Revisiting the Electrochemical Oxidation of Ammonia on Carbon-supported Metal Nanoparticle Catalysts

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Abstract

The ammonia electro-oxidation reaction (AOR) has been studied due to its promising applications in ammonia electrolysis, wastewater remediation, direct ammonia fuel cells, and sensors. However, it is difficult to compare and analyze the reported electrocatalytic activity of AOR reliably, likely due to the variation in catalyst synthesis, electrode composition, electrode morphology, and testing protocol. In this paper, the electro-oxidation of ammonia on different carbon-supported precious metal nanoparticle catalysts was revisited. The effect of experimental conditions, electrochemical test parameters, electrocatalytic activity, thermodynamics, and possible deactivation mechanism of the catalysts were investigated. Pt/C catalyst possesses the highest electrocatalytic activity, while Ir/C and Rh/C show lower overpotential. The onset potential of the AOR is related to the hydrogen binding energy of the catalyst. N_{ads} is one major cause of deactivation accompanied with the formation of surface O/OH_{ads} at high potentials. The coulombic efficiency of N_{ads} formation on Pt is about 1% initially and gradually decreases with reaction time. Increase in ammonia concentration leads to increase in current density, while increase in hydroxyl ions concentration can enhance the current density and reduce the overpotential simultaneously. The slopes of AOR onset potential and hydrogen adsorption/desorption potential of Pt/C as a function of pH follow Nernst equation. In contrast, potentials measured at different current densities exhibit non-Nernstian behavior, suggesting a critical role of the local pH change.

Keywords: ammonia electro-oxidation; Pt catalyst; ammonia electrolysis; ammonia fuel cells; ammonia sensors

1. Introduction

Due to rapid increase in environmental and energy issues, it is required to replace conventional fossil fuels with renewable energy sources. Ammonia is regarded as a potential energy carrier for renewable energy due to its higher volumetric energy density and easier handling and transportation than hydrogen.[1, 2] Over the past few decades, the electrochemical oxidation of ammonia has attracted much attention due to its potential application in fuel cells,[3-7] ammonia electrolysis,[8-10] wastewater remediation,[11-15] and sensors,[16, 17]. Ammonia can be electrochemically oxidized into nitrogen by noble transitional metal electrocatalysts (i.e. Pt, Ir, Rh, Pd) in alkaline solutions.[18, 19] The half-reaction is expressed as

Among these candidate metals, Pt based catalysts have been found to be the most promising catalysts.[19] However, the electrochemical oxidation of ammonia on Pt has a sluggish kinetics due to the complicated multistep electron and proton transfer process as well as difficult dimerization reaction.[20] In order to achieve high activity, tremendous efforts have been made on the development of more active electrocatalysts, include alloying of Pt with other metals (e.g., Ir, Rh, Pd, Ru) that have a potential synergistic effect with Pt for ammonia oxidation,[13, 21-23] enhancing the number of active sites by controlling the surface structure of the electrocatalysts (preferential orientation, shape, morphology, etc.),[24-26] as well as using metal oxides (e.g., CeO₂, antimony-tin oxide) to enhance local hydroxide concentration.[27, 28] Yet, none catalysts have shown satisfactory performance comparable to the hydrogen oxidation reaction. Besides, Pt catalysts suffer from activity degradation due to poisonous N_{ads} species.[19, 29] Therefore, further development of highly active and durable catalysts is demanded.

Another concern lies in the lack of consistency in the electrocatalytic activity for ammonia

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4 oxidation reaction (AOR) reported by the literature. Cyclic voltammetry (CV) has been widely
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6 adopted as a simple method to identify the electrocatalytic activity of a catalyst. However, the
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8 reported activity of different Pt catalysts in the literature varies largely.[5, 7, 21, 23, 27, 30-33]
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10 This deviation is even larger for Pt-based alloy catalysts. For instance, Miura et al. discovered
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12 that $\text{Pt}_{0.2}\text{Ir}_{0.8}$ was the best electrocatalyst for AOR,[21] while Vidal-Iglesias et al. found that
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14 $\text{Pt}_{75}\text{Ir}_{25}$ and $\text{Pt}_{75}\text{Rh}_{25}$ produce higher current densities than that for Pt nanoparticles and other Pt
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16 alloys in the lower overpotential region.[5] It is later reported that the maximum fuel cell
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18 performance was obtained using a Pt:Ir catalyst with atomic ratio of 50:50.[7] It is thus difficult
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20 to compare and analyze the reported electrocatalytic activity of AOR reliably, likely due to the
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22 variation in catalyst synthesis, electrode composition, testing protocol, electrode morphology,
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24 crystal structure, etc. Further design and preparation of more active and durable catalysts
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26 requires a reliable electroactivity baseline for AOR. Therefore, it is highly desirable to revisit the
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28 electrochemical oxidation of ammonia and examine its real performance.
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36 In this work, carbon supported metal nanoparticle (Pt, Ir, Rh) catalysts are synthesized using
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38 a modified poly-ol method. These catalysts exhibit small particle size and uniform particle size
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40 distribution, allowing us to compare and analyze the performance of these catalysts. These
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42 catalysts are evaluated for AOR in alkaline solution using CV. The electrocatalytic activity,
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44 thermodynamics, possible deactivation mechanism of these catalysts are studied and elucidated
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53 **2. Experimental**

54 **2.1. Materials**

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56 H_2PtCl_6 hydrate (ca. 40% Pt, Catalog No. AC195370050), IrCl_3 trihydrate (53-56% Ir,
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Catalog No. AC195500050), RhCl_3 hydrates (ca. 38% Rh, Catalog No. AC195520010), ethylene glycol (99.5%, Catalog No. AC295530250) were purchased from Acros Organics. Vulcan XC-72 carbon black was donated by Cabot Corp. (Lot No. 3709428). Isopropanol (Certified ACS, Catalog No. A416-20), ethanol (Histological, Catalog No. A405-20), ammonium hydroxide (Catalog No. A669-212) and 1 N KOH solution (Catalog No. SP208-500) were obtained from Fisher Chemical. Nafion solution (5 wt%, Catalog No. 527084) was purchased from Sigma-Aldrich.

2.2. Catalyst synthesis

Carbon-supported Pt, Ir, and Rh catalysts were prepared by a modified polyol reduction method.[7, 23] H_2PtCl_6 hydrate, IrCl_3 trihydrate, and RhCl_3 hydrates were used as metal precursors. Vulcan XC-72 was first dispersed in ethylene glycol by ultrasonication in a Branson CPX2800 bath sonicator for 1 h at a concentration of 2 mg mL^{-1} , followed by addition of certain amount of metal precursors to achieve the desired 20 wt% loading. The pH was adjusted above 8 with 1 M KOH solution. Then, the mixture was stirred at 300 rpm and refluxed for 3 h (160°C for Pt, 180°C for Ir and Rh). After the reaction was complete, the solids were collected by filtration with a Sartorius $0.2 \mu\text{m}$ nylon filter membrane and washed with copious DI water (18 M Ω) and ethanol. Finally, the obtained catalysts were dried in a vacuum oven (MTI EQ-DZF-6050-UL) at 80°C for 24 h.

2.3. Characterization

The morphology of the catalysts was characterized using a JEOL 2100F transmission electron microscopy (TEM). The particle size distribution was obtained based on randomly

measuring more than 200 primary nanoparticles in TEM images using ImageJ. The electrochemical performance was obtained in a three-electrode electrochemical cell using a glassy carbon rotating disk electrode (RDE) (0.196 cm^2 , Pine Instruments E3 series). The RDE was polished with $0.3\text{ }\mu\text{m}$ and $0.05\text{ }\mu\text{m}$ alumina suspension (Electron Microscopy Sciences) to obtain a mirror-like finish. To prepare the catalyst ink, the catalyst and 20 wt% Nafion ionomer were added into an isopropanol/water mixture (1:4 v:v) and sonicated for 30 mins. A $10\text{ }\mu\text{L}$ dispersion was dropped onto the glassy carbon electrode and dried at ambient condition. The mass loading of the precious metal was estimated to be about $30.6\text{ }\mu\text{g cm}^{-2}$. A Pt wire (CH Instruments, 99.99%, 0.5 mm diameter, 23 cm long) was used as the counter electrode, and Hg/HgO (1 M KOH, CH Instruments) or reversible hydrogen electrode (RHE, HydroflexTM) was used as the reference electrode. All potentials reported in this work are referred to the SHE scale, unless otherwise stated. Electrochemical tests were measured by a Solartron 1480E potentiostat. Prior to the electrochemical tests, the Pt and Rh catalysts were electrochemically cleaned from -0.9 V to 0.3 V vs. Hg/HgO in 1 M KOH or from 0 V to 1.2 V vs. RHE in 0.1 M HClO_4 at 500 mV s^{-1} until the CV curve remained stable and electrochemically reduced at -0.9 V vs. Hg/HgO (1 M KOH) for 1 min before AOR test. Ir catalysts were electrochemically cleaned from -0.9 V to -0.1 V vs. Hg/HgO in 1 M KOH or from 0 V to 0.8 V vs. RHE in $0.05\text{ M H}_2\text{SO}_4$ to avoid Ir oxidation at 500 mV s^{-1} until the CV curve remained stable and electrochemically reduced at -0.9 V vs. Hg/HgO (1 M KOH) for 1 min before AOR test.

3. Results and Discussion

The representative TEM images and corresponding particle size distribution of the catalysts are shown in Fig. 1. It can be seen that the metal nanoparticles are well dispersed on the carbon

support except that there is some nanoparticle aggregation for the Rh/C catalyst. The average particles size for Pt/C, Ir/C, Rh/C are calculated to be about 2.7, 2.2, 3.7 nm, respectively. Although there is slight difference in particle size and distribution, this difference is not significant enough to cause major deviation in electrocatalytic activity. The catalysts were used to study the electrochemical oxidation of ammonia in alkaline solution.

Insert Fig. 1.

Electrochemical measurements were conducted by CV scans at a scan rate of 20 mV s⁻¹ in HClO₄ for Pt/C and Rh/C catalysts and H₂SO₄ for Ir/C catalyst, shown in Fig. 2. The electrochemical surface area (ECSA) was determined by measuring the integration of hydrogen adsorption-desorption area after double layer correction, assuming charge densities of 210 μC cm⁻²_{Pt}, 218 μC cm⁻²_{Ir}, and 221 μC cm⁻²_{Rh}, respectively.[34, 35] The ECSA for Pt/C, Ir/C, and Rh/C were calculated to be about 72, 85, and 67 m² g⁻¹, respectively. The high surface area is consistent with the uniform distribution of nanoparticles, as shown in the TEM results.

Insert Fig. 2.

3.1. Electrochemical oxidation of ammonia on Pt/C electrode

The electrochemical performance of AOR by a Pt/C electrode was evaluated by CV scan in 1 M KOH in the presence and absence of 1 M NH₃ at room temperature and corresponding CV curves are shown in Fig. 3. The Pt/C electrode was electrochemically cleaned and fully reduced before any electrochemical measurement. A starting voltage of -0.46 V vs. SHE, which is close

to the zero charge potential of Pt, was used in all CV scans for AOR to avoid H^+ adsorption, OH^- adsorption, and ammonia oxidation.[36] Comparing CV curves in the presence and absence of NH_3 (Fig. 3a), it can be seen that the hydrogen adsorption/desorption peak shifted to a lower potential (from -0.59 V vs. SHE with KOH to -0.7 V vs. SHE with NH_3 and KOH), which suggests that the presence of ammonia/ammonium ions may influence the hydrogen binding energy and consequently hydrogen adsorption/desorption potential. The onset potential of AOR (defined as the potential when the anodic current density starts increasing), is around -0.46 V vs. SHE, which is very close to potential of zero charge (PZC) of Pt and more than 300 mV higher than theoretical value (-0.77 V vs. SHE at pH 14). This may imply that ammonia oxidation takes place only after hydrogen atoms desorb from the Pt surface.[37] There is a small pre-peak (at about -0.4 vs. SHE) prior to the major AOR peak, which has been ascribed to the ammonia adsorption on Pt surfaces.[25, 37] However, the origin of this pre-peak is still not completely clear and beyond the scope of this work. The AOR peaked at about -0.153 V vs. SHE and started to deactivate at potentials above that. It is also observed that the AOR current density of Pt/C catalyst decreases with the number of CV cycles. Several authors have reported the deactivation of Pt catalyst and ascribed this deactivation to N_{ads} poisoning and diffusion.[6, 19, 29, 38] The origin of this deactivation was investigated and the results are presented later.

The difference in cathodic scan between -0.8 V and -0.5 V (highlighted by the dashed circle in Fig. 3a) suggests the existence of poisonous adsorbates AOR.[19] Since the deactivated electrode cannot be recovered after 10 mins hold at OCV (Fig. 3b), diffusion is not likely the dominant cause of degradation as a function of cycle number. A facile method to recover the catalyst by applying a reduction potential at -0.8 V is demonstrated and shown in Fig. 3b. After holding at -0.8 V for 1 min, the deactivated Pt/C electrode can be fully recovered and its CV

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4 curve is identical to that of a fresh electrode. The residual poisonous adsorbates after ammonia
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6 oxidation test may be one major cause for deviation in AOR performance reported in the
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8 literature. Thus, it is necessary to recover the catalyst after each electrochemical test if the same
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10 electrode will be used in subsequent tests. Otherwise, a fresh electrode should be used and a
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12 proper electrochemical cleaning procedure should be followed. (See experimental section for
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14 more details.)
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26 As mentioned earlier, AOR suffered from deactivation from possible adsorption of
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28 intermediates. To investigate the effect of intermediates on AOR, cyclic voltammograms in 1 M
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30 ammonia and 1 M KOH solution with a constant lower potential limit of -0.8 V and various
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32 upper switch potentials were measured and first-cycle CV curves are shown in Fig. 4a. It is seen
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34 that the anodic current density almost overlap for all scans. The cathodic current density below -
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36 0.6 V is larger for scans with higher upper potentials, suggesting that reduction of oxidative
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38 species or desorption of intermediate species is related to the upper potentials. As shown in Fig.
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40 S1, the deactivation as a function of cycle numbers was very obvious if the upper potential was
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42 higher than peak potential (>-0.1 V), and this deactivation increased with the upper potential
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44 limit. In contrast, when -0.2 V was used as the upper potential limit, there was almost no
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46 deactivation after 10 CV cycles. One deactivation cause is the formation of strongly adsorbed
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48 N_{ads} that blocks the active sites. The deactivation rate caused by N_{ads} is expected to be
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50 proportional to the number of N_{ads} species, which should be related to the total charge consumed
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52 in AOR. However, as can be seen in Fig. 4a and Fig. S1, the total charge consumed at higher
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upper potential limits are not significantly higher than that at lower upper potential limits (due to rapid drop in current density above -0.1 V), which means that N_{ads} is probably not the solely dominant poisonous species at potentials above -0.1 V. Probable candidate poisonous species include OH_{ads} and surface oxide, as it has been reported that OH has a higher adsorption energy on Pt than NH_3 . [39] Several research groups have reported that the presence of OH_{ads} and chemisorbed surface oxide can greatly hinder electrocatalytic reactions, like oxygen reduction reaction. [40-42] As the potential increases, hydroxide ions starts to adsorb on Pt surface in alkaline solution at around 0.5 V vs. RHE (-0.326 V vs. SHE) and surface coverage of OH_{ads} increases significantly. Above 0.8 V vs. RHE (-0.026 V vs SHE), Pt surface begins to form a thin oxide film. [41] These results are consistent with our experimental observation and suggest that OH_{ads} and surface oxide could be the major cause of deactivation for AOR at potential >-0.15 V vs. SHE. To further validate our assumption, Pt/C catalyst was pre-oxidized at 0.2 V vs. SHE for 1 min in 1 M KOH and then this oxidized Pt/C catalyst was used for CV scan between -0.3 V and 0.2 V in 1 M KOH and 1 M NH_3 . As can be seen in Fig. 4b, the oxidized Pt/C only exhibited a very small ammonia oxidation peak around -0.06 V, which can be attributed to ammonia oxidation into NO_x on oxidized Pt. [19, 43] A similar peak is also observed for fresh Pt/C electrode above 0 V. The electrode can be fully recovered after the oxidized Pt/C electrode is reduced at -0.8 V for 1 min, indicating a reversible poisoning effect of O/ OH_{ads} . Thus, the practical operating voltage of ammonia electrolyzers or fuel cells should be carefully examined because of the detrimental effect of O/ OH_{ads} species on AOR.

To study the poisoning effect of N_{ads} , AOR was tested by CV using an upper potential limit of -0.25 V to prevent poisoning from O/ OH_{ads} . The first-cycle CV curves (Fig. 4c) are almost identical in the region above -0.5 V. However, as shown in Fig. S2, AOR still suffered slightly

from deactivation as a function of cycle numbers. Since the influence of O/OH_{ads} can be excluded, this deactivation can be ascribed to strongly adsorbed N_{ads} atoms. Closer examination of cathodic scan of Pt/C (Fig. 4d) in 1 M KOH and 1 M NH₃ solution scanned between -0.8 V and -0.25 V displays that the H_{ads} peak decreases with cycle number. The suppression of hydrogen adsorption peak is likely because of blocking Pt surface by N_{ads}. This assumption is supported by the fact that N_{ads} atom binds more strongly on Pt than H_{ads}. [19, 44] In addition, there is an increase in the cathodic current below -0.65 V vs. SHE, probably due to the reduction of N_{ads} from the Pt surface. These results indicate that the oxidative adsorbates from AOR, most likely N_{ads}, are the major cause of poisoning. To quantify the rate of poisoning, ammonia oxidation was carried out on Pt/C at -0.25 V vs. SHE for different time. Then, the cathodic scan from -0.5 V to -0.8 V vs. SHE was performed and shown in Fig. 4e. With the increase in reaction time, the hydrogen adsorption peak gradually declines and the charge required to remove N_{ads} raises. The surface coverage of N_{ads} as a function of reaction time can be estimated by Eq. 2.

$$\theta_{N_{ads}} = 1 - \frac{q_{H_{ads}}}{q_{H_{ads,0}}} \quad (2)$$

The charge of hydrogen adsorption peak (H_{ads}) and surface coverage of N_{ads} versus reaction time is shown in Fig. 4f. It can be seen that after 30 min of reaction at -0.25 V almost 90% of the catalyst surface was covered by N_{ads}. Interestingly, the plot of charge of H_{ads} possesses very similar decay trend with the chronoamperometric curve (Fig. S3a), suggesting that N_{ads} is the dominant factor for catalyst degradation during chronoamperometric tests at -0.25 V. The coulombic efficiency of forming N_{ads} can be calculated based on normalization of the charge to remove N_{ads} by the total charge of AOR and shown in Fig. S3b. It is shown that the coulombic efficiency of forming N_{ads} is initially about 1% (30 s reaction time) and gradually decreases to

0.36% (1800 s reaction time). Considering the fact that AOR was only carried out for less than half an hour, this rate of poisoning is quite significant. It is, thus, not surprising Pt/C exhibited very rapid degradation within a few minutes during chronoamperometry tests for ammonia oxidation.[31] A catalyst with lower N_{ads} binding energy is expected to have lower formation rate of passive N_{ads} and faster dimerization reaction between two N atoms. Nevertheless, designing such a catalyst remains a challenge, because lowering N_{ads} binding energy also results in lower NH_x binding energy, which may be detrimental to dimerization of NH_x species. Revising AOR by different Pt alloy catalysts is highly desirable to unveil the correlation between the binding energy of intermediate species and the rate of poisoning.

Insert Fig. 4.

Fig. 5a shows the cyclic voltammograms of ammonia oxidation by Pt/C catalyst in 1 M KOH and 1 M NH_3 at different scan rates. The current density increased with scan rate and the peak current density was linearly proportional to the square root of the scan rates (Fig. 4b), which suggests that AOR follows a diffusion-controlled mechanism.[45] The Tafel analysis is a powerful tool to discover the rate determining steps involved in an electrochemical reaction. Tafel analysis is performed by plotting the potential vs. the log of kinetic current density (i_k). Because the diffusion-limiting current density is at least one order higher than what have been observed in our experiments,[31] the measured current density is in close proximity to be used directly as i_k . Typical Tafel plots of Pt/C catalyst at different scan rates are shown in Fig. 5b. A Tafel slope around 30 mV dec^{-1} is observed for all scan rates. This result suggests that the dimerization of NH_2 species can be the rate-determining step and AOR dominantly takes place

on Pt(100) plane.[25] As reported in the literature, Tafel slope can also be obtained by analysis of a plot of the peak potential (E_p) vs. the logarithm of the scan rate.[25] However, instead of one linear relationship, two linear regions are observed and shown in Fig. S4. The contradictory result in Fig. S4 is probably because E_p is not only affected by AOR kinetics, but also by surface coverage of OH/ O_{ads} and N_{ads} , mass transport, etc.

Insert Fig. 5.

Fig. 6 shows the anodic and cathodic portions of the cyclic voltammograms measured on Pt in 1 M KOH solution with the various ammonia concentrations. All these solutions have almost the same pH (measured to be about 14), because NH_3 is a weak base. As can be seen in Fig. 6a, the AOR peak current density increases with the NH_3 concentration. Plot of current density as a function of NH_3 concentration (Fig. 6b) reveals that the current density increases linearly at low NH_3 concentrations (1 mM to 10 mM) and then begins to level off at higher NH_3 concentrations. At low NH_3 concentrations, the reaction is governed majorly by ammonia diffusion, while at higher NH_3 concentration the reaction is also limited by the reaction kinetics, diffusion of reaction products, local pH change, as well as possible surface poisoning by N_{ads} . One would expect that the thermodynamic voltage of AOR should be dependent on the concentration of the reactants according to Nernst equation,

$$E = E_0 - 2.303 \frac{RT}{3F} \log \frac{[NH_3][OH^-]^3}{[N_2]^{1/2}} \quad (3)$$

where E is the equilibrium potential, E_0 the standard equilibrium potential, R the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T the temperature (in K), F the Faraday constant (96485 C mol^{-1}). However, it is surprising that the CV curves of NH_3 concentration above 5 mM overlapped in the

voltage region above -0.3 V. This again suggests that AOR in the relatively large overpotential region is governed not only by the ammonia diffusion but also by other factors, like reaction kinetics, diffusion of hydroxide and reaction products, as well as possible surface poisoning. Closer examination of the region between -0.8 V vs. -0.3 V (Fig. 6c) reveals that the hydrogen desorption peak and onset potential of AOR shift to lower potential with increase in ammonia concentration. The negative shift in hydrogen desorption peak indicates the decrease in hydrogen binding energy (HBE) with increase in ammonia concentration.[35, 46] Plot of hydrogen desorption peak for Pt (100) as a function of $\log[\text{NH}_3]$ shows a linear correlation with a slope of about -26 mV dec^{-1} . It is worth noting that this slope is steeper than literature reported slopes of 12 mV per pH for peak shift as a function of pH change,[35] suggesting that ammonia has a significant role in changing the HBE. Interestingly, the slope for onset potential of AOR vs. $\log[\text{NH}_3]$ was determined to be about $-22.6 \text{ mV dec}^{-1}$, which is very close to the theoretical value ($-2.303RT/3F = -19.7 \text{ mV dec}^{-1}$) according to Eq. 3. In addition, it may be hypothesized that there is a correlation between onset potential of AOR and the HBE, because AOR seems to take place only after hydrogen atoms desorb from the Pt surface.

Insert Fig. 6.

The effect of pH on AOR by Pt/C catalyst was determined by conducting the experiments in 1 M NH_3 with different KOH concentrations, and cyclic voltammograms are shown in Fig. 7. It can be observed that with the increase in pH (i.e. KOH concentration) the AOR peak current density increases significantly and also the ammonia oxidation peak shifts negatively. The addition of hydroxide ions can not only promote the reaction rate of ammonia oxidation, but also

causes a negative shift in the thermodynamic potential. According to Nernst equation (Eq. 3), the AOR potential should shift negatively by ca. 59.2 mV per pH increase. Fig. 7c shows that the onset potential and pre-peak potential shift negatively at a slope of about 60 mV pH⁻¹, which is consistent with our prediction. However, the peak potential exhibits a non-Nernstian dependence of pH with a slope of about 83 mV pH⁻¹, suggesting a complicated role of pH on AOR. Katsounaros *et al.* has recently reported a similar non-Nernstian slope of about 90-100 mV per pH, and this non-Nernstian slope has been attributed to a change of the local pH at the solid–liquid interface.[37] Furthermore, it is striking that this non-Nernstian slope is not a constant, but strongly dependent on the applied overpotential. The potential at different current densities as a function of pH is shown in Fig. 7d. It can be seen that the slope increases with the current density. For instance, the peak shifts per pH at 0.05, 0.1, 0.2, 0.3, and 0.5 mA cm⁻² are 65.6, 75.1, 83, 82.7, 98.1 mV per pH change, respectively. The local pH is strongly dependent on the current density.[47] At low current densities, the local pH is only slightly altered because a small amount of hydroxide is consumed. In contrast, at high current densities the depletion of hydroxide ions can lead to significant drop in local pH near the solid–liquid interface. These results suggest that the non-Nernstian slope is very likely correlated to the local pH. The peak potential only shifted negatively by 83 mV per pH, possible due to the influence of mass transport, surface coverage of OH⁻, and poisonous N_{ads} species. Although exact causes of this non-Nernstian slope cannot be elucidated in this work, the complicated role of pH (i.e. OH⁻), particularly local pH near active sites, needs to be taken into consideration in future studies.

Insert Fig. 7.

Cyclic voltammograms of Pt/C catalyst in N₂-saturated 1 M KOH and 1 M NH₃ solution at different rotating rates are shown in Fig. 8a. The AOR peak appears at around -0.15 V for all rotation rates, and all CV curves are almost identical. Magnified view of AOR peak reveals that the peak current density first increases with rotating rate, peaks at 800 rpm, then decreases. This result is quite striking, considering that stationary-electrode voltammetry (Fig. 5a) shows AOR is diffusion controlled. The initial increase with rotating rate is likely due to improved mass transport. When the rotating rate further increases, some weakly bonded intermediates products (i.e. N₂H₄, etc.) during ammonia oxidation may escape from the Pt surface and cannot be further oxidized, leading to loss in current density. However, it is worth noting that the deviation in current density at different rotating rates is small (within 10%). This phenomenon illustrates that AOR is a complex electrochemical process, controlled by multi-step electron transfer, multi-path reaction kinetics, and mass transport of different species. The nature of these intermediate species and their adsorption strength is still unknown. A through study including identification of intermediate species via *in-situ* mass spectroscopy technique combined with computational calculations could unveil further details on the nature of these intermediates and their role on AOR.

Insert Fig. 8

3.2. Electrochemical oxidation of ammonia on Ir/C electrode

Ir has been reported as the second best catalyst for AOR, and has been extensively studied as catalyst alone or alloying with Pt.[5, 19, 48] The electrochemical performance of AOR by Ir/C electrode was evaluated by CV scan in 1 M KOH in the presence and absence of 1 M NH₃ at

room temperature and corresponding CV curves are shown in Fig. 9. As can be seen in Fig. 9a, the hydrogen adsorption/desorption peak shifts to a lower potential (at around -0.7 V vs. SHE), suggesting that the presence of ammonia/ammonium ions can also influence the hydrogen binding energy of Ir and consequently hydrogen adsorption/desorption potential. The onset potential of AOR is around -0.53 V vs. SHE, suggesting a lower overpotential (240 mV) for AOR on Ir than Pt (310 mV). It is worth noting that the PZC of Ir is about 100 mV lower than that of Pt, which is consistent with the difference of onset potential for AOR.[49] The PZC is related to the hydrogen adsorption/desorption behavior. Typically, hydrogen adsorption/desorption occurs below the PZC.[35] The HBE of Ir is lower than that of Pt, therefore, the onset potential of AOR for Ir/C catalyst is also more negative than that for Pt/C. These findings underline that the onset potential of AOR is strongly dependent on the HBE of a catalyst. The AOR on Ir/C peaked at about -0.22 V with a current density of only about 1 mA cm⁻², much lower than that for Pt/C. This probably is caused by the poor kinetics and larger binding energy of N_{ads} on Ir.[19] Unlike Pt/C, there is no pre-peak present prior to the main AOR peak. The absence of this pre-peak may suggest that the adsorption of ammonia on Ir is masked by the ammonia oxidation that occurs at an earlier onset potential than on Pt/C or that the pre-peak observed on Pt/C may not be attributed to ammonia adsorption. This is an interesting finding that should be carefully studied in the future, as it may lead to better understanding on kinetics processes of AOR. Similar to Pt/C, Ir/C also suffers from severe performance loss upon CV cycling. The same recovering procedure was used for Ir/C, however, the catalyst could not be successfully recovered, as illustrated in Fig. 9b. When the electrode was reduced at -0.9 V vs. SHE, even formation of bubbles were observed due to hydrogen evolution reaction. In contrast to Pt catalyst, the deactivation of Ir catalyst is irreversible. In addition, there is a dramatic decrease

in hydrogen desorption peak, possibly due to either surface poisoning or loss of ECSA.

Insert Fig. 9.

To investigate the origin of the irreversible deactivation of Ir/C catalyst, cyclic voltammograms of Ir/C in 1 M ammonia and 1 M KOH solution with a constant lower potential limit of -0.8 V and various upper switch potentials were measured and shown in Fig. 10a and Fig. S5. It is necessary to use a fresh electrode for each electrochemical test, because the catalyst cannot be recovered. It is shown in Fig. 10a that the anodic current density almost overlap for all first-cycle scans. However, the deactivation as a function of cycle numbers is very obvious if the upper potential is higher than peak potential of -0.2 V vs. SHE, and this deactivation increases with the upper potential limit (Fig. S5). In contrast, when -0.3 V vs. SHE is used as the upper potential limit, there is only minor deactivation. Similar to Pt, the major poisonous species at high potentials are likely OH_{ads} and surface oxides. As the potential increases, hydroxide ions started to adsorb on Ir surface at around 0.4 V vs. RHE (-0.426 V vs. SHE) and Ir is oxidized into $\text{Ir}(\text{OH})_3$. Above the potential raised above 0.77 V vs. RHE (-0.056 V vs SHE), $\text{Ir}(\text{OH})_3$ can further be oxidized into anhydrous IrO_2 . [50] The hydrogen adsorption/desorption peak declines due to the irreversible loss of ECSA. These findings are consistent with our experimental results, as Ir can go through an irreversible phase change to form $\text{Ir}(\text{OH})_3$ and IrO_2 at higher potentials. To further validate our assumption, the Ir/C catalyst was pre-oxidized at 0.2 V vs. SHE for 1 min in 1 M KOH and subject to CV scan between -0.3 V and 0.2 V in 1 M KOH and 1 M NH_3 . As can be seen in Fig. 10b, the oxidized Pt/C exhibits a very small activity toward ammonia oxidation. Even after the pre-oxidized electrode was reduced at -0.9 V for 1 min, its AOR

activity still could not be fully recovered. Although Ir exhibits lower overpotential than Pt, it suffers from many disadvantages, i.e. slow AOR kinetics, larger strong binding energy of N_{ads} , severe deactivation due to irreversible phase change. To avoid irreversible losses of Ir catalyst performance, potentials more positive than -0.2 vs. SHE should not be applied. This consideration is important for the operation of ammonia electrolysis, fuel cells, and sensors.

Insert Fig. 10.

3.3. Electrochemical oxidation of ammonia on Rh/C electrode

As reported previously, 4d transition metals, such as rhodium, ruthenium, and palladium exhibited negligible AOR activity.[19] In this work, Rh/C catalyst was chosen to revisit its AOR performance, because it has shown excellent performance when alloying with Pt.[8] Fig. 11 shows typical cyclic voltammograms of Rh/C in 1 M KOH and 1 M NH_3 . Similar to Pt/C and Ir/C, upon the addition of ammonia, the hydrogen adsorption/desorption peak for Rh/C also shifts to a lower potential (at around -0.6 V vs. SHE). Interestingly, a small shoulder peak around -0.52 V is present (indicated in Fig. 11 by a black arrow) after hydrogen desorption peak and a much higher peak around -0.6 V can be found, which may be due to ammonia oxidation on Rh.[19] The HBE of Rh is much lower than that of Pt,[35] thus, the oxidation of ammonia may occur much earlier on Rh (-0.6 V) than on Pt (-0.46 V). However, as reported in the literature, no steady-state production of N_2 has been found for Rh catalyst,[19] consistent with our observation of very low activity. Based on computational calculations, it was suggested by de Voors et al. that NH_3 can rapidly be dehydrogenated to N_{ads} , suppressing further reaction.[19] A pre-peak that has been reported to be related to ammonia adsorption of Pt/C catalysts is not observed, indicating a weaker adsorption of ammonia. Therefore, one could hypothesize that the weak

adsorption of ammonia and strong adsorption of N_{ads} atoms on Rh lead to minimum ammonia electrooxidation. Although Rh has remarkably slow reaction rate of AOR,[51] it suffers less from degradation, as indicated by the overlapping CV curves over several cycles.

Insert Fig. 11.

4. Conclusion

In this work, we have revisited the electrochemical oxidation of ammonia in alkaline solution on a series of carbon supported nanoparticle catalysts, such as Pt/C, Ir/C, and Rh/C. The electrochemical performance was revealed by carefully treating the electrode prior to each electrochemical measurement. The Pt/C catalyst possessed the highest electrocatalytic activity, while Ir/C and Rh/C had lower overpotential for AOR. The onset potential of AOR was found to be related to the HBE. N_{ads} is one major deactivation cause. In addition, the formation of surface O/OH_{ads} at high potentials can significantly inhibit the reaction. The poisoning due to O/OH_{ads} on Pt is reversible and can be recovered, while the oxidation of Ir undergoes an irreversible phase change. Due to strong binding energy of N_{ads} on Pt, the coulombic efficiency of poisonous N_{ads} was about 1%. AOR is a diffusion-controlled process and has a Tafel slope of about 30 mV dec⁻¹, indicating the dimerization of NH₂ species as the rate-determining step. Increase in ammonia concentration only lead to increase in peak current density, but not a significant shift in the potential. Increase in KOH concentration (i.e. pH) can enhance the peak current density and reduce the overpotential simultaneously. The pH dependence of AOR onset potential for Pt/C catalyst follows Nernst equation. In contrast, non-Nernstian slopes are observed for potentials measured at different current densities, suggesting a critical role of the local pH change. In

summary, although promising, electro-oxidation of ammonia on monometallic PGMs suffers from sluggish kinetics, deactivation due to strong adsorption of poisonous species (i.e. N_{ads} , O/OH_{ads}). Future work needs to be done to revisit Pt alloy catalysts to unveil the correlation between binding energy of different intermediates and electrocatalytic activity as well as the rate of poisoning. A through study including identification of adsorbate species via *in-situ* spectroscopy techniques combined with computational calculations and mathematical modeling could unveil further details on the mechanism of the reaction. However, the important experimental considerations reported in this study should be maintained to guarantee the reliability of the electrochemical measurements.

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Figure Captions

Fig. 1. TEM images and particle size histogram of (a) Pt/C, (b) Ir/C, and (c) Rh/C catalysts.

These catalysts possess uniform dispersion of metal nanoparticles on the carbon black support except that there is some aggregation for the Rh/C catalyst.

Fig. 2. Cyclic voltammograms of Pt/C (solid line) and Rh/C (dotted line) in 0.1 M HClO₄ and Ir/C (dashed line) in 0.05 M H₂SO₄ at a scan rate of 20 mV s⁻¹. Hydrogen adsorption/desorption region is observed from 0.02 to 0.4V vs. RHE. ECSA can be determined by measuring the integration of hydrogen adsorption-desorption area after double layer correction.

Fig. 3. CV curves of (a) Pt/C catalyst in 1 M KOH in the presence and absence of 1 M NH₃ at a scan rate of 20 mV s⁻¹ and (b) fresh, deactivated, and recovered Pt/C electrode in 1 M KOH and 1 M NH₃ at a scan rate of 20 mV s⁻¹. The onset potential of Pt/C catalyst is around -0.46 V vs. SHE and the peak potential about -0.153 V vs. SHE. It is also observed that the Pt/C catalyst degrades as a function of CV cycle number and can be recovered by cathodic reduction at -0.8 V vs. SHE.

Fig. 4. Cyclic voltammograms measured on Pt/C electrode in 1 M KOH and 1 M ammonia solution (a) with a constant lower potential limit of -0.8 V and various upper potential limits (1st cycle). (b) Cyclic voltammograms measured on fresh Pt/C electrode, oxidized Pt/C electrode, and oxidized Pt/C electrode after reduction. (c) Cyclic voltammograms measured on Pt/C electrode in 1 M KOH and 1 M ammonia solution with a constant upper potential limit of -0.25 V and various lower potential limits (1st cycle). (d) CV curves of Pt/C electrode 1 M KOH and 1 M ammonia solution scanned from -0.8 V to -0.25 V and from -0.8 V to -0.4 V vs. SHE. (e) Cathodic linear sweep measured on Pt/C electrode after holding in 1 M KOH and 1 M ammonia solution at -0.25 V vs. SHE for different time. (f) Integration of charge of hydrogen adsorption peak around -0.58 V vs. SHE and calculated N_{ads} surface coverage as a function of different

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4 reaction time at -0.25 V vs. SHE. High surface coverage of O/OH_{ads} above -0.15 V vs. SHE was
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6 found to be the dominant factor for catalyst deactivation, while strongly adsorbed N_{ads}
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8 intermediates can also passivate the Pt surface.
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11 **Fig. 5.** (a) CV curves of Pt/C catalyst in 1 M KOH and 1 M NH₃ at different scan rates. Insert:
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13 plot and fit of anodic peak current vs. $v^{1/2}$. (b) Tafel plots of Pt/C catalyst at different scan rates
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15 (1, 10, 100 mV s⁻¹). The peak current density increased linearly with scan rate, indicating a
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17 diffusion-controlled mechanism for AOR. Tafel analysis shows a Tafel slope of 30 mV dec⁻¹.
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21 **Fig. 6.** (a) Representative CV curves of Pt/C catalyst in 1 M KOH with different concentrations
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23 of NH₃. (b) Plot of anodic peak current density vs. NH₃ concentration (insert: plot and fit of
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25 anodic peak current density vs. NH₃ concentration at low NH₃ concentrations). (c) Magnified CV
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27 curves of Pt/C catalyst in 1 M KOH with different concentrations of NH₃ between -1 V and -0.2
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29 V vs. SHE. (d) Plot and fit of hydrogen desorption peak and onset potential of AOR as a function
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31 of log[NH₃]. The peak current density increased linearly at low NH₃ concentrations (1 mM to 10
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33 mM) and then began to level off at higher NH₃ concentrations. The addition of ammonia leads to
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35 negative shift in hydrogen desorption peak, i.e. reduction in HBE.
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41 **Fig. 7.** (a) CV curves of Pt/C catalyst in 1 M NH₃ with different KOH concentrations. (b) Plot of
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43 anodic peak current density vs. KOH concentration and pH. (c) Plot and fit of onset potential,
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45 pre-peak potential, and peak potential of AOR as a function of solution pH. (d) Plot and fit of
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47 potential at different current densities as a function of solution pH. Hydroxide ions not only can
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49 promote reaction rate of ammonia oxidation, but also cause a negative shift in the
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51 thermodynamic potential. The pH dependence of ammonia oxidation does not follow the Nernst
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53 equation.
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58 **Fig. 8.** (a) Cyclic voltammograms of Pt/C electrode in N₂-purged 1 M NH₃ and 1 M KOH
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4 solution at various rotation rates at a scan rate of 20 mV s^{-1} . Insert: Magnified view of AOR
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6 peak. (b) Plot of peak current density as a functional of rotation rate. The peak current density
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8 first increases then decreases with rotating rate.
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11 **Fig. 9.** CV curves of (a) Ir/C catalyst in 1 M KOH in the presence and absence of 1 M NH_3 at a
12 scan rate of 20 mV s^{-1} and (b) fresh, deactivated, and recovered Ir/C electrode in 1 M KOH and 1
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14 M NH_3 at a scan rate of 20 mV s^{-1} . Ir/C catalyst has lower activity than Pt/C and suffers from
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16 irreversible degradation over several CV cycles.
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21 **Fig. 10.** Cyclic voltammograms measured on Ir/C electrode in 1 M KOH and 1 M ammonia
22 solution (a) with a constant lower potential limit of -0.8 V and various upper potential limits (1st
23 cycle). (b) Cyclic voltammograms measured on fresh Ir/C electrode, oxidized Ir/C electrode, and
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25 oxidized Ir/C electrode after reduction. Irreversible formation of Ir(OH)_3 and IrO_2 was found to
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27 be the dominant factor for catalyst deactivation at potential $> -0.2 \text{ V}$ vs. SHE.
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33 **Fig. 11.** CV curves of Rh/C catalyst in 1 M KOH in the presence and absence of 1 M NH_3 at a
34 scan rate of 20 mV s^{-1} . A shoulder peak after hydrogen desorption peak at -0.6 V is indicated by
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36 a black arrow, which may be attributed to ammonia oxidation on Rh.
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Possible causes:

- Catalyst oxidation
- Catalyst poisoning due to N_{ads}
- Diffusion

Figure 1

Figure 1. Li *et al.*

Figure 2

Figure 2. Li *et al.*

Figure 3

Figure 3. Li *et al.*

Figure 4

Figure 4. Li *et al.*

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Fig. 5.

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Figure 6. Li *et al.*

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Figure 10. Li *et al.*

Figure 11

Figure 11. Li *et al.*