

Electrochemical Properties of Pt Coatings on Ni Prepared by Atomic Layer Deposition

Robert R. Hoover^{*} and Yuriy V. Tolmachev^{**,z}

Department of Chemistry, Kent State University, Kent, Ohio 44242, USA

Presented herein is an approach to fabrication of Pt coatings on non-noble metals with (sub)monolayer thickness. The Pt coatings were prepared using atomic layer deposition (ALD) in which Ni-disk substrate is exposed to MeCpPtMe₃ and H₂ in alternating cycles. The structure and electrocatalytic activity of the coatings were characterized using elemental analysis and various electrochemical techniques. We found that the ALD results in micrometer-size Pt islands up to ca 3.7 monolayers of Pt loading and continues more uniformly at higher loadings. The islandlike growth at low Pt loadings is attributed to the presence of adsorbed O on atomically rough facets of polycrystalline Ni substrate. The thin films of Pt on Ni show enhancement factors in the oxygen reduction similar to what has been reported for PtNi alloys. Potential applications of the methodology demonstrated in this work for the development of the third-generation polymer electrolyte fuel cell catalytic layers with ultralow Pt loading are briefly discussed.

© 2008 The Electrochemical Society. [DOI: 10.1149/1.3002372] All rights reserved.

Manuscript submitted July 23, 2008; revised manuscript received September 9, 2008. Published November 7, 2008.

The strategy to reduce the Pt loading in polymer electrolyte fuel cells (PEFCs) using smaller and smaller Pt nanoparticles has been actively pursued ever since the advent of the PEFC technology.¹ Unfortunately, it seems now that this approach has reached a plateau, because Pt nanoparticles smaller than 2-3 nm show lower electrocatalytic activity in oxygen reduction reaction $\left(\text{ORR}\right)^{4,5}$ and decreased stability.⁶ An alternative approach to reduction of the Pt loading is to decrease the number of bulk (nonsurface) Pt atoms in the catalytic particles. The largest possible noble metal loading reduction without sacrifice in power density can be achieved using a (sub)monolayer-thick Pt shell on a non-noble nanostructured core. Adzic et al. has demonstrated some advantages of this strategy by the example of Pt (sub)monolayers on Ru,⁸ Pd,⁹ and alloy¹⁰ nanoparticle cores prepared via spontaneous deposition or Cu underpotential (UPD) displacement. Pt shells have also been produced through partial corrosion of Pt alloys with less noble metals¹¹⁻¹³ or by electroless plating.^{14,15} The core-shell concept has been expanded beyond supported nanoparticles to carbon-free three-dimensional nanoporous cores.¹⁵ In all these cases, however, the cores still contain noble metals, thus offsetting the cost reduction due to lower Pt loading. Conventional methods of preparing Pt thin films, such as UPD displacement,⁹ thermal decomposition,¹⁶ chemical vapor deposition (CVD),¹⁷⁻¹⁹ and physical vapor deposition,^{20,21} are not suitable for making conformal monolayer-thick Pt shells on non-noble metal cores either due to a parasitic displacement reaction²²⁻²⁴ in the case of liquid-phase depositions or due to a poorly controlled conformity and thickness in the case of both liquid- and gas-phase processes affected by mass-transport of the Pt precursor.²¹ Atomic layer deposition (ALD) is a gas-phase process that allows for a conformal growth even in high-aspect-ratio nanostructures with a precise deposit-thickness control. This is because the rate of ALD growth is controlled by adsorption coverage rather than mass transport of the precursor.²⁵ More specifically, instead of exposing the substrate to a mixture of two reactants as in CVD, the precursor is adsorbed on the substrate first and then decomposed by reacting it with another gas. This process is repeated in cyclic fashion until the desired film thickness is reached.

The only successful published ALD of Pt uses (methylcyclopentadienyl) trimethylplatinum, MeCpPtMe₃, as the Pt precursor and O₂ as the reactive gas at temperatures above 200°C.²⁵⁻²⁸ Oxides have been used as the substrates in these studies, and thousands of ALD cycles were typically performed. It is not likely that a uniform coverage of Pt can be achieved on oxide substrates using ALD at monolayer thicknesses, because the Pt cohesion energy typically exceeds the Pt-oxide (and Pt-carbon) adhesion energy. Also, the substrate in fuel cell catalytic layers should possess a good electronic conductivity. Both the adhesion and conductivity requirements favor the use of metals as the supports for the Pt shell. Under oxidative conditions, however, a non-noble metal substrate would oxidize and there would be little hope of making uniform Pt deposits at monolayer coverages. However, MeCpPtMe₃ has been used successfully in combination with H₂ in CVD of nanometer-thick Pt films onto oxides, carbon, and polymers at temperatures as low as 90°C. ^{17-19,29} The reaction in question can be described by the following equation¹⁸

$$MeCpPtMe_3(ads) + 4H_2(g) = MeC_5H_9(g) + 3CH_4(g) + Pt(ads)$$
[1]

We decided to adopt this chemistry for a reductive Pt ALD compatible with non-noble metal substrates. Pt CVD using MeCpPtMe₃ and H₂ has been reported at temperatures as low as 25 °C when Pt substrate is used.¹⁸ However, thermal decomposition of the precursor occurs above 300 °C.²⁷ Thus, this compound has a potentially large ALD temperature window.

Ni was selected as the non-noble substrate in this work because it shows promotion in the catalytic activity of Pt in oxygen reduction^{11,30,36} and methanol oxidation,^{37,38} improved tolerance to methanol in ORR,^{39,41} and CO tolerance,^{42,44} and because the native oxide layer on Ni can be relatively easily reduced.

The deposits were characterized using inductively coupled plasma-mass spectrometry (ICP-MS) and electrochemical techniques which allowed us to determine the amounts of Pt deposited, the surface area of the Pt films, the presence of uncoated Ni patches, as well as the electrocatalytic activity and stability of the Pt monolayers.

Experimental

ALD of platinum onto nickel.— The apparatus used for ALD is illustrated in Fig. 1. It consists of a quartz tube (10 cm long and with a 12 mm inner diameter) with an outlet leading to a silicone oil bubbler which prevents air from getting into the system. The inlet is connected to a system of valves which can control the delivery of hydrogen, ultrahigh-purity (UHP, 99.999%) nitrogen, or nitrogen saturated with precursor to the quartz tube. The precursor (ca 50 mg of solid MeCpPtMe₃, Strem Chemicals) is seated atop a glass frit inside a glass vessel through which the nitrogen can be purged and saturated with the precursor vapor (50 mTorr at 30°C).¹⁸ All delivery lines, valves, and joints exposed to the precursor are made of glass, poly(tetrafluoroethylene), or poly(vinylidene difluoride).

Prior to Pt ALD, two nickel disks purchased from Pine Instruments (Grove City, PA), 6.00 mm diameter and 4.0 mm tall, polished to a scratch-free mirror finish, degreased in chloroform, and

^{*} Electrochemical Society Student Member.

^{**} Electrochemical Society Active Member.

^z E-mail: ytolmach@kent.edu



Figure 1. A schematic representation of the ALD system (not to scale).

rinsed with acetone and with Nanopure water are placed inside the quartz tube. Hydrogen is purged through it for several minutes, and the tube is then heated with a Bunsen burner for 1 h to a temperature in excess of 500°C. The purpose of this high temperature is to reduce the native oxide layer on the Ni surface.⁴⁵⁻⁴⁸ After cooling to room temperature, heating tape is wrapped around the portion of the tube where the disks are located. The flow of H₂ is continued during this step. The following steps are followed to deposit platinum onto the disks.

1. The heating tape power is set to keep the Ni disks temperature at 50° C. The hydrogen flow is switched to UHP nitrogen at a flow rate of 6.0 L/min. This step lasts 5 min.

2. The UHP nitrogen is replaced with UHP nitrogen saturated with precursor. The flow rate is reduced to about 100 mL/min to allow for proper saturation of precursor. This step lasts for 4 min.

3. The nitrogen saturated with precursor is replaced with the pure nitrogen at 6.0 L/min. This step lasts for 5 min.

4. The pure nitrogen is replaced by pure hydrogen at a flow rate of about 100 mL/min. The heating tape power is increased so that it raises the temperature of the disks to 170° C. This step lasts for 5 min.

5. The heating tape power is turned off, and the flow of H_2 continues. This step lasts for 2 min.

6. H_2 is switched to N_2 flow at 6.0 L/min. This step lasts for 3 min.

7. Nitrogen purge continues, and the heating tape power necessary to raise the temperature to 50° C is applied. This step lasts for 2 min.

Steps 2–6 are repeated for the prescribed number of cycles. The purpose of step 4 is to reduce the adsorbed precursor to Pt (at lower temperatures) and to remove submonolayers of oxide⁴⁶ that form on the Ni surface during the course of the cycle from oxygen and water impurities as discussed below.

Determining the amount of platinum deposited .- The disk to be used for determination of platinum-layer thickness was placed on a clean Petri dish. The etching solution was prepared by combining 100 µL of ACS-certified plus-grade (37%) HCl with 50 µL of ACScertified plus-grade (70%) HNO3 and mixing thoroughly. After 2 min, 50 μ L of this mixture was transferred (using an Eppendorf pipet) to the top face of the disk. The droplet of the etching solution was spread to cover the face completely without touching the sides of the cylindrical disk. After 2 min, this 50 µL droplet was sucked into an Eppendorf pipet and transferred into a glass flask. This was repeated with the two remaining 50 µL portions of the etching solution, which were combined with the first 50 µL aliquot in the glass flask. In the next step, the disk's face was rinsed repeatedly with seven 50 µL portions of Nanopure water. Nanopure water was then added to the glass flask for a final volume of 5.00 mL. The Pt concentration in the produced solutions was determined by ICP-MS,⁴⁹ and the Pt amount was then converted into the number of monolayers on the disk surface, assuming that there are 1.3 \times $10^{15}\,{\rm Pt}$ atoms per cm^{2} 50 and that the roughness factor is one. The complete removal of Pt from Ni was verified occasionally by recording hydrogen oxidation current on the Ni disks in the rotating disk electrode (RDE) setup (see below).

The details for the ICP-MS analysis are as follows. A Thermo Finnigan Element 2 ICP double sector field mass spectrometer was used for all measurements. ²⁰⁹Bi internal standard was employed using a mixing tee that added 200 ppb Bi solution to each sample. The flow rate of the sample was 10.0 times faster than the flow rate of Bi standard, so one volume of Bi solution was added to every nine volumes of sample. This allowed all measured ¹⁹⁴Pt and ¹⁹⁵Pt intensities to be normalized by their corresponding ²⁰⁹Bi signals. Two calibration curves were created (for ¹⁹⁴Pt and ¹⁹⁵Pt isotopes) using standard solutions of Pt in water (the blank Pt signal corresponding to 8×10^{-4} ppb). The agreement between the two curves for the concentrations of the unknown samples was within 5%. In order to test the repeatability of the analysis, a 50 ppb standard solution was measured five times over the course of the analyses. A 4.5% standard deviation in the ¹⁹⁴Pt/²⁰⁹Bi ratio was seen for these five replicate measurements.

Electrochemical characterization.— The disk used for electrochemical investigation was removed from the deposition chamber and transferred to an MTI 36 rotating ring-disk electrode tip assembly (Pine Instruments, Grove City, PA). The tip was attached to the rotating shaft, then immersed and sealed in a glass cell with a separate compartment for the reference electrode. An Ag/AgCl electrode, $E = +300 \pm 1$ mV vs reference hydrogen electrode (RHE, in 0.10 M HClO₄), was used for the reference electrode; however, in this article all potentials are referred to RHE. A 0.10 M solution of HClO₄ prepared from ultrapure perchloric acid (J. T. Baker) and Nanopure water (Barnsted) was used as the electrolyte. A separate pure Pt RDE (also from Pine Instruments) was used for pure Pt comparisons. This electrode contains a permanently embedded Pt disk with a diameter of 4.57 mm.

Cyclic voltammetry.— Cycling voltammograms (CV) were acquired at 50 mV/s scan rate under pure nitrogen from +50 to +1100 mV vs RHE. The disk was not rotated during these measurements.

Rotating disk and rotating ring-disk electrode measurements. Hydrogen oxidation.— Hydrogen-oxidation polarization curves were done on the disk while rotating at various rotation rates as pure hydrogen was bubbled through the electrolyte. The data were acquired by holding the disk at +1100 mV vs RHE for 1 min, then scanning from +1100 to + 50 mV at 20 mV/s.

Oxygen reduction.— Oxygen-reduction polarization curves were done on the disk as rotating at various rotation rates as pure oxygen was bubbled through the electrolyte. The technique consisted of holding the disk at 1100 mV vs RHE for 10 s, then stepping to +100 mV for 3 s then scanning from 100 to 1100 mV at 20 mV/s. Simultaneously, the platinum ring surrounding the disk was held at 1300 mV vs RHE. At this potential, hydrogen peroxide is oxidized under limiting current conditions, and the yield of peroxide produced on the disk can be calculated using the collection efficiency of the system (N = 0.24).

CO stripping.— In order to determine the platinum surface area, oxidation of an adsorbed carbon monoxide monolayer was preformed. This was done by first holding the potential of the disk electrode at 500 mV under nitrogen, then bubbling CO for 2 min while observing the transient current that flows as a result of the CO introduction. Five hundred millivolts is higher than the typical CO adsorption potential used in such experiments; however, holding the disk at lower potentials did not passivate Ni electrode fully, and the positive background currents were too large for accurate CO-displacement charge measurement. After CO adsorption, the potential was kept at 500 mV for 30 min while the solution-phase CO was removed by purging with nitrogen. A CV was then run at



Figure 2. Pt loading (determined by ICP-MS) per geometric surface area on Ni disks not subjected to electrochemical treatment vs the number of ALD cycles completed.

50 mV/s from 500 to 1100 mV. The CO coverage was calculated from the stripping charge using CO-displacement charge as the correction according to Ref. 51 and 52.

Nickel depassivation/dissolution.— In order to determine whether or not the nickel surface is completely coated with platinum, an experiment referred to as nickel depassivation/dissolution was performed. This consists of first holding the disk electrode at -1000 mV for 200 s in order to reduce the protective nickel-oxide passive layer that covers Ni on the surface of the disk, then stepping to 0 mV and holding for 500 s to remove the hydrogen that was produced during the reduction. After this, CV from 50 to 1100 mV at 50 mV/s is recorded. The disk electrode is rotated at >4000 rpm during the entire experiment to ensure no bubbles accumulate on the disk surface.

Results and Discussion

Amount of Pt deposited .- The amount of Pt on Ni determined by ICP-MS and converted to the number of monolayers (ML) assuming a roughness factor of one is shown in Fig. 2 as a function of the number of ALD cycles. There is a linear relationship between the number of cycles and the amount of Pt deposited. The slope of this line yields 0.42 ± 0.05 monolayers per cycle. Taking into account the actual roughness factor of 1.47 ± 0.07 (see below), we obtain 0.28 \pm 0.04 Pt monolayers per cycle, which is close to the 0.20-0.25 value calculated on the basis of the ratio of the size of Pt atom and methycyclopentadiene ligand. The data shown in Fig. 2 were obtained with Ni disks not subjected to any electrochemical treatment. When the other disk from the same ALD experiment was analyzed after the electrochemical measurements described below, consistently lower Pt loadings were found. We believe that this is due to the dissolution of Pt monolayers on Ni. Even though we did not systematically study the effect of electrochemical treatment on the stability of Pt monolayers, we noticed that no Pt loss was observed if the Pt potential remained within 50–900 mV, which is similar to the corrosion behavior of bulk Pt. 49,53

Pt surface area and Ni holes.— The CO stripping voltammograms as well as the CV values of CO-free Pt on Ni electrodes are shown in Fig. 3. These data clearly show that both H-UPD charge on bare Pt as well as the stripping charge on the CO-covered electrode increase with an increase in the number of ALD cycles. The Pt surface area (also referred to as real area) determined by both the charge due to CO stripping^{51,52} as well as the charge due to H-UPD adsorption/desorption^{54,55} is shown in Fig. 4 as a function of effective Pt film thickness (number of monolayers) from Fig. 2.



Figure 3. CO stripping cyclic voltammograms for Pt on Ni ALD deposits. Also included are CO stripping cyclic voltammograms for pure Pt and pure Ni. Experimental conditions: electrolyte is 0.10 M HClO₄, CO adsorption potential is 500 mV, and scan rate is 50 mV/s.

Figure 4 shows that the roughness factor (Pt real area normalized by the disk geometric area) increases proportionally to the Pt loading per geometric disk area up to ca 5.5 ML geometric loading and remains constant at higher loadings. The fact that the roughness factor for multilayer coverage is constant (for loading greater than five monolayers) suggests a conformal deposition without propagation of dendrites, as happens during diffusion-limited growth. The limiting value of the roughness factor (1.47 ± 0.07) is most likely determined by the roughness of the Ni substrate. The fact that the break point is observed at 5.5 ML geometric loading (3.7 ML = 5.5 ML/1.47 of real-area loading) and not at 1 ML suggests that the Pt ALD starts with formation of islands several atoms high before a complete coating is produced. Nevertheless, our results show that ALD produces a much smoother and more uniform coating than sputtering even for smooth substrates. For example, in the case of Pt sputtered onto glassy carbon, the break point in the roughness factor appears only at 5 nm thickness (ca 20 ML).

The islandlike growth leads to the question of whether Ni gaps, uncoated by Pt, remain on the surface at the low loadings studied in this work. Being a non-noble metal, Ni has a thermodynamic propensity to dissolve at potentials negative of 0 RHE in acidic solu-



Figure 4. Roughness factor (the ratio of electrochemical Pt area to the geometric Ni disk area) as a function of Pt loading determined via CO stripping (solid square), H-UPD desorption (solid circle), and H-UPD adsorption (open circle). Also shown is the roughness factor for bulk Pt (solid line). Dashed lines are eye guides only. Each X-axis value corresponds to a particular number of cycles in Fig. 2.



Figure 5. Ni depassivation curves from the samples used in Fig. 3. Ni depassivation curves were produced by first holding the disk at -1000 mV for 300 s, holding at +50 mV for 500 s, and then running the cyclic voltammogram from +50 to + 1100 mV at 50 mV/s.

tions. Such behavior is not seen in Fig. 3 even for a bare Ni electrode. The reason for that is the passivation of the Ni surface by a NiO oxide layer. In order to detect the presence of uncoated NiO patches on the electrodes, depassivation/dissolution experiments were performed (see the Experimental section for details). As one can see from Fig. 5, after cathodic reduction of the passivating oxide layer, Ni dissolution becomes apparent at +50 mV and goes through a maximal rate around 500 mV due to reappearance of the oxide at more positive potentials. The maximal current of Ni dissolution correlates inversely with the number of ALD cycles, suggesting that the area of the uncoated NiO patches becomes smaller as more Pt is deposited. In fact, there is little Ni dissolution for samples made with more than 30 ALD cycles (ca 8 ML of Pt per real surface area).

Hydrogen oxidation on RDE.— In order to determine the size of the NiO gaps between the Pt islands, RDE polarization curves of hydrogen oxidation (HOR) were acquired (see Fig. 6). The electrooxidation of hydrogen is fast in the RDE timescale on Pt but negligibly slow on passivated Ni electrode. A well-defined diffusionlimited current for HOR is observed with bulk Pt electrodes over a broad potential range (+0.1 < E < + 0.7 V); the drop of the current at higher potentials is due to slower HOR on Pt oxide than on metallic Pt.



Figure 6. Hydrogen oxidation polarization curves. Cathodic scans at 20 mV/s after holding at +1100 mV vs RHE for 60 s. Data was acquired at 2500 rpm rotation rate in 0.10 M HClO₄ saturated at 1.00 atm H_2 .

Our electrodes with active Pt islands and inactive NiO gaps should behave as partially blocked RDEs in HOR. Figure 6 shows that the 15 and 30 cycle depositions yield limiting current densities (normalized by the geometric area of the disk) close to that of bulk Pt. Furthermore, the analysis of the dependence of the limiting current on rotation rate (not shown) reveals that these electrodes follow the Levich relationship with the expected value of the slope. These two electrodes do not show the partial blocking effect, probably because the average gap size is significantly smaller than the thickness of the diffusion boundary layer (20 µm for conditions in Fig. 6). The small difference (<5%) between the limiting current for the 15 and 30 ALD-cycle electrode and the bulk Pt electrode is most likely due to the edge rounding (and thus higher geometric surface area than the projected area used to calculate the current density) that we have been unable to completely prevent during polishing of the electrodes. Also, the "edge effect," i.e., radial diffusion, might have contributed more in the case of a smaller bulk Pt electrode.

The 8 and 4 cycle depositions, however, yield limiting currents significantly below that of bulk Pt. Furthermore, the behavior of the limiting current on rotation rate (data not shown) resembles more the Koutecky–Levich rather than the Levich relationship. The slopes in the Koutecky–Levich coordinates for all four ALD electrodes are similar within 6%. The most likely explanation for this is the presence of inactive NiO gaps between active Pt islands. Because an accurate general solution to the problem of current on a partially blocked RDE is presently lacking, ⁵⁷⁻⁶⁴ we can make only an order-of-magnitude estimate of the sizes of active, d_A , and blocked, d_B , sites. Within the limitations of the model of Landsberg et al.⁶¹⁻⁶³

$$\frac{1}{i_d} = \frac{1}{i_d^L} + \frac{\sum A_n}{nFDC}$$
[2]

where i_d is the measured diffusion-limited current density per geometric area of the electrode, i_d^L is the diffusion-limited current on a fully active electrode, *n* is the number of electrons in the reaction, F is the Faraday constant, *D* is the O₂ diffusion coefficient, *C* is the O₂ concentration, and A_n represents numerical coefficients with a dimension of length which depends on d_A and d_B . The analysis based on the equation above, using the experimental values of ΣA_n and the dependence of $2\Sigma A_n/(d_A + d_B)$ vs $d_A/(d_A + d_B)$ calculated in Ref. 62, is shown in Table I. Also shown therein are the values calculated using an explicit formula suggested by Mort⁶⁴

$$\frac{1}{i_{d}} = \frac{1}{i_{d}^{L}} + \frac{(1 - \theta^{1/2})^{2}}{\theta} \frac{d_{A}}{nFDC}$$
[3]

where θ is the coverage of the active site. Both approaches yield values on the order of micrometers for the active and blocked sites, and the agreement is reasonably good considering the approximate nature of the models.

It is quite unsettling that depositions with less than 15 cycles (<5 ML loading per geometric area) result in micrometer-wide NiO gaps, because the distance between deposited Pt atoms in the case of the ideal ALD should be on the order of the radius of the precursor, i.e., 0.56 nm. Nevertheless, this conclusion is in agreement with the data in Fig. 4, which suggest that ALD follows an islandlike growth up to ca 3.7 ML of Pt and continues conformally at higher loadings. One possible explanation for this finding could be the presence of patches of oxide (sub)monolayers^{46-48,65-70} on the nickel surface during ALD. This oxide probably forms due to oxygen and water contamination (at the ppm level) in the "ultrahigh-purity" nitrogen used as the carrier gas. We realized this possibility early in our work, and this is the reason 150°C was used during the hydrogen purge step. In fact, without the increased temperature during the reduction step, essentially no Pt deposits. It is possible that even with the 150°C hydrogen purge, the oxygen on Ni is present as patches, causing a low sticking probability of the Pt precursor in these regions.⁴⁴ Because the size of the blocking patches (micrometers) is comparable to the typical grain size in a polycrystalline metal sample, we speculate that they may be facets with high atomic roughness, which are

Table I. Analysis of the sizes of active, d_A , and blocked, d_B , sites for HOR for the electrodes shown in Fig. 6.							
Ι	II^{a}	$\mathrm{III}^{\mathrm{b}}$	IV ^c	V^d	VI ^e	V^{f}	VI^f
Number of ALD cycles	θ	$d_{\rm A}/d_{\rm B}$	$d_{\rm A}/(d_{\rm A}+d_{\rm B})$	$2\Sigma A_{\rm n}/(d_{\rm A}+d_{\rm B})$	ΣA_{n} (µm)	$d_{\rm A}$ (µm)	$d_{\rm B}~(\mu{\rm m})$
4	0.10	1.88	0.35	1.17	3.31	2.0 0.71	3.7 1.3
8	0.53	0.46	0.68	0.19	1.24	8.9 8 8	4.2 4.1

^a From the real Pt area in Fig. 4.

^b From the relationship for a square grid of squares: $1/\theta = 2(d_A/d_B)^2 + (d_A/d_B) + 1$.

^c From column III.

^d From Table I in Ref. 62 for the values in column IV.

^e Experimentally from the intercepts of Koutecky–Levich plots for electrodes in Fig. 6 (data not shown).

^f The upper value is from Landsberg's analysis (columns IV-VI), and the lower is from Morf's $[d_A = \sum A_n \theta/(1 - \theta^{1/2})^2$ and column III].

known for higher initial sticking coefficient and heat of O adsorption than those of $Ni(111)^{67-70}$ as well as resistance to reduction by ^{/2,/3} It is likely that the Pt nucleation on different Ni facets re-H₂. quires different numbers of reductive ALD cycles.

Oxygen reduction behavior .-- Pt monolayer skins on PtNi alloys are known for improved performances in ORR compared to pure Pt. 11,32,33 To test the electrocatalytic properties of the Pt thin films on Ni prepared in this work, oxygen-reduction polarization curves were acquired using an RDE.

The curves in Fig. 7 show that larger oxygen-reduction currents are seen at a given potential as the number of ALD cycles increases. This behavior is similar to what has been discussed earlier with regard to HOR on such partially blocked electrodes. For 15 ALD cycles or more, the ORR limiting currents reach values close to that of bulk Pt (the latter agrees with literature values^{74.76} within 2%), suggesting that the NiO gaps are much smaller than the diffusionlayer thickness (16 μ m for the data in Fig. 7) and that the coatings are smooth in this length scale. One striking difference between HOR (Fig. 6) and ORR (Fig. 7) RDE polarization curves is the faster drop in current in both kinetic and diffusion regions with the decrease in Pt loading. For the 8 and 4 cycle depositions, the ORR currents at 850 mV in Fig. 7 (0.862 and 0.050 mA/cm², respectively) are sufficiently small compared to the limiting diffusion current (6.00 mA/cm²), so that mass-transport correction may be neglected. The kinetic current for 15 and 32 cycle depositions under these conditions is 10.6 mA/cm² (see below). If the lower kinetic

current at lower Pt loading is simply due to the blocking effect, then the ratios of kinetic currents would be the same as the ratio of the roughness factors from Fig. 4, i.e., 2.0 for 30 vs 8 cycles and 7.5 for 30 vs 4 cycles. If mass-transport corrections and radial diffusion effects are taken into account for low Pt loading electrodes, these ratios should be even lower. The experiment gives 12 and 200 for the two ratios, respectively. In other words, the fast drop in kinetic current with reduction of Pt loading in our samples cannot be explained by the reduction of Pt surface area and mass-transport effects. Similar observations have been reported for nanometer-sized Pt islands on glassy carbon in perchloric⁵⁶ but not sulfuric acid^{56,77} and have been attributed to the electronic effect. Because our Pt islands are 2 orders of magnitude larger than in these cited works, we need an alternative explanation. This can be a contamination of Pt sites by NiO, which is more pronounced for small Pt coverage.

The raw data in Fig. 7 show that the Pt thin film on Ni for 30 ALD cycles shows a clear enhancement of the oxygen-reduction current compared to bulk Pt, i.e., behavior similar to PtNi alloys. In order to quantitatively assess the apparent enhancement, the kinetic current density, j_k , normalized by real Pt surface area was determined for the 16 and 32 cycle depositions as well as for the pure Pt sample (see Fig. 8).

The kinetic current density was calculated from the following relationship³

$$j_{k} = \frac{i \cdot i_{d}}{i_{d} - i} \times \frac{l}{rf}$$
[4]



Figure 7. RDE oxygen-reduction polarization curves for Pt and Pt/Ni electrodes. 0.10 M HClO₄ saturated at 1.00 atm O₂, 1600 rpm, 20 mV/s anodic scan. The current is normalized per the geometric area of the disk electrode. The notations for the curves for different samples are the same as in Fig. 6.

where i and i_d are measured mixed and diffusion-limited current densities per geometric surface area and rf is the roughness factor.



Figure 8. Tafel plots of data from Fig. 7. Kinetic current density, j_k , refers to the real Pt surface area.

Even though this approach is not completely rigorous because it assumes the same spatial scale for mass-transport and heterogeneous kinetics, it is appropriate in the current situation, because the roughness factors are similar and the diffusion-layer thicknesses are larger than the inactive NiO gaps in all three experiments. Such correction is not accurate for 8 and 4 ALD cycle depositions; therefore, these data are not discussed in this context.

As can be seen from the figure, the Tafel slopes for all three samples are similar, i.e., change gradually from 60 to 120 mV/dec as the overpotential increases, with a break point around 0.9 V. This behavior is typical for ORR on Pt in HClO₄ solutions.^{56,78} Both the 30 and the 15 cycle depositions show a greater kinetic current density when compared to that of pure Pt. For example, j_k is 1.47 mA/cm² for bulk Pt at 900 mV vs RHE, but it is 2.72 mA/cm² for both the 30 and 15 cycle depositions. This corresponds to a 1.85-fold catalytic enhancement. Our value for j_k in the case of polycrystalline Pt agrees with literature,^{11,55} but our value for ORR enhancement is lower than what is usually reported for smooth polycrystalline PtNi alloys at this same potential, i.e., 2-3.11,35,36 The smaller enhancement factor found in our work agrees with a previously noted trend of decreasing the promoting effect of Ni substrate with a thicker Pt shell.^{11,35,36}

It is also worth comparing the Pt mass-specific activity of our catalyst with other Pt (sub)monolayer catalysts. When compared with a smooth Pt_{ML}/Pd(111),^{79,80} our catalyst (15 ALD cycles, 5 ML of Pt) shows a two-times larger area-specific enhancement but a two-times smaller mass-specific enhancement (because our catalyst has 5 rather than 1 ML of Pt). When compared with Pt_{ML}/Pd/C nanoparticles, our catalyst shows less of a difference. For example, Adzic et al. reported, for 800 mV, 10.5 mA/ μ g for Pt_{ML}/Pd/C 9 and 23 mA/ μ g for Pt_{ML}/AuNi₁₀/C,¹⁰ which is an order of magnitude improvement over conventional nanoparticles than for 3 nm Pt/C nanoparticles $(1 \text{ mA}/\mu g)$.¹⁰ Our catalyst displays a comparable Pt mass-specific activity at 800 mV, i.e., 17 mA/µg. This trend is also present at 850 mV, i.e., 8 mA/µg for $Pt_{ML}/AuNi_{10}/C^{10}$ and 5 mA/ μ g for our Pt on Ni. Apparently, the discrepancy in comparison of our catalyst with other Pt monolayers on smooth and nanoparticle supports is due to a so-called particle-size effect. The latter may be either the intrinsic drop in the area-specific activity of nanoparticles or an artifact due to mass transport in an assembly of nanoparticles.^{4,55,81}

Because the purpose of PEFC ORR electrocatalysts is to reduce O_2 to water rather than peroxide, we measured the H_2O_2 yield with our catalysts using a rotating ring-disk electrode. In all cases, the peroxide yield of Pt on Ni electrodes was similar to bulk Pt and to other PtNi electrocatalysts,^{82,83} i.e., smaller than 1% for potentials positive of +300 mV and increasing at more negative potentials. The latter increase is due to inhibition of O_2 absorption on Pt in the presence of adsorbed H.⁸⁴

Electrocatalytic oxidation of adsorbed CO.— Figure 3 shows that decreasing the real Pt loading on Ni below eight monolayers (30 ALD cycles) accelerates the electro-oxidation of adsorbed CO. Better performance of PtNi alloys and Pt thin films on Ni toward electro-oxidation of adsorbed CO has been reported earlier and has been attributed to an electronic effect.⁴²⁻⁴⁴ In addition to this previously proposed explanation, we also want to discuss the possibility of a bifunctional mechanism with Pt providing the CO adsorption and diffusion sites and with Ni being responsible for the reactive OH species.³⁷ Indeed, according to the mechanism of Pt growth on Ni proposed in this work, the deposit consists of Pt islands in a NiO sea. The smaller size of Pt islands at lower Pt loading should result in faster CO diffusion to the island edges and, thus, a faster CO oxidation. Similar arguments have been proposed to explain the superior activity of PtRu alloys compared to Ru islands on Pt.85 However, the size of our Pt islands is on the order of micrometers, and because the surface diffusion of CO is rather slow at such distances, the complete removal of CO at a 0.2 V lower potential in the CV timescale via the bifunctional mechanism is unlikely.

Conclusions

We showed that ALD using MeCpPtMe3 and H2 can yield conformal Pt deposits on a non-noble metal at monolayer loadings. In the case of Ni substrate and 99.999% pure N₂ as the carrier gas, micrometer-size gaps are present between Pt islands up to 3.7 ML of real-area Pt loading. This is probably due to adsorption of oxygencontaining species on Ni during deposition. The coating becomes virtually pinhole free at Pt real-area loading over 8 ML. The Pt thin films show similar enhancement in ORR to PtNi alloys.

The reductive Pt ALD demonstrated in this work can be potentially used for fabrication of ultralow Pt loading PEFC catalytic layers using carbon-free nanoporous supports with nanometersmooth surfaces not subject to the particle-size effect⁴ that also may not require ionomer due to surface H2O diffusion on a continuous Pt coating.⁸⁶ We believe that a more uniform Pt coating at (sub)monolayer loadings can be achieved using vacuum ALD. Also, the use of a more corrosion-resistant coating on the substrate under the Pt (which can be easily produced via ALD) may be needed for a durable PEFC catalyst.

Acknowledgments

This work was partially supported by Kent State University, Ohio Board of Regents, Ohio Third Frontier program, and the U.S. Department of Energy. The authors thank A. Lutton and J. Olesik of the School of Earth Sciences of the Ohio State University for the **ICP-MS** measurements.

Kent State University assisted in meeting the publication costs of this article

References

- 1. S. Gottesfeld and T. A. Zawodzinski, in Advances in Electrochemical Science and Engineering, Vol. 5, R. C. Alkire and D. M. Kolb, Editors, pp. 195-301, Wiley-VCH, New York (1997).
- 2. P. Costamagna and S. Srinivasan, J. Power Sources, 102, 242 (2001).
- C. N. Kostelansky, J. J. Pietron, M. S. Chen, W. J. Dressick, K. E. Swider-Lyons, D. E. Ramaker, R. M. Stroud, C. A. Klug, B. S. Zelakiewicz, and T. L. Schull, J. 3. Phys. Chem. B, 110, 21487 (2006).
- 4. H. A. Gasteiger, S. S. Kocha, B. Sompalli, and F. T. Wagner, Appl. Catal., B, 56, 9 (2005).
- K. J. J. Mayrhofer, B. B. Blizanac, M. Arenz, V. R. Stamenkovic, P. N. Ross, and N. M. Markovic, J. Phys. Chem. B, 109, 14433 (2005).
- 6. R. Borup, J. Meyers, B. Pivovar, Y. S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, et al., Chem. Rev. (Washington, D.C.), 107, 3904 (2007).
- Y. Tolmachev, U.S. Pat. application no. 20070105005 (2007). K. Sasaki, J. L. Zhang, J. Wang, F. Uribe, and R. Adzic, *Res. Chem. Intermed.*, **32**, 543 (2006).
 - 9. M. B. Vukmirovic, J. Zhang, K. Sasaki, A. U. Nilekar, F. Uribe, M. Mavrikakis, and R. R. Adzic, Electrochim. Acta, 52, 2257 (2007).
 - J. Zhang, F. H. B. Lima, M. H. Shao, K. Sasaki, J. X. Wang, J. Hanson, and R. R. Adzic, J. Phys. Chem. B, 109, 22701 (2005). 11. V. R. Stamenkovic, B. S. Mun, K. J. J. Mayrhofer, P. N. Ross, and N. M. Markovic,
 - J. Am. Chem. Soc., 128, 8813 (2006).
 - 12. S. Koh, C. Yu, P. Mani, R. Srivastava, and P. Strasser, J. Power Sources, 172, 50 (2007).
 - 13. S. Koh and P. Strasser, J. Am. Chem. Soc., 129, 12624 (2007).
 - 14. J. Yang, J. Y. Lee, L. X. Chen, and H.-P. Too, J. Phys. Chem. B, 109, 5468 (2005). 15. R. Zeis, A. Mathur, G. Fritz, J. Lee, and J. Erlebacher, J. Power Sources, 165, 65 (2007).

 - J. I. Park and J. Cheon, J. Am. Chem. Soc., 123, 5743 (2001).
 Z. L. Xue, M. J. Strouse, D. K. Shuh, C. B. Knobler, H. D. Kaesz, R. F. Hicks, and R. S. Williams, J. Am. Chem. Soc., 111, 8779 (1989).
 - 18. Z. L. Xue, H. Thridandam, H. D. Kaesz, and R. F. Hicks, Chem. Mater., 4, 162 (1992).
 - 19. J. Goswami, P. Majhi, C. G. Wang, and S. K. Dey, Integr. Ferroelectr., 42, 13 (2002).
 - 20. A. F. Gulla, M. S. Saha, R. J. Allen, and S. Mukerjee, J. Electrochem. Soc., 153, A366 (2006).
 - 21. L. Gancs, T. Kobayashi, M. K. Debe, R. Atanasoski, and A. Wieckowski, Chem. Mater., 20, 2444 (2008).
 - 22. H. P. Liang, H. M. Zhang, J. S. Hu, Y. G. Guo, L. J. Wan, and C. L. Bai, Angew. Chem., Int. Ed., 43, 1540 (2004).
 - Y. Vasquez, A. K. Sra, and R. Schaak, J. Am. Chem. Soc., 127, 12504 (2005)
 - S. Papadimitriou, A. Tegou, E. Pavlidou, S. Armyanov, E. Valova, G. Kokkinidis, and S. Sotiropoulos, Electrochim. Acta, 53, 6559 (2008).
 - 25 T. Aaltonen, M. Ritala, T. Sajavaara, J. Keinonen, and M. Leskelae, Chem. Mater. 15, 1924 (2003).
 - 26. T. Aaltonen, A. Rahtu, M. Ritala, and M. Leskela, Electrochem. Solid-State Lett.,

6, C130 (2003).

- 27. T. Aaltonen, M. Ritala, Y. L. Tung, Y. Chi, K. Arstila, K. Meinander, and M. Leskela, J. Mater. Res., 19, 3353 (2004).
- Y. Zhu, K. A. Dunn, and A. E. Kaloyeros, J. Mater. Res., 22, 1292 (2007).
 T. Ngo, L. Brandt, R. S. Williams, and H. D. Kaesz, Surf. Sci., 291, 411 (1993).
- 30. M. K. Min, J. H. Cho, K. W. Cho, and H. Kim, Electrochim. Acta, 45, 4211 (2000).
- 31. S. Mukerjee and S. Srinivasan, in Handbook of Fuel Cells-Fundamentals, Technology and Applications, Vol. 2, W. Vielstich, H. A. Gasteiger, and A. Lamm, Editors, Chap. 34, pp. 502-519, John Wiley & Sons, New York (2003).
- 32. N. Wakabayashi, M. Takeichi, H. Uchida, and M. Watanabe, J. Phys. Chem. B, 109, 5836 (2005).
- V. Stamenkovic, B. S. Mun, K. J. J. Mayrhofer, P. N. Ross, N. M. Markovic, J. 34.
- Rossmeisl, J. Greeley, and J. K. Norskov, *Angew. Chem., Int. Ed.*, **45**, 2897 (2006). V. R. Stamenkovic, B. S. Mun, M. Arenz, K. J. J. Mayrhofer, C. A. Lucas, G. F. Wang, P. N. Ross, and N. M. Markovic, *Nature Mater.*, **6**, 241 (2007).
- 35. V. Stamenkovic, T. J. Schmidt, P. N. Ross, and N. M. Markovic, J. Electroanal. Chem., 554, 191 (2003).
- 36. V. Stamenkovic, T. J. Schmedt, P. N. Ross, and N. M. Markovic, J. Phys. Chem. B, 106. 11970 (2002).
- 37. K. W. Park, J. H. Choi, B. K. Kwon, S. A. Lee, Y. E. Sung, H. Y. Ha, S. A. Hong, H. Kim, and A. Wieckowski, J. Phys. Chem. B, 106, 1869 (2002).
- T. C. Deivaraj, W. X. Chen, and J. Y. Lee, J. Mater. Chem., 13, 2555 (2003).
- J. F. Drillet, A. Ee, J. Friedemann, R. Kotz, B. Schnyder, and V. M. Schmidt, 39. Electrochim. Acta, 47, 1983 (2002).
- 40. H. Yang, C. Coutanceau, J.-M. Leger, N. Alonso-Vante, and C. Lamy, J. Electroanal. Chem., 576, 305 (2005).
- 41. E. Antolini, J. R. C. Salgado, A. M. dos Santos, and E. R. Gonzalez, Electrochem. Solid-State Lett., 8, A226 (2005).
- 42. D. W. McKee and M. S. Pak, J. Electrochem. Soc., 116, 516 (1969).
- 43. M. Watanabe, in Handbook of Fuel Cells-Fundamentals, Technology and Applications, Vol. 2, W. Vielstich, H. A. Gasteiger, and A. Lamm, Editors, Chap. 28, pp. 408-415, John Wiley & Sons, New York (2003).
- 44. H. Igarashi, T. Fujino, Y. M. Zhu, H. Uchida, and M. Watanabe, Phys. Chem. Chem. Phys., 3, 306 (2001). 45. J. A. Rodriguez, J. C. Hanson, A. I. Frenkel, J. Y. Kim, and M. Perez, J. Am. Chem.
- Soc., 124, 346 (2002).
- 46. M. Lorenz and M. Schulze, Surf. Sci., 454, 234 (2000). 47
- G. Fanjoux, B. Lescop, and A. Le Nadan, Surf. Interface Anal., 34, 555 (2002).
- 48. B. Lescop, J. P. Jay, and G. Fanjoux, Surf. Sci., 548, 83 (2004). 49. X. P. Wang, R. Kumar, and D. J. Myers, Electrochem. Solid-State Lett., 9, A225 (2006).
- A. E. Thomas and A. Wieckowski, J. Electroanal. Chem., 399, 207 (1995). 50.
- 51. M. J. Weaver, S. C. Chang, L. W. H. Leung, X. Jiang, M. Rubel, M. Szklarczyk, D. Zurawski, and A. Wieckowski, J. Electroanal. Chem., 327, 247 (1992).
- R. Gomez, J. M. Feliu, A. Aldaz, and M. J. Weaver, Surf. Sci., 410, 48 (1998). 52. V. Komanicky, K. C. Chang, A. Menzel, N. M. Markovic, H. You, X. Wang, and D. 53.
- Myers, J. Electrochem. Soc., 153, B446 (2006). T. Biegler, D. A. J. Rand, and R. Woods, J. Electroanal. Chem. Interfacial Elec-54.
- trochem., 29, 269 (1971). 55. K. J. J. Mayrhofer, D. Strmcnik, B. B. Blizanac, V. Stamenkovic, M. Arenz, and N.

- M. Markovic, Electrochim. Acta, 53, 3181 (2008).
- 56. A. Sarapuu, A. Kasikov, T. Laaksonen, K. Kontturi, and K. Tammeveski, Electrochim. Acta, 53, 5873 (2008).
- 57. V. Y. Filinovsky, Electrochim. Acta, 25, 309 (1980).
- 58. E. Levart, J. Electroanal. Chem. Interfacial Electrochem., 187, 247 (1985).
- 59. L. Nyikos, T. Pajkossy, and S. A. Martemyanov, Sov. Electrochem., 25, 1381 (1989).
- M. A. Jakab, D. A. Little, and J. R. Scully, J. Electrochem. Soc., 152, B311 (2005). 60.
- R. Landsberg and R. Thiele, *Electrochim. Acta*, 11, 1243 (1966).
 F. Scheller, S. Muller, R. Landsberg, and H.-J. Spitzer, *J. Electroanal. Chem.* Interfacial Electrochem., 19, 187 (1968).
- F. Scheller, R. Landsberg, and H. Wolf, Z. Phys. Chem., 243, 345 (1970).
- 64
- W. E. Morf, Anal. Chim. Acta, 330, 139 (1996).
 P. H. Holloway and J. D. Hudson, Surf. Sci., 43, 123 (1974).
 P. H. Holloway and J. D. Hudson, Surf. Sci., 43, 141 (1974). 65.
- 66.
- A. D. Karmazyn, V. Fiorin, and D. A. King, J. Am. Chem. Soc., 126, 14273 (2004). 67.
- T. P. Pearl, S. B. Darling, and S. J. Sibener, Surf. Sci., 491, 140 (2001). 69. K. Yagi-Watanabe, Y. Ikeda, Y. Ishii, T. Inokuchi, and H. Fukutani, Surf. Sci., 482,
- 128 (2001). 70. I. L. Bolotin, A. Kutana, B. Makarenko, and J. W. Rabalais, Surf. Sci., 472, 205 (2001).
- 71. M. Walker, C. R. Parkinson, M. Draxler, M. G. Brown, and C. F. McConville, Surf. Sci., 600, 3327 (2006).
- E. Vesselli, L. De Rogatis, A. Baraldi, G. Comelli, M. Graziani, and R. Rosei, J. Chem. Phys., 122, 144710 (2005).
- 73. T. Ikari, T. Matsuoka, K. Murakami, T. Kawamoto, K. Yamada, A. Watanabe, M. Naitoh, and S. Nishigaki, Surf. Sci., 601, 4418 (2007).
- V. Stamenkovic, T. J. Schmidt, P. N. Ross, and N. M. Markovic, J. Phys. Chem. B, 74. 106, 11970 (2002).
- 75. U. A. Paulus, A. Wokaun, G. G. Scherer, T. J. Schmidt, V. Stamenkovic, N. M. Markovic, and P. N. Ross, *Electrochim. Acta*, **47**, 3787 (2002).
- 76. H. Ye, J. A. Crooks, and R. M. Crooks, Langmuir, 23, 11901 (2007).
- 77. A. Schneider, L. Colmenares, Y. E. Seidel, Z. Jusys, B. Wickman, B. Kasemo, and R. J. Behm, Phys. Chem. Chem. Phys., 10, 1931 (2008).
- 78. J. X. Wang, N. M. Markovic, and R. R. Adzic, J. Phys. Chem. B, 108, 4127 (2004).
- 79. J. L. Zhang, M. B. Vukmirovic, Y. Xu, M. Mavrikakis, and R. R. Adzic, Angew. Chem., Int. Ed., 44, 2132 (2005).
- J. Zhang, M. B. Vukmirovic, K. Sasaki, F. Uribe, and R. R. Adzic, J. Serb. Chem. Soc., 70, 513 (2005).
- 81. Y. H. Shih, G. V. Sagar, and S. D. Lin, J. Phys. Chem. C, 112, 123 (2008).
- 82. U. A. Paulus, A. Wokaun, G. G. Scherer, T. J. Schmidt, V. Stamenkovic, N. M. Markovic, and P. N. Ross, Electrochim. Acta, 47, 3787 (2002).
- 83. H. Yang, W. Vogel, C. Lamy, and N. Alonso-Vante, J. Phys. Chem. B, 108, 11024 (2004).
- 84. N. M. Markovic, H. A. Gasteiger, and P. N. Ross, J. Phys. Chem., 99, 3411 (1995). 85. J. S. Spendelow, P. K. Babu, and A. Wieckowski, Curr. Opin. Solid State Mater. Sci., 9, 37 (2005)
- 86. U. A. Paulus, Z. Veziridis, B. Schnyder, M. Kuhnke, G. G. Scherer, and A. Wokaun, J. Electroanal. Chem., 541, 77 (2003).