ELECTROCHEMISTRY

Conformation-modulated three-dimensional electrocatalysts for high-performance fuel cell electrodes

Jong Min Kim^{1,2,3}, Ahrae Jo⁴, Kyung Ah Lee², Hyeuk Jin Han^{1,5}, Ye Ji Kim^{1†}, Ho Young Kim², Gyu Rac Lee¹, Minjoon Kim¹, Yemin Park¹, Yun Sik Kang^{2‡}, Juhae Jung², Keun Hwa Chae⁶, Eoyoon Lee⁷, Hyung Chul Ham⁷, Hyunchul Ju⁴, Yeon Sik Jung¹*, Jin Young Kim²*

Unsupported Pt electrocatalysts demonstrate excellent electrochemical stability when used in polymer electrolyte membrane fuel cells; however, their extreme thinness and low porosity result in insufficient surface area and high mass transfer resistance. Here, we introduce three-dimensionally (3D) customized, multiscale Pt nanoarchitectures (PtNAs) composed of dense and narrow (for sufficient active sites) and sparse (for improved mass transfer) nanoscale building blocks. The 3D-multiscale PtNA fabricated by ultrahigh-resolution nanotransfer printing exhibited excellent performance (45% enhanced maximum power density) and high durability (only 5% loss of surface area for 5000 cycles) compared to commercial Pt/C. We also theoretically elucidate the relationship between the 3D structures and cell performance using computational fluid dynamics. We expect that the structure-controlled 3D electrocatalysts will introduce a new pathway to design and fabricate high-performance electrocatalysts for fuel cells, as well as various electrochemical devices that require the precision engineering of reaction surfaces and mass transfer.

INTRODUCTION

Electrochemical energy produced by hydrogen and fuel cell technologies are considered key to global efforts to shift energy sources away from carbon-based fuels. While current electrochemical technologies for power generation have demonstrated their feasibility in certain applications such as green transportation, there is widespread agreement that breakthroughs in electrochemical materials are critical to realize practical levels of performance, durability, and cost-effectiveness in electrochemical energy conversion systems such as fuel cells (1). In particular, power delivery from polymer electrolyte membrane fuel cells (PEMFCs) is limited by the sluggish kinetics of the oxygen reduction reaction (ORR), where molecular oxygen is electrochemically reduced to water to generate an electrical potential (1–3).

The ideal design of electrodes for fuel cells involves a delicate balance in the relative proportions of transport media and catalyst particles, and their distribution and arrangement, to form a more effective conducting network (4). Uncontrolled microfeatures in conventional Pt/C electrodes often cause structure-related problems in fuel cell devices. For example, an ionomeric additive is generally incorporated in the electrodes to enhance proton conductivity, but

*Corresponding author. Email: ysjung@kaist.ac.kr (Y.S.J.); jinykim@kist.re.kr (J.Y.K.) †Present address: Department of Materials Science and Engineering, Massachusetts Institute of Technology (MIT), Cambridge, MA 02139, USA.

*Present address: Fuel Cell Laboratory, Korea Institute of Energy Research (KIER), Daejeon 34129, Republic of Korea Copyright © 2021 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. No claim to original U.S. Government Works. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC).

a large variation in the impregnation depth of the cast ionomers can result in inefficient local proton transport and also introduce an unnecessary barrier to gas diffusion (4). More seriously, the corrosion instability of the carbon support resulting from electrochemical oxidation can lead to the detachment, dissolution, and sintering of Pt nanoparticles. This can lead to the degeneration of the electrochemical active surface area (ECSA) and a consequent degradation in catalytic performance and durability after prolonged periods of operation (5–7).

To address these challenges and develop highly durable electrodes, nanostructured, thin-film (NSTF) electrocatalysts have been proposed, which are uniformly coated with high-efficiency electrolyte layers (1, 8-10). Compared to conventional electrocatalysts, NSTF electrocatalysts can enhance energy production by ensuring more efficient charge delivery and better utilization of electrode materials. The thin electrocatalyst structures are also attractive because of their rapid charge transport kinetics, made possible by their short conduction distances, which obviates the use of an ionomer. In addition, the conductive, continuous thin-film scaffolds act as efficient electron pathways without relying on a carbon support, effectively mitigating electrochemical degradation, and resulting in electrodes with long-term stability. Despite these advantages, the small Pt surface area and low pore volume in NSTF electrocatalysts remain as critical issues to be solved, because they make the electrode more susceptible to water flooding (11).

To realize the full potential of these electrocatalyst materials, three-dimensional (3D) hierarchical structures need to be designed to achieve both sufficient ECSA and full accessibility to the electrochemical reactants (5, 12). 3D nanostructures provide superior electrochemical performance because the geometric constraints of simple monotonous geometries make it difficult to balance these factors (13–19). Conversely, heterogeneous nanoarchitectures based on multiple building blocks can yield novel 3D electrocatalysts. Such multicomponent hierarchical architectures can exploit design flexibility to combine seemingly incompatible attributes into a single

¹Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Republic of Korea. ²Center for Hydrogen and Fuel Cell Research, Korea Institute of Science and Technology (KIST), Seoul 02792, Republic of Korea. ³Materials Architecturing Research Center, Korea Institute of Science and Technology (KIST), Seoul 02792, Republic of Korea. ⁴Department of Mechanical Engineering, Inha University, Incheon 22212, Republic of Korea. ⁵Department of Mechanical Engineering and Materials Science, Yale University, New Haven, CT 06511, USA. ⁶Advanced Analysis Center, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 02792, Republic of Korea. ⁷Department of Chemistry and Chemical Engineering, Education and Research Center for Smart Energy and Materials, Inha University, Incheon 22212, South Korea.

catalyst entity. However, simultaneously achieving a large specific surface area, efficient mass transfer, and superior electrochemical performances and durability better than traditional electrodes has not been demonstrated yet.

In this study, we introduce a distinctive class of electrocatalysts with 3D orthogonal grid patterns, constructed via additive printing of individual Pt nanowire building blocks, for use as fuel cell electrocatalysts. Specifically, these 3D-modulated structures, designated Pt nanoarchitectures (PtNAs), can be built by the sequential stacking of 2D arrays of Pt nanowires using nanotransfer printing (nTP). nTP is a powerful synthetic technique for obtaining various 3D architectural designs and for optimizing the geometry and functionality of 3D assemblies (20-22). These PtNAs provide clear advantages. They have less tortuous mass transfer pathways and a more efficient use of active materials compared to commercial Pt/C. The top-performing PtNA was found to have a specific activity of more than 1.88 times in half-cells and a maximum power density that is 43% greater than that of conventional Pt/C catalysts in a single cell. These newly designed PtNA catalysts were probed using both theoretical and experimental analyses, and the observed outstanding performance and durability reveal the important relationship between 3D structural parameters and catalytic performance.

RESULTS

Geometric control of 3D PtNA catalysts via nTP

Figure 1A illustrates the nTP fabrication of the 3D PtNA catalysts. This additive and high-resolution printing technique enables the fabrication and transfer of 2D Pt nanopatterns, i.e., nanowire arrays, which can then be stacked into 3D structures. First, a 2Darrayed Pt nanopattern is transferred to a substrate. Then, additional 2D patterns are sequentially brought into contact on the previously formed pattern, forming crossed-wire 3D structures based on the design of electrocatalysts. The final 3D electrocatalyst can be easily transferred to a membrane and assembled into a stack with other structural elements, e.g., a gas diffusion layer (GDL), sub-gaskets, and bipolar plates, to create an electrochemical device suitable for fuel cell applications. The transfer process of the final 3D electrocatalysts using a sacrificial substrate will be described in detail later. In addition, we demonstrated various nanoarchitectures of elements (Cu, Ir, SnO₂, Ni, Au, TiN, Cr, and Ag) (fig. S1), which means our work is not limited to Pt catalysts and can deal with a variety of materials, composites, and structuring.

From an industrial point of view, this process can be implemented over large areas and, in this regard, we demonstrated an nTP process with close to 100% yield on a large area (18 cm by 11 cm) (fig. S2). The large-area capability indicates that the process can be directly applied to real industry, beyond laboratory-scale systems. Furthermore, our group demonstrated a sputtering-based nTP process (23), in which mass activity can be greatly improved through application of Pt alloy materials via a sputtering process.

Structural characteristics of the 3D nanostructured Pt catalysts

The 3D orthogonal grid structures were composed of multiple layers of 2D patterns, each consisting of periodic line patterns on a nano-to-micro length scale. Three master pattern substrates were prepared by block copolymer lithography (pitch, 50 nm/width, 20 nm) and photolithography (pitch, 200 nm/width, 50 nm and pitch, 1.2 µm/width, 200 nm) followed by plasma etching. Figure 1B shows scanning electron micrographs (SEMs) of the transfer-printed nanopatterns with a monolayer, depending on the master substrates. As discussed below, the 3D manufacture and organization of the Pt structures via nTP was effective regardless of the dimensions of the master mold patterns. Mono-, double-, and multipatterned Pt structures were also built by alternating the building blocks (Fig. 1, B to D) through sequential printing. Although this work focused on Pt nanowires with widths of 20, 50, and 200 nm, there are no realistic limitations to pattern size (down to even sub-10 nm). Furthermore, the nTP process was also applicable to a variety of complex structures such as multistacked nanostructures with different alignment angles and even freestanding nanostructures (Fig. 1E).

Pt metallic nanostructures were formed by the direct deposition of materials onto nanopatterned polymer substrates via glancing angle deposition (GLAD). In this method, the plane of the substrate is not placed perpendicularly to the direction of material deposition. This misalignment yields discrete nanostructures selectively on the protruded parts of the patterns, while avoiding material deposition in the recessed regions of the substrate patterns, thanks to the shadowing effect. The optimum deposition angle was between 70° and 85° (relative to the normal direction to the substrate plane), depending on the pattern size and the template depth.

After the nanowire fabrication process, the 3D Pt structures were annealed at 600°C in an Ar atmosphere to obtain polycrystalline Pt structures with increased grain size (Fig. 2A). The heat treatment also removed the remaining polymer residues on the surface of the Pt nanostructure. In the fast Fourier transform (FFT) image of the horizontal-plane high-resolution transmission electron microscope (HRTEM) image of the thermal-treated Pt nanowires (pitch, 200 nm/width, 50 nm), the diffraction patterns of the (111) and (002) planes can be clearly observed, while the diffraction pattern of the (220) plane is not observed (Fig. 2, B and C). This indicates that most of the crystal planes along the horizontal direction consist of (111) and (002) plane families, which suggests that most of the direction perpendicular to the crystal planes seen on the HRTEM image is the (220) plane. This result indicates that the exposed crystal planes on the top surface of the Pt nanowires are mainly the (220) plane. Also, the selected-area electron diffraction (SAED) pattern in the low-resolution TEM (LRTEM) image revealed a very weak intensity (220) diffraction pattern, compared to (111) and (002), results that are consistent with the abovementioned FFT analysis on HRTEM (fig. S3). These HRTEM and LRTEM images with FFT and SAED patterns demonstrate that the exposed crystal planes of the Pt nanowires are mainly composed of Pt(110) planes relative to other crystal planes. A higher proportion of Pt(110) planes is beneficial for fuel cells because the ORR is highly reactive on that crystal plane (24, 25).

Electron diffractograms obtained after annealing showed that the Pt nanopatterns were successfully converted into highly crystalline structures. Through the Scherrer equation based on x-ray diffraction (XRD) data, it was found that the average grain size increased from 5.2 to 10.0 nm after annealing (fig. S4). On the basis of the HRTEM analysis, we confirmed that the (110) plane was preferred on the exposed surface; however, it was difficult to observe clear information about the preferred (110) plane in the XRD results. This is because HRTEM analysis provides surface-specific information of individual Pt nanowires, while XRD analysis provides crystal information through the entire depth of the samples. These

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Fig. 1. Geometric control of 3D PtNAs via nTP. (A) A schematic illustration of the fabrication process for the 3D Pt electrocatalysts using the nTP process. Scanning electron micrography images of (B) a monolayer, (C) double layers, and (D) multilayers of PtNAs (left: pitch, 50 nm/width, 20 nm; center: pitch, 200 nm/width, 50 nm; and right: pitch, 1.2 µm/width, 200 nm). (E) Complex PtNAs stacked with a 45°, 30°, and freestanding nanostructure.

dissimilar probe ranges of the different characterization tools are the basis for the seemingly inconsistent results. Further analysis of the preferred (110) plane on the surface identified in HRTEM will be reconfirmed through in situ TEM-ASTAR (automatic crystal orientation and phase mapping).

Note that changing the deposition angle allows control of the types of facets and their relative portions. The ability to control the faceting of the Pt nanostructures is highly important in the preparation of catalytic substances, because adsorbates can change the relative stabilities of different crystal facets (25, 26). To investigate the crystal facets on the surface of Pt nanostructures formed by the

GLAD process, we carried out in situ TEM-ASTAR analysis during thermal treatment (Fig. 2, D and E), and it was performed over a wide coverage area containing more Pt nanowires for accuracy (27, 28). As a result, for pristine Pt nanowires, it was shown that (110) planes were preferred to the surface, as confirmed through HRTEM, and the (110) planes were still exposed to the surface in the same manner under the heat treatment at 600°C. In contrast, the exposed Pt surfaces in Pt/C were random (fig. S5). The grain size of Pt nanowires was observed to increase because of the thermal treatment, which is consistent with the increase in grain size measured in XRD results. In addition, from the crystalline orientation



Fig. 2. Characterization of fabricated PtNAs by TEM. (A) A schematic illustration shows dense PtNWs (pitch, 200 nm/width, 50 nm). (**B**) High-resolution TEM image of the Pt nanowire and corresponding (**C**) FFT of the whole HRTEM image (yellow box). (**D** and **E**) In situ TEM-ASTAR crystal orientation mapping of dense PtNWs along *z* directions during thermal treatment at 600°C. The inset indicates a color-coded inverse pole figure. The mapping time required to obtain an image is about 40 min, and it was observed in the same sample although not in the same position because of the change in position during the thermal treatment and mapping process. The lower part shows the corresponding crystalline orientation distribution diagram.

distribution diagram for the corresponding in situ TEM-ASTAR mapping results, it was confirmed again more quantitatively that (110) planes were preferred to the surface, which is known to be the most active plane for ORR (24, 25).

Generally, the Pt(111) plane is the energetically preferred growth plane of polycrystalline Pt during general thin-film deposition. However, it is understood that the relatively unfavorable Pt(110) planes can be formed by a combination of shadowing effect and differences in atom mobility during the GLAD process. In the early stage of the GLAD process, randomly grown textures are formed on the surface. Among them, unfavorable textures with low adatom mobility, e.g., Pt(110) planes, can have faster vertical growth rates, and consequently, the vertically grown textures grow larger and larger because of the shadow effect produced by the tilt angle (24, 29). This results in the predominant formation of unfavorable crystal planes. Similarly, Khudhayer et al. (24) reported highly active single-crystal Pt nanorod arrays for ORR formed by the GLAD process and demonstrated through crystal simulation and XRD pole-figure analysis that the exposed surface of Pt nanorods was covered by Pt(110) planes, which is consistent with our TEM-ASTAR and HRTEM analysis results.

Surface chemical analysis performed with x-ray photoelectron spectra (XPS) revealed that the Pt nanowire arrays formed by the GLAD process had dissimilar surface states from those of Pt nanoparticles formed by wet chemistry. The XPS analysis results (Fig. 3, A and B) indicate that the proportion of metallic Pt(0) in the Pt nanowires was 65.77%, which is substantially higher than the



Fig. 3. Characterization of fabricated PtNAs by XPS and XAFS. (**A**) XPS of Pt (4f) and (**B**) the ratio of Pt and Pt oxidation products in Pt/C and dense PtNA. (**C**) Pt L₃-edge x-ray adsorption near-edge structure spectra of Pt/C and dense PtNA. (**D**) The coordination number for Pt-Pt and (**E**) Fourier transform magnitude spectra are shown for the Pt L₃ edge of Pt/C and dense PtNA.

41.72% of the commercial Pt/C. The fractions of Pt(II) and Pt(IV) in the Pt nanowires were 24.81 and 9.43%, while those for commercial Pt/C were 39.76 and 18.52%, respectively. These results suggest that the surface of the Pt nanowires formed by nTP can minimize the formation of oxides on the surface compared to commercial Pt/C synthesized by wet chemistry.

X-ray adsorption spectroscopy was also performed to investigate the local atomic and electronic structures of our fabricated PtNA. The white line in x-ray adsorption near-edge structure (XANES) data indicates the d-band vacancy (Fig. 3C). A decrease in the white line intensity of our PtNA relative to that of a Pt/C catalyst indicates that our PtNA feature is an electron-rich phase on the surface, which corresponds to the XPS results. Curve fitting of the extended x-ray absorption fine structure (EXAFS) spectra established that the Pt-Pt coordination number (CN) of the PtNA was 11.6, which is considerably higher than that (8.1) of Pt/C (Fig. 3, D and E, and Table S1). It is well known that Pt nanoparticles (2 to 5 nm) supported on carbon black typically have spherical or hemispherical shapes with a large fraction of undercoordinated sites on the Pt surface (low CN) (5, 30, 31). Unlike Pt nanoparticles, the fabricated PtNAs have continuous 3D nanostructures (high CN), i.e., well-defined extended surfaces, effectively reducing the population of undercoordinated sites on the Pt surface. Considering that the EXAFS analysis results reflect both the top-surface and bulk information with a probe depth of ~100 nm (32), we expect that the surface undercoordinated site ratio of PtNA will be significantly lower than that of Pt/C. Because the undercoordinated Pt surface sites lead to low ORR activity because of their strong oxygen binding energy, PtNA with a high CN can bind oxygen species more weakly than Pt/C, achieving enhanced ORR performance (30). Furthermore, the electrochemical dissolution of Pt can be accelerated by undercoordinated Pt sites such as step, corner, and edge sites (30, 33). In other words, the larger the coordination number, the more stable it is. For these reasons, 3D Pt catalysts are expected to have high

durability and excellent activity, which will be discussed in the later part of this paper.

Electrochemical characterizations

Two sets of electrochemical experiments were performed to characterize the electrocatalyst functionality and utility of the 3D PtNA, in both half- and full-cell reactions, where the electrochemical kinetic parameters can be quantitatively determined. Cu foil was used as a sacrificial substrate to transfer the 3D PtNA onto glassy carbon electrodes or polymer electrolytes, as illustrated in Fig. 4A.

Half-cell characteristics were evaluated using a rotating disk electrode (RDE) for PtNA that had a single-scale pattern of pitch, 200 nm/width, 50 nm (designated as dense PtNA) and a commercial Pt/C catalyst. The activities of the Pt/C and dense PtNA catalysts were measured to be 0.196 and 0.566 mA cm⁻², corresponding to mass activities of 0.110 and 0.156 A/mg (at 0.9 V), respectively (Fig. 4, B to D). The kinetic current densities are shown as Tafel plots in Fig. 4B, and the Tafel slopes of the ORRs of Pt/C (66 mV/dec) and dense Pt/C (64 mV/dec) indicated that they have the same reaction mechanisms. It should be noted that the ORR activity of the 3D PtNA was higher than that of Pt/C despite its smaller surface area. Regarding the performance of Pt/C, we confirmed that it is similar to the mass and specific activities reported in other literatures (24, 34, 35). Integration of the hydrogen desorption region of

the cyclic voltammogram (CV) yielded ECSAs of 56.1 m^2/g for the Pt/C catalysts and 27.5 m^2/g for the dense PtNA. Thus, even with a 49% lower ECSA, the dense PtNA catalysts had specific activity and mass activity 188 and 42% higher than those of Pt/C, respectively. Furthermore, compared with the previously reported specific activity values of unsupported Pt thin-film electrocatalysts (e.g., NSTF Pt and Pt nanorods) and bulk Pt (9, 24), it was confirmed that the specific activity of dense PtNA is higher than Pt/C, lower than bulk Pt, and within the specific activity range similar to Pt thin-film electrocatalysts (Table S2). The dense PtNA showed improved mass activity compared to Pt thin-film electrocatalysts because of its high surface area.

The enhanced activity of the dense PtNA can be attributed to three factors: (i) the highly active Pt(110) crystal facets with a smaller fraction of undercoordinated sites (TEM and EXAFS; Figs. 2 and 3), (ii) the metal-rich phase on the surface (XPS and XANES; Fig. 3), and (iii) ionomer-free conditions. For the first and second factors, we additionally performed the density functional theory (DFT) calculation to support our results (fig. S6). When comparing the closed-packed Pt(111) plane with the Pt(110) plane considering the high CN and electron-rich surface, it was confirmed that the Pt(110) plane has optimal oxygen binding energy favorable to ORR activity compared to Pt(111). For the third factor, molecular dynamics and DFT simulation performed by Jinnouchi *et al.* (*36*) reported that ionomers fold to enlarge the polymer-metal attractive interaction



Fig. 4. Liquid half-cell test. (A) The transfer process for fabricated PtNA on glassy carbon or membrane substrates to prepare samples for electrochemical evaluation. (**B**) The ORR and (**C**) CV curves of Pt/C and dense PtNA are compared. The inset indicates the corresponding Tafel plot. (**D**) Mass and specific activities of Pt/C and dense PtNA. The ORR curves during the accelerated degradation test (ADT) (0.6 to 1.1 V, 6000 cycles) for (**E**) Pt/C and (**F**) dense PtNA. (**G**) ECSA retention rate of Pt/C and dense PtNA during the ADT. The ORR curves were acquired in a solution of O₂-saturated 0.1 M HClO₄, and the CV and ADT tests were conducted in a solution of Ar-saturated 0.1 M HClO₄.

induced by the large number of CF_2 groups, and this leads to a highly dense layer adjacent to the Pt surface and in turn reduces O_2 concentration close to the Pt surface to nearly zero. That is to say, in the case of ionomer-free PtNA, local O_2 resistance at the Pt surface can be eliminated, which leads to the improvement of ORR activity. These three features can explain the superior ORR activity of the dense PtNA compared to Pt/C, despite its lower surface area.

As a next step, we evaluated the electrochemical durability of PtNA in an accelerated degradation test (ADT) of 6000 cycles (Fig. 4, E to G). We adopted a potential range of 0.6 to 1.1 V and a scan rate of 5 mV/s to apply a harsh degradation environment. In general, it is well known that the lower the scan rate, the more severe the degree of degradation (*37*, *38*). After 6000 cycles, the CV data showed that the ECSA of the Pt/C was reduced by 91% while that of the dense PtNA was reduced by only 34%. PtNA, with a higher atomic CN than conventional Pt/C particles, can substantially reduce the surface area loss that occurs owing to Pt dissolution and redeposition (0.6 < E < 1.00 V). Furthermore, its carbon-free condition may also allow excellent durability under carbon corrosion conditions (>1.00 V) (*5*, *39*).

Then, to assess the electrochemical performance of the PtNA catalysts under more realistic single-cell operating conditions, we fabricated membrane electrode assemblies (MEAs) and evaluated their fuel cell performance in terms of maximum power density and current density at 0.6 V. For mass activities that are typically benchmarked at 0.9 V by using liquid half-cell, losses can be attributed to activation overpotential, while the maximum power density and current density at 0.6 V in fuel cells represent contributions from the resistive components of the cell and the transport efficiencies of gases, electrons, and protons to the catalyst sites (40). Thus, these two parameters provide an overall assessment of the performance of the electrode of the PEMFCs.

We compared the single-cell PEMFC performance of the dense PtNA catalysts as a function of the number of stacked layers (fig. S7). All of the measurements were carried out in a fully humidified atmosphere and ambient pressure. The maximum power densities were 420, 491, and 492 mW cm⁻² for 10, 20, and 40 layers, respectively. The maximum power densities were 420, 491, and 492 mW cm⁻² for the 10, 20, and 40 layers, respectively. However, performance reached a plateau at >20 layers, which can be attributed to the dominance of mass transfer issues occurring for thick electrodes (41, 42). From these results, it is speculated that the optimum number of layers is about 20 for dense PtNAs.

To confirm the increase in mass transfer resistance resulting from the increased number of layers, we next carried out electrochemical tests at lower humidity conditions (fig. S8). For the 40-layer PtNA, compared to the results from the relative humidity (RH) 100% condition, a higher current density voltage upswing was observed under the RH 50% condition. The performance at RH 50% was markedly higher than that at RH 100%, particularly in regions of high current density. This result indicates that the observed falloff in high current density can be attributed to water flooding in the cathode, resulting from the highly dense nanostructure of the dense PtNA. This water flooding is the cause of the performance saturation at higher numbers of stacked layers. When humidity was further lowered to RH 30%, the degree of hydration was insufficient for the electrochemical operation of the MEA, resulting in performance degradation. These results suggest that further modulation of the 3D structural design would result in better performance.

To expedite mass transfer by augmenting the channel, so that water can be more easily transported, we prepared a 3D Pt catalyst with a larger feature size (sparse PtNA; pitch, 1.2μ m/width, 200 nm) as shown in Fig. 5A. Morphologically, we expected that a sparse PtNA would have a relatively higher porosity than a dense PtNA, because of the larger-sized building blocks (eight times higher and four times wider) and lower nanowire density. In terms of electrochemical performance, the sparse PtNA exhibited inferior performance, especially in the low current densities regime, i.e., activation loss regime, in the *I-V* curves shown in Fig. 5B.

To address this issue, we hypothesized that building multiscale 3D Pt structures that incorporated features of various scales would enhance both the degree of utilization and the specific effective surface area. We designed and fabricated a multiscale PtNA by alternately stacking narrower (and denser) and wider (and sparse) Pt nanowire building blocks using nTP (Fig. 5A and fig. S9). We then compared their polarization and power density plots with those of conventional Pt/C catalysts.

Measurements were performed in a fully humidified atmosphere of H_2/air at 80°C under ambient pressure and at 150 kPa. With similar Pt loading, the performance levels of the PtNAs containing multiscale features were higher than those of Pt/C at both pressures (Fig. 5, B and C). The current density of the Pt/C electrode was 350 mA cm⁻² at 0.6 V under ambient pressure. Under the same conditions, the current densities of electrodes composed of sparse, dense, and multiscale PtNA were 191, 390, and 390 mA cm⁻², respectively. Although the ECSAs of our PtNAs were less than that of Pt/C, as shown in fig. S10, both the dense and multiscale 3D Pt structures exhibited approximately 10% higher performance than Pt/C at 0.6 V.

The maximum power densities of the 3D Pt electrodes with the dense (421 mW cm⁻²) and multiscale structures (430 mW cm⁻²) were 40 and 43% higher than that of the Pt/C (300 mW cm⁻²), respectively. These results demonstrate that the multiscale 3D Pt structures significantly improved electrode performance in regions of high current density, where mass transfer losses are dominant. It needs to be noted that the differences in performance among the dense, sparse, and multiscale PtNA were more noticeable under high-pressure conditions. Although the ECSA of the multiscale PtNA (19.69 m²/g) was 37% less than that of the dense PtNA (31.7 m²/g) (fig. S10), it exhibited a 9% greater maximum power density (535 mWcm⁻²) at 150 kPa than the latter. This is because the enhanced mass transfer of the multiscale PtNA became more pronounced under a high current density, such as those occurring at a back pressure of 150 kPa.

To more fully characterize the mass transfer characteristics of our structures, we calculated the oxygen gain and the difference in power density compared to Pt/C (Fig. 5, D and E). Oxygen gain was calculated by measuring the difference in potential that occurs when the device is exposed to oxygen or air. The oxygen gain values indicated that mass transfer in the multiscale PtNA was much greater than in either the Pt/C or dense PtNA and was similar to that of the sparse PtNA. These results suggest that the mass transfer characteristics of the 3D Pt catalyst can be improved by controlling the internal geometry of the electrode. Furthermore, with an increase in current density, the multiscale PtNA demonstrated larger differences in power density than the Pt/C and other (dense or sparse) PtNAs, confirming that the multiscale PtNA had both excellent mass transfer and moderate ECSA.



Fig. 5. Multiscale PtNA and single-cell test. (A) A schematic illustration showing a multiscale PtNA. Polarization curves of Pt/C and various PtNA-based MEAs are shown under an atmosphere of H₂/air (B) without outlet pressure and (C) with a total outlet pressure of 150 kPa. (D) Oxygen gains were calculated using the potential difference observed upon exposure to oxygen or air, respectively. (E) The differences in power density between Pt/C and various PtNAs MEAs are shown for a H₂/air atmosphere with a total outlet pressure of 150 kPa. CV curves of (F) Pt/C and (G) multiscale PtNA are shown before and after ADT (1.0 to 1.5 V, 5000 cycles).

We think that the current state is not optimal and there is room for performance improvement. For this, we suggest three strategies to reduce fuel cell losses: (i) rational design of electrode architecture (activation and mass transfer loss), (ii) improved contact resistance between electrode and membrane (ohmic loss), and (iii) introduction of high-efficiency Pt alloy materials (activation loss). Further efforts are being put into developing the design of strategies that can improve the performance of 3D PtNA catalytic activity in the vast structure-activity design space (see figs. S11 to S16).

Single-cell ADT tests were also carried out to evaluate the long-term stability of our multiscale PtNA (Fig. 5, F and G) in a single-cell configuration. To simulate the operation of a practical automotive PEMFC, the ADT was performed by cycling the electrode potential

between 1.0 and 1.5 V for 5000 cycles. After cycling, the multiscale PtNA lost only 5% of its initial ECSA, while the Pt/C electrode lost ~69% of its initial ECSA. The maximum power density retention of the Pt/C declined by about 72.5% after the ADT, compared with 18.1% for the multiscale PtNAs (fig. S17). The difference in degradation rates during ADT for the half-cell and MEA is due to the different scan rates and potential ranges. At 1.0 to 1.5 V, where only carbon corrosion is mainly observed, the excellent durability of the unsupported multiscale PtNA is more noticeable, compared to the carbon-supported Pt/C, due to its carbon-free nature.

For the post-ADT studies, we statistically calculated the change in Pt nanoparticle size distribution in the Pt/C using TEM images and investigated changes in the morphology of the multiscale PtNA using SEM images as well (figs. S18 and S19). In the Pt/C, the average size of Pt nanoparticles increased significantly, from 2.9 to 6.5 nm after ADT. However, in the multiscale PtNA catalyst layer on the membrane, although some wrinkles and cracks were found, the pattern width remained almost the same before and after ADT. The dense Pt nanowires in the multiscale PtNA had a linewidth of about 50 nm before the test, as shown in Fig. 5A, and almost the same pattern width of 50 nm was observed even after ADT, which is consistent with the ECSA retention results of the multiscale PtNA (5% loss of ECSA).

We also investigated the XPS spectra of the Pt 4f of the Pt/C and multiscale PtNA and found that the intensity of the Pt 4f of the Pt/C significantly decreased after the test because of the severe Pt nanoparticle degradation resulting from the corrosion of the carbon support (fig. S20). In contrast, the intensity of the Pt 4f of the multiscale PtNA decreased very slightly compared to the Pt/C, which was also consistent with the results of the ECSA reduction rate in CV. In addition, it was observed that the binding energies of Pt 4f shifted negatively after ADT for both PtNA and Pt/C. During the ADT, it is understood that the effect of grain and particle growth of Pt/C may have influenced the peak shift of XPS spectra and the change on the shift from PtNA samples may be attributed to the grain size increase in Pt NWs induced by the coalescence and sintering of Pt atoms without significant change in pattern width, verified by dark-field TEM images (fig. S21). These results confirmed the superior durability of the multiscale PtNA compared to carbon-supported Pt/C.

Computational fluid dynamics

Numerical simulations based on computational fluid dynamics were used to help understand how the electrochemical properties of the overall 3D pattern are influenced by local pattern biases at different scales (here, binary patterns). 3D, two-phase fuel cell simulations were conducted with a conventional Pt/C catalyst and a dense PtNA, a sparse PtNA, and a multiscale PtNA. Detailed descriptions of the 3D fuel cell model are available in our previous papers (43–45). The computational domains and mesh configuration are shown in fig. S22. The ECSAs and porosities of the 3D Pt structure catalyst structures were first calculated and then applied to the 3D model.

The sparse PtNA catalyst was modeled as an array of elliptic nanowires. Each Pt nanowire was defined by a width, *D*, a height, *H*, and a length, *L*, using the Ramanujan approximation (46) as follows

$$A_{\text{sparse}} = \frac{1}{2} \times \pi \times \left[3 \times (D/2 + H) - \sqrt{(3 \times D/2 + H)(D/2 + 3 \times H)} \right] \times L + D \times L$$
(1)

The number of nanowires required for a cell area of 1 cm by 1 cm was $N_{\text{sparse}} = 8334$ per individual mesh, and one pair of meshes included a one-directional mesh and its perpendicular analog. Then, 10 pairs of meshes were stacked to form the catalyst layer, i.e., 20 meshes or 1600 nm total thickness. Thus, the ECSA of the sparse PtNA was estimated to be

$$ECSA_{sparse} = (A_{sparse} \times N_{sparse}) \times 20 \text{ meshes} = 8.06 \times 10^{-5} \text{ m}^2 (2)$$

Conversely, nanowires in the dense PtNA were assumed to be semicircular bars (50 nm by 10 nm by 10 nm, $N_{dense} = 50,000$), corresponding to an ECSA for a 1 cm by 1 cm cell defined by

$$ECSA_{dense} = (A_{dense} \times N_{dense}) \times 20 \text{ meshes} = 12.0 \times 10^{-5} \text{ m}^2 \quad (3)$$

Last, individual pairs of meshes in the multiscale PtNA were modeled as a combination of dense and sparse nanowires. Hence, the ECSA for a multiscale PtNA with a thickness of 900 nm (10 densesparse pairs) was calculated as follows

$$ECSA_{multiscale} = \frac{1}{2}ECSA_{sparse} + \frac{1}{2}ECSA_{dense} = 10.03 \times 10^{-5} m^{2}$$
(4)

Based on these ECSAs, the electrochemically active surface area per unit of catalyst volume, a_{Pt} , and catalyst porosity, ε , were estimated and are listed in Table 1. As with the experimental data, the dense PtNA exhibited a large electrochemically active surface area per catalyst layer volume and a relatively small pore volume.

Figure 6A compares the simulated and experimental polarization curves of the four different cathode catalyst designs. In general, the model accurately captured key experimental trends, particularly the steeper ohmic polarization characteristics of the Pt/C catalyst, which results in two intersections of the curves at low and high current densities. This phenomenon implies that the thin catalyst layers of the 3D Pt structure resulted in a substantially lower ohmic potential drop. The high cell performance of the Pt/C catalyst in the low current density regime ($<300 \text{ mA cm}^{-2}$) is consistent with its large ECSA. By contrast, the low performance of the Pt/C catalyst at high current densities (>800 mA cm⁻²) is the combined result of larger ohmic and mass transfer resistances due to the thicker catalyst layer (6 µm). Note that the multiscale PtNA design outperformed the other designs over a wide range of current densities. This indicates that a combination of dense and sparse nanowires, and the resulting pore structure, provided sufficient ECSA for oxygen transport and the ORR.

To better understand the nonmeasurable polarization behaviors of our 3D electrode systems, individual voltage losses associated with ORR kinetic polarization and ohmic polarization due to proton and electron transfer across the cathode catalyst were calculated from the simulation results and are plotted in Fig. 6B. The Pt/C catalyst showed the largest ECSA and slightly lower kinetic polarization than the three 3D Pt designs. By contrast, ohmic polarization due to proton transfer through the catalyst layer was greatly reduced in the dense PtNA because of its very thin catalyst layer (200 nm). The contribution of electron transport to the ohmic polarization was almost negligible, because of the sufficiently high electronic conductivity of the cathode catalyst layer.

The average oxygen concentrations in the cathode catalyst layers are compared in Fig. 6C. While severe oxygen depletion was observed in the Pt/C catalyst, due to its low porosity and thick catalyst layer, the average oxygen concentrations in the dense, sparse, and multiscale PtNA were similar. This demonstrates the trade-off between the thickness of the catalyst layer and the porosity of the 3D Pt designs. Although the sparse PtNA exhibited high porosity, alleviating the effects of oxygen depletion, the sparse PtNA had a 16-fold greater thickness than the dense PtNA, which offset any advantages of the high porosity.

The degree of liquid saturation in the cathode catalyst layer and GDL are plotted in Fig. 6D. Local liquid saturation was averaged along the flow (y) and in-plane (z) directions. A higher liquid saturation of around 0.36 was predicted in the dense PtNA because of its lower overall pore volume, while the average liquid saturation

Description		Value	Ref.
Exchange current density (^{ref})	Anode CL	2350 A m ⁻²	(47)
	Cathode CL	$6.0 \times 10^{-4} \text{ A m}^{-2}$	(47)
Reference H_2/O_2 molar concentration (C^{ref})		40.88 mol m ⁻³	(48)
Transfer coefficients (α)	Anode CL	$\alpha_a = \alpha_c = 1$	(40)
	Cathode CL	$\alpha_c = 1$	(48)
Activation energy (E _a)	Anode CL	10 kJ mol ⁻¹	(47)
	Cathode CL	70 kJ mol ⁻¹	(49)
Reaction order in the electrode (r)	Anode CL	1/2	(40)
	Cathode CL	3/4	(48)
Porosity of the GDL (ε_{GDL})		0.6	Assumed
Porosity of the anode CL (ε_{CL})		0.5	Assumed
Porosity and permeability of the dense PtNA (K_{na})		50%, $1.0 \times 10^{-12} \text{ m}^2$	Estimated
Porosity and permeability of the sparse PtNA (K_{sp})		$86.9\%, 3.0 \times 10^{-11} \mathrm{m}^2$	Estimated
Permeability of the anode CL (K_{aCL})		$1.0 \times 10^{-13} \mathrm{m^2}$	Assumed
Permeability of the GDL (K_{GDL})		$5.0 \times 10^{-13} \mathrm{m}^2$	Assumed
ECSA per catalyst layer volume of dense PtNA catalyst layer (ana)		$6.0 \times 10^7 / m$	Estimated
ECSA per catalyst layer volume of sparse PtNA catalyst layer (a_{sp})		5.038×10^{6} /m	Estimated
ECSA per catalyst layer volume of multiscale PtNA catalyst layer (a _{mul})		1.114×10 ⁷ /m	Estimated
Dry membrane density (ρ _{dry, mem})		2000kg m^{-3}	(50)
Equivalent weight of electrolyte in membrane (EW)		1.1 kg mol ⁻¹	(50)
Faraday constant (F)		96,487 C mol ⁻¹	
Universal gas constant (R)		8.314 J mol ⁻¹ K ⁻¹	
Catalyst coverage coefficient (n _c)		1.5	
Effective electronic conductivity in the narrow and sparse PtNA (σ_{PtNA})		$1.2 \times 10^5 \mathrm{S m^{-1}}$	Estimated
Effective electronic conductivity in the Pt/C (σ_{CL})		1000 S m ⁻¹	(48)
Effective electronic conductivity in the GDL (σ_{GDL})		10,000 S m ⁻¹	(48)
Effective electronic conductivity in the graphite BP ($\sigma_{Graphite}$)		20,000 S m ⁻¹	(48)
Surface tension (σ)		0.0625 N m ⁻¹	(48)
Contact angle of GDL, CL (θ)		92°, 92°	
Liquid water density (ρ^{l} at 65°C)		980 kg m ⁻³	
Liquid water viscosity (μ ^l)		$3.5 \times 10^{-4} \mathrm{N \ s \ m^{-2}}$	(48)
Thermal conductivity of the hydrogen (k _{H2})		0.2 W m ⁻¹ K ⁻¹	(50)
Thermal conductivity of the oxygen (k_{02})		0.0296 W m ⁻¹ K ⁻¹	(50)
Thermal conductivity of the water vapor ($k_{\rm H2O}$)		0.0237 W m ⁻¹ K ⁻¹	(50)
Thermal conductivity of the nitrogen (k_{N2})		0.0293 W m ⁻¹ K ⁻¹	(50)
Thermal conductivity of membrane (k _{mem})		0.95 W m ⁻¹ K ⁻¹	(48)
Thermal conductivity of GDL/CL		5.0/1.0 W m ⁻¹ K ⁻¹	(48)
Thermal conductivity of graphite		20 W m ⁻¹ K ⁻¹	(48)

Table 1. Kinetic, physiochemical, and transport properties.

values for the Pt/C catalyst, sparse PtNA, and multiscale PtNA were 0.13, 0.16, and 0.32, respectively. However, because the pore volume of the dense PtNA was only 10.8% that of the sparse PtNA and 5.0% of the Pt/C catalyst, the degree of water saturation was lower than expected. This was due to a relatively strong convective flow in the dense PtNA that enhanced the water removal efficiency of the catalyst layer.

To estimate the effects of convection on water accumulation in the cathode catalyst layer, the magnitudes of the transverse gas velocity in the cathode were averaged (fig. S23). A larger transverse gas velocity was induced in the dense PtNA because of the thin catalyst layer (200 nm) and consequently low momentum resistance. In contrast, convection in the Pt/C catalyst was much weaker owing



Fig. 6. Numerical simulations based on computational fluid dynamics. (A) Comparison of simulated (lines) and measured (symbols) polarization curves under an operating pressure of 1 atm, (B) individual voltage losses due to ORR kinetic polarization and ohmic polarization across the cathode catalyst layer, (C) the average oxygen concentrations in the cathode catalyst layer as a function of operating current density, and (D) comparison of through-plane liquid saturation profiles for three different cathode catalyst layer designs at 1.0 A cm⁻².

to the thickness of its catalyst layer (6 μ m). The above results indicate that ultrathin catalyst layers in the 3D Pt structures lead to relatively strong transverse convection effects in the catalyst layer. This results in better removal of accumulated water from the interior of the cathode. Among the four catalyst designs, the multiscale PtNA offered significant benefits in terms of oxygen transfer and ESCA for ORR while the accumulation of moderate amounts of water enabled the formation of an efficient proton transfer path along the catalyst layer thickness direction.

DISCUSSION

In summary, we demonstrated that multiscale PtNA can be fabricated as high-performance electrocatalysts for PEMFC via the 3D-stack printing of aligned Pt nanowire building blocks with controlled diameter and spacing. The electrochemical characterizations indicated that single-pattern PtNAs were suboptimal in terms of ECSA and mass transfer, suggesting the design and construction of multiscale PtNA composed of dense and sparse building blocks to maximize their electrochemical performance. Using a combination of theoretical and experimental studies, the degree of utilization and the specific effective surface area of the catalyst was also assessed to determine the optimal structure, deducing exemplary multiscale 3D PtNA catalysts. The maximum power density of the resulting multiscale 3D Pt electrodes was 43% higher than that of Pt/C, and the ADT for 5000 cycles revealed that the multiscale PtNA lost only 5%

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of its initial ECSA, which is markedly superior to the 69% loss for the Pt/C electrode.

MATERIALS AND METHODS

Preparation of master molds

The master template with widths of 20 nm was fabricated by block copolymer self-assembly. For the block copolymer self-assembly to form 20-nm-wide patterns, PS-b-PDMS (polystyrene-block-polydimethylsiloxane) block copolymer (48 kg/mol) and hydroxyl-terminated PDMS brush polymer (5 kg/mol) were purchased from Polymer Source Inc. (Canada). The hydroxyl-terminated PDMS solution [2 weight % (wt%)] dissolved in heptane solvent was spin-coated on the prepatterned Si substrate and then the sample was thermal-annealed at 150°C and then washed with heptane to remove unattached polymer brush. The PS-b-PDMS block copolymer was dissolved in a mixed solvent of toluene, heptane, and PGMEA (propylene glycol methyl ether acetate) (1:1:1 by volume) with 0.8 wt% and spin-cast on the prepared substrate and solvent-annealed with toluene vapor for 10 hours in the chamber at room temperature to form well-ordered line and space patterns. After the annealing process, the sample was etched by CF₄ plasma followed by O₂ plasma treatment. The master templates with widths of 50 and 200 nm were fabricated using KrF photolithography. All of the prepared master templates were subjected to the same PDMS brush treatment as the method used in the block copolymer self-assembly process to lower the surface energy for replication.

High-resolution nTP process

For replication, polymethyl methacrylate (PMMA; Polysciences, 100 kg/mol) was dissolved in a mixed solvent of toluene, acetone, and heptane at 4 wt% (4.5:4.5:1 by volume). The PMMA polymer solution was spin-cast onto the master molds and a polyimide adhesive film (3M Inc.) was attached to the top surface of the PMMA and then detached from the master mold with the inverted surface topography. Pt nanowires were formed on the nanopatterned PMMA replica by GLAD using an e-beam evaporator. After Pt deposition, the fabricated Pt nanowires/nanopatterned PMMA replica was exposed to a mixed solvent vapor of acetone and heptane (1:1 by volume) at 55°C for 25 s and then brought into contact with the substrates, e.g., Cu foil. Then, the PMMA replica was washed by dipping it into the toluene solvent. After the PtNAs were formed on the Cu foil using the sequential printing process, the thermal treatment was performed at 600°C for 5 min in an Ar atmosphere. The total amount of Pt loading in the PtNAs was measured using inductively coupled plasma mass spectrometry. To verify that this measured value was valid, we additionally carried out a numerical calculation of the Pt loading of PtNA, based on structural variables, and confirmed that the experimentally measured and calculated values were in a similar range (figs. S24 and S25). To transfer the PtNA to a glassy carbon electrode or Nafion membrane for electrochemical evaluation, a PMMA polymer solution (4 wt%) was spincoated on the fabricated PtNA/Cu foil substrate, and it was floated in 0.1 M ammonium persulfate solution [(NH₄)₂S₂O₈, Sigma-Aldrich] to remove the Cu foil substrate. Thereafter, the PMMA-coated PtNA floating in the solution was transferred to an arbitrary substrate such as glassy carbon electrode or Nafion electrolyte and then the PMMA was removed by toluene washing as described in Fig. 4A.

Material characterizations

The morphologies and microstructures of the fabricated PtNAs were investigated by field-emission scanning microscopy operated at 15 kV (Hitachi S-4800, JEOL 7600F) and TEM (JEOL JEM-ARM200F microscope) operated at 200 kV. The crystal orientation mapping was carried out by TEM-ASTAR (ASTAR: NanoMEGAS, TEM: Tecnai F20 G2) operated at 200 kV with 1° of precession angle. The chemical oxidation states of the Pt surface were investigated by an x-ray photoelectron spectrometer (K-Alpha, Thermo VG Scientific). The crystal information and grain size were analyzed with a multipurpose thin-film x-ray diffractometer (Rigaku). X-ray absorption data were measured at the 1D XRS KIST-PAL beamline in the Pohang Accelerator Laboratory. The Fourier transforms of EXAFS data were obtained by processing the Pt L₃-edge result using the IFEFFIT software package.

Electrochemical half-cell tests

Electrochemical half-cell tests were carried out using an AutoLab potentiostat (Eco Chemie Inc., Netherlands) with a three-electrode cell. A Pt plate and a saturated calomel electrode were used as the counter and the reference electrodes, respectively. All of the electrochemical results were calibrated versus reversible hydrogen electrode. To prepare the Pt/C catalyst ink, 5 mg of Pt/C catalysts (20 wt%, Premetek) was used in 500 μ l of isopropyl alcohol and 50 μ l of Nafion solution (5 wt% solution, Sigma-Aldrich). Then, 5 μ l of catalyst ink was dropped onto a glassy carbon RDE to form the working electrode. To grave the working electrode, as described above. CV was

carried out in Ar-saturated 0.1 M HClO₄ electrolyte over the range of 0.05 to 1.2 V at a scan rate of 20 mV/s. ORR curves were measured in an O₂-saturated 0.1 M HClO₄ electrolyte over the range of 0.05 to 1.05 V at a scan rate of 10 mV/s, and the RDE was rotated at 1600 rpm. An ADT was performed in an Ar-saturated 0.1 M HClO₄ electrolyte over the range of 0.6 to 1.1 V at a scan rate of 5 mV/s.

MEA tests

To prepare the MEA for a single-cell test, the anode catalysts (Pt/C, Pt 46.2 wt%, Tanaka, 0.1 mg/cm²) were loaded by a spray-coating method onto the membrane. The commercial Pt/C catalyst (Pt/C, Pt 46.2 wt%, Tanaka, 0.08 mg/cm²) was loaded using a spray-coating method, and the fabricated catalyst was loaded using the PMMAbased transfer method to prepare the dense, sparse, and multiscale PtNA (0.08 mg/cm²) samples for cathode catalyst layers. The active areas were 1 cm^2 , and Nafion 211 was used as the membrane. The catalyst-coated membranes were placed between two GDLs (SGL 39 BC), and the whole MEAs were inserted into single-cell modules composed of two graphite plates. To evaluate their electrochemical performance, the I-V polarization curves were measured using a single-cell test station (CNL Energy Co.). The anode and cathode were placed in a H₂/air (RH 100%) or H₂/O₂ (RH 100%) flow, at a flow rate of 200/600 standard cubic centimeters per minute under ambient pressure and 150-kPa back pressure, respectively. The cell temperature was maintained at 80°C. CV curves were measured by sweeping the potential range from 0.05 to 1.2 V at a scan rate of 50 mV/s with a potentiostat device (Solartron Analytical, AMETEK). The ADT was carried out by sweeping the potential range from 1.0 to 1.5 V at a scan rate of 500 mV/s for 5000 cycles.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/ content/full/7/30/eabe9083/DC1

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