

# **Heteroatom-doped Carbon Nanostructures as Catalysts for Electrochemical Halogen Production Technologies**

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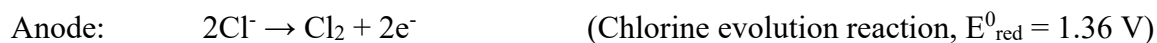
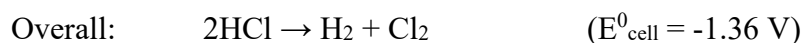
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## Abstract

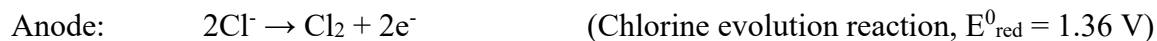
Hydrochloric acid electrolysis is a widely used chlorine manufacturing process. The energy requirements of HCl electrolysis can be significantly reduced by replacing the traditional H<sub>2</sub>-evolving cathode with an oxygen depolarized cathode (ODC). Successful operation of this technology requires good ORR characteristics of ODC catalysts, along with high resistance to poisoning in the presence of Cl<sup>-</sup> anions. State-of-the-art ORR catalyst, namely Pt/C, is highly susceptible to poisoning in the presence of Cl<sup>-</sup>. Alternative precious metal catalysts such as Rh<sub>x</sub>S<sub>y</sub>/C demonstrate somewhat higher Cl<sup>-</sup> poisoning resistance but the exorbitant cost of Rh limits its economic viability. We have evaluated the use of nitrogen-doped carbon nanostructures (CN<sub>x</sub>) and iron-nitrogen coordinated carbon-supported materials (FeNC) as ODC catalysts by investigating the effect of Cl<sup>-</sup> exposure on the ORR activity of these materials. Interestingly, while Pt/C, Rh<sub>x</sub>S<sub>y</sub>/C and FeNC catalysts show a loss in ORR activity, the activity of CN<sub>x</sub> significantly improves after exposure to Cl<sup>-</sup> anions. A combination of electrochemical measurements and spectroscopic characterization is used to fundamentally investigate this enhancement in ORR activity of CN<sub>x</sub>.

## 1. Introduction

Electrolysis of hydrochloric acid is a widely used process for the manufacture of chlorine gas, which is an essential chemical in a majority of industrial processes that produce many indispensable products including polymers such as polyvinyl chloride, polyurethanes and chloroaromatics. Traditional HCl electrolysis suffers from its high energy requirements, however, significant amount of energy can be saved by replacing the traditional H<sub>2</sub>-evolving electrode with an oxygen depolarized cathode (ODC) where O<sub>2</sub> is reduced instead of protons via the oxygen reduction reaction (ORR) [1]. The reactions corresponding to the traditional HCl electrolysis process are as shown below:



HCl electrolysis using ODC technology reduces the energy consumption per ton of Cl<sub>2</sub> produced from ~1500 kWh to ~800 kWh [1]. The reactions occurring in this process include:



Even though Cl<sup>-</sup> anions are not in direct contact with the cathodic ORR catalyst, they are known to crossover to the cathode side during shut down and maintenance procedures [1, 2]. Successful operation of ODCs, therefore, depends on the nature of the catalyst – its activity and stability towards ORR in the presence of Cl<sup>-</sup> ions [3]. Platinum based materials are generally shown to be

the most effective catalysts for ORR [4, 5]. However, there are many concerns involved in the use of Pt-based catalysts for ODCs. Platinum is known to get poisoned by halides leading to a loss of its ORR activity and increase in peroxide formation [6-12].

Severe corrosion of Pt-based materials has resulted in several attempts to discover more stable materials to be used as ODC catalysts. These include the use of palladium metal supported on carbon [13], palladium oxide coated titanium electrodes [14], carbon supported Pt and Pt/Ru catalysts [15], crystalline gold catalysts [16, 17], nickel-cobalt oxides with the composition  $\text{Co}_2\text{NiO}_4$  and transition metal sulfides [18-20]. Metal porphyrins and phthalocyanines have also been described as good electrodes for ORR in chlor-alkali cells [21-23]. However, problems with the stability and durability of these materials still need to be addressed.

Some of these problems have been partially addressed by the development of rhodium based materials as catalysts for ODCs [2]. Allen et al. have described the synthesis of rhodium sulfide catalysts supported on high surface area carbon black by reacting a rhodium metal precursor with a thionic species in an aqueous medium [24]. Gulla et al. have proposed the use of supported rhodium sulfide catalysts as ODCs for HCl electrolysis. They have also shown that these materials are stable in a hydrochloric acid environment or in the presence of chloride ions [25, 26]. Although these catalysts exhibit a very good performance in terms of activity and stability, the exorbitant cost of Rh limits the economic viability of the ODC technology [27].

In this work, we have evaluated the use of nitrogen-doped carbon nanostructures ( $\text{CN}_x$ ) and iron-nitrogen coordinated carbon-supported materials (FeNC) as ODC catalysts in  $\text{Cl}_2$  manufacturing processes. These catalysts have previously been shown to demonstrate good ORR performance in acidic media [28, 29]. Our current focus is to further investigate their resistance to poisoning in

the presence of  $\text{Cl}^-$  ions and determine their applicability as ODC catalysts in low temperature electrocatalytic chlorine production technologies.

## 2. Materials and Methods

### 2.1 Catalyst synthesis:

$\text{CN}_x$  catalyst was synthesized using the methodology reported by Matter et al. [28] Briefly, MgO nanopowder (Sigma Aldrich) was doped with 2 wt% Fe from Fe(II) acetate (Sigma Aldrich), using incipient wetness impregnation method. The Fe/MgO precursor was dried overnight at 110 °C and ball-milled at 200 rpm for 3 hours. The ball-milled precursor was used as a substrate for chemical vapor deposition (CVD) of acetonitrile at 900 °C for 2 hours. A schematic of the lab-scale set-up used for chemical vapor deposition is shown in Figure 1. The material obtained after CVD was subjected to acid washing in 1 N  $\text{H}_2\text{SO}_4$  at 60 °C for 1 hour to remove the non-conductive Fe/MgO support. The acid washing mixture was vacuum filtered, washed with deionized water and allowed to dry overnight in an oven at 70 °C. The sample thus obtained is the nitrogen-doped carbon catalyst, denoted as  $\text{CN}_x$ . Chloride-exposed  $\text{CN}_x$  (denoted as  $\text{CN}_x\text{-Cl}$ ) was synthesized by soaking 40 mg of  $\text{CN}_x$  catalyst in 200 ml of 0.3 M HCl for 1 hour at room temperature. The mixture is vacuum filtered and dried overnight in an oven, to obtain the  $\text{CN}_x\text{-Cl}$  sample.

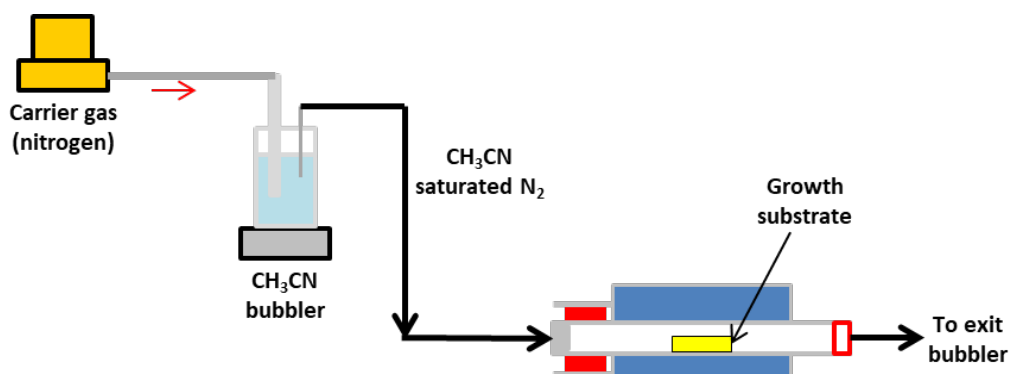


Figure 1: Schematic of chemical vapor deposition set up used for  $\text{CN}_x$  synthesis

FeNC catalyst was synthesized using the procedure reported by Dodelet and coworkers [30]. Fe acetate and phenanthroline were impregnated onto Black Pearls carbon support in 150 ml of an ethanol-water mixture, under continuous stirring at 70 °C. When the suspension reached one-third of its initial volume, the precursor was dried overnight in an oven at 110 °C, following which it was ball-milled at 200 rpm for 3 hours. The precursor was subjected to shock heat treatment under argon atmosphere for 1 hour at 1050 °C, and under ammonia atmosphere for 20 minutes at 950 °C to obtain the FeNC sample.

## **2.2 Electrochemical testing:**

Catalyst activity towards oxygen reduction reaction (ORR) was determined using electrochemical measurements performed with the help of a standard three-electrode rotating disk electrode (RDE) system consisting of a working electrode, a reference electrode and a counter electrode. The working electrode was made of glassy carbon (Pine Research Instrumentation, Inc.), the reference electrode was a reversible hydrogen electrode (RHE, Hydroflex®) and the counter electrode was a graphite rod (Pine Research Instrumentation, Inc.). A Biologic potentiostat was used to apply potential and measure the corresponding current on the working electrode. All potentials reported herein are referenced with respect to RHE, unless otherwise specified. Chloride poisoning resistance was determined for four samples – 10% Pt/C (commercial, E-TEK), 30% Rh<sub>x</sub>Sy/C (commercial, De Nora Tech, Inc.), FeNC and CN<sub>x</sub>.

To determine ORR activity, the system was first equilibrated by running fast cyclic voltammograms (CVs) between 1.2 and 0 V at 50 mV/s in oxygen-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte until the CVs overlapped with each other. Slow CVs were then collected in the same range of potentials at 10 mV/s, with the electrode rotating at 1000 or 1600 rpm. The above

procedure was repeated in argon-saturated electrolyte to subtract the non-Faradaic current from the oxygen CVs.

In-situ chloride poisoning experiments were performed using the same procedure as above, in chloride containing 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte. The source of chloride ions was NaCl. ORR activity is expressed in terms of (a) onset potential, which is the potential at a background-subtracted current density of -0.1 mA/cm<sup>2</sup><sub>geometric</sub>, and (b) half-wave potential ( $E_{1/2}$ ).

### **2.3 Catalyst characterization:**

CN<sub>x</sub> catalysts, before and after exposure to Cl<sup>-</sup> ions, were characterized using different techniques to understand structure-property relationships.

X-ray photoelectron spectroscopy (XPS) was used to determine the nature of species present on the surface of the samples. XPS spectra were collected using a Kratos Axis Ultra DLD Spectrometer with Al K $\alpha$  monochromatic X-ray radiation (1486.6 eV). Spectra were collected using a pass energy of 20 eV and the data was calibrated using C-1s binding energy of 284.5 eV [31].

Temperature programmed desorption experiments were performed under an inert atmosphere of helium. The catalyst samples were packed in a quartz reactor and placed inside a furnace. To analyze the exit gases, the reactor exit was connected to an MKS Cirrus bench-top residual gas analyzer. The system was allowed to flush with helium at room temperature until the signals in the mass spectrometer stabilized. The temperature of the furnace was increased gradually @ 10 °C/min up to 900 °C and the signal corresponding to HCl (36 a.m.u) was monitored.

### 3. Results and Discussion

#### 3.1 Electrochemical testing:

The results from electrochemical ORR half-cell measurements to determine the chloride poisoning resistance of the four catalysts – Pt/C, Rh<sub>x</sub>S<sub>y</sub>/C, FeNC and CN<sub>x</sub> are reported in Figure 2(a-d) [27]. Pt/C catalyst (Figure 2(a)) deactivates almost completely, with the ORR half-wave potential shifting negative from 0.81 V to 0.32 V after exposure to 100 mM Cl<sup>-</sup>. Rh<sub>x</sub>S<sub>y</sub>/C catalyst shows higher resistance to chloride poisoning as compared to Pt/C, with a 140 mV negative shift in the ORR half-wave potential. Amongst the non-precious metal catalysts, while FeNC shows some

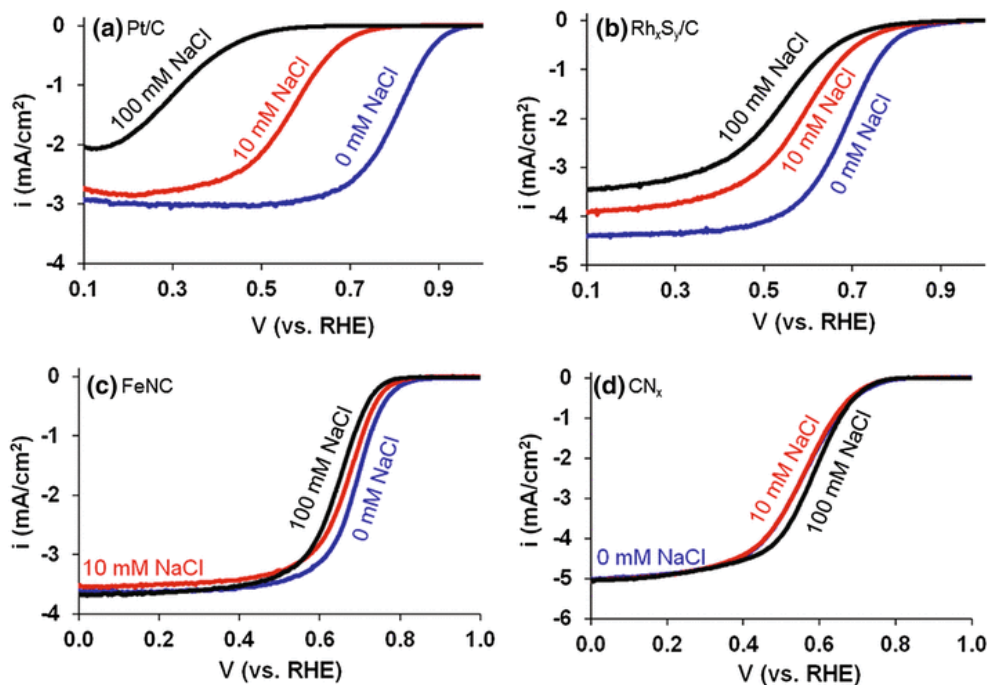


Figure 2: Cathodic polarization curves of (a) Pt/C, (b) Rh<sub>x</sub>S<sub>y</sub>/C, (c) FeNC and (d) CN<sub>x</sub> samples for ORR before and after exposure to chloride ions in the electrolyte (O<sub>2</sub> saturated, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 1600 rpm and 10 mV/s)

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deactivation in the presence of chloride ions as indicated by the negative shift of the ORR half-wave potential by 50 mV, CN<sub>x</sub> catalyst exhibits an improvement in ORR activity after exposure



to chloride (Figure 2(c) and (d)). The ORR onset and half-wave potentials of  $\text{CN}_x$  exhibit no change after exposure to 10 mM  $\text{Cl}^-$  ions, but shift positive by 20 mV and 30 mV, respectively, at  $\text{Cl}^-$  concentration of 100 mM in the electrolyte [27].

To further explore the ORR enhancement effect of chloride on  $\text{CN}_x$  catalyst, the activity of ex-situ chloride-soaked  $\text{CN}_x$ , i.e., the  $\text{CN}_x\text{-Cl}$  sample is determined (Figure 3) [31]. Activity measurements performed in 0.5 M  $\text{H}_2\text{SO}_4$  electrolyte show an increase in ORR half wave potential of the catalyst from 0.54 V in  $\text{CN}_x$  to 0.66 V (an increase of 120 mV) in the  $\text{CN}_x\text{-Cl}$  sample. The ORR onset potential of  $\text{CN}_x$  also increases by 60 mV after exposure to chloride anions [31]. Characterization of  $\text{CN}_x$  and  $\text{CN}_x\text{-Cl}$  samples reported in the following section help investigate the nature of species responsible for this significant improvement in ORR activity.

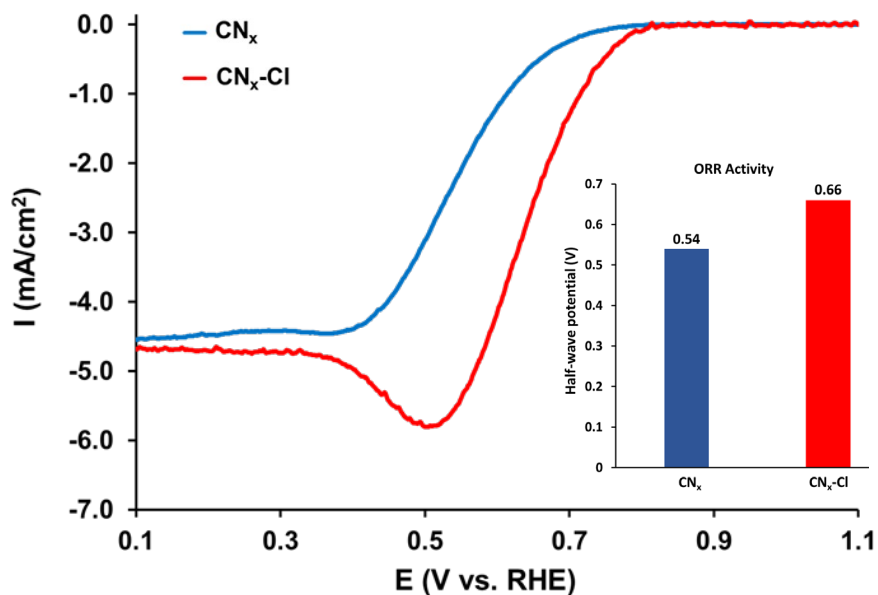


Figure 3: ORR cathodic polarization curves and inset: half-wave potentials of the  $\text{CN}_x$  and  $\text{CN}_x\text{-Cl}$  catalysts. ( $\text{O}_2$  saturated, 0.5 M  $\text{H}_2\text{SO}_4$ , 1600 rpm, 10 mV/s).

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### 3.2 Catalyst characterization:

XPS data collected in the Cl-2p region for  $\text{CN}_x$  and  $\text{CN}_x\text{-Cl}$  samples has been reported in Figure 4. XPS spectrum in the Cl-2p region has been fitted by using a spin orbit splitting of 1.6 eV between the  $2p_{1/2}$  and  $2p_{3/2}$  components. The absence of chlorine species in the  $\text{CN}_x$  sample is evident from the absence of any peaks in the Cl-2p region of catalyst. The XPS spectrum in Cl-2p

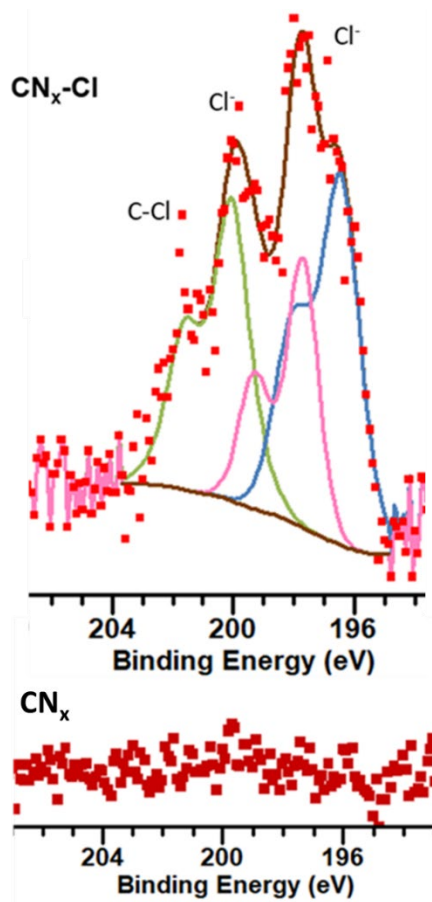


Figure 4: XPS spectra obtained in the Cl 2p region for  $\text{CN}_x$  and  $\text{CN}_x\text{-Cl}$  catalysts

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region for  $\text{CN}_x\text{-Cl}$  can be deconvoluted into three distinct species – (a) C-Cl at  $2p_{3/2}$  binding energy peak of 200 eV, (b) anionic chloride in a positively charged local environment of a pyridinium

ring ( $\text{N}^+\text{Cl}^-$ ) at  $2p_{3/2}$  binding energy of 197.7 eV and (c) anionic physisorbed chloride at  $2p_{3/2}$  binding energy of 196.4 eV [31].

The presence of three distinct chlorine functionalities was further confirmed by performing temperature programmed desorption (TPD) of chlorine species from  $\text{CN}_x\text{-Cl}$  sample, under inert conditions [31]. The desorption profile of chlorine species monitored as HCl signal (36 a.m.u.) in the mass spectrometer also indicated the presence of three different chlorine species. The first desorption peak at  $\sim 210^\circ\text{C}$  corresponds to the most weakly-bound chloride species, namely, physisorbed chloride. The second and third peaks at  $\sim 330^\circ\text{C}$  and  $\sim 600^\circ\text{C}$  correspond to chloride species desorbing from  $\text{N}^+\text{Cl}^-$  and C-Cl functionalities, respectively. The results obtained from TPD measurements are, therefore, in agreement with the XPS results [31]. The possible explanation for the enhanced ORR activity of  $\text{CN}_x\text{-Cl}$  is the formation of additional active sites in

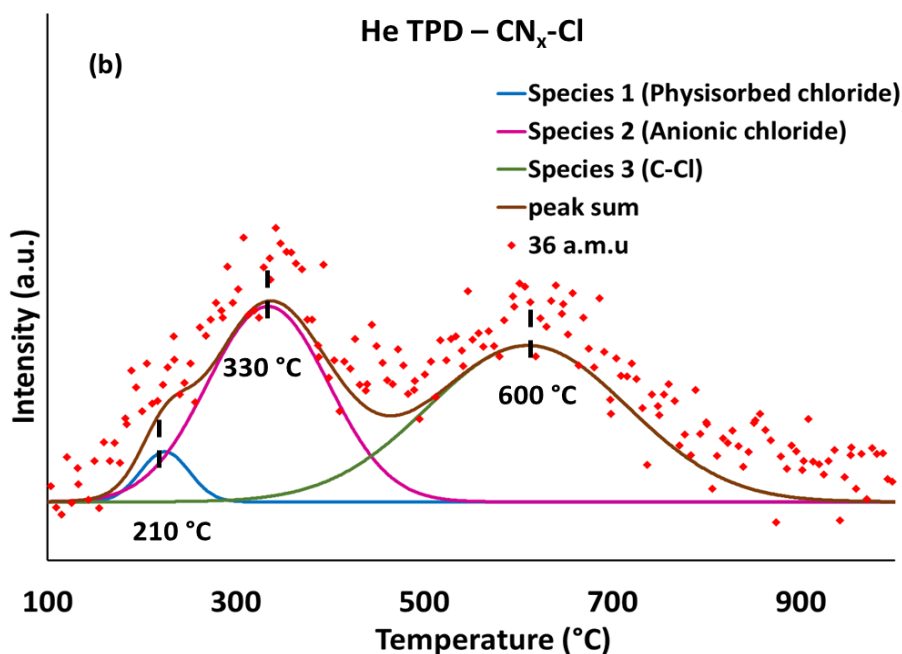


Figure 5: Deconvoluted TPD profile for  $\text{CN}_x\text{-Cl}$  catalyst (He,  $10^\circ\text{C}/\text{minute}$ )

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the form of C-Cl functionalities. The difference in electronegativity between C and Cl bonds creates a partial positive charge on the C atom, which enables side-on adsorption of oxygen molecule for oxygen reduction reaction [31].

#### **4. Conclusions**

This work shows the promise of using nitrogen-doped carbon nanostructures as catalysts for oxygen depolarized cathode technology for chlorine production. While Pt/C, Rh<sub>x</sub>S<sub>y</sub>/C and FeNC catalysts deactivate after exposure to chloride anions, CN<sub>x</sub> materials show an enhancement in ORR activity after Cl<sup>-</sup> exposure. The activity enhancement in CN<sub>x</sub> is attributed to the creation of additional ORR active sites in the material in the form of C-Cl functionalities after exposure to Cl<sup>-</sup> anions. We have, therefore, also described a simple way of incorporating chlorine functionalities in nitrogen-doped carbon nanostructures to enhance the ORR activity of the material.

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