

Enhancing Fuel Cell Durability with Heteroenergetic TaO_x-Carbon Support

Suyeon Choi,[†] Doosun Hong,[†] HyunWoo Yang, Jeonghan Roh, Jaeyoung Yoo, Changsoo Lee, MinJoong Kim, Young Hwa Yun, Kihoon Bang, Jong Min Kim, EunAe Cho, Sang Soo Han,^{*} Donghun Kim,^{*} and Hyuck Mo Lee^{*}



Cite This: *ACS Energy Lett.* 2024, 9, 4265–4272



Read Online

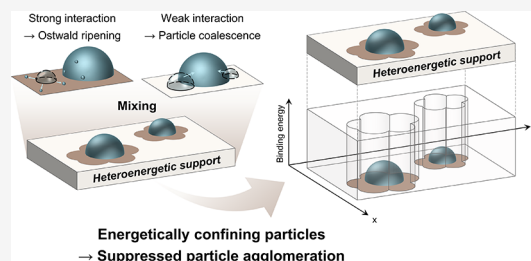
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: Attaining the high durability of supported metal catalysts in heterogeneous catalysis remains a significant challenge. Here, we introduce a mixed tantalum oxide-carbon support for an oxygen reduction reaction catalyst in alkaline fuel cells, aiming to address the degradation arising from suboptimal metal–support interactions. The composite support, conceptualized as a heteroenergetic support, comprises two distinct components exhibiting substantially disparate affinities for metal nanoparticles (NPs). This unique configuration ensures the effective stabilization of the metal NPs on the support. The Au-doped Pd NPs on the mixed tantalum oxide-carbon support exhibit fully sustained mass activity even after a 10000-cycle accelerated durability test. This exceptional durability is ascribed to the effective suppression of the particle agglomerations, as elucidated through transmission electron microscopy and X-ray photoelectron spectroscopy. Our study highlights the efficacy of a heteroenergetic support as a compelling approach for achieving ultradurability in catalytic operations and indicates the broad applicability of this strategy for diverse reactions.



Supported metal catalysts are indispensable in various industrial processes and play critical roles in chemical production and renewable energy generation. These catalysts rely on support materials to provide a framework for anchoring or dispersing catalytically active metal particles, ensuring the maximum exposure of active sites for efficient catalysis. However, during operation, supports often suffer from metal particle detachment, migration, and coalescence, leading to diminished efficacy over time. Additionally, Ostwald ripening, where smaller metal particles dissolve and redeposit onto larger particles, further exacerbates the degradation of supported metal catalysts.^{1–8}

A notable example of this degradation is observed in the current state-of-the-art Pt/C catalysts in anion exchange membrane fuel cells (AEMFCs), which exhibit inadequate durability for prolonged operation.^{9–11} Despite the renowned stability of Pt against dissolution at high pH,¹² Pt/C catalysts experience destabilization in an alkaline environment due to significant Pt aggregation and detachment.^{13–16} To address this challenge, several studies have attempted to mitigate the loss of support functionality by modulating the metal–support interaction (MSI).^{17–21} For instance, the deposition of Pt onto tin-doped indium oxide affected the stability of catalysts with strong MSIs;¹⁷ moreover, the synergistic effect within Pt–CaMnO₃ prevented Pt agglomeration, resulting in significantly improved catalytic durability compared to Pt/C.¹⁸ In addition,

Pd was uniformly supported on defective TiO₂ to enhance both the activity and durability.²¹ While these approaches have shown improved durability compared to commercial Pt/C, they have not achieved the ultimate stability.

In this paper, we present a novel approach utilizing a mixed tantalum oxide-carbon support as an alternative to suppress the substantial aggregation and detachment of metal nanoparticles (NPs). Drawing inspiration from studies on preventing particle agglomerations in thermal catalysts,^{22–24} we employ a support composed of a mixture of two distinct materials with significantly different binding affinities to the catalyst material—a heteroenergetic support. This heteroenergetic support is characterized by one component having a strong interaction with the metal and the other component having a weak interaction with the metal; as a result, this support is capable of effectively stabilizing the metal particles, thereby enhancing the catalytic durability.²² We applied this strategy to AEMFCs by incorporating a mixed tantalum oxide-carbon support with Au-

Received: July 17, 2024

Accepted: July 31, 2024



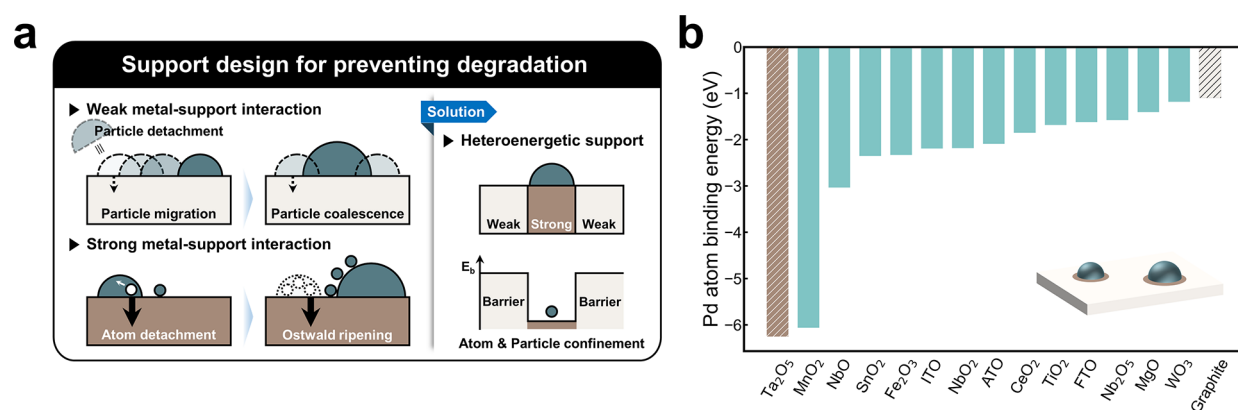


Figure 1. Heteroenergetic support design using DFT calculations. (a) Schematic illustration of a heteroenergetic support. (b) DFT calculation results for the interaction (binding energy) of Pd atoms with 14 commonly used metal oxides, alongside graphite. On the *x*-axis, ATO, ITO, and FTO denote antimony-doped tin oxide, indium tin oxide, and fluorine-doped tin oxide, respectively.

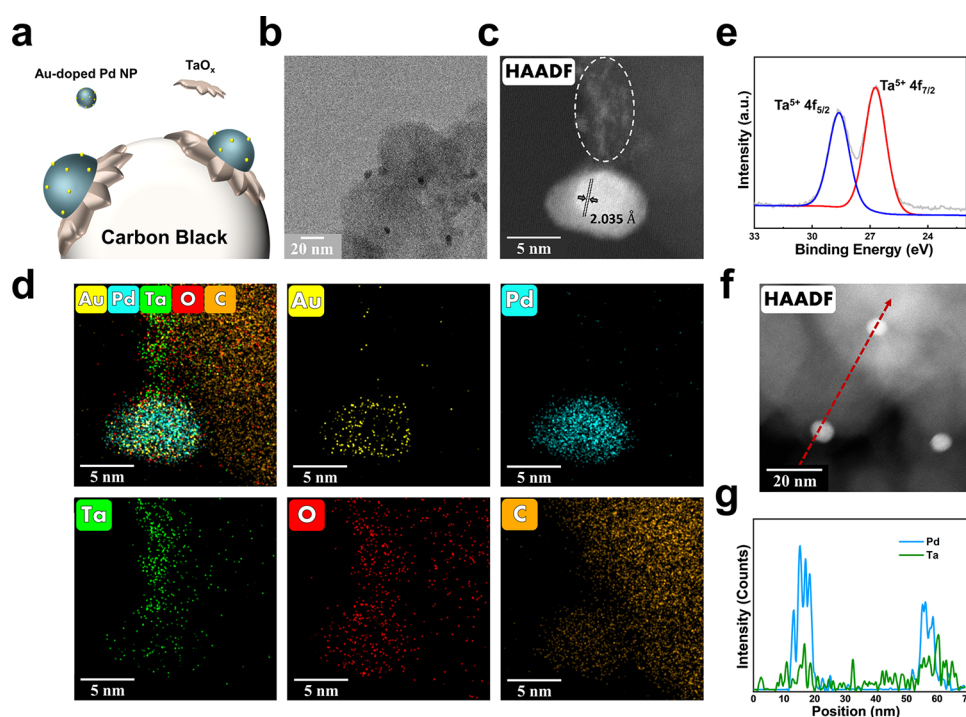


Figure 2. Characterization of the Au-Pd NPs on the mixed TaO_x and carbon support. (a, b) Schematic illustration and TEM image of Au-Pd/TaO_x/C. (c, d) HAADF-STEM image and the corresponding EDS elemental mappings of Au-Pd/TaO_x/C. (e) XPS spectrum of the Ta 4f level on Au-Pd/TaO_x. (f, g) HAADF-STEM image of Au-Pd/TaO_x/C at a lower magnification and the line scanning profile of Pd and Ta.

doped Pd metal NPs, resulting in zero loss in mass activity (MA) even after a 10000-cycle accelerated durability test (ADT). Through comprehensive transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) analyses, we confirmed that this exceptional durability could be attributed to the highly stabilized metal particles on the heteroenergetic support. Our study provides a novel approach to designing supports for highly stable supported metal catalysts, which offers an alternative to the conventional use of single support materials with suboptimal MSIs.

HETEROENERGETIC SUPPORT DESIGN USING DFT CALCULATIONS

In this section, the concept of the heteroenergetic support and its relevance in material selection are elucidated by using density functional theory (DFT) calculations. The durability

loss observed in supported metal catalysts often stems from three primary mechanisms: metal particle detachment, particle migration and coalescence (PMC), and Ostwald ripening. Weak interactions between the metal particles and the support typically facilitate both particle detachment and PMC. To mitigate these degradation pathways, enhancing the strength of MSIs by substituting supports with strong MSIs is a common approach.¹ However, this approach may trigger Ostwald ripening, which also contributes to degradation. A support material exhibiting a stronger interaction than the cohesive energy of the small metal particles can catalyze atom detachment from these particles, which initiates Ostwald ripening.^{4,25,26} The Sabatier principle of MSI for stabilizing supported metal catalysts emphasizes the importance of optimizing MSIs, while also implies inherent limitation for improving the durability.²²

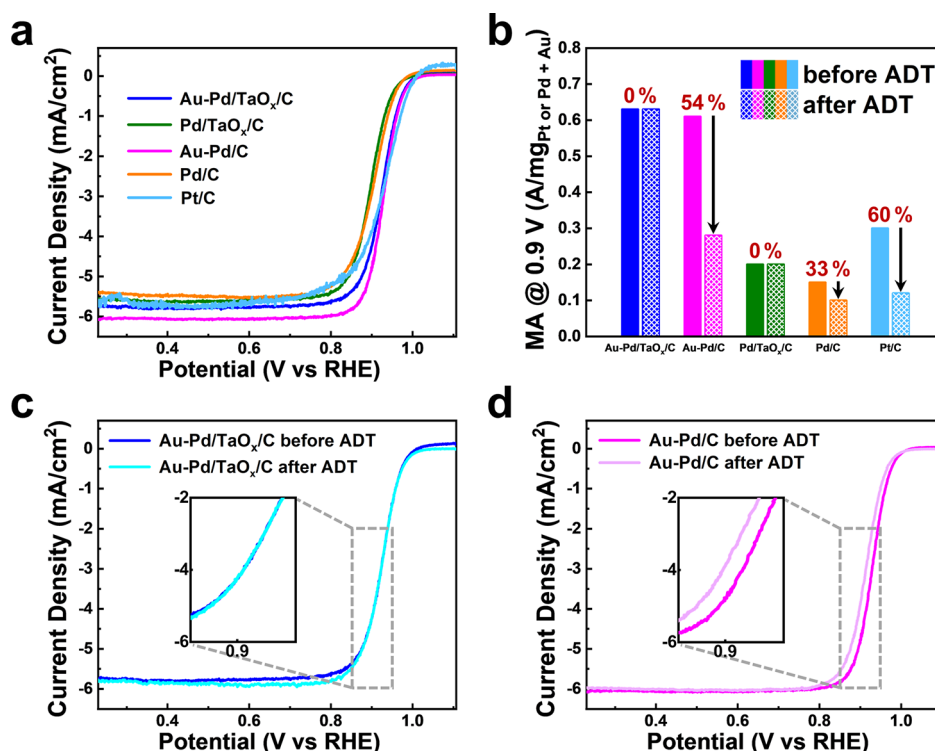


Figure 3. Degradation results for the ORR catalytic performance of Au-Pd/TaO_x/C and other comparative catalysts in half-cell measurements. (a) ORR polarization curves of Au-Pd/TaO_x/C and other catalysts. (b) MA comparisons of Au-Pd/TaO_x/C and other catalysts before and after ADT. ORR curves acquired before and after the ADT of (c) Au-Pd/TaO_x/C and (d) Au-Pd/C.

To achieve ultradurable supported metal catalysts beyond the Sabatier limit, the concept of a heteroenergetic support was recently proposed by Hu et al.,²² although experimental validation was lacking. A heteroenergetic support consists of a mixture of two materials with significantly different binding affinities to catalyst materials (Figure 1a). When these materials are alternately distributed, the particles preferentially settle on the material with a stronger binding energy, while the material with a weaker binding energy acts as a barrier against atom migration, thus suppressing the second elementary step of Ostwald ripening. Consequently, a heteroenergetic support provides a promising avenue for mitigating all three degradation mechanisms (particle detachment, PMC, and Ostwald ripening), potentially maximizing catalyst robustness.

In this study, we applied a heteroenergetic support strategy to address the degradation challenges encountered in the oxygen reduction reaction (ORR) within AEMFCs. Leveraging the inherent stability of Pd and various metal oxides in alkaline environments,^{27–32} Pd and several metal oxides are considered potential candidates for supported metal catalysts. Carbon, which is a prototypic support in this domain, was also considered. Using DFT calculations, we computed the binding energies of Pd atoms on 14 commonly used metal oxides and graphite (a representative carbon support material),^{17,33–42} as shown in Figure 1b. Structural information on the modeled candidates, including space group, exposed surface plane, dopant composition, and binding energies, is summarized in Table S1 and Figure S1. Among the candidates, Ta₂O₅ exhibited the strongest interaction, while graphite displayed the weakest interaction. Based on these screening results, mixed tantalum oxide-carbon emerged as a potentially effective material for a heteroenergetic support.

SYNTHESIS AND CHARACTERIZATION OF THE METAL NPs ON THE MIXED TaO_x-CARBON SUPPORTS

We synthesized Au-doped Pd NPs and deposited them onto supports consisting of tantalum oxide (TaO_x) and carbon black (CB), as depicted in Figure 2a. Note that both pure Pd NPs and Au-doped Pd NPs were experimentally examined, considering the known enhancement of Pd activity through Au doping for the ORR in AEMFCs.^{43–46} The synthesis of Au-doped Pd NP catalysts involved a three-step process: (1) the simultaneous synthesis of Pd NPs and TaO_x via chemical reduction using oleylamine, (2) the subsequent Au doping on the surface of the Pd NPs, ensuring even deposition without agglomeration by controlling the reduction rate of the Au precursor with trioctylphosphine, and (3) the deposition of the synthesized Au-Pd/TaO_x NPs onto CB, forming a heteroenergetic support consisting of TaO_x and CB. To provide a comparative perspective, we prepared Pd/TaO_x/C, Au-Pd/C, and Pd/C as references to clarify the effect of the heteroenergetic support and Au doping.

TEM imaging confirmed the uniform dispersion of the NPs on the support, as shown in Figure 2b. For a more comprehensive characterization, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was employed at higher magnification (Figure 2c), using lattice fringe spacing to identify the NPs. Lattice fringe analysis revealed a slight increase in the lattice fringe within the NPs (measuring 2.035 Å); this lattice corresponded to the (200) plane of Pd and the increase was attributed to Au doping since Au has a larger lattice fringe (2.039 Å) than Pd (1.967 Å). Notably, the identified Pd particle came into direct contact

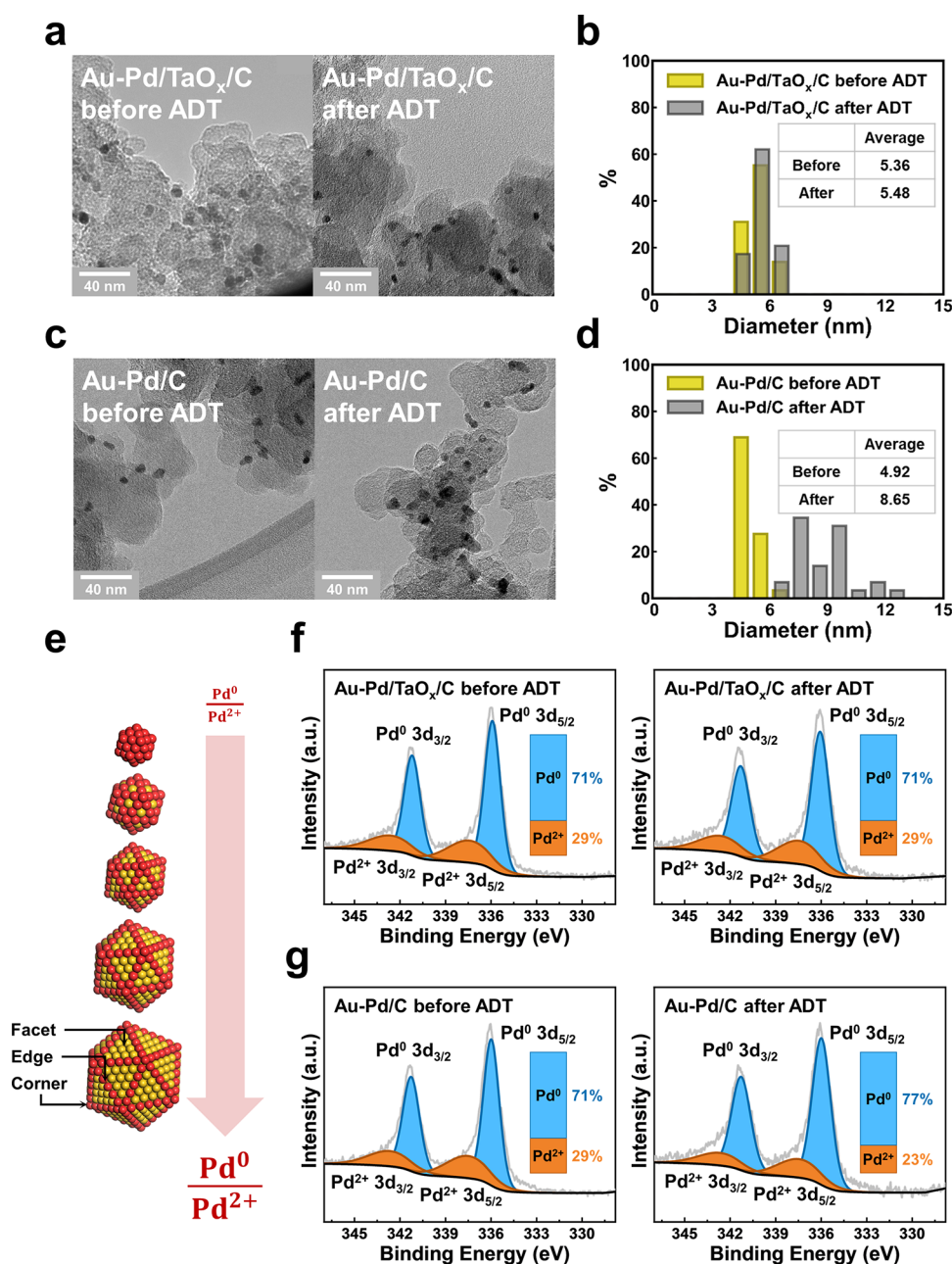


Figure 4. Suppression of the NP enlargement enabled by a heteroenergetic support (TaO_x-C). (a) TEM images and (b) NP size distribution before and after ADT of Au-Pd/TaO_x/C. (c) TEM images and (d) NP size distribution before and after ADT of Au-Pd/C. (e) Schematic of the NPs with varying diameters, highlighting atoms in corners and edges (red) and atoms on facets (yellow). XPS spectra of the Pd 3d level before and after ADT of (f) Au-Pd/TaO_x/C and (g) Au-Pd/C.

with the support material devoid of discernible crystallinity (Figure 2c, highlighted by a circle with a dotted white line).

To gain a deeper understanding of the composition of the catalyst and support, energy-dispersive X-ray spectroscopy (EDS) mapping of Au, Pd, Ta, and C was performed (Figure 2d). The analysis confirmed the presence of Au-doped Pd NPs, as evidenced by the overlapping distribution of Pd and Au; these results were consistent with the lattice fringe analysis. The poorly crystalline material observed in the HAADF-STEM image of Figure 2c was identified as tantalum oxide, as corroborated by the distribution of Ta and O. The broad peaks observed in the XRD analysis of tantalum oxide further confirmed its amorphous nature (Figure S2). XPS analysis confirmed that the oxidation state of tantalum oxide (Ta⁵⁺ 4f

peaks) was Ta₂O₅, as shown in Figure 2e.⁴⁷ In addition, EDS mapping indicated that tantalum oxide was adjacent to CB; thus, the support consisted of amorphous tantalum oxide and CB. Based on these analyses, we characterized the Au-Pd/TaO_x/C system with Au-doped Pd NPs anchored on tantalum oxide owing to their strong interaction with Pd according to DFT calculations.

Importantly, the NPs were predominantly distributed over the tantalum oxide regions of the support. The EDS line scanning results for Pd and Ta in low-magnification HAADF-STEM images further confirmed the alignment of the Pd and Ta signals, supporting the selective positioning of Pd NPs on the TaO_x portion (Figure 2f,g and Figure S3). The preferential adhesion of NPs to regions with stronger binding energies was

the desired outcome of the heteroenergetic support. Notably, irrespective of the presence of Au doping, Pd/TaO_x/C promoted the deposition of Pd NPs onto the tantalum oxide portion of the support (Figure S5).

■ EXCEPTIONAL CATALYTIC DURABILITY OF Au-Pd/TaO_x/C

Electrochemical measurements were conducted on the four synthesized catalysts (Au-Pd/TaO_x/C, Pd/TaO_x/C, Au-Pd/C, and Pd/C) and commercial Pt/C in an alkaline environment. First, we explored the impact of Au doping on the ORR performance by comparing linear sweep voltammetry (LSV) curves of these five catalysts (Figure 3a). Both Au-Pd/TaO_x/C and Au-Pd/C exhibited ORR activities superior to those of Pt/C; their ORR activities surpassed those of Pd/TaO_x/C and Pd/C, respectively. Specifically, Au-Pd/TaO_x/C had a half-wave potential of 0.925 V and a limiting current of 5.79 mA/cm², while Pd/TaO_x/C had a half-wave potential of 0.897 V and a limiting current of 5.62 mA/cm²; these results highlight the efficacy of Au doping in enhancing ORR activity.

To assess the role of the heteroenergetic support in enhancing catalyst durability, we measured MA at 0.9 V before and after 10000 cycles of ADT (Figure 3b). Au-Pd/TaO_x/C exhibited an unchanged MA after ADT, confirming its remarkable stability, consistent with our prediction regarding the synergistic effect of the heteroenergetic support. Pd/TaO_x/C, featuring the same heteroenergetic support as Au-Pd/TaO_x/C, also displayed sustained MA after ADT. However, both Au-Pd/C and Pd/C, where Pd particles were deposited on CB without TaO_x, exhibited significant decreases in MA of 54% and 33%, respectively.

The durability of Au-Pd/TaO_x/C was further confirmed by comparing the LSV curves before and after ADT. For Au-Pd/TaO_x/C, both the half-wave potentials and limiting currents remained constant after ADT (Figure 3c). The inset of Figure 3c depicts that the mixed kinetic-diffusion control region showed no changes even after 10000 cycles of ADT. Conversely, the LSV curve of Au-Pd/C was negatively shifted after ADT, indicating a decrease in the half-wave potential (Figure 3d). Similar to the above analysis of the Au-Pd NPs, Pd/TaO_x/C did not degrade, while Pd/C clearly degraded (Figure S8). Both the MA and LSV analyses revealed that incorporating TaO_x with CB significantly enhanced the catalytic durability. Additional experiments with extended ADT cycles (up to 50000) showed that Au-Pd/TaO_x/C exhibited only slight LSV degradation after 50000 cycles as well as a much slower rate in the MA reduction compared to Au-Pd/C, demonstrating the effectiveness of the heteroenergetic support (Figure S9). We also evaluated the performance and durability of the AEMFC single cell device using Au-Pd/TaO_x/C as the cathode catalysts, confirming the feasibility of these synthesized catalysts in a real device with high efficacy (Figure S10).

■ SUPPRESSION OF THE NP AGGREGATION ENABLED BY THE MIXED TaO_x-CARBON SUPPORT

To investigate whether the enhanced durability stems from the preservation of the NP size with the heteroenergetic support, we conducted TEM and XPS analyses. Our hypothesis posited that Au-Pd/C and Pd/C, supported solely on CB, would experience NP enlargement during the ORR due to weak catalyst–support interactions.^{48,49} In contrast, Au-Pd/TaO_x/C

and Pd/TaO_x/C, which feature a heteroenergetic support, were expected to maintain their NP size without undergoing significant Ostwald ripening or PMC. Analysis of the NP size distribution before and after ADT, based on TEM images, revealed a significant increase in the average diameter of the Pd NPs in Au-Pd/C, from 4.92 to 8.65 nm, while the NP sizes in Au-Pd/TaO_x/C remained almost unchanged (Figure 4a–d). Similar trends were observed for Pd/TaO_x/C and Pd/C (Figure S11). Consequently, the exceptional durability observed for Au-Pd/TaO_x/C and Pd/TaO_x/C could be attributed to the use of a heteroenergetic support, which effectively stabilized the NPs. The amount of Pd dissolution measured after a 10000-cycle ADT is similar regardless of the presence of a heteroenergetic support, suggesting that the enhanced durability is not due to the prevention of dissolution (Figure S12).

In addition to the local characterization using TEM, an XPS analysis was also conducted to confirm the universal suppression of NP enlargement in our systems. The evolution of the Pd⁰/Pd²⁺ ratio obtained from XPS analysis provided information on the changes in the NP size. The Pd⁰/Pd²⁺ ratio exhibits an inverse correlation with the oxophilicity of the surface, which is also related to the NP size. Since the atoms on the NP corners and edges are more oxophilic than those on facets, smaller NPs have greater oxophilicity and smaller Pd⁰/Pd²⁺. An increase in the Pd⁰/Pd²⁺ value after ADT indicates an increase in the NP size and a decrease in the activity (Figure 4e).^{50–52} We calculated Pd⁰/Pd²⁺ using the Pd 3d peak from the XPS analysis and confirmed that both of the Pd⁰/Pd²⁺ values obtained for each of the Pd 3d_{5/2} and Pd 3d_{7/2} were identical. When Au-Pd/TaO_x/C was maintained at 2.45 (Pd⁰:Pd²⁺ = 71:29), the Pd⁰/Pd²⁺ values of Au-Pd/C increased from 2.45 (Pd⁰:Pd²⁺ = 71:29) to 3.35 (Pd⁰:Pd²⁺ = 77:23) after ADT (Figure 4f,g). The difference in the trend of Pd⁰/Pd²⁺ between Au-Pd/TaO_x/C and Au-Pd/C indicated that the suppression of the NP enlargement was a global characteristic of our heteroenergetic support-based systems, consistent with the results of the TEM analyses.

The thermal stabilities of the Au-Pd/TaO_x/C and Au-Pd/C were also evaluated by comparing their ORR activities before and after thermal treatment (Figure S13).⁵³ Minimal changes in ORR activity were observed for Au-Pd/TaO_x/C after heat treatment, providing additional evidence for the effect of a heteroenergetic support on durability.

In conclusion, we introduce an approach utilizing a mixed TaO_x-C support as an effective strategy to prevent significant aggregation and the detachment of metal particles. We employ a support consisting of a blend of two distinct materials with markedly different binding affinities to the catalyst material—a heteroenergetic support. By applying this strategy to AEMFCs, we incorporated a mixed TaO_x-C support with Au-doped Pd metal NPs, resulting in no loss of MA even after subjecting the catalyst to a 10000-cycle ADT. Through comprehensive TEM and XPS analyses, we confirmed that this exceptional durability could be attributed to the effective suppression of NP aggregation (both Ostwald ripening and PMC) and NP detachment due to the heteroenergetic support. Our study provides a novel approach for modulating MSIs to achieve highly stable supported metal catalysts, diverging from the conventional reliance on single support materials with suboptimal MSIs.

METHODS

Details of the methods used for DFT calculations, material synthesis and characterization, and electrochemical measurements are provided in the [Supporting Information](#).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenerylett.4c01946>.

Computational and experimental methods, characterization of Au doping, investigation of Au doping effect, structure information on screened metal oxides, XRD images of TaO_x and the catalysts, HAADF-STEM images and the corresponding EDS elemental mappings of Pd/TaO_x/C and Au-Pd/C, CV curves and Tafel plots, stability evaluation of Au-Pd/TaO_x/C through a 50000-cycle ADT, ORR polarization curves before and after ADT of Pd/TaO_x/C, Pd/C, and Pt/C, ICP-MS analysis of Pt/C, Pd/C, Au-Pd/TaO_x/C, and Au-Pd/C after ADT, stability analyses of Pd/TaO_x/C and Pd/C, single cell test of Au-Pd/TaO_x/C, and ORR polarization curves after thermal treatments ([PDF](#))

AUTHOR INFORMATION

Corresponding Authors

Sang Soo Han – Computational Science Research Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea; orcid.org/0000-0002-7925-8105; Email: sangsoo@kist.re.kr

Donghun Kim – Computational Science Research Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea; orcid.org/0000-0003-0326-5381; Email: donghun@kist.re.kr

Hyuck Mo Lee – Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon 34141, Republic of Korea; orcid.org/0000-0003-4556-6692; Email: hmlee@kaist.ac.kr

Authors

Suyeon Choi – Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon 34141, Republic of Korea

Doosun Hong – Computational Science Research Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea

HyunWoo Yang – Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon 34141, Republic of Korea

Jeonghan Roh – Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon 34141, Republic of Korea; orcid.org/0000-0003-4080-580X

Jaeyoung Yoo – Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon 34141, Republic of Korea; orcid.org/0000-0002-9351-2421

Changsoo Lee – Hydrogen Research Department, Korea Institute of Energy Research, Daejeon 34129, Republic of Korea

MinJoong Kim – Hydrogen Research Department, Korea Institute of Energy Research, Daejeon 34129, Republic of Korea; orcid.org/0000-0002-2330-546X

Young Hwa Yun – Hydrogen Research Department, Korea Institute of Energy Research, Daejeon 34129, Republic of Korea

Kihoon Bang – Computational Science Research Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea

Jong Min Kim – Materials Architecturing Research Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea

EunAe Cho – Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon 34141, Republic of Korea; orcid.org/0000-0002-2871-6903

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acsenerylett.4c01946>

Author Contributions

[†]S.C. and D.H. contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Research Foundation of Korea funded by the Ministry of Science and ICT (NRF-2021M3A7C2089739 and NRF-2022-M3H4A7046278).

REFERENCES

- (1) van Deelen, T. W.; Hernández Mejía, C.; de Jong, K. P. Control of metal-support interactions in heterogeneous catalysts to enhance activity and selectivity. *Nat. Catal.* **2019**, *2*, 955–970.
- (2) Zaman, S.; Wang, M.; Liu, H.; Sun, F.; Yu, Y.; Shui, J.; Chen, M.; Wang, H. Carbon-based catalyst supports for oxygen reduction in proton-exchange membrane fuel cells. *Trends Chem.* **2022**, *4*, 886–906.
- (3) Li, S.; Liu, J.; Liang, J.; Lin, Z.; Liu, X.; Chen, Y.; Lu, G.; Wang, C.; Wei, P.; Han, J.; et al. Tuning oxygen vacancy in SnO₂ inhibits Pt migration and agglomeration towards high-performing fuel cells. *Appl. Catal. B: Environ.* **2023**, *320*, No. 122017.
- (4) Ouyang, R.; Liu, J.-X.; Li, W.-X. Atomistic theory of Ostwald ripening and disintegration of supported metal particles under reaction conditions. *J. Am. Chem. Soc.* **2013**, *135*, 1760–1771.
- (5) Van den Berg, R.; Parmentier, T. E.; Elkjær, C. F.; Gommès, C. J.; Sehested, J.; Helveg, S.; de Jongh, P. E.; de Jong, K. P. Support functionalization to retard Ostwald ripening in copper methanol synthesis catalysts. *ACS Catal.* **2015**, *5*, 4439–4448.
- (6) Arnal, P. M.; Comotti, M.; Schüth, F. High-temperature-stable catalysts by hollow sphere encapsulation. *Angew. Chem., Int. Ed.* **2006**, *45*, 8224–8227.
- (7) Pang, J.; Yin, M.; Wu, P.; Song, L.; Li, X.; Zhang, T.; Zheng, M. Redispersal and stabilization of Cu/MFI catalysts by the encapsulation method for ethanol dehydrogenation. *ACS Sustain. Chem. Eng.* **2023**, *11*, 3297–3305.
- (8) Paz Herrera, L.; Freitas de Lima e Freitas, L.; Hong, J.; Hoffman, A. S.; Bare, S. R.; Nikolla, E.; Medlin, J. W. Reactivity of Pd–MO₂ encapsulated catalytic systems for CO oxidation. *Catal. Sci. Technol.* **2022**, *12*, 1476–1486.
- (9) Ramaswamy, N.; Mukerjee, S. Alkaline anion-exchange membrane fuel cells: Challenges in electrocatalysis and interfacial charge transfer. *Chem. Rev.* **2019**, *119*, 11945–11979.

- (10) Firouzjaie, H. A.; Mustain, W. E. Catalytic advantages, challenges, and priorities in alkaline membrane fuel cells. *ACS Catal.* **2020**, *10*, 225–234.
- (11) Gottesfeld, S.; Dekel, D. R.; Page, M.; Bae, C.; Yan, Y.; Zelenay, P.; Kim, Y. S. Anion exchange membrane fuel cells: Current status and remaining challenges. *J. Power Sources* **2018**, *375*, 170–184.
- (12) Pourbaix, M. *Atlas of electrochemical equilibria in aqueous solutions*, 2nd English ed.; National Association of Corrosion Engineers: 1974.
- (13) Hyun, J.; Kim, H.-T. Powering the hydrogen future: Current status and challenges of anion exchange membrane fuel cells. *Energy Environ. Sci.* **2023**, *16*, 5633–5662.
- (14) Ul Hassan, N.; Mandal, M.; Huang, G.; Firouzjaie, H. A.; Kohl, P. A.; Mustain, W. E. Achieving high-performance and 2000 h stability in anion exchange membrane fuel cells by manipulating ionomer properties and electrode optimization. *Adv. Energy Mater.* **2020**, *10*, No. 2001986.
- (15) Hyun, J.; Yang, S. H.; Doo, G.; Choi, S.; Lee, D.-H.; Lee, D. W.; Kwen, J.; Jo, W.; Shin, S.-H.; Lee, J. Y.; et al. Degradation study for the membrane electrode assembly of anion exchange membrane fuel cells at a single-cell level. *J. Mater. Chem. A* **2021**, *9*, 18546–18556.
- (16) Lafforgue, C.; Maillard, F.; Martin, V.; Dubau, L.; Chatenet, M. Degradation of carbon-supported platinum-group-metal electrocatalysts in alkaline media studied by in situ Fourier transform infrared spectroscopy and identical-location transmission electron microscopy. *ACS Catal.* **2019**, *9*, 5613–5622.
- (17) Zhao, S.; Wangstrom, A. E.; Liu, Y.; Rigdon, W. A.; Mustain, W. E. Stability and activity of Pt/ITO electrocatalyst for oxygen reduction reaction in alkaline media. *Electrochim. Acta* **2015**, *157*, 175–182.
- (18) Han, X.; Cheng, F.; Zhang, T.; Yang, J.; Hu, Y.; Chen, J. Hydrogenated uniform Pt clusters supported on porous CaMnO_3 as a bifunctional electrocatalyst for enhanced oxygen reduction and evolution. *Adv. Mater.* **2014**, *26*, 2047–2051.
- (19) Elezovic, N.; Babic, B.; Radmilovic, V.; Vracar, L. M.; Krstajic, N. Nb– TiO_2 supported platinum nanocatalyst for oxygen reduction reaction in alkaline solutions. *Electrochim. Acta* **2011**, *56*, 9020–9026.
- (20) Elezovic, N.; Radmilovic, V.; Kovac, J.; Babic, B.; Gajic-Krstajic, L. M.; Krstajic, N. Pt nanoparticles on tin oxide based support as a beneficial catalyst for oxygen reduction in alkaline solutions. *RSC Adv.* **2015**, *5*, 15923–15929.
- (21) Li, J.; Zhou, H.; Zhuo, H.; Wei, Z.; Zhuang, G.; Zhong, X.; Deng, S.; Li, X.; Wang, J. Oxygen vacancies on TiO_2 promoted the activity and stability of supported Pd nanoparticles for the oxygen reduction reaction. *J. Mater. Chem. A* **2018**, *6*, 2264–2272.
- (22) Hu, S.; Li, W.-X. Sabatier principle of metal-support interaction for design of ultrastable metal nanocatalysts. *Science* **2021**, *374*, 1360–1365.
- (23) Xue, Q.; Li, Z.; Yi, H.; Jiang, Z.; Yan, B.; Wang, Y.; Luo, G. Controlling sintering and carbon deposition with post-coated MgO confined group VIII metal-based catalysts towards durable high-temperature steam reforming. *Appl. Catal. B: Environ.* **2022**, *318*, No. 121874.
- (24) Chen, J.; Liu, C.-H.; Pham, H. N.; Toops, T. J.; Datye, A. K.; Kyriakidou, E. A. Designing ultrastable Pt/ CeO_2 - Al_2O_3 nanosheet catalysts for three-way catalysts applications. *Chem. Eng. J.* **2023**, *477*, No. 147086.
- (25) Hansen, T. W.; DeLaRiva, A. T.; Challa, S. R.; Datye, A. K. Sintering of catalytic nanoparticles: Particle migration or Ostwald ripening? *Acc. Chem. Res.* **2013**, *46*, 1720–1730.
- (26) Hemmingson, S. L.; Campbell, C. T. Trends in adhesion energies of metal nanoparticles on oxide surfaces: Understanding support effects in catalysis and nanotechnology. *ACS Nano* **2017**, *11*, 1196–1203.
- (27) Zadick, A.; Dubau, L.; Sergeant, N.; Berthome, G.; Chatenet, M. Huge instability of Pt/C catalysts in alkaline medium. *ACS Catal.* **2015**, *5*, 4819–4824.
- (28) Zadick, A.; Dubau, L.; Demirci, U. B.; Chatenet, M. Effects of Pd nanoparticle size and solution reducer strength on Pd/C electrocatalyst stability in alkaline electrolyte. *J. Electrochem. Soc.* **2016**, *163*, F781.
- (29) Schalenbach, M.; Kasian, O.; Ledendecker, M.; Speck, F. D.; Mingers, A. M.; Mayrhofer, K. J.; Cherevko, S. The electrochemical dissolution of noble metals in alkaline media. *Electrocatalysis* **2018**, *9*, 153–161.
- (30) Speck, F. D.; Zagalskaya, A.; Alexandrov, V.; Cherevko, S. Periodicity in the electrochemical dissolution of transition metals. *Angew. Chem., Int. Ed.* **2021**, *60*, 13343–13349.
- (31) Zhang, W.; Chang, J.; Yang, Y. Strong precious metal–metal oxide interaction for oxygen reduction reaction: A strategy for efficient catalyst design. *SusMat* **2023**, *3*, 2–20.
- (32) Sun, Q.; Li, X.-H.; Wang, K.-X.; Ye, T.-N.; Chen, J.-S. Inorganic non-carbon supported Pt catalysts and synergetic effects for oxygen reduction reaction. *Energy Environ. Sci.* **2023**, *16*, 1838.
- (33) Back, S.; Bagherzadeh Mostaghimi, A. H.; Siahrostami, S. Enhancing oxygen reduction reaction activity using single atom catalyst supported on tantalum pentoxide. *ChemCatChem* **2022**, *14*, No. e202101763.
- (34) Lv, L.; Zha, D.; Ruan, Y.; Li, Z.; Ao, X.; Zheng, J.; Jiang, J.; Chen, H. M.; Chiang, W.-H.; Chen, J.; et al. A universal method to engineer metal oxide–metal–carbon interface for highly efficient oxygen reduction. *ACS Nano* **2018**, *12*, 3042–3051.
- (35) Gao, R.; Wang, J.; Huang, Z.-F.; Zhang, R.; Wang, W.; Pan, L.; Zhang, J.; Zhu, W.; Zhang, X.; Shi, C.; et al. Pt/ Fe_2O_3 with Pt–Fe pair sites as a catalyst for oxygen reduction with ultralow Pt loading. *Nat. Energy* **2021**, *6*, 614–623.
- (36) Kumari, S.; Sautet, P. Highly dispersed Pt atoms and clusters on hydroxylated indium tin oxide: A view from first-principles calculations. *J. Mater. Chem. A* **2021**, *9*, 15724–15733.
- (37) Asara, G. G.; Paz-Borbón, L. O.; Baletto, F. Get in touch and keep in contact: Interface effect on the oxygen reduction reaction (ORR) activity for supported PtNi nanoparticles. *ACS Catal.* **2016**, *6*, 4388–4393.
- (38) Wang, X.; Yang, Z.; Zhang, Y.; Jing, L.; Zhao, Y.; Yan, Y.; Sun, K. MnO_2 supported Pt nanoparticles with high electrocatalytic activity for oxygen reduction reaction. *Fuel Cells* **2014**, *14*, 1.
- (39) Yang, L.; Hou, S.; Zhu, S.; Shi, Z.; Wang, X.; Jiang, J.; Chu, Y.; Bai, J.; Wang, Y.; Zhang, L.; et al. Stabilizing Pt electrocatalysts via introducing reducible oxide support as reservoir of electrons and oxygen species. *ACS Catal.* **2022**, *12*, 13523–13532.
- (40) Zhang, L.; Wang, L.; Holt, C. M.; Navessin, T.; Malek, K.; Eikerling, M. H.; Mitlin, D. Oxygen reduction reaction activity and electrochemical stability of thin-film bilayer systems of platinum on niobium oxide. *J. Phys. Chem. C* **2010**, *114*, 16463–16474.
- (41) He, C.; Sankarabramanian, S.; Ells, A.; Parrondo, J.; Gumeci, C.; Kodali, M.; Matanovic, I.; Yadav, A. K.; Bhattacharyya, K.; Dale, N.; et al. Self-anchored platinum-decorated antimony-doped-tin oxide as a durable oxygen reduction electrocatalyst. *ACS Catal.* **2021**, *11*, 7006–7017.
- (42) Kim, G. Y.; Yoon, K. R.; Shin, K.; Jung, J. W.; Henkelman, G.; Ryu, W. H. Black tungsten oxide nanofiber as a robust support for metal catalysts: High catalyst loading for electrochemical oxygen reduction. *Small* **2021**, *17*, No. 2103755.
- (43) Qiao, S.; Shou, H.; Xu, W.; Cao, Y.; Zhou, Y.; Wang, Z.; Wu, X.; He, Q.; Song, L. Regulating and identifying the structures of PdAu alloys with splendid oxygen reduction activity for rechargeable zinc–air batteries. *Energy Environ. Sci.* **2023**, *16*, 5842–5851.
- (44) Jiao, W.; Chen, C.; You, W.; Chen, G.; Xue, S.; Zhang, J.; Liu, J.; Feng, Y.; Wang, P.; Wang, Y.; et al. Tuning strain effect and surface composition in PdAu hollow nanospheres as highly efficient ORR electrocatalysts and SERS substrates. *Appl. Catal. B: Environ.* **2020**, *262*, No. 118298.
- (45) Jiao, W.; Chen, C.; You, W.; Zhao, X.; Zhang, J.; Feng, Y.; Wang, P.; Che, R. Hollow palladium-gold nanochains with periodic concave structures as superior ORR electrocatalysts and highly efficient SERS substrates. *Adv. Energy Mater.* **2020**, *10*, No. 1904072.
- (46) Liu, S.; Ren, H.; Yin, S.; Zhang, H.; Wang, Z.; Xu, Y.; Li, X.; Wang, L.; Wang, H. Defect-rich ultrathin AuPd nanowires with

Boerdijk–Coxeter structure for oxygen reduction electrocatalysis. *Chem. Eng. J.* **2022**, 435, No. 134823.

(47) Chen, Y.; Yan, Y.; Wu, J.; Wang, C.; Lin, J. Y.; Zhao, J. S.; Hwang, C. S. Electroforming-free, flexible, and reliable resistive random-access memory based on an ultrathin TaO_x film. *ACS Appl. Mater. Interfaces*. **2020**, 12, 10681–10688.

(48) Meier, J. C.; Galeano, C.; Katsounaros, I.; Witte, J.; Bongard, H. J.; Topalov, A. A.; Baldizzone, C.; Mezzavilla, S.; Schüth, F.; Mayrhofer, K. J. J. Design criteria for stable Pt/C fuel cell catalysts. *Beilstein J. Nanotechnol.* **2014**, 5, 44–67.

(49) Shao, M.; Peles, A.; Shoemaker, K. Electrocatalysis on platinum nanoparticles: Particle size effect on oxygen reduction reaction activity. *Nano Lett.* **2011**, 11, 3714–3719.

(50) Luo, M.; Zhao, Z.; Zhang, Y.; Sun, Y.; Xing, Y.; Lv, F.; Yang, Y.; Zhang, X.; Hwang, S.; Qin, Y.; et al. PdMo bimetallic for oxygen reduction catalysis. *Nature* **2019**, 574, 81–85.

(51) Back, S.; Yeom, M. S.; Jung, Y. Active sites of Au and Ag nanoparticle catalysts for CO₂ electroreduction to CO. *ACS Catal.* **2015**, 5, 5089–5096.

(52) Zhou, M.; Guo, J.; Zhao, B.; Li, C.; Zhang, L.; Fang, J. Improvement of oxygen reduction performance in alkaline media by tuning phase structure of Pd–Bi nanocatalysts. *J. Am. Chem. Soc.* **2021**, 143, 15891–15897.

(53) Li, O. L.; Shi, Z.; Lee, H.; Ishizaki, T. Enhanced electrocatalytic stability of platinum nanoparticles supported on sulfur-doped carbon using in-situ solution plasma. *Sci. Rep.* **2019**, 9, 12704.