precursor solution was diluted to 7.0 mg in 200 ml water. Following synthesis, Pd/CuNWs were also washed in 1 M hydrochloric acid, water, and 2-propanol.

Scanning electron microscopy (SEM) images were taken at 20 kV on a Phillips XL-30 FEG microscope. Transmission electron microscopy (TEM) images were taken at 300 kV on a Phillips CM300 microscope. X-ray diffraction (XRD) patterns were taken over 60 min at 40 kV and 35 mA on Bruker D8 Discover with a 2θ of 15–87°. Catalyst compositions were determined by inductively coupled plasma mass spectrometry (ICP-MS), taken on a Thermo Scientific iCAP Q, and confirmed by energy dispersive X-ray spectroscopy experiments during SEM.

Electrochemical measurements were conducted in a RDE half-cell containing a 0.1 M potassium hydroxide (KOH) electrolyte. The RDE half-cell utilized a glassy carbon working electrode, Au mesh counter electrode, and mercury/mercurous chloride reference electrode (Koslow Scientific). Rotation of the working electrode was

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controlled by a modulated speed controller (Pine Instruments) and data were collected on a multichannel potentiostat (Princeton Applied Research, VMP2). RDE experiments used a mercury / mercurous chloride reference electrode which was converted to a reversible hydrogen electrode (RHE) at the intersection between HOR and HER on BPPt. KOH electrolytes were replaced every 30 min to minimize electrolyte deterioration.²⁴

Catalyst inks of Pd/CuNWs and PdNTs (Cu) consisted of 0.98 mg of total metal (M) per 1 ml of water and 2-propanol, at a 3:1 ratio. Working electrodes were coated with 20 μl of ink, resulting in Pd/CuNW and PdNT (Cu) loadings of 12.5 $\mu\text{g}_{\text{PDM}} \text{cm}_{\text{elec}}^{-1}$ and 80.8 $\mu\text{g}_{\text{PDM}} \text{cm}_{\text{elec}}^{-1}$ (100 $\mu\text{g}_{\text{M}} \text{cm}_{\text{elec}}^{-1}$), necessary to reach diffusion limited currents in HOR and ORR experiments. Inks of carbon supported Pd (Pd/C) and Pt/C consisted of 0.35 mg_{PDM} per 1 ml of water and 2-propanol at a 3:1 ratio; coating with 10 μl of ink resulted in electrode loadings of 18 $\mu\text{g}_{\text{PDM}} \text{cm}_{\text{elec}}^{-1}$. Cu nanoparticles (CuNPs, US Research Nanomaterials, Inc.) were prepared on a bulk polycrystalline Pd electrode (BPPd) by pipetting 10 μl of ink (water to 2-propanol ratio of 3:1) onto the electrode surface; CuNP loading (1–100 $\mu\text{g} \text{cm}_{\text{elec}}^{-2}$) was controlled by varying the ink concentration.

Repeated cyclic voltammograms were completed at 100 mV s^{-1} in an argon-saturated 0.1 M KOH electrolyte in the scan range 0.05–1.2 V vs. RHE as an electrochemical break-in.²⁵ Voltammograms were also taken in an extended scan range (0.05–1.5 V vs. RHE) at 50 mV s^{-1} as a comparison to bulk polycrystalline Cu (BPCu). The electrochemically active surface areas (ECSAs) of Pd and Pt were determined by carbon monoxide oxidation voltammograms since more than a monolayer of hydrogen adsorbed onto Pd during cyclic voltammograms.²⁶ Carbon monoxide oxidation voltammograms were completed by: adsorbing carbon monoxide at 0.3 V vs. RHE for 10 min; purging the electrolyte with argon for 10 min while continuing to hold the working electrode at 0.3 V vs. RHE; and immediately completing a voltammogram at 20 mV s^{-1} starting in the anodic direction. Validity of the ECSA calculation was confirmed on BPPd and BPPt, which had surface roughness factors of 1.22 and 1.25.

HOR and ORR experiments were completed at 1600 rpm in a 0.1 M KOH electrolyte at 20 mV s^{-1} . Activities were corrected for internal resistance from impedance spectroscopy measurements between 10 kHz and 0.1 mHz. Activities were also corrected for mass transport by the Koutecky Levich equation, except in the case of HER since there was no diffusion limited current. Previous studies found that Pt HOR in acid was too fast kinetically to be measured in RDE, that the Pt/C HOR response matched the Nernstian diffusion limited overpotential.⁶ For all examined catalysts in base, however, the Nernstian diffusion limited overpotential was not reached; RDE measurements, therefore, were valid in this case.^{6,7} Hydrogen, from the underpotential deposition region or HER, can persist on the surface of Pd at positive potential, inflating the HOR response.²⁶ As a precaution, Pd and Pt catalysts were cycled at potentials greater than 0.3 V vs. RHE prior to HOR experiments. HOR responses were taken in the cathodic direction, preventing the adsorption of excess hydrogen. After the HOR/HER response was taken, the catalyst was repeatedly cycled at positive potential in argon to desorb extra hydrogen. The process was then repeated to ensure data reproducibility. All catalysts reached but did not exceed the diffusion limited current for HOR. HOR/HER responses were fit to the Butler-Volmer equation with $\alpha = 0.5$ to derive exchange current density values in the potential range -0.05 to +0.05 V vs. RHE. The α value was previously determined, but was also verified by fitting to the data in this study.⁷ The Butler-Volmer equation equally fit the HOR/HER portions, validating the exchange current densities and RDE experiments.⁷

Results and Discussion

Spontaneous galvanic displacement of CuNWs yielded Pd/CuNWs and PdNTs (Cu) 12.5 and 80.8 wt% Pd. Displacement produced nanostructures with similar morphologies to the Cu template: Pd/CuNWs were 100 nm in diameter with a length of 40–50 μm ; and PdNTs (Cu) were 5–10 μm in length, with an outer diameter of 100 nm and a wall

Figure 1. SEM and TEM images of (a-b) Pd/CuNWs and (c-d) PdNTs (Cu).

thickness of 9 nm (Figure 1). SAED patterns also found that Pd displacement maintained the same growth directions of the CuNWs, previously found to be single twinned in the [1, -1, 0] direction (Figure 2).^{21,22} XRD patterns further confirmed compression of the Pd lattice following displacement (Figure 2). Pd/CuNWs and PdNTs (Cu) had lattice constants of 3.86 and 3.87 Å, slightly compressed relative to the “pure” lattice constant of 3.89 Å. A CuNW lattice constant of 3.61 Å, matching Cu metal, was maintained following Pd displacement.

Catalysts were examined for HOR activity in RDE half-cells (Figure 3). The kinetic activities (denoted i_k) were fitted to the Butler-Volmer equation to determine exchange current densities (denoted i_0 , Figure 4). Pd/CuNWs and PdNTs (Cu) each produced area exchange current densities roughly 20 times greater Pd/C. Although PdNTs (Cu) had a low ECSA, partial displacement lowered the Pd content, improving ECSA and the HOR mass exchange current density. Pd/CuNWs produced a mass exchange current density 7.4 times greater than Pd/C and 95% of the activity of Pt/C. Pt/CuNWs were previously synthesized and studied as hydrogen oxidation electrocatalysts in alkaline electrolytes.¹⁸ Pd/CuNWs produced mass and specific exchange current densities 57 and 49% of the previously studied material.

The extended surface structure, lattice compression, surface Cu, and Pd facets were examined as potential contributors to the high HOR activity of Pd/CuNWs. Discussions of these potential factors are included in the following paragraphs.

BPPd produced an area exchange current density 11 times greater than Pd/C.^{7,18} Although a more detailed trend between HOR activity and Pd particle size has not been established in this study, it appeared clear that: Pd nanoparticles produced low area activity compared to BPPd; and that the Pd/CuNWs and PdNTs (Cu) benefitted from the high area activity of extended Pd surfaces.

The synthesized catalysts, however, also exceeded the area exchange current density of BPPd by 78–90%, potentially due to a compressed Pd lattice. XRD patterns found a 0.5–1% lattice compression compared to “pure” Pd (Figure 2). This compressive strain potentially tuned Pd electronically by widening the Pd d-band and shifting the d-band center further from the Fermi level, thereby weakening the hydrogen chemisorption and improving HER/HOR activity.^{7,16} Previous studies have also examined Pd-Cu systems, including Pd-Cu alloys and Pd overlayers on Cu, and found a shift in the d-band center further from the Fermi level.^{27–30} The Pd lattice of the Pd/CuNWs was also

Figure 2. (a) XRD pattern of Pd/CuNWs, PdNTs (Cu), and CuNWs and (b) SAED pattern of PdNTs (Cu).

slightly more compressed than that of the PdNTs (Cu). The greater lattice compression may have allowed for the higher area activity, 6% greater than PdNTs (Cu).

Marković et al. previously examined the effect of hydroxyl adsorption on HOR activity, finding an improvement in Pt catalysts with

added oxophilic sites.²⁰ Cyclic voltammograms of the synthesized materials consisted of Pd and Cu characteristics (Figure 5a, 5b). Cu features were observed in the Pd double charging layer: Cu → Cu(I) oxidation peak at 0.5 V vs. RHE; Cu → Cu(I) and Cu(I) → Cu(II) oxidation peak at 0.85 V vs. RHE; and Cu(II) → Cu(I) reduction peak

Figure 3. iR and mass transport corrected (—) HOR/HER activity of (a) Pd/CuNWs, (b) PdNTs (Cu), (c) Pd/C, (d) BPPd, and (e) Pt/C in conjunction with the activity fitted to the Butler Volmer equation (---) at 1600 rpm and 20 mV s⁻¹ in a hydrogen saturated 0.1 M KOH electrolyte. Figure inset included the measured (—) and internal resistance corrected (---) linear polarization scans; the Nernstian diffusion limited overpotential, the current for HOR is limited solely by diffusion, was provided as a reference. More information is available in the Experimental section. Units for the inset axes mirror the main figures (x-axis E [V vs. RHE], y-axis I [mA cm_{disk}⁻²]).

Figure 4. HOR mass and area exchange current densities of Pd/CuNWs, PdNTs (Cu), Pd/C, BPPd, and Pt/C.

at 0.45 V vs. RHE.²⁵ Overall, Pd/CuNW and PdNT(Cu) have similar hydrogen binding energy (HBE) (Figure 5a) which is consistent

with their similar HOR activity. The CO stripping data (Figure 5c, 5d) show that CO stripping peak occurs earlier on Pd/CuNWs than PdNT(Cu) even though they have similar HOR activity. The CO stripping data also show that PdNT (Cu) has similar CO stripping onset potential as Pd/C but significantly higher activity (Figure 4). Both observations suggest that OH adsorption is not the dominating factor for determining HOR activity.^{20,31}

Exposure of particular Pd facets may have influenced HOR activity, but was not due to active synthesis control. Any preferential surface facets due to templating of the CuNW growth direction would likely have been diluted by the rough surface formed by galvanic displacement. Although low index Pt facets were examined for HOR in base, such data was unavailable for Pd.³²

Catalysts were also examined for ORR activity in base in RDE half-cells. At 0.9 V vs. RHE, Pd/CuNWs and PdNTs (Cu) exceeded the area ORR activities of Pd/C and BPPd by 3 and 2 times (Figure 6). By thinning the noble metal layer and improving the Pd ECSA, the Pd/CuNWs also exceeded the ORR mass activities of Pd/C and Pt/C by 8 and 83%. Previously, an alkaline Pd ORR particle size effect was observed; Pd/CuNWs and PdNTs (Cu) likely benefitted

Figure 5. Cyclic voltammograms of (a) Pd/CuNWs and PdNTs (Cu) 20 mV s⁻¹ and (b) a polycrystalline Cu electrode at 50 mV s⁻¹ in a 0.1 M KOH electrolyte. Carbon monoxide oxidation voltammograms of (c) Pd/CuNWs and PdNTs (Cu) and (d) Pd/C and Pt/C at 20 mV s⁻¹.

Figure 6. (a) Anodic polarization scans and (b) mass and area activities of Pd/CuNWs, PdNTs (Cu), Pd/C, BPPd, and Pt/C at 20 mVs⁻¹ and 1600 rpm in an oxygen saturated 0.1 M KOH electrolyte.

Table I. ECSAs, HOR mass and area exchange current densities, and ORR mass and area activities.

	ECSA [m ² g _{Pd} ⁻¹]	i ₀ HOR [A mg _{Pd} ⁻¹]	i ₀ HOR [mA cm _{Pd} ⁻²]	i _m ORR [A mg _{Pd} ⁻¹]	i _s ORR [mA cm _{Pd} ⁻²]
Pd/CuNWs	32.6	0.33	1.01	0.37	1.14
PdNT (Cu)	6.2	0.06	0.96	0.07	1.14
Pd/C	90.0	0.04	0.05	0.34	0.38
BPPd	—	—	0.18	—	0.53
Pt/C	59.6	0.35	0.58	0.20	0.34

from the extended network and avoided the Pd particle size effect.³³ Lattice compression also potentially improved ORR activity by an alloying effect, weakening oxygen and hydroxide chemisorption.^{34,35} HOR and ORR data are summarized in Table I.

Conclusions

Pd/CuNWs and PdNTs (Cu) were developed as HOR catalysts in base. The synthesized nanostructures were 20 times more active for HOR than Pd/C on an area-specific basis. Although PdNTs (Cu) had a low ECSA (6.2 m² g_{Pd}⁻¹) compared to the nanoparticles, partial galvanic displacement produced Pd/CuNWs, reducing the Pd content and improving the Pd ECSA to 32.6 m² g_{Pd}⁻¹. The improvement in ECSA allowed for the Pd/CuNWs to achieve a mass exchange current density of 0.33 A mg_{Pd}⁻¹, 7.4 times greater than Pd/C and within 95% of Pt/C. Pd/CuNWs were demonstrated as potentially a more promising catalyst than Pt by being comparable in activity at a significantly reduced cost, one half to one third the metal price over the past five years.

The high HOR activity of Pd/CuNWs was potentially due to a combination of the extended surface, lattice compression, and the presence of surface copper. The extended network catalyst was able to produce an area exchange current density 90% larger than BPPd. Electronic tuning by lattice compression also potentially benefitted, allowing for area activities greater than BPPd. Small amounts of surface Cu, stable in base, may have also have weakened Pd-H binding or modified hydroxyl adsorption and benefitted the area activity of the Pd/CuNWs as well.

Pd/CuNWs have also been studied as ORR catalysts in base. By using partial galvanic displacement and improving the Pd surface area, Pd/CuNWs produced mass activities 8 and 83% greater than Pd/C and Pt/C. The high area-specific activity observed was potentially due to the extended nature of the catalyst and lattice compression due to Cu alloying. The synthesized catalysts further produced area-specific activities 2.2 times greater than BPPd.

Extended surface nanostructures have been shown to improve the HOR and ORR activity of Pd. In RDE half-cells, Pd/CuNWs produce slightly higher ORR mass activity than Pd/C and comparable HOR mass activity to Pt/C. Pd/CuNWs can potentially become enabling elements in AEMFCs and allow for significant catalyst cost reduction.

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