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Influence of metal precursors on the catalytic activity and structure of non-precious metal electrocatalysts for oxygen reduction reaction

Hui-Juan Zhang^{a,b}, Hai-Chuan Kong^b, Xianxia Yuan^{b,*}, Qi-Zhong Jiang^b, Junhe Yang^a, Zi-Feng Ma^{b,*}

^a School of Materials Science and Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China

^b Department of Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China

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ABSTRACT

The influence of 3d transition metal precursors has been studied to prepare non-precious metal catalysts (MTETA/C) for the oxygen reduction reaction (ORR) in acid electrolyte. All these 3d transition metal precursors are chelated with triethylenetetramine (TETA) and supported on BP 2000, then pyrolyzed at 800 °C in the presence of Ar. The catalysts are characterized in terms of structure and catalytic activity by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and electrochemical techniques. Variations of the electrocatalytic activity of these non-precious metal catalysts indicate that the metal precursors have obvious effects on the catalytic activity and this may be related to the N atoms and O species on the carbon surface indicated by XPS. Here, metal chloride is beneficial to prepare these catalysts for the ORR in acidic electrolyte. Furthermore, pyridinic N and pyrrolic N on the carbon surface facilitate the reduction of oxygen on these Fe-based and Co-based catalysts, respectively.

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1. Introduction

Great efforts have been put into the development of new and low-cost catalysts for the ORR, which could replace the expensive Pt-based catalysts. Among various types of non-precious metal fuel cell cathode catalysts, heat-treated carbon-supported transition metal based nitrogen-containing compounds have been extensively studied and are considered to be promising candidates for the active and reliable catalyst [1–5].

There are several methods to produce this type of non-precious metal catalysts: (1) heat treatment of a complex adsorbed on a carbon support, in which the transition metal is

coordinated by nitrogen atoms in the macrocycle ligands, such as porphyrins [1,2]; (2) heat treatment of a mixture composing of the metal salts and a nitrogen-containing polymer such as polypyrrole and polyacrylonitrile with and without carbon support [6–9]; (3) heat treatment of the metal salts supported on carbon materials in NH₃ or CH₃CN atmosphere [10–13]. Although the exact nature of the active site in this type of catalysts for the ORR is controversial, it is believed that there are four elements to influence the activity of these non-precious metal catalysts: (1) a choice of transition metal, usually in the form of metal salts; (2) a nitrogen source, such as porphyrins, polypyrrole, NH₃ and CH₃CN; (3) a source of carbon support, such as BP 2000; and (4) heat treatment,

* Corresponding authors. Tel.: +86 21 54742827; fax: +86 21 54741297.

E-mail addresses: yuanxx519@yahoo.com.cn, yuanxx@sjtu.edu.cn (X. Yuan), zfma@sjtu.edu.cn (Z.-F. Ma).

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usually higher than 800 °C. For example, effect of the central metal for metal phthalocyanines on the ORR activity was reported as $\text{Fe} > \text{Co} > \text{Ni} > \text{Cu} \approx \text{Mn}$ [14]. Dodelet's group reported that the catalytic activity increased according to the following order: $\text{Cr} > \text{Fe} > \text{Co} \gg \text{V}$, where the catalysts were obtained from pyrolysis of transition metal hydroxides supported on carbon in acetonitrile vapor [15]. However, they also illustrated the increasing ORR activity as $\text{Fe} > \text{Co} > \text{Cr} > \text{Mn}$, when transition metal acetates, ammonia and perylene-tetracarboxylic dihydride (PTCDA) were employed as the metal precursor, nitrogen source and carbon source, respectively [16]. Dahn obtained the catalytic activity orders of the TM-C-N (TM = V, Cr, Mn, Fe, Co and Ni) catalysts toward the ORR as follows: $\text{Fe} > \text{Co} > \text{Cr} > \text{Ni} > \text{Mn} > \text{V}$ in 0.1 M HClO_4 solution, and $\text{Co} > \text{Ni} > \text{Mn} > \text{V} > \text{Cr}$ in 0.1 M KOH solution [17]. All these results show that transition metals play important roles in improving the catalytic active.

Recently, we developed a new class of non-precious metal catalyst (MTETA/C) and its method through pyrolysis of a simple metal- N_4 chelate supported on carbon under an Ar atmosphere [18–21]. Prompted by the facts that metal porphyrin catalysts have good catalytic activity and with its catalytic active site as metal- N_4 moiety, we adopted CoCl_2 and triethylenetetramine (TETA, a cheap and simple ligand, which also has four nitrogen atoms in its molecular, N_4) as the starting materials for the first time to substitute porphyrins and phthalocyanines to prepare non-precious metal ORR catalysts [18–20]. We found that the catalytic activity of the MTETA/C catalysts decreased in the order of $\text{Fe} > \text{Co} > \text{Zn} > \text{Mn} \gg$ metal-free $\gg \text{Cu} \gg \text{Ni}$ [21]. This suggests that Co and Fe play more important role than the other 3d transition metals in improving the catalytic active of the catalyst. Therefore, further exploration of the transition metal precursors (Co salts and Fe salts) for these non-precious metal catalysts is necessary for the actual applications in this study.

Here, effects of the 3d transition metal precursors on the catalytic activity and structure of the non-precious metal catalysts MTETA/C in acid electrolyte are investigated, where TETA is chosen as the nitrogen source. The obtained catalysts are physically characterized by X-ray diffraction (XRD) measurement and X-ray photoelectron spectroscopy (XPS). The catalytic activities toward the ORR are evaluated by rotating disk electrode (RDE) and cycle voltammograms (CVs).

2. Experimental

2.1. Catalysts preparation

All these non-precious metal catalysts were prepared via methods outlined in prior publications [18–21]. Briefly, desired amounts of the 3d transition metal salts (MX, M = Co or Fe; X = Cl, NO_3 or SO_4) were dissolved in ethanol absolute, respectively. The TETA were added into the above solutions to form metal- N_4 chelates under stirring conditions, followed by the addition of carbon support (Black Pearl 2000, BP 2000). The ethanol absolute solvents were removed in a rotary evaporator, and the resulting powders were then heat treated at 800 °C for 90 min under an Ar atmosphere with a ramping rate of 5 °C min^{-1} . The carbon-supported non-precious metal

catalysts were denoted as MX-TETA/C. The nominal amount of metal loaded on the carbon support was kept at 10 wt%.

2.2. Physical characterization

The XRD was performed on an automated Rigaku diffractometer equipped with a Cu $K\alpha$ radiation. The data acquisition was recorded in the scanning angle range of 20–80° at a scan rate of 6° min^{-1} . The PDF (powder diffraction file database) from the ICDD (International Centre for Diffraction Data) was used as a reference to interpret peak assignments on the XRD spectra.

The electronic structures of C, N and O on the catalyst surface were evaluated using XPS, which was carried out using a PHI ESCA 5700 system (Physical Electronics) with Al $K\alpha$ radiation (1486.6 eV). The electron binding energies were referred to the C 1s spectrum of carbon contamination at 284.5 eV.

2.3. Electrochemical characterization

The electrochemical activity of the catalysts towards the ORR was investigated by the RDE and CV techniques, which was carried out in a conventional single compartment three-electrode test cell at room temperature. A Pt-wire counter electrode, a saturated-calomel reference electrode and the catalyst-coated glassy carbon (GC) electrode were used for the measurement. The prepared 0.5 M H_2SO_4 solution was used as the electrolyte. The potentials discussed below have been corrected to the normal hydrogen electrode (NHE) potential.

The catalyst ink was prepared by blending 5 mg finely ground catalyst powders with 0.5 mL distilled water and 50 μL 5 wt% Nafion solution in an ultrasonic bath. Then 10 μL this ink was deposited onto the glassy carbon disk for air-drying. Catalytic activity for the ORR was evaluated in the oxygen-saturated acidic electrolyte. Firstly, the electrode was electrochemically cleaned by sweeping the potential between 1.04 V and 0.04 V at a sweep rate of 50 mV s^{-1} . Then CVs were

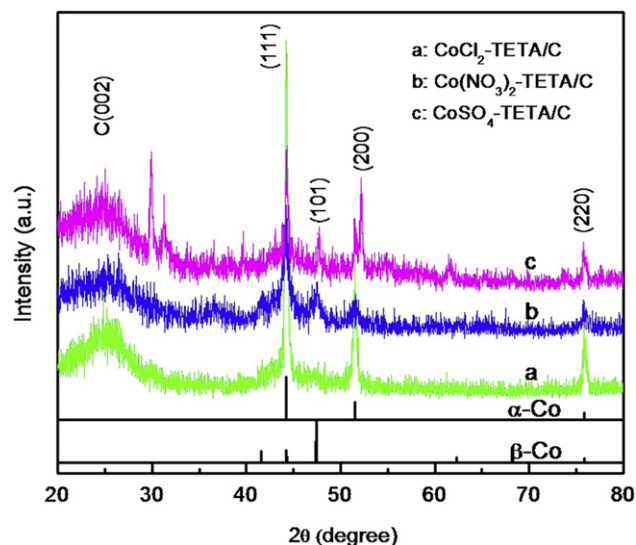


Fig. 1 – XRD patterns of the CoX-TETA/C libraries ($\text{X} = \text{Cl}$, NO_3 or SO_4). A series of standard characteristic diffraction peaks are also shown for comparison.

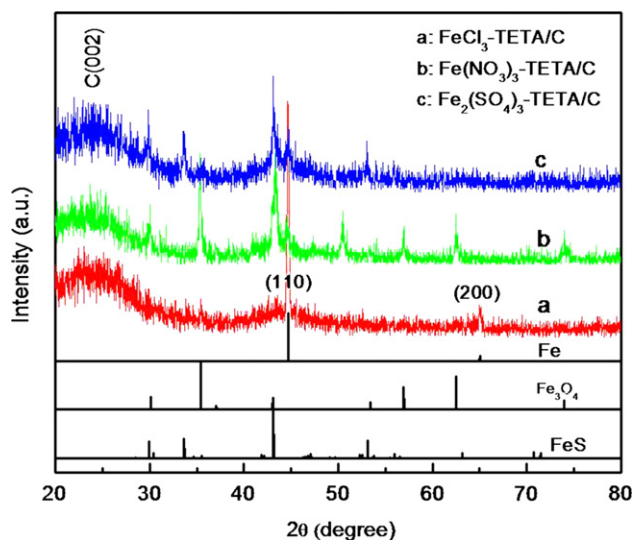


Fig. 2 – XRD patterns of the FeX-TETA/C libraries (X = Cl, NO₃ or SO₄). A series of standard characteristic diffraction peaks are also shown for comparison.

recorded by scanning the potential between 1.04 V and 0.04 V at a scan rate of 5 mV s⁻¹. One cycle was completed with the electrode stationary (0 rpm) and another cycle was completed with the electrode rotated at 900 rpm.

3. Results and discussion

3.1. XRD analysis

The structure and phase analysis of the CoX-TETA/C (X = Cl, NO₃ and SO₄) libraries are shown in Fig. 1. Each catalyst clearly exhibits a broad diffraction peak located at 24.5°, which corresponds to the C(002) plane diffraction of BP 2000. All these catalysts exhibit the characteristics of single-phase face-centered cubic (fcc) crystalline structure Co with the Co(111), Co(200) and Co(220) reflections (PDF 15-0806). Furthermore, there is also β-Co (PDF 89-4308) with Co(101) diffraction in the Co(NO₃)₂-TETA/C catalyst. In the CoSO₄-TETA/C catalyst, there exists Co (PDF 15-0806) and Co₃S₈ (PDF 65-6801) diffractions.

Fig. 2 indicates the XRD patterns of the FeX-TETA/C libraries (X = Cl, NO₃ and SO₄). A series of standard characteristic

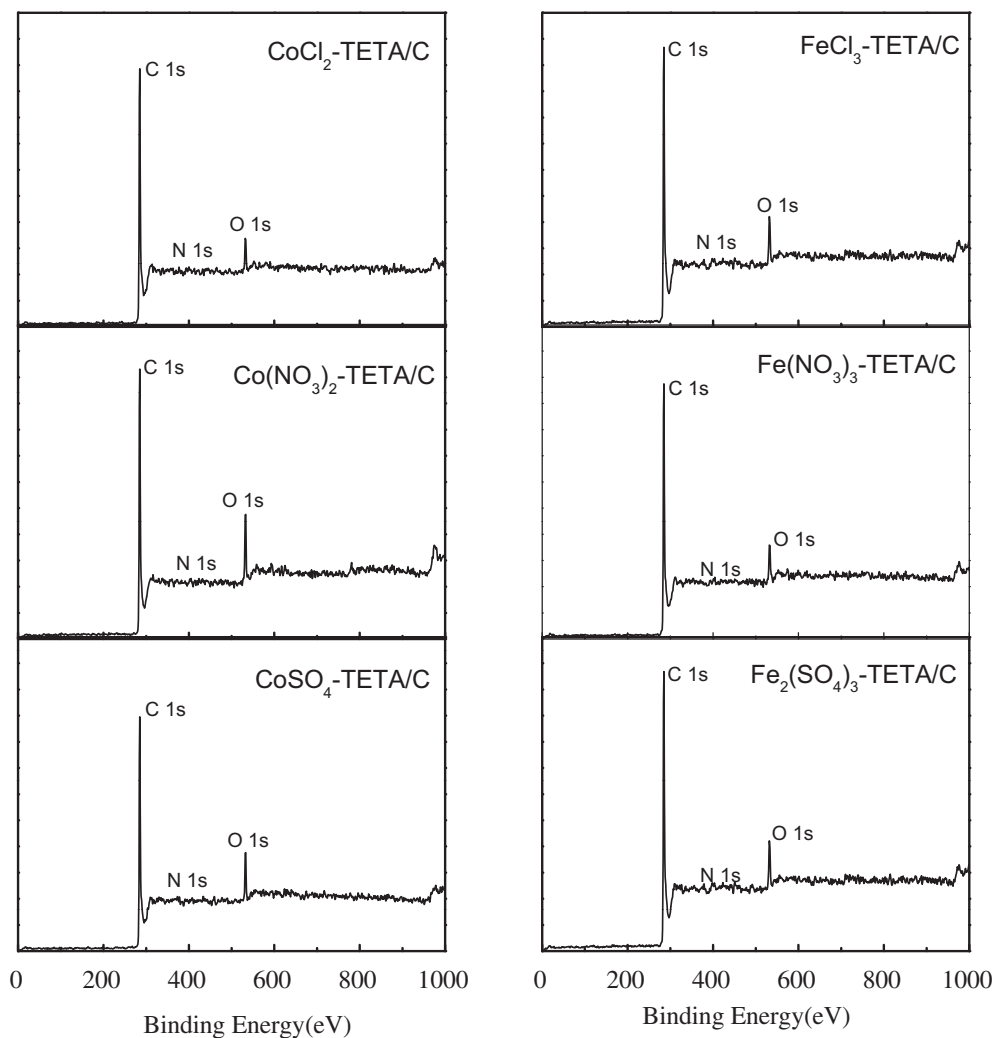


Fig. 3 – XPS survey for the MX-TETA/C libraries (M = Fe or Co; X = Cl, NO₃ or SO₄).

diffraction peaks are shown for comparison. In the FeX-TETA/C libraries, there are Fe nanoparticles (PDF 65-4899) with Fe(110) and Fe(200) phases in the FeCl₃-TETA/C catalyst. Except for the diffraction of Fe nanoparticles, Fe₃O₄ nanoparticle could be detected by its characteristic diffractions (PDF 65-3107) in the Fe(NO₃)₃-TETA/C catalyst; and FeS nanoparticles (PDF 65-0408) are also shown in the Fe₂(SO₄)₃-TETA/C catalyst.

3.2. XPS analysis

The XPS survey spectra of these non-precious metal catalysts are given in Fig. 3. Each catalyst clearly shows a predominant C 1 s peak at 285 eV, a weak O 1 s peak at 532 eV and a much weaker N 1 s peak at 400 eV. These weak peaks of O 1 s and N 1 s in the XPS spectra presumably arise from the physically adsorbed oxygen-containing functional groups and nitrogen-containing species on the carbon surface [22]. The weak spectra can also come from encapsulation of the encapsulated MN₄-based complexes [23].

Regarding the C(1 s) region, shown in Fig. 4, a peak shifts to a higher binding energy (284.7 eV) in each catalyst, as

compared to the carbon supports exhibit similar spectra with a main peak at 284.5 eV, a binding energy that has been observed for a number of carbon supports such as Norit SX Ultra [24] and Vulcan SC-72R [25]. This could be attributed to the adulteration of nitrogen atoms and oxygen species on the carbon support. The corresponding high-resolution C 1 s spectra show three peak components at 284.7 eV, 285.9 eV and 288.6 eV, which are assigned to the carbon component in C–C, C–O and O=C–O, respectively.

The XPS spectra of N 1 s are not always simple to decipher. However, it is important to understand their origins and relate these with the observed oxygen reduction activity. Several different N coordinations with different but close binding energies are reported in the literature [25,26], which include: (1) pyridinic N with its peak at 398.3–399.5 eV (an N atom at the edge of a graphene layer contributing to the n band with one electron); (2) pyrrolic N with its peak at 399.9–400.7 eV (an N atom at the edge of a graphene layer contributing to the z band with two electrons); and (3) graphitic N with its peak at 401–403 eV (an N atom is assigned to highly coordinated graphitic nitrogen atoms bound to three carbon atoms in

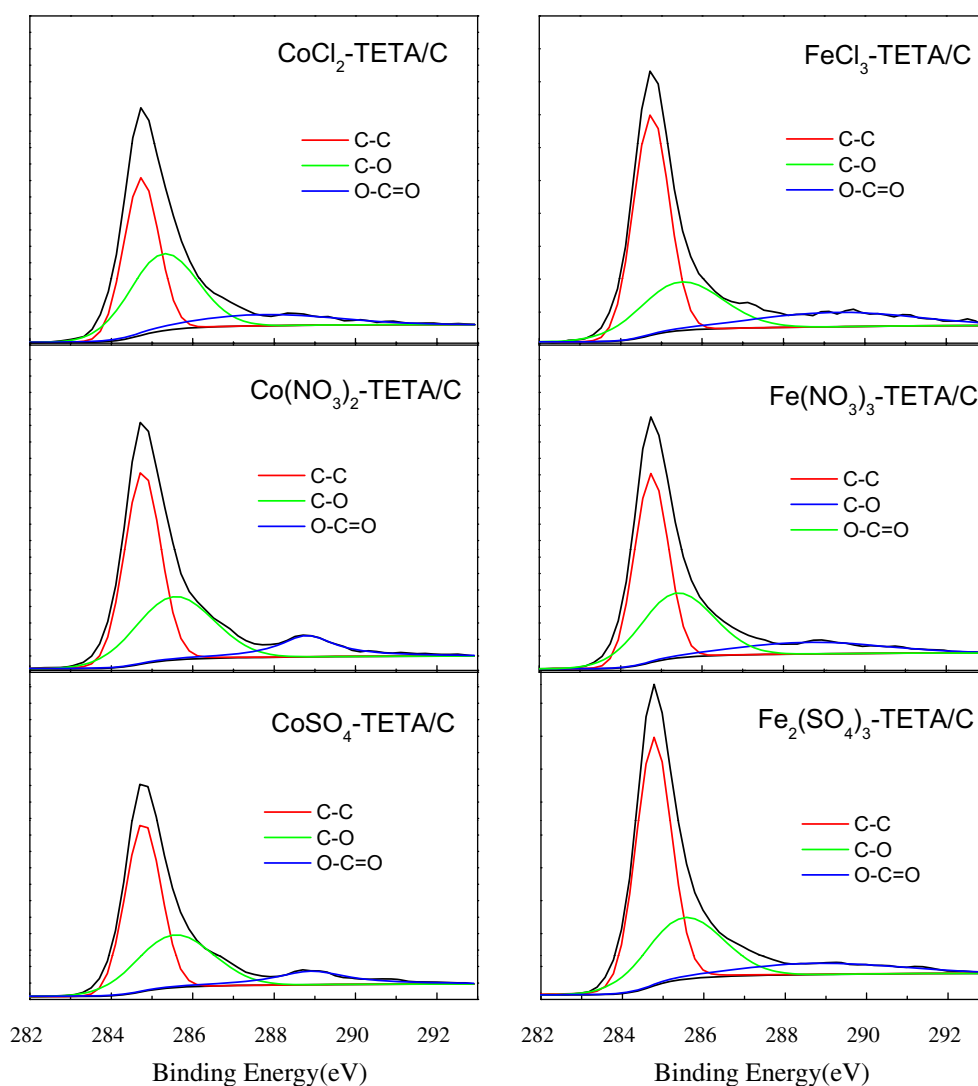


Fig. 4 – High-resolution C 1 s for the MX-TETA/C libraries (M = Fe and Co; X = Cl, NO₃ or SO₄).

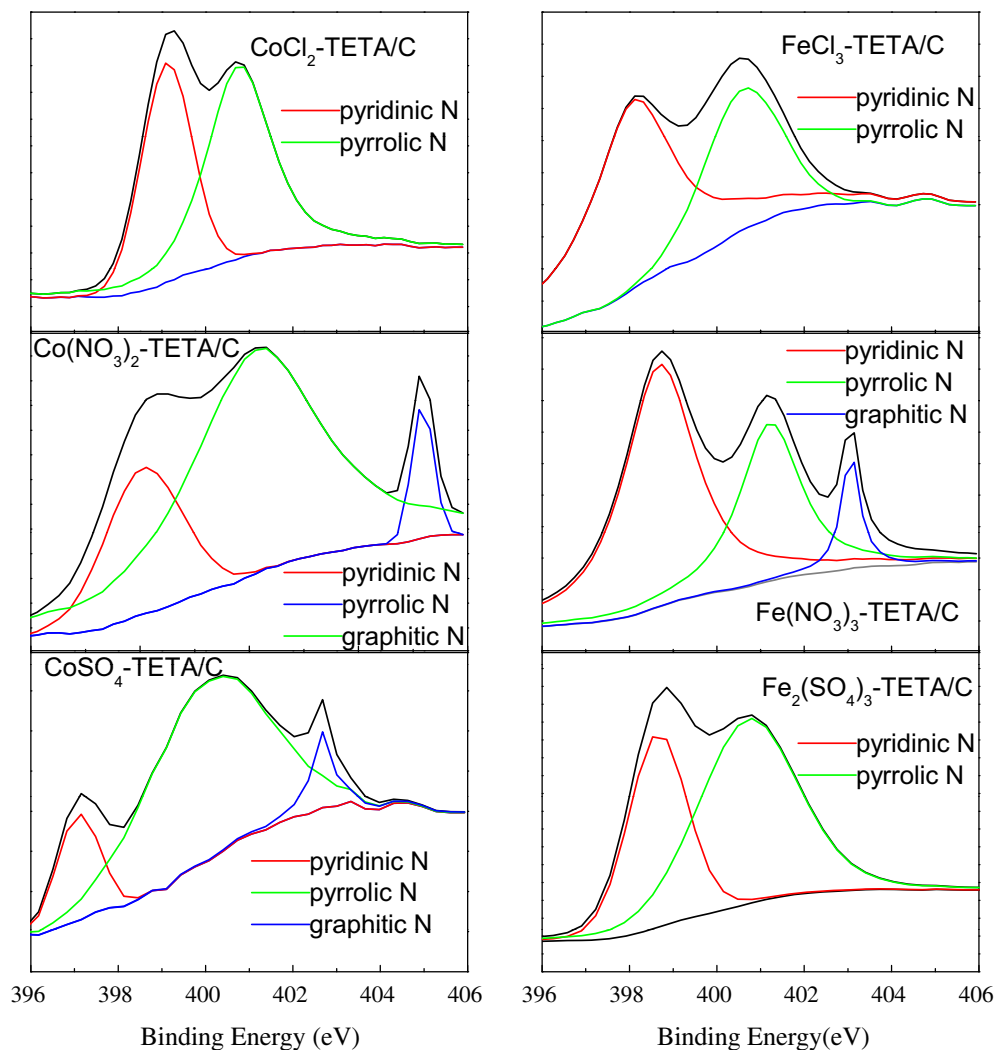


Fig. 5 – XPS of N 1s for the MX-TETA/C libraries (M = Fe or Co; X = Cl, NO₃ or SO₄).

different locations in the center of the graphene layer). Fig. 5 displays the XPS of N 1s both in the CoX-TETA/C libraries and FeX-TETA/C libraries. For each catalyst, the components of the N 1s peak can mainly be deciphered into pyridinic N and pyrrolic N. We can clearly see that the contributions of these types of N are different, for example, in the CoX-TETA/C libraries, there is more content of pyrrolic N than the content of pyridinic N, while in the FeX-TETA/C libraries, the contrary is the case. A small amount of graphitic N can be seen in the Co(NO₃)₂-TETA/C, CoSO₄-TETA/C and Fe(NO₃)₃-TETA/C catalysts. This indicates the incorporation of nitrogen within the graphene sheets. Initially, the N atoms could preferentially incorporate into the hexagon graphene, as reflected by the pyridinic N XPS peak. The continuous presence of N atoms in the furnace could introduce N-containing pentagon defects inside the hexagon matrix [22]. Pyridinic N has one lone pair of electrons in addition to the one electron donated to the conjugated π bond system, imparting a Lewis basicity to the carbon. It is capable of adsorbing molecular oxygen and its intermediates in the oxygen reduction reaction. Sidik performed the quantum mechanical calculations for oxygen reduction on cluster models of graphite sheets containing

substitutional N, and they showed that in acidic media, a strong Lewis basicity of carbons doped with pyridinic N facilitated the reductive adsorption reaction of O₂ without the irreversible formation of oxygen functionalities, due to an increased electron-donor property of carbon [27].

The XPS O 1s narrow-scan spectra of oxygen are presented in Fig. 6. All these spectra can be decomposed into two components: O_A(531.8 eV) and O_B(533.3 eV). Similar spectra are also obtained for other non-precious metal catalysts [28]. O_A with a binding energy of 531.8 eV is assigned to C=O (aldehydes, ketones and lactones), whereas O_B with a binding energy of 533.3 eV is assigned to the C-OH and/or C-O-C groups [23,29]. The phenomenon in Fig. 6 is that O_A content is more than that of O_B in all of these catalysts, especially in the Fe₂(SO₄)₃-TETA/C catalyst, which means that there are more C=O functional group on the carbon surface.

3.3. Electrochemical characterization

Fig. 7 shows the CVs of the prepared non-precious metal catalysts in oxygen-saturated 0.5 M H₂SO₄ solution. It is a traditional way to represent the relative catalytic activity of

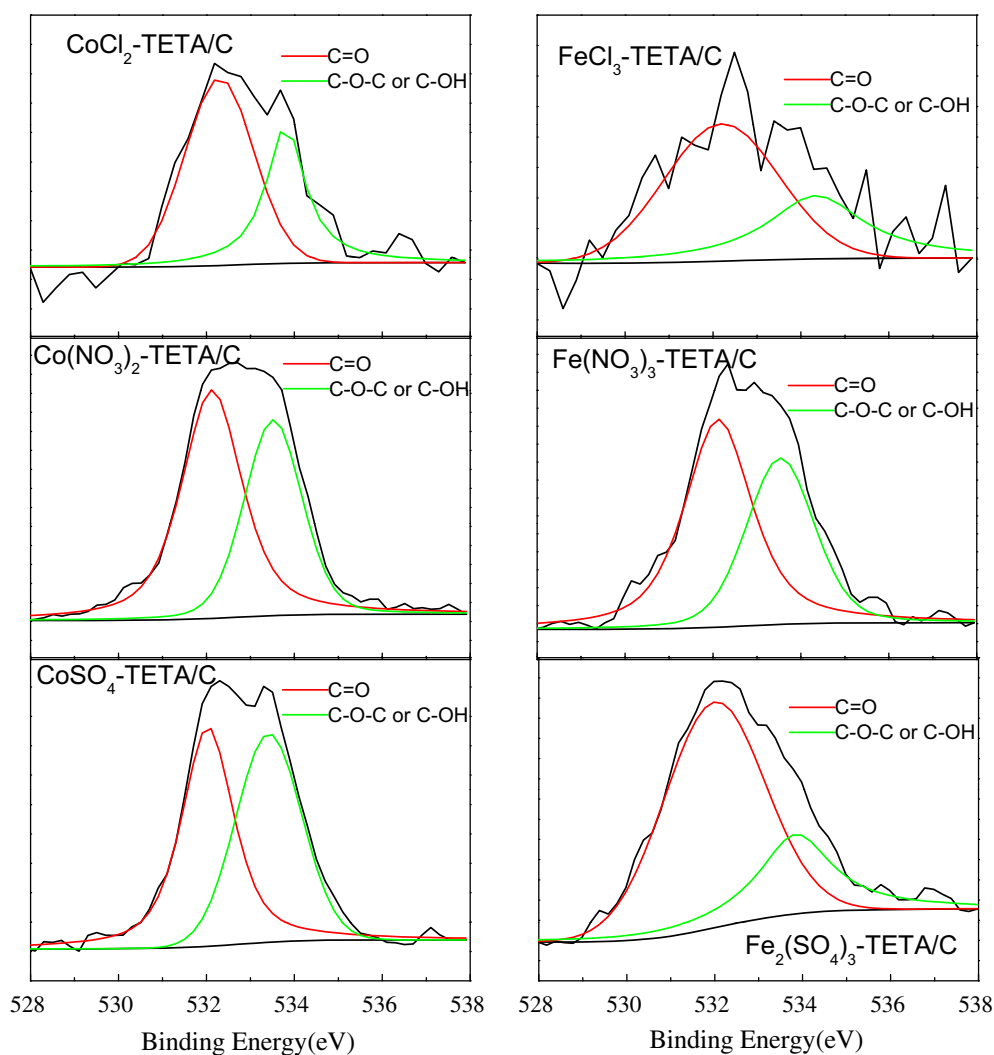


Fig. 6 – XPS of O 1s for the MX-TETA/C libraries (M = Fe or Co; X = Cl, NO₃ or SO₄).

catalysts with the ORR peak potential where the maximum oxygen reduction current occurs. Fig. 7 indicates that both the peak potential and peak current of oxygen reduction for the CoX-TETA/C libraries is $\text{CoCl}_2\text{-TETA/C} \gg \text{CoSO}_4\text{-TETA/C} \approx \text{Co(NO}_3)_2\text{-TETA/C}$; but for the FeX-TETA/C libraries, the

peak potential of oxygen reduction is $\text{FeCl}_3\text{-TETA/C} > \text{Fe(NO}_3)_3\text{-TETA/C} > \text{Fe}_2(\text{SO}_4)_3\text{-TETA/C}$ and the peak current of oxygen reduction is $\text{Fe(NO}_3)_3\text{-TETA/C} > \text{FeCl}_3\text{-TETA/C} > \text{Fe}_2(\text{SO}_4)_3\text{-TETA/C}$. Here, we can conclude that the metal precursors (metal salts) have obvious effects on

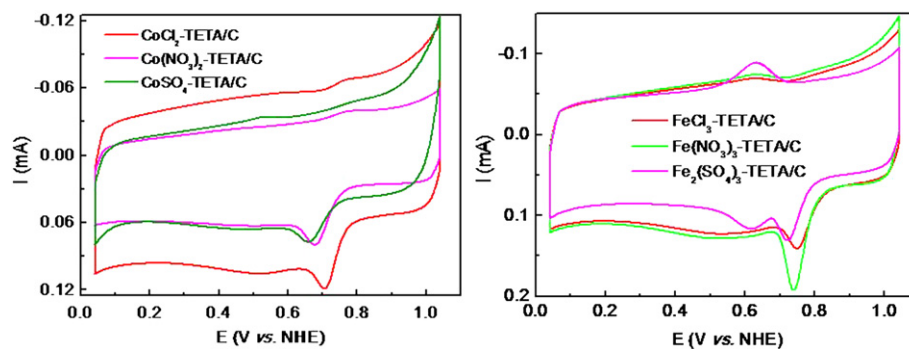


Fig. 7 – Cycle voltammograms of the MTETA/C catalysts (M = Fe or Co; X = Cl, NO₃ or SO₄) in oxygen-saturated 0.5 M H₂SO₄ solution at a scan rate of 5 mV s⁻¹.

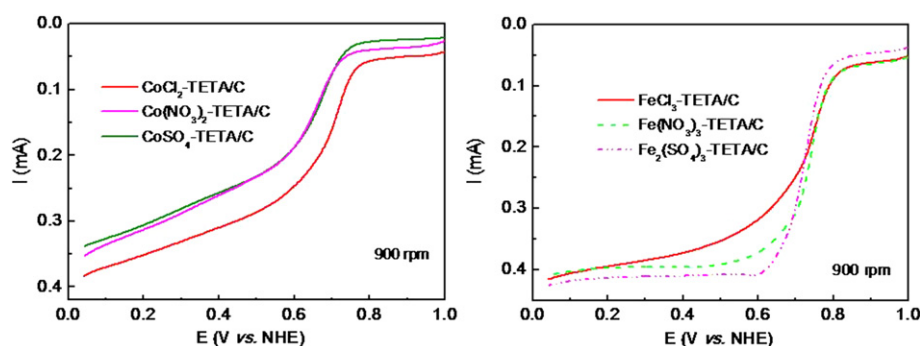


Fig. 8 – Current-potential polarization curves of the MX-TETA/C catalysts ($M = \text{Fe}$ or Co ; $X = \text{Cl}$, NO_3 or SO_4) in oxygen-saturated 0.5 M H_2SO_4 solution at a rotation rate of 900 rpm.

improving the catalytic activity and it may be related to forming the N atoms and O species on the carbon surface. Apparently, metal chloride (i.e. CoCl_2 and FeCl_3) is preferred to prepare the non-precious metal catalysts MTETA/C with high activity for the ORR in acidic solution.

Fig. 8 shows the current-potential polarization curves of oxygen reduction on the prepared non-precious metal catalysts at room temperature. It illustrates that the catalytic activity in the CoX-TETA/C libraries increases as $\text{CoCl}_2\text{-TETA/C} > \text{CoSO}_4\text{-TETA/C} \approx \text{Co}(\text{NO}_3)_2\text{-TETA/C}$ and for the FeX-TETA/C catalysts, it is very difficult to compare the catalytic activity among the whole potential region. It is observed that the half potential for oxygen reduction on the FeX-TETA/C libraries shifts positively as compared to the CoX-TETA/C catalysts. There are no well-expressed limiting current plateaus for these non-precious metal catalysts, except for the $\text{Fe}_2(\text{SO}_4)_3\text{-TETA/C}$ catalyst and $\text{Fe}(\text{NO}_3)_3\text{-TETA/C}$ catalyst. A similar shape of polarization curves was reported for oxygen reduction on carbon-supported metal macrocycle catalysts [9]. The ill-defined limiting currents from the RDE experiment are probably resulted from the thick and highly porous electrode.

4. Conclusions

Here, we study the effects of 3d transition metal precursors (i.e. cobalt salts and iron salts) on the structure and catalytic activity of non-precious metal catalysts for the oxygen reduction reaction (ORR) in acid electrolyte. The non-precious metal catalysts are prepared by chelating these 3d transition metal precursors with TETA and supporting on BP 2000, then pyrolyzing at 800 °C in the presence of Ar. The catalysts characterized by XRD and XPS show that there are metal particles, N and O species on the catalysts surface. Electrochemical measurements indicate that the metal precursors have obvious effects on the catalytic activity and metal chloride is beneficial to prepare these non-precious metal catalysts with desired activity for the ORR in acidic solution among the studied ones. The higher catalytic activity is explained by the N-containing species and O functional species on the carbon surface. Furthermore, pyridinic N facilitates the reduction of oxygen on these Fe-based catalysts, and on the

other hand, pyrrolic N on the carbon surface is in favor of oxygen reduction on these Co-based catalysts.

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