Vertically Aligned Titanium Nitride Nanorod Arrays as Supports of Platinum–Palladium–Cobalt Catalysts for Thin-Film Proton Exchange Membrane Fuel Cell Electrodes

Shangfeng Jiang,[a, b] Baolian Yi,[a] Hongjie Zhang,[a, b] Wei Song,[a] Yangzhi Bai,[a, b] Hongmei Yu,[a] and Zhigang Shao*[a]

The degradation of the carbon supports and high platinum (Pt) loading significantly hinder the wide adoption of proton exchange membrane fuel cells. In conventional electrodes, the ionomer binders introduce an undesirable, high oxygen-transport resistance and cover the catalysts active sites. Herein, an advanced catalytic layer based on vertically aligned titanium nitride nanorod arrays (TiN NRs) is prepared, without additional ionomer or binders in the cathode. After supporting the thin-film platinum–palladium–cobalt (PtPdCo) catalyst (Pt loading: 66.9 μm cm⁻²) onto TiN NRs, the ordered electrodes were investigated as the cathode of a single cell without additional ionomer in the catalytic layer. With this electrode architecture, the as-synthesized electrode performs with a maximum power density of 390.5 mW cm⁻² and cathode mass-specific power density of 5.84 W mg⁻¹. The 2000 potential cycles accelerated degradation test shows that the PtPdCo–TiN electrode is more stable than the commercial gas diffusion electrode.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) that directly convert chemical energy to electrical energy have high energy-conversion efficiency, low or zero emission, low operating temperature, and quick startup. Thus, they are considered as one of the most promising energy-conversion devices for portable, stationary, and transportation applications.[1] However, several barriers hinder the wide adoption of fuel cells, including high cost and durability. Many researchers have focused on the development of Pt alloy or core–shell structures with non-noble metals, whereas some researchers have focused on the fabrication of ordered-structure electrodes.[2–6] For the commercial application of fuel cells, the development of an effective membrane electrode assembly (MEA) is significant, because fuel cell performance not only relates to the intrinsic catalytic activity of the as-prepared catalysts, but also depends on the structure of the catalyst layer formed by these electrocatalysts.[7] A conventional catalytic layer is established by carbon-supported Pt-based catalysts (Pt/C) and ionomer, which results in the poor durability and high cost of fuel cells.[8] The reasons for loss of the electrochemically active surface area (ECSA) of Pt/C can be summarized as follows: 1) loss of platinum nanoparticles from the carbon support, resulting in corrosion of the carbon support; 2) platinum nanoparticle dissolution and Ostwald ripening; and 3) platinum–nanoparticle aggregation driven by surface-energy minimization.[2] Although some new oxygen reduction reaction (ORR) electrocatalysts with high activity and high durability have been developed, the most widely used catalyst supports are still high-surface-area carbon materials, which cause a significant degradation of a single cell or stack performance for carbon corrosion.[9] The additional ionomer binder film around the Pt/C catalysts adds to the oxygen-transport resistances and covers the catalyst active sites, which reduces the Pt utilization.[10]

Many efforts have been made to improve the ionomer- and carbon-free catalytic layer with a low amount of Pt without sacrificing the performance and durability of fuel cells. The widely known “3M” nanostucture thin film (NSTF) electrode is one of the successful examples. The vertically aligned organic whiskers with sub-micrometer thicknesses are covered with a continuous thin layer of Pt or Pt alloy catalysts, which show a significant activity improvement over the Pt/C-based catalyst layer.[11] As NSTF electrodes are ionomer free (without additional ionomer), the water film is believed to be the secondary proton-conduction pathway.[12] In addition to 3M NSTF electrodes, ordered-structure metal-oxide supports such as TiO₂, WO₃, or others have been employed in the advanced catalytic layer structure, owing to their high corrosion resistance and the strong metal–support interaction with Pt-based catalysts. Zhang et al. used ordered-structure titanium nanotubes as the catalyst support in the catalyst layer of PEMFCs, which showed high stability even when maintained at 1.6 V versus NHE for
Some research groups have also investigated the support-free Pt nanotube arrays for PEMFCs without additional Nafion\textsuperscript{®} ionomer.\textsuperscript{[14]} Detailed results suggest that the ordered thin-layer structure can enhance the mass transport and proton conductivity, thus generating high performance without using a proton-conducting ionomer.

Transition-metal nitrides, as non-carbon support materials, in particular titanium nitrides (TiNs), are widely studied in terms of fuel cell application.\textsuperscript{[15]} Nanostructured TiN should be a candidate catalyst support for PEMFCs, owing to its high electrical conductivity and relative corrosion resistances.\textsuperscript{[16–18]} Pan et al.\textsuperscript{[17]} employed hollow and porous TiN nanotubes as the catalyst supports for the ORR, which showed better performance and higher durability compared with commercial Pt/C. Meanwhile, mesoporous TiN has served as a non-carbon support of PtAg alloys for the ORR in alkaline media, which exhibits much higher mass activity and durability than Pt/C catalysts.\textsuperscript{[19]}

The Pt ORR activity and durability are enhanced by the incorporation of other metallic elements (e.g. Pd, Fe, Co, Ni, and Cu)\textsuperscript{[3, 5, 20, 21]} which can be attributed to their geometric and electronic effects or the Pt d-center downshift.

Herein, we present an ordered-structured electrode based on TiN nanorods (NRs) as the catalyst support of a thin-film PtPdCo catalyst. The TiN NRs, with an extended-surface catalyst coating, were directly grown on the surface of carbon fibers. Figure S1 shows the species transport pathways for oxygen and protons in both conventional Pt/C electrodes and the proposed TiN NR-based electrode. In the proposed electrode, without additional ionomer in the cathode, the water film possibly acted as the proton-conduction pathway. The proposed benefits of this approach are as follows: 1) the removal of ionomers or binders for better fuel transport; 2) elimination of carbon supports; 3) a thin-film, extended-surface PtPdCo catalyst; and 4) low-tortuosity pathways for transportation.

Titanium dioxide NR arrays were first hydrothermally grown on carbon paper and then annealed in ammonia gas to convert them into TiN NRs. The ternary PtPdCo catalysts were sputtered onto the surface of TiN NRs by using physical vapor deposition (PVD), and annealed in a 5%H\textsubscript{2}/Ar atmosphere to enhance the crystallization of the catalysts. To confirm the electrochemical performance, the as-synthesized PtPdCo–TiN electrode was employed as the cathode of a single cell. Furthermore, an advanced degradation test (ADT) showed that the as-prepared PtPdCo–TiN electrode was more stable than the commercial Pt/C in the 2000-cycle test.

### 2. Results and Discussion

The schematic illustration in Figure 1 shows the synthesis process of PtPdCo–TiN NRs on carbon paper. In a typical experimental process, TiN NRs grow on carbon paper in three steps: 1) fabrication of TiO\textsubscript{2} seeds on one side of a carbon paper; 2) hydrothermal growth of TiO\textsubscript{2} NRs on carbon paper; and 3) conversion of TiO\textsubscript{2} NRs into TiN NRs, through ammonification at 900 °C for 2 h.

The corresponding phase transmission of the as-synthesized samples was monitored by using X-ray diffraction (XRD). The hydrothermally grown NR arrays were found to be mainly composed of the rutile phase after being heated at 550 °C for 2 h (Figure 2). After increasing the temperature to 900 °C under an ammonia atmosphere, the as-prepared products mainly consisted of the face-centered cubic-structured TiN phase, as shown by the peaks in Figure 2, except for the peak at 2θ = 54.38°, which was attributed to rutile TiO\textsubscript{2}. In accordance with the energy-dispersive X-ray photoelectron spectroscopy (XPS) results (Figure 3). A broader peak between 42 and 46° in the TiO\textsubscript{2} XRD pattern is attributed to the carbon paper.\textsuperscript{[22]} Owing to the low loading of the PtPdCo catalyst, the (111), (200), and (220) planes are presented in the XRD pattern of PtPdCo–TiN, but the phase is not specified.

In addition to XRD, XPS was used to analyze the chemical state and concentration of the Ti and N atoms in the NR arrays (as shown in Figure 3). After annealing at 900 °C in NH\textsubscript{3}, the XPS spectra of the NR arrays prove the presence of N atoms. The N 1s spectra can be divided into two peaks with binding energies at 396.5–396.8 eV and 397.6 eV, which are consistent with the values of the Ti–N and Ti–O–N bonding energies.\textsuperscript{[23, 24]} N substituted an O atom in the crystal lattice, and the atomic concentration ratio of Ti/N was calculated to be 1.06, according
to the XPS data. The Ti2p spectra of the samples annealed in an ammonia atmosphere can be assigned as Ti–N (2p3/2 = 455.6–455.9 and 2p1/2 = 461.4–461.8 eV), Ti–O–N (2p3/2 = 457.1–457.5 and 2p1/2 = 463.1–463.5 eV), and Ti–O (2p3/2 = 458.7–459.3 and 2p1/2 = 464.4–465.0 eV). Detailed results suggest that the surface chemical states of the as-synthesized NRs are composed of Ti–N, Ti–O–N, and Ti–O.

Figure 4a shows the field-emission scanning electron microscopy (FESEM) images of TiO2 NRs grown on carbon paper. The average diameters of TiO2 NRs are around 120 nm and the average length of a single TiO2 NR is around 1.2 μm (Figures 4a and 4d). The as-synthesized TiO2 NRs were further calcined in an NH3 flow at 900 °C to be transformed into TiN NRs. The morphologies of the TiN NRs without obvious alteration in the NR structure can be seen in Figure 4b. More details of TiN NR can clearly be seen in the transmission electron microscopy (TEM) image, which is displayed in Figure 4e. The TiN NR, with a uniform diameter along the length axis, shows a relatively smooth surface. After the PtPdCo catalyst is deposited on the surface, the TiN NRs are annealed in a 5% H2/Ar atmosphere at 400 °C for 2 h. The morphologies of the PtPdCo–TiN NRs are shown in Figure 4c and the thickness of the NR film was around 1.2 μm before being hot-pressed to form a MEA (Figure 4d). TEM images in Figure 4f reveal that the fresh PtPdCo–TiN NRs were uniformly coated with thin catalyst layer along the length axis.

It can be seen that the catalyst forms whiskerettes on the surface of the TiN NRs with lengths of 6–7 nm (Figure 4f). Hydrogen treatment of the catalysts will help to restructure the surface and rearrange the surface atoms, thus changing the initial activity of the catalyst.[26] After annealing at 400 °C in 5%H2/Ar, the PtPdCo whiskerettes become a thin-film catalyst layer with a thickness of around 5 nm, which coats the surface of the TiN NRs uniformly, as shown in Figures 4g and 5. More details about the thin PtPdCo catalyst layer along the length axis of the TiN NR can be seen in the high-resolution transmission electron microscopy (HRTEM) image (Figure 5). The high-angle angular dark-field (HAADF) scanning transmission electron microscopy (STEM) images show that the three elements of Pt, Pd, and Co are distributed uniformly along the surface of the TiN NRs.

Figure 6 shows the Pt 4f, Pd 3d, and Co 2p XPS spectra for the PtPdCo–TiN electrode after heat treatment. The most intense peak of Pt 4f7/2 is assigned to metallic Pt0. The second peak is assigned to Pt(II), as in PtO and Pt(OH)2, and the third

Figure 3. N1s and Ti2p XPS spectra of the NRs after annealing under an NH3 atmosphere at 900 °C for 2 h.

Figure 4. FESEM images of a) TiO2 NRs, b) TiN NRs calcined under NH3 at 900 °C, d) PtPdCo–TiN NRs calcined at 400 °C, and TEM images of e) TiN NRs, f) fresh PtPdCo–TiN NRs, and g) PtPdCo–TiN NRs after annealing at 400 °C.

Figure 5. HAADF–STEM characterization and elemental mapping of a PtPdCo–TiN NR.
is assigned to Pt(IV). The binding energy of Pt⁴f (4f⁷/₂ = 71.2 eV; 4f⁵/₂ = 74.68 eV) for PtPdCo–TiN was slightly shifted in the positive direction in comparison with that of the referenced bulk Pt⁴f (4f⁷/₂ = 70.15 eV; 4f⁵/₂ = 73.46 eV).[27] The slight shift in bulk metallic Pt⁴f to higher binding energies may be attributed to a significant contribution from the interaction among three metals. It can be noted that Co is an electropositive element, as compared with Pt or Pd, and the electronegativity difference between Co, Pd, and Pt (1.88, 2.20, and 2.28, respectively) produces an electron-withdrawing effect of Pd and Pt from the neighboring Co atoms in the catalyst, which results in upshifting of the Pt binding energy. The XPS results reveal that the PtPdCo catalyst may exhibit an alloy structure. The atomic concentration ratio of Pt/Pd/Co is calculated to be 28.68:0.87:0.78, according to the XPS data.

To investigate the electrochemical performance, cyclic voltammetry (CV) was conducted in a traditional three-electrode system. Figure 7a shows that the CV curves of PtPdCo–TiN electrode have a 72 mV positive shift. Meanwhile, PtPdCo–TiN has a discernible positive shift (ca. 50 mV) in the oxide reduction peak as compared to the Pt/C catalyst,[28] demonstrating that the oxygen is somewhat easier to reduce on the PtPdCo catalyst. The enhancement in activity of PtPdCo–TiN may be attributed to the modified surface electronic structure and a negative shift in the d-band center position induced by strain and ligand effects through alloying.[29] The ORR activity increases relative to that of Pt–TiO₂–C, as mentioned before,[30]

![Figure 6](image_url)  
**Figure 6.** Pt 4f, Pd 3d, and Co 2p XPS spectra of a PtPdCo–TiN sample after heat treatment.

![Figure 7](image_url)  
**Figure 7.** The CV curves of a PtPdCo–TiN electrode a) before and after annealing at 400 °C for 2 h. ADT of b) a PtPdCo–TiN electrode and c) a commercial GDE in N₂-saturated 0.5 M H₂SO₄ solution with a scan rate of 50 mV s⁻¹.
by adding the Pd and Co elements. The durability of the as-synthesized samples was examined by using ADTs in the potential range of 0.0–1.2 V (vs. RHE) for 2000 cycles at a scan rate of 50 mV s⁻¹ (Figures 7b and 7c). The ECSA values of PtPdCo–TiN and the commercial gas diffusion electrode (GDE) before the test were 60.2 and 84.9 μm², respectively. After the ADT, the remaining ECSA of the PtPdCo–TiN electrode was 72.6%, which is larger than that of the commercial GDE (59.5%). This result indicates that the PtPdCo–TiN electrode is more stable than the commercial GDE. After the ADT, the surfaces of the TiN NRs were converted into TiO₂ through electrochemical oxidation. The formation of an electrochemically less active and electrically less conductive TiO₂ layer leads to a significant loss of capacitance. Thus, the double layer of the PtPdCo–TiN electrode shows a significant decrease after 2000 CV cycles.

We now present the single-cell characterization of the TiN NR-based order-structured electrode. Here, the as-prepared electrode, without additional proton-conducting ionomers in the catalytic layer, was used as the cathode of a single cell (shown in Figure S2). The water film is believed to be the secondary ion-conduction pathway. Thus, various humidification conditions were investigated. The proposed order-structured electrode yields a power density as high as 390.5 mW cm⁻² at 90% related humidity (RH, shown in Figure 8). The cell performance was higher than that of the comparable homemade GDE, as mentioned before, even with a lower Pt loading (as illustrated in Figure S2). The reason for the highest cell performance occurring when the conditions were not fully humidified could be attributed to the hydrophilicity of the thin-film electrode. The cell performance of the as-prepared electrode is relatively poor under fully humified conditions, especially in the high-current-density region (the Nyquist plots in Figure S4 prove this phenomenon). Thus, the importance of water management is highlighted for the improvement of the order-structured electrode performance.

One problem that arises in the present TiN NR-based electrode is the relatively low cell performance. The charge-transfer resistance of the TiN NR-based electrode is higher than the commercial GDE, which is the reason for the poor performance. The other reason is that the TiN NRs directly grew on the surface of carbon paper (Figure S3). In addition, the PtPdCo–TiN electrode is susceptible to water flooding (Figure S4); thus, the absence of a microporous layer (MPL) will make the problem worse. One suggestion for solving this issue is to prepare the oriented TiN NRs on a titanium plate, sputtering the catalyst onto the TiN NRs as the 3M NSTF before transferring it to a Nafion membrane. Thus, an order-structured electrode with a better electrode structure than the proposed one would enable us to improve the cell performance.

Hence, to improve performance and stability, the following factors may be considered. 1) An ordered thin catalyst layer structure may be used; the ordered structure within a thin layer benefits mass transport, thereby generating a high performance without additional Nafion ionomer. 2) The PtPdCo catalysts need to be highly accessible by the fuels; the as-synthesized electrodes are free of Nafion ionomer and PTFE and the catalysts are uncovered (without Nafion or binder), and the fuels can easily gain access to the gas–liquid–solid interface (three-phase boundary). 3) Three metals (Pt, Pd, and Co) interact in thin-layer catalysts; the enhancement in the PtPdCo–TiN activity may be attributed to the modified surface electronic structure and a negative shift in the d-band center position induced by the strain and ligand effects through alloying. The lower d-band center position decreases the adsorption energy between the adsorbents and PtPdCo catalyst, thereby enhancing the OH removal and ORR activity. In addition, the high stability of PtPdCo–TiN electrode should be related to the alloying effect. 4) The electrode structure should be optimized, as the thin-film electrode is easily flooded by water, thus a MPL is necessary.

3. Conclusions

In summary, vertically aligned TiN NRs were employed as a thin-film PtPdCo catalyst support. ADT results suggested that the stability of the PtPdCo–TiN electrode after 2000 cycles (72.6% ECSA remaining) was higher than the commercial GDE (59.5% ECSA remaining). With a low Pt loading (66.9 μm²), the as-prepared electrode as the cathode of a single cell yielded a maximum power density of 390.5 mW cm⁻² and a cathode mass-specific power density of 5.84 W mg⁻¹. These values are greater than the commercial Pt/C-based GDE (without additional Nafion ionomer in cathode). The results suggest that the order-structured electrode based on TiN NRs is a viable approach, but it is necessary to further improve the cell performance through structure optimization.

Experimental Section

Preparation of TiN NRs

Vertically aligned TiO₂ NRs on carbon paper were synthesized by using a two-step method in a typical experimental process, TiO₂ NRs were first hydrothermally grown on carbon paper. The
carbon papers (TGP-H-060, Japan) were cleaned in a mixture of de-ionized water, ethanol, and acetone (1:1:1 in volume ratio) for 30 min and dried at room temperature. Then, the cleaned carbon paper was impregnated with 0.05 wt. titanium (IV) chloride aqueous solution on one side for 10 min (under ice bath) and dried. To generate TiO₂ nanoparticles on the surface of the carbon paper, the dried carbon paper was further heated in a furnace in air at 350 °C for 10 min, and this process was repeated several times to ensure uniformity. A tetrabutyl titanate (1.1 mL) solution was dropped into concentrated hydrochloric acid (37 mL), which was diluted with de-ionized water (37 mL) whilst stirring. After stirring for several minutes, the carbon paper coated with TiO₂ seeds was immersed into the mixture and then, together, these were transferred into a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was heated at 150 °C for different durations, and then cooled back to room temperature. Finally, the sample was annealed in a furnace in air at 550 °C for 2 h, which was followed by heat treatment in an ammonia flow (at a flow rate of 60 mL min⁻¹) at 900 °C for 2 h; the samples were donated as TiN-900.

**Preparation of the PtPdCo–TiN Electrode**

The catalysts were deposited onto TiN NRs by using a PVD method, with a working pressure of 1.0 Pa and an input power of 120 W. For the preparation of the PtPdCo–TiN electrode, Co nanoparticles were first sputtered onto the TiN NRs (Co–TiN) and the whole deposition process was maintained for 15 min. Second, Pd nanoparticles were deposited onto Co–TiN NRs for 6 min (PdCo–TiN) and then Pt nanoparticles were deposited onto the PdCo–TiN NRs for 12 min (PtPdCo–TiN). After the deposition process, the samples were heated at 400 °C under 5% H₂/Ar atmosphere with a flow of 30 mL min⁻¹, and these conditions were maintained for 2 h. The total metal loadings of Pt, Pd, and Co in a PtPdCo–TiN electrode sample, as detected by inductively coupled plasma–optical emission spectroscopy (ICP–OES), were 66.9, 35.1, and 1.8 µg cm⁻², respectively.

**Physical Characterization**

FESEM (supra 55; Germany) and TEM (JEM-2000EX at 120 KV) were employed to observe the morphology and structure of the samples. HRTEM (JEM-2100F; Japan) was carried out by using a FEI Tecnai G2F30 microscope operating at 300 KV. The HAADF–STEM image was also studied by using a FEI Tecnai G2F30 microscope. The crystal phase and the composition of the products were measured by using XRD (Bruker D8, Cu Kα radiation) and XPS (Thermo Scientific ESCALab250 Xi spectrometer, Al Kα in twin anode), respectively. The metal contents of the electrodes were measured by using ICP–OES (Leeman Plasma-Spec-I).

**Half-Cell Test**

Electrochemical measurements were conducted by using a conventional three-electrode cell with PtPdCo–TiN or a commercial GDE as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt foil as the counter electrode. N₂-purged 0.5 M H₂SO₄ solution was used as the electrolyte. The ADTs were performed in the potential range of 0.0–1.2 V (vs. RHE) for 2000 cycles with a scan rate of 50 mV s⁻¹ at room temperature. The ECSA was calculated by integrating the areas of the Pt-hydrogen region, assuming 0.21 mC cm⁻² for the desorption charge of a monolayer of hydrogen atoms on a clean Pt surface.[13]

**MEA Preparation and Single-Cell Test**

The MEA employed a homemade catalyst-coated membrane (CCM, membrane: Nafion 212; Pt loading: 0.2 mg cm⁻²) as the anode and PtPdCo–TiN was used as the cathode. Afterwards, it was hot-pressed at 140 °C and 0.2 MPa (gauge) for 2 min. The effective geometric area of the single cell was 4 cm².

During the performance test, the cell operating temperature was maintained at 65 °C. Fully humidified hydrogen and oxygen (99.99% pure) with corresponding flow rates of 50 and 200 ML min⁻¹ at 0.05 MPa (backpressure) were supplied to the anode and cathode, respectively. The high performance of a single cell under partially humidified conditions at the cathode side was also investigated. After fully activated, the KFM-2030 impedance meter (Kikusui, Japan) was used to obtain current–voltage (i–V) curves. The electrochemical impedance spectroscopy (EIS) test was carried out by using a Solartron 1287 electrochemical interface in conjunction with a Solartron 1260 frequency response analyzer in a frequency range from 0.1 Hz to 10 kHz.

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