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Effect of Ammonia on the Electrocatalysis of Oxygen Reduction Reaction in Base

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We investigated the effect of ammonia on the activity of seven benchmark oxygen reduction reaction (ORR) electrocatalysts, Pt/C, Pd/C, Au/C, Ag/C, commercial Fe–N–C, zeolitic imidazolate framework (ZIF)-based Fe–N–C (Fe-ZIF), and ZIF-based Fe, Co–N–C (Fe,Co-ZIF) in alkaline media and direct ammonia fuel cell (DAFC) relevant conditions using a rotating disk electrode. We found that ammonia exposure causes considerable ORR activity loss for all studied electrocatalysts. Should we rank the electrocatalysts in terms of their ORR activity loss and their irreversible ORR activity loss as the result of exposure to ammonia (from the highest loss to the lowest loss), we get Au/C > Pt/C > Ag/C > commercial Fe–N–C > Fe-ZIF > Fe,Co-ZIF and Pd/C > Au/C > Ag/C > commercial Fe–N–C > Fe-ZIF > Fe,Co-ZIF > Pd/C, respectively. The ammonia oxidation reaction activity and adsorptive properties of the Gerischer-Mauser reaction intermediates do not govern the trend of the ORR activity loss of Pt/C, Pd/C, Au/C, and Ag/C electrocatalysts. Notably, we found that Pt/C electrocatalyst shows the lowest irreversible ORR activity loss, while Fe-ZIF and Fe,Co-ZIF electrocatalysts show the lowest overall ORR activity loss. Our comprehensive study suggests that Pt-based, Fe-ZIF, and Fe,Co-ZIF electrocatalysts are promising cathode candidates for future DAFCs.

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Hydrogen carriers have recently attracted significant attention as alternative fuels to gaseous hydrogen for the realization of a low-carbon/carbon-neutral civilization. This attention is a result of the fact that hydrogen as a fuel faces critical technological challenges in transportation, storage, and dispensation, which impedes its extensive application. Among hydrogen carriers, ammonia is an up-and-coming candidate to replace hydrogen because of its various advantages, such as low production cost, full availability, produc-
sion, storage, and transportation infrastructures that are well-established worldwide, ease in liquefaction under mild conditions (8.46 atm at 20 °C or −33.4 °C at atmospheric pressure), and high volumetric energy density.6,7

In response to the above technical trend, the development of direct ammonia fuel cell (DAFC) as an energy conversion device that directly utilizes ammonia as a fuel has significantly accelerated. The advances in DAFC technology, particularly over the past few years, have been awe-inspiring.6 As the ammonia oxidation reaction (AOR), the reaction which happens in the anode side of a DAFC, operates most efficiently in alkaline media and direct ammonia fuel cell (DAFC) relevant conditions using a rotating disk electrode, the ammonia tolerance of the ORR electrocatalysts will be a critical metric in designing high-performance DAFCs. Moreover, the adsorption of nitrogen-containing species during the AOR in the cathode of a DAFC could poison the ORR electrocatalysts. This poisoning can ultimately result in instability, as well as a decrease in DAFC performance. To the best of our knowledge, the impact of ammonia on the ORR electrocatalysis in alkaline media and DAFC relevant conditions has not been addressed systematically yet. We note that should the effect of ammonia on the ORR electrocatalysis in alkaline media be significant, as we will show in the case, the ammonia tolerance of the ORR electrocatalysts will be a critical metric in designing high-performance DAFCs.

We would like to mention that the current study is motivated in part by our recent observation that the ORR polarization curves recorded in either 1 M potassium hydroxide (KOH) or (1 M KOH + 0.1 M ammonia) electrolytes were not identical for Pt/C and a commercial Fe–N–C (Acta 4020) electrocatalysts. Both electrocatalysts lost some ORR activity as a result of exposure to ammonia.6 Interestingly, we observed the ORR activity loss to be smaller for Acta 4020 electrocatalyst than for Pt/C electrocatalyst, which prompted us to use the former as the cathode electrocatalyst in our DAFC development efforts.6 However, in our previous study, we did not quantify the amount of the ORR activity loss of Pt/C and Acta 4020 electrocatalysts as a function of exposure time to ammonia in alkaline media and DAFC relevant conditions. Also, we did not investigate the cause of the ORR activity loss of the electrocatalysts, and whether their ORR activity loss is recoverable or not.6,8

In this work, we quantify and analyze the effect of ammonia on the activity of seven benchmark ORR electrocatalysts (Pt/C, Pd/C, Au/C, Ag/C, commercial Fe–N–C, zeolitic imidazolate framework (ZIF)-based Fe–N–C (Fe–ZIF), and ZIF-based Fe,Co–N–C (Fe,Co-ZIF)) in alkaline media and DAFC relevant conditions using a rotating disk electrode (RDE). From the noble metal electrocatalysts active for the ORR in alkaline media, namely Pt, Pd, Au, Ag, Ir, Ru...
and, Rh,8,26–28 we chose only to investigate Pt, Pd, Au, and Ag. We made this informed decision since Ir, Ru, and Rh are poor ORR electrocatalysts compared to Pt, Pd, Au, and Ag in alkaline media.7,8,26–28 From a practical point of view, the high cost and scarcity of Ir and Rh compared to others also make them much less attractive ORR electrocatalysts.7,8,26–28 We also decided to investigate Fe–N–C (commercially made), Fe-ZIF, and Fe,Co-ZIF electrocatalysts as they are very promising low-cost ORR electrocatalysts.29–36 We show that the loss of ORR activity as a result of exposure to ammonia is quite significant for all of the electrocatalysts studied. However, Fe-ZIF and Fe,Co-ZIF electrocatalysts are the most promising electrocatalysts in terms of ammonia tolerance. We also demonstrate that among the noble metal electrocatalysts, Pt/C is most promising because its loss of ORR activity is mostly reversible, which is consistent with the formation of weakly-adsorbed nitrogen-containing species at its surface. Overall, our study highlights and quantifies the profound negative impact of ammonia exposure on the performance of the benchmark ORR electrocatalysts under DAFCE relevant conditions and provides essential guidance for the choice and design of ammonia-tolerant ORR electrocatalysts for DAFCs.

**Experimental**

**Chemicals and materials.**—We obtained Pt/C (5 weight percent (wt.% Pt supported on Vulcan XC-72, Premetek Co.), Pd/C (10 wt. % Pd supported on Vulcan XC-72, Premetek Co.), Au/C (20 wt.% Au supported on Vulcan XC-72, Premetek Co.), Ag/C (40 wt.% Ag supported on Vulcan XC-72, Premetek Co.), Acta 4020 (Fe–N–C electrocatalyst from Acta Company), and Pajarito (Fe–N–C electrocatalyst from Pajarito Powder, LLC) commercially and we used them as received. We purchased potassium hydroxide (KOH, 99.99%), isopropanol (IPA, 99.9%), and Nafion ionomer solution (LQ-1105–1100 EW, 5 wt.% from Sigma-Aldrich, Fisher Chemical, and Fuel Cell Store respectively and we used them as received.

**Synthesis of Fe-ZIF electrocatalyst.**—The ZIF-derived Fe–N–C electrocatalyst exclusively contains atomically dispersed FeN4 active sites, which is based on our previous effort.29–36 Typically, we dissolved 3.39 g of zinc nitrate hexahydrate (Zn(NO3)2·6H2O) and 0.145 g (0.5 mmol) of cobalt (II) nitrate hexahydrate (Co(NO3)2·6H2O) in 300 ml methanol solution. We prepared another 300 ml methanol solution containing 3.94 g of 2-methylimidazole (C4H6N2). Then, we mixed these two solutions and heated the mixture at 60 °C for 24 h. We collected the precipitate, and thoroughly washed it with ethanol, then dried the precipitate at 60 °C in a vacuum oven. The resulting Fe-ZIF crystals then underwent thermal activation at a temperature of 1100 °C under N2 flow for 1 h in a tube furnace to obtain the final Fe-ZIF electrocatalyst.

**Synthesis of Fe,Co-ZIF electrocatalyst.**—Fe,Co-ZIF electrocatalyst contains atomically dispersed FeN4 and CoN4 sites, which both are highly active for the ORR. The synthesis includes the following two steps:

**Synthesis of Co-N-C@surfactant nanocrystals.**—In the typical synthesis of Co-ZIF-8@F127 precursor,30 we dissolved F127 surfactant (0.5 g) in methanol (100 ml) to form a clear solution, and then we added into the solution 1.8 g (6 mmol) of Zn(NO3)2·6H2O and 0.145 g (0.5 mmol) of cobalt (II) nitrate hexahydrate (Co(NO3)2·6H2O). We subsequently injected 100 ml of methanol containing 1.6 g (19.5 mmol) 2-methylimidazole (C4H6N2) into the above solution under stirring for 5 min at room temperature. After stirring for 30 min at 60 °C in a reflux system, we collected the nanocrystals by centrifugation. After drying in a vacuum oven at 60 °C for 12 h, we obtained pink solid Co-ZIF-8@F127 crystals as a precursor for subsequent processes. Finally, we directly carbonized the as-obtained Co-ZIF-8@F127 crystals at 900 °C for 3 h under constant nitrogen flow with a ramp rate of 30 ° C min−1.

**Fe3+-adsorption and thermal activation.**—We dispersed a controlled amount of Co-N-C@F127 powder in Fe(NO3)3·9H2O in isopropanol solution for the following procedure.34 After 15 min of ultrasonication and 2 h of magnetic stirring, we collected the product that adsorbed Fe3+ by centrifugation, and then we dried it at 60 °C in a vacuum oven for 5 h. We dispersed 30 mg of dried powder in 10 ml n-hexane, and then we added 10 μl of Fe(NO3)3·9H2O (100 mg ml−1). Then, we performed thermal activation at 1100 °C for 1 h under N2 flow to generate the final Fe,Co-ZIF electrocatalyst.

**Experimental setup and preparation of working electrodes.**—We performed the electrochemical measurements in a three-electrode cell with a standard single-junction mercury/mercury oxide (Hg/HgO: PINE Instrument Company) electrode as the reference electrode, a graphite rod (6.35-mm outside diameter; Graphite Store) as the counter electrode, and a glassy carbon disk (5-mm outer diameter, PINE Instrument Company) as the working electrode. We prepared Pt/C, Pd/C, Au/C, Ag/C, Acta 4020, Pajarito, Fe-ZIF, and Fe,Co-ZIF-covered working electrodes using a three-step procedure.35 First, we prepared the electrocatalyst ink by mixing appropriate amounts of deionized (DI) water, IPA, 5 wt.% Nafion ionomer solution, and electrocatalyst (see Table S1 which is available online at stacks.iop.org/JES/167/164510/mmedia for the detailed composition of Pt/C, Pd/C, Au/C, Ag/C, Acta 4020, Pajarito, Fe-ZIF, and Fe,Co-ZIF inks). Second, we placed the electrocatalyst ink in an ice bath and sonicated the ink for four hours. Finally, we pipetted 10 μl of the well-dispersed electrocatalyst ink onto a mirror-polished glassy carbon disk electrode to achieve the desired loading (see Table I for the loading of Pt/C, Pd/C, Au/C, Ag/C, Acta 4020, Pajarito, Fe-ZIF, and Fe,Co-ZIF-covered working electrodes). We performed our experiments in 0.1 M KOH, which acts as the electrolyte, and Nafion only plays the role of an electrocatalyst binder. We note that researchers frequently use Nafion as the electrocatalyst binder in rotating disk electrode tests in alkaline electrolytes to investigate the ORR, the AOR, the oxygen evolution reaction (OER), the hydrogen evolution reaction (HER), the hydrogen oxidation reaction (HOR), and the nitrogen reduction reaction (NRR) since Nafion has outstanding oxidation/reduction resistance, mechanical stability, and film-forming properties.6,8,38–42

**Electrochemical measurements.**—By recording cyclic voltammetry (CV) scans in argon-saturated (0.1 M KOH) electrolyte at a rotation speed of 1600 rpm and a scan rate of 100 mV s−1, we determined the electrochemical surface areas (ECSAs) of the noble metal ORR electrocatalysts.7,41 We calculated the ECSAs of Pt/C electrocatalyst from the average of charges associated with desorption and adsorption of underpotential deposited (UPD) hydrogen region in the CV scan with proper double-layer correction.7,41,43 We measured the ECSAs of Pd/C and Au/C electrocatalysts from the
ammonia) electrolyte as the electrolyte that would mimic the cathode environment of a DAFC, which experiences significant technologically tolerable cross-over of ammonia from the anode side. Assuming anode and cathode flow rates are comparable in a DAFC, 0.1 M ammonia concentration corresponds to about 2 percent fuel loss (for 5 M ammonia concentration in the anode feed), which is similar to the 2 percent fuel loss in state-of-the-art hydrogen fuel cells.\textsuperscript{37} We used the average current density observed in the last minute of this experiment as a measure of the ORR activity of Pt/C electrocatalyst after exposure to ammonia, which subsequently allowed us to calculate the activity loss of Pt/C electrocatalyst as a result of exposure to ammonia. Fourth, we recorded two hundred CV scans in ammonia-free argon-saturated (0.1 M KOH) electrolyte to clean the surface of Pt/C electrocatalyst electrochemically and to remove any weakly-adsorbed nitrogen-containing species from the surface of the ammonia contaminated Pt/C electrocatalyst. We used the last recorded CV scan as a measure of the final state of Pt/C electrocatalyst, which subsequently allowed us to calculate the ECSA loss of Pt/C electrocatalyst as a result of exposure to ammonia. In addition, we note that one expects to observe pronounced differences between the first and the last recorded CV scans of Pt/C electrocatalyst after exposure to ammonia, should weakly-adsorbed nitrogen-containing species be present on the surface of Pt/C electrocatalyst. Therefore, we also compared the first and the last recorded CV scans for Pt/C electrocatalyst after exposure to ammonia. Fifth, we performed a constant potential (0.85 V vs RHE) activity test in ammonia-free oxygen-saturated (0.1 M KOH) electrolyte for one hour. We used the average current density observed in the last minute of this experiment as a measure of the ORR activity of Pt/C electrocatalyst after exposure to ammonia and potential cycling, which subsequently allowed us to calculate the irreversible activity loss of Pt/C electrocatalyst as a result of exposure to ammonia.

We also performed control experiments to demonstrate that there was no loss of ORR activity and ECSA for Pt/C electrocatalyst in an alkaline environment in the absence of ammonia. These experiments were identical to the main experiments described above, with the exception that in the third step, no ammonia was present. We summarized the more detailed version of the experimental procedure used in this study in Tables S2 and S3. We repeated the experiments three times, each time with a freshly prepared Pt/C electrocatalyst sample, to ensure reproducibility and statistical accuracy.

Control experiments confirm that there is no loss of ORR activity and ECSA for Pt/C electrocatalyst after performing the one-hour ORR experiment in ammonia-free 0.1 M KOH electrolyte (Fig. S1). Figure 1 shows the results of the experiments performed to evaluate the effect of exposure to ammonia on the performance of Pt/C electrocatalyst. Figure 2 depicts the ORR activity loss, ECSA loss, the ORR irreversible activity loss, and initial ORR area-specific activity of Pt/C electrocatalyst. By close inspection of Figs. 1 and 2, we can make the following observations and conclusions. First, the ORR activity of Pt/C electrocatalyst at the constant potential of (0.85 V vs RHE) decreases substantially in the presence of ammonia, indicating that there is significant poisoning of the electrocatalyst in the presence of ammonia (Figs. 1a, 1b, and 2). Second, the CV experiment performed after the ORR experiment in an ammonia containing electrolyte indicates that Pt/C electrocatalyst only loses a small portion of its ECSA due to exposure to ammonia (Figs. 1c and 2), suggesting that ECSA loss is responsible for only a small portion of the ORR activity loss. Third, we see significant differences between the first and the last recorded CV scans after exposure to ammonia for Pt/C electrocatalyst confirming the existence of weakly adsorbed nitrogen-containing species at the surface of Pt/C electrocatalyst after exposure to ammonia (Fig. 1d). Fourth, the ORR activity loss of Pt/C electrocatalyst is mainly recoverable, and the small irreversible ORR activity loss observed is identical, within experimental uncertainty, to the ECSA loss of the electrocatalyst (Figs. 1b and 2). These experiments confirm that the ECSA loss of Pt/C
electrocatalyst, most probably caused by surface-site blocking of strongly adsorbed nitrogen-containing species, is responsible for the small irreversible ORR activity loss of the electrocatalyst. Fifth, we note that previous experimental studies have shown that Pt has the highest electrocatalytic activity for the ORR relative to other metals.8,26–28 Interestingly, previous experimental studies have also established that Pt is the most active metal for ammonia oxidation,8,20,22–25,48,49 so we expect the ORR and the AOR to co-occur on a Pt surface, resulting in a voltage loss due to parasitic currents. These previous experimental reports, combined with the above-described results, lead us to conclude that parasitic currents and weakly adsorbed nitrogen-containing species at the surface of Pt/C electrocatalyst are mainly responsible for the significant loss of the ORR activity of Pt/C electrocatalyst in the presence of ammonia.

Effect of ammonia exposure on the ORR activity of Pd/C, Au/C, and Ag/C electrocatalysts.—Next, we performed similar experiments to investigate the effect of ammonia exposure on the ORR activity of Pd/C, Au/C, and Ag/C electrocatalysts. Control experiments performed for Pd/C, Au/C, and Ag/C electrocatalysts confirm that similar to Pt/C electrocatalyst, there is no loss of ORR activity and ECSA for these electrocatalysts after performing the ORR for one hour in ammonia-free 0.1 M KOH electrolyte (Figs. S2 to S4). For the sake of brevity, we only present the ORR experimental results at the constant potential of (0.85 V vs RHE) and comparison of the first and the last recorded CV scans after exposure to ammonia for these electrocatalysts in Fig. 3 (we show the detailed experimental results in Figs. S5 to S7). We also present a comparison of the ORR activity loss, ECSA loss, irreversible ORR activity loss, and initial ORR area-specific activity for these electrocatalysts in Fig. 2.

We can extract the below key observations and conclusions from Figs. 2 and 3. First, the initial ORR area-specific activity of Pt/C, Pd/C, Au/C, and Ag/C electrocatalysts decreases as follows: Pt/C > Pd/C > Au/C > Ag/C (Fig. 2). Second, like Pt/C electrocatalyst, the constant potential ORR activity of Pd/C, Au/C, and Ag/C electrocatalysts decreased substantially in the presence of ammonia due to significant poisoning of the electrocatalysts (Figs. 2 and 3). The activity loss was >85% for all of the noble metal electrocatalysts, and >95% for the Au/C electrocatalyst, in the presence of 0.1 M ammonia. Third, the CVs collected after the ORR experiment in an ammonia-containing electrolyte indicate that, unlike the Pt/C electrocatalyst, Pd/C, Au/C, and Ag/C electrocatalysts lose a significant portion of their initial ECSA after ammonia exposure (Figs. 2 and S5 to S7). More specifically, Pd/C loses the largest ECSA (=63.5%) when compared to Au/C (=42.7%) and Ag/C (=24.0%). This observation indicates that the loss of ECSA is at least partially responsible for the ORR activity loss of Pd/C, Au/C, and Ag/C electrocatalysts in the presence of ammonia. Fourth, we see significant differences between the first and the last recorded CV

![Figure 1. Representative electrochemical experimental results for Pt/C electrocatalyst (metal loading: 4 μg cm−2). (a) Polarization curve recorded in oxygen-saturated 0.1 M KOH electrolyte before exposure to ammonia. (b) Constant potential (0.85 V vs RHE) experimental results in oxygen-saturated (0.1 M KOH + 0.1 M ammonia) electrolyte, recovered ORR activity at (0.85 V vs RHE) in oxygen-saturated 0.1 M KOH electrolyte after exposure to ammonia and potential cycling, and ORR activity at (0.85 V vs RHE) of a representative control sample in oxygen-saturated 0.1 M KOH electrolyte depicted for comparison. (c) Comparison of CV scans before and after exposure to ammonia in argon-saturated 0.1 M KOH. (d) Comparison of the first and the last recorded CV scans after exposure to ammonia (see Table S2 for more experimental details).](image-url)
scans after exposure to ammonia for Pd/C, Au/C, and Ag/C electrocatalysts confirming the existence of weakly adsorbed nitrogen-containing species on their surface (Fig. 3). Fifth, we performed experiments to see whether the ORR activity of Pd/C, Au/C, and Ag/C electrocatalysts can be recovered. Unlike Pt/C electrocatalyst, ORR activity losses of Pd/C, Au/C, and Ag/C electrocatalysts were irreversible (Figs. 2 and 3). In the case of Pd/C, Au/C, and Ag/C electrocatalysts, the irreversible ORR activity loss observed for each electrocatalyst was identical, within experimental uncertainty, to the ECSA loss of that electrocatalyst. This observation confirms that the ECSA loss of Pd/C, Au/C, and Ag/C electrocatalysts, most likely caused by surface-site blocking of strongly adsorbed nitrogen-containing species, is responsible for the irreversible ORR activity loss of the electrocatalysts. Sixth, Pt/C electrocatalyst shows the smallest amount of irreversible ORR activity loss among all noble metal electrocatalysts studied in this work.

Prior experimental studies have already established that Pd is a very inefficient AOR electrocatalyst. At the same time, Au and Ag are not able to mediate the AOR at a potential of 0.85 V vs RHE.\textsuperscript{20,25} Thus, ECSA loss is mainly responsible for the ORR activity loss of Pd/C electrocatalyst, and parasitic currents and weakly adsorbed nitrogen-containing species at the surface of Pd/C electrocatalyst are responsible for the reversible ORR activity loss. Also, ECSA loss is responsible for a portion of the ORR activity loss of Au/C and Ag/C electrocatalysts, and weakly adsorbed nitrogen-containing species on the surface of Au/C and Ag/C electrocatalysts are responsible for the reversible ORR activity loss of the electrocatalysts.

**Effect of ammonia exposure on the ORR activity of Acta 4020, Pajarito, Fe-ZIF, and Fe,Co-ZIF electrocatalysts.**—We then performed experiments to investigate the effect of ammonia exposure on the ORR activity of Fe-based electrocatalysts, including Acta 4020, Pajarito, Fe-ZIF, and Fe,Co-ZIF electrocatalysts. Control experiments performed for these Fe-based electrocatalysts confirm that there is no loss of ORR activity after performing the one-hour ORR experiment in ammonia-free 0.1 M KOH electrolyte (Figs. S8 to S11). Here, we only present the constant potential ORR experimental results and the comparison of the first and the last recorded CV scans after exposure to ammonia for these electrocatalysts in Figs. 4 and 5, respectively (we show the detailed experimental results in Figs. S12 to S15). In addition, we present a comparison of the ORR activity loss, irreversible ORR activity loss, and initial ORR area-specific activity that is lower than their initial ORR activity (Fig. 4). Second, the initial ORR area-specific activity of Acta 4020, Pajarito, Fe-ZIF, and Fe,Co-ZIF decreases as follows: Fe-ZIF > Acta 4020 > Pajarito ≈ Fe,Co-ZIF. The ORR activity loss in the presence of ammonia drops as follows: Acta 4020 > Pajarito > Fe-ZIF ≈ Fe,Co-ZIF. Similarly, the irreversible ORR activity loss drops as follows: Acta 4020 > Pajarito > Fe-ZIF ≈ Fe,Co-ZIF (Fig. 6). Our results, therefore, demonstrate that Fe-ZIF and Fe,Co-ZIF electrocatalysts show better ammonia tolerance than the two commercially available Fe–N–C electrocatalysts (i.e., Acta 4020 and Pajarito). We note that Fe and Co active sites in Fe-ZIF and Fe,Co-ZIF electrocatalysts are expected to be in well-coordinated atomically dispersed FeN\textsubscript{4} or CoN\textsubscript{4} states.\textsuperscript{34} In contrast, Fe and Co active sites in commercially available Fe–N–C electrocatalysts are produced through traditional co-pyrolysis of Fe, N, and C sources, and they can be in a variety of uncontrolled states (FeN\textsubscript{x} (x = 1 to 4) and metallic crystalline species).\textsuperscript{34,50,51} Consistent with our observation, one expects that the well-coordinated FeN\textsubscript{4} or CoN\textsubscript{4} active sites in Fe-ZIF and Fe,Co-ZIF electrocatalysts to be less vulnerable to adsorption of nitrogen-containing species than Fe and Co active sites in commercially available Fe–N–C electrocatalysts. Third, we see significant differences between the first and the last recorded CV scans after exposure to ammonia for Acta 4020, Pajarito, Fe-ZIF, and Fe,Co-ZIF electrocatalysts confirming the existence of weakly adsorbed nitrogen-containing species at their surface (Fig. 5). The CV scan of each electrocatalyst after exposure to ammonia is identical to its CV scan recorded before exposure to ammonia. However, based on these CV scans alone, we cannot rule out the permanent loss of the ORR active sites of the electrocatalysts as a result of ammonia exposure, as these sites do not show oxidation/reduction peaks in CV scans. We strongly believe that surface-site blocking by strongly adsorbed nitrogen-containing species is responsible for the irreversible ORR activity loss of the electrocatalysts. Fourth, we investigated the AOR activity of Fe-based electrocatalyst samples (the samples were...
similar to the ones used for the ORR activity tests) by performing a constant potential (0.85 V vs RHE) AOR activity test in argon-saturated (0.1 M KOH + 0.1 M ammonia) electrolyte for one hour. During the experiment, we observed no AOR current, which confirms that these electrocatalysts cannot mediate the AOR at a potential of 0.85 V vs RHE. This observation, combined with the results above, lead us to conclude that the irreversible loss of the ORR active sites is responsible for a portion of the ORR activity loss of Fe-based electrocatalysts, and weakly adsorbed nitrogen-containing species at the surface of Fe-based electrocatalysts are responsible for the remainder of the ORR activity loss.

Figure 3. Constant potential (0.85 V vs RHE) experimental results in oxygen-saturated (0.1 M KOH + 0.1 M ammonia) electrolyte, recovered ORR activity at (0.85 V vs RHE) in oxygen-saturated 0.1 M KOH electrolyte after exposure to ammonia and potential cycling, and ORR activity at (0.85 V vs RHE) of a representative control sample in oxygen-saturated 0.1 M KOH electrolyte depicted for comparison. (a) Pd/C electrocatalyst (metal loading: 3 μg cm⁻²). (b) Au/C electrocatalyst (metal loading: 6 μg cm⁻²). (c) Ag/C electrocatalyst (metal loading: 80 μg cm⁻²). Comparison of the first and the last recorded CV scans after exposure to ammonia. (d) Pd/C electrocatalyst (metal loading: 3 μg cm⁻²). (e) Au/C electrocatalyst (metal loading: 6 μg cm⁻²). (f) Ag/C electrocatalyst (metal loading: 80 μg cm⁻²).

We end this section by reporting some additional key observations. If we rank the electrocatalysts studied in this work in terms of their ORR activity loss and their irreversible ORR activity loss as the result of exposure to ammonia (from the highest loss to the lowest loss), the order is Au/C > Pt/C ≈ Pd/C > Ag/C > Acta 4020 ≈ Pajarito > Fe-ZIF ≈ Fe,Co-ZIF and Pd/C > Au/C > Ag/C > Acta 4020 ≈ Pajarito > Fe-ZIF ≈ Fe,Co-ZIF > Pt/C. Interestingly, Pt/C
electrocatalyst shows the lowest irreversible ORR activity loss, while Fe-ZIF and Fe,Co-ZIF electrocatalysts show the lowest overall ORR activity loss in the presence of ammonia. These observations indicate that Pt-based, Fe-ZIF, and Fe,Co-ZIF electrocatalysts are promising candidates for the cathode of DAFCs.

Insights obtained from previous studies on electrocatalytic AOR on metallic surfaces and future research directions.—The electrocatalytic AOR at metallic surfaces has been studied extensively, both experimentally and theoretically, due to its critical role in several important fields, including DAFCs,6,8–11,52–54 hydrogen production through electrolysis of ammonia,55–57 electrochemical wastewater cleanup,58–61 and electrochemical ammonia sensors.25,62,63 Gerisher and Mauerer suggested the most accepted mechanism for the AOR at metallic surfaces in 197064 with the following elementary steps (Scheme 1):

\[
NH_3 + OH^- + * \rightarrow NH_2^* + H_2O + e^- \quad [1]
\]
\[
NH_2^* + OH^- \rightarrow NH^* + H_2O + e^- \quad [2]
\]
\[
NH^* + OH^- \rightarrow N^* + H_2O + e^- \quad [3]
\]

Based on the G-M mechanism, NH_3 is dehydrogenated by hydroxyl ions in elementary steps 1, 2, and 3, forming water molecules while simultaneously releasing an electron at each elementary step. An adsorbed nitrogen atom (N*) behaves as a poison for N_2 formation because of typically substantial kinetic barriers for N–N bond formation to release N_2. Therefore, N–N bond forms through the recombination of NH_x^* and NH_y^* species, thereby producing an H_xNNH_y^* species. According to the G-M mechanism, this species is subsequently dehydrogenated to N_2, which then desorbs from the surface of the active site. Typically, one of the reactions presented in Eq. 4 is the rate-determining step (RDS).

\[
NH_x^* + NH_y^* \rightarrow H_xNNH_y^* + *(x, y = 1 or 2) \quad [4]
\]
\[
H_xNNH_y^* + (x + y)OH^- \rightarrow N_2 + (x + y)H_2O + (x + y)e^- + * \quad [5]
\]

We note that the G-M mechanism is quite a reliable mechanism as quantum-chemical density-functional theory (DFT) calculations performed based on this mechanism can successfully predict the experimentally observed electrocatalytic AOR activity trends at different metallic surfaces.20,25 More specifically, three key conclusions emerged from these calculations. First, consistent with Sabatier principle, metals with a low affinity for N^*, and hence a low
dehydrogenation capacity, such as Au and Ag, do not mediate electrocatalytic AOR since the active intermediates are not formed considerably at the surface of these metals. Second, consistent with Sabatier principle, metals with a high affinity for N*, such as Os and Re, do not mediate electrocatalytic AOR since the active intermediates are not stable compared to N* at the surface of these metals. Third, Pt has the highest electrocatalytic activity for the AOR of any of the single metal electrocatalysts, since it has a good dehydrogenation capacity, a sufficiently low affinity for the formation of N*, and a relatively small RDS activation energy barrier compared to other metals that can mediate electrocatalytic AOR.

We note that based on the above DFT calculations, the trend in the strength of adsorption of the G-M reaction intermediates (N*, NHx*, and HxNNHx*) is Pd ≈ Pt >> Au ≈ Ag. Based on this trend, one expects significant amounts of the G-M reaction intermediates to form on Pd and Pt. Also, as mentioned before, Pt is the most active metal electrocatalyst for the AOR, Pd is a poor electrocatalyst for the AOR, and Ag and Au are inactive towards the AOR at a potential of 0.85 V vs RHE. Based on these trends, one may expect that Au and Ag show much lower ORR activity loss and ECSA loss than Pt and Pd as a result of exposure to ammonia. However, this expectation is not consistent with our experimental observations. If we rank the noble metal electrocatalysts in terms of their ORR activity loss and ECSA loss, we get: Au/C > Pt/C ≈ Pd/C > Ag/C and Pd/C > Au/C > Ag/C >> Pt/C, respectively. Clearly, the AOR activity or adsorptive properties of the G-M reaction intermediates does not govern the trend of ORR activity loss and ECSA loss of noble metal electrocatalysts.

Following the above discussion, the results presented in this work generate a range of interesting questions for future investigation. For instance, we have not yet identified the weakly/strongly adsorbed nitrogen-containing species and their adsorption strength. These species could be different from the G-M reaction intermediates due to the possibility of cross-coupling of intermediates formed from ammonia and oxygen. We note that interactions between ammonia and oxygen adsorbates can be revealed by changes to the shape of the ORR Tafel plots and measuring the change in the hydrogen peroxide side product yield using the ring of a rotating ring disc electrode. Identification of weakly/strongly adsorbed nitrogen-containing species can be done via in situ surface-sensitive spectroscopy techniques such as sum-frequency generation spectroscopy (SFG) or polarization modulation-infrared reflection-absorption spectroscopy (PM-IRRAS). Furthermore, quantum-chemical DFT calculations could provide more insight into the binding strength of these species, and their role in the ORR activity loss of the electrocatalysts studied in this work.

Additionally, we observe significant ECSA loss for Pd/C, Au/C, and Ag/C electrocatalysts. We believe that strongly adsorbed nitrogen-containing species are responsible for the ECSA loss of these electrocatalysts; however, we cannot rule out the remote possibility of ammonia-driven sintering of these electrocatalysts in an oxygen-saturated electrolyte. In-situ spectroscopic characterization of the adsorbed intermediates at the surface of these...
electrocatalysts with techniques such as SFG or PM-IRRAS,65–67 combined with characterization of the morphology/structure of these electrocatalysts with techniques such as atomic force microscopy (AFM),65,67 electrochemical scanning tunneling microscopy (electrochemical-STM), 65–67 or transmission electron microscopy (TEM)65,67 as well as investigating the possibility of forming transition metal ammine complexes using inductively coupled plasma mass spectrometry (ICP-MS) 65,67 may provide valuable insights regarding the mechanisms of ECSA loss of these electrocatalysts and how to mitigate the ECSA loss of these electrocatalysts.

Finally, we note that the most efficient DAFCs reported in the literature by us and others operate at temperatures ranging from 80 °C to 100 °C.6–8 We also note that although the performance of DAFCs has been improved significantly in recent years, the DFAC durability still requires considerable improvement. The best reported DAFC durability is the continuous DAFC operation for 60 h at a constant current density of 100 mA cm\(^{-2}\), with an average degradation rate of \(\sim 4 \text{ mV h}^{-1}\). This rate of voltage drop is high and can be a result of a variety of factors such as flooding of the cathode electrocatalyst layer on its side adjacent to HEM by the aqueous solution crossing from the anode, dry-out on the cathode electrocatalyst layer surface adjacent to the air stream, degradation of HEMs and HEIs at elevated temperatures and low relative humidities, and loss of the ORR activity of the cathode electrocatalyst due to ammonia cross-over from the anode side to the cathode side.6,7,68

These complications currently do not allow us to decouple and investigate ammonia’s effect on the ORR electrocatalysis in DAFCs at temperatures relevant to practical applications. Upon significant improvements in the durability of DAFCs and eliminating all other degradation mechanisms, one can investigate the effect of ammonia on the ORR electrocatalysis at elevated temperatures, which should be the topic of future investigations.

Conclusions

In summary, we quantified and analyzed the effect of ammonia on the performance of seven benchmark ORR electrocatalysts (Pt/C, Pd/C, Au/C, Ag/C, commercial Fe–N–C, Fe-ZIF, and Fe,Co-ZIF) in alkaline media and DAFC relevant conditions. Our study shows that ammonia exposure has a considerable negative impact on the ORR performance of these electrocatalysts, regardless of whether they contain noble or non-noble metals. Consequently, ammonia crossover in DAFCs must be minimized by using HEMs with low ammonia permeability or new cathode electrocatalysts with high ammonia tolerance must be developed. Should we rank the electrocatalysts in terms of their ORR activity loss in ammonia and their irreversible ORR activity loss (from the highest loss to the lowest loss), the order is: Au/C > Pt/C > Pd/C > Ag/C > commercial Fe–N–C > Fe-ZIF > Fe,Co-ZIF and Fe,Co-ZIF, respectively.

These observations indicate that Pt-based, Fe-ZIF, and Fe,Co-ZIF electrocatalysts are promising candidates for future electrocatalyst development efforts for the cathode of DAFCs. Interestingly, the AOR activity or adsorptive properties of G-M reaction intermediates does not govern the trend of ORR activity loss and ESCA loss of noble metal electrocatalysts studied in this work. This observation signifies the importance of identifying the adsorbed nitrogen-containing species at the surface of these electrocatalysts in future studies, as this may enable one to design ORR electrocatalysts with high ammonia tolerance for advanced DAFCs.

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Figure 6. ORR activity loss, irreversible ORR activity loss, and initial ORR area-specific activity at (0.85 V vs RHE) of Acta 4020, Pajarito, Fe-ZIF, and Fe,Co-ZIF electrocatalysts.

\[
\begin{align*}
NH_3 + OH^- & \leftrightarrow NH_2^+ + H_2O + e^- \quad (1) \\
NH_2^+ + OH^- & \rightarrow NH_3 + H_2O + e^- \quad (2) \\
NH_3 + OH^- & \rightarrow N_2 + H_2O + e^- \quad (3) \\
NH_2^+ + NH_3 & \rightarrow H_2NNH_2^+ + (x, y = 1 \text{ or } 2) \quad (4) \\
H_y NNH_2^+ + (x + y)OH^- & \rightarrow N_2 + (x + y)H_2O + (x + y)e^- + (5)
\end{align*}
\]

Scheme 1. The Gerisher-Mauerer (G-M) Mechanism for Electrocatalytic AOR at Metallic Surfaces (the * indicates either free surface sites or adsorbed reaction intermediates).
We thank Pajarito Powder, LLC, for providing us free samples of their commercial Fe–N–C electrocatalyst.

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