

Platinum/tantalum carbide core-shell nanoparticles with sub-monolayer shells for methanol and oxygen electrocatalysis

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ABSTRACT

Core-shell architectures provide great opportunities to improve catalytic activity, but achieving nanoparticle stability under electrochemical cycling remains challenging. Herein, we synthesized core-shell nanoparticles comprising atomically thin Pt shells over earth-abundant TaC cores and used them as highly durable electrocatalysts for the methanol oxidation reaction (MOR) and the oxygen reduction reaction (ORR) needed to drive direct methanol fuel cells (DMFCs). Characterization data showed that a thin oxidic passivation layer protected the TaC core from undergoing dissolution in the fuel cell-relevant potential range, enabling the use of partially covered Pt/TaC core-shell nanoparticles MOR and ORR with high stability and enhanced catalytic performance. Specifically, at the anode the surface-oxidized TaC enhanced MOR activity compared conventional Pt nanoparticles. At the cathode, the Pt/TaC catalyst featured increased tolerance to methanol crossover. These results show unique synergistic advantages of the core-shell particles and open opportunities to tailor catalytic properties for electrocatalytic reactions.

Direct methanol fuel cells (DMFCs), involving the methanol oxidation reaction (MOR) at the anode and the oxygen reduction reaction (ORR) at the cathode, offer unique advantages, particularly for small devices, over hydrogen fuel cells due to methanol's high volumetric energy density and ease of storage.¹⁻³ However, despite using state-of-the-art precious metal catalysts in both electrodes, the kinetics of MOR and ORR are sluggish and limit the overall cell performance.^{2,4-6} Therefore, enhancing activity, and stability, while minimizing the use of critical materials is necessary for the large scale implementation of DMFCs. Pt/transition metal carbide (TMC) core-shell nanoparticles pioneered by Román-Leshkov and co-workers show promise in this respect.⁷ For example, Ti-doped WC (TiWC) core covered with Pt or PtRu shell showed superior performance in ORR and MOR, respectively, when compared to benchmark Pt-based catalysts.^{7,8} However, the TiWC core undergoes dissolution when it is in direct contact with acidic electrolytes under ORR conditions, which is hardly avoidable during DMFC operation.⁸

The chemical stability of various TMCs have been comprehensively studied by Chen and co-workers, who demonstrated that the durability of TMCs is correlated with the stability of the oxide passivation layer on the surface that forms spontaneously over these materials under oxidizing potentials.^{9,10} In general, TMCs with parent metals that bind strongly to oxygen are more stable under electrochemical cycling. Recently, Göhl, Ledendecker, and co-workers showed that the transition metal-carbon bond enthalpies govern the electrochemical stability of TMCs and experimentally showed that titanium, tantalum, and zirconium carbides have high stability in acid,^{11,12} which is in line with previous observations.^{9,10} On the other hand, because thermal carburization of oxide-based precursors is an essential step for the synthesis of TMC-based nanoparticles, a strong interaction between the transition metal and oxygen is unfavorable in terms of synthetic feasibility because of the increasingly higher temperatures required for carburization. Among the TMCs that are stable in acid, tantalum carbide has a relatively low oxygen binding energy.¹⁰ Thus, we surmised that tantalum carbide is a suitable core material for Pt/TMC core-shells, satisfying both synthetic viability and stability in acidic environments. Meanwhile, synthesis of tantalum carbide nanoparticles still requires the temperature above 1200 °C,^{13,14} and to the best of our knowledge, tantalum carbide interfaced with Pt has not been synthesized directly owing to the low Tammann temperature of Pt, which would promote significant sintering at the temperature needed for TaC synthesis.

In this study, Pt/TaC core-shell nanoparticles were synthesized for the first time and were applied as highly active and stable electrocatalysts for both MOR and ORR, targeting their potential applications in DMFCs. The synthesis used a high-temperature self-assembly method pioneered by our group,⁷ which enabled Pt monolayers (MLs) to form over the nanosized TaC particles during thermal carburization and mitigated the needed synthesis temperature down to below 1000 °C. Pt/TaC catalysts with sub-ML shell coverages had superior activity in MOR compared to that of bare Pt. In addition, Pt/TaC nanoparticles showed significantly enhanced ORR performance in the presence of methanol, which is necessary due to methanol crossover under realistic DMFC operating conditions. Lastly, the high stability of Pt/TaC under electrochemical operation conditions was investigated using various analytical techniques.

Results

Synthesis and characterization of Pt/TaC nanoparticles

The synthesis route of Pt/TaC core-shell nanoparticles via a high-temperature self-assembly method is summarized as a scheme in Fig. 1. Firstly, TaO_x nanoparticles were prepared in a reverse microemulsion by hydrolysis of tantalum isopropoxide. The Pt precursor was added in a separate, smaller reverse microemulsion batch serving as the shell component. Then, the particles were encapsulated by a silica shell and subjected to thermal carburization at 970 °C in a tube furnace under flow of a gas mixture of 80% H₂ and 20% CH₄, to reduce and carburize TaO_x. Prior work had reported TaO_x carburization temperatures above 1200 °C;^{13,14} however, we hypothesize that Pt facilitates the TaO_x reduction via H₂ spillover and decomposition of CH₄ which serves as the carbon source, thereby substantially decreasing the carburization temperature.¹⁵⁻¹⁸ Pt/TaC nanoparticles supported on carbon were subsequently obtained by dissolving the silica shell using ethanol-diluted hydrofluoric acid solution and then dispersing the particles onto a carbon black support. Pt/TaC nanoparticles with four different shell thicknesses were prepared by using different amounts of Pt precursors. As a reference catalyst, we used commercial carbon-supported Pt nanoparticles (20 wt.%, Premetek), which are hereafter denoted as Pt_{comm}.

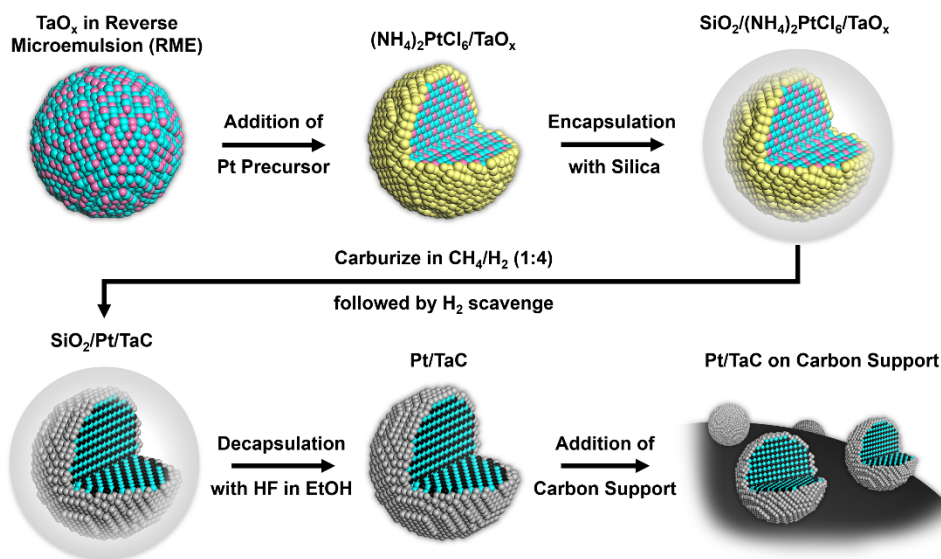


Fig. 1. Synthesis of Pt/TaC core-shell nanoparticles. Schematic overview of the synthetic procedure based on the self-assembly of Pt on TaC during thermal carburization. Silica encapsulation was carried out prior to the carburization to inhibit nanoparticle sintering at high temperature, and the silica shell was removed before incorporation of carbon supports. Color codes: cyan Ta, magenta O, yellow (NH₄)₂PtCl₆, gray Pt, black C.

From the powder X-ray diffraction (PXRD) patterns displayed in Fig. 2a, signals from phase-pure TaC (PDF no. 00-035-0801) were clearly observed while reflections from Pt were not apparent. From the crystallite sizes calculated from PXRD patterns and the Pt:Ta ratio obtained from inductively coupled plasma-mass spectroscopy (ICP-MS), Pt shell thicknesses of the nanoparticles were estimated as 0.2, 0.6, 0.9, and 1.2 ML (see Supplementary Table 1 for details), and the Pt/TaC nanoparticles were named Pt/TaC_0.2 ML, Pt/TaC_0.6 ML, Pt/TaC_0.9 ML, and Pt/TaC_1.2 ML, respectively. The uniformity of the synthesized particles was imperfect; the morphologies of Pt/TaC were characterized by transmission electron microscopy (TEM) analysis, which clearly showed carbon-supported nanoparticles ranging in size from 5 to 20 nm (Fig. 2b and Supplementary Fig. 1). However, the nanoparticles were expected to manifest different electrocatalytic behaviors in average with regard to the calculated Pt ML-coverage. The wetting of Pt on the TaC surface was confirmed by aberration-corrected scanning transmission electron microscopy (STEM) and the corresponding elemental maps acquired by energy-dispersive X-ray spectroscopy (EDX) displayed in Figs. 2c and d (and by additional images shown in Fig. 5a in the later section), respectively.

In order to obtain insights on the chemical state of Pt and TaC with varying shell thicknesses, diverse X-ray techniques were employed. Figure 2e shows the X-ray absorption near edge structure (XANES) spectra of Pt_{comm} and Pt/TaC nanoparticles obtained at the Pt L₂-edge. Although XANES at the Pt L₃-edge is mostly measured as it gives a large amount of information on the 5d states, the L₂-edge was selected because the Ta L₁- and L₂-edges are located close to the Pt L₃-edge and are entangled in the measurement. Nonetheless, prior literature reports indicate that XANES data obtained at the Pt L₂-edge represent the electronic structures reasonably well.¹⁹⁻²² Note the white line intensity was significantly larger for Pt/TaC as compared to that of Pt_{comm}, and increases further with decreasing shell thicknesses. This observation was in line with the trend in the Pt 4f spectra acquired by X-ray photoelectron spectroscopy (XPS) analysis, which showed a larger positive shift for smaller shell thicknesses (Supplementary Fig. 2). Based on the work functions of Pt and TaC,²³⁻²⁵ it is unlikely that Pt would lose charge to TaC and, previously, we thoroughly discussed the genesis of the Pt d-band broadening and the corresponding increase in the white line intensity when the coupling matrix element of TMC's parent metal is larger than that of Pt.²² According to the work by Hammer and Nørskov, Ta has a larger coupling matrix element than Pt, and this leads to broadening of the Pt d-band when the formation of a chemical bond between Pt and Ta takes place.^{26,27} Therefore, we expect a downshift of the Pt d-band center with regard to the Fermi level, given that the d-band filling should be conserved.

The observed trend in Pt-surface coverage was indirectly corroborated by comparing the signals from the carbidic and oxidic features in the Ta 4f XPS spectra (Supplementary Fig. 3). When the nominal Pt-shell thickness increases, the shell increases in homogeneity and a smaller amount of native oxide can be found. In order to investigate the geometric characteristics of the Pt shell on the TaC core, extended X-ray absorption fine structure (EXAFS) analysis was carried out (Fig. 2f). It is known that an increase/decrease in interatomic distance of Pt atoms results in broadening/narrowing of Pt d-band and a consequent downshift/upshift of the d-band center.²⁷⁻²⁹ By fitting the EXAFS spectra (detailed fitted parameters are displayed in Supplementary Table 2), we could compare Pt-Pt distances among Pt_{comm} and Pt/TaC nanoparticles. Although the lattice parameter of face-centered cubic (fcc) Pt (0.39 nm) is smaller than that of TaC (0.44 nm), the presence of the TaC core did not induce notable changes to the Pt-Pt distance. This result indicates that the modifications of the Pt d-band structure observed by both XANES and XPS are mostly attributable to the electronic interaction between Pt and TaC.

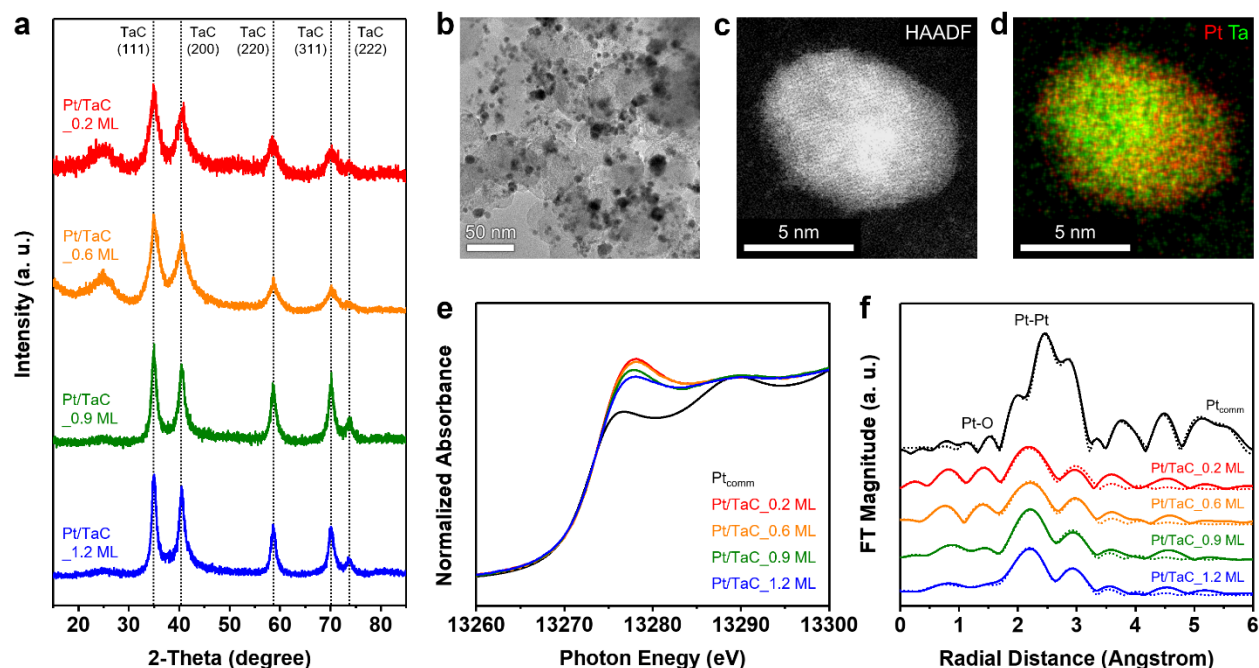


Fig. 2. Materials characterization of Pt/TaC core-shell nanoparticles. (a) PXRD patterns of Pt/TaC core-shell nanoparticles with various shell thicknesses. All patterns were collected from powder samples at a scan rate of 4 °C/min, and the patterns were indexed with regard to the crystal structure of TaC (PDF no. 00-035-0801). (b) Low-magnification TEM image of Pt/TaC_0.6 ML. (c) High-magnification STEM image of Pt/TaC_0.6 ML obtained by using a high-angle annular dark-field (HAADF) detector and (d) corresponding elemental EDX map showing the distributions of Pt and Ta. (e) XANES and (f) Fourier transform of EXAFS spectra of Pt_{comm} and Pt/TaC nanoparticles acquired at the Pt L₂-edge in transmittance mode; solid and dotted lines in the panel (e) show experimental data and the fitted results, respectively.

Methanol oxidation characteristics of Pt/TaC nanoparticles

Considering the potential application of Pt/TaC at the anode for DMFCs, catalyst performance in MOR was first characterized by cyclic voltammetry (CV) measurements in 0.1 M HClO₄ containing 1.0 M methanol (insets of Figs. 3a and b). We compared current densities at 0.5, 0.6, and 0.7 V vs. the reversible hydrogen electrode (RHE; all of the electrochemical potentials are hereafter noted with regard to RHE unless otherwise stated) to obtain specific and mass activities, because background corrections were not viable in the potential range below 0.45 V (Supplementary Fig. 4).³⁰⁻³² Figures 3a and b compare specific and mass activities of Pt_{comm} and Pt/TaC nanoparticles in MOR. Pt/TaC with relatively thin (0.2 ML and 0.6 ML) shell manifested higher MOR activities (both mass and specific) as compared to Pt_{comm}, while those with 0.9 ML

and 1.2 ML-thick shells showed lower activity. At 0.5 V, Pt/TaC_0.2 ML was the most active catalyst, but Pt/TaC_0.6 ML had superior activity at higher potentials. Since potential interference from capacitive currents are expected to be larger when the overall current density is smaller (i.e., at lower potentials), we selected Pt/TaC_0.6 ML as the best-performing catalysts and used it for further investigations. First, we carried out chronoamperometry measurements of Pt_{comm} and Pt/TaC_0.6 ML catalysts at 0.5, 0.6, and 0.7 V (Supplementary Figs. 5a and b). Specific and mass activities were calculated using the current density at 10 min, and they are displayed in Supplementary Fig. 5c and Fig. 3c, respectively. At steady-state, Pt/TaC_0.6 ML clearly featured higher MOR activity compared to Pt_{comm}.

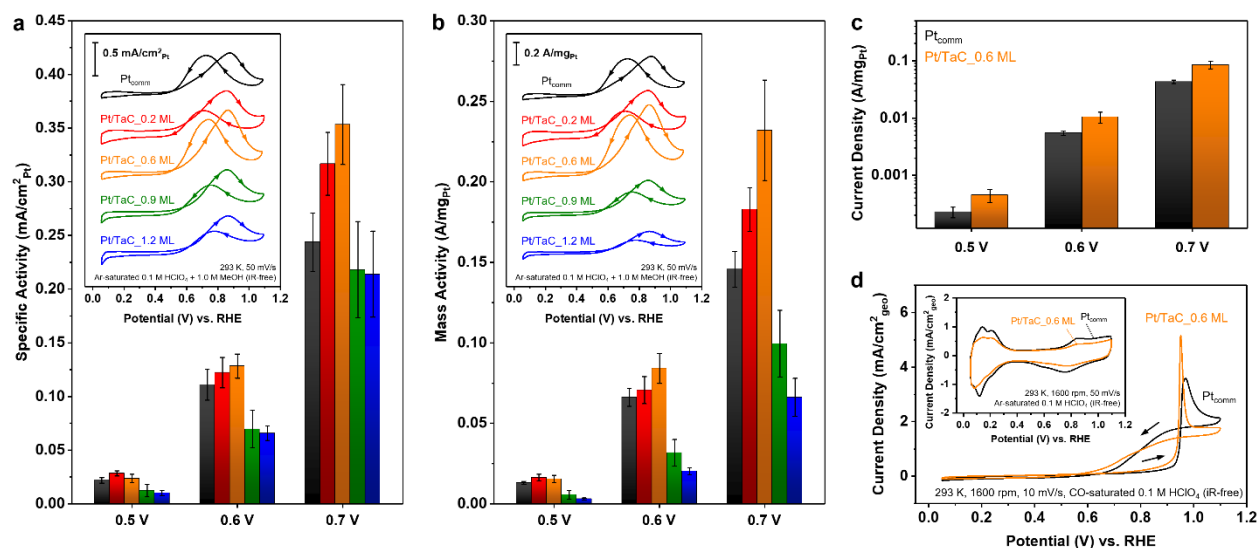


Fig. 3. Electrochemical methanol and CO oxidation characteristics. (a) Specific and (b) mass MOR activities of Pt_{comm} and Pt/TaC core-shell nanoparticles obtained by MOR CV diagrams displayed in the insets; the CV measurements were carried out in Ar-saturated 0.1 M HClO₄ containing 1.0 M MeOH at a scan rate of 50 mV/s without convection. Calculation of activities were performed after the subtraction of background currents. (c) Summary of mass MOR activities of Pt_{comm} and Pt/TaC_0.6 ML from steady-state measurements at various potentials (data shown in Supplementary Fig. 5). (d) CO bulk oxidation characteristics of Pt_{comm} and Pt/TaC_0.6 ML in CO-saturated 0.1 M HClO₄ measured at a scan rate of 10 mV/s and a rotation speed of 1600 rpm; the inset shows CV diagrams obtained without the presence of CO. Error bars show standard deviations obtained from at least three independent measurements.

In light of these results, we then explored the origin of the high MOR activity of Pt/TaC catalysts. It is known that MOR mostly proceeds via methanol dehydrogenation followed by CO

oxidation.³³ Kinetically, the CO oxidation step is rate-limiting on Pt surfaces.³⁴ Figure 3d shows CO bulk oxidation characteristics of Pt_{comm} and Pt/TaC_0.6 ML measured in a CO-saturated 0.1 M HClO₄ electrolyte. CO oxidation on Pt/TaC_0.6 ML took place at an earlier potential relative to that on Pt_{comm}, indicating that Pt/TaC has weaker CO binding. This is consistent with the Pt characterization results showing an increased white line intensity in XANES and positive shift of Pt 4f spectra in XPS. CO oxidation on Pt takes place via a Langmuir-Hinshelwood mechanism where neighboring, adsorbed -OH groups react with adsorbed -CO to form CO₂.³⁵ The inset of Fig. 3d shows the CV curves of Pt_{comm} and Pt/TaC_0.6 ML measured in Ar-saturated 0.1 M HClO₄, from which negligible differences in -OH formation on Pt_{comm} and Pt/TaC could be observed. From these results, a change in CO adsorption characteristics by the presence of TaC could be regarded as one of the reasons for superior MOR performance in Pt/TaC nanocatalysts. Indeed, electronic interactions between TaC core and Pt shell, which presumably leads to the downshift of Pt d-band center, can reduce CO adsorption strength on the Pt surface and enhance the overall CO oxidation performance. We additionally obtained CO stripping results of Pt_{comm} and Pt/TaC_0.6 ML and verified that Pt/TaC is more resistant to CO poisoning (Supplementary Fig. 6).

In addition to the weaker CO binding, the specific MOR activities of Pt/TaC with nearly complete Pt-coverage (0.9 ML and 1.2 ML) were similar, but both were lower than that of Pt_{comm} (Fig. 3a). Given that the Pt shell exhibited a similar electronic structure changes as those found for subML coverages (Fig. 2e), it appears that electronic interactions between TaC and Pt alone cannot explain the enhanced MOR performance for Pt/TaC_0.6 ML. We hypothesize the TaC surface exposed to the electrolyte plays a critical role in enhancing MOR activity. In the MOR potential region, an oxide passivation layer forms spontaneously on the surface of TaC,¹⁰ enriching the surface with -OH groups. For shell thicknesses below 1 ML, CO oxidation can be facilitated by a bifunctional effect^{32,36} at the interface between Pt and surface-exposed TaC, where the reaction between -CO on Pt and -OH on passivated TaC may take place (Supplementary Fig. 7a). This surface composition matches well with the narrow CO bulk oxidation peak of Pt/TaC_0.6 relative to that of Pt_{comm}. The CO oxidation potential is dependent to facets and coordination environment in Pt_{comm},^{37,38} and interfacial sites between Pt and TaC would provide a relatively uniform environment for CO oxidation. Meanwhile, when the shell coverage of Pt/TaC is close to or slightly larger than 1 ML, the influence of adsorbed -OH on the exposed TaC surface is not significant anymore. However, oxidation of TaC might occur to some extent through pinholes in

the Pt shell, which is analogous to our previous observations from Pt/TiWC²² and XPS results showing the presence of native TaO_x even when the thickness of Pt shell is 1.2 ML (Supplementary Fig. 3). The oxide layer that forms between TaC and Pt seems to be decreasing the overall electrical conductivity of the catalysts, leading to lower electrocatalytic activity for the Pt/TaC_0.9 ML and Pt/TaC_1.2 ML catalysts (Supplementary Fig. 7b). Indeed, this hypothetical interpretation of our experimental observations regarding the origin of the MOR activity trend of the core-shell nanoparticles with regard to the Pt shell coverage is currently the subject of active investigations in our groups.

Oxygen reduction characteristics and electrochemical stability of Pt/TaC

We evaluated Pt/TaC nanoparticles as catalysts for the cathodic ORR. Figure 4a shows the ORR polarization curves of Pt_{comm} and Pt/TaC with different shell thicknesses. Specific and mass activities were calculated at 0.9 V using the Koutecky-Levich equation,³⁹ and the results are summarized in Fig. 4b. Pt/TaC nanoparticles were not as active as Pt_{comm} for the ORR, even when normalizing the current densities by the mass of Pt. Based on the comparison among the Pt/TaC catalysts, the optimum Pt shell thickness was 0.6 ML in terms of the ORR performance, and Pt/TaC_0.6 ML was thereby selected for further studies. To gain insights into the role of the TaC in the reaction kinetics, ORR polarization curves were obtained under various rotation rates (Supplementary Fig. 8), and electron transfer numbers of Pt_{comm} and the best-performing Pt/TaC core-shell nanoparticles (Pt/TaC_0.6 ML) were calculated by a Koutecky-Levich analysis (details are provided in the Supplementary Information).³⁹⁻⁴¹ We obtained identical electron transfer numbers (4.08 electrons) for both Pt_{comm} and Pt/TaC_0.6 ML (Supplementary Fig. 9) indicating that the reaction mechanism does not change in the presence of TaC. Similar Tafel slopes were also observed from the ORR characteristics of all catalysts investigated in this study (Supplementary Fig. 10), though the Tafel slopes of Pt/TaC core-shell nanoparticles were larger than that of Pt_{comm} and the slope increased with thicker Pt shells.

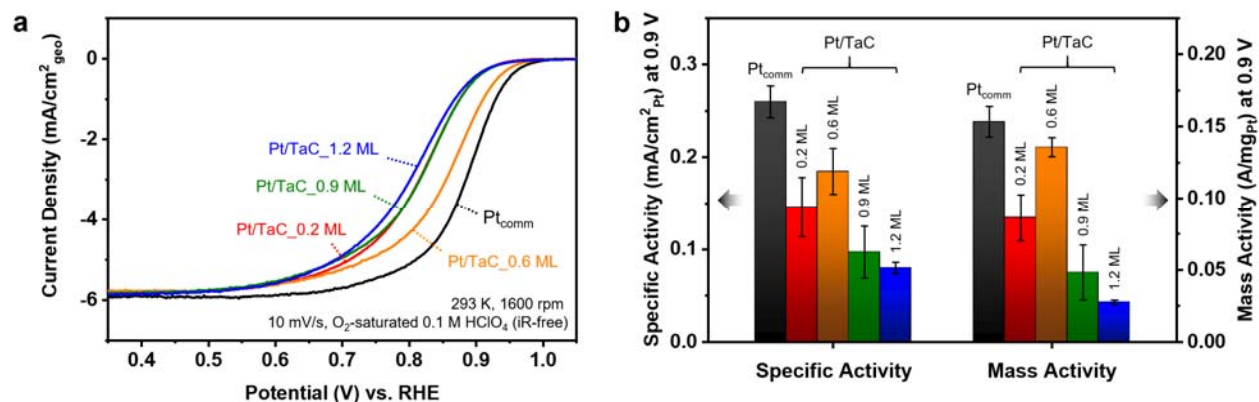


Fig. 4. Electrochemical oxygen reduction characteristics. (a) ORR polarization curves of Pt_{comm} and Pt/TaC core-shell nanoparticles with various shell thicknesses. All of the measurements were carried out in O₂-saturated 0.1 M HClO₄ at a scan rate of 10 mV/s and a rotation speed of 1600 rpm. The polarization curves were obtained by subtraction of capacitive currents. (b) Specific and mass ORR activities of Pt_{comm} and Pt/TaC core-shell nanoparticles at 0.9 V. Error bars show standard deviations obtained from at least three independent measurements.

Next, we explored the stability of Pt/TaC at conditions relevant to DMFC operation. Since the stability of fuel cell catalysts are mostly challenged by oxidative degradation at high potentials, we carried out various analyses under ORR conditions. First, Pt/TaC_0.6 ML was characterized before and after the accelerated stress test (AST; 10,800 potential cycles in 0.1 M HClO₄ within the potential range of 0.4 to 1.0 V at a scan rate of 1.0 V/s) by using identical location (IL)-STEM with corresponding elemental EDX mappings (Fig. 5a and Supplementary Fig. 11). The changes in morphology were negligible even after 10,800 potential cycles, and the elemental EDX maps clearly show that the locations of Pt and Ta did not change during the AST.

Moreover, excellent stability of the TaC core was corroborated by comparing Pt/TaC_0.6 ML and Pt/TiWC reported in our previous studies^{7,8} using scanning flow cell (SFC)-ICP-MS measurements during 1,000 potential cycles in AST conditions (Supplementary Figs. 12 and 13). The average thickness of Pt/TiWC was ~2 ML, indicating that significant portion of the particles are completely covered with Pt shell. However, the amount of dissolved core metals after the potential cycles was smaller in the case of Pt/TaC_0.6 ML by approximately two orders of magnitude, and the difference was even larger (up to around three orders of magnitude) when the dissolution amount observed during the initial stabilization at open circuit is included. Meanwhile, although the fraction of dissolved Pt shell was slightly smaller for Pt/TaC_0.6 ML, its shell was more vulnerable to dissolution during the potential cycles. This is likely attributable to its low

shell-coverage, as a core completely covered with the shell is protected from surface oxidation,⁸ which weakens chemical adhesion between the core and shell.⁷ The highly durable characteristics of Pt/TaC nanoparticles with different dimensions and shell coverages will be discussed in a separate study focusing on electrochemical stability.⁴²

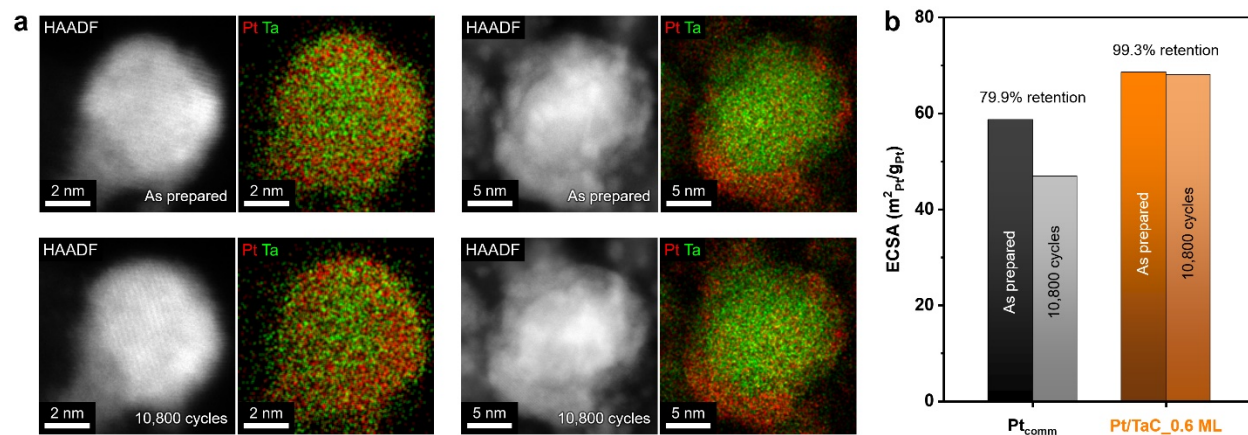


Fig. 5. Structural stability of Pt/TaC core-shell nanoparticles. (a) IL-STEM images and corresponding elemental EDX maps of Pt/TaC_0.6 ML before and after 10,800 AST cycles in Ar-saturated 0.1 M HClO₄ from 0.4 to 1.0 V with a scan rate of 1.0 V/s. (b) ECSAs of Pt_{comm} and Pt/TaC_0.6 ML before and after the AST in O₂-saturated 0.1 M HClO₄ electrolyte at the same potential range and the scan rate. ECSAs were calculated from the H_{upd} region in Supplementary Fig. 14.

We studied the development of the electrochemically active surface area (ECSA) of Pt_{comm} and Pt/TaC nanoparticles before and after the AST (Fig. 5b and Supplementary Fig. 14). Based on the adsorption/desorption charges in the H_{upd} region, the ECSA decreased around 20% for Pt_{comm}, and less than 1% for Pt/TaC_0.6 ML. Interestingly, the CV curves of Pt_{comm} and Pt/TaC_0.6 ML before and after the AST showed a unique difference (Supplementary Fig. 14). In the case of Pt_{comm}, both currents originating from adsorption and desorption of hydrogen and oxygen species decreased in similar proportions. On the other hand, for Pt/TaC_0.6 ML the current decrease was most apparent within the potential region related to oxygen species. Additionally, the H_{upd} profile changes for Pt/TaC_0.6 ML suggest the possibility of rearrangement or dissolution/redeposition of Pt atoms on the TaC surface during potential cycling.⁴³⁻⁴⁵ As Pt favors to form chemical bonds with metals in TMCs rather than carbon or oxygen in the passivation layer,⁷ Pt might rearrange as the surface oxidation of the TaC core occurs. The decrease in ORR performance after the AST was

more significant in Pt/TaC than Pt_{comm} (Supplementary Fig. 15), and this could be attributed to the thickening of TaO_x passivation layer and the rearrangement of Pt atoms, as the ORR activity of Pt is strongly dependent on exposed facets and the coordination environment at the surface.^{44,45}

Oxygen reduction characteristics of Pt/TaC under the presence of methanol

Even in the most advanced DMFCs, diffusion of methanol from the anodic to the cathodic chamber through the membrane is inevitable.^{46,47} This methanol crossover causes MOR to take place at the cathode, which results in the negative shift of cathodic potential and CO poisoning that significantly decreases the overall cell voltage.^{48,49} Therefore, it is important to develop methanol-resistant ORR catalysts for DMFC cathodes. While state-of-the-art PtRu alloy catalysts can manage methanol crossover and CO poisoning to some extent, the kinetics for the ORR are sluggish under these conditions.^{32,50,51}

We investigated the ORR characteristics of Pt/TaC in the presence of methanol in order to evaluate the feasibility of Pt/TaC under more realistic DMFC cathodic conditions. Supplementary Fig. 16 shows ORR polarization curves of Pt_{comm} and Pt/TaC_0.6 ML measured in O₂-saturated 0.1 M HClO₄ containing 1.0 M methanol. Since MOR and ORR compete for the same catalytic sites, we could not calculate activities by removing background currents Ar-saturated electrolyte. We therefore averaged the forward and backward scans and then calculated specific and mass activities, which are summarized in Figs. 6a and b, respectively. Pt/TaC showed significantly higher activities compared to those of Pt_{comm}. In particular, mass activity of Pt/TaC was more than two times that of Pt_{comm} at the potential above 0.7 V (Supplementary Fig. 17). This difference could be attributed to higher CO oxidation and MOR performances of Pt/TaC. Since the electrolytes used in the electrochemical analysis of both catalysts had identical methanol concentration and were saturated with O₂, Pt/TaC which can manage methanol faster than Pt_{comm} would be able to reduce a larger number of oxygen molecules per active site. As a result, Pt/TaC manifested a significantly higher ORR activity than Pt_{comm} in the presence of methanol, and the feasibility of Pt/TaC catalysts for both electrodes of DMFC could be clearly verified.

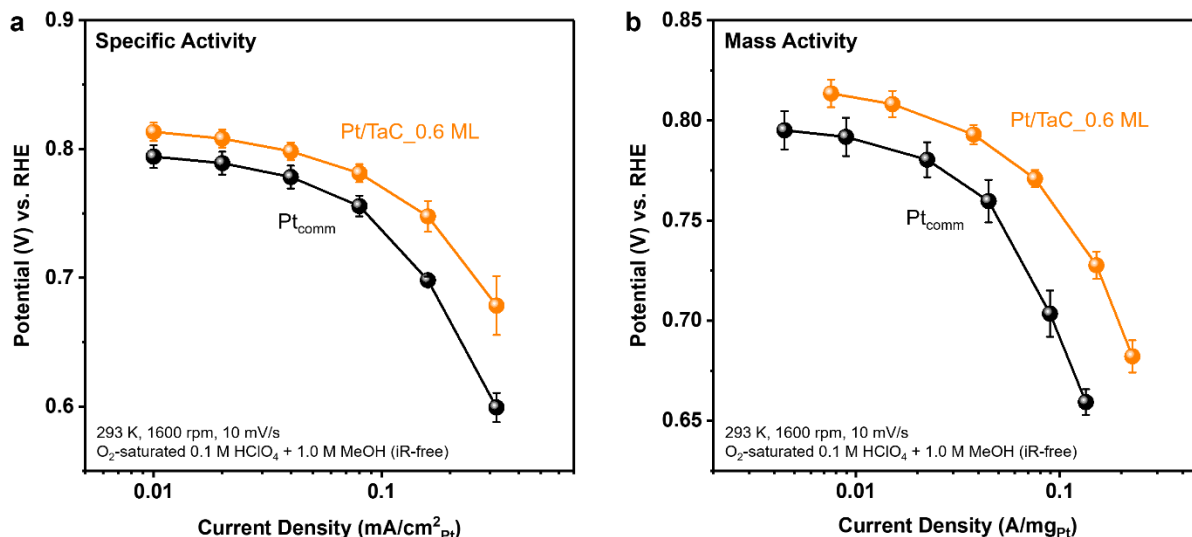


Fig. 6. Electrocatalytic oxygen reduction characteristics under the presence of methanol. (a) Specific and (b) mass ORR activities of Pt_{comm} and Pt/TaC_0.6 ML (obtained from ORR curves shown in Supplementary Fig. 16) measured in O₂-saturated 0.1 M HClO₄ containing 1.0 M MeOH at a scan rate of 10 mV/s and a rotation speed of 1600 rpm. Calculation of activities were performed after averaging the forward and backward scans, and the error bars show standard deviations obtained from at least three independent measurements.

Discussion

In this study, Pt/TaC core-shell nanoparticles were synthesized and applied as electrocatalysts for the MOR and ORR. TaC was chosen as a core material due to its high stability at low pH values and at high potentials. Pt/TaC nanoparticles with sub-monolayer shell thicknesses showed superior MOR activity compared to that of Pt_{comm} as a result of weaker CO binding strength on Pt and the participation of surface-oxidized TaC in the reaction. In the presence of methanol, Pt/TaC showed a significantly higher ORR activity compared to Pt_{comm}. Stability of Pt/TaC during electrochemical cycling was also thoroughly investigated based on a variety of analytical techniques, which unveiled that the portion of dissolved core material during 10,800 cycles of AST was around 3 orders of magnitude smaller than that of the previous reported Pt/TiWC system. This work shows that Pt/TaC could serve as an early-stage platform for designing stable core-shell nanoparticles for applications in diverse electrochemical and catalytic systems, given their high versatility and wide room for further enhancements by compositional and structural engineering. Furthermore, our

study opens up opportunities to tailor the property of core-shell nanoparticles by demonstrating that core materials that are sufficiently stable can take part in catalysis and modify reaction kinetics.

Data availability

The data generated or analyzed during this study are included in the published article and its Supplementary Information file. Source data are provided with this paper.

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Author contributions

Z.W., J.S.K., Y.S.-H., M.L., and Y.R.-L. conceived this study. Z.W. synthesized the materials and performed physicochemical characterizations. J.S.K. designed and conducted electrochemical analysis. D.G. and P.P. carried out the stability-related in situ analysis. D.S.G. and D.Z. performed

quantitative analysis of the EXAFS spectra. The manuscript was written by J.S.K., Z.W., Y.R.-L.,
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Competing interests

The authors declare no competing interests.

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