Platinum Nanorod Arrays with Preferred Morphological and Crystal Properties for Oxygen Reduction Reaction

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Vertically aligned platinum (Pt) nanorod arrays produced by glancing angle deposition technique (GLAD) have been investigated for their morphological, crystallographic, and electrochemical properties for oxygen reduction reaction (ORR) in hydrogen polymer electrolyte membrane (PEM) fuel cells. These single-layer and single-crystal catalyst nanorods without any carbon support have been produced at lengths varying between 20–600 nm, which correspond to Pt loadings of 0.016–0.48 mg/cm². GLAD nanorods have been grown on tilted azimuthally rotating substrates in a sputter deposition unit at an oblique angle of 85° as measured from the substrate normal. Electrodes of sputtered Pt thin films deposited at normal incidence and commercially available carbon supported Pt nanoparticles (Pt/C) were also prepared for comparison. The scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD) results reveal that Pt nanorods are well-isolated, vertically aligned, and single-crystal. The single-crystal property allows enhanced electrochemical activity and reduced surface oxidation, while the isolated nature of the rods in lateral directions can provide a channeled porosity for effective transportation of oxygen. Possible crystal orientations at the sidewalls as well as at the tip-facets of Pt nanorods have also been investigated. Cyclic voltammetry (CV) results show that well-defined multiple peaks exist in the CV profiles of Pt nanorods, which are absent or weak in conventional Pt/C and Pt film electrodes. These multiple CV peaks are due to the electrochemically more active crystal orientations in Pt nanorods compared to those of Pt/C and Pt thin film. In addition, Pt nanorod electrocatalysts exhibit a more positive reduction peak potential (less overpotential) and greater stability against electrochemically-active surface area loss compared to that of Pt/C due to their decreased oxophilicity, single-crystal property, and the dominance of the preferred crystal orientation for ORR.

Keywords:

1. INTRODUCTION

Fuel cell technology is one of the most promising alternative energy systems for an environmentally friendly, sustainable energy economy.1,2 Among the various types of fuel cells, polymer electrolyte membrane (PEM) fuel cells have attracted great interest as a primary source of electricity especially for electric vehicles, because they can operate with various types of energy carriers including hydrogen, ethanol, and methanol, run at relatively low temperatures (≈80°C), have high power density, and can vary their output quickly to meet changes in power demand.3-6 However, PEM fuel cells require an expensive platinum (Pt) catalyst, which raises the cost of the fuel cell. Current estimates of PEM fuel cell system costs, when extrapolated to mass production, exceed $70/kW. To compete economically with the internal combustion engine, however, the cost must approach $30/kW.7

The oxygen reduction reaction (ORR) at the cathode is a sluggish reaction, unlike the anodic hydrogen oxidation reaction (HOR), and typically the major contributor to the efficiency losses in an operating PEM fuel cell. Loadings may reach as high as 0.6 mg Pt/cm² at the cathode side to reduce these losses. State-of-the-art high surface area carbon supported Pt (Pt/C) catalyst suffer from low area and mass specific activities for practical fuel cell applications.8 In addition to the cost and low-efficiency issues, the carbon support causes additional challenges which can be summarized as follows: Oxidation of the carbon support causes the catalyst loss,9 carbon supports...
facilitate the formation of peroxide species that leads to degra-
dation of the membrane polymer,\textsuperscript{10} and carbon separates over
time from the ionomer, leading to loss of effectiveness.\textsuperscript{9} There-
fore, extensive effort is currently underway to develop a high-
performance, durable, carbon-free, and low cost (low Pt loading)
electrocatalyst materials. For example, in recent years, there have
been several efforts for fabricating non-precious catalysts,\textsuperscript{11} Pt-
based alloys,\textsuperscript{8} or de-alloying of Pt-M nanoparticles\textsuperscript{12-13} in order to
enhance the electrocatalytic activity (area and mass specific
activities) toward ORR.

Carbon-free unsupported Pt nanoparticles (Pt-black) can avoid
the problems associated with the carbon; however, the rest of the
issues listed above (especially the high loadings required for Pt-
black at about 2 mg/cm\textsuperscript{2}) remain unsolved. In recent years, a few
other carbon-free catalyst electrode approaches have also been
proposed, where Pt thin films of submicron thickness are directly
coated on the membrane, gas diffusion layer (GDL),\textsuperscript{14-19} colum-
nar titanium support\textsuperscript{20} or on an organic whisker support layer.\textsuperscript{21}
By this way, the carbon-related problems mentioned above can be
avoided and promising results have been demonstrated. How-
ever, the fuel cell performance (mW/cm\textsuperscript{2}) of such continuous Pt
film approaches\textsuperscript{14-19} generally falls behind that of conventional fuel cells with higher loadings (usually ≥ 0.4 mg/cm\textsuperscript{2}) due to the
cells the continuous non-porous and polycrystalline structure of the
Pt thin film. Recently, the work from 3 M\textsuperscript{21} has demonstrated
the improved durability and area-specific activity of the nano-
structured thin film (NSTF) whisker support material, which is a
monolayer of oriented crystalline whiskers of an organic pigment
material, in combination with the large-grained polycrystalline Pt
thin film catalysts that encapsulate or coat whiskers. However,
the 3 M catalyst\textsuperscript{21} suffers from a lower mass activity compared to
Pt/C as calculated from Mayrhofer et al.\textsuperscript{22} In addition, the poly-
crystalline nature of Pt thin has important disadvantages: first,
it is prone to oxidation due to polycrystalline structure; second
(Pt(111)) is the energetically favorable growth plane of Pt films,
which has a poorer electrochemical activity than that of Pt(110)
and Pt(100) planes due to the relatively strong adsorption of bi-
sulfate ions as confirmed in the previous studies.\textsuperscript{23,24} although
the type of electrolyte may change the activity sequence of Pt(111)
and Pt(100).\textsuperscript{25} In a recent study, Chen et al.\textsuperscript{26} reported that
enhanced ORR electrocatalytic activity of Pt nanotubes in 0.5 M
H\textsubscript{2}SO\textsubscript{4} might be attributed to preferential exposure of certain
crystal facets of nanotubes. Therefore, in addition to the recent
non-precious or Pt-alloy catalyst approaches mentioned above, as
an alternative method, controlling/engineering the morphologi-
cal properties (the electrode porosity), promoting a single-crystal
property, and most importantly the crystal orientation of ele-
mental Pt-based catalysts by promoting the crystal orientation of
Pt(110) and Pt(100) over Pt(111) can significantly enhance the
electrochemical activity of PEM fuel cell cathodes.

In this study, we investigate the fabrication of vertically
aligned Pt catalyst nanorod arrays utilizing a glancing angle
deposition (GLAD) technique and their crystal, morphological,
and electrochemical properties as a potential catalyst material for
ORR. Scanning electron microscopy (SEM), transmission elec-
tron microscopy (TEM), and X-ray diffraction (XRD) have been
utilized to study the morphology and crystallographic structure
of Pt nanorods. Using cyclic voltammetry (CV) measurements,
we have evaluated the electrochemical properties of a carbon-
free, single-layer Pt nanorod arrays as well as the comparison
conventional Pt/C and polycrystalline Pt thin film electrodes.

GLAD technique provides a novel capability for growing 3D
nanostructure arrays with unique material properties.\textsuperscript{27-30} It offers
a simple, single-step, cost and time efficient method to fabricate
nanostructured arrays of various materials in the periodic table
as well as alloys and oxides. GLAD method uses the “shadow-
ning effect,” which is a “physical self-assembly” process through
which obliquely incident atoms/molecules can only deposit to the
tops of higher surface points, such as to the tips of a nanostruc-
tured array or to the hill-tops of a rough or patterned substrate.
Recently, Gall et al.\textsuperscript{31} has compared the fuel cell performance of
conventional polycrystalline Pt thin films and Pt particles pro-
duced by GLAD and demonstrated that the particle-electrodes exhibit a higher mass-specific performance than continuous-layer
and conventional Teflon-bonded Pt-black (TBPBE) electrodes at
high current densities. The results of Gall et al. suggest that
GLAD technique provides the unique ability to control Pt poros-
ity that allows efficient reactant flow especially for high-current
density operations.

2. EXPERIMENTAL DETAILS

A schematic of the custom-made GLAD experimental setup
(Excel instruments, India) in the present study is shown in
Figure 1. We have employed a DC magnetron sputter GLAD
method\textsuperscript{27-30} for the fabrication of Pt nanorod arrays for dif-
gerent growth times of 3, 7, 30, 60 and 80 minutes, which cor-
respond to 20, 50, 200, 400 and 600 nm long Pt nanorods,
respectively. Nanorods were deposited on native oxide p-Si (100)
(resistivity 12–25 Ω-cm) substrates (2 × 2 cm\textsuperscript{2}), using a 99.999%
purity Pt cathode (diameter about 2.54 cm). The substrates were
mounted on the sample holder located at a distance of about
12 cm from the cathode. The base pressure of about 2.4 ×
10\textsuperscript{−6} Torr was achieved using a turbo-molecular pump backed
by a mechanical pump. In all deposition experiments, the power
was 150 Watts with an ultra pure Ar working gas pressure of
2.4 × 10\textsuperscript{−4} Torr. Pt nanorods were deposited at a glancing angle
of θ = 85° (with respect to substrate normal) on silicon wafer
substrates coated with a flat 50 nm thick Pt thin film on top and a
50 nm thick Cr layer between the Pt thin film and Si substrate.
Pt thin film served as a continuous electrical conducting layer, while
chromium acts as an adhesion layer to the silicon substrate in

Fig. 1. A schematic of the glancing angle deposition (GLAD) technique
used for the fabrication of Pt nanorod arrays.
order to avoid delamination during electrochemical tests. During GLAD, the substrates were also rotated azimuthally around the surface normal with a speed of 2 rpm. Conventional Pt thin film samples with a thickness of 400 nm was also deposited at normal incidence (θ = 0°) for comparison. The deposition rate of the glancing angle depositions of Pt nanorods (i.e., nanorod length per growth time) was about 7.5 nm/min as measured by the analysis of cross-sectional scanning electron microscopy (SEM) images.

We measured the weight loadings of Pt nanorods using our recently developed quartz crystal microbalance (QCM) setup (Inficon-Q-pod QCM monitor, crystal: 6 MHz gold coated standard quartz). For this purpose, we deposited GLAD Pt nanorods directly on QCM crystals and measured the loading values by comparing the oscillation frequencies of the blank and coated crystals. The surface morphology of Pt nanorods was investigated using SEM analysis (JEOL-JEM 6330F, JEOL Ltd, Tokyo, Japan). Crystalllographic structure of the nanorods were determined utilizing TEM analysis (JEOL, JEM 2100F, Ltd, Tokyo, Japan) and θ–2θ X-ray diffraction (XRD, Bruker D8 discover) systems. For TEM, Pt nanorods were removed from the Si substrate and then dispersed onto a holey carbon film on a Cu grid (from Pacific Grid-Tech). The microstructure of a single nanorod was studied using TEM operating at 200 kV. In addition, selective area electron diffraction (SAED) was employed to characterize the crystal structure of the nanorod.

The electrochemical tests (cyclic voltammetry) were performed at room temperature to characterize the catalyst activity of the Pt nanorods. CV measurements have also been performed on Pt thin film and Pt/C electrocatalysts for comparison. The test cell was a typical three-electrode system, consisting of a working electrode (Pt nanorods, Pt/C or Pt thin film), a Pt wire counter electrode, and a silver/silver chloride (Ag/AgCl) as the reference electrode. As described above, 400 nm Pt thin film, 20, 50, 200, 400 and 600 nm long GLAD Pt nanorods were deposited on flat Pt-film samples coated on Cr/Si wafers. The area of the working electrode was ~0.20–0.36 cm², and the area of the counter electrode was higher to allow for a more uniform current density distribution through the working electrode. The electrolyte was deaerated or oxygen-saturated 0.5 M H₂SO₄ solution (calculated pH ≈ 0). The potential during CV measurements was changed from ~300 to +1200 mV in 0.5 M H₂SO₄ at a scan rate of 50 mV/seconds.

Although some argue, 0.5 M H₂SO₄ solution is believed to be analogous to the acidic electrolyte in polymer electrolyte membrane fuel cells. In addition, we have chosen the sulfuric acid ionomer in the fuel cell electrode, it is therefore beneficial to decrease the ORR inhibiting effect of adsorbed sulfonate by maximizing the fraction of exposed crystal faces with weak sulfonate adsorption (e.g., (110) and Pt(100)). In another recent study, it was found that the magnification of CVs measured in perchloric, sulfuric, and phosphoric acids in the potential range 600–1000 mV (vs. RHE) reveals that the onset of oxide species formation shifts toward more positive potential by as much as 220 mV with the trend perchloric < sulfuric < phosphoric acids. Since the onset of oxides partially determines the stability of the catalyst under potential cycling, sulfuric acid appears to be a better candidate for carrying out simulated fuel cell durability tests. Therefore, the samples are scanned multiple times in 0.5 M H₂SO₄ at a potential range ~300 to 1200 mV and a scan rate 50 mV/s to establish the stability and reproducibility in the acidic environment.

Conventional carbon supported Pt nanoparticles electrode (Pt/C 20% wt Pt on carbon-black, Clean Fuel Cell Energy, LLC) was prepared as described by Schmidt et al. Briefly, aqueous suspension of 1 mgcat/ml was obtained by ultrasonic mixing for about 20 minutes. Glassy carbon disk electrode (5 mm diameter, ~0.2 cm² geometrical surface area; Pine Instrument Inc., NC) was polished and served as a substrate for the supported catalyst. A 20 μl aqueous Pt catalyst suspension was pipetted onto the glassy carbon substrate leading to Pt loading of ~20 μg/cm². After evaporation of the water at room temperature, 20 μl of a diluted Nafion™ solution (5% wt, Clean Fuel Cell Energy, LLC) was pipetted on the electrode surface in order to attach the catalyst particles onto the glassy carbon substrate. The Nafion loading was about 0.1 μm which is in the range where Nafion resulted diffusion limitations is considered to be negligible. After preparation, the electrodes were immersed in deaerated (Argon, Airgas) 0.5 H₂SO₄ under potential control of 500 mV. Then the potential was cycled between ~300 to 1200 mV in order to produce electrochemically clean electrode surface. For ORR experiments, the electrolyte was saturated with ultra high purity oxygen (Airgas).

3. RESULTS AND DISCUSSION

3.1. Surface Morphology and Pt Loading

Figure 2 shows the top view and side view SEM images of Pt nanorod arrays of different lengths. In these images, an isolated columnar morphology of Pt nanorods can be clearly seen (Figs. 2(b–f)) unlike the relatively smooth and continuous morphology of conventional Pt thin film (Fig. 2(a)) deposited at normal incidence. At initial times of GLAD growth, the number density of the rods are larger, and they have diameters as small as about 5–10 nm. As they get longer and some of the rods stop growing, their diameters grow up to about 200 nm. The average gap between the rods also changes with their length from 5–10 nm, initially, up to 50–100 nm at later stages. The average diameter and gap of the rods can be changed through the control of deposition parameters such as deposition angle, sputter power, substrate temperature, and surface roughness of the substrate. The isolated nature of the rods in lateral directions leads to a channeled porosity aligned in the vertical direction to the substrate surface. This novel geometry can greatly help the effective transport of hydrogen molecules to the catalyst sites in the anode and, more importantly, with proton and oxygen transport in the cathode layer. Moreover, high resolution top view SEM analysis of Pt nanorods shown in Figure 2 reveals that some of the rods in fact have 6-fold symmetric faceted tips, which indicates that an individual column has a single-crystal structure.

Figures 3(a–c) show the bright-field TEM image of an individual vertical Pt column, the corresponding diffraction pattern, and...
Fig. 2. Top and cross-section scanning electron microscopy (SEM) views of (a) 400 nm thick conventional flat Pt thin film grown by normal incidence sputter deposition and GLAD Pt nanorod arrays grown at lengths of (b) 20 nm (c) 50, (d) 200 (e) 400, (f) 600 nm.

Fig. 3. Bright-field transmission electron microscopy (TEM) image of an individual Pt nanorod (a), the corresponding selective area electron diffraction (SAED) pattern (b), and high resolution bright-field TEM image of a nanorod tip (c). The single set of diffraction spots in the SAED pattern in (b) and the high resolution TEM image (c) show that the individual Pt nanorods have a single crystal structure.

high resolution bright-field TEM image of a nanorod tip, respectively. The diffraction spots are perfectly matched by the theoretical diffraction pattern for a face centered cubic lattice, indicating that the individual Pt nanorod has a single-crystal structure and thus does not have any grain boundaries (A polycrystalline material would give a TEM diffraction pattern with rings of different crystal orientations). Grain boundaries in crystalline materials have been shown to be easy diffusion pathways for oxygen and therefore can act as initiation sites for both surface and bulk

oxide formation and oxidation-related degradation. It has been shown that Pt dissolution can significantly inhibit the ORR, and even lead to Pt dissolution leading to loss of electrochemically-active surface area. Single-crystal property of Pt nanorods also agrees well with previous studies which reported that an individual metallic nanorod fabricated by GLAD is typically single-crystal. Single-crystal rods do not have any interior grain boundaries and have faceted sharp tips. This property is expected to lead to enhanced electrochemical activity and reduced surface oxidation, which can greatly increase the robustness and resistance to oxidation-degradation of the electrode layer in the fuel cell environment.

QCM setup was used to measure the Pt loading of the prepared samples. We measured the weight loadings of 20, 50, 200, 400, and 600 Pt nanorods to be about 0.016, 0.04, 0.16, 0.32, and 0.48 mg/cm², respectively. The Pt loadings are very important for calculating the electrochemical active surface area (ECSA) as well as the porosity of the electrodes. The porosity of Pt nanorods of different lengths (20 to 600 nm) has been calculated from the relationship porosity = 1 – (nanorod-loading/dense-film-loading). Weight loadings of the corresponding dense Pt thin films were also measured utilizing QCM setup. It was found that the porosity of all Pt nanorod electrodes did not significantly change with the length of the nanorods and is close to about 54 ± 5%. It should be noted that the similar porosity value of Pt nanorod electrodes of different lengths does not mean that all the electrode have the same ECSA. In spite of the similar porosity values, due to the channeled morphology of the nanorods, interaction of the electrochemical solution with the nanorod electrode can strongly depend on the length of the nanorods, which will be discussed in more detail in the following section.

3.2. Crystal Orientation Analysis

XRD is a versatile technique for the study of orientation of crystal planes parallel to the substrate surface (i.e., texture) of thin films and nanostructured coatings. In addition to single-crystal property highlighted in the previous section, we observed that the crystal orientations of Pt nanorod arrays are significantly different than that of a polycrystalline continuous film which was deposited at normal incidence by otherwise using similar deposition conditions as the GLAD Pt nanorods. XRD results in Figure 4 reveal that Pt nanorods are mainly oriented in the [100] direction perpendicular to the substrate plane parallel to the nanorod axis utilizing cross-sectional SEM images to be ranging from 54° to 45°, indicating that the facets we are seeing on the tips are more likely to be oriented in [111], [110], and [011] directions (Fig. 5). Therefore, the facets of the tips of the nanorods are expected to have (111) and (110) type crystal planes as shown in Figure 5. For the facets observed at the tips of the nanorods (Fig. 2), the tilt angle α of the facets was measured from the line parallel to the nanorod axis utilizing cross-sectional SEM images to be ranging from 54° to 45°, indicating that the facets we are seeing on the tips are more likely to be oriented in [111], [110], and [011] directions. In a recent study, we have shown that GLAD Pt nanorods are highly hydrophilic and this implies that the electrochemical solution can significantly interact with the high-surface-area side walls of the nanorods. Therefore, also incorporating the facets at the tips of the nanorods shorter than 400 nm long, we believe that competition happening beyond 400 nm. This might be attributed to an increase in the number of the nanorods which are oriented in Pt(220) over those with dominant Pt(200). Nanorods, oriented in [220] direction, become larger in diameter and higher in length so that they start to shadow other nanorods which are oriented in [200], and eventually become the dominant orientation.

We have also theoretically investigated the possible crystal orientations of the side walls of Pt nanorods and facets of the tips of Pt nanorods by calculating the angles between different planes of Pt nanorods utilizing Crystal-Maker software (Crystal-Maker Software Ltd.). Pt has a face centered cubic (fcc) crystal structure, which makes several crystal planes identical due to the symmetry. For example, (100), (010) and (001) planes of Pt are all identical, and in the following sections we will call them (100) type planes. Similarly, (110), (101), and (011) planes of Pt have the same atomic configuration (we will call them (110) type planes).

For nanorods up to 400 nm long, which are single-crystal and oriented in [100] direction perpendicular to the substrate (Fig. 4), Pt(100) plane makes angles of 90°, 90°, 55°, 45°, 45°, and 90° with the crystal planes (001), (010), (111), (110), (101), and (011), respectively. This implies that the side walls are most likely oriented in (001) and (010) which are identical to [100] orientation. (011) plane, which is a (110) type plane, also makes 90° angle with (100). Hence, the side walls of Pt nanorods are expected to have (100) and (110) type crystal planes as shown in Figure 5. For the facets observed at the tips of the nanorods (Fig. 2), the tilt angle α of the facets was measured from the line parallel to the nanorod axis utilizing cross-sectional SEM images to be ranging from 54° to 45°, indicating that the facets we are seeing on the tips are more likely to be oriented in [111], [110], and [011] directions. Therefore, the facets of the tips of the nanorods are expected to have (111) and (110) type planes. In a recent study, we have shown that GLAD Pt nanorods are highly hydrophilic and this implies that the electrochemical solution can significantly interact with the high-surface-area side walls of the nanorods. Therefore, also incorporating the facets at the tips of the nanorods shorter than 400 nm long, we believe that...
saturated 0.5 M H₂SO₄ at a scan rate 50 mV/s. In deaerated
respectively) scanned between 20, 50, 200, 400 and 600 nm long Pt nanorods (Figs. 6(b–f), thic
Figure 6 shows the room temperature CV results of 400 nm
but electrochemically more active crystal orientations.
through their length or by introducing a surface roughness as in
ture of Pt nanorods can also be simply controlled by either
Therefore, other than deposition parameters listed above, tex-
oriented tip-facets and Pt(100) planes at the nanorod sidewalls.
comparation of results in Figure 6, it can be seen clearly that Pt nanorod
electrochemical activity of ORR compared to Pt[110] and Pt[100]
anorods is attributed to larger crystallite size, single-crystal
plane, and the dominance of the preferred crystal orientations for
3.3. Electrochemical Characterization
Figure 6 shows the room temperature CV results of 400 nm
thick flat Pt thin film and Pt/C electrodes (Fig. 6(a)) as well as
at a scan rate 50 mV/s. In deaerated
solution, during the anodic scan, hydrogen is desorbed between
−200 and +200 mV and surface platinum oxides are formed
above +800 mV. During the cathodic scan, the surface platinum
oxides are reduced between +800 and +400 mV and hydrogen
is adsorbed between +200 and −200 mV. It should be noted that
the CV responses for Pt nanorods in oxygen-saturated solu-
tion exhibit significantly higher current densities compared to
those in a deaerated solution at the same scan rate, indicat-
ing the catalytic activity of Pt nanorods toward ORR. Figure 6 shows
that there are no visible peaks for ORR indicating that
Pt thin film is relatively inactive. This may be attributed to the
dominant crystal orientation of Pt[111] which has a poor elec-
trochemical activity of ORR compared to Pt[110] and Pt[100]
orientations, and also higher surface oxidation rate of Pt
thin films. As we increased the length (Pt loading) of Pt nanorods
from 20 to 400 nm, the oxygen reduction peak started show-
ing up and became stronger for 400 nm Pt nanorods as shown
in Figures 6(b–f). The enhanced electrochemical activity of Pt
nanorods as they get longer is believed to be due to the larger
fraction of the exposed Pt[110] and Pt[111] crystal orientations
at large-surface area sidewalls, which were reported to have a
superior electrochemical activity for oxygen reduction reaction
compared to Pt[111] planes, and also due to the large crystal-
lite size of longer nanorods. 600 nm long Pt nanorods have
larger diameter tips compared to others (Fig. 2(f)), and therefore
the enhanced electrochemical activity (see Fig. 6(e)) for these
nanorods can be attributed to the presence of Pt(100) and Pt(110)
oriented tip-facets and Pt(100) planes at the nanorod sidewalls.
Therefore, our results demonstrate that GLAD technique is a
promising approach to control the crystal orientation, and pro-
mote the growth of catalyst surfaces with Pt(110) and Pt(100)
planes which are the most active surfaces for oxygen reduction reaction in PEM fuel cells.
We compared the CV profiles of our nanorod catalysts with
that of the conventional fuel cell electrocatalyst (Pt/C) as shown
in Figure 6. Carbon-supported Pt particles are mainly ori-
ented in the [111] direction and hence the hydrogen adsorp-
tion/desorption features between +200 and −200 mV are
different from the bulk polycrystalline Pt. From comparison
of results in Figure 6, it can be seen clearly that Pt nanorod
electrocatalysts can reduce oxygen to water at a more posi-
tive potential (0.56 V) than that of the Pt/C (0.48 V). Com-
pared to Pt/C, the enhanced ORR electrochemical activity of Pt
nanorods is attributed to larger crystal size, single-crystal
property, and the dominance of the preferred crystal orientations
for ORR.
The 600 nm Pt nanorods and conventional Pt/C samples are
scanned multiple times from −300 to 1200 mV potential range
in deaerated 0.5 M H₂SO₄ at a scan rate 50 mV/s to establish the
stability of the Pt-nanorods samples in the acidic environment.
Figure 7 shows a series of CVs from 600 nm Pt nanorods over
1500 cycles and a series of CVs from Pt/C over 1000 cycles at
room temperature. It can be clearly seen that the CV current of
Pt/C decreases considerably (Fig. 7(a)) which reflects the loss of
Pt surface area (~60% of surface area left after 1000 cycles),
while the 600 nm Pt nanorods shows insignificant change in the
CV current (see Fig. 7(b)) where ~90% of surface area left after
1500 cycles, indicating the stability of our catalyst in the acidic
environment. We should note that there is a shift in the final Pt/C
peak positions toward those of the Pt nanorods that might be
attributed to a decrease in Pt oxophilicity due to an increase in
Fig. 6. Room temperature cyclic voltammetry (CV) results in oxygen-saturated 0.5 M H₂SO₄ at a scan rate of 50 mV/s of (a) 400 nm thick polycrystalline Pt thin film and Pt/C, and single crystal GLAD Pt nanorod arrays of lengths (b) 20 nm, (c) 50 nm, (d) 200 nm, (e) 400 nm, and (f) 600 nm.

Pt/C platinum particles sizes with cycling, due to ripening process, as recently summarized by Shao-Horn et al. This behavior has been also observed by a recent study by Debe et al.

Finally, the CV was employed to calculate the electrochemical active surface area (ECSA) of different catalysts. The electrochemical active surface area was determined at room temperature (∼20 °C) from the integration of the hydrogen adsorption and desorption regions, which appear between −200 and +200 mV. Assuming 210 μm of Pt surface area for a full monolayer of adsorbed hydrogen (saturation coverage) and after double-layer and hydrogen evolution corrections, ECSA can be calculated from the equation:

\[
\text{ECSA} = \frac{\text{Charge (µC/cm}^2\text{)}}{210(µC/cm}^2\text{)}\frac{\text{Pt loading (g/cm}^2\text{)}}{\text{gPt/cm}^2}
\]

The results show that ECSA of 20, 50, 200, 400, and 600 Pt nanorods with Pt loadings in the range of 16–500 µg/cm² are 16, 14.8, 12.8, 8, and 6.5 m² Pt/g, respectively. The decreasing ECSA with increasing nanorod length may be attributed to increases in the nanorod diameter concurrent with increases in
length which decreases the surface area to volume ratio of the rods. Incomplete wetting of the nanorods with increasing nanorod length can also reduce the measured ECSA. ECSA value of the conventional Pt/C electrode has been calculated to be 65 m²/Pt/g Pt, which is in good agreement with the reported values in the literature and significantly higher than those of nanorods. Therefore, in order to get a fair and more in-depth comparison of Pt nanorods with high surface area Pt/C catalyst, rotating disk electrode (RDE) measurements at various temperatures (20–60 °C) are currently in progress in our laboratory. RDE measurements will allow us to calculate the most important kinetics parameters including electron-transfer constant rate, activation energy, Tafel slopes at low and high current densities, and other crucial kinetic parameters important to ORR activity for PEM fuel cell applications.

4. CONCLUSION

We have employed detailed SEM, XRD, TEM, and CV measurements to investigate the morphological, crystallographic, and electrochemical properties of Pt nanorod arrays produced by glancing angle deposition technique. SEM results reveal GLAD Pt nanorods are well-isolated and vertically aligned. TEM results indicate that individual Pt nanorods are single-crystal, which is a property that significantly enhances resistance to surface oxidation. Compared to the polycrystalline Pt thin film and the conventional Pt/C electrodes, the well-defined multiple peaks that exist in CV profiles of Pt nanorods are due to the electrochemically active preferential crystal plane orientations in Pt nanorods. Our detailed crystal structure analysis shows that Pt nanorods mainly have Pt(100) and Pt(110) type crystal planes at their large surface area sidewalls and tip facets, which has a superior electrochemical activity for oxygen reduction reaction compared to Pt(111) planes. In addition, CV profiles reveal that our catalyst is electrochemically more active than the conventional Pt/C electrocatalyst by reducing oxygen to water at more positive potential than that of Pt/C catalyst. The enhanced electrochemical activity of Pt nanorods as they get longer is believed to be due to the larger fraction of the exposed Pt(100) and Pt(110) crystal orientations at large surface area sidewalls and also due to larger crystallite size of longer nanorods. Moreover, series of CV cycles show that the surface of Pt nanorod arrays electrocatalyst was observed to be significantly more stable than the Pt/C electrocatalyst in the acidic environment. The single-crystal property of the individual Pt nanorods and their resistance to surface oxidation are believed to be the main reasons for their stable electrochemical activity. Glancing angle deposited Pt nanorods with preferential crystal orientations for enhanced electrochemical properties and stability can lead to engineering of new Pt-based alloys and non-precious catalyst materials with desired crystal and morphological properties for ORR in PEM fuel cell applications.

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References and Notes