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Enhancement in Oxygen Reduction Reaction Activity of CN_x in Acidic Media through Chloride-ion Exposure

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Abstract

Nitrogen-doped carbon nanostructures (CN_x) are promising cathode catalysts for oxygen reduction reaction (ORR) in polymer electrolyte membrane (PEM) fuel cells. Incorporation of chlorine into CN_x catalysts using a facile methodology can lead to a significant improvement in the ORR activity of these materials in acidic media, as confirmed by electrochemical half-cell measurements. Chlorine containing CN_x is synthesized by soaking CN_x catalyst in powder form in 0.3 M HCl to obtain CN_x-Cl. Near edge X-ray absorption fine structure (NEXAFS) spectra collected in the C K-edge region and Fourier transform infrared (FT-IR) spectra confirm the formation of C-Cl bonds in CN_x-Cl. X-ray photoelectron spectroscopy (XPS) reveals the presence of three distinct chloride species in the CN_x -Cl sample – (i) organic chloride (C-Cl), (ii) anionic chloride in the positively charged environment of a pyridinium ring (N⁺Cl⁻) and (iii) physisorbed ionic chloride. Results from temperature programmed desorption studies under inert atmosphere corroborate the conclusions from XPS depth profiling analysis. The improvement in ORR activity after exposure of CN_x catalyst to chloride anions can be attributed to creation of additional active sites in the form of C-Cl functionalities. The difference in electronegativities of C and Cl atoms creates a net positive charge on adjacent carbon site leading to side-on adsorption of oxygen molecule and breakage of O-O bond during ORR.

Keywords: PEM fuel cells, ORR, CN_x, chlorination, N-doped carbon

1. Introduction

Polymer electrolyte membrane (PEM) fuel cells offer a promising technology for clean and sustainable energy generation applications. Slow kinetics of the oxygen reduction reaction (ORR) taking place on the cathode of a PEM fuel cell necessitates use of large amounts of platinum-based catalyst, thus reducing the economic viability of PEM fuel cell technology. Non-precious metal catalysts (NPMCs) of the type Me-N-C (Me = transition metal such as Fe or Co) which contain a metal-centered active site have been thoroughly studied and shown to be promising alternatives to platinum for ORR^[1]. Another class of NPMCs includes nitrogen-doped carbon nanostructures (CN_x) that were first demonstrated by Ozkan and co-workers to be active for ORR in acidic media^[2]. They further incorporated phosphorus into CN_x to form CN_xP_y catalysts that showed improved ORR catalytic activity and selectivity towards formation of water^[3]. It was also established that unlike Me-N-C catalysts, CN_x materials do not have a metal centered active site^[4] by demonstrating their resistance to poisoning in the presence of methanol^[5], CO^[6], H₂S^[7], cyanide^[6a] and chloride^[8]. More recently, they identified phosphate anion as a poisoning probe and concluded that there are two possible active sites in CN_x catalysts^[9]: (a) pyridinic-N itself, or (b) carbon next to the pyridinic-N.

Doping of carbon nanostructures using heteroatoms that have a higher electronegativity than carbon ($\chi = 2.55^{[10]}$) creates a partial positive charge on the adjacent carbon atom, thus facilitating side-on adsorption of O₂ molecules on the catalyst surface and weakening of O-O bonds, resulting in high ORR activity^[11]. Doping of carbon with nitrogen ($\chi = 3.04^{[10]}$) is thus found to be very effective in improving ORR catalytic activity of carbon nanostructures. Doping of additional heteroatoms such as boron, phosphorus, sulfur and halogens into CN_x-type materials have also been shown to enhance their ORR catalytic activity^[3a, 12].

Amongst all halogens, most studies in literature have focused on doping fluorine on carbon nanostructures for applications in ORR catalysis in alkaline media^[13]. Qiao et al. synthesized carbon-based catalysts simultaneously doped with nitrogen and fluorine by annealing graphene oxide and ammonium fluoride together^[14]. They attributed the enhancement in ORR activity of the catalyst to additional doping with fluorine apart from nitrogen, leading to the formation of C-F bonds and a synergistic effect between F and N dopants. Alwarappan and co-workers also

reported the use of nitrogen and fluorine co-doped graphene synthesized using a two-step wet chemical process as an efficient ORR electrocatalyst in alkaline medium, and studied the synergistic effect of dual dopant atoms^[15].

There are a very few studies in literature that focus on using facile methodologies to synthesize nitrogen and chlorine co-doped carbon nanostructures for applications as ORR electrocatalysts in acidic media^[11b]. One popular methodology used for preparation of halogenated graphene nanoplatelets is by ball milling graphite flakes in the presence of halogen gas (F_2 , Cl_2 , Br_2)^[11a, 16]. Jeon et al. prepared edge-halogenated graphene nanoparticles using ball-milling and showed excellent ORR activity of these materials in alkaline medium^[11a]. Pumera and co-workers described the synthesis of halogenated graphene by exfoliation of graphene oxide in a halogen atmosphere at very high temperatures^[17]. Wu et al. also demonstrated solution phase synthesis of halogenated graphene or or or class of the un-doped sample^[18]. Since handling of toxic halogen gases can be hazardous in a laboratory, it is important to explore safer ways of chlorine incorporation into nitrogen-doped carbon nanostructures.

In this work, we have used a facile methodology to incorporate chlorine into CN_x catalysts and attempted to explore the role of chlorine in enhancing the ORR catalytic activity of these materials. Pristine CN_x catalyst is synthesized using chemical vapor deposition of acetonitrile (CH₃CN) on Fe/MgO substrate followed by acid washing to remove the metallic precursor. To incorporate chlorine, the pristine CN_x sample is soaked in 0.3 M HCl, vacuum filtered and dried to obtain CN_x -Cl. Several catalyst characterization techniques such as Fourier transform infrared (FT-IR) spectroscopy, near edge X-ray absorption fine structure (NEXAFS), X-ray photoelectron spectroscopy (XPS) as well as temperature programmed desorption have been employed to gain insights into the nature of the different chlorine species incorporated into CN_x catalysts that cause an enhancement in ORR activity.

2. Results and Discussion

2.1 Effect of chloride exposure on electrocatalytic activity

Electrochemical ORR activity measurements were performed in 0.5 M H₂SO₄ electrolyte on two samples – CN_x and CN_x -Cl. A comparison of the results indicates that ORR activity significantly improved after CN_x was soaked in 0.3 M HCl (Figure 1(a)). ORR kinetic parameters of the samples have been compared in Table 1. The ORR onset potential (E_{onset} , determined at a current density of -0.1 mA/cm²) increased by 60 mV for CN_x -Cl sample as compared to its pristine counterpart (740 mV). Similarly, the value of half-wave potential ($E_{1/2}$) shifted positive by 120 mV for CN_x -Cl indicating improved ORR activity, as compared to the pristine sample (660 mV vs. 540 mV respectively). Kinetic current density obtained at 0.7 V also improved significantly from 0.31 mA/mg_{catalyst} to 2.22 mA/mg_{catalyst} after soaking the CN_x sample in 0.3 M HCl. Cyclic voltammograms (CVs) collected in oxygen saturated electrolyte for CN_x -Cl samples are shown in the supplementary information (Figure S1) where the enhancement effect of chloride ion exposure on CN_x is clearly visible. The ORR activity of CN_x -Cl sample as compared to that of state-of-the-art 10% Pt/C (ETEK) catalyst is presented in Figure S2. It is seen that, although chloride exposure enhances the ORR activity of CN_x significantly, CN_x -Cl still does not perform as well as 10% Pt/C, with a difference in E_{onset} of 106 mV and a difference in $E_{1/2}$ of 110 mV.

Figure 1(b) shows Tafel plots for both samples and values of Tafel slopes (Table 1) suggest similar ORR rate-determining steps for CN_x and CN_x -Cl. Thus, electrocatalytic measurements clearly indicate that soaking CN_x in 0.3 M HCl solution significantly improved the ORR activity of the catalyst.

Koutecky-Levich (K-L) plots depicted in Figure 2(a) were used to determine the selectivity of both CN_x and CN_x -Cl catalysts towards formation of water. The value of selectivity calculated in terms of number of electrons transferred per oxygen molecule (n), using the slope of K-L plots was found to be 3.7 at 0.25 V for both CN_x and CN_x -Cl samples. This observation suggests that ORR on these catalysts takes place primarily via a direct 4 electron or 2+2 electron reduction pathway to form water.

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Stability measurements performed on CN_x and CN_x -Cl catalysts are expressed in terms of ORR half-wave potentials ($E_{1/2}$) determined after 200, 500, 1000, 1500, 2000 and 3000 cycles. As evident from Figure 2(b), no significant loss in ORR activity was observed even after 3000 cycles for either sample. Accelerated durability testing thus demonstrates the exceptional stability of both CN_x and CN_x -Cl samples in acidic media.

2.1.1 Electric double layer capacitance measurements

Cyclic voltammograms obtained at different scan rates between 1.2 and 1.0 V on the pristine CN_x electrode, before and after exposure to 0.3 M chloride anions, are shown in Figure 3(a) and 3(b). Figure 3(c) illustrates the plot of capacitive current ($I_{capacitive}$) at 1.1 V vs. scan rate, the slope of which equals the value of double layer capacitance of the electrode before and after exposure to chloride anions. The electric double layer capacitance of CN_x increases from 4.1 mF in pristine H₂SO₄ electrolyte to 7.7 mF in H₂SO₄ electrolyte containing 0.3 M Cl⁻ anions. The observed increase in electric double layer capacitance can be attributed mainly to the adsorption of chloride anions on CN_x electrode since adsorbed ions generally increase the interfacial capacitance^[9]

2.2 Characterization of Cl-containing species through vibrational spectroscopy

Fourier transform infrared (FT-IR) spectrum collected on CN_x -Cl using CN_x as the background spectrum is shown in Figure 4. The two IR bands observed at 714 and 661 cm⁻¹ can be associated with the presence of C-Cl stretching vibrations and anionic chloride species, respectively, that form after soaking the CN_x sample in 0.3 M HCl ^[19].

Raman spectra of both pristine and soaked samples show first order D and G bands (Figure 5). The D-band corresponding to disordered sp² hybridized carbon is centered at 1360 cm⁻¹ while the G-band corresponding to the presence of crystalline graphitic carbon appears at 1574 cm⁻¹ for both CN_x and CN_x -Cl samples^[20]. Second order Raman bands at ~2700 cm⁻¹ (2D band^[20d, 21]) and ~2938 cm⁻¹ (G+D bands^[22]) are also present in both pristine and HCl-soaked CN_x samples. The degree of graphitization obtained by calculating the ratio of area under the G band to area under D band was found to be very similar for CN_x and CN_x -Cl samples (0.41 and 0.44, respectively). This indicates that the improvement in ORR activity is not a result of additional

defect sites that may be created in the carbon matrix due the vast difference in sizes of C and Cl atoms^[11c].

2.3 Near edge X-ray absorption fine structure (NEXAFS)

NEXAFS spectroscopy was used to acquire information about the atomic environment of C in pristine and HCl-soaked CNx samples. NEXAFS spectra of CNx and CNx-Cl are shown in Figure 6. Both samples exhibit a peak at ~285.7 eV which can be assigned to transition of C 1s core electron into unoccupied C-C π^* states in the carbon ring structure of CN_x materials^[23]. The feature at ~288.9 eV observed in both pristine and soaked CN_x samples can be attributed to the presence of oxygenated (CO) functional groups while that at ~293.7 eV represents C-C σ^* ring transitions ^[23a, 23c, 24]. The pristine sample contains an additional feature at ~286.4 eV indicating the presence of C-OH groups^[25]. This feature is absent in the CN_x -Cl sample likely due to the protonation of C-OH groups in CN_x after exposure to 0.3 M HCl. There is also an additional shoulder observed at ~288 eV in CN_x -Cl which is absent in the CN_x sample. This feature at ~2.3 eV above the C-C π^* transition can be attributed to the formation of C-Cl bonds formed after chlorination, as is also reported in literature^[26]. This observation is also consistent with the presence of C-Cl bonds observed in both FT-IR spectrum and Cl 2p region of XPS which is described in the following sections.

2.4 Surface characterization using X-ray photoelectron spectroscopy (XPS)

XPS analysis was performed on both CN_x and CN_x -Cl to investigate the nature of surface species in the catalysts. XPS survey spectra obtained for both samples are shown in the supplementary information (Figure S3). Surface atomic composition analysis shown in Table 2 revealed that the surfaces of both samples contain a significant amount of carbon and nitrogen as also observed previously^[9]. The relative amount of nitrogen present on the surface remains the same before and after exposure to chloride anions. However, CN_x-Cl contains a small amount of chlorine species on the surface which is absent in the CN_x sample. Consequently, a decrease in the surface atomic concentration of oxygen after exposure to chloride anions is observed. Consistent with our previous works, no iron was detected on the surface of either sample^[4,9].

XPS spectra obtained in the C-1s region are presented in Figure S4. Both samples exhibit the presence of graphitic C=C species at binding energy of 284.4 eV and sp³ hybridized carbon (C- C) species at binding energy of 285.1 $eV^{[27]}$. The peak at 286.7 eV in both samples corresponds to the presence of C-O and C-N functionalities while the highest binding energy peaks (>290 eV) are attributed to the presence of sp^2 hybridized graphitic carbon or carboxyl (C=O) functionalities^[27a, 28]. It is important to note here that the C 1s peaks corresponding to C-Cl, C-N and C-O lie fairly close together and are difficult to reliably deconvolute^[29]. It is therefore important to examine the XPS spectra in the Cl 2p region to identify various chlorine species on the catalyst surface.

XPS spectra collected in the Cl 2p region for both CN_x and CN_x -Cl samples is shown in Figure 7(a). The CN_x sample does not contain any detectable chlorine species on the surface. Cl 2p spectra of the CN_x -Cl sample is deconvoluted by fitting two spin orbit split peaks ($2p_{1/2}$ and $2p_{3/2}$) for each of the different chemical states of chlorine. $2p_{1/2}$ and $2p_{3/2}$ peaks of each of these species are separated by a spin-orbit splitting of 1.6 eV and area under the $2p_{1/2}$ component is half of that under the $2p_{3/2}$ component. Full width at half maximum (FWHM) of $2p_{1/2}$ and $2p_{3/2}$ components is constrained to be the same for each species.

Three distinct chemical states of chlorine are identified in the CN_x -Cl sample. The first species observed with $2p_{3/2}$ binding energy peak at 200 eV indicates the presence of C-Cl functionalities in the sample^[30]. This observation is consistent with spectra obtained using FT-IR and NEXAFS that confirm the presence of organic chloride species. The second and third chlorine component peaks appear at $2p_{3/2}$ binding energies of 197.7 eV and 196.4 eV respectively, indicating the presence of two different ionic chloride species in the sample^[31]. Specifically, the ionic chloride peak at higher binding energy (197.7 eV) can be attributed to the presence of anionic chloride species present in a more positively charged local environment associated with the pyridinium ring (N⁺Cl^{32]}. Table 3 shows the relative distribution of various chloride species present in CN_x-Cl sample.

Figure 7(b) shows XPS spectra in the N 1s region of both CN_x and CN_x -Cl samples. As noted earlier, the surface atomic composition of nitrogen remains the same in both samples, however, the relative distribution of various nitrogen species changes after exposure of CN_x to 0.3 M HCl. Both samples contain three distinct nitrogen species. Pyridinic-N appears at a binding energy of 398.2 - 398.4 eV while quaternary nitrogen is represented by binding energy peaks at 400.7 –

400.9 eV^[9, 33]. The peak at binding energy > 402 eV can be assigned to pyridinic N⁺O⁻ species or simply to positively charged nitrogen functionalities^[34].

Interestingly, as shown in Table 3, soaking the CN_x sample in 0.3 M HCl results in a decrease in the pyridinic-N content, with a corresponding increase in its quaternary nitrogen content. It should also be noted that it is not possible to differentiate between quaternary nitrogen species and pyridinic-NH species using $XPS^{[33b]}$. Thus, the observed increase in quaternary nitrogen content can be attributed to formation of pyridinic-NH functionalities by dissociative adsorption of HCl on adjacent C and N sites, resulting in the protonation of pyridinic-N species. The protonation of pyridinic-N sites in acidic media was proposed by Popov and co-workers as a possible degradation mechanism of NPMCs^[33b, 35]. This protonated pyridinic-N site is stabilized by formation of C-Cl species on the carbon atom adjacent to the pyridinic-N. This phenomenon has also been previously reported by Mamtani et. al. for explaining adsorption of phosphate anions on CN_x leading to poisoning of ORR active sites in CN_x catalyst^[9]. It also explains the formation of C-Cl functionalities as observed in the XPS Cl 2p spectra of CN_x -Cl sample. The difference in electronegativity of C and Cl in the C-Cl bond can lead to creation of a partial positive charge on C atoms adjacent to the Cl atom, thus facilitating adsorption of oxygen on the catalyst surface to perform $ORR^{[12a, 14, 18]}$.

It is also worthwhile to note from Table 3 that the amount of positively charged pyridinic-N functionalities remains similar before and after exposure to chloride anions. This is possibly due to the conversion of pyridinic N^+O^- species in CN_x partially into pyridinic N^+CI^- sites after soaking the pristine catalyst in 0.3 M HCl. This observation is also consistent with the presence of anionic chloride species at $2p_{3/2}$ binding energy of 197.7 eV in the deconvoluted XPS Cl 2p spectra of CN_x -Cl sample shown in Figure 7(a).

To gain further insight into the nature of chloride species that result in enhanced ORR activity of CN_x catalyst, the surface of CN_x -Cl sample was etched using an argon ion gun following which XPS spectra were collected in the N 1s and Cl 2p regions. Figure 8(a) shows the Cl 2p region of XPS spectra of CN_x -Cl before etching, after 15 s of etching and after 120 s of etching. The relative composition of ionic chloride species at the lower binding energy (196.4 eV) reduces significantly after 15 s of etching, and these species completely disappear after 120 s of etching

the catalyst surface. This implies that the ionic chloride species at lower binding energy are predominantly surface species that likely form due to physisorption of chloride anions on CN_x catalyst during the process of soaking in 0.3 M HCl. Additionally, as the etching time increases, the relative abundance of C-Cl functionalities increases (Table 4). Ionic chloride species at higher binding energy (197.7 eV) persist even after 120 s of etching time. This is also confirmed from the N 1s region of XPS spectra of CN_x -Cl depicted in Figure 8(b) where the pyridinic N⁺O⁻/ N⁺Cl⁻ species continue to exist after 120 s of etching.

2.5 Evolution of chloride species observed through temperature programmed desorption

Temperature programmed desorption (TPD) was performed under an inert atmosphere on both CN_x as well as CN_x -Cl samples. The signal corresponding to 36 a.m.u (HCl) was monitored using a mass spectrometer and the results are shown in Figure 9(a). As expected, no peaks are observed in the spectrum of CN_x sample due to the absence of chlorine species. On the other hand, CN_x -Cl sample shows TPD spectra that can be deconvoluted into desorption of three different species as evident from Figure 9(b). This observation is consistent with the results of XPS indicating the presence of three distinct chlorine species in the soaked sample. The first desorption peak at ~210 °C corresponds to the most easily desorbed species and hence may be attributed to the physisorbed chloride species observed in XPS. The second and third desorption peaks appear at ~330 °C and ~600 °C, respectively. Since the strength of C-Cl bonds is greater than that of N-Cl bonds^[10, 36], it can be concluded that the second peak corresponds to desorption of chloride species from N-Cl functionalities while the third peak at ~600 °C appears due to dissociation of the organic chlorine (C-Cl) functionalities. The results from TPD studies are thus in agreement with those obtained using XPS, and also indicate that the C-Cl bonds formed in CN_x -Cl sample are fairly stable in nature.

3. Conclusions

In this work, we have successfully used a facile methodology to incorporate chlorine into CN_x catalyst leading to enhancement in its ORR activity. Electrocatalytic measurements reveal a significant positive shift in onset potential, half wave potential as well as kinetic current density at 0.7 V after soaking the CN_x sample in dilute HCl. Similar Tafel slopes obtained before and

after chloride exposure suggest that there is no change in the rate determining step of ORR. Accelerated durability testing shows no change in the ORR activity of either catalyst even after 3000 cycles. Increase in electric double layer capacitance after chloride exposure under in situ conditions confirms the adsorption of chloride anions on the surface of CN_x . FT-IR spectrum of CN_x -Cl shows vibrations corresponding to the presence of C-Cl bonds in the sample while analysis of Raman spectra suggests no change in the degree of graphitization after exposure of CN_x catalyst to chloride anions in 0.3 M HCl. Consistent with FT-IR, NEXAFS spectrum collected in the C K-edge region also shows a feature corresponding to the formation of C-Cl bonds in CN_x -Cl sample.

XPS and TPD analysis reveals the presence of three distinct chlorine species in the sample – organic chlorine (C-Cl), ionic chloride in the form of N⁺Cl⁻ and physisorbed chloride species. C-Cl bonds are formed by dissociative adsorption of HCl leading to protonation of a pyridinic-N site and chlorination of the carbon atom next to the pyridinic-N site. The difference in electronegativity between C and Cl atoms leads to the development of a partial positive charge on the carbon atom which helps facilitate ORR. Therefore, the improvement in ORR activity can likely be attributed to the formation of additional active sites in CN_x -Cl sample in the form of C-Cl bonds. We hope that the insights gained in this study will help in designing highly active non-precious metal based ORR catalysts and developing facile methodologies to improve the ORR activity of carbon-based materials for applications in PEM fuel cells.

4. Experimental Section

Catalyst synthesis

 CN_x catalysts were grown over iron-doped magnesia (2% Fe/MgO) substrate which was prepared using incipient wetness impregnation of iron (II) acetate (Sigma Aldrich) onto MgO nanopowder (Sigma Aldrich). The growth substrate was then dried overnight in an oven at 110 °C and ground using a rotary ball mill at 200 rpm for 3 h. 900 mg of the ball-milled substrate was subjected to chemical vapor deposition in a furnace at 900 °C using acetonitrile (CH₃CN). The catalyst precursor hence obtained was suspended in 0.5 M H₂SO₄ at 60 °C for 1 h to remove the Fe/MgO substrate as well as any surface iron impurities. This was followed by vacuum filtration and washing of the precursor with approximately one liter of deionized water after which the sample was dried overnight in an oven at 70 °C to obtain pristine CN_x catalyst.

40 mg of the CN_x sample was soaked in 0.3 M HCl at room temperature under continuous stirring, following which it was vacuum filtered and dried overnight in an oven at 70 °C to obtain the ex-situ chloride enhanced CN_x sample, namely, CN_x -Cl.

Electrochemical Testing

ORR activity of the catalysts was determined using a standard three-electrode system comprising of a glassy carbon disk (working electrode, 0.2472 cm^2), a reference hydrogen electrode (RHE, ET070 Hydroflex) and a platinum coil counter electrode. Catalyst ink was prepared by adding 48 µl of 5 wt% Nafion[®] solution and 175 µl of ethanol (200 proof) to 5 mg of catalyst sample in a 2 ml vial. The vial was kept in an ice-cooled ultrasonication bath until a uniformly dispersed catalyst ink was obtained. 9 µl of the catalyst ink was then applied to the glassy carbon disk, corresponding to a catalyst loading of ~800 µg/cm².

For measuring ORR activity, cyclic voltammograms (CVs) were first performed at a scan rate of 50 mV/s from 1.2 to 0 to 1.2 V vs. RHE in oxygen saturated 0.5 M H₂SO₄ electrolyte until reproducible CVs were obtained. CVs were then collected at a scan rate of 10 mV/s at different rotation rates of the working electrode - 400, 800, 1000, 1200 and 1600 rpm. The electrolyte was then saturated with argon for 15 minutes. Fast and slow CVs were collected at a rotating speed of 1600 rpm in the same potential range. CV collected in the argon-saturated electrolyte serves as a blank for the oxygen CVs. All potentials mentioned in this work are referenced with respect to RHE.

ORR activity was expressed in terms of: (a) onset potential (E_{onset}), which is the potential at a background-subtracted current density of -0.1 mA/cm²_{geometric}; (b) half wave potential ($E_{1/2}$) and (c) specific kinetic current (i_k) at 0.7 V calculated using the Koutechy-Levich equation (eq. I)

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_{lim}}$$
(eq. I)

Here, *i* is the measured current density, i_k is the kinetic current density and i_{lim} is the limiting current density.

Koutecky-Levich analysis also helped determine the selectivity of the catalysts by using the definition of i_{lim} (eq. II)

$$i_{lim} = 0.62 n F C_{O_2} (D_{O_2})^{2/3} \vartheta^{-1/6} \omega^{1/2}$$
(eq. II)

Here, *n* is the number of electrons transferred per molecule of oxygen, F is Faraday's constant (96485 C/mol), C_{O_2} is the bulk concentration of oxygen in the electrolyte (1.13 X 10⁻⁶ mol/cm³), D_{O_2} is the diffusion coefficient of oxygen (1.8 X 10⁻⁵ cm²/s), ϑ is the kinematic viscosity of the electrolyte (1.009 X 10⁻² cm²/s) and ω is the angular rotation rate (rad/s)^[37]. The value of *n* is determined using the slope of 1/*i* vs. $1/\omega^{1/2}$ curve. An *n* value of 4 is equivalent to a complete (2+2 or direct 4 electron) reduction of oxygen to water, while a value of 2 indicates complete formation of H₂O₂.

Tafel analysis was also performed using eq. III, in order to gain insights into the ORR rate determining step of the samples.

$$V = V_0 + b \log \frac{i_k}{i_0}$$
(eq. III)

where V_0 represents the equilibrium potential (1.23 V), b represents the Tafel slope and i_0 is the exchange current density.

Stability of CN_x and CN_x -Cl catalysts was determined by performing accelerated durability testing where the catalyst coated electrode was cycled between 1.0 and 0.6 V vs. RHE in an argon saturated electrolyte^[8]. The electrode was kept stationary and the voltage scan rate used was 50 mV/s during cycling. ORR activity was measured after 200, 500, 1000, 1500, 2000 and 3000 cycles. Electric double layer capacitance values reported in this work were obtained under in situ conditions by measuring the capacitance of the CN_x catalyst-coated electrode in both the presence and absence of chloride anions in the electrolyte. CVs were first collected in argon saturated H₂SO₄ electrolyte by performing potential sweeps across a non-Faradaic region at

different scan rates - 2.5, 5, 10, 20, 40, 50 and 100 mV/s - with the electrode rotating at 1600 rpm. NaCl was then added to the electrolyte corresponding to a concentration of 0.3 M chloride anions. CVs were collected again in the chloride ion-containing argon-saturated electrolyte at different scan rates with the electrode rotating speed of 1600 rpm. Capacitive current $(I_{canacitive})$ is linearly proportional to the scan rate (ϑ) as shown in eq IV.

$$I_{capacitive} = C\vartheta$$

(eq. IV)

Here *C* represents the double layer capacitance of the catalyst coated electrode.

Vibrational Spectroscopy

Vibrational Spectroscopy
 Fourier transform infrared (FT-IR) spectra was collected on CN_x as well as CN_x-Cl using a Thermo NICOLET 6700 FTIR spectrometer employing a KBr beam splitter and a liquid nitrogen cooled MCT detector. Both samples were diluted with KBr in a ratio of 1:300 (sample:KBr) by mass and pelletized using a 13 mm dye. 512 interferograms were collected on each of the samples with a resolution of 4 cm⁻¹. The IR spectrum of CN_x was used a background for the CN_x-Cl sample.
 Laser Raman spectra on both the pristine as well as soaked samples were obtained at room temperature using a Horiba Scientific LabRAM HR Raman microscope system. A 514.5 nm laser was used for data collection. The system was calibrated before data collection using while light at 0 cm⁻¹ and a silicon reference at 520.7 cm⁻¹. Spectra were analyzed using MagicPlot program.

Near Edge X-ray Absorption Fine Structure

Near edge X-ray absorption fine structure (NEXAFS) spectra at C K-edge were obtained for both CN_x and CN_x-Cl samples at the CSX-2 (23-ID-2) beamline of the National Synchrotron Light Source II (NSLS- II). Samples in powdered form were pressed on indium foil and mounted on a copper sample plate using double-sided carbon tape. The sample plate was mounted into a load lock before it was introduced to the measurement chamber. Spectra were collected in the total electron yield (TEY) mode by measuring the drain current of the sample. NEXAFS measurements were performed under vacuum conditions at room temperature. The spectra were

acquired in an energy range from 275 eV to 375 eV with an energy step size of 0.1 eV and asynchronously normalized with respect to the photodiode scan. Energy calibration was verified with respect to the C-C π^* transition in graphene oxide reference compound^[23a].

X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) data was obtained using a Kratos Axis Ultra DLD Spectrometer with Al K α monochromatic X-ray radiation (1486.6 eV). Spectra were collected using a pass energy of 20 eV at room temperature under vacuum conditions, and calibrated using the standard C 1s binding energy of 284.5 eV. An argon ion gun was used to etch the surface of CN_x-Cl and provide depth profiling. XPS spectra were collected after etching the sample for 15 s and 120 s. Peak fitting and analysis of surface atomic composition were performed using the CasaXPS program. Shirley-type background correction was performed and Lorentzian-Gaussian combination was used for curve fitting.

Temperature Programmed Desorption

Temperature programmed desorption was performed under a helium environment using an MKS Cirrus bench-top residual gas analyzer. 10 mg of each of the CN_x and CN_x -Cl sample was placed in a vertical quartz tube reactor, the exit stream of which was heated and fed into the mass spectrometer. The reactor was initially flushed with He until its signal stabilized. The system was then heated at the rate of 10 °C/min from room temperature to 900 °C. Signal corresponding to HCl (36 a.m.u) was monitored to check for desorption of chloride ions from the samples. Data smoothening and curve fitting were performed using SigmaPlot and Origin software packages respectively.

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Figure 1. (a) Polarization curves and (b) mass transport corrected Tafel plots of CN_x and CN_x -Cl catalysts. (O₂ saturated, 0.5 M H₂SO₄, 1600 rpm, 10 mV/s and 800 μ g_{catalyst}/cm²_{geometric})



Figure 2. (a) K-L plots obtained at different potentials to determine ORR selectivity on CN_x and CN_x -Cl samples towards formation of water, and (b) Stability measurements expressed in terms of half-wave potentials after cycling CN_x and CN_x -Cl catalysts between 0.6 and 1.0 V vs. RHE (0.5 M H₂SO₄, 1600 rpm and 800 μ g_{catalyst}/cm²_{geometric})



Figure 3. Cyclic voltammograms at various scan rates for CN_x in (a) H_2SO_4 electrolyte and (b) H_2SO_4 electrolyte containing 0.3 M Cl⁻ collected across a potential window without Faradaic processes. The capacitive current at 1.1 V as a function of scan rate for both cases is presented in

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Figure 4. Transmission IR spectra for CN_x -Cl sample at room temperature. The spectrum for pristine CN_x was used as the background



Figure 5: Raman spectra of (a) CN_x and (b) CN_x -Cl



Figure 6. NEXAFS spectra of CN_x and CN_x-Cl catalysts in the C K-edge region



Figure 7. XPS spectra obtained in (a) Cl 2p and (b) N 1s regions for CN_x and CN_x-Cl catalysts



Figure 8. (a) Cl 2p (b) N 1s XPS spectra for CN_x -Cl before etching and after etching the catalyst surface for 15 s and 120 s



Figure 9. (a) TPD profiles of CN_x and CN_x -Cl catalysts, (b) deconvoluted TPD profile for CN_x -Cl catalyst (He, 10°C/minute)

Sample	E _{onset} (Potential @ -0.1 mA/cm ²)	Half-wave potential (E _{1/2})	i _K @ 0.7 V vs. RHE	Tafel slope
	V vs. RHE		mA/mg _{catalyst}	mV/dec
CN _x	0.74	0.54	0.31	105
CN _x -Cl	0.80	0.66	2.22	97

Table 1. Comparison of ORR kinetic parameters for CN_x and CN_x -Cl samples

Table 2. Surface elemental composition (atomic %) of CN_x and CN_x -Cl samples as determined by XPS

Sample	С	Ν	0	Cl
CN _x	90.35	6.97	2.68	0.00
CN _x -Cl	90.47	6.95	2.08	0.50

Table 3. Cl 2p and N 1s distribution of CN_x and CN_x -Cl samples as determined by XPS

Relative % distribution of Cl					
Sample	C-Cl (2p _{3/2} = 200 eV)	Ionic Cl ⁻ (2p _{3/2} = 197.7 eV)	Ionic Cl ⁻ (2p _{3/2} = 196.4 eV)		
CN _x	0	0	0		
CN _x -Cl	33	25	42		
Relative % distribution of N					
Sample	Pyridinic N ⁺ O ⁻ / N ⁺ Cl ⁻ (> 402 eV)	Quaternary-N (400.7-400.9 eV)	Pyridinic-N (398.2-398.4 eV)		
CN _x	21	55	24		
CN _x -Cl	22	59	19		

Relative % distribution of Cl					
Etching time	C-Cl (2p _{3/2} = 200 eV)	Ionic Cl ⁻ (2p _{3/2} = 197.7 eV)	Ionic Cl ⁻ (2p _{3/2} = 196.4 eV)		
Pre-etch	33	25	42		
15 secs	48	32	20		
120 secs	56	44	0		
Relative % distribution of N					
Etching time	Pyridinic N ⁺ O ⁻ / N ⁺ Cl ⁻ (> 402 eV)	Quaternary-N (400.7-400.9 eV)	Pyridinic-N (398.2-398.4 eV)		
Pre-etch	22	59	19		
15 secs	13	54	33		
120 secs	9	56	35		

Table 4. Cl 2p and N 1s distribution of CN_x-Cl obtained using XPS after etching the sample surface.