Inhibition of Surface Chemical Moieties by Tris(hydroxymethyl)aminomethane: A Key to Understanding Oxygen Reduction on Iron–Nitrogen–Carbon Catalysts

Y. Chen,[†] K. Artyushkova,^{*,†,‡} S. Rojas-Carbonell,[†] A. Serov,[†] I. Matanovic,^{†,‡} C. Santoro,[†] T. Asset,[†] and P. Atanassov^{*,†,‡}

[†]Department of Chemical and Biological Engineering, Center for Micro-Engineered Materials (CMEM), University of New Mexico, Albuquerque, New Mexico 87131, United States

[‡]Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States

Supporting Information

ABSTRACT: The effect of tris(hydroxymethyl)aminomethane (Tris) on the activity of metal–nitrogen–carbon (M–N–C) platinum metal group-free (PGM-free) catalysts for oxygen reduction reaction (ORR) is studied. Electrochemical tests performed in the acidic and alkaline electrolyte and comparison between electrochemical observations for metal-free and metal-containing catalysts along with density functional calculations showed the multiplex mechanism of oxygen reduction in which numerous species perform partial and full reduction of oxygen to peroxide or water, respectively. The important role of protons in the mechanism of oxygen reduction is highlighted.

KEYWORDS: platinum group metal-free electrocatalyst, transition metal–nitrogen-carbon catalysts, oxygen reduction reaction, active site poisoning, ORR inhibition, probing active sites

INTRODUCTION

Metal–nitrogen–carbon (M–N–C) materials are among the most studied candidates to replace costly platinum group metal (PGM) catalysts^{1,2} for oxygen reduction reaction (ORR). Numerous methods for M–N–C synthesis proposed in the literature are based on pyrolysis (high-temperature treatment) of macrocycles,¹ metal–organic frameworks,² and other organic precursors.³ To optimize the synthesis of M–N–C structures with best activity and durability,^{4–6} it is essential to understand the mechanism of oxygen reduction reaction and to identify the active sites responsible for different pathways of the ORR.^{4,6–9} Catalyst inhibition or catalyst poisoning are powerful methods to indisputably confirm the role of various metal, carbon, and nitrogen moieties in the individual steps of ORR, such as (1) reduction of oxygen to hydrogen peroxide, (2) the reduction of hydrogen peroxide to water, and (3) the reduction of oxygen directly to water. Some early studies attempted to introduce traditional inhibitors into the electrolyte during oxygen reduction progress, such as carbon monoxide, cyanide, fluoride, thiocyanate, alcohols, thiol, chloride, sulfate, and sulfide.^{10–15} Another approach was based on the introduction of the blocking ligands during the material synthesis, in particular, the hydrogen sulfide-rich atmosphere during heat treatment,¹⁰ or sulfur, thio-urea, and thiophene mixed with precursors before pyrolysis.¹⁶ However, these methods have the disadvantage of the excessively strong interaction of these inhibitors with the catalyst resulting in incomplete removal of adsorbed com-

pounds, which in turn leads to difficulties in the deconvolution of the active sites in the PGM-free catalysts.

In the latest work focused on the mechanism of ORR through the characterization of inhibited active sites, Kneebone et al. used Mössbauer spectroscopy, nuclear resonance vibrational spectroscopy, and density functional theory to study the influence of Fe–N–C activity toward oxygen reduction under the selective interaction of catalyst active centers with NO.¹⁷ Mamtani et al. have used phosphate anion to probe the active sites of nitrogen-doped metal-free carbon nanostructures.⁸ They observed a correlation between the increase in the level of protonation of the pyridinic sites and decrease of the activity toward oxygen electroreduction. Recently, Malko et al.¹⁸ studied the poisoning effect of NO₂[–], NO, and NH₂OH on the electrocatalytic activity of Fe–N–C catalysts in the acid and alkaline media.

Herein, we report for the first time the use of tris(hydroxymethyl)-aminomethane (Tris) as a specific molecular probing agent of active sites in Fe–N–C catalysts. Two catalysts, one metal-free (N–C) and one metal-containing (Fe–N–C), were fabricated by identical synthetic procedure from the same carbon–nitrogen precursor, aminoantipyrene (AAPyr), without and with Fe salt (AAPyr and FeAAPyr, respectively).^{19–21} Study of inhibition and recovery of metal-containing catalysts in the

Received: January 4, 2018

Accepted: April 10, 2018

Published: April 10, 2018

Figure 1. DFT optimized geometries of TrisH adsorbed on (a) Fe–N, (b) graphitic N, (c) pyridinic-N, (d) hydrogenated pyridinic-N site, and (e) Pt (111). For clarity, for Fe–N–C only atoms belonging to part of the unit cell are shown.

acidic and alkaline electrolyte and comparison between metal-free and metal-containing PGM-free catalysts allowed us to correlate the nature of their active sites with individual steps of oxygen reduction reaction.

EXPERIMENTAL SECTION

Catalysts Preparation. The catalysts used in the presented work were prepared using the sacrificial support method (SSM) as previously presented.^{14,22} Aminoantipyrine (AAPyr) was employed in both cases as a nitrogen-rich organic precursor for the synthesis. Fe-AAPyr was prepared by mixing iron nitrate and AAPyr. In the case of metal-free catalyst (AAPyr), the only organic precursor was used. In both cases, the monodispersed silica with a surface area of $250 \text{ m}^2 \text{ g}^{-1}$ was impregnated with mentioned above precursors. The material was then homogenized using ball milling for 30 min. High-temperature treatment was done in a quartz tube in an inert atmosphere of UHP nitrogen. The gas flow was constant at 100 mL min^{-1} . The temperature was increased from room temperature to 950°C with a ramp rate of $25^\circ \text{C min}^{-1}$. The sample was heat treated for 45 min. The silica template was etched using 20 wt % HF overnight ($\sim 12 \text{ h}$). The catalyst was then washed with DI water until the neutral pH of the supernatant was reached. The catalyst was then dried.

Electrochemical Measurements. RRDE was the technique used to determine the electrocatalytic performances of FeAAPyr and AAPyr in acidic media with/without the addition of Tris. The ink was prepared as previously presented.^{23,24} Five mg of PGM-free catalyst was added to a plastic vial with 1 mL of 150 μL of 0.5 wt % Nafion solution and 850 μL of IPA: H_2O 1:1 ratio. The mixture was sonicated few times to obtain a uniformly dispersed ink. The latter was drop cast to the disk electrode using a micropipette. The catalyst loading on the disk was $200 \mu\text{g cm}^{-2}$. The ink was left to dry at room temperature, and then linear sweep voltammetry (LSV) was performed. LSV was run from 0.8 to -0.2 V vs (Ag/AgCl) at a scan rate of 5 mV s^{-1} for Fe-AAPyr sample, while from 0.65 to -0.35 V for AAPyr sample. A graphite rod electrode (PINE research) was used as the counter electrode. After every test, a calculated amount of Tris was added, and the pH was controlled to be lower than 1. Two series of electrochemical inhibition studies were done independently. The first set of experiments tested electrode made from FeAAPyr catalyst with the following concentrations of Tris in 0.5 M H_2SO_4 and in 1 M KOH: 0.001 M, 0.01 M, 0.1 M, 0.8 M. The second study tested both FeAAPyr and AAPyr in 1 M HClO_4 using the following concentrations of Tris: 0.1 M, 0.15 M, 0.2 M, 0.25 M, 0.3 M, 0.4 M, 0.5 M, 0.6 M, 0.7 M, 0.8 M. After LSV was recorded in the 0.8 M solution of Tris, the electrolyte was changed to a freshly prepared 0.5 M H_2SO_4 , 1 M HClO_4 or 1 M KOH while the working electrode was immersed and kept 1600 rpm rotating in deionized (DI) water for 5 min (DI water

was changed 3 times). After washing, the working electrode was used for ORR measurements in the Tris-free electrolytes. The tests under this condition are designated as “R” (recovery or refresh). The reference tests of commercial Pt were performed in Tris in 0.5 M H_2SO_4 using the following concentrations of Tris: 0.001 M, 0.01 M, 0.1 M, 0.8 M. The ink formulation was modified for the commercial Pt/C (Aldrich, 10 wt % of Pt), to achieve a $40 \mu\text{g cm}^{-2}$ loading while maintaining an identical Nafion (N) over Carbon (C) ratio with the PGM-free ink ($\text{N/C} = \text{ca. } 0.15$).

Computational Details. The calculations were performed using plane-wave pseudopotential implementation of Density Functional Theory (DFT)^{25,26} with the Perdew–Burke–Ernzerhof (PBE) functional^{27,28} with the use of Vienna Ab initio Simulation Package (VASP).^{29,30} Fe–N_x and graphitic nitrogen sites were modeled using extended surfaces with the dimensions of $17.04 \text{ \AA} \times 17.04 \text{ \AA}$, $\gamma = 60^\circ$ and a vacuum region of 20 $\text{\AA}$. Pyridinic and hydrogenated pyridinic nitrogen were modeled using the nanoribbons, which were constructed from 4×2 orthorhombic super cells with the size of $9.84 \text{ \AA} \times 23.52 \text{ \AA}$ and with a vacuum regions of 15 $\text{\AA}$ in the *z*- and *y*-direction. Pt(111) surface was modeled using three layers of Pt atoms in the unit cell of the size $11.2 \times 11.2 \text{ \AA}$ and a vacuum region of 20 $\text{\AA}$. The electronic energies were calculated using tetrahedron method with Blöchl correction³¹ and $3 \times 3 \times 1$ k-point Monkhorst-Pack³² mesh in the case of the extended surfaces and $8 \times 1 \times 1$ k-points in the case of the super cells used to model edge defects. In all the cases, plane-wave basis cut off was set to 700 eV. Adsorption energies of Tris and protonated Tris (TrisH) at different defects (ΔE_{ad}) were calculated using the following formula:

$$\Delta E_{\text{ad}} = E_{\text{surface+ad}} - [E_{\text{surface}} + E_{\text{ad}}]$$

where $E_{\text{surface+ad}}$ is the energy of Tris or TrisH adsorbed on the certain defect, E_{surface} is the energy of the extended surface or a nanoribbon, and E_{ad} is the energy of the Tris/TrisH molecule in the gas phase. In each case, we considered multiple adsorption orientations, but the results reported in work correspond to most preferable adsorption orientation.

RESULTS AND DISCUSSION

We first used density functional theory (DFT) to understand the interaction of Tris and TrisH with different defects that exist in Fe–N–C materials. At the acidic pH, Tris with pK_a value of 8.07 is present in its protonated form, which we denote TrisH, while at alkaline pH it is present in deprotonated form Tris. The interaction of Tris and TrisH with different defects was calculated as shown in Figure 1. The defects considered in the calculations are responsible for $2 \times 2e^-$ or $4e^-$ mechanism of oxygen reduction to water (metal–nitrogen directly

coordinated), $2e^-$ reduction of oxygen to peroxide (hydrogenated pyridinic, pyrrolic nitrogen and graphitic nitrogen) and reduction of peroxide to water (pyridinic nitrogen).^{7,33}

The DFT results show that the interaction energy between the Fe–N₄ site and Tris of -0.25 eV is significantly smaller than that of oxygen (see Table 1). Therefore, we assume that

Table 1. Adsorption Energy of Tris, Protonated Tris (TrisH), and Oxygen in eV as Calculated Using DFT

site	TrisH	Tris	O ₂
(a) Fe–N _x	$-1.96(x = 4)$ $-2.18(x = 2)$	-0.25 ($x = 4$)	-1.01^a to -1.43^b ($x = 4$) -1.68^a ($x = 2$)
(b) graphitic-N	-1.07	-0.02	-0.13^a to -0.41^b
(c) pyridinic-N	-3.65	-0.41	-0.08^a to -0.28^b
(d) hydrogenated pyridinic-N /pyrrolic N	-0.53	-0.26	-0.21^b to -0.25^b
(e) Pt (111)	-3.07		-0.44 to -0.81^c

^aValues calculated using PBE functional and as published in ref 34.

^bValues calculated using vdW-DF functional as published in ref 35.

^cValues are taken from refs 36–38.

Tris form does not bind to metal-containing active sites and is not involved in the inhibition process, by opposition to TrisH (-1.96 eV). From the comparison of the adsorption energies of TrisH and O₂ on different defects (Table 1), it can be concluded that TrisH has the strongest interaction with pyridinic-N and Fe–N_x sites, followed by the graphitic-N and hydrogenated nitrogen defects (pyrrolic and hydrogenated pyridine). At the same time, only pyridinic nitrogen serves as a possible site for Tris binding that is strong enough to compete with the binding of oxygen. Fe–N_x and pyridinic nitrogen are the most preferred sites for TrisH binding and for these sites

the binding energy of TrisH is significantly larger than that of oxygen.

Electrocatalytic activity of FeAAPyr in the reaction of oxygen reduction was evaluated by Rotating Ring Disk Electrode (RRDE) in the 0.5 M H₂SO₄ and 1 M KOH (Figure 2). The information derived from linear sweep voltammograms (LSVs) as a function of Tris concentration is presented in Figure 3. LSV for commercial Pt/C was also acquired as a reference. According to DFT, there is a strong energy of adsorption between Pt and TrisH (-3.07 eV, see Table 1 and Figure 1e), which is comparable to the energy of adsorption of TrisH to pyridinic N. In Pt/C where ORR occurs via direct $4e^-$ mechanism, addition of TrisH causes very significant decreases in half-wave potential due to blockage of Pt sites by the absorbed inhibitor (Figure 3h), while limiting disk current decreases insignificantly at lower concentrations than 0.1 M and drops significantly at 0.8 M of Tris (Figure 2c). This indicates that at larger concentrations of Tris, i.e., above 0.1 M, solubility of oxygen in the electrolyte decreases due to the increased concentration of inhibitor. This explanation is further supported by the negligible (and independent of the Tris concentration) ring current (Figure 2f). Indeed, this result confirms that oxygen reduction reaction on Pt follows a direct $4e^-$ pathway and that Tris addition does not have any effect on the hydrogen peroxide yield. Because the limiting current is dependent on the reactant concentration in solution and on the exchanged number of electrons. The constant value of the later confirms that Tris is decreasing O₂ solubility in solution at concentrations above 0.1 M. Washing away Tris from the working Pt/C electrode results in full recovery of both half-wave potential and disk current at 0.2 V.

For FeAAPyr catalyst, the addition of even 0.001 M Tris to electrolyte results in 25 mV shift of half-wave potential to a lower value in acidic solution and no change in alkaline. In

Figure 2. LSV on (a, c, e) disk electrode and (b, d, f) ring electrode in different concentrations of Tris, where “R” denotes refreshed Tris-free electrolyte and washed RRDE. Data of (a, b) FeAAPyr in acid, (c, d) FeAAPyr in alkaline, and (e, f) Pt/C in acid, respectively.

Figure 3. Electrochemical parameters extracted from LSV. Disk and ring current density for FeAAPyr in (a, d) acid, (b, e) FeAAPyr in alkaline, and (c, f) 10% Pt/C in acid. Changes in parameters for three systems: (h) decrease in half-wave potential; (i) decrease in disk current density; and (g) change in % generated H_2O_2 .

acidic electrolyte, there is a 45 mV downshift in the half-wave potential at 0.1 M of Tris, but no further decrease in half-wave potential is observed when Tris concentrations were increased up to 0.8 M. The rate of change in half-wave potential is quite different in alkaline electrolyte (Figure 3h), where 0.1 and 0.8 M Tris induce much smaller shift in half-wave potential of only 15 and 35 mV, respectively. The rate of decrease in the disk limiting current density is very similar for both acidic and alkaline solutions (Figure 3i) with maximum decrease observed for 0.8 M Tris concentration induced by decreased solubility of oxygen (as observed on Pt/C), especially at high concentrations of an inhibiting agent. The larger effect on disk current density in alkaline media versus acidic even at low concentrations of Tris points to the higher solubility of Tris in alkaline electrolyte.

After washing the working electrode with deionized water, a very small increase in $E_{1/2}$ (~ 5 mV) was registered in the acidic electrolyte, which indicates the irreversible inhibition of active sites participating in the ORR by the Tris added (Figure 3h). At the same time, the half-wave potential is almost fully recovered in alkaline media. However, in both cases, the diffusion limiting current for the “recovered” catalysts are lower than observed before Tris-addition. This is easily explained by the higher peroxide yield (Figures 2b, d and 3g) that induces a decrease of the overall number of electrons exchanged during the reaction

and, therefore, a diminished diffusion limiting current. Differences in peroxide yield arise from the addition of Tris, which results in drastically different behavior due to a different mechanism of oxygen reduction, particularly in the first step of oxygen reduction to hydrogen peroxide. A significant difference between ORR in acidic and alkaline media is based on an inner-sphere and outer-sphere mechanism. In alkaline media, surface hydroxyl groups promote surface-independent outer-sphere electron transfer, whereas in acidic media immediate involvement of active sites such as metal coordinated to nitrogen in inner-sphere electron transfer is of direct relevance.^{39–41}

In acidic media, Tris is present in its protonated form TrisH ($\text{pK}_a = 8.07$); the addition of low concentrations of Tris, i.e., between 1 mM and 0.1 M results in a similar decrease in a ring current due to TrisH inhibiting hydrogen peroxide producing sites. At large Tris concentration of 0.8 M, there is a significant decrease in hydrogen peroxide production due to a combination of decreased oxygen solubility and inhibition of H_2O_2 producing sites by bound TrisH. However, after washing the working electrode, the ring current density increased from 0.02 mA cm^{-2} to 0.10 mA cm^{-2} at 0.5 V vs RHE (Figure 3d). This phenomenon of hydrogen peroxide recovery after catalyst washing is a clear indication of Tris reversible weak binding to the active centers participating in the first step of ORR mechanism. Moreover, DFT calculations show that the proton

Figure 4. LSV data of (a, c) Fe-AAPyr and (b, d) AAPyr materials. (a, b) Disk current density and (c, d) ring current density.

from TrisH is being transferred to pyridinic nitrogen due to the lower pK value of the pyridinic nitrogen (6.5 for pyridinic nitrogen and 8.06 for Tris molecule). The interaction energy between protonated pyridinic nitrogen, and Tris molecule is only -0.26 eV. In previous studies, protonation of pyridine has shown to inhibit oxygen reduction reaction.⁸ Pyridinic nitrogen has shown to catalyze the second step of hydrogen peroxide reduction to water. This implies that after the catalyst washing, TrisH is removed, but pyridinic nitrogen remains in its protonated form, therefore, explaining the lower half-wave potential and higher hydrogen peroxide yield of the “recovered” catalysts compared to their “fresh” counterpart (Figures 2a, b). Furthermore, on the basis of the DFT results in Table 1, TrisH can be more easily removed from protonated pyridinic nitrogen, pyrrolic nitrogen, and graphitic nitrogen, while Fe-N_x sites may be irreversibly blocked by TrisH.

In alkaline media, Tris is present in its deprotonated form. The interaction energy between the Fe-N₄ site and Tris was determined to be -0.25 eV, significantly smaller than that of TrisH (Figure S1, Table S1). DFT has shown competitive binding of Tris and oxygen to pyridinic nitrogen. Enhanced hydrogen peroxide generation at all concentrations of Tris is observed (Figure 3g). This can be attributed to the presence of Tris bound to pyridinic nitrogen within the outer Helmholtz sphere of the catalyst surface, which enhances the first step of oxygen reduction to peroxide.^{40,41}

In conclusion, in acidic electrolyte, TrisH interacts strongly with active sites that catalyze both complete and partial reduction of oxygen, and, therefore, it should inhibit both steps of ORR. As observed in the experiment performed in an acidic electrolyte, the addition of TrisH results in a decrease of both half-wave potential and the ring current confirming direct blocking of active sites for both complete and partial oxygen reduction by TrisH. In alkaline electrolyte, Tris can only competitively bind to pyridinic nitrogen which has been shown to catalyze the reduction of hydrogen peroxide to water.⁷ The half-wave potential recorded in alkaline media is changed very

slightly by the addition of Tris. However, there is an enhancement of hydrogen peroxide production, observed experimentally when Tris is added to the alkaline electrolyte. One explanation could be that specific adsorption of Tris leads to selective blocking of pyridinic nitrogen moieties, which act as catalytic sites for hydrogen peroxide reduction to water. This effect of selective site blocking can be synergistic to a local increase of $-OH$ groups in proximity of Tris-bound to pyridinic nitrogen surface groups, which can be beneficial to oxygen reduction to hydrogen peroxide in alkaline electrolyte. In acidic electrolyte TrisH affects both partial oxygen reduction to peroxide and complete oxygen reduction to water, as evidenced by the observation that both half-wave potential and the peroxide yield decrease for Tris concentrations exceeding 0.1 M. In contrast, in alkaline electrolyte Tris promotes the first step of reaction of producing hydrogen peroxide and inhibits the second step of H_2O_2 reduction to water. This alternate effect on selectivity allows one to use Tris as a homogeneous, electrolyte-based “titration agent” to selectively study kinetics of individual steps of ORR on various catalytically active moieties present in M-N-C catalysts.

To address the role of metal on oxygen reduction mechanism we have tested inhibition of the electrocatalytic activity of FeAAPyr and AAPyr by Rotating Ring Disk Electrode (RRDE) method in the 1 M $HClO_4$ acidic electrolyte with the addition of Tris as the inhibiting agent (Figure 4). The electrochemical information derived from linear sweep voltammograms (LSVs) as a function of Tris concentration is presented in Figure S2. Like the experiments reported in Figure 2, in the case of FeAAPyr, the shift to lower values in half-wave potential with increasing concentration of Tris was observed (Figure S2 a). When 0.8 M Tris is added to the acidic electrolyte, similar shift of 50 mV is observed in both 0.5 M H_2SO_4 and 1 M $HClO_4$. Very insignificant recovery in half-wave potential indicates the irreversible inhibition of active sites participating in the ORR. After this initial decrease in ORR activity upon addition of 0.1 M Tris, increasing the Tris concentration resulted in the

insignificant decrease of the limiting current density (Figure 5a).

Figure 5. Schematic diagram of ORR mechanism changes before and after Tris introduced into the solution. Catalytically active surface moieties are depicted schematically with no intention of implying any special positioning of distribution in the actual material. “Dashed” lines suppressed reactions subject to reversible or irreversible inhibition.

As can be seen in Figure 4c, the ring current density decreased with the increase of the Tris concentration from 0 to 0.8 M. Partial recovery of electrochemical production of H_2O_2 after washing the catalyst is an indication of weak adsorption of Tris on hydrogen peroxide-producing active sites.

The similar set of experiments were performed with metal-free (AApyr) electrocatalyst to discriminate further the active sites participating in ORR. It was found that upon exposure of metal-free catalyst (AApyr) to Tris, both half-wave and disk current densities gradually decrease (Figure 4b, d). In general, the overall half-wave potential is not recovered after washing, in contrast to ring current densities, which approaches the values obtained in the Tris-free electrolyte.

In both Fe–N–C and N–C materials, pyridinic nitrogen and hydrogenated nitrogen (pyrrolic and hydrogenated pyridine) are part of the $2 \times 2e^-$ mechanism, in which hydrogenated nitrogen reduces oxygen to H_2O_2 , while pyridinic nitrogen reduces H_2O_2 to water. Comparison between inhibition and recovery of ORR performance in metal-free and metal-containing electrocatalysts shows that the moieties that reduce oxygen directly to water ($\text{Fe}-\text{N}_x$) have a higher affinity to TrisH compared to the active centers reducing oxygen to hydrogen peroxide (pyridinic and hydrogenated nitrogen). The metal-containing catalyst contains sites that have stronger binding of TrisH as established by the drastic decrease in the half-wave potential. TrisH also adsorbs onto both hydrogenated nitrogen and pyridinic nitrogen more strongly than O_2 , inhibiting, thus, both the first and the second step of the ORR. However, upon Tris removal by washing, protonation of pyridine results in the creation of sites that reduce oxygen to hydrogen peroxide, which manifests itself as a recovery in the hydrogen peroxide yield. In metal-containing electrocatalysts, $\text{Fe}-\text{N}_x$ moieties are the most active toward the full reduction of oxygen to water via either $4e^-$ or $2 \times 2e^-$ mechanism. At the

same time, TrisH binds strongly and irreversibly to these sites, more strongly than O_2 , and inhibits the oxygen reduction reaction. After removal of the TrisH by washing, most of the sites are protonated and contribute to the production of hydrogen peroxide.

To summarize, in Figure 5, we suggest the possible mechanism of oxygen reduction and changes in surface chemistry that occur when inhibitor Tris is introduced into the acidic solution. In this diagram, we show that the $\text{Fe}-\text{N}_x$ centers are being irreversibly blocked by TrisH resulting in slower direct $4e^-$ oxygen reduction to water. At the same time protonation of pyridinic nitrogen results in the enhanced kinetics of the first step of reduction of oxygen to hydrogen peroxide.

CONCLUSION

Poisoning effect of Tris(hydroxymethyl)aminomethane (Tris) on the electrocatalytic activity of M–N–C toward ORR in the acidic and alkaline environment was comprehensively studied experimentally and computationally. The experiments in acidic electrolyte also allowed to analyze the role of metal in M–N–C by studying the effect of the inhibitor on the electrochemical behavior of metal free and metal-containing electrocatalyst. The introduction of Tris into the electrolyte inhibits iron–nitrogen and nitrogen–carbon active sites. Rotating ring disk electrode experiments and density functional theory calculations show that the $\text{Fe}-\text{N}_x$ sites could be irreversibly poisoned while N–C sites can be recovered by the removal of Tris. Density functional theory calculations also show that the protonation of pyridinic nitrogen could contribute to the recovery of the hydrogen peroxide generation in both metal-free and metal containing electrocatalysts in acidic media. As Tris is a commonly used chemical in electrochemistry research, the described phenomena reveal new avenues for mechanistic studies of PGM-free oxygen reduction catalysts.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsam.8b00020.

Figures S1 and S2 and Table S1 (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: kartyush@unm.edu.

*E-mail: plamen@unm.edu.

ORCID

K. Artyushkova: 0000-0002-2611-0422

I. Matanovic: 0000-0002-9191-8620

P. Atanassov: 0000-0003-2996-472X

Author Contributions

The manuscript was written through contributions of all authors. S.R.-C. discovered the inhibitor effect; Y.Ch., S.R.-C., C.S., and T.A. were primarily responsible for the electrochemical evaluation; S.R.-C., A.S., and T.A. for synthesis; I.M. for DFT calculations; Y.Ch., T.A., K.A., and P.A. for planning, analysis, and writing. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thankfully acknowledge the computational resources for this project from the Tri-Lab computing resources of LANL, operated by Los Alamos National Security, LLC, for the National Nuclear Security Administration of U.S. Department of Energy (Contract DE-AC52-06NA25396), computational resources of NERSC, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231, and CNMS, which is a DOE Office of Science User Facility. VASP license was provided by Theoretical division, LANL. This paper has been designated LA-UR-17-30624.

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