



High-Performance Ammonia Oxidation Catalysts for Anion-Exchange Membrane Direct Ammonia Fuel Cells

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High-Performance Ammonia Oxidation Catalysts for Anion-Exchange Membrane Direct Ammonia Fuel Cells

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Low-temperature direct ammonia fuel cells (DAFCs) can use carbon-neutral ammonia as a fuel, which has attracted increasing attention recently due to ammonia's low source-to-tank energy cost, easy transport and storage, and wide availability. However, current DAFC technologies are greatly limited by the kinetically sluggish ammonia oxidation reaction (AOR) at the anode. Herein, we report an AOR catalyst, in which ternary PtIrZn nanoparticles with an average size of 2.3 ± 0.2 nm were highly dispersed on binary composite support comprising of cerium oxide (CeO₂) and zeolitic imidazolate framework-8 (ZIF-8)-derived carbon (PtIrZn/CeO₂-ZIF-8) through a sonochemical-assisted synthesis method. The PtIrZn alloy, with the aid of abundant OH_{ad} provided by CeO₂ and high particle dispersibility contributed by porous ZIF-8 carbon (surface area: ~ 600 m² g⁻¹), has shown highly efficient catalytic activity for the AOR in alkaline media, superior to that of commercial PtIr/C. The rotating disk electrode (RDE) results indicate a lower onset potential (0.35 vs. 0.43 V, reversible hydrogen electrode at room temperature, and a decreased activation energy (~ 36.7 vs. 50.8 kJ mol⁻¹) relative to the PtIr/C catalyst. Notably, the PtIrZn/CeO₂-ZIF-8 catalyst was assembled with a high-performance hydroxide anion-exchange membrane to fabricate an alkaline DAFC, reaching a peak power density of 91 mW cm⁻². Unlike in aqueous electrolytes, supports play a critical role in improving uniform ionomer distribution and mass transport in the anode. PtIrZn nanoparticles on silicon dioxide (SiO₂) integrating with carboxyl-functionalized carbon nanotube (CNT-COOH) were studied as the anode in a DAFC. A significantly enhanced peak power density of 314 mW cm⁻² was achieved, indicating critical roles of alloying Zn with PtIr. Density functional theory calculations further elucidate that Zn atoms in the PtIr alloy can reduce the theoretical limiting potential of *NH₂ dehydrogenation to *NH by up to ~ 0.1 V, which can be attributed to a Zn-modulated upshift of the Pt-Ir d-band that facilitates the N-H bond breakage.

1. Introduction

Hydrogen is a promising and sustainable fuel since it only produces water when consumed in a fuel cell. It can be produced through the water-splitting by utilizing renewable and clean solar and wind electricity.^{1, 2} However, the hydrogen economy's advent cannot be realized until technical barriers related to hydrogen transportation, distribution, and storage are overcome. Alternatively, the concept of an ammonia (NH₃)

economy has recently gained eminence due to the following reasons.³⁻⁶ First, ammonia as a cost-effective hydrogen carrier and carbon-free fuel is in a liquid state at near ambient conditions, and it enables a complete cycle of synthesis and consumption that would not produce greenhouse gas emissions. Second, the infrastructure and supply chain for ammonia as a transport fuel is already in existence or can be easily modified. Third, dissociating ammonia for hydrogen generation and then using the hydrogen in a fuel cell or a direct ammonia input to a fuel cell can be realized for electricity generation as a power source with high energy density for transportation applications.^{1, 7, 8} Particularly, low-temperature direct ammonia fuel cells (DAFCs) can directly utilize ammonia to the anode, which has great promise for vehicle applications, because of its fast start-up superiority in comparison to high-temperature DAFCs (e.g., ammonia-fueled solid oxide fuel cells, SOFCs, and protonic ceramic fuel cells, PCFCs).^{7, 9, 10} Nevertheless, the development of DAFCs is at an earlier stage when compared with the direct hydrogen fuel cells. This is mainly due to a more complex and sluggish anodic ammonia oxidation reaction (AOR) than hydrogen oxidation reaction (HOR).¹¹

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Earlier researches indicated that Pt, Ir, and their alloys can catalyze the AOR in alkaline media at the low temperature.^{12, 13} The standard potential of the AOR is -0.77 V vs. SHE (0.056 V vs. RHE), very close to that of hydrogen oxidation reaction at -0.83 V (0 V vs. RHE) in alkaline media at 25 °C. However, the overpotential on Pt-based catalysts at room temperature is larger than 0.40 V, which significantly reduces the energy conversion efficiency for DAFC applications.^{13, 14} Accordingly, it is anticipated that the AOR could commence in the hydrogen zone (0 to 0.40 V vs. RHE) if a more efficient catalyst were used. The modulation of the *H oxidation potential is a way to design an efficient AOR catalyst. It was reported that the hydrogen adsorption could be suppressed by incorporating Pt with high hydrogen-overpotential metals (e.g., Zn).^{15, 16} Therefore, the knowledge gained from Pt-Zn alloys provides a guide in this work to explore ternary Pt-Ir-Zn alloys for the AOR. Also, our density functional theory calculations predicted that Zn atoms in the PtIr alloy could reduce the theoretical limiting potential of *NH₂ dehydrogenation to *NH, because a Zn-modulated upshift of the Pt-Ir d-band facilitates the N-H bond breakage. Driven by the theoretical understanding, we synthesized a new PtIrZn ternary catalyst for the AOR in this work.

Besides, catalyst supports play a critical role in uniformly dispersing metal nanoparticles, improving catalyst utilization, and offering a unique metal-support interaction for intrinsic activity enhancement. Our previous report has demonstrated that silicon dioxide (SiO₂) and carboxyl functionalized carbon nanotube (CNT-COOH) as composite support can be used for effective Pt alloy nanoparticle deposition.¹³ The interfaces between SiO₂ and Pt alloys facilitate AOR activity because SiO₂ could supply abundant OH_{ad} to the nearby metallic catalytic sites.¹⁷ However, the nanoparticle dispersion on this composite support is not very uniform.¹³ Therefore, improving the nanoparticle dispersion has assured us to develop novel composite support in this work. In light of this, cerium oxide (CeO₂) and zeolitic imidazolate framework-8 (ZIF-8)-derived carbon were newly explored for the PtIrZn nanoparticle catalyst. CeO₂ is widely used to support metal nanoparticles because the Ce³⁺ in CeO₂ can work as a Lewis base to modify reactants' adsorption properties and intermediates.¹⁸ Thus, the CeO₂-Pt alloy interfaces can facilitate the AOR.^{13, 19} However, CeO₂ generally possesses a low surface area (<50 m² g⁻¹), which is not sufficient for high-loading nanoparticle deposition and effective mass transfer. In contrast, the ZIF-8 derived carbon typically exhibits a large surface area and dominant porosity, ideal for Pt-based alloy nanoparticle deposition.²⁰⁻²²

Morphology characterization results have demonstrated that the ternary PtIrZn nanoparticles were uniformly deposited on the CeO₂-ZIF-8 support. To provide a more comprehensive understanding of these two different composite supports, we also used SiO₂-CNT-COOH composite support for depositing PtIrZn nanoparticles. Both catalysts were and further evaluated in DAFCs by using a high-performance anion-exchange membrane.^{7, 23} Electrochemical results displayed a similar intrinsic AOR activity (onset potential) on both CeO₂-ZIF-8 and SiO₂-CNT-COOH composite supports. The DAFC tests demonstrated that the PtIrZn/SiO₂-CNT-COOH could greatly enhance electrical conductivity and mass transfer in the anode, yielding a remarkable power density of 314 mWcm⁻². We believe the new knowledge for ammonia oxidation combined with the design and

synthesis of advanced electrocatalyst alloys and supports in this work would advance the DAFC technology for possible transportation and other applications.

2. Results and discussion

2.1 Catalyst synthesis and characterization

A facile synthetic route for ternary PtIrZn nanoparticles (NPs) deposited on a binary composite support (e.g., CeO₂/ZIF-8-derived carbon and SiO₂/CNT-COOH) was developed by reducing the metal precursors via sodium borohydride under an ultrasonic environment (**Figure 1**). In the case of the CeO₂/ZIF-8 carbon support, diluted alkaline-treated CeO₂ acts as not only a support for metal NPs,²⁴ but also a reservoir for adsorbing OH species.²⁵ ZIF-8 derived carbon with unique micropores shows a large surface area (~600 m² g⁻¹, **Figure S1**),¹⁸ which are effective metal precursors (i.e., PtCl₄²⁻, IrCl₆²⁻, and Zn²⁺) adsorption during the synthesis. Also, the dominant N dopants in ZIF-8 derived-carbon provides sufficient defects to assist the dispersion of Pt-based nanoparticles due to the electron-donation from nitrogen defects to Pt.^{18, 26, 27} ZIF-8 derived carbon shows an average particle size of 200 ± 12.7 nm, as can be seen from the scanning electron microscopy (SEM) images (**Figure S2a, b**). Crystal structures of ZIF-8 precursors are converted into the carbon phase during a typically thermal activation process at 1100°C for one hour under Ar atmosphere, verified by analyzing their X-ray diffraction (XRD) patterns (**Figure S2c, d**).

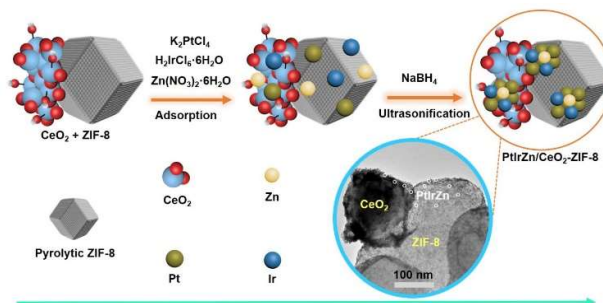


Figure 1. Schematic illustration for the synthesis of CeO₂ and ZIF-8 supported ternary PtIrZn nanoparticles.

During the synthesis, deionized water and ethanol were used to disperse the composite support and then adsorb the metal precursors in the support. Simultaneously, acoustic cavitation²⁸ was employed to control the nucleation and growth of PtIrZn ternary NPs with uniform size and distribution. Additionally, compared to platinum-group-metal (PGM) precursors (PtCl₄²⁻ and IrCl₆²⁻) for the PtIr/CeO₂-ZIF-8 (**Figure S3**), the smaller Zn²⁺ is easily adsorbed onto the pyrolytic ZIF-8 carbon support and interacts with the PGM ones. In doing so, the uniformly dispersed ternary PtIrZn alloy NPs were uniformly dispersed on the composite support consisting of CeO₂ (~100 ± 8.9 nm) and ZIF-8 derived carbon (**Figure S4**). The PGM (Pt or Pt-Ir) loadings for all the synthesized catalysts are 10 wt% vs. the support unless otherwise noted. Molar ratios of Pt:Ir:Zn in the PtIrZn/CeO₂-ZIF-8 are varied at 1:1:0.2 (PtIrZn₁), 1:1:0.6 (PtIrZn₂), and 1:1:1 (PtIrZn₃). Other control samples, such as PtIr/CeO₂-ZIF-8 and PtZn/CeO₂-ZIF-8 in molar ratio of Pt:Ir and Pt:Zn = 1:1, as well as

PtIrNi₂/CeO₂-ZIF-8 and PtIrCu₂/CeO₂-ZIF-8 in molar ratio of Pt:Ir:Ni and Pt:Ir:Cu = 1:1:0.6, were synthesized via an identical procedure and the corresponding metal precursors.

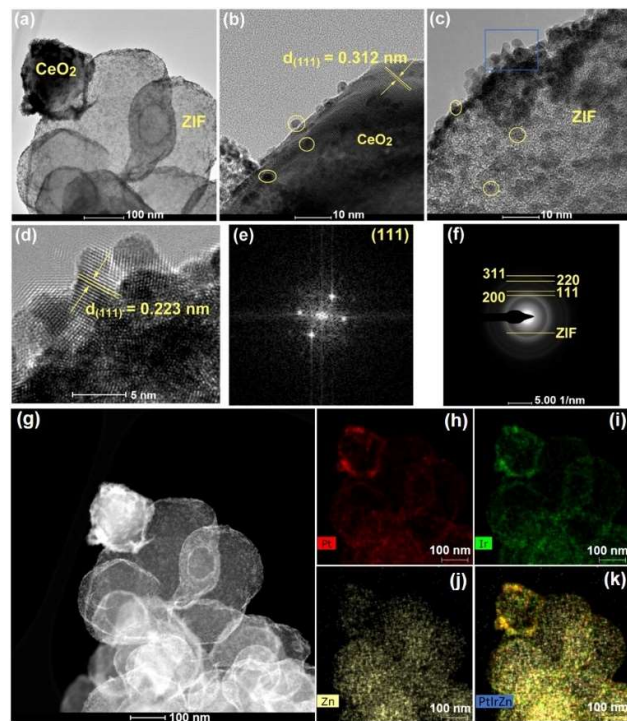


Figure 2. Morphology, structure, and composition of the PtIrZn₂/CeO₂-ZIF-8 catalyst (molar ratio of Pt/Ir/Zn = 1:1:0.6). (a) TEM images, (b, c) HR-TEM images, (d) the enlarged area selected from (c), (e) the FFT patterns of the corresponding nanoparticle in (d), (f) ED pattern from the selected area in (c), (g) HAADF-STEM image of (a), and the corresponding EDS elemental mappings of Pt (h), Ir (i), Zn (j), and integrated mapping of Pt, Ir, and Zn (k).

Transmission electron microscopy (TEM) images show that the PtIr NPs have an average dimension of 7.1 ± 0.3 nm (Figure S3c, d). An interplanar spacing of 0.225 nm measured with these PtIr NPs in Figure S5a and 5c suggests a lattice contraction compared to that of the pure Pt (ca. 0.227 nm).²⁹ Typically, PtIr alloys have a lattice parameter of ca. 2.25 Å in the (111) plane (Figure S5b, d), which agrees with the PtIr NPs on the composite support.³⁰ The electron diffraction (ED) pattern in Figure S5f shows that the indices (e.g., 111 and 200) are in good agreement with the face-centered cubic (fcc) lattice of PtIr NPs.³¹ The high angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) and the corresponding elemental maps show that the Pt and Ir atoms are well dispersed throughout the PtIr NP on the composite support (Figure S5g).

Unlike PtIr/CeO₂-ZIF-8 sample, more uniform Pt alloy NP dispersion is found for the PtIrZn₂/CeO₂-ZIF-8 (Figure 2a-c and Figure S6). This is likely due to the ZIF-8 derived carbon and OH⁻ abundant CeO₂ are much easier to trap the smaller Zn²⁺ that could assist the adsorption and distribution of Pt and Ir precursors (i.e., PtCl₄²⁻ and IrCl₆²⁻) via electrostatic effect.³²⁻³⁴ The diameter of PtIrZn NPs was estimated to be 2.3 ± 0.2 nm, smaller than that of commercial PtIr/C (Figure S7, PtIr particle size: 2.7 ± 0.3 nm). The strong metal-support interactions between PtIrZn and CeO₂ support (Figure 2b) could be due to the semiconductor properties of CeO₂ for reducing PtIrZn

alloy NPs.²⁴ The unique PtIrZn/CeO₂ interfaces could strengthen the interactions for metal-to-oxide and metal-to-metal bonds, thus restraining phase separation.^{18, 24} The lattice spacing of $d = 0.312$ nm is consistent with the (111) plane of fluorite-phase CeO₂ (Figure 2b).^{18, 35} Different to the PtIrZn NP deposited on CeO₂ support, a higher loading of PtIrZn is observed on the ZIF-8 derived carbon support (Figure 2c), which can be attributed to its high surface area (~ 600 m² g⁻¹) and porosity. The HR-TEM image (Figure 2d) and FFT pattern (Figure 2e) display the interplanar spacing of 0.223 nm corresponding to d_{111} of fcc-PtIrZn alloy, illuminating a lattice contraction occurs in PtIrZn NPs in contrast with that of the PtIr NPs (ca. 0.225 nm) from commercial PtIr/C (Figure S7) and PtIr/CeO₂-ZIF-8 (Figure S5). The ED pattern in Figure 2f shows that the indices (e.g., 002, 111, and 200) are in accordance with the ZIF-8 derived carbon and fcc lattice of PtIrZn NPs. Also, the uniformly distributed PtIrZn NPs on the composite support can be further confirmed by the elemental mappings using energy-dispersive X-ray spectroscopy (Figure 2(g-k)). Some Zn atoms can also be observed in the carbon support due to the incomplete thermal removal of Zn from the ZIF-8 structure.³⁶

X-ray diffraction (XRD) patterns were used to identify the crystal structure of these prepared catalysts. As shown in Figure S8a, the peak at $\sim 26^\circ$ of Pt/ZIF-8 sample is attributed to the C (002) of the ZIF-8 derived carbon.³⁷ Other diffraction peaks at $2\theta = 39.6, 47.4, 67.1, 81.2$ and 83.6° correspond to the Miller indices of (111), (200), (220), (311) and (222) of fcc Pt for all the prepared Pt-based catalysts (Figure S8).²⁶ XRD peaks at $28.6^\circ, 33.1^\circ, 47.5^\circ, 56.3^\circ, 59.1^\circ, 69.4^\circ, 79.1^\circ$, and 88.4° in the CeO₂-involved catalysts can be ascribed to the Miller indices (111), (200), (220), (311), (222), (400), (331), and (420) of the cubic lattice of CeO₂ (JCPDS No. 81-0792, fluorite structural type), respectively (Figure 3a, Figure S8 and S9).¹⁹

After introducing Ir, Zn, and IrZn into the Pt base, XRD patterns verify the bimetallic PtIr and PtZn and ternary PtIrZn alloys with the face-centered cubic (fcc) crystal structure (Figure 3a,b and Figure S9). Furthermore, fcc Pt peaks in these alloys shift toward higher angles, suggesting a reduced d space due to the alloying. Precisely, the d spaces of PtIrZn₁, PtIrZn₂, and PtIrZn₃ were calculated to be 0.2237, 0.2226, and 0.2223 nm, respectively, lower than that of PtIr alloys (0.2252 nm). The contraction can be explained by the replacement of Pt by the smaller Ir and Zn atoms, leading to the decreased lattice spacing. Raman spectra (Figure S10a) have shown the identical D and G bands of the ZIF-8 derived carbon, as well as the CeO₂ peak.

X-ray photoelectron spectroscopy (XPS) results for several Pt-based catalysts (Figure 3c and Figure S10-S13) were summarized in Table S1 concerning their chemical states and surface species. The atomic concentrations of Pt and Ir in the PtIrZn₂/CeO₂-ZIF-8 are determined to be 9.2 at.% and 7.3 at.%, respectively, which are higher than other catalysts, suggesting a stronger interaction between binary support and Pt alloys.

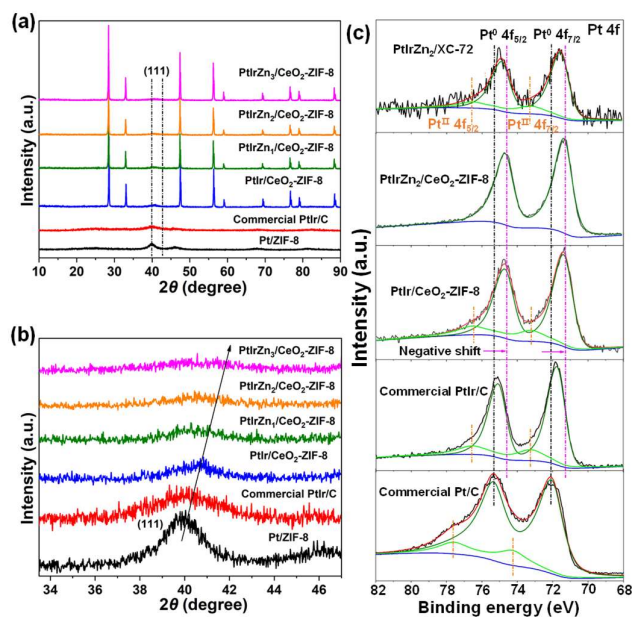


Figure 3. XRD patterns of (a) Pt/ZIF-8, commercial PtIr/C, PtIr/CeO₂-ZIF-8, PtIrZn₁/CeO₂-ZIF-8, PtIrZn₂/CeO₂-ZIF-8, and PtIrZn₃/CeO₂-ZIF-8, and (b) the corresponding enlarged region from 33° to 47° for these Pt-based catalysts. (c) High-resolution Pt 4f XPS spectra of various Pt-based catalysts.

In addition to pyridinic-, graphitic-, and oxidized-N,^{38,39} the N 1s XPS peak at 399.7 eV could be ascribed to N species bonded to M sites,⁴⁰⁻⁴² likely Pt-N or Ir-N in the catalyst (**Figure S11**). Pyridinic N's existence can act as anchor points for Pt and Ir atoms,^{26,40} increasing average binding energy of N 1s. In **Figure 3c**, the high-resolution Pt 4f spectra of all tested samples except for the PtIrZn₂/CeO₂-ZIF-8 can be deconvoluted into two doublets assigned to metallic Pt⁰ and oxidized Pt(II), respectively.⁴¹ Differently, two peaks with binding energies of 71.34 and 74.70 eV are observed in the Pt 4f XPS spectrum of PtIrZn₂/CeO₂-ZIF-8, indicating the dominant metallic Pt species. Introducing metals (e.g., Ir and Zn) with smaller electronegativity into Pt could result in a negative shift of binding energies for Pt in its alloys,¹⁹ as can be demonstrated by the binding energy shifts of Pt 4f_{5/2} (0.24 and 0.42 eV) and Pt 4f_{7/2} (0.30 and 0.48 eV) for the PtIr/C and PtIrZn₂/XC-72, respectively, when compared to Pt/C catalyst (**Table S2**). It should be noticed that the binding energy shifts of Pt 4f_{5/2} (0.60 eV) and Pt 4f_{7/2} (0.70 eV) for the PtIr/CeO₂-ZIF-8 are significantly larger than those of the PtIr/C catalyst, indicating the intense electron interactions between Pt and CeO₂ support, as well as the coordinated N, which would be beneficial for electrocatalytic properties.^{20,38}

2.2 Catalyst activity for the AOR

The AOR activity of all catalysts was assessed using a rotating disk electrode (RDE) in 1.0 M KOH + 0.1 M NH₃ electrolyte. The synergy between CeO₂ and ZIF-8 was confirmed by a noticeable AOR activity enhancement when Pt nanoparticles were deposited on various supports (**Figure S14a**). In alkaline electrolytes, CeO₂ is a reservoir for OH adsorption. The adsorbed OH groups at the catalyst surface could participate in the AOR,^{17,25} leading to an enhanced AOR activity. Several commonly used carbon materials, including carbon black (XC-72), carboxyl-functionalized CNT (CNT-COOH), and ZIF-8 derived

carbon, were integrated with CeO₂ for Pt nanoparticle deposition as AOR catalysts. The electrochemical impedance spectroscopy (EIS) results (**Figure S14b**) demonstrate that these studied supports display different charge transfer resistance. Overall, the CNT-containing support present the smallest resistance, while the ZIF-8 carbon based one shows the largest resistance, which is likely due to their electrical conductivity. However, the ZIF-8 carbon displayed the highest AOR activity (**Figure S14a**). This is because the large surface area (**Figure S1**) and sufficient defects in the ZIF-8-derived carbon benefit the uniform dispersion of Pt nanoparticles. Additionally, the optimization of carbon content in the composite support was performed, and it was found that 33.3 wt% ZIF-8 derived carbon in the support led to the highest AOR activity (**Figure S14c**). This composition was then used for all further experiments. The chronoamperogram (CA) results, i.e., i-t curves (**Figure S15**), of all Pt catalysts, are consistent with their corresponding AOR activity determined by cyclic voltammetry (CV) using a sufficiently low scanning rate. Accordingly, the best-performing composite support of CeO₂ and ZIF-8 was used for further studies.

To enhance the catalytic activity of Pt catalysts, Ir or Zn were alloyed with Pt at a molar ratio of 1:1. The improved AOR activities of both PtIr/CeO₂-ZIF-8 and PtZn/CeO₂-ZIF-8 were demonstrated in terms of the increased current density at 0.5 V vs RHE (**Figure 4a, b** and **Table S3**).^{13,43} A dramatically reduced onset potential (0.417 V vs. RHE) for PtIr/CeO₂-ZIF-8 compared to that of Pt/CeO₂-ZIF-8 (0.504 V) is attributed to favorable NH₃ adsorption and dehydrogenation.^{44,45} Also, a reduced onset potential (0.468 V) for PtZn/CeO₂-ZIF-8 is likely due to that alloying Zn could inhibit the competitive hydrogen adsorption.^{46,47} Furthermore, Ir and Zn were then simultaneously alloyed with Pt to prepare a ternary catalyst. Compared to the binary PtIr/CeO₂-ZIF-8 (peak current density, J_p : 15.7 A g⁻¹, onset potential, E_{onset} : 0.417 V) and PtZn/CeO₂-ZIF-8 catalysts (19.9 A g⁻¹ and 0.468 V), the PtIrZn₂/CeO₂-ZIF-8 catalyst demonstrated a significantly improved AOR activity (**Figure 4a**) in terms of both the increased J_p (31.8 A g⁻¹) and the reduced E_{onset} (0.345 V). The AOR activity is significantly superior to the commercial PtIr/C catalyst (25.1 A g⁻¹ and 0.428 V). Note that the PGM loading is used to quantify the current for all studied catalysts.

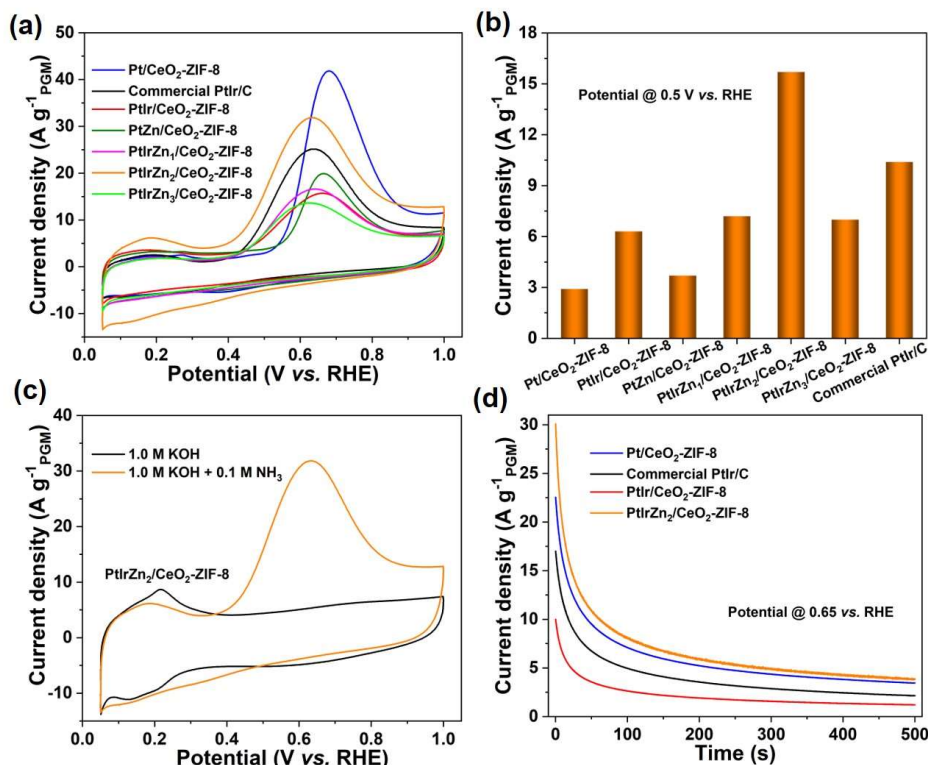


Figure 4. CV curves for different catalysts in Ar-saturated 1.0 M KOH + 0.1 M NH₃ at 5 mV s⁻¹ and 900 rpm under ambient conditions: (a) Comparison between Pt, PtIr, PtZn, PtIrZn₁, PtIrZn₂, PtIrZn₃ deposited on the CeO₂-ZIF-8 support and the commercial PtIr/C catalyst. (b) AOR activity comparison for various catalysts in (a) at 0.5 V vs. RHE. (c) CV curves of the PtIrZn₂/CeO₂-ZIF-8 catalyst in the presence and absence of NH₃. (d) Chronoamperograms (CA) of the Pt/CeO₂-ZIF-8, commercial PtIr/C, PtIr/CeO₂-ZIF-8, and PtIrZn₂/CeO₂-ZIF-8 in Ar-saturated 1.0 M KOH with 0.1 M NH₃ at 900 rpm at 0.65 V vs. RHE under ambient conditions.

Zn has a high overpotential for hydrogen evolution.¹⁵ Therefore, the introduction of Zn into Pt or PtIr could suppress the hydrogen adsorption, as evidenced in the CV curves recorded in Ar-saturated 0.1 M KOH solutions for various catalysts, including Pt/CeO₂-ZIF-8, PtIr/CeO₂-ZIF-8, PtZn/CeO₂-ZIF-8, and PtIrZn₂/CeO₂-ZIF-8. (Figure S16). The hydrogen adsorption/desorption occurs over 0 to 0.40 V vs. RHE, where the adsorption of ammonia would compete against the hydrogen adsorption. The addition of Zn might inhibit the competitive hydrogen adsorption (Table S4), leading to a decrease in onset potential (Figure 4a).

In general, the amount of an introduced third metal (e.g., Zn or Ni¹³) in the ternary alloys will result in effects on their electronic structure, therefore affecting NH₃ adsorption and N–H bond activation differently. Although the PtIrZn₂/CeO₂-ZIF-8 catalyst performs the best, other studied Zn contents in PtIrZn catalysts (e.g., PtIrZn₁/CeO₂-ZIF-8 and PtIrZn₃/CeO₂-ZIF-8) do not exhibit enhanced activity compared to the PtIr/CeO₂-ZIF-8 catalyst (Figure 4a, b and Table S3). Because only Pt or Ir sites can adsorb NH₃ for subsequent dehydrogenation at room temperature, energy factors relating to bond cleavage and geometric factors are sensitive to the Zn content. An appropriate amount of Zn added into the PtIr system is needed to maintain Pt–Ir sites' density for N–H bond activation and breaking. Considering both the J_p and the E_{onset} (Table S3), the PtIrZn₂/CeO₂-ZIF-8 (molar ratio of Pt/Ir/Zn = 1:1:0.6) was regarded as the optimal ternary PtIrZn AOR catalyst, which was further studied in the next sections.

The synergy between CeO₂ and ZIF-8 was further confirmed by the enhanced AOR activity of PtIrZn₂ nanoparticles supported on CeO₂-ZIF-8 (current density: 15.7 A g⁻¹ at 0.5 V) when compared to the individual CeO₂ (current density: 3.6 A g⁻¹ at 0.5 V), and ZIF-8-derived carbon (current density: 10.9 A g⁻¹ at 0.5 V vs. RHE) supports (Figure 4d and Table S5). The higher AOR activity of PtIrZn₂/CeO₂-ZIF-8 catalyst is attributed to fast scavenging of the *NH species adsorbed on Pt alloy sites by reaction with OH adsorbed on adjacent CeO₂ sites at lower oxidation potential.^{13, 25} More significantly, the optimal PtIrZn catalyst supported on CeO₂-ZIF-8 binary support shows much better AOR activity relative to commercial XC-72 support (Figure S16 and S17). Thus, the interfaces between the active metal sites (i.e., PtIrZn) and advanced support (i.e., CeO₂-ZIF-8) are the critical factors for the enhanced AOR activity. Likewise, another composite support consisting of SiO₂-CNT-COOH yield enhanced AOR activity.¹³ The PtIrZn nanoparticles (e.g., Figure 2b) directly attached to the CeO₂ may have enhanced intrinsic AOR activity because the supplied OH groups from CeO₂ readily accept a proton and facilitate the critical NH₃ dehydrogenation (e.g., NH_{3,ad} + OH⁻ → NH_{2,ad} + H₂O + e⁻). Meanwhile, the ZIF-8-derived carbon typically exhibits a large surface area and porosity, maximizing the Pt alloy utilization and enriching CeO₂ and PtIrZn NP interfaces.

Figure 4c presents typical CV curves for the optimal PtIrZn catalyst in 0.1 M KOH in the presence and absence of NH₃, showing an NH₃ oxidation peak in the potential range of 0.30–0.95 V. A small pre-peak at around 0.22 V before the AOR peak is likely attributed to

the chemical adsorption of NH_3 .^{48, 49} The deactivation at higher potential ranges (0.64–0.92 V) is due to the strongly adsorbed reaction intermediates (e.g., *N and *NO) that block the active Pt alloy surface.^{13, 43} CA results (Figure 4d and Figure S17) further determine that the optimal PtIrZn catalyst has the highest current density (e.g., 3.9 A g⁻¹ after 500 s) at 0.65 V, superior to PtIr/CeO₂-ZIF-8 (1.2 A g⁻¹) and commercial PtIr/C (2.2 A g⁻¹) catalysts. It should be pointed out that these CAs show a rapid drop of the current until attaining a steady-state. At the beginning of the reaction, the active sites (i.e., Pt or PtIr) are likely free for adsorbing NH_3 molecules. However, the initial activity drop is due to the reduction of Pt site density due to the poisoning with *N or *NO_x species rate as the reaction proceeds.^{13, 50}

To further determine the superiority of ternary PtIrZn, the most studied Ni and Cu were selected as the third metals alloying with PtIr. As discussed above, Zn's optimal addition into PtIr can suppress the hydrogen adsorption, acting as a critical role to facilitate the AOR (Figure S16 and Table S4). In contrast, Ni and Cu's addition to PtIr affects the hydrogen adsorption-desorption behaviors differently (Figure S18a). As a result, the AOR activity for these three ternary alloys is in order of PtIrZn > PtIrNi > PtIrCu, with the corresponding onset potentials of 0.345, 0.414, and 0.418 V, respectively (Figure S18b and Table S5). This activity order was further demonstrated by their current densities (i.e., 15.7, 7.7, and 6.3 A g⁻¹) at 0.5 V (Figure S18c) from CVs and their corresponding CA results (Figure S18d).

Overall, the AOR activity of the best-performing PtIrZn₂/CeO₂-ZIF-8 catalyst (molar ratio of Pt/Ir = 1:1, E_{onset} : 0.345 V vs RHE, J_p : 31.8 A g⁻¹) is superior or comparable to those of many reported catalysts, such as PtZn nanocubes/C catalyst (E_{onset} : ~0.5 V vs RHE, J_p : 405 A g⁻¹),⁴⁶ PtIr/N-reduced graphene oxide (rGO) (molar ratio of Pt/Ir = 1:3, E_{onset} : ~0.37 V vs RHE),⁵¹ PtIrNi/SiO₂-CNT-COOH (molar ratio of Pt/Ir = 9:1, E_{onset} : ~0.399 V vs RHE, J_p : 124.0 A g⁻¹),¹³ PtIrNi/CeO₂-CNT-COOH (molar ratio of Pt/Ir = 9:1, E_{onset} : ~0.465 V vs RHE, J_p : 34.0 A g⁻¹),¹³ CuPtRh nanowires (mass ratio of Pt/Ru = 7:1, E_{onset} : ~0.49 V),⁵² and Ir and Ni(OH)₂-decorated Pt nanocubes (mass ratio of Pt/Ir = 98:2, E_{onset} : ~0.51 V)⁵⁰. Detailed comparisons of aforementioned AOR catalysts in terms of E_{onset} and/or J_p were compared in Table S5.

The PtIrZn₂/CeO₂-ZIF-8 catalyst also shows good stability for the AOR. The continuous CV cycling over the potential range of 0.05–0.7 V at 500 mV s⁻¹ was conducted in Ar-saturated 1.0 M KOH solutions to evaluate the catalyst's degradation. After 2000 cycles, the PtIr/C benchmark rapidly lost 65% of its initial electrochemically active surface area (ECSA).¹³ In contrast, the PtIrZn₂/CeO₂-ZIF-8 catalyst exhibited much better cycling stability, retaining more than ~85% of the initial ECSA (Figure S19a). The ECSA reduction of these two catalysts is in good agreement with their AOR activity losses (Figure S19a). The PtIrZn₂/CeO₂-ZIF-8 catalyst shown only 32 mV positive shift of peak potential and a loss of ~3.0 % peak current density, whereas the PtIr/C benchmark displayed ~46 mV positive shift of peak potential and a loss of 51% peak current density.¹³ Therefore, both the chronoamperometric durability (Figure 4d) and the cycling stability (Figure S19) of PtIrZn₂/CeO₂-ZIF-8 have exceeded the PtIr/C catalyst.

2.3 Critical factors of AOR rates

In addition to the catalyst, AOR can be affected by critical reaction conditions, such as the operating temperature, NH_3 concentration,

and KOH concentration.^{43, 53} The effect of operating temperature was investigated on the best-performing PtIrZn₂/CeO₂-ZIF-8 catalyst and the commercial PtIr/C reference (Figure 5a). The oxidation peak current densities of both catalysts rise rapidly with temperature elevating up to 80 °C, attributable to the improved kinetics of NH_3 oxidation.⁵³ Strikingly, the AOR onset potential of the PtIrZn catalyst shifts from 0.33 V at 25 °C to 0.25 V at 80 °C, and its J_p increases from 38 to 418 A g⁻¹. The CV curves (Figure 5a) also exhibit a 102 mV negative shift of the peak potential from 25 to 80 °C. With an increase of temperatures, the *N intermediate can form less positive potential, allowing a higher reaction rate at a lower overpotential.¹³ The N–N dimerization reactions become more accessible at higher temperatures.^{43, 44} Steady-state CA results of the PtIrZn₂/CeO₂-ZIF-8 (Figure S20a) at different temperatures are consistent with its CV results, further confirming the advantage of the elevated temperatures for the AOR. Figure 6b shows the Arrhenius plots for the PtIrZn₂/CeO₂-ZIF-8 and the commercial PtIr/C catalysts at 0.5 V. Good linear relationships are achieved by plotting log(J) and 1/ T , indicating that the reaction mechanism is not changed with temperature increasing.⁵³ According to the Arrhenius law, their activation energy can be calculated using the equation.^{53, 54} The activation energies at 0.5 V were calculated to be 36.7 and 50.8 kJ mol⁻¹ for the PtIrZn₂/CeO₂-ZIF-8 and commercial PtIr/C catalysts, respectively (Figure 5b). The lower activation energy of the PtIrZn catalyst unveils its higher intrinsic activity, faster charge transfer process, and less energy-consuming to the reaction in theory.⁵³

AOR activity of the PtIrZn₂/CeO₂-ZIF-8 catalyst is increased with the NH_3 concentration (Figure 5c). The current density was increased from 9.4 to 17.6 A g⁻¹ when concentrations of NH_3 are from 0.05 to 1.0 M at 0.5 V (Figure 5d). Higher NH_3 concentrations lead to faster current attenuation (Figure S20b), which can be attested by a lower remaining current density at 1.0 M NH_3 (4.8 A g⁻¹) than 0.5 M NH_3 (5.1 A g⁻¹) after 500 s. These results indicate that more poisonous adsorbates could be accumulated in an electrolyte with a higher NH_3 concentration during the AOR.

Given a constant NH_3 concentration and under room temperature, the OH⁻ concentration in electrolytes can substantially influence the AOR rates. Figure 5d and Figure S20c (CA characterization) show the effect of KOH concentration on the AOR activity of the PtIrZn₂/CeO₂-ZIF-8 catalyst, as measured by RDE. Higher OH⁻ concentration can lower the AOR onset potential. It also increases the peak current density (Figure 5e). When OH⁻ concentrations are increased from 1.0 to 5.0 M, the onset potentials are reduced from 0.345 to 0.314 V, and the peak current densities are increased from 31.8 to 65.1 A g⁻¹. The improved AOR activity at higher OH⁻ concentration is likely due to smaller charge transfer resistance (R_{ct} = 16.6, 19.8, and 60.4 Ω for 5.0, 3.0, and 1.0 M KOH, respectively, Figure 5f).^{7, 55}

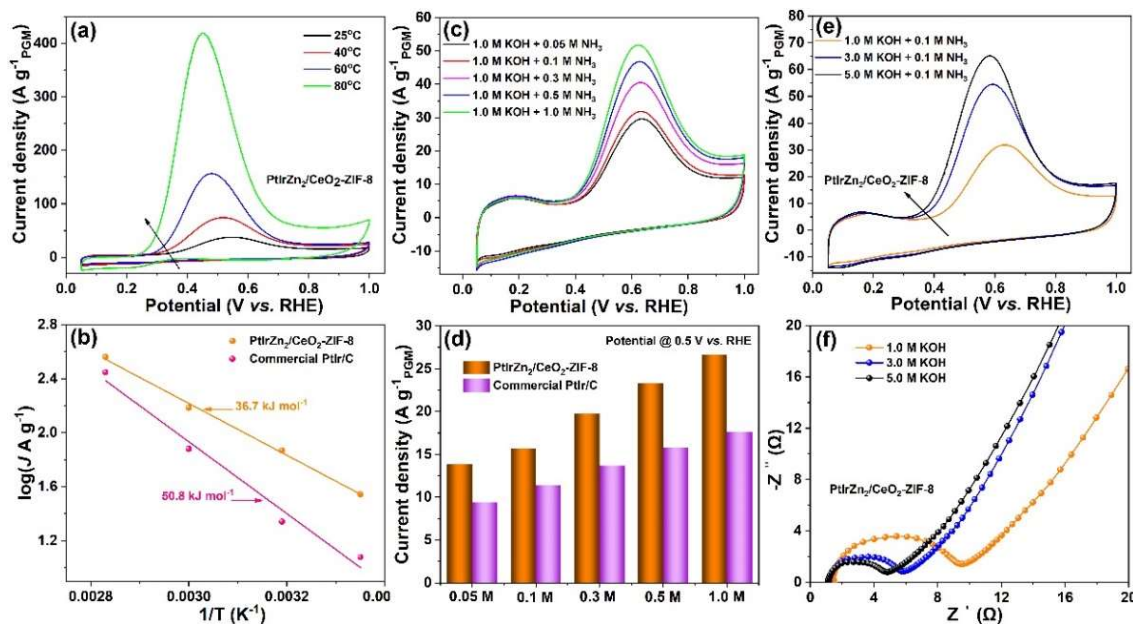


Figure 5. (a) CV curves at 5 mV s^{-1} and 900 rpm for the PtIrZn₂/CeO₂-ZIF-8 catalyst in Ar-saturated 1.0 M KOH + 0.1 M NH₃ operating at different temperatures. (b) Arrhenius plots for NH₃ oxidation on PtIrZn₂/CeO₂-ZIF-8 and commercial PtIr/C catalysts at 0.5 V vs. RHE. (c) CVs for the AOR in 1.0 M KOH electrolytes with different NH₃ concentrations under room temperature. (d) AOR activity comparisons at 0.5 V vs. RHE for PtIrZn₂/CeO₂-ZIF-8 and commercial PtIr/C at different NH₃ concentrations. Note: the PtIr/C benchmark were compared according to our previous report.¹³ (e) CVs for the AOR in various electrolytes containing 0.1 M NH₃ and different KOH concentrations at room temperature. (f) Nyquist plots of EIS spectra measured for the PtIrZn₂/CeO₂-ZIF-8 catalyst in different KOH concentrations at the open circuit potential.

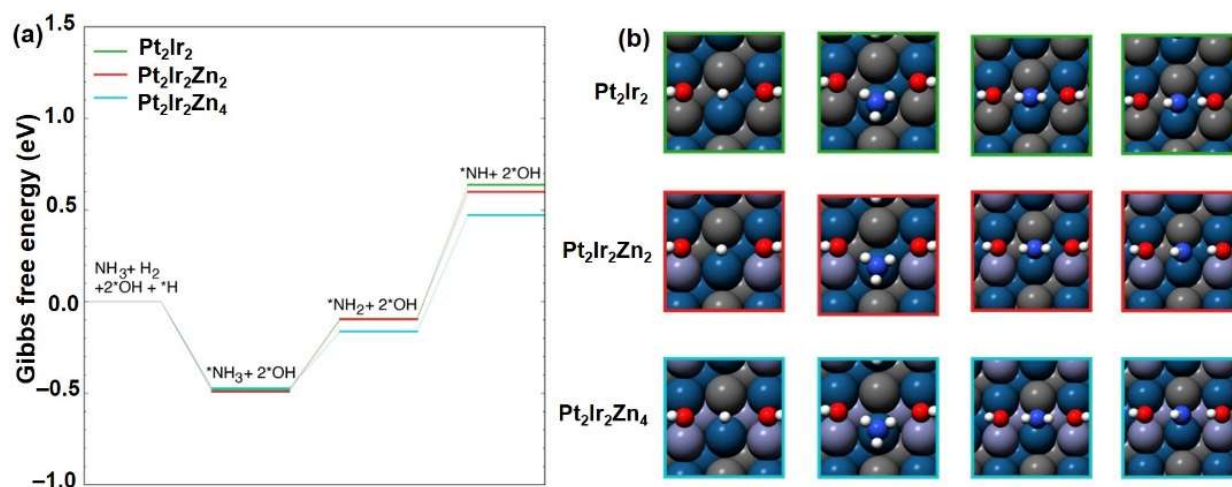


Figure 6 (a) Free energy diagrams of NH₃ oxidation on Pt₂Ir₂ and its ternary alloy with Zn at 0 V vs. RHE. (b) Geometric structures of clean, *NH₂, and *NH intermediates on Pt₂Ir₂ and its alloys with Zn. (Grey: Pt, dark blue: Ir, purple: Zn, red: O, white: H, and blue: N)

2.4 Theoretical studies of the AOR

To understand Zn's role in the ternary PtIrZn catalyst for the AOR, we performed DFT calculations for appropriate reaction steps on three models, including a bimetallic Pt₂Ir₂ and Pt₂Ir₂Zn₂ systems with a relatively low and medium Zn content (Pt₂Ir₂Zn_{1c} and Pt₂Ir₂Zn_{1mc}). All models were simulated in the fcc phase. The (100)-termination was chosen because of its unique structure toward N-N coupling, a crucial step for ammonia oxidation⁵⁶. Because of Zn's strong oxophilicity and the abundance of OH_{ad} from the CeO₂ support, the surface bridge

sites are pre-covered with $\frac{1}{4}$ ML *OH species. The limiting potential of *NH₂ to *NH with the hydrogen bonding interaction with OH is a useful indicator for capturing the onset potential of the AOR on Pt(100) and its alloys.^{13, 56} *NH-*NH dimerization is the dominant pathway toward N₂ formation. **Figure 6** shows the free energy diagram of the initial steps of NH₃ oxidation at 0 V. Compared to the Pt-Ir bridge site on Pt₂Ir₂(100), a low concentration of Zn (preferred at the surface because of a strong interaction with *OH) stabilizes the *NH₂ and *NH intermediates only slightly with a reduction of the limiting potential < 0.03 V. The Zn atom has a weaker

d-d coupling to the Pt-Ir group d-orbitals, which will shift up the d-band and facilitate the hydrogenation of *NH_2 species. Fortunately, the sp-electron transfer from the electron-rich Zn atoms to the Pt-Ir site has an opposite effect. As the Zn concentration increases in the $Pt_2Ir_2-Zn_{mc}$ model, the stabilization of *NH is 0.1 eV more than the *NH_2 species, which leads to a 0.1 V reduced onset potential of the PtIrZn catalyst as observed experimentally. We attributed this effect to Zn-induced electronic structure change as the average of d-band center is increased from -0.7 eV in the Pt_2Ir_2 to -0.52 eV in the $Pt_2Ir_2-Zn_{mc}$. Another effect is the competitive adsorption between *H and *NH_3 . At Pt(100), the adsorption/desorption of *H occurs at the potential of 0.2–0.4 V, which overlaps with the operating potential of AOR at ~ 0.3 V. The strongly binding *H might block the active Pt-Ir site for the NH_3 adsorption. The free energy of *NH_3 adsorption at the Pt-Ir site is 0.6 eV stronger than Pt(100). Although Zn stabilizes both intermediates on PtIrZn catalysts, it becomes more favorable for *H removal with *NH_3 adsorption, resulting in a less positive potential of *H oxidation. This result is impressive since it is generally believed that Zn destabilizes the *H , prohibiting the HER. Our DFT calculations suggest that incorporating Zn into PtIr leads to a stronger *NH_3 adsorption than *H adsorption, which is kinetically favorable for the AOR.

2.5 Low-temperature direct ammonia fuel cell performance

The typical set-up for a DAFC was illustrated in **Figure 7a**. NH_3 reacts with OH^- and is oxidized at the anode to provide electrons and generate N_2 ($2NH_3 + 6OH^- = N_2 + 6H_2O + 6e^-$, $E^0 = -0.77$ V vs. SHE). O_2 consumes electrons and generates OH^- ($O_2 + 2H_2O + 4e^- = 4OH^-$, $E^0 = 0.401$ V vs. SHE) at the cathode.¹¹ In theory, the overall reaction can generate a cell voltage up to 1.17 V, which is only slightly lower than an H_2 - O_2 fuel cell.

Unlike in aqueous electrolytes, high-performance OH^- -exchange membranes and ionomers developed at the University of Delaware were integrated with these studied PtIrZn catalysts for fabricating membrane electrode assemblies (MEAs) for DAFC studies.^{7, 57} The cathode is an Acta 4020 catalyst (i.e., 3.5 wt% transition iron metal on carbon support) for the oxygen reduction reaction (ORR). During the DAFC studies, we selected four PtIr-based catalysts concerning the variations of supports (i.e., $CeO_2/ZIF-8$ -carbon, $SiO_2/CNT-COOH$, and commercial XC-72) and metal nanoparticles (i.e., PtIr and PtIrZn₂, 1.0 mg_{PGM} cm⁻²). RDE measurements (**Figure 7b**) indicate that their AOR activities in an aqueous electrolyte ($KOH+NH_3$) follow the order: PtIrZn₂/SiO₂-CNT-COOH > PtIr/SiO₂-CNT-COOH > PtIrZn₂/CeO₂-ZIF-8 > commercial PtIr/C, as evidenced by their current densities of 32.4, 24.7, 15.7, and 10.4 A g⁻¹ at 0.5 V, respectively.

The polarization curves of DAFCs at 95 °C by using different anode catalysts were recorded in **Figure 7c**. The open-circuit voltages (OCVs) with these studied PtIrZn₂/CeO₂-ZIF-8, PtIr/SiO₂-CNT-COOH,

and PtIrZn₂/SiO₂-CNT-COOH anodes are 0.64, 0.70, and 0.70 V, respectively, comparable to that of the commercial PtIr/C (0.69 V). MEA testing results show a different trend to their AOR onset potentials evaluated by RDE (**Figure 7b**). A similar phenomenon was found on the peak power densities, showing 91 mW cm⁻² for the PtIrZn₂/CeO₂-ZIF-8, 241 mW cm⁻² for the PtIr/C, 282 mW cm⁻² for the PtIr/SiO₂-CNT-COOH, and 314 mW cm⁻² for the PtIrZn₂/SiO₂-CNT-COOH. From the high-frequency resistance (HFR) result recorded by the EIS module of the fuel cell test station, the HFR of MEA with the PtIrZn₂/CeO₂-ZIF-8 catalyst is 110 mΩ cm⁻², which is much larger than those of MEAs with PtIrZn₂/SiO₂-CNT-COOH and PtIr/SiO₂-CNT-COOH, which are 65 mΩ cm⁻² for both. The HFR of MEA with commercial PtIr/C is 50 mΩ cm⁻². The resistance comparison of MEAs is inconsistent with Nyquist plots recorded by using RDE (**Figure S21**). Since the loading and thickness of the catalyst layer of MEA are higher than that of RDE, the resistance will significantly influence the performance.

Nevertheless, the improved cell performance of the PtIrZn₂/SiO₂-CNT-COOH relative to the PtIr/SiO₂-CNT-COOH further determines the significance of introducing Zn into PtIr alloys. The higher power density of DAFCs with the catalysts supported on SiO₂/CNT-COOH support also justifies the critical role of supports in boosting charge and mass transports within thick cathodes (**Figure 7c**). The relatively poor DAFC performance with the PtIrZn₂/CeO₂-ZIF-8 anode may be due to the high resistance caused by non-uniform ionomer distribution and less efficient mass transport caused by dominant micropores in ZIF-8-derived carbon. In contrast, the SiO₂-CNT-COOH composite support can provide more efficient charge and mass transports, which is critical for enhanced MEA performance.⁵⁸

Compared to previous DAFC performance in literature, the PtIrZn₂/SiO₂-CNT-COOH anode performs the best (**Table S6**). Notably, given the significant activity difference between the PtIrZn/SiO₂-CNT-COOH and the commercial PtIr/C (**Figure 8b**), we should expect further improved DAFC performance with continuously studying MEA design and fabrication. It should be noted that, apart from intrinsic activity, the catalyst morphology and structures are essential for MEA performance. It is often challenging to directly transfer high RDE activity in aqueous electrolytes to solid-state electrolyte-based MEA performance because of the complicated triple-phase interfaces for charge and mass transports in a thick and porous cathode.⁵⁹ Based on the obtained knowledge on H_2 - O_2 and direct methanol fuel cells,^{60–62} DAFC performance can be improved by increasing the PGM loading on supports, optimizing the interaction between PtIrZn alloy NPs and the support, engineering the interfaces of the catalyst and the ionomer for OH^- transfer within the cathode, and improving cathode structures with better ammonia permeability.^{7, 9, 63}

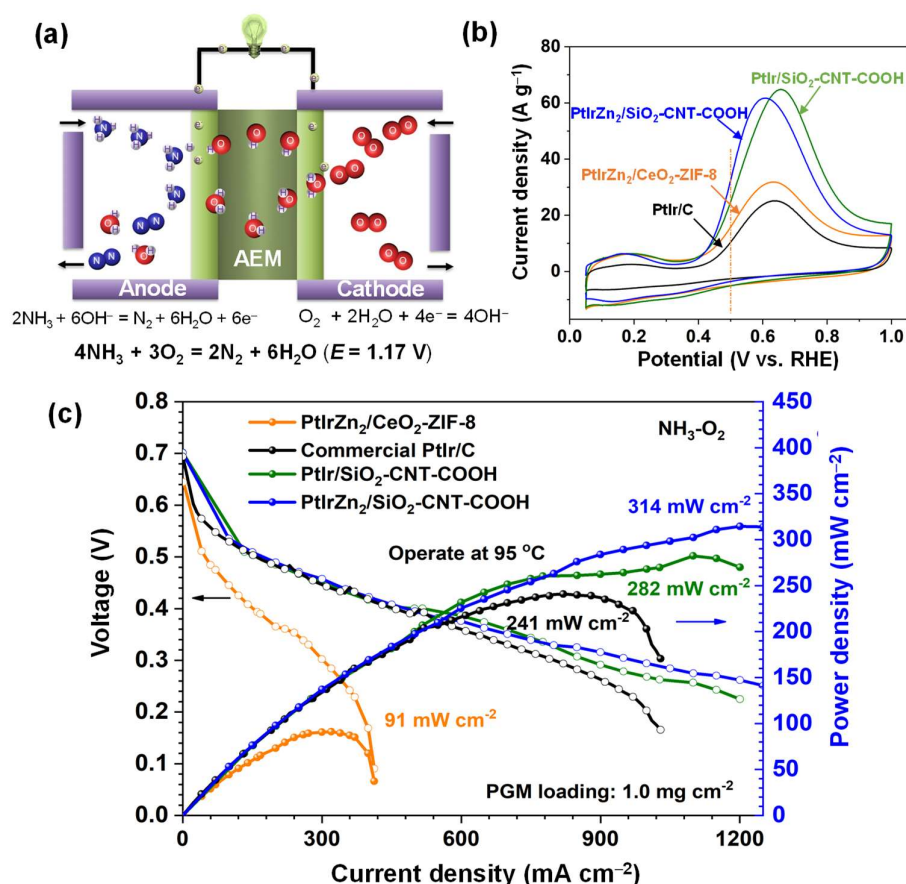


Figure 7. (a) Schematic view of components and working principles of a DAFC. (b) AOR activity comparison of PtIrZn₂/CeO₂-ZIF-8 (Pt-Ir, 10 wt%), PtIr/SiO₂-CNT-COOH (Pt-Ir, 10 wt%), PtIrZn₂/SiO₂-CNT-COOH (Pt-Ir, 20 wt%), and PtIr/C (Pt-Ir, 40 wt%) in 1.0 M KOH + 0.1 M NH₃ at 5 mV s⁻¹ and 900 rpm under ambient conditions. (c) Polarization curves and power density curves of DAFCs with PtIrZn₂/CeO₂-ZIF-8, PtIr/C, PtIr/SiO₂-CNT-COOH, and PtIrZn₂/SiO₂-CNT-COOH anodes. The ORR cathode catalyst is a Fe-based commercial Acta 4020. The anode contains 1.0 mg_{PGM} cm⁻² with 10 wt% PAP-TP (terphenyl-based) ionomer. The cathode contains 2.0 mg cm⁻² of Acta 4020 with 20 wt% PAP-TP ionomer. The hydroxide exchange membrane (HEM) is PAP-TP (81 μm thickness). Testing conditions: cell temperature of 95°C, 7.0 M NH₃ in 1.25 M KOH aqueous solution (5.0 mL min⁻¹) at 1.0 bar backpressure; O₂ (500 mL min⁻¹) at 2.0 bar backpressures.

3. Conclusions

In summary, inspired from theoretical understanding, we designed and synthesized a PtIrZn ternary alloy catalysts supported on various composite supports for the AOR in DAFCs. In particular, well-defined PtIrZn alloy nanoparticles can be uniformly dispersed on a composite support consisting of CeO₂, and ZIF-8 derived carbon, with an average diameter of 2.3 ± 0.2 nm. In principle, CeO₂ can serve Lewis base and provide OH for facilitating the AOR. The high surface areas, dominant porosity, and N dopant in the ZIF-8-derived carbon can be favorable for generating fine alloy nanoparticles during the synthesis. The

combination of CeO₂ and ZIF-8 carbon can enrich the CeO₂-Pt alloy interfaces, thus enhancing the AOR activity. Similarly, we further employed SiO₂-CNT-COOH composite support for preparing the ternary PtIrZn catalyst. Unlike CeO₂, SiO₂ processes high surface areas and plays a similar role in facilitating the AOR by providing OH groups. It should be noted that the combination of CeO₂ and CNTs was explored as well, but both have low surface areas and cannot achieve uniform metal NP dispersion.

RDE results shown that the optimal PtIrZn catalyst at a molar ratio of 1:1:0.6 shows superior AOR activity and stability in alkaline media relative to the commercial PtIr/C. DFT

calculations suggest that Zn atoms' addition into the PtIr alloy modulates the electronic structure of Pt-Ir active ensembles on the (100) surface for facilitating dehydrogenation steps adsorbed NH₃. Similar to the Zn's role in enhancing AOR activity, Ni or Cu were also introduced into the PtIr baseline. Their AOR activities are in the order of PtIrZn > PtIrNi > PtIrCu. The kinetics of AOR is strongly dependent on the operation temperature, NH₃ concentration, and KOH concentration in aqueous electrolytes. The increasing temperature results in a significantly increased current density and reduced overpotentials. The AOR activity is also enhanced with NH₃ concentrations, but a higher concentration of NH₃ may accelerate the catalyst deactivation. Higher OH⁻ concentration lowers the AOR onset potential and increases the peak current density, likely due to the fast AOR kinetics and smaller charge transfer resistances.

Multiple studied PtIrZn catalysts and the commercial PtIr/C were further evaluated in DAFCS by using OH⁻ exchange membrane and ionomers. At first, the PtIrZn₂/CeO₂-ZIF-8 (Pt-Ir, 10 wt%) anode catalyst does not present encouraging DAFC performance and only exhibited a moderate peak power density of 91 mW cm⁻² due to a large charge transfer resistance and low mass transport. When PtIrZn alloy NPs were deposited on an alternative composite support consisting of high-surface-area SiO₂ and highly electrically conductive CNT-COOH, the PtIrZn/SiO₂-CNT-COOH anode catalyst achieved a compelling peak power density of 314 mWcm⁻², much higher than PtIr/SiO₂-CNT-COOH (282 mWcm⁻²) and PtIr/C (241 mWcm⁻²) controls. The enhanced DAFC performance further justifies the importance of innovative supports and PtIrZn catalysts for the AOR in actual MEAs. Further engineering electrode structures and MEA fabrication concerning advanced catalyst and support designs, catalyst/ionomer interfaces, and porosity for NH₃ permeability could dramatically improve DAFC performance for promising transportation and other applications.

Author Contribution

G.W., Y.Y., H. X., J.Y., and Y.L. proposed the concept and designed all experimental and theoretical studies. Y.L., Z.Q., and M.C. carried out materials synthesis and characterization. H.S.P. and Q.M. performed DFT calculation. S.H. and D.S. conducted electron microscopy studies. S.K. analyzed XPS data. T.W. and Y. Z. tested fuel cell performance. G.W., Y.Y., H. X., and Y. L. wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

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Broader Context

The development of clean hydrogen fuel cells is crucial for our energy and environment sustainability, and, however, still face grand challenges in terms of difficulties of hydrogen production, transportation, distribution, and storage. Alternatively, ammonia, a carbon-neutral fuel, is an ideal hydrogen carrier, which can be readily transported and stored using existing infrastructures, and then directly utilized for energy applications through a direct ammonia fuel cell (DAFC). However, the kinetically sluggish ammonia oxidation reaction (AOR) in DAFCs requires substantial precious metal catalysts (e.g., Pt and Ir), leading to prohibitively high cost. This research is dedicated to reducing the cost of DAFCs by developing advanced AOR catalysts with reduced precious metal loadings and improved catalytic performance. High-performance DAFCs in the future can provide power sources without CO₂ emission for a variety of applications, including electric vehicles, portable electronics, and stationary residences.