Nanorod arrays of chromium (Cr) were grown on glassy carbon (GC) electrodes by a dc magnetron sputtering glancing angle deposition (GLAD) technique. The Cr nanorods were used as low-cost, high surface area, metallic supports for a conformal layer of Pt thin film catalyst, as a potential low-loading electrocatalyst for the oxygen reduction reaction (ORR) in polymer electrolyte membrane (PEM) fuel cells. A dc magnetron sputtering small angle deposition (SAD) technique was utilized for a conformal coating of Pt on Cr nanorods. The ORR activity of SAD-Pt/GLAD-Cr electrodes was investigated using cyclic voltammetry (CV) and rotating-disk electrode (RDE) techniques in a 0.1 M HClO₄ solution at room temperature. A reference sample consisting of GLAD Cr nanorods coated with a Pt thin film deposited at normal incidence (θ = 0°) was prepared and compared with the SAD-Pt/GLAD-Cr nanorods. Compared to GLAD Cr nanorods coated with Pt thin film at θ = 0°, the SAD-Pt/GLAD-Cr nanorod electrode exhibited higher ECSA and area-specific and mass-specific ORR activity. These results indicate that the growth of catalyst layer on the base-metal nanorods by the SAD technique provides a more conformal and possibly a nanostructured coating, significantly enhancing the catalyst utilization.

INTRODUCTION

The oxygen reduction reaction (ORR) at the cathode electrode of polymer electrolyte membrane (PEM) fuel cell is an important and well-studied electrochemical reaction because the slow kinetics of ORR causes it to be the dominant source of PEM voltage losses. 1 Typical cathode and anode electrocatalysts are platinum catalyst nanoparticles (3-5 nm in size) supported on carbon black. 2 In addition to the cost issue, this type of electrocatalyst faces other challenges related to the carbon support, summarized as follows: Oxidation of the carbon support causes catalyst loss, 3 the carbon support facilitates the formation of peroxide species that lead to degradation of the membrane polymer, 4 and carbon separates from the ionomer over time, leading to loss of catalyst utilization. 3 Therefore, extensive effort is currently underway to develop high-performance, durable, carbon-free, and low cost (low Pt loading) electrocatalyst materials. 1 For example, the 3M Company has demonstrated the improved durability and area-specific activity of nanostructured thin film Pt (NSTF Pt) electrocatalyst layers consisting of large-grained polycrystalline Pt thin film deposited on and encapsulating oriented crystalline whiskers of an organic pigment material. 5 A potential disadvantage of their support material, however, is the decomposition of the organic whiskers at elevated temperature (≥ 350 °C), which limits thermal treatment, such as catalyst annealing, to temperatures lower than 350 °C. 6 Bonakdarpour et al. 6 fabricated titanium (Ti) nanocolumns on glassy carbon (GC) disks using GLAD. The Ti nanocolumns were used as supports for Pt thin films deposited at a normal incidence angle (θ = 0°). While the reported ORR specific activity (500 μA/cm² at 0.9 V) of these catalysts is lower than that reported for the 3M electrocatalyst (NSTF Pt), this activity is higher than that of the conventional Pt/C electrocatalyst. Furthermore, Gasda et al. 7 deposited Pt thin films at normal incidence (θ = 0°) on chromium nitride (CrN) nanoparticles and electrochemically-etchable carbon nanorod array supports fabricated by the GLAD technique. 7-9 Compared to the 3M NSTF Pt, one of the potential drawbacks of the above approaches 5-9 is that Pt tends to accumulate mainly on
the tips of relatively dense nanoparticle/nanorod/nanocolumn supports, which results in lower catalyst utilization and dissolution of base metal, which in some cases can lead to complicated redox processes and deactivation of the electrode for ORR.

In this work, we investigate the use of a combination of GLAD and small angle deposition (SAD) techniques to fabricate chromium (Cr) nanorod array supports conformally coated with a thin layer of Pt. The GLAD method provides a novel capability for growing 3D nanostructure arrays with interesting material properties such as single crystallinity and the formation of uncommon crystal planes.\textsuperscript{10-13} During GLAD, a flux of atoms produced by physical vapor deposition (e.g., sputtering) is incident on a rotating substrate (around its substrate normal) tilted at oblique angles, generally higher than 70°. This technique uses the “shadowing effect” which is a “physical self-assembly” through which some of the obliquely incident atoms may not reach certain points on the substrate due to the concurrent growth of parallel structures.\textsuperscript{12,13} This leads to the formation of isolated nanostructures that can be in the shapes of rods, springs, zigzags, or spheres.\textsuperscript{13} The conformal coating of base-metal GLAD nanorods with a thin layer of Pt is achieved using the SAD technique, developed by Karabacak et al.,\textsuperscript{14,15} by controlling the substrate tilt angle. The main difference between SAD and GLAD techniques is that in SAD the incidence angle of the deposition flux is typically less than 45° and is adjusted based on the substrate surface pattern. In the SAD technique, the sidewalls and bottom portions of the support nanorods are effectively exposed to the deposition flux through the use of a small tilt angle and rotation of the substrate. This can lead to conformal coatings of very thin layers of catalyst on the support nanorods.\textsuperscript{14}

In addition, since SAD uses a small substrate tilt angle, the incident flux of atoms will deposit on the sidewalls of the nanorods at high oblique angles as measured from the sidewall surface normal. For example, a nanostructured coating at the sidewalls can be achieved using a small substrate tilt angle, less than 30°, where the local incident angle on the sidewalls becomes larger than 70°, promoting the shadowing effect and formation of a nanostructured film. However, when the substrate tilt angle is too small and the deposition angle is close to normal incidence ($\theta \sim 0^\circ$), most of the deposition occurs close to the tips of the nanorods, quickly clogging the gaps, which then leads to the formation of a continuous capping layer with poor coating of the sidewalls and bottoms of the nanorods.\textsuperscript{16} Moreover, also due to the shadowing effect at the sidewalls during SAD, the film can have unusual crystallographic orientations. The crystal orientation can be controlled through the deposition parameters, such as tilt angle, substrate temperature, deposition rate, length and separation of nanorods, electrical biasing of the substrate, working gas pressure, and substrate rotation speed.

**EXPERIMENTAL WORK**

A DC magnetron GLAD sputtering system (Excel instruments, India) was employed for the fabrication of Cr nanorod arrays for a growth time of 15 minutes, which resulted in about 100 nm long Cr nanorods. The depositions were performed on glassy carbon disk inserts (5 mm OD x 4 mm thick, Pine Instrument) and silicon wafers using a 99.99 % pure Cr cathode (diameter ~ 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 7.5 x $10^{-7}$ Torr was achieved using a turbo-molecular pump backed by a mechanical pump. The substrates were tilted so that the angle between the surface normal of the target and the surface normal of the substrate was 87°. The substrate was attached to a stepper motor and rotated at a speed of 2 rpm for growing vertical nanorods. During Cr deposition experiments, the power was 200 W with an ultra high purity Ar (99.99%) atmosphere at a pressure of $2.4 \times 10^{3}$ Torr. The deposition rate of GLAD Cr nanorods (i.e., nanorod length per growth time) was approximately 8.2 nm/min as measured by the analysis of cross-sectional SEM images.
After the deposition of the GLAD Cr nanorods, the substrates were tilted towards the Pt sputter source for coating with a Pt film by the SAD technique. Pt was deposited on the Cr nanorods for 60 seconds by utilizing dc sputter deposition from a 99.99% pure Pt cathode (diameter ∼2.54 cm) at a deposition angle of \( \theta = 30^\circ \). For comparison purposes, Pt was also deposited on GLAD Cr nanorods at normal incidence (\( \theta = 0^\circ \)) for 50 seconds. It should be noted that different deposition times were used to obtain similar Pt loadings on all the samples for comparison of their ORR activities. The substrates (arrays of Cr nanorods on GC and silicon wafer) were rotated around the substrate normal axis with a speed of 2 rpm. The deposition was performed under a base pressure of approximately \( 4 \times 10^{-7} \) Torr. During Pt deposition experiments, the sputter power was 150 Watts with an Ar pressure of \( 3.2 \times 10^{-3} \) Torr. The Pt loadings of the prepared samples were measured by quartz crystal microbalance (QCM, Inficon Q-pod QCM monitor, crystal: 6 MHz gold coated standard quartz). For the QCM measurements, Pt coatings were deposited directly on quartz crystals and the loading values were determined by comparing the oscillation frequencies of the blank and the coated crystal.

The electrochemical tests (CV and RDE) were performed in deaerated and oxygen-saturated 0.1 M HClO\(_4\) at room temperature for characterizing the ORR activity of the Pt/Cr nanorods electrocatalysts. The test setup was a typical three-electrode system (Pine Instrument bipotentiostat, North Carolina, USA), consisting of a working electrode (Pt/Cr nanorods on glassy carbon of 0.196 cm\(^2\) area), a Pt wire counter electrode, and a Ag/AgCl reference electrode. The area of the working electrode samples was 0.196 cm\(^2\), while the area of the counter electrode was higher to allow for a more uniform current density distribution through the working electrode. For CV measurements, the working electrodes were scanned from 0.05 to 1.20 V in O\(_2\)-free 0.1 M HClO\(_4\) at a scan rate 50 mV/s. For chemical stability in the acidic environment, the electrodes were also scanned multiple times in the 0.6 to 1.2 V range at 50 mV/s. For the evaluation of ORR kinetics, RDE measurements were recorded between 0.05 and 1.05 V at a scan rate of 20 mV/s in O\(_2\)-saturated 0.1 M HClO\(_4\) at room temperature and a rotation speed of 1600 rpm. To eliminate the effect of pseudo-capacitive currents on the calculated ORR activities, the background currents obtained using O\(_2\)-free 0.1 M HClO\(_4\) were subtracted from the currents obtained in O\(_2\)-saturated electrolyte.

**RESULTS AND DISCUSSION**

Figure 1 shows the cross-sectional SEM images of the isolated vertical GLAD Cr nanorods before and after Pt deposition. Analysis of cross-sectional SEM images (Fig. 1a) showed the average length of Cr nanorods to be approximately 100 nm. A Pt thin film was deposited on GLAD Cr nanorods at \( \theta = 0^\circ \) (normal incidence) and \( 30^\circ \) (SAD deposition) as shown in Figs. 1b and c, respectively. The above samples will be referred to as Pt(0\(^\circ\))/Cr, Pt(30\(^\circ\))/Cr nanorods, respectively, in the remainder of the paper. Careful examination of Fig. 1b reveals that the Pt deposited at normal incidence is concentrated at the tips of the Cr nanorods, while a more uniform and conformal coating of Pt on the Cr nanorods was observed for the SAD-deposited Pt film, as shown in Fig. 1c. These observations were further confirmed by the EDX line mapping results, shown in Fig. 2, that were measured along the axis of the nanorods starting from their tips (i.e. tip being at the 0 nm position of Fig. 1). The Pt coverage percentage was estimated by the ratio of the coated portion, where the intensity of Pt is higher than that of Cr in Fig. 2, to the total length of nanorods. Figure 2a reveals that the Pt film deposited at normal incidence mainly accumulates at the tips of Cr nanorods with smaller amount deposited at the bottom. The estimated coverage of normal incidence deposited Pt on Cr nanorods is calculated to be ~30-40%. On the other hand, the coverage of SAD Pt is estimated to be about 75-80%. These results indicate that the SAD technique results in a more conformal thin film compared to normal incidence deposition.
Based on previously reported BET measurements on GLAD carbon nanorods, $^{17}$ Pt nanorods of 500 nm length are expected to have an effective surface area enhancement factor (SAEF, ratio of real surface area to substrate geometric area) of about 40. This can be used for estimating the SAEF for GLAD Cr nanorods coated SAD Pt thin films with the assumption that the total surface area of Cr/Pt nanorods is linearly dependent on their length. Based on that, the approximate SAEF of Pt/Cr nanorods was calculated to be $\sim 8$ ($=40 \times (100/500)$). Based on the estimated SAEF of Pt(30°)/Cr nanorods, the thickness of the Pt thin film on GLAD Cr nanorods is estimated to be approximately 3 to 5 nm, based on the calculated SAEF of Pt(30°)/Cr divided by the thickness of the thin film on a planar substrate.

Figure 3a compares the room temperature steady-state CV profiles of bare GLAD Cr nanorods and Cr nanorods coated with Pt thin film deposited at $\theta = 0^\circ$ and $30^\circ$ with the same Pt loading of 0.04 mg/cm². The cyclic voltammogram of Cr nanorods shown in Fig. 3a agrees with those presented in the literature for Cr in acidic electrolyte. $^{18-21}$ The Pt thin films on Cr nanorods exhibit a shift in the onset potential for oxide formation compared to Pt alone (≥ 0.86 V vs. ~0.8 V for Pt alone, $^{11}$), indicating an electronic interaction between the Pt and the Cr. The Pt(30°)/Cr electrode has an oxide reduction peak potential of 0.78 V, which is 50 mV more positive than the oxide reduction peak observed for Pt(0°)/Cr electrode, as shown in Fig. 3a. This can be attributed to a stronger electronic interaction between the thin, conformal Pt film with the Cr nanorods for the SAD thin film as compared to the thicker and less conformal films formed at 0°, $^{22}$ The greater conformality of the SAD film is also evidenced by the large CV peak intensities (i.e., a larger surface area is being exposed to the electrolyte).
and relatively well-defined hydrogen adsorption/desorption peaks (enhanced electrochemical activity with different crystal planes). This strong interaction between the Pt and Cr may result in significant changes in the electronic states of surface Pt atoms inhibiting/reducing the formation of OH species which are considered poisoning species for ORR. 23-26

![Graph](image)

**Figure 3:** (a) Room temperature CVs in O2-free 0.1 M HClO4 at a scan rate 50 mV/s for GLAD Cr nanorods coated with a thin film of Pt deposited at θ = 0° and 30° (SAD Pt) all with a Pt loading of 0.04 mg/cm2. The solid black line shows the CV profile of GLAD Cr nanorods without the Pt coating and (b) Room temperature RDE profiles in oxygen-saturated 0.1 M HClO4 at a scan rate 20 mV/s and rotation speed 1600 rpm for GLAD Cr nanorods coated with a thin film of Pt deposited at θ = 0° and 30° (SAD Pt).

The ECSA of the prepared electrodes was determined by integrating the charge in the hydrogen adsorption region derived from CV profiles between the double layer region and the onset of hydrogen evolution, after subtracting the double layer charge. The Pt(30°)/Cr electrode exhibits an ECSA of 16 m2/gPt compared to 12.2 m2/gPt for the films deposited at 0°. The larger ECSA for the SAD film as compared to the films deposited at 0° further supports the SEM and EDX results discussed above. The RDE results in Fig. 3b show that the Pt(30°)/Cr nanorods exhibit an \( E_{1/2} \) of ~0.9 V, while the GLAD Cr nanorods coated with Pt thin films at θ = 0° has an \( E_{1/2} \) of ~0.86 V. The ORR kinetic currents (\( I_k \)) at 0.9 V were extracted from these RDE data using the well-known mass-transport correction for RDE measurements. 2 It should be noted that the assumptions implicit in this equation valid over the current range of 0.1 \( I_{lim} < I < 0.8 \) \( I_{lim} \) and thus this equation is valid for calculating \( I_k \) at 0.9V. 25 The area- (SA) and mass- (MA) specific activities are derived by normalizing the kinetic currents by the ECSA and the Pt loading of the catalyst applied to the electrode, respectively. At 0.9 V, the SA of GLAD Cr nanorods coated with the SAD Pt thin film deposited at \( \theta = 30° \) is approximately 885 µA/cm², which is about 68% higher than that the GLAD Cr nanorods coated with the Pt thin film deposited at 0° with SA of 525 µA/cm², as shown in Table I. It can be seen from Table I that the GLAD Cr nanorods coated with the SAD Pt thin film have ORR mass activities normalized to Pt loading of ~0.150 A/mg, which is higher than the ~0.064 A/mg observed for Pt(0°)/Cr. The improved activity might be attributed to a better Pt conformality, especially at the sidewalls of the nanorods, and a preferential exposure of certain crystal facets.
Table I: Summary of the evaluated electrocatalytic activity (area-specific and mass-specific activities at 0.90 V) of Cr nanorods coated with SAD ($\theta = 30^\circ$) Pt thin film catalyst in 0.1 M HClO$_4$ and comparison to the literature values for various Pt-based catalysts.

<table>
<thead>
<tr>
<th>Method</th>
<th>Sample</th>
<th>Pt loading (mg/cm$^2$)</th>
<th>ECSA (m$^2$/g)</th>
<th>T ($^\circ$C)</th>
<th>Scan rate (mV/s)</th>
<th>$I_\text{s}$ (μA/cm$^2$)</th>
<th>$I_\text{m}$ (A/mg)</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>RDE</td>
<td>Pt(0$^\circ$)/Cr nanorods</td>
<td>0.040</td>
<td>12.2</td>
<td>20</td>
<td>20</td>
<td>525</td>
<td>0.064</td>
<td>This work</td>
</tr>
<tr>
<td>RDE</td>
<td>Pt(0$^\circ$)/Ti nanorods</td>
<td>50 nm thick Pt film</td>
<td>SEF* $\sim$ 11</td>
<td>21</td>
<td>5</td>
<td>500</td>
<td>-</td>
<td>[6]</td>
</tr>
<tr>
<td>RDE</td>
<td>SAD Pt(30$^\circ$)/Cr nanorods</td>
<td>0.040</td>
<td>16</td>
<td>20</td>
<td>20</td>
<td>885</td>
<td>0.150</td>
<td>This work</td>
</tr>
<tr>
<td>RDE</td>
<td>200 nm long Pt nanorods</td>
<td>0.160</td>
<td>12</td>
<td>20</td>
<td>10</td>
<td>1,080</td>
<td>0.130</td>
<td>[11]</td>
</tr>
<tr>
<td>TF-RDE</td>
<td>20% Pt/C</td>
<td>0.020</td>
<td>60</td>
<td>20</td>
<td>20</td>
<td>288</td>
<td>0.180</td>
<td>[11]</td>
</tr>
<tr>
<td>TF-RDE</td>
<td>NSTF Pt</td>
<td>0.042</td>
<td>8</td>
<td>20</td>
<td>20</td>
<td>750</td>
<td>0.060</td>
<td>[25]</td>
</tr>
</tbody>
</table>

SEF: Surface Enhancement Factor

The ORR specific activity of Pt(30$^\circ$)/Cr is compared with the literature values for conventional Pt/C, solid GLAD Pt nanorods, and nanostructured thin film Pt (3M NSTF Pt) electrocatalysts (Table I). It was found that the Pt(30$^\circ$)/Cr nanorod array electrode exhibits higher $SA$ than conventional Pt/C and 3M Pt NSTF electrocatalysts. This enhancement might be attributed to (1) the dominance of the preferred crystal orientation of the SAD Pt coating at the nanorod sidewalls for ORR and (2) the change in the electronic states of surface Pt atoms induced by the electronic interaction between Pt and Cr nanorods which reduces/inhibits the formation of OH species which are considered poisoning species for ORR.

In addition to the above possible advantages, the higher $SA$ of Pt(30$^\circ$)/Cr electrode compared to Pt/C and 3M Pt NSTF catalysts might be arising from its larger crystallite size, in the range of 5-100 nm (i.e., film thickness–planar size along the Cr nanorod length), which results in average coordination numbers of surface Pt and corresponding surface electronic properties approaching those of polycrystalline Pt. Furthermore, the mass-activity ($MA$) of Pt(30$^\circ$)/Cr nanorod array electrode is higher than that of the 3M Pt NSTF, based on the reported area-specific activity at 0.9 V and ECSA of 8 m$^2$/g, but it is still lower than the reported values in the literature for Pt/C electrocatalyst. Compared to the solid GLAD Pt nanorods with $MA$ of 0.13 A/mg, a significant enhancement in $MA$ value for the Pt(30$^\circ$)/Cr electrode is expected since a small amount of Pt was used to coat the base nanorod support (GLAD Cr nanorods). The small $MA$ enhancement of 0.02 A/mg is attributed to the incomplete coating of GLAD Cr nanorods by SAD Pt thin film, especially at the bottom of the nanorods as shown by EDX analysis above, and to the excessive thickness of the Pt film. In addition, there is a possibility that the crystallographic structure of the sidewalls of Pt(30$^\circ$)/Cr nanorods is different than that of solid GLAD Pt nanorods where the ORR activity is dominated by Pt(110), which is the most active surface for ORR. We believe that the $MA$ parameter can be further improved by increasing the separation of Cr nanorods so that the SAD approach can be more effective in reaching the bottom of the nanorods, resulting in a more conformal coating of Pt thin film on the nanorods and a better Pt utilization. This approach may also enhance the electrode porosity resulting in better oxygen transport within the catalyst layer.
CONCLUSION
SAD-Pt/GLAD-Cr nanorods exhibit higher electrochemically-active surface area (ECSA) and area- and mass-specific ORR activities as compared to GLAD Cr nanorods coated with a Pt thin film deposited at normal incidence (θ = 0°). The improved ORR activity and enhanced catalyst utilization of SAD-Pt/GLAD-Cr electrode might be attributed to a better Pt conformality, especially at the sidewalls of the nanorods, and a preferential exposure of certain crystal facets.

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