Periodic Pt Nanorod Arrays with Controlled Porosity for Oxygen Reduction Reaction

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Nanorod arrays of platinum were fabricated on flat (Sample A) and patterned glassy carbon electrodes at room temperature using glancing angle deposition (GLAD) technique. Pt nanorod arrays were tested by cyclic voltammetry (CV) and rotating-disk electrode (RDE) techniques as a potential polymer electrolyte membrane fuel cell cathode electrode for oxygen reduction reaction (ORR). Patterned substrates with honeycomb geometry were obtained utilizing modified-nanosphere lithography method using polystyrene (PS) nanoparticles of diameters 250 (Sample B) and 500 (Sample C) nm. The RDE results demonstrate that samples B and C have higher diffusion limiting current density values of 5.8 and 6 mA/cm² at potential range of 0.2–0.7 V compared to 5.6 mA/cm² for sample A. ORR polarization curves show that the specific-area activity (SA), normalized to the Pt ECSA, of sample A at 0.9 V is about 1,060 μA/cm² that is about 18.7% higher than for the nanorods of sample B and C with SA of 893 μA/cm². However, samples B and C exhibit significantly higher specific-area activities at lower potentials, for example at 0.75 V, SA = 41,773 and 95,870 μA/cm², respectively, which are 2.8 and 6.5 times higher than 14,693 μA/cm² of sample A. The higher ORR activity at low potential region in the polarization curve of periodic and well-separated GLAD Pt nanorods is attributed to the enhanced electrode porosity which facilitates the oxygen mass transport to the active catalytic sites.

Keywords: Periodic GLAD Pt Nanorods, Sputtering, ORR Electro catalysts, PEM Fuel Cell Electro catalysts, Modified Nanosphere Lithography Technique.

1. INTRODUCTION

Polymer electrolyte membrane (PEM) fuel cells are electrochemical energy conversion devices which have demonstrated great promise as future energy sources for electric vehicles, as they convert chemical energy to electrical energy with a significantly higher efficiency and lower environmental impact than in standard combustion processes.1,2 Compared to anodic hydrogen oxidation reaction (HOR), the oxygen reduction reaction (ORR) in acid electrolytes is a slow four-electron transfer reaction resulting in high overpotential losses at the cathode side under typical PEM fuel cell operating conditions.3,4 Controlling the electrode porosity is one of the most critical needs to minimize the resistance to oxygen mass transport within the cathode electrode at high current density region in the polarization curve of an operating PEM fuel cell, resulting in high power densities with high efficiency.1 The enhanced Pt utilization with low oxygen mass transport resistance was observed on sputter-deposited cathode electrodes due to their thin catalytic layer.5–7 Bonakdarpour et al.8 fabricated titanium (Ti) nanorods directly on glassy carbon (GC) disks by glancing angle deposition (GLAD) technique. They used GLAD Ti nanorods as supports for conventional normal angle deposited (θ = 0°) Pt thin film electrocatalyst, which showed enhanced ORR activity compared to planar Pt thin films without nanorod support. Recently, Gasda et al.9 compared the fuel cell performance of conventional polycrystalline Pt thin films and Pt particles produced by GLAD technique and demonstrated that the particle-electrodes exhibit a higher mass activity than continuous-layer film and conventional Teflon-bonded Pt-black (TBPB) electrodes at high current densities. The results of Gasda et al.9 suggest that the GLAD technique combines the advantages of thin film electrodes with the ability to fabricate porous electrodes allowing efficient reactant flow especially for high-current density operations. This work has been extended to develop new electrodes based on normal angle deposited Pt on GLAD CrN nanoparticles10 and electrochemically etched carbon nanorods11,12 supports also fabricated by...
GLAD technique. However, these electrodes listed above typically suffer from poor porosity which might have a negative effect on oxygen mass transport in an operating PEM fuel cell. In addition, another potential drawback of the ones that included normal angle deposited Pt film on GLAD nanostructures is that Pt tends to accumulate mainly on the tips of relatively dense nanorod/nanoparticle layer, which results in lower catalyst utilization.

More recently, we have studied the electrocatalytic ORR activity of vertically-aligned GLAD Pt nanorods utilizing cyclic voltammetry (CV) and rotating-disk electrode (RDE) techniques in a 0.1 M HClO4 solution at temperatures ranging from 20 to 60 °C. It was found that the GLAD Pt nanorods exhibit higher area-specific activity, higher reaction rate constant, comparable activation energy, and greater stability against electrochemically-active surface area loss compared to conventional Pt/C electrode. The enhanced ORR activity of Pt nanorods was attributed to their larger crystallite size, single-crystal property, and the dominance of Pt(110) crystal planes on the nanorod sidewalls, which was reported to be the most active plane for ORR. However, there is still an urgent need to enhance and control the electrode porosity in order to improve oxygen transport and further enhance the ORR electrocatalytic activity of nanostructured GLAD fuel cell electrodes especially at the low potential region of a polarization curve. This can be achieved by utilizing substrate surface patterning approaches, which can lead to the formation of periodic and well isolated GLAD nanostructures.

The GLAD technique provides a novel capability for growing room-temperature nanostructured arrays with interesting material properties. It offers a simple, single-step, low-temperature, cost- and time-efficient method to fabricate nanostructured arrays of various elemental materials as well as alloys and oxides. The GLAD technique uses the "shadowing effect," which is a "physical self-assembly" process through which obliquely incident atoms/molecules can only deposit on the tops of higher surface points, such as to the tips of a nanostructured array or on the highest points of a rough or patterned substrate. Porosity of the nanorod arrays is basically a function of the average diameter and separation of nanorods. Due to their vertically aligned shapes, the porosity will not strongly depend on the length of the rods. Diameter, separation and, therefore, porosity of the nanorods can be controlled through a number of parameters such as deposition angle, substrate rotation speed, and control of the substrate surface roughness (e.g., the gas diffusion layer (GDL) or membrane layer). In addition, surface patterning on substrates has also been shown to provide additional control over nanorods diameter, separation, and shape, which will in turn provide insight on which roughness values of GDL and PEM substrates would result in nanorod coatings with the best electrochemical properties. Such and similar surface engineering approaches may open the way up for utilizing GLAD nanorods as model electrodes with controlled porosity to evaluate the relationship between the oxygen mass transport limitations and electrode porosity.

Nanosphere lithography technique (NSL) has been successfully applied to pattern the substrates which can be used to fabricate nano-patterned metallic surfaces. These surfaces have received increasing attention in nanotechnology due to their potential applications such as in catalysis. NSL is a low cost and simple technique for growing two-dimensional (2D) periodic nano-particles arrays. It is based on self-assembly of polystyrene (PS) or silica nanospheres onto a substrate to form a closely packed monolayer or bilayer, which is employed as a deposition mask. In addition to the above advantages of low cost and simplicity, NSL offers precise control over surface pattern at the nanometer scale simply by using spheres of different diameters. To ensure a uniform periodicity and well controlled separation of GLAD nanorods, NSL can be utilized to fabricate patterned substrates on which periodic and well separated GLAD nanorods can be grown. For commercial applications, once the optimum gaps are obtained by NSL, for desired PEM fuel cell activity of GLAD nanorods, the polymeric membrane or GDL layer can be roughened or patterned by high-throughput, large-scale surface patterning techniques such as plasma etching or nano-imprinting to mimic the isolated-seed morphology formed by NSL.

The aim of this study is to investigate the electrochemical activity and kinetics toward ORR of periodic and well separated Pt nanorods produced by GLAD technique on patterned glassy carbon (GC) electrodes fabricated by modified nanosphere lithography (m-NSL) technique, in an acidic electrolyte utilizing Cyclic Voltammetry (CV) and rotating-disk electrode (RDE) techniques. GLAD Pt nanorods grown on flat GC substrates were also prepared for comparison. Scanning electron microscopy (SEM) has been utilized to study the morphology of the Pt nanorods. CV and RDE experiments were performed at room temperature to characterize the ORR activity of the Pt nanorods deposited on both flat and patterned substrates for comparison.

2. EXPERIMENTAL WORK

Prior to Pt deposition by GLAD, silicon and glassy carbon substrates were patterned using m-NSL technique as shown in Figure 1. Our modified NSL method involves three principal steps. First, colloidal spheres are formed on a substrate via a self-assembly process to form a monolayer. Second, the voids among the spheres are filled with the seed material of choice (i.e., Ag) using normal angle deposition. Finally, the spheres are removed to leave behind a nanostructured pattern, such as dots on the substrate. The polystyrene (PS) spheres in our investigation were purchased from Bang Laboratories, Inc. as 10%...
spheres at normal angle of \( \theta = 0^\circ \) in a vacuum deposition chamber (Fig. 1(c)) with a base pressure of \( 10^{-7} \) Torr, which was achieved using a turbo-molecular pump backed by a mechanical pump. The operating pressure was \( 6 \times 10^{-5} \) Torr. The substrates were also rotated azimuthally around the surface normal with a speed of 2 rpm. Thickness and deposition rate of the deposited film were measured utilizing a quartz-crystal microbalance attachment (QCM, Inficon-Qpod QCM monitor, crystal: 6 MHz gold coated standard quartz). After deposition of Ag in the voids among the spheres, the PS nanospheres were removed from the substrate by dissolving them in toluene with the aid of sonication for 5 minutes. Finally, the samples were rinsed with Milli-Q water to remove/sift off the PS nanospheres completely from the substrate, leaving behind a honeycomb pattern of Ag seeds, as depicted in Figure 1(d).

We have employed a DC magnetron sputter technique (Excel Instrument, India) to fabricate vertically-aligned Pt nanorods on the flat and patterned GC substrates. Because of the shadowing effect during GLAD, nanorods will nucleate on the nanoparticle “seeds” formed by the NSL process providing a uniform and well-separated structure. A growth time of 30 minutes resulted in 200 and 175 nm long nanorods on flat and patterned substrates, respectively. Sample A refers to GLAD Pt nanorods on flat substrate, while GLAD Pt nanorods grown on patterned substrate utilizing m-NSL with 250 and 500 nm in diameter PS nanoparticles are named as sample B and C, respectively, in the remainder of the paper. The schematic of the GLAD experimental setup is shown in Figure 2. Pt nanorods were deposited at a glancing angle of \( \theta = 85^\circ \) (with respect to substrate normal) on silicon wafers and glassy carbon disk inserts (5 mm OD x 4 mm thick, Pine Instrument), using a 99.99 % pure Pt cathode (diameter about 2.54 cm). The substrates located at a distance of about 12 cm from the cathode, was mounted on a sample holder which was attached to a stepper motor and rotated at a speed of 2 rpm around the substrate normal axis. The depositions were performed under a base pressure of \( 2.4 \times 10^{-5} \) Torr that was achieved using a turbo-molecular pump backed by a mechanical pump. During Pt deposition, the sputter power was 150 W with an ultrapure Ar working gas pressure of 2.4 mTorr. The Pt nanorod deposition rate (i.e., nanorod length per growth time) was approximately 7.5 nm/min as measured by the analysis of cross-sectional SEM images. For weight measurements, Pt nanorods were deposited directly on quartz crystals and loading values were determined by comparing the oscillation frequencies of the blank and the coated crystal. The weight loading of GLAD Pt nanorod deposited on flat and patterned substrates was approximately 0.16 mg/Pt/cm². The surface morphology of Pt nanorods was investigated using SEM analysis (FESEM-6330F, JEOL Ltd, Tokyo, Japan). For SEM analysis, Pt

by weight in solution (i.e., as a suspension in water) with 250 and 500 nm in diameter. For substrate preparation, the silicon and GC substrates were sonicated in acetone for 10 minutes, then thoroughly cleaned with standard RCA I process, that is, a treatment with 1:1:5 solution of \( \text{NH}_3 \cdot \text{OH} (25\%) : \text{H}_2 \text{O}_2 (30\%) : \text{H}_2 \text{O} \) at 80 °C for 10 minutes. This treatment creates flat and hydrophilic substrates. Then the substrates were rinsed with DI-water. For mask preparation, a petri dish was filled with Milli-Q water and a cleaned glass slide was partially immersed into the water at an angle of 30°. Then the 1:1 with ethanol diluted PS particle suspension was transferred onto the water surface by dropping it onto the glass slide. When the particle suspension on the glass slide flowed down and reached the water surface, unordered monolayer formed at the water-air interface. By adding a drop of a surfactant, e.g., 2% sodiumdodecylsulfate (SDS), a hexagonal close packed (hcp) arrangement of the spheres was achieved. Finally the masks were transferred to the prepared substrates which were attached to a motorized stage (Pacific Laser Equipment, Santa Ana, CA) used to pull the substrate out of the petri dish at a very low speed as shown in Figures 1(a) and (b).

The seed material in our study was silver (Ag) and was deposited by thermal evaporation in the voids among the
nanorods were deposited on Si(100) wafer pieces which were mounted on the substrate holder in the same Pt deposition experiments on the glassy carbon samples.

Electrochemical measurements (CV and RDE) were performed at room temperature to characterize the ORR activity and kinetics of the periodic Pt nanorods catalyst using a three-electrode cell and a potentiostat (Pine Instrument, CH Instruments bipotentiostat). The measurement setup was a typical three-electrode system, consisting of a working electrode (Pt nanorods on glassy carbon), a Pt wire counter electrode located in a separate fitted compartment, and a silver/silver chloride (Ag/AgCl) reference electrode. The measured potential of this reference electrode is converted to reversible hydrogen electrode (RHE) scale in the remainder of the paper. The electrolyte was deaerated or O2-saturated 0.1 M HClO4 (GFS Chemical, Inc., veritas double-distilled in >18 MΩ-cm−1 Millipore water). Both the argon (Ar, for deaeration) and O2 gases used were ultrahigh purity (99.999% Ar, 99.99% O2, Air Gas). An interchangeable, removable glassy carbon disk (5 mm OD × 4 mm thick) of a ring-disk electrode (RDE, 6.5 mm ID, 7.5 mm OD) from Pine Instruments was used as a substrate for preparing the Pt nanorod electrodes. This interchangeable electrode allowed us to use the same ring assembly with different disk inserts. The geometric area of the glassy carbon disk working electrode was ~0.196 cm². After scaling in the ring-disk housing and immersion in the electrolyte, the glassy carbon/Pt nanorods working electrodes were scanned from 0.05 to 1.4 V at a scan rate of 50 mV/s. Prior to measuring CVs for electrochemical surface area determination and ORR, the working electrodes were scanned in the above potential range at 100 mV/s for 20 cycles to produce an electrochemically-clean electrode surface. The RDE measurements were performed at room temperature in an oxygen-saturated 0.1 M HClO4 solution with potential range of 0.05 to 1.05 V at scan rates of 20 mV/s and rotation rate of 1600 rpm.

3. RESULTS AND DISCUSSION

Figure 3(a) shows a mono-layer of 250 nm diameter PS nanoparticles that were deposited on Si and GC substrates by the m-NSL method. PS nanoparticles of different sizes (250 and 500 nm in diameter) have been used in these experiments to demonstrate the effect of separation of GLAD nanorods on their electrochemical activity. The monolayer is regular hexagonal shape in structure and looks sufficiently uniform and closely packed. It should be noted that uniform hcp structure was obtained on a substrate area of ~1 cm². This result shows that under proper conditions, it is possible to form large area, uniform, and closely packed PS monolayer using our recently developed m-NSL setup. After deposition of silver seeds and lifting PS nanoparticles off using toluene, periodically arranged silver dots in honeycomb-like were obtained and used as artificial seeds for the subsequent GLAD growth of the Pt nanorods as shown in Figure 3(b). From the cross sectional SEM view in Figure 3(c), the average height of the silver seeds was found to be about 40 nm with an average diameter of ~25 nm. The average height and diameter of silver seeds produced by m-NSL using 500 nm PS nanoparticles were measured from SEM images (not shown in here) to be around 40 and 30 nm, respectively.

Top view and cross-section SEM images in Figure 4(a) reveal that GLAD Pt nanorods deposited on flat substrates (sample A) by GLAD have an isolated columnar morphology. In the initial stages of GLAD growth which is governed by surface diffusion processes, number density of
the rods is large, and the rods have diameters ranging from 5–25 nm, yielding a relatively low porosity near the substrate with narrow pores (~5 nm). However, as the rods get longer due to the shadowing effect, they also grow in the lateral direction to diameters up to about 100 nm. During this stage, the average gap between the rods also changes with increasing length from initially 5–10 nm to 25–75 nm. When a critical length close to about 100 nm is reached, some of the rods cease to grow in the vertical direction, and the rest of them continue to grow upwards with almost constant diameter and gap values, leading a more straight rod-like geometry. The average length of these nanorods is about 200 nm with spacing and diameter ranging between 25–75, and 25–100 nm, respectively.

Figures 4(b) and (c) show the top and cross-section SEM views of GLAD Pt nanorods grown on patterned substrates which were fabricated using m-NSL with PS nanoparticles of 250 and 500 nm in diameter, corresponding to sample B and C, respectively. The nanorods replicate the honeycomb dot pattern and have approximately an equal length of 175 nm, excluding the height of the pattern, with an average diameter of 125 and 150 nm for sample B and C, respectively. Despite the fact that they have the same Pt loading, the nanorods on patterned substrates are shorter and bigger in diameter than those on flat substrate. This is due to the presence of Ag seeds on which Pt nanorods grown. In addition to that, it should be noted that the increase in film thickness does not only lead to an increase in the structure diameter, but also to the development of a triangle cross-section of the growing nanostructures as shown in Figures 4(b) and (c). The SEM images in Figures 4(b) and (c) indicate that there is a significant amount of deposition among GLAD nanorods grown on patterned substrate which occurs because the height of silver seeds (40 nm) is insufficient to shadow the whole interseed region, resulting in initial incomplete shadowing between neighboring seeds. As film growth proceeds, deposition between the silver seeds is suppressed since the larger growth rate on the seeds increases the atomic shadowing. The average diameter, length, and separation of these nanorods were measured from SEM images in Figures 4(b) and (c) to be 15, 40, and 20 nm, respectively. However, it should be noted that the presence of short Pt nanorods among periodic and well separated Pt nanorods is believed to further enhance the electrochemical surface area available for ORR.

The gaps among Pt nanorods deposited on flat substrate (sample A) increases dramatically with the nanorods length from ~5 to 75 nm as can be seen from SEM images in Figure 4(a). On the other hand, it should be noted that the nanorods grown on patterned substrates are not equidistantly distributed across the substrate surface due to the honeycomb-like template substrate. As indicated by Figures 4(b) and (c), in different growth directions, the distances between adjacent nanorods are different. Therefore, the gaps among Pt nanorods grown on patterned substrate of sample B exhibit relatively uniform minimum/maximum widths of 50 and 175 nm for closely adjoining nearest-neighbor nanorods (i.e., nanorods located at the side walls of the honeycomb structure) and for farthest-neighboring, respectively, as shown in Figure 4(b). Nanorods in sample C have relatively larger minimum/maximum gaps of 75 to 350 nm as depicted in Figure 4(c). Therefore, the average separation of GLAD
nanorods grown on patterned substrates is significantly enhanced compared to the nanorods on flat substrate, indicating that the porosity of GLAD Pt nanorod electrode can be controlled by growing them on patterned substrates.

Cyclic voltammetry (CV) profiles of sample A, B, and C with Pt loading of 0.16 mg/cm² are presented in Figure 5(a). During room temperature CV measurements, the working electrodes were scanned between 0 to 1.4 V in O₂-free 0.1 M HClO₄ at a scan rate of 50 mV/s. It was found that GLAD Pt nanorods grown on flat and patterned GC substrates are electrochemically active. The CV results are reproducible and represent adsorption and desorption of hydrogen on all the working electrodes, indicating the availability of a clean Pt surface for carrying out electrochemical reactions. The electrochemical surface area (ECSA) of the Pt in the working electrodes was calculated from the hydrogen adsorption charge in the negative-going potential scan (0.4-0.06 V) after correction for double-layer charging. The measured charge was converted to ECSA using the following equation:

\[ \text{ECSA (cm}^2/\text{gPt}) = \frac{\text{Charge} (\mu\text{C/cm}^2)}{210 (\mu\text{C/cm}^2) \cdot \text{Pt loading (gPt/cm}^2)} \] (1)

The measured ECSA values of sample A, B, and C are found to be 12, 12.6, and 13 m²/g, respectively. One may expect that GLAD Pt nanorods on flat substrate (sample A) would have higher ECSA than those of GLAD Pt nanorods grown on patterned substrates (sample B and C) for the
Fig. 5. Comparison of (a) Room temperature CV profiles obtained on sample A, B, and C. CVs recorded at 50 mV/s in O₂-free 0.1 M HClO₄. (b) Room temperature RDE profiles for sample A, B, and C in O₂-saturated 0.1 M HClO₄ at a scan rate of 20 mV/s and rotation rate of 1600 rpm, and (c) ORR polarization curves which were extracted from RDE results in (b) for samples A, B, and C during the anodic sweep (0 to 1.05 V versus RHE). The currents in (b) and (c) were normalized to geometric surface area and Pt ECSA, respectively.

Following reasons: first, larger diameter of the nanorods in sample B and C is expected to decrease the surface area to volume ratio of the rods. Second, better electrode porosity of sample B and C is also expected to decrease ECSA due to the lower number density of the nanorods. However, the enhanced ECSA of sample B and C might be attributed to a significant amount of deposition among periodic and well separated nanorods which results in fabricating additional nanorods on flat spots among these nanorods. These additional nanorods have the same morphology to those deposited on flat GC substrate in sample A and they can act as additional active sites available for the reactants, which in turn, enhances the ECSA. In our previous study, we showed that GLAD Pt nanorods deposited on flat substrate are highly hydrophilic, enabling penetration of aqueous electrolyte and/or ionomer into the nanorod arrays. Hence, we believe that increasing the separation of GLAD Pt nanorods grown on patterned substrate may further enhance the wettability of sample B and C and results in an increase in the measured ECSA. By a careful examination of CVs in Figure 5(a), it was found that samples B and C have oxide reduction peak potential values of 0.786 and 0.793 V, respectively, at the high current density region of the plots. These potential are 6 and 13 mV more positive than the oxide reduction peak observed on sample A, indicating that the nanorods in sample B and C exhibit lower overpotential than sample A due to the enhanced electrode porosity. In addition, this might also be attributed to the increased oxophilicity for smaller nanorods in sample A which leads to a decrease in specific activity of the ORR, because the oxygenated species (OH₂/or O₂) can effectively block the active sites required for the adsorption of O₂ and/or splitting of the O–O bond. This is investigated in more detail in the following analysis.

Figure 5(b) compares the positive-going RDE profiles of the ORR kinetics current densities on sample A, B, and C at a scan rate of 20 mV/s and rotation rate of 1600 rpm in O₂-saturated 0.1 M HClO₄ with Pt loading of 0.16 mg/cm² for all the working electrodes. As can be seen in Figure 5(b) that the ORR on all samples is under mixed kinetics-diffusion control in the potential range between 0.75 and 1.0 V, followed by diffusion-limited current region observed from 0.2 to 0.7 V. A very slight reduction in the limiting current of all the working electrodes was observed at potentials less than 0.2 V in the region of hydrogen adsorption, indicates the formation of H₂O₂ and a change in the ORR pathway from a four- to a two-electron mechanism. The values of diffusion limiting current density, normalized to geometric surface area, of 5.6, 5.8, and 6.0 mA/cm² were observed in Figure 5(b) for sample A, B, and C, respectively. These values are within 10% of the theoretical diffusion limiting current expected at 1,600 rpm and room temperature (5.7 mA/cm²), which is calculated using Levich equation.
indicating adequate coverage of the GC electrodes by the GLAD Pt nanorods and minimal effects of oxygen diffusion within the electrode films.\textsuperscript{2,4,10} The higher values of diffusion limiting current of patterned samples B and C is attributed to the more effective oxygen mass transport than dense and not well-separated GLAD Pt nanorods grown on flat GC substrate (sample A).

The ORR polarization curves of samples A, B, and C were extracted from RDE profiles shown in Figure 5(b) using the well-known mass-transport correction for RDE measurements:\textsuperscript{2-4}

\[
I_k = \frac{(I_{\text{lim}} \times I)}{(I_{\text{lim}} - I)}
\]  
(2)

where \(I\) is the measured current at a specified potential, \(I_{\text{lim}}\) is the measured limiting current, and \(I_k\) is the kinetic current. Specific activities can be determined by calculation of \(I_k\) using Eq. (2) and normalization to measured Pt ECSA. Figure 5(c) represents the ORR polarization curves for samples A, B, and C in the potential range between 0.7 and 0.99 V. The GLAD Pt nanorods on flat GC substrate (sample A) exhibits higher electrocatalytic activity toward ORR at high potential region compared to the nanorods grown on patterned substrates (sample B and C). For example, at 0.9 V, the specific-area activity of sample A is about 1,060 \(\mu A/cm^2\) is about 18.7\% higher than for the nanorods in sample B and C with SA of 893 \(\mu A/cm^2\). The enhanced ORR activity of Pt nanorods was attributed to the dominance of Pt(110) crystal planes on the well-developed nanorod sidewalls, which was reported to be the most active plane for ORR.\textsuperscript{31,32} It seems that the effect of the increased oxophilicity, described above, of the nanorods with smaller diameter of sample A than those in sample B and C is compensated and overcome by the dominance of the preferred crystal planes for ORR. However, at high current density, samples B and C show higher performance compared to sample A. For example, the specific area activities at 0.75 V of samples B and C extracted from Figure 5(c) were found to be about 41,773 and 95,870 \(\mu A/cm^2\), respectively, which are significantly higher than 14,693 \(\mu A/cm^2\) of sample A. This enhancement in ORR activity on samples B and C at high current region is believed to be associated with the enhanced electrode porosity due to the substrate patterning which facilitates oxygen mass transport throughout the catalyst layer.

4. CONCLUSION

Periodic and well separated Pt nanorods were fabricated by GALD deposition on patterned GC substrates prepared by m-NSL technique. Pt nanorods deposited on flat GC electrode was also prepared to be compared with the periodic and well-separated Pt nanorods for their electrochemical activity toward ORR in 0.1 M HClO\(_4\) electrolyte at room temperature utilizing CV and RDE techniques. Deposition of Pt nanorods on flat GC substrate (sample A) yields a dense electrode layer near the substrate base with gap size of \(\sim\)5 nm, followed by the formation of columnar Pt nanorods with gap size increases up to 75 nm. In contrast, the patterned B and C electrodes exhibit gap sizes with minimum/maximum width values of 50/175 and 75/350 nm for closely adjoining nearest-neighbor nanorods (i.e., nanorods located at the side walls of the honeycomb structure) and for farthest-neighboring, respectively. The ORR Polarization curves, extracted from RDE profiles, of samples A, B, and C yield that sample A show higher area-specific activity than those of sample B and C at high potentials (\(\geq 0.9\) V). However, samples B and C exhibit higher performance at low potential region which is attributed to the effective oxygen mass transport within the wider pores for the periodic and well-separated GLAD Pt nanorods compared to the nanorods of sample A grown on flat substrate.

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References and Notes


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