

**Supercritical Fluid Assisted Preparation of Co Promoted N
Doped Carbon Aerogel Electrocatalysts for Oxygen
Reduction Reaction and Investigation of the
Nature of Active Sites**

by

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**Supercritical Fluid Assisted Preparation of Co Promoted N-Doped Carbon
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Investigation of the Nature of Active Sites**

Koç University

Graduate School of Sciences and Engineering

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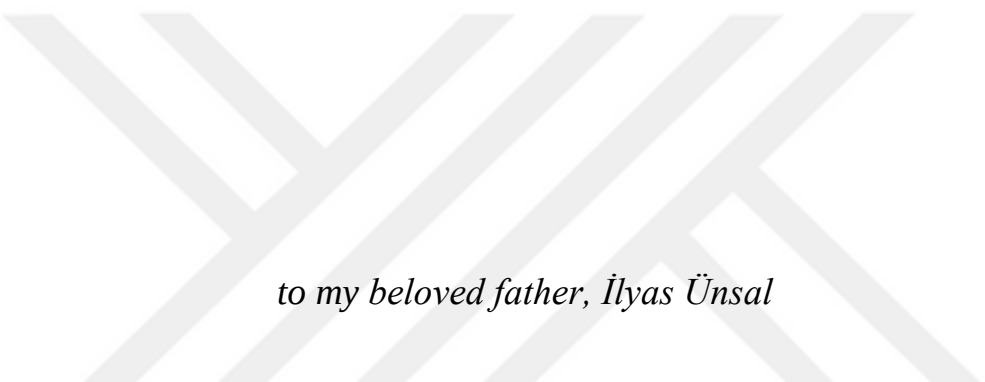
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to my beloved father, İlyas Ünsal

ABSTRACT

Oxygen Reduction Reaction (ORR) plays an important role in various devices that are under development for energy conversion and storage such as fuel cells and metal-air batteries. Although carbon supported Pt and its alloys are considered as the best ORR catalysts up to now, high cost and limited supply of noble metals severely hinders the widespread commercialization of these devices. Thus, development of Pt-free carbon based nanomaterials for ORR has been attracting increased attention. Among others, transition metal containing (usually Co, Fe) N-doped carbon materials are the most promising candidates. In this study, a new highly active family of non-noble Co promoted N-doped Carbon Aerogel catalysts (N-Co-CA) were developed which prepared by a supercritical CO₂ assisted technique combined with NH₃ treatment. The catalyst displayed similar activity as a commercial Pt/C catalyst with a superior methanol tolerance. The active sites are created during the complex transformation of an organic aerogel to a carbon aerogel in the presence of cobalt by ammonia as the source of nitrogen and pyrolysis medium.

In the first part, the effect of various parameters on structural and electrocatalytic properties were investigated. The effect of pyrolysis temperature was examined in the range of 700 °C to 1000 °C, and the mass activity for the ORR had a maximum at 800 °C. The TEM images revealed the existence of Co nanoparticles covered by carbon shells in the samples pyrolyzed at 800 to 1000°C. The effect of Co content on ORR activity was also investigated by varying the Co loading between 8.4 wt% and 23.7 wt%. An optimum in Co loading associated with the ORR activity was detected although the changes in the ORR activity of the samples having different Co contents are not very pronounced. Additionally, the roles of the Co and N doping in enhancing the activities of the N-Co-CA catalysts were studied. N-doped Co-promoted carbon aerogel pyrolyzed at 800 °C under NH₃ flow (9.06 mA/mg_{cat}) exhibited nearly double the mass activity of N-doped carbon aerogel pyrolyzed at the same temperature (5.21 mA/mg_{cat}) at 0.8 V vs a reversible hydrogen electrode (RHE). The former catalyst exhibited the 4e⁻ reaction pathway with a superior methanol tolerance as compared to commercial 20 wt% Pt/C catalyst for ORR in alkaline media. Moreover, the effect of N source on ORR activity was investigated.

To prepare the samples in this set, urea was added to the initial solution as N source in different ratios, and TEM images displayed the presence of donut-shape Co nanoparticles. The samples prepared with NH_3 treatment displayed greater mass activities compared to the samples prepared with urea. The higher activities of the samples prepared with post NH_3 treatment can be attributed to possible catalytic role of Co to form C-N active sites structures for ORR during NH_3 treatment.

In the second part, the nature of the active sites in N-Co-CA catalyst for the ORR was investigated by selectively adding or removing the spectator species via base/acid/ H_2 treatments. Based on rotating disc electrode (RDE) and X-ray photoelectron spectroscopy (XPS) measurements, a strong correlation was found between the relative distribution of graphitic-N species and the mass activity. RDE and XPS data also suggested that the formation of graphitic-N sites is promoted by the presence of Co species. The results revealed that the introduction of Co during the synthesis is crucial although it is not solely responsible for the ORR activity.

ÖZET

Oksijen indirgeme reaksiyonu (OİR), yakıt pilleri ve metal-hava bataryaları gibi çeşitli enerji dönüşüm ve depolama cihazlarının yaygınlaşabilmesi için kritik bir role sahiptir. Ancak, ORR çok yavaş bir kinetiğe sahip olduğundan dolayı, bu reaksiyon için bir katalizör kullanımı gereklidir. Uygun katalizör aşırı-potansiyeli düşürecek ve OİR performansını artıracaktır. Şimdiye kadar en iyi ORR katalizörü olarak karbon destekli platin (Pt) ve Pt alaşımları kabul ediliyordu. Fakat soy metallerin yüksek maliyeti ve sınırlı tedariki, bu cihazların ticarileşmesini ciddi bir biçimde engellemektedir. Bu nedenle, ORR için Pt içermeyen karbon bazlı nano-materyallerin geliştirilmesi ile ilgili yapılan çalışmalar giderek artmaktadır. Diğer ORR için geliştirilen platinsiz nano-yapılar arasında, geçiş metali içeren (genellikle Co, Fe) nitrogen (N) katkılı karbon materyaller en umut verici materyallerdir. Bu tezde, süperkritik deposizyon yöntemi ile amonyak (NH_3) muamelesinin birleşimiyle hazırlanan, OİR için oldukça aktif, N-katkılı Co-teşvikli karbon aerogel katalizörleri (N-Co-CA) incelenmiştir. Sentezlenen katalizör, üstün bir metanol toleransına sahip olup ticari Pt/C katalizörünün aktivitesine çok yakın bir aktivite sergilemiştir. Katalizördeki OİR'dan sorumlu aktif bölgelerin, organik aerogelin Co katalizörlüğünde, NH_3 (10%) gazı ile pirolizi sırasında karbon aerogele dönüşürken oluştuğu düşünülmektedir.

İlk bölümde, çeşitli parametrelerin katalizörün yapısal ve elektrokatalitik özelliklerine etkisi araştırılmıştır. Piroliz sıcaklığı 700 °C'den 1000 °C'ye yükseldikçe, ORR için en fazla kütle aktivitesi 800 °C'de hazırlanan örnekte gözlenmiştir. TEM görüntüleri, 800 ila 1000 °C'de pirolize edilen numunelerde karbon kabuklarıyla kaplı Co nano-parçacıkların varlığını ortaya çıkarmıştır. Farklı Co içeriğine sahip olan numunelerin OİR aktivitesindeki değişiklikler çok belirgin olmamakla birlikte, OİR aktivitesi ile ilişkili Co içeriği açısından optimal bir değer saptanmıştır. Ek olarak, N-Co-CA katalizörünün yüksek ORR aktivitesindeki Co ve N katkısının rolü incelenmiştir. NH_3 akışı altında 800 °C'de pirolize edilen N-katkılı Co-promoteli karbon aerogel (9.06 mA / mg_{kat}), aynı sıcaklıkta piroliz edilen N-katkılı karbon aerogelin 0.8 V'da tersinir hidrojen elektrotuna göre (RHE) olan kütle aktivitesinin (5.21 mA / mg_{kat}) neredeyse iki katını göstermiştir. 800°C'de hazırlanan N-katkılı Co-teşvikli karbon aerogel, 4e⁻ reaksiyon yolunu izlemiş

ve OİR için ticari olarak kullanılan kütlege % 20 Pt/C katalizörüne kıyasla alkali ortamlarda üstün bir metanol toleransı göstermiştir. Ayrıca, N kaynağının OİR aktivitesi üzerindeki etkisi araştırılmıştır. Bu takımdaki örnekler, N kaynağı olarak başlangıç çözeltisinde çeşitli oranlarda üre eklenmesiyle sentezlenmiştir ve TEM görüntüleri, numunelerde içi oyuk şekilli Co nano-parçacıkların varlığını ortaya çıkarmıştır. NH₃ muamelesi ile hazırlanan örnekler, üre ile hazırlanan örneklerle kıyasla daha fazla OİR kütle aktivitesi göstermiştir. NH₃ muamelesi ile hazırlanan örneklerin üre ile hazırlanan örneklerle kıyasla daha iyi OİR aktivelerine sahip olması, Co'nun NH₃ muamelesi sırasında OİR için aktif C-N yapılarının oluşturulmasında katalitik rol sağlamış olabileceği ile ilişkilendirilmiştir.

İkinci kısımda, N-Co-CA katalizöründeki OİR için aktif yapıların doğası, OİR aktivitesinde etkili olmayan yapıların baz / asit / H₂ muameleleri ile seçici olarak eklenmesi veya çıkarılması ile araştırılmıştır. Döner disk elektrot (RDE) ve X-ışını fotoelektron spektroskopisi (XPS) ölçümlerine dayanarak, grafitik-N yapılarının göreceli dağılımı ve OİR kütle aktivitesinin arasında güçlü bir korelasyon bulundu. Ayrıca, RDE ve XPS verileri grafitik-N yapılarının oluşumunun Co varlığı ile desteklendiğini göstermektedir. Sonuçla, sentez sırasında Co varlığının, OİR aktivitesinden bizzat sorumlu olmasa bile, büyük bir öneme sahip olduğunu ortaya koymaktadır.

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NOMENCLATURE

a_{ox}	activity of the oxidized species
a_{red}	activity of the reduced species
A	Cross sectional area of the electrode (cm^2)
B	Koutecky-Levich constant
C_o	Bulk concentration of oxidized species (M, mol/cm^3)
C_R	Bulk concentration of reduced species (M, mol/cm^3)
C_o^*	Concentration of oxidized species at the electrode surface (M)
C_R^*	Concentration of reduced species at the electrode surface (M)
CA	Carbon aerogel
CE	Counter electrode
$Co(acac)_3$	Cobalt(III) acetylacetonate
D_j	Diffusion coefficient of species j (cm^2/s)
E	potential of an electrode (V)
E^0	Standard potential of an electrode (V)
E_{RHE}	Potential of an electrode versus reversible hydrogen electrode (V)
E_{SHE}	Potential of an electrode versus standard hydrogen electrode (V)
E_{eq}	Equilibrium potential of an electrode (V)
E_{half}	Half-wave potential measured in voltammetry (V)
F	Faraday constant; charge on one mole of electrons
F	Formaldehyde
CV	Cyclic voltammetry
EDX	Energy-dispersive X-ray
ΔG^0	standard Gibbs free energy change in a chemical process (kJ/mol)
ΔH^0	standard Enthalpy change in a chemical process (kJ/mol)
HAADF-STEM microscopy	High-angle annular dark field scanning transmission electron microscopy
HRTEM	High resolution Transmission Electron Microscopy
i	Current (A)
i_a	Anodic current (A)

i_c	Cathodic current (A)
i_K	Kinetic current (A)
i_l	Limiting current (A)
i_0	Exchange current (A)
j	Current density (A/cm ²)
j_k	Kinetic current density (A/cm ²)
j_0	Exchange current density (A/cm ²)
K	Equilibrium constant
k	Rate constant
k^0	Standard rate constant
k_b	Rate constant for backward reaction
k_f	Rate constant for forward reaction
N_j	Total number of moles of species j in a system (mol)
n	Number of electron transferred in an electrode reaction
NHE	Normal hydrogen electrode
O	Oxidized form of the standard system
ORR	Oxygen Reduction Reaction
P	Pressure (atm)
P_c	Critical pressure (atm)
P_r	Reduced pressure (atm)
PEMFC	Polymer electrolyte membrane fuel cell
R	Gas constant (J/ mol K)
R	Reduced form of the standard system
R	Resorcinol
RDE	Rotating Disk Electrode
RE	Reference electrode
RFA	Resorcinol formaldehyde aerogel
scCO ₂	Supercritical carbon dioxide
SCD	Supercritical deposition
SCF	Supercritical fluid
T	Temperature (°C)
T_c	Critical temperature (°C)

T_r	Reduced temperature ($^{\circ}\text{C}$)
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
U	Urea
WE	Working electrode
XRD	X-ray diffraction
XRF	X-ray fluorescence

Greek Letters

α	the transfer coefficient for ORR
η	Overpotential (V)
λ	Wavelength of the X-ray
ω	Rotation speed (rpm)

Chapter 1

INTRODUCTION

One of the greatest threats to our planet is climate change, which is due in part to excessive consumption of fossil fuels as our main energy source [1]. A related problem is the limited supply of these fossil fuels, and so we are facing a looming global energy crisis. In response to these problems there has been extensive research over the last few years with a focus on renewable energy technologies such as metal – air batteries [2, 3], fuel cells [4, 5], electrocatalytic [6] and photocatalytic [7] water splitting. These technologies rely on the oxygen electrochemistry by either the oxygen reduction reaction (ORR) or oxygen evolution reaction (OER). Pt and Pt-based alloy catalysts are currently considered as the best ORR catalysts [8-14]. However, high cost of Pt and limited supply of precious metals severely hinder the widespread commercialization of devices [15-17]. To overcome this obstacle, tremendous efforts are being devoted to develop precious metal free ORR catalysts such as transition metal chalcogenides [18], oxides [19, 20], oxynitrides [21, 22] nitrides [23], carbides[24], metal-free heteroatom-doped carbon materials [25] and nitrogen doped carbon supported transition metal catalysts [26-28]. Among these catalysts, Co or Fe containing nitrogen-doped carbon materials are promising candidates, and up to now, various N-M-C (M stands for Co or Fe) catalysts have been synthesized with high activities for ORR [29-37].

A current challenge preventing the rational design of synthetic routes for such catalysts is a lack of understanding of the exact nature of the active site(s) in the N-M-C (M: Fe or Co) catalysts. The active centers in Co-containing materials have been less studied compared to Fe-containing materials, and it is still unclear whether the cobalt is the crucial center of the active site(s), or only catalyze the process of nitrogen (N) doping into carbon. It is because N-Co-C catalysts usually consists of a variety of species within

the carbon matrix depending on the preparation method such as Co-N_x species, a family of C-N sites (pyridinic N, pyrrolic N, graphitic-N and pyridinic N-oxides), dispersed cobalt oxides and carbon shell covered Co nanoparticles, which have been considered as active sites for ORR. In recent years, graphitic-N [38, 39], pyrrolic N [40], pyridinic-N [41], Co-N_x [42, 43], cobalt oxides [44] species were proposed as active sites for the ORR based on spectroscopic and computational [45] studies. However, there is no consensus in the literature on whether some of these species are active sites or spectator species.

Various N-doped carbon materials such as carbon nanotubes [46], ordered mesoporous carbon [47], graphene [48], graphene aerogels [49] and carbon aerogels [50-52] have been synthesized and displayed promising ORR activities. Among these materials, nanostructured carbon aerogels (CAs) have been receiving increased attention due their unique properties such as high surface area, low mass density, high porosity and high electrical conductivity. Carbon aerogels are obtained by pyrolysis of organic aerogels that are generally produced by supercritical drying of organic gels [53]. CAs have the advantages of a three-dimensional hierarchical morphology that can be tuned by changing the process parameters during the polymerization, the gelation, the curing and the pyrolysis steps. Therefore, CAs with such a tunable morphological diversity are attractive alternatives to conventional N-doped carbons in preparation of cobalt or iron based ORR catalysts.

There are several conventional techniques available to prepare supported metal catalysts such as wet impregnation and ion-exchange. However, each of these techniques have some limitations and may not be suitable for highly porous materials such as aerogels because of the high surface tension of liquids which can cause the collapse of the nano-sized pores of the aerogels [54]. Supercritical deposition (SCD) is an alternative route for the preparation of aerogel supported metals, which consists of the dissolution of a metal complex in a supercritical fluid with subsequent adsorption on a porous support followed by the conversion of the metal complex to its metal form [54-60]. Supercritical CO₂ (scCO₂) is the most commonly used supercritical fluid due a relatively low critical temperature and other desirable characteristics such as being non-toxic, non-flammable, inexpensive and environmentally friendly. Up to now, SCD technique has been used to

synthesize a variety of supported monometallic, bimetallic, trimetallic or metal oxide nanoparticles for various catalytic applications. For instance, carbon supported Pt nanoparticles prepared by SCD have exhibited promising electrocatalytic properties and have outperformed commercial catalysts in some cases [61, 62]. Therefore, SCD may also be an attractive route to prepare precious metal free transition metal-containing N-doped carbon (N-M-C) electrocatalysts with high activities.

Here, we used a SCD assisted technique to synthesize N-Co-CA catalyst. We prepared highly active Co promoted N-doped CA catalysts and evaluated the effect of pyrolysis temperature, cobalt loading and nitrogen source on ORR activity. We further compared the catalytic activity of the N-Co-CA catalysts with those of the N-CA, Co-CA and CA catalysts to study the role of the Co and N doping in enhanced activity of the N-Co-CA catalysts. The durability and methanol tolerance of the N-Co-CA catalysts were also tested and compared to a commercial Pt/C. Moreover, to understand the nature and catalytic sites of the synthesized catalysts, various base/acid treatments were performed in order to selectively remove the possible spectator species and the morphologies and ORR activities of the samples were characterized and compared at each step of the treatments using XRD, XPS, TEM, HAADF-STEM and rotating disc electrode (RDE) measurements.

Chapter 2 presents an overview of an electrode process, thermodynamic and kinetics of ORR along with the techniques used in electrocatalytic ORR. Subsequently, a brief review of N-doped non-noble metal ORR catalyst (N-M-C) and its active site nature are given in Chapter 2. The properties and applications of carbon aerogels (CA), N-doped CAs and N-doped non-noble metal CAs are also briefly reviewed. Chapter 2 also introduces the features of supercritical fluids and the supercritical deposition (SCD) technique.

Experimental methodology is given in Chapter 3. The synthesis procedures of all samples and the post acid-base treatments are described in this chapter. Subsequently, techniques used for the characterization of catalysts are presented.

In Chapter 4, experimental results are given. In the first part, the effect of various parameters on structural and electrocatalytic properties of the samples are discussed in

detail based on the physical and electrochemical characterization results of the samples. In the second part, the results of post acid-base treatment are presented, and active site nature of N-Co-CA catalyst is discussed.

Chapter 5 concludes the thesis with a brief summary and gives perspectives for future work.



Chapter 2

LITERATURE REVIEW

2.1 Overview of an Electrode Process

2.1.1 Types of Electrochemical Cells and Basic Definitions

Electrochemical cells can be classified as *galvanic* and *electrolytic* cells (Figure 2.1)[63]. In galvanic cells (e.g. the Leclanche Zn-MnO₂ cells, fuel cells), the reaction takes place spontaneously when electrodes are connected by a conductor. These cells generally used for converting chemical energy into electricity. However, an electrolytic cell requires electrical energy to carry out the chemical reactions. Thus, external voltage greater than open-circuit voltage is applied. The electrolytic cells are commonly used in electroplating, electrefining and the production of chlorine and aluminum (electrolytic synthesis).

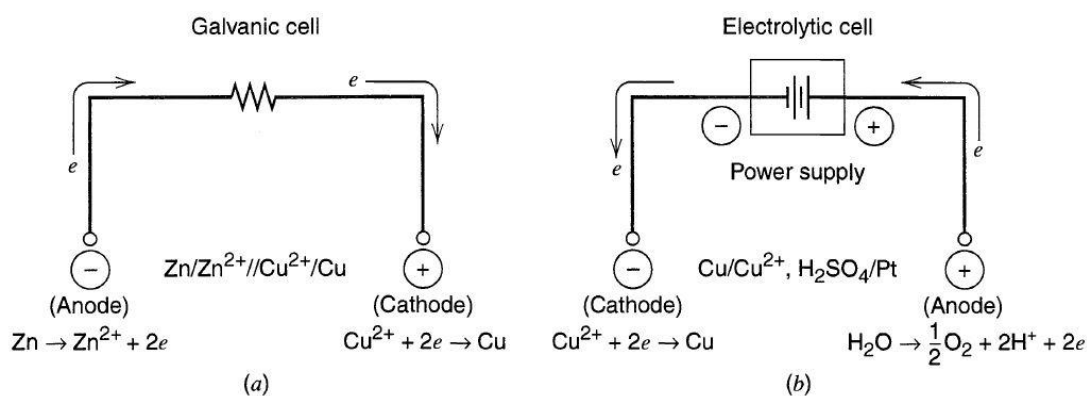


Figure 2.1 (a) Galvanic and (b) Electrolytic Cells[63]

The nature of single electrode reactions and its behavior do not depend on the type of the cell (either galvanic or electrolytic), which the electrode belongs.

Therefore, the chemical changes occurring with the faradaic reactions at electrodes in contact with electrolytes is defined as *electrolysis* [63]. Conventionally, the electrode where the reduction takes place is named as the *cathode* and the electrode where the oxidation takes place is called the *anode*. *Cathodic current* (i_c) is the current formed by the flow of electrons from the electrode to the solution, while *anodic current* (i_a) is the electron flow from the solution into the electrode. In galvanic cells, cathode is positive with respect to anode whereas in electrolytic cells cathode is the negative electrode with respect to anode (Figure.2.1)

2.1.2 Rate of Electrode Reactions

The electrode reactions are more complex than the reactions taking place in gas phase or in the solution, which occurs homogeneously within the medium at a uniform rate. Since the electrode reactions occur only at the electrode-electrolyte interface, which makes them heterogeneous reactions, interpreting their reaction rate is more complex. Other than usual kinetic parameters, the reaction rate of electrode reactions also depend on many surface effects and the mass transfer to the electrode. An overall electrode reaction can be represented as



where the O and R are the oxidized and reduced species in the solution. The general pathways for an electrode reaction is schematized in Figure 2.2. The rate of an electrode reaction depends on the rates of below processes [64]

- Mass transfer (diffusion of O or R from the bulk solution to electrode surface)
- Electron transfer on the surface of the electrode
- Chemical reactions on the electrode surface following or preceding the electron transfer
- Adsorption, desorption, crystallization reactions on the surface of electrode.

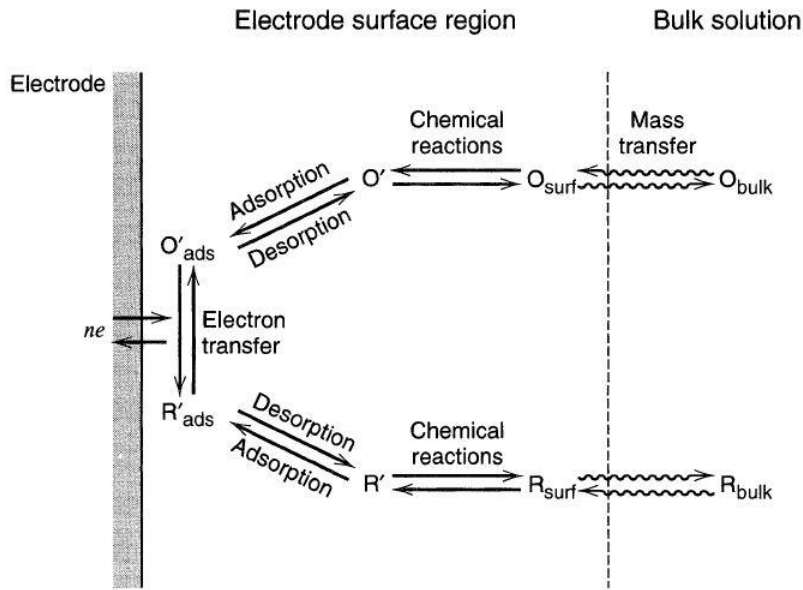


Figure 2.2 Schematic of a General Electrode Reaction [63]

The rate of electrode reactions directly proportional to current(i). Current is defined as:

$$i \text{ (ampers)} = \frac{dQ}{dt} \text{ (coulombs/s)} \quad (2.1)$$

$$\frac{Q(\text{Coulombs})}{nF(\text{Coulombs/mol})} = N \text{ (mol electrolyzed)} \quad (2.2)$$

$$\text{Rate}(\text{mol s}^{-1}) = \frac{dN}{dt} = \frac{i}{nF} \quad (2.3)$$

where Q is the amount of electricity required to oxidize or reduce the species in electrochemical cell, F is Faraday constant, n is the number of electrons consumed in the electrode reaction.

The rate of the electrode reactions are usually described with the unit of mol s^{-1} per unit area; thus,

$$\text{Rate}(\text{mol s}^{-1}\text{cm}^{-2}) = \frac{i}{nFA} = \frac{j}{nF} \quad (2.4)$$

where A is the electrode area (cm^2) and the j is the current density (A/cm^2).

$$j = i/A \quad (2.5)$$

2.2 Electrochemical Oxygen Reduction Reaction (ORR)

2.2.1 Thermodynamics of Oxygen Reduction Reaction

In the fields of electrochemistry, oxygen electrocatalysis is the one of the most widely investigated topics owing to its importance for electrochemical energy conversion and storage devices. The oxygen reduction reaction (ORR) is the cathodic branch of oxygen electrode reactions in electrochemical systems.

Table 2.1 Thermodynamic Electrode Potentials of ORR in Different Mediums[65]

Electrolyte	ORR Reactions	Thermodynamic Electrode Potential
Acidic Medium	$O_2 + 4H^+ + 4e^- \rightleftharpoons H_2O$	$E^\circ = 1.229 \text{ V vs SHE}$
	$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	$E^\circ = 0.695 \text{ V vs SHE}$
	$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	$E^\circ = 1.776 \text{ V vs SHE}$
Alkaline Medium	$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	$E^\circ = 0.401 \text{ V vs SHE}$
	$O_2 + H_2O + 2e^- \rightleftharpoons HO_2^- + OH^-$	$E^\circ = -0.076 \text{ V vs SHE}$
	$HO_2^- + H_2O + 2e^- \rightleftharpoons 3OH^-$	$E^\circ = 0.878 \text{ V vs SHE}$

The ORR consists of multiple adsorption-desorption steps with many intermediates, mainly depending on the natures of the catalysts, electrode material and electrolyte. It has very sluggish reaction kinetics and its mechanism is quite complicated. Although great efforts have been devoted over decades, the reaction mechanism of ORR has not been well understood due to complexity of the reaction. Molecular O_2 can be reduced by following $2e^-$ or $4e^-$ pathways depending on the nature of the catalyst and electrolyte type. Typical ORR processes in different mediums with their corresponding thermodynamic electrode potentials at standard conditions are displayed in Table 2.1

Compared to acidic medium, ORR is more enhanced in alkaline medium both thermodynamically and kinetically [66]. Moreover, higher pH of alkaline electrolyte provides a less corrosive environment for the catalyst.

In nonstandard conditions, Nernst Equation governs the equilibrium potential of oxygen electrode reactions[65].

$$E = E^o - \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}} \quad (2.6)$$

where E^o is the equilibrium cell voltage, T is the temperature (K), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), F is the Faraday constant ($96,485 \text{ J mol}^{-1} \text{ V}^{-1}$), n is the number of electrons transferred and a is activity of the oxidized and reduced species. The electrode potential can be expressed with respect to Reversible Hydrogen Electrode (RHE) potential in the specific circumstance of alkaline media at 25°C and 1 atm [65].

$$E_{\text{RHE}} = E_{\text{SHE}} + 0.059 \times \text{pH} \quad (2.7)$$

The pH dependence of $E_{\text{O}_2}/E_{\text{OH}^-}$ in terms of SHE and RHE is given in Figure 2.3.

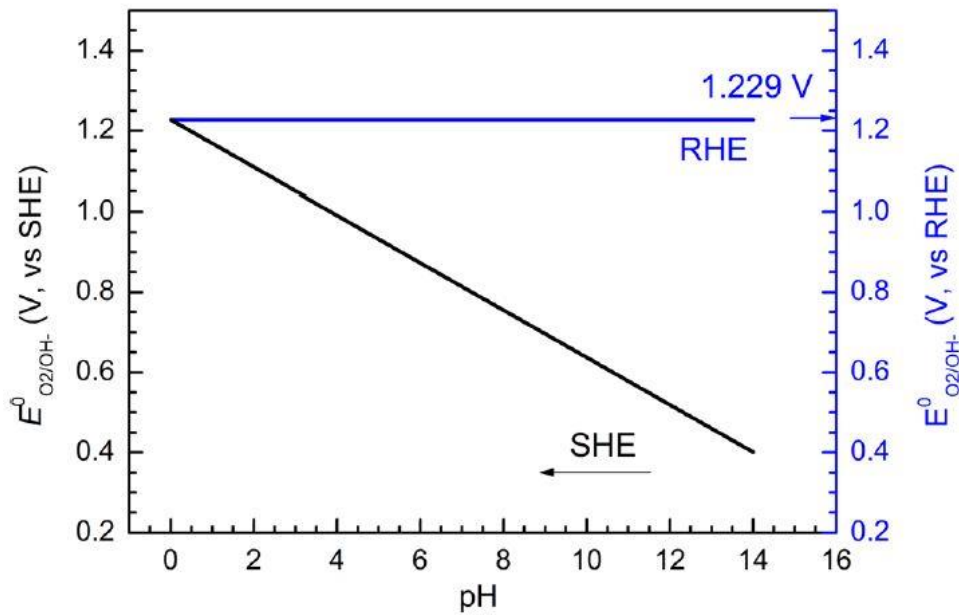


Figure 2.3 RHE and SHE Scales of O_2/OH^- Redox Couple in The Electrolytes Having Different pH Values [65]

2.2.2 Kinetics of Oxygen Reduction Reaction

ORR is highly irreversible reaction and it is desired to have the ORR as close to the reversible conditions as possible with a high reaction rate. In other words, ORR should take place near to the equilibrium cell voltage with an overpotential (η) which is very close to zero. Overpotential is defined as the additional potential (beyond the thermodynamic potential) as shown in Equation 2.8 required to drive the reaction at a certain rate (Equation 2.3) [63]. To minimize the overpotential, the use of electrocatalysts has significant importance.

$$\eta = E - E^o \quad (2.8)$$

The current-overpotential relationship is given in Equation 2.9 [63]

$$i = F A k^o \left[C_O^* e^{\frac{-n\alpha F \eta}{RT}} - C_R^* e^{\frac{(1-\alpha)n F \eta}{RT}} \right] \quad (2.9)$$

where i is the current, A is the electrode area, k^o is the standard rate constant, C_O^* , C_R^* are the surface concentrations, C_O , C_R are the bulk concentrations, F is the Faraday constant, n is the number of electrons transferred in the rate determining step, α is the transfer coefficient, η is the overpotential of ORR, R is the gas constant, and T is the temperature in Kelvin. This relation is called as the *Butler –Volmer* (B-V) formulation of electrode kinetics[64]. B-V theory links

- Faradaic current which is the current occurs due to chemical reactions
- Electrode potential
- Concentration of electroactive species at the electrode surface.

The k^o represents the value at $E=E^O$ where the forward and backward rate constants are the same. While small k^o can be attributed to sluggish kinetic, the system with a large k^o can achieve the equilibrium in a short time so it has the fast kinetic. Depending on the reaction complexity the k^o value can be altered from 10 to 10^{-9} cm/s [63].The systems having single electron transfer have large k^o (i.e.hydrogen oxidation reaction). Since the

reduction of molecular oxygen (following either $2e^-$ or $4e^-$ pathway) includes significant molecular rearrangement upon electron transfer with complicated reaction mechanism, its k^0 is low [63].

2.2.2.1 Exchange Current Density

Equation 2.9 is usually written in terms of exchange current (i_0), which is defined as the current that flows with the same value in opposite direction at equilibrium, becoming the net current zero. In other words, the exchange current will be equal to the anodic (i_a) and cathodic (i_c) currents at $E=E^0$. At equilibrium, the surface concentrations will be equal to bulk concentrations and the exchange current is defined where the bulk concentration of oxidized and reduced species are the same (i.e. $C_O = C_R = C$); that is,

$$i_0 = F A k^0 C \quad (2.10)$$

i_0 is directly proportional with the k_0 and it is commonly used as a kinetic parameter instead of k_0 . In terms of i_0 , the current- overpotential relation given in Equation 2.9 becomes:

$$i = i_0 \left[\frac{C_O^*}{C_O} e^{\frac{-n\alpha F\eta}{RT}} - \frac{C_R^*}{C_R} e^{\frac{(1-\alpha)nF\eta}{RT}} \right] \quad (2.11)$$

The relation given in Equation 2.11 is depicted in Figure 2.4 for a general $O + ne^- \rightleftharpoons R$ system. The cathodic (i_c) and anodic (i_a) currents are displayed as the dashed line while the solid line shows the net total current that are the sum of i_c and i_a . At large negative over-potentials, anodic component becomes negligible. Thus, for ORR, total current is essentially the same as i_c . As going beyond the equilibrium potential, E_{eq} , the magnitude of the current increases rapidly due to exponential factor. However, after a point increasing the over-potential does not affect the magnitude of current. The current in this region called as *limiting current* (i_l), which is controlled by mass transfer rather than heterogeneous kinetics. It indicates that the exponential term in Equation 2.11 is

moderated by the ratio of the surface to bulk concentration of the species in the limited current region.

When mass transfer effect is eliminated (i.e. by mixing the solution well or keeping the current very low), the surface and bulk concentrations will be almost identical and the Equation 2.11 will reduce to

$$i = i_o \left[e^{\frac{-n\alpha F\eta}{RT}} - e^{\frac{(1-\alpha)nF\eta}{RT}} \right] \quad (2.12)$$

which is known as *Butler Volmer Equation*. [63]

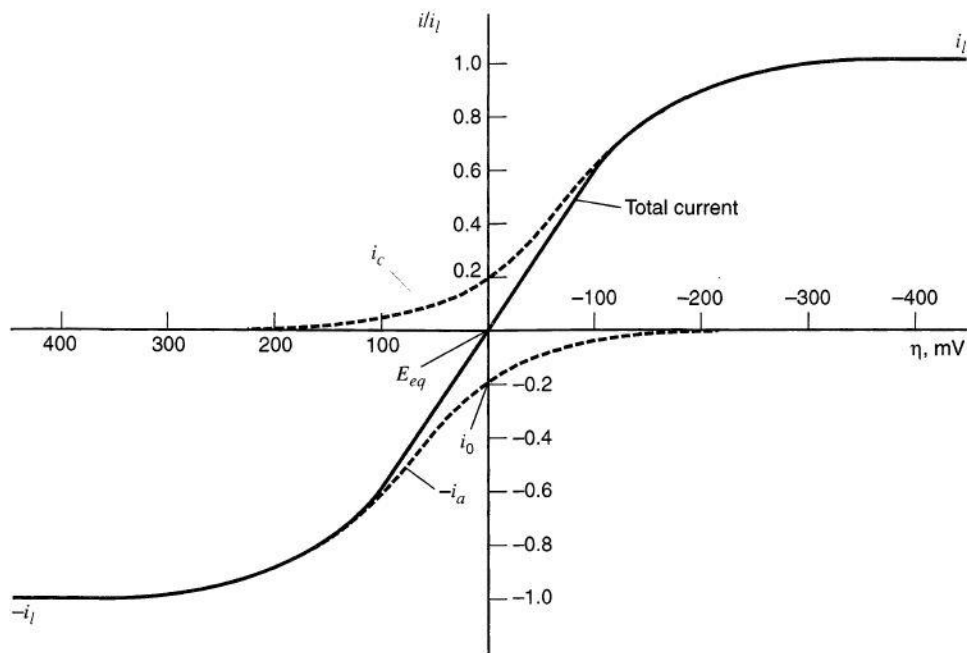


Figure 2.4 A Typical Current-Overpotential Curves for The System $O + ne^- \rightleftharpoons R$ [63]

The exchange current density (j_0) for ORR is related to type of electrode and catalysts where the reaction occurs, the concentration of reactants (i.e. partial pressure of O_2), actual electroactive area as well as the measurement conditions. ORR displays higher exchange current density on a Pt electrode compared to other noble metals (i.e. Au). Since

the actual electroactive surface area of the Pt electrode is significantly different from that of geometric area and the partial pressure of O₂ is not 1 atm the intrinsic exchange current density should be used instead of apparent exchange current density ($j_{0,apparent}$); that is,

$$j_{0,apparent} = (ECSA)_c j_{0,ORR} \left(\frac{P_{O_2}}{P_{O_2}^o} \right)^{\alpha_0} \quad (2.13)$$

where $(ECSA)_c$ is electrochemical active surface area of the cathode catalyst, $j_{0,ORR}$ is the intrinsic exchange current density, $P_{O_2}^o$ is partial pressure of O₂ at standard conditions, P_{O_2} is the actual O₂ pressure, α_0 is the transfer coefficient for ORR. The temperature dependency of exchange current density is also governed by Arrhenius equation, which is

$$j_{0,ORR} = j_{0,\infty} e^{-(E_a/RT)} \quad (2.14)$$

where $j_{0,\infty}$ is the exchange current density at temperature goes to infinity, E_a is the activation energy.

2.2.1.2 Tafel Slope

For large overpotential values, the term given in parenthesis in Equation 2.12 reduces to

$$i = i_o \left[e^{\frac{n\alpha F\eta}{RT}} \right] \quad (2.15)$$

or

$$\eta = \frac{2.3RT}{n\alpha F} \log(i_o) - \frac{2.3RT}{n\alpha F} \log(i) \quad (2.16)$$

The plot of η vs $\log(i)$ gives a linear relationship, which is given by Tafel in 1965 in the form of

$$\eta = a + b \log(i) \quad (2.17)$$

where the Tafel constants are

$$a = \frac{2.3RT}{n\alpha F} \log(i_o) \quad b = -\frac{2.3RT}{n\alpha F}$$

The higher the Tafel slope indicates the faster overpotential increase with the current density. Therefore, for an electrochemical reaction the low Tafel slope is desirable to obtain a high current at low overpotential. Depending on the electrode materials used and on the potential range, for ORR, two Tafel slopes are obtained, 60 mV/dec and 120 mV/dec, respectively[67]. α is an important factor determining the Tafel slope.

2.3 Techniques Used in Electrocatalytic O₂ Reduction Reaction

2.3.1 Steady- State Polarization

For an electrode reaction, the potential shifts from its equilibrium value which leads to the electrochemical reaction and passage of current is called as *polarization*. The polarization curves are obtained by changing the electrode potential and recording the stable current response or vice versa. The curves give the relation between the current density and electrode potential, which follows the Butler Volmer Equation (Equation 2.12). For instance, **Figure 2.5** displays steady state polarization curves of a polymer exchange membrane fuel cell at 23°C and 80°C. For both high ORR performance and fuel cell efficiency, it is desirable to obtain high current densities at lower ORR overpotential or higher cell voltage values. The cell voltage obtained at any current density at 80°C is higher than the one obtained at 23 °C in **Figure 2.5**, which indicates that the fuel cells display better performance at 80 °C compared to 23 °C. Moreover, the Tafel slope and α can be obtained by fitting the polarization curves or plotting η vs $\log(j)$.

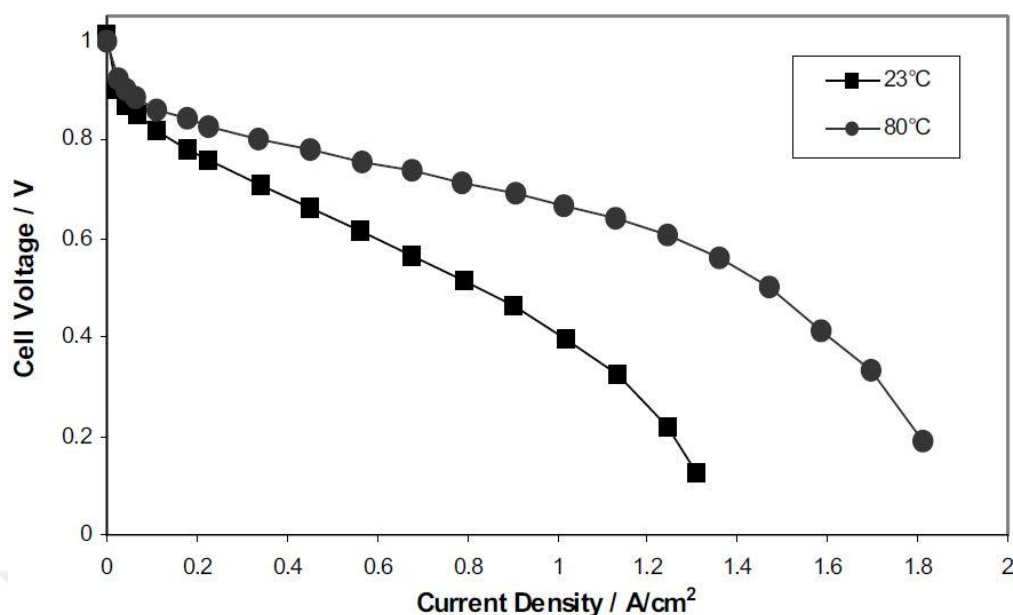


Figure 2.5 Polarization Curves Obtained at Different Temperatures
MEA Active Area is 4.4 cm^2 . H_2/Air With 100% Relative Humidity [68]

2.3.2 Cyclic Voltammetry

Cyclic voltammetry (CV) is used to provide information about electrochemical reactions and response of electrocatalysts in an electrolyte. **Figure 2.6** represents the cyclic voltammogram of a Pt electrode in N_2 saturated acidic electrolyte. Solid black line displays the range swept in negative direction to $\sim 0.1 \text{ V}$ vs RHE in negative direction starting from $\sim 1.2 \text{ V}$ vs RHE. The 0.0 V vs RHE is the potential where the hydrogen evolution starts. The extended dashed lines on the left hand side and the right hand side represent the hydrogen evolutions and oxygen evolution regions, respectively, which both are generally considered as irreversible. The areas above and below the zero current lines are approximately equal.

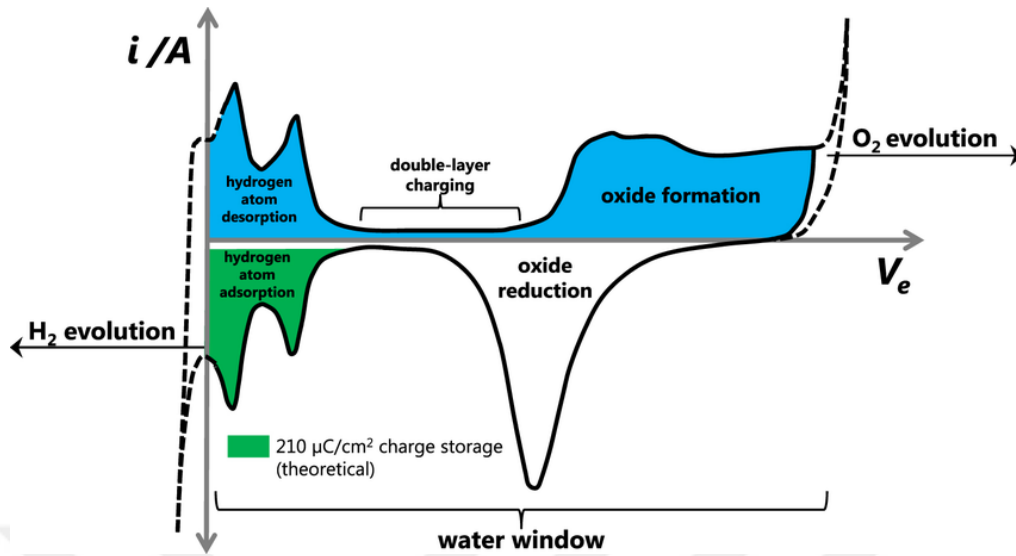
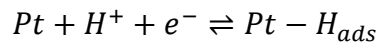
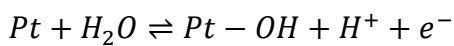


Figure 2.6 Cyclic Voltammogram of a Pt Electrode in N₂ Saturated Acidic Electrolyte[69]

On the left-hand side, the hydrogen adsorption and desorption regions are displayed with green and blue shaded areas, respectively. H⁺ ions are adsorbed on Pt electrode surface as the potential goes to the negative direction, while they start to desorb from the surface as moved in the positive potentials [69]. The reactions occur in this region can be given as;



On the right-hand side, the blue area represents where the platinum oxides are formed and they are reduced below the zero-current line in the white region. The reactions in these regions are:



The middle region is the double layer capacitance region where no electron transfer occur and the current is approximately constant. The double layer capacitance charging occurs at entire potential ranges simultaneously with other processes[69].

2.3.3 Rotating Disk Electrode (RDE)

Rotating disk electrode (RDE) is a hydrodynamic working electrode utilized in a three electrode cell system. The cell contains working electrode (WE), counter electrode (CE) and reference electrode (RE) as represented in **Figure 2.7**. WE is the electrode in which the main reaction occur. For ORR measurements, glassy carbon electrodes are commonly used. A RE should have a stable potential and ideally no current passes through so that the potential of WE can be controlled and measured with respect to RE. The most common and practical reference electrodes used in such systems are Saturated Calomel Electrode ($\text{Hg}/\text{Hg}_2\text{Cl}_2$ SCE), Silver/Silver Chloride (Ag/AgCl) (filled with KCl or NaCl), Mercury/Mercury oxide (Hg/HgO). SCE and Ag/AgCl electrodes are generally recommended for acidic electrolytes with low pH values while Hg/HgO is more preferable for highly basic electrolytes for long term usages [64]. The Ag/AgCl and SCE electrodes have limited life times in very alkaline solutions because hydroxide ions diffuse into the electrode filling solution and form silver hydroxy/oxide species on the silver wire and brown-black color is observed on the silver wire [70]. This contamination causes some shifts in the electrode potential but it can be prevented, to some extent, by using a double junction to slow the hydroxide diffusion from electrolyte to silver wire. The potential values in polarization curves obtained by RDEs are generally presented in terms of reversible hydrogen electrode (RHE) due to its independency of electrolyte pH. CE is an inert (i.e. Pt) material which enables current flow between WE and itself. The current flows between WE and CE during RDE experiment.

RDE is the most common technique to measure the ORR activity of a catalyst by simulating the ORR in an O_2 saturated electrolyte. In RDE, the catalyst is deposited on glassy carbon electrode, which is the WE, was tested in O_2 saturated electrolyte environment. To study ORR in acidic medium, HClO_4 and H_2SO_4 are commonly used electrolytes in different molarities while to study ORR in alkaline medium, aqueous KOH is preferred as the electrolyte. With RDE, the oxygen transport limitation can be controlled by rotating the WE in different speeds.

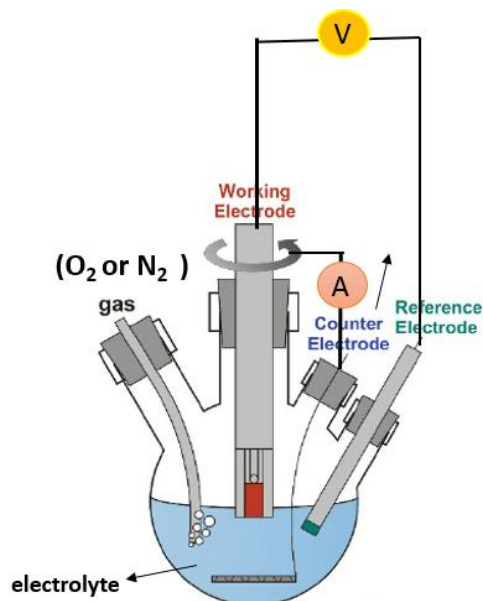


Figure 2.7 Experimental Setup for a Three-Electrode Cell

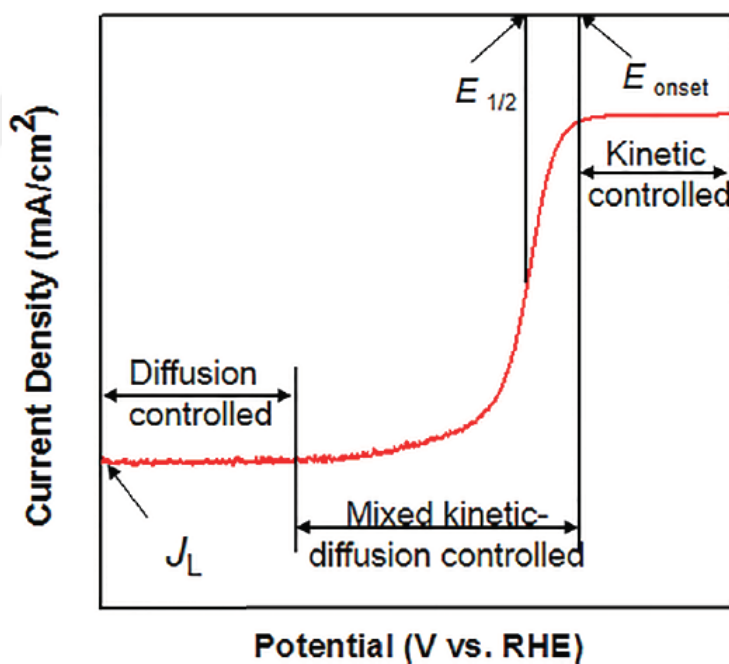


Figure 2.8 A typical ORR Polarization Curve [71]

Figure 2.8 shows a typical ORR polarization curve. The curve is divided into three region, which are the kinetic controlled, the diffusion controlled and the mixed region [71]. In the kinetic controlled region, the ORR is slow and the current density increases slightly as potential decreases. In the mixed controlled region, the reaction accelerates

and the current density increases with by changing potential under both kinetic and diffusion control. The region where the current density reaches a platform is the diffusion limited region. In this region, since the rate of ORR is very fast due to high overpotentials, the reaction rate is governed by the diffusion rate of O₂ molecule to the electrode.

The onset potential (E_{onset}) and the half-wave potential (E_{half}) are two important parameters to evaluate the activity of an ORR catalyst. Commonly, E_{onset} is defined as the potential in which the cathodic current reaches 0.1 mA/cm² [42] and the E_{half} is defined as the potential where the half of limited current density observed. Moreover, kinetic current density (J_K) is another parameter used to evaluate the ORR catalysts, which can be calculated by the Koutecky-Levich (K-L) equation. For ORR, K-L plots (J^{-1} vs $\omega^{-1/2}$) are generated at various electrode potentials to calculate the number of electrons transferred (n) using the slopes of their best linear fits according to K-L equation given below [42]:

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} = \frac{1}{J_K} + \frac{1}{B\omega^{1/2}} \quad (1)$$

$$B = 0.62nFC_0D_0^{2/3}\nu^{-1/6} \quad (2)$$

$$J_K = nFkC_0 \quad (3)$$

where J is the measured current density, J_K and J_L are the kinetic and diffusion-limiting current densities, ω is the angular velocity of the disk ($\omega = 2\pi N$, where N is the linear rotation speed), n is the number of transferred electrons, F is the Faraday constant (96 485 C mol⁻¹), C_0 is the bulk concentration of O₂ (1.2×10^{-6} mol mL⁻¹), ν is the kinematic viscosity of the electrolyte (0.01 cm² s⁻¹), D_0 is the O₂ diffusion coefficient (1.9×10^{-5} cm² s⁻¹), and k is the electron-transfer rate constant. The number of electrons transferred (n) and J_K can be determined from the slope and the intercept of the K-L plots, respectively.

2.4 N-doped Non-noble Metal ORR Catalyst (N-M-C)

Up to now, Pt-based catalysts are considered as the best ORR catalysts [8-14]. However, due to the high cost and durability problems of Pt catalysts, tremendous efforts have been devoted to replace them with precious metal free ORR catalysts such as transition metal chalcogenides [18], oxides [19, 20], oxynitrides [21, 22] nitrides [23], carbides [24], metal-free heteroatom-doped carbon materials [25] and nitrogen doped carbon supported transition metal catalysts [26-28].

Among others, Co or Fe containing nitrogen-doped carbon materials are one of the most promising candidates. The first report on this type of catalyst by Jasinski et al. demonstrated that metal phthalocyanine complexes are active for ORR and they may be used as a substitute for expensive Pt-based catalysts [29]. Following the discovery by Jasinski et. al., it was found that with thermal treatment of these phthalocyanine- and porphyrin-based materials, remarkable increases in the catalyst stability and activity could be achieved [30]. Subsequently, Gupta et al. demonstrated that the enhanced ORR activity obtained by thermal treatment of metal macrocycles could also be achieved by heat-treating a mixture of a Co(II) salt and polyacrylonitrile which results in nitrogen-doped carbon-supported cobalt catalysts; thus, it has been proven that the precursor for the pyrolysis step does not have to be a metal in a macrocycle structure (such as phthalocyanine and porphyrin) to obtain an non-noble metal catalyst that has high activity for ORR [31]. Following these studies, various N-M-C (M denotes Co or Fe) catalysts have been synthesized with high activities for ORR [32-34].

The performance of catalyst is directly related to the synthetic procedure, choice of precursors and type of carbon supports. N containing polymers (i.e, melamine [36], polyaniline(PANI) [35]), small organic molecules (i.e pyrrole [52], acetonitrile, 1-methylimidazole [37]) and the inorganic N sources (i.e NH_3 gas [32, 34], NaN_3 [33]) are commonly used nitrogen sources for N-M-C catalysts. As transition metal precursor, nitrate salts are commonly used such as $\text{Co}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$ [42]. Generally, synthesis procedure of such catalyst begins with a preparation of a solution containing the mixture of transition metal, nitrogen and carbon precursors. After the solvent is removed, the remaining solid powder is subjected to heat treatment at high temperatures in the range

of 700- 1000 °C. In some studies[42, 72], the heat treatment step is followed by acid treatment step to remove the unstable species and the undesired functional groups from the catalyst pores so that the more exposure active sites can improve the ORR activity. Moreover, since the acid treatment might block the active sites with some functional groups introduced by acid depending on its type (i.e.HNO₃, H₂SO₄), the acid treatment is generally followed by a second-heat treatment to further eliminate the undesired functional groups caused by acid washing.

2.4.1 Nature of Active Site in N-M-C Catalyst

A current challenge preventing the rational improvement of synthetic routes for such catalysts is a lack of understanding of the exact nature of the active site(s) in the N-M-C (M: Fe or Co) catalysts. The nature of active sites for ORR in Fe containing catalyst has been widely investigated and in recent years, there is growing a consensus that FeN_x species in the carbon matrix are the main active sites in the N-Fe-C catalyst. based on the results obtained by Mössbauer spectroscopy [73], extended X-ray absorption fine structure (EXAFS) [74], X-ray photoelectron spectroscopy(XPS) [72] as well as the computational studies [75]. However, the active centers in Co-containing materials have been less studied and it is still unclear whether the cobalt is the crucial center of the active site(s), or only catalyze the process of nitrogen doping into carbon. For instance, Niwa et.al. [76] and Shin et.al. [40] revealed that Co component in the catalyst is not part of the active site by XAS and XPS measurements, respectively. However, Qian et al. [42] proposed that the main active site in N-Co-C catalyst is Co-N related species based on the XPS results. On the other hand, in the recent years, Yao et al. found that CoN–C moieties are actual ORR active sites rather than Co-N nanoparticles themselves according to XPS measurements [77].

The reason of this inconsistency is that N-Co-C catalysts usually include a variety of species including Co nanoparticles and clusters [78], carbon shell covered Co nanoparticles [79, 80], dispersed cobalt oxides [81] and Co-N_x species [42, 43, 82] along with a family of N species (pyridinic N, pyrrolic N, graphitic-N and pyridinic N-oxides) as shown in **Figure 2.9** within the carbon matrix depending on the preparation method. Among these species, graphitic-N [38, 39, 76] , pyrrolic N [40] pyridinic-N [41], Co-N_x

[42, 43], cobalt oxides [44] species were proposed as active sites for the ORR based on spectroscopic and computational [45] studies. However, there is no definite agreement in the literature on whether some of these species are active sites or spectator species.

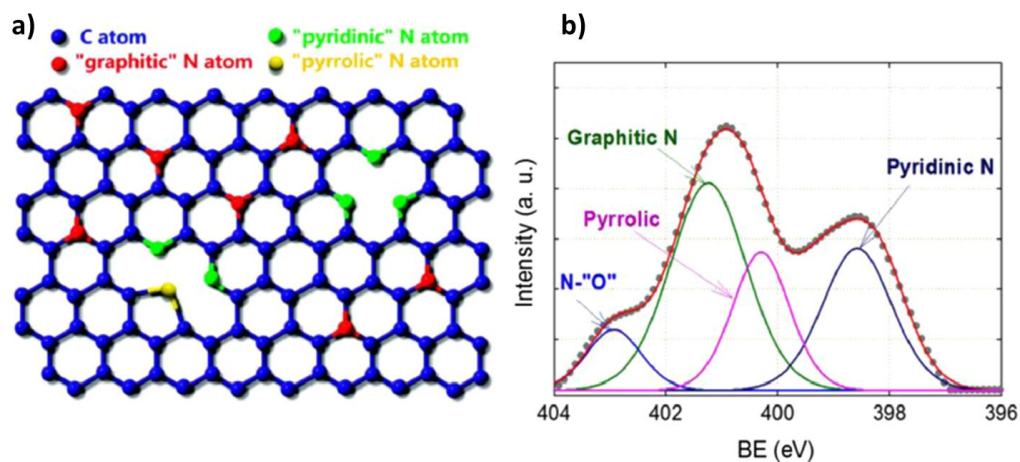


Figure 2.9 a) Nitrogen Doping into Graphene Plane at Different Location [83] b) Typical Binding Energies of N Atoms in Different Doping Environment Determined by XPS [35].

2.5 Carbon Aerogels

Aerogels are highly porous materials which are synthesized by replacing the liquid component of a gel material with gas as its name represents. Their pores are in the mesoporous range and they have high specific surface area and low mass density.

Carbon aerogels (CAs) are obtained via pyrolysis of the organic aerogels at high temperatures (500-2500 °C) in an inert atmosphere [84]. The preparation of organic aerogels begins with the preparation of wet gels which are synthesized through polycondensation of organic monomers and followed by supercritical drying. The first organic aerogel was developed by Pekala et. al. [53] in 1989 via polycondensation of resorcinol-formaldehyde with the addition of acid or base catalysts. Different organic aerogels can also be prepared by adding different monomers in the sol-gel step (i.e melamine-formaldehyde aerogels, phenol-furfural etc.)[85].

In the pyrolysis step, the organic aerogel loses its functional groups and a highly pure carbon structure is originated. CAs become electrically conductive when the pyrolysis temperature is greater than 750 °C [86], which makes them suitable for electrocatalytic applications. The electrical conductivity of CAs are in the range of 1 to 15 S/cm and their carbon structure is stable in both alkaline and acidic mediums. They have also advantages of high surface area (400-1200 m²g⁻¹), high porosity (in the mesoporous range) and low bulk density which distinguish them from other carbon-based materials. Moreover, their tunable physical and pore properties, which can be tuned by changing the synthesis parameters during sol-gel, gelation and pyrolysis steps, allow to use them in wide variety of applications. For instance, they have been studied in the literature as supercapacitors, catalyst supports, adsorbents and insulation materials [87-89].

2.5.1 N-doped Carbon Aerogels

Although carbon aerogels combine the conductivity of nanocarbon with aforementioned favorable properties, their almost inert electronic environment makes them too inert to be used directly in energy-related applications [90]. An effective way to use the carbon aerogels in energy-related materials is doping them with electrochemically active heteroatoms such as N, P, B and S [90]. Recently, many studies have revealed that N doping into carbon aerogels significantly improves their electrocatalytic activities and energy storage performances [52, 91, 92]. Moreover, it is also demonstrated that N doping enhances the adsorption properties of CAs by inducing their surface alkalinity; thus they are also promising candidates as adsorbent materials [93]. For example, recently, Yu et.al.[94] revealed the improved CO₂ adsorption capacity of N-doped carbon aerogels.

N-doped CAs can be prepared by adding various N containing compounds such as urea [95], melamine [96, 97], 3-hydroxyaniline [97], 3-hydroxypyridine [97] to the initial mixture before polycondensation. Another option to incorporate the nitrogen atom to the structure of CAs can be pyrolysing the aerogel in a nitrogen rich reactant gas (i.e NH₃ gas). Depending on the nitrogen source, composition and synthesis condition, N-doped CAs display different functional groups (i.e pyridinic N, pyrrolic N, graphitic N, pyrindinic N oxides) with different compositions.

2.5.2 N-doped Non-noble Metal Carbon Aerogels

N doped CAs have been also used as a support for noble metal ORR catalyst [98]. However, after the discovery of promising ORR activities of noble metal free carbon catalysts, more studies have focused on the use CAs as a non-noble metal catalyst support for ORR [50, 51, 90]. For example, You et.al.[90] demonstrated high ORR activities of CoO_x containing N doped CAs, which were prepared by using commercial melamine sponge, in alkaline medium. In their methodology, the melamine sponge simultaneously functioned as green N precursor for surface N doping and 3D support. The resulting Co-N-CA catalysts displayed 3D hierarchical, interconnected macro and bimodal mesoporosity (6.3 nm and <4 nm), high surface area ($1383 \text{ m}^2 \text{ g}^{-1}$), and highly dispersed, semi-exposed CoO_x nanoparticles with the diameter of 12.5 nm. Their catalysts displayed superior electrocatalytic oxygen reduction (ORR) activities comparable to the commercially Pt/C catalysts with outstanding durability.

Kreek et.al.[50] is another group who studied the ORR on cobalt-containing nitrogen-doped CAs in alkaline medium. They prepared their catalysts through the sol-gel polymerization of organic precursors (resorcinol derivatives and melamine), followed by insertion of Co by using an ion-exchange process and pyrolysis. They revealed that the N-doped Cobalt CA catalysts induce the $4e^-$ reduction of O_2 with the promising activity and high durability for ORR. Their study also showed that concentrations of the precursors used during synthesis had a large effect on the structure and physicochemical properties of the materials and the activity of the catalyst increased with increasing Co content.

Furthermore, Wang et. al.[51] studied the a three dimensional (3D) N-doped carbon aerogels with trace amount Fe (ca. 0.60 wt%) for ORR both in alkaline and acidic medium. They prepared the catalyst by using carbon aerogel as the main raw material with facile KOH activation and a solid-state pyrolysis technique. In their case, the pyrolysis temperature and trace amount of Fe played crucial roles in the ORR activity. The best catalyst displayed onset and half-potentials of 0.918 and 0.798 V vs RHE in alkaline solution and 0.801 and 0.592 V vs RHE in acidic media, respectively. The methanol tolerance and long-term stability for the catalyst were also better than those of

Pt/C. Furthermore, they displayed that the main active sites for ORR were Fe-N_x sites, and the robust 3D structure with hierarchical pores, unique chemical composition, and uniform Fe-N_x active sites in the catalyst contributed to the superior ORR performance.

2.6 Supercritical Fluids

A supercritical fluid (SCF) is a fluids which is simultaneously compressed and heated above its critical temperatures (T_c) and critical pressure (P_c). The term supercritical is generally used to denote the fluids at around their reduced temperature ($T_r = T/T_c$) in the range of 0.95-1.10 and reduce pressure ($P_r = P/P_c$) between 1.01–1.5[99]. In supercritical region, there is a single homogenous phase regardless of its pressure and temperature. As demonstrated in **Table 2.2**, SCFs have liquid-like density and gas-like viscosity. Mass transfer rates in SCFs are also significantly faster compared to that of liquid solvents, which enable easier penetration to the pores of the highly porous nanostructures.

Table 2.2 Physical properties of gases, liquids and SCFs [99]

Fluid Properties	Liquid	SCF	Gas
Diffusivity ($\text{m}^2 \text{s}^{-1}$)	10^{-9}	$2-7 \times 10^{-8}$	$1-4 \times 10^{-5}$
Density (g cm^{-3})	0.6-1.6	0.2-0.9	$0.6- 2 \times 10^{-3}$
Viscosity (Pa s^{-1})	10^{-3}	$1-9 \times 10^{-5}$	$1-3 \times 10^{-5}$

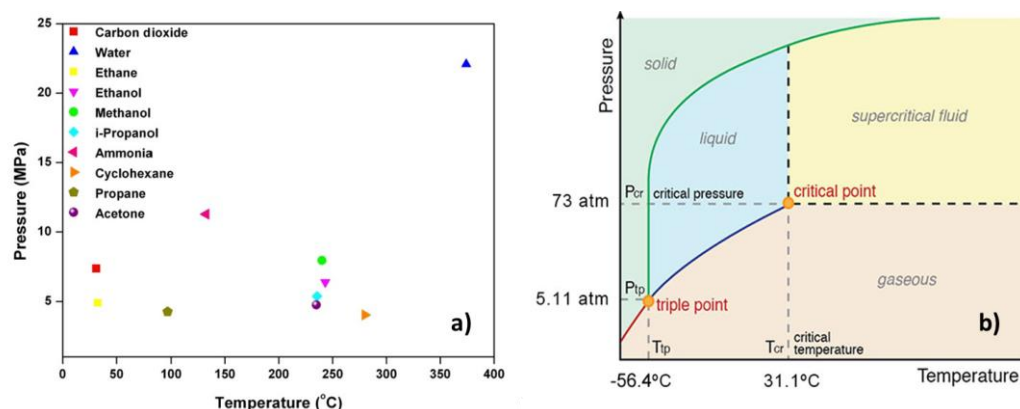


Figure 2.10 a) Critical Points of Various Fluids[99] b) Phase Diagram of CO₂

Critical points of various SCFs are displayed in **Figure 2.10-a**. Thanks to its relatively low T_c (31.1 °C) and P_c (7.38 MPa), supercritical CO₂ (scCO₂) is the most commonly used SCF. The phase diagram of CO₂ is given in **Figure 2.10-b**. scCO₂ is an attractive medium for a variety of applications due to its nice properties such as being abundant, cheap, non-toxic, and environmentally friendly.

2.6.1 Supercritical CO₂ Assisted Preparation of Supported Metal Catalyst

Many conventional techniques are available to prepare supported metal catalysts such as wet impregnation and ion-exchange. However, each of these techniques have some limitations and may not be suitable for highly porous materials such as aerogels because of the high surface tension of liquids which can cause the collapse of the nano-sized pores of the aerogels [54]. Therefore, an alternative way to synthesize aerogel supported metal catalysts is loading the desired precursor with the assistance of scCO₂. This technique is commonly called as supercritical deposition (SCD), which consists of the dissolution of a metal complex in a supercritical fluid with subsequent adsorption on a porous support followed by the conversion of the metal complex to its metal form [54-60]. Supercritical CO₂ (scCO₂) is the most commonly used supercritical fluid due to a relatively low critical temperature and other desirable characteristics such as being non-toxic, non-flammable, inexpensive and environmentally friendly. Relatively low surface tension of scCO₂ provides better penetration and wetting of the pores compared to

conventional liquid solvents while preventing the collapse of the nano-sized pores in aerogel supported catalysts during preparation.[100] Moreover, no solvent residue remains in the processed product upon depressurization, because of the gaseous state of CO₂ under ambient conditions. Up to now, SCD technique has been used to synthesize a variety of supported monometallic [62, 101-106], bimetallic [107-110], trimetallic [111] or metal oxide [112, 113] nanoparticles for various catalytic applications. Carbon supported Pt nanoparticles prepared by SCD have exhibited promising electrocatalytic properties and have outperformed commercial catalysts in some cases [61, 62]. Carbon supported Pt and Pt alloy nanoparticles prepared using SCD were shown to be very active towards the ORR [54, 62, 103-105] and higher activities were obtained as compared to electrocatalysts prepared using conventional routes [105, 114-116]. Therefore, SCD may also be an attractive route to prepare precious metal free transition metal-containing N-doped carbon (N-M-C) electrocatalysts with high activities.

Chapter 3

EXPERIMENTAL METHODOLOGY

3.1. Materials

Resorcinol (99%), acetone (99.9%) and cobalt (III) acetylacetonate (99.99% trace metal basis) were purchased from Sigma-Aldrich. Sodium carbonate (99.99%) was purchased from Merck and formaldehyde (36%) was purchased from Lachema. The chemicals were used as received. Carbon dioxide (99.998% purity) and nitrogen was purchased from Messer Air Liquide. Ammonia (%10 balanced with He) was purchased from Elite gaz.

3.2 Synthesis of Resorcinol Formaldehyde Aerogels (RFAs)

RFAs were synthesized by the sol-gel route introduced by Pekala [53] which involves the polymerization of resorcinol (R) and formaldehyde (F) with an alkali catalyst, $\text{Na}_2(\text{CO})_3$, (C) in water (W) followed by gelation. Initial molar ratios of resorcinol/catalyst (R/C), resorcinol/water (R/W) and resorcinol/formaldehyde (R/F) were set as 0.5, 200 and 0.02 during the synthesis. After the desired amount of R was dissolved in W, appropriate amounts of C and F were added with the aforementioned initial ratios and the resulting solution was mixed for 5 minutes. The solution was then transferred into airtight tubes. The tube was kept at ambient temperature for one day, at 50 °C for one day and then at 90 °C for three days. After the aging was completed, the resulting hydrogel was placed in an acetone bath for 2 days to replace the water in the pores with acetone. Finally, the acetone inside the gel was removed by supercritical extraction using scCO_2 at 13.8 MPa and 50 °C in an Applied Separations Speed SFE extraction unit resulting in RFAs.

3.3 Cobalt Loading on RFAs by Supercritical Deposition (SCD)

A custom-made stainless steel vessel with a volume of 57 mL was used in SCD experiments. The vessel was equipped with two sapphire windows (2.5 cm in diameter (Sapphire Engineering, Inc., Pocasset; MA), a T-type thermocouple assembly (Omega Engineering), a pressure transducer (Omega Engineering), a vent line, and a rupture disk assembly (Autoclave Engineers) which was sealed with poly(ether ether ketone) O-rings. For each experiment, a certain amount (between 50 and 150 mg) of Cobalt(III) acetylacetonate ($\text{Co}(\text{acac})_3$) was placed in the vessel along with a stirring bar, with 150 mg of crushed RFA. The solubility of a $\text{Co}(\text{acac})_3$ in scCO_2 at 70 °C and 20 MPa is 5×10^{-5} in terms of mole fraction [117]. A stainless steel screen was placed in the middle of the vessel in order to separate the RFA substrate and the stirring bar. The system was sealed and heated to 80 °C using a circulating heater/cooler (Cole Parmer, Model 12108-15). Then, the system was pressurized to 20 MPa with CO_2 using a syringe pump (ISCO, 260D) and was kept at these conditions until all of the precursor inside the vessel had adsorbed into the RFA. $\text{Co}(\text{acac})_3$ placed into the vessel dissolved slowly in scCO_2 and adsorbed onto the substrate from the fluid phase. Initially, a dark green color was observed through the sapphire windows, which indicates the dissolution of some of the cobalt precursor in scCO_2 . As $\text{Co}(\text{acac})_3$ in the fluid phase was adsorbed on RFA, undissolved $\text{Co}(\text{acac})_3$ at the bottom of the vessel dissolved and adsorbed on RFA. Finally, there was no $\text{Co}(\text{acac})_3$ left at the bottom of the vessel and the green color disappeared. The mass increase in the RFAs after deposition was lower than the mass of the precursor that was put in the vessel at the beginning, which indicates that some precursor should be in reduced form on the RFA. Moreover, compared to weight of Co which corresponds weight of reduced form of $\text{Co}(\text{acac})_3$ placed in the vessel, the mass increase in the RFAs after deposition was higher and this shows that and not all Co was in the reduced form on the RFA and the precursor was partially reduced during SCD. As final step, the system was depressurized slowly (0.6 MPa min^{-1}) using a needle valve (Autoclave Engineers), and the impregnated RFA sample was removed from the vessel.

3.4 Preparation of N-CA /Co-CA, / N-Co_{xxx}-CA-YYY

To obtain N-doped carbon aerogel supported cobalt catalysts, the impregnated RFA samples were subjected to pyrolysis under flowing NH_3 gas with a flow rate of 100

$\text{cm}^3 \text{min}^{-1}$ (NTP) at various temperatures ranging from 700 °C to 1000 °C in a tube furnace (Model F1125 Thermolyne Tube Furnace) for 6 h. The resulting materials are referred to as N-Co_{xxx}-CA-YYY, where xxx denotes the amount of precursor in milligrams used during SCD, YYY denotes the pyrolysis temperature in °C. Moreover, a Co-CA and an N-doped CA sample were prepared by pyrolysis in flowing N₂ and NH₃, respectively. A diagram which shows the synthesis procedure is given in Figure 1.

3.5. Preparation of U-RFA _{α} and Co_{xxx}-UCA _{α} -YYY Samples

In the Co_{xxx}-UCA _{α} -YYY catalysts, N doping was carried out by addition of urea to the initial solution before the gelation step. Firstly, different urea containing resorcinol formaldehyde aerogels (U-RFA _{α}) were prepared by changing the U:F ratio in the range of 1:3 to 1:20 in the solution where α shows the number of the sample according to its U:F ratio. For all samples, the initial mole ratios of R/C, R/W and R/(U+F)) were set as 0.5, 200 and 0.02 during the synthesis. After the desired amount of R and U were dissolved in W, appropriate amounts of C and F were added with the aforementioned initial ratios and the resulting solution was mixed for 5 minutes. For aging, acetone exchange and supercritical extraction, the same procedure described in section 3.2 were followed, and the resulting U-RFA gels were named as U-RFA₁, U-RFA₂, U-RFA₃, and U-RFA₄ for mole ratios of U:F which were 1:20, 1:10, 1:5, and 1:3, respectively. 100 mg of Co(acac)₃ precursor was loaded on 150 mg U-RFA₂ and U-RFA₄ by SCD and after pyrolysis under N₂ flow at 800 °C for 6 h, they were named as Co₁₀₀-UCA₂-800 and Co₁₀₀-UCA₄-800, respectively.

3.6 Post Acid-Base Treatments

For base treatment, a certain amount of N-Co₁₀₀-CA-800 sample was submerged in a 17.5 M NaOH solution at room temperature for 1 day. The resulting sample was rinsed with deionized water until the pH was neutralized. After the sample was dried at ambient conditions, it was treated with N₂ gas at 800 °C for 4 h. Following this, the acid treatment was performed by using 40 ml of aqua regia solution (volume ratio of HCl/HNO₃ = 3). The sample was treated with the aqua regia solution at room temperature overnight. Afterwards, the resulting sample was rinsed with deionized water until a neutral pH was attained; the sample was then left to dry under ambient conditions. As the

final step, the sample was treated with H₂ (%10 balanced with N₂) for 2 h at 800 °C using calibrated mass flow controllers (Brooks Instruments).

3.7 Physical Characterization

N₂ adsorption data were collected using a Micromeritics ASAP 2020 instrument to determine the pore sizes, pore volumes and the Brauner, Emmet and Teller (BET) surface areas of the catalysts. The N₂ adsorption/desorption isotherms were obtained with a relative pressure (P/P_0) ranging from 10^{-7} to 0.99999. Using the Barrett, Joyner and Halenda (BJH) method, the pore size distributions of the samples were determined. Pore sizes were obtained from the desorption isotherms. The t-plot method was used to obtain micropore areas and micropore volumes. Thermogravimetric analysis (TGA) was performed in a TA Instruments TGA Q500 to determine the cobalt content of the catalysts by heating the samples to 800 °C under 60 ml min⁻¹ air flow. The solid product after TGA corresponded to Co₃O₄ as determined by XRD. (supporting Info). The cobalt content in the catalyst was also determined by ICP-MS, which was performed using Agilent 7700x ICP-MS (Agilent Technologies Inc., Tokyo, Japan) equipped with octopole reaction system with Helium collision cell for spectral interference removal. Prior to measurement, metal content of the catalyst was leached in acid solution. For the acid leaching, a certain amount of sample was placed in aqua regia solution (3:1 mixture of HCl and HNO₃, respectively) and stirred for 1 day at room temperature. ICP-MS was operated with a MicroMist concentric nebulizer, a Quartz spray chamber and Ni sampling/skimmer cones. Daily instrumental optimizations were performed using 1 µg/L tuning solution for the short-term stability of the instrument. External calibration solutions were prepared by using Spex Certiprep Multi-element calibration standards. Calculations of the analytical results for ICP-MS were completed using MassHunter software. C and N contents of the catalysts were determined by ThermoScientific Flash 2000 CHNS Analyzer. XRD measurements were performed using a Bruker D8 Advance Diffractometer equipped with a Cu K α source in the 2 θ range of 20°–90° with a low background silicon sample holder. The morphologies of the samples were characterized by transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM). TEM specimens were prepared by first, grinding the samples carefully in a mortar and pestle set, and then dispersing them in ethanol to obtain a

uniform suspension. A Quantifoil 200 mesh copper TEM grid coated with a holey carbon film was then immersed in the suspension, removed with a droplet of suspension on the grid surface, allowed to dry in air, and then kept in a vacuum desiccator overnight to remove any residual moisture. High-resolution phase contrast TEM imaging and high-angle annular dark-field (HAADF) STEM imaging were performed using an FEI Talos F200X operating at an accelerating voltage of 200 kV. This instrument is equipped with a Super-X silicon drift detector (SDD) system that allows for rapid acquisition of energy-dispersive X-ray spectroscopy (EDXS) data. STEM spectrum imaging experiments were performed by acquiring full EDXS spectra at each point in a scanned area. X-ray maps for C, O, N, Co were extracted from these spectrum images by integrating the intensities in the K peaks, and the quantified chemical maps were obtained using Bruker Quantax EDS software. The surface characteristics of the catalysts were examined by X-ray photoelectron spectrometry (XPS), which was conducted using Thermo Scientific K-Alpha spectrometer with an Aluminum anode (Al K α = 1468.3 eV) at an electron take-off angle of 90° (between the sample surface and the axis of the analyzer lens). The binding energies were calibrated with respect to the C 1s peak at 284.5 eV. The peak fit analysis was performed using the XPS Advantage 5.9 data system. Raman measurements were conducted with Raman microscope (Renishaw inVia) using an excitation wavelength of 532 nm and a 50x objective. The spectra from the samples were corrected with respect to Silicon peak at 520 cm⁻¹. All spectra were recorded between 1000–2000 cm⁻¹ for 60 seconds. To avoid local heating and damaging of the samples, the laser power was kept at less than 1 mW.

3.8 Electrochemical Characterization

The electrochemical measurements were conducted using a three-electrode electrochemical cell connected to a potentiostat (Pine Instrument Company Model AFCBP1) at ambient temperature. A glassy carbon (GC) rotating disk electrode (RDE, 0.196 cm² in diameter, Pine Instruments) was used as the working electrode. A Pt wire and a Ag/AgCl electrode saturated with KCl solution (Pine Instruments) were used as the counter electrode and reference electrode, respectively. 0.1 M KOH solution was used as electrolyte. Prior to use, the RDE was polished sequentially with 0.3 and 0.05 μ m alumina slurries (Bruker) to obtain a mirror finish. The electrode was rinsed with absolute

ethanol and deionized water to remove any traces of alumina grit from the electrode surface, and the electrode was then left to dry under ambient conditions. Catalyst ink was prepared by dispersing 6 mg of catalyst powder into a solution containing milli Q water, isopropanol, and nafion solution (15 wt %) at a volume ratio of 3:1:0.05. A homogenous dispersion of the ink was obtained by sonicating for at least 30 min. Then, 10 μL of the as-prepared catalyst ink was cast onto the RDE surface with a micro-pipette, and the solvent was evaporated in air at ambient temperature, which resulted in a catalyst loading of 0.3 mg cm^{-2} . For comparison, a commercial 20 wt % Pt/C catalyst (Alfa Easer) ink was also prepared using the procedure described above and deposited onto the RDE surface with a catalyst loading of $20.1 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$. The reference electrode was calibrated before each measurement and values are reported with respect to a reversible hydrogen electrode (RHE). For the RHE calibration, a platinum electrode was used as the working electrode in a H_2 -saturated electrolyte. The potential was swept close to the thermodynamic potential for the H^+/H_2 reaction and the value of the potential where the current crossed zero was recorded as the potential for this reaction (**Figure S1**). Cyclic voltammograms (CVs) were performed with a scan rate of 50 mV s^{-1} in N_2 saturated electrolyte. The ORR activity was recorded by cathodic scans of the RDE in an O_2 -saturated 0.1 M KOH solution between 0.2 V - 1.1 V vs RHE at 5 mV s^{-1} . The rotational speed was varied from 400 rpm to 2500 rpm. Prior to the electrochemical measurement, the electrolyte was saturated with O_2 or N_2 for at least 30 min and after saturation, a blanket of O_2 or N_2 was kept over the solution surface. Before recording the data, the RDE was swept for at least for 5 cycles at a scan rate of 50 mV s^{-1} in the same potential range until the cyclic voltammogram become reproducible. The electron transfer numbers (n) were calculated by using the slopes of K-L plots at various potentials as described in Section 2.3.3. The chronoamperometry was carried out at a constant potential of 0.60 V vs. RHE in O_2 -saturated 0.1 M KOH for 30,000 s with a rotation rate of 1600 rpm.

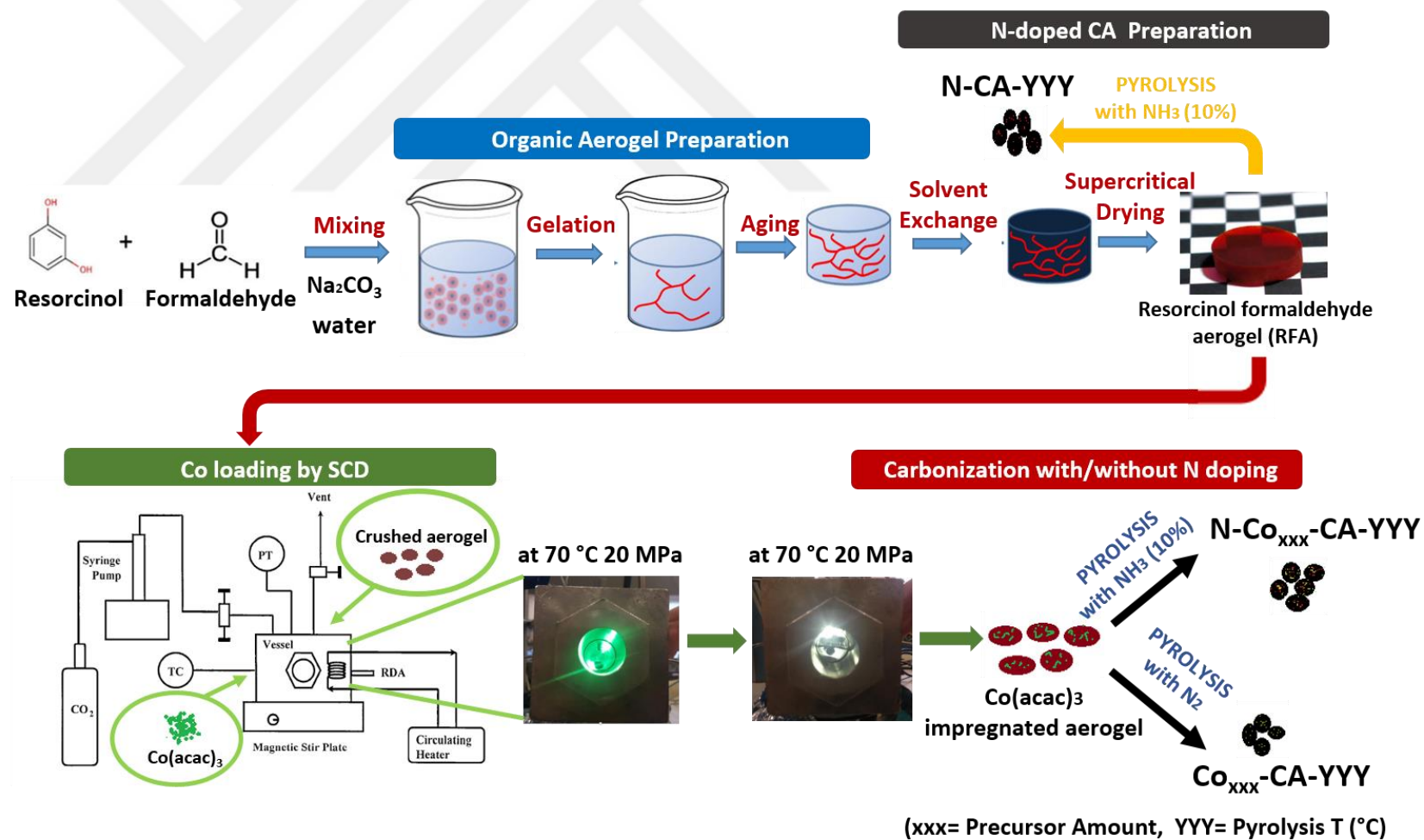


Figure 3. 1 The scheme of the scCO₂ Assisted Preparation of N-CA-YYY, Co_{xxx}-CA-YYY and N-Co_{xxx}-CA-YYY Catalysts

Chapter 4

RESULTS AND DISCUSSION

4.1 The Effect of Various Parameters on Structural and Electrocatalytic Properties

Synthetic procedures for the sample sets are described briefly in **Figure 3.1**. Four sets of samples were prepared. In the first set, N doped cobalt catalysts were prepared at three different pyrolysis temperatures ranging from 700 to 1000 °C while keeping the initial amount of Co(acac)₃ in scCO₂ constant. For each sample in the first set, 100 mg of precursor was placed into the vessel and all of the precursor was loaded into the RFAs (150 mg) by SCD. Ammonia gas (10% in He balance) was used as the N source during pyrolysis. In the second set, samples with different Co loadings were synthesized by varying the initial amount of precursor used from 50 to 150 mg during SCD. All of samples in the second set were pyrolyzed at 800 °C in NH₃ (10%) flow. In the third set, only nitrogen (N-CA) and cobalt doped (Co-CA) samples were synthesized to examine the effect of cobalt and nitrogen on the ORR separately. While for the first three set NH₃ gas was used as nitrogen source, in the fourth set, different portions of urea was added into solution before polycondensation to investigate the effect of nitrogen source on ORR activity. Cobalt loading was performed in similar to previous sets and all samples in the fourth set pyrolyzed in inert N₂ flow.

4.1.1 Effect of Pyrolysis Temperature

The elemental composition and textural properties of the samples prepared in different pyrolysis temperatures are summarized in **Table 4.1**. The bulk compositions (wt%) of C and N were analyzed by C-N-H elemental analysis while cobalt compositions were obtained by TGA. As indicated in **Table 4.1**, as the pyrolysis temperature increased

from 800 to 1000 °C, nitrogen content in the sample decreased since thermal treatment at 900 °C and above resulted in breaking up of C–N bonds and removing the nitrogen from the catalyst [48].

Table 4.1 Textural Properties and Elemental Composition of Samples Pyrolyzed in Different Temperatures Under 10% NH₃ Flow

<i>Sample</i>	<i>C</i> (wt%)	<i>N</i> (wt%)	<i>Co</i> (wt%)	<i>S</i> _{BET} (m ² g ⁻¹)	<i>D</i> _{BHJ,desorp.} (nm)	<i>V</i> _{pore} (cm ³ g ⁻¹)	<i>V</i> _{micro} (cm ³ g ⁻¹)
<i>N-Co₁₀₀-CA-700</i>	67.5 ^a	1.8 ^a	NA	587	26.7	2.8	0.10
<i>N-Co₁₀₀-CA-800</i>	78.8 ^a	1.9 ^a	17.9 ^b / 15.4 ^c	638	19.2	2.4	0.11
<i>N-Co₁₀₀-CA-900</i>	81.2 ^a	1.5 ^a	16.8 ^b	607	21.6	2.6	0.12
<i>N-Co₁₀₀-CA-1000</i>	79.1 ^a	1.0 ^a	18.3 ^b	593	20.8	2.4	0.12

^a by CHN Elemental Analysis, ^b by TGA, ^c by ICP-MS

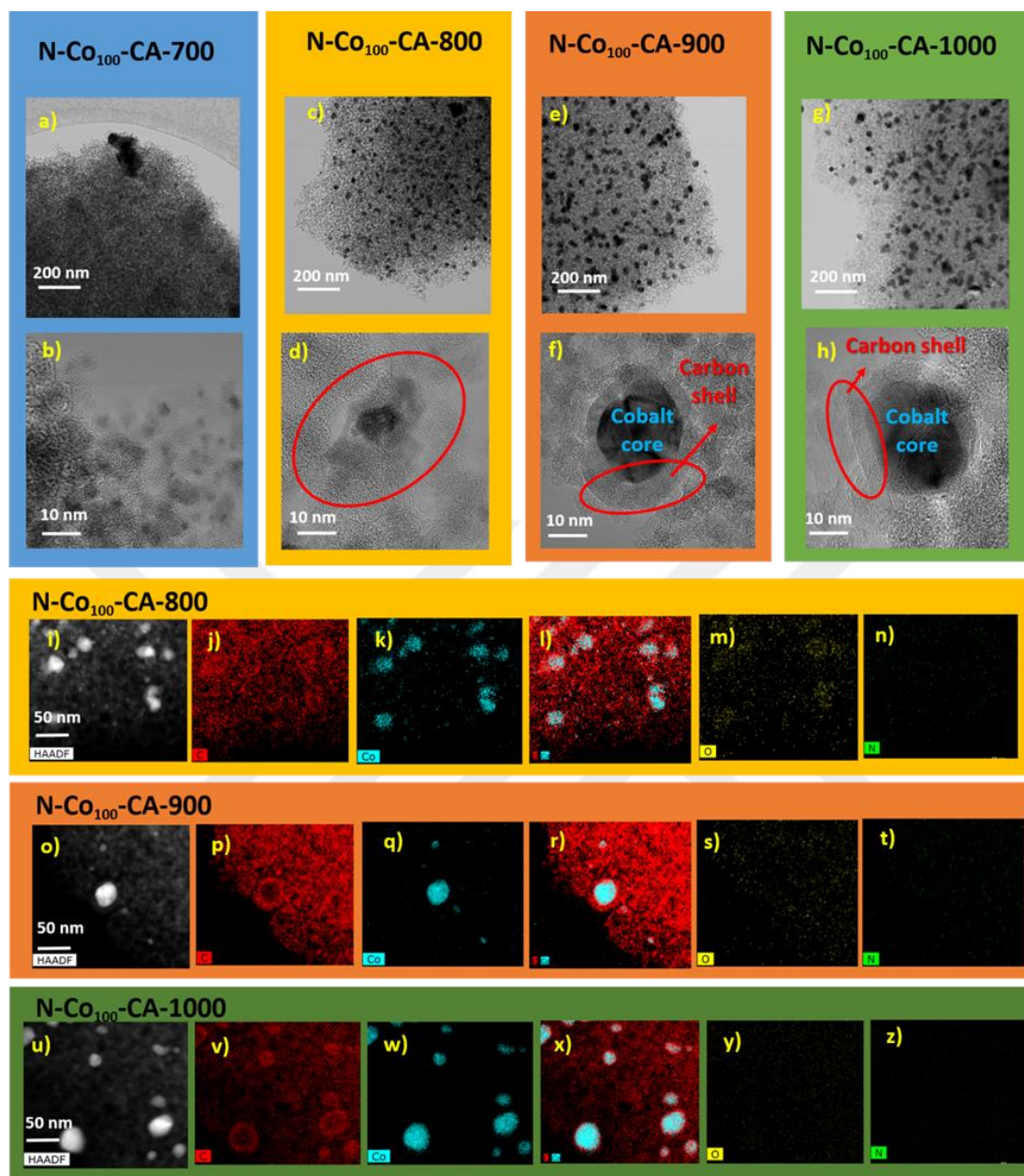


Figure 4.1 TEM Images of N-Co₁₀₀-CA-YYY, Where YYY=700°C (a-b), 800 °C (c-d) 900°C (e-f), 1000°C (g-h). HAADF-STEM Images and Their Corresponding Elemental C, Co,O,N Mapping of N-Co₁₀₀-CA-800 (i-l), N-Co₁₀₀-CA-900 (m-p), N-Co₁₀₀-CA-1000 (q-t)

Figure 4.1(a-h) are examples of the TEM images obtained from the Co₁₀₀-CA-YYY samples pyrolyzed at different temperatures under NH₃ flow. The observed morphology indicates the existence of Co nanoparticles covered by carbon shells for the samples pyrolyzed at temperatures higher than 700 °C. The lack of any clear core-shell structure

in the sample pyrolyzed at 700 °C is probably due to the insufficient carbonization of the organic aerogel which is also reflected by its lower carbon content (~67 wt%) compared to the samples pyrolyzed at higher temperatures (~80 wt%) (**Table 3.1**). Formation of core-shell structures starts at 800 °C and becomes more evident as the pyrolysis temperature increases to 1000 °C. HAADF-STEM images of the samples pyrolyzed at 900 and 1000 °C clearly illustrates the core-shell structure of these samples with their corresponding elemental mappings for Co and C. To verify the presence of core-shell nanoparticles in the sample pyrolyzed in 800 °C, the cobalt content was analyzed using TGA and ICP-MS. By ICP-MS, the weight percentage of Co in N-Co₁₀₀-CA-800 was measured as 14.3 wt% while TGA analysis revealed 17.9 wt% Co in the same sample. The likely reason for this difference is that Co nanoparticles which are encased by carbon shells could not be leached by the acid pre-treatment for ICP analysis. This is consistent with the TEM images of the sample after acid leaching in **Figure 4.2**; thus, the ICP measurements gave a lower value of the cobalt content. However, during TGA, all the carbon was removed from the samples by heating them flowing air at 800 °C; at that temperature, all the carbon is eliminated as CO and/or CO₂, and all of the cobalt in the samples is converted to Co₃O₄, as indicated by **Figure A.2**. The remaining solid product which corresponds Co₃O₄ was used to obtain the Co compositions given in **Table 4.1** with superscript “b”.

Table 4.2 Bulk and Surface Co, N Compositions of Samples Pyrolyzed in Different Temperatures

<i>Sample</i> (wt%)	<i>N_{bulk}</i>	<i>N_{surface}</i>	<i>Co_{bulk}</i>	<i>Co_{surface}</i>
<i>N-Co₁₀₀-CA-700</i>	1.83 ^a	1.69 ^b	NA	5.89 ^b
<i>N-Co₁₀₀-CA-800</i>	1.90 ^a	1.82 ^b	17.9 ^c	3.62 ^b
<i>N-Co₁₀₀-CA-900</i>	1.52 ^a	1.39 ^b	16.8 ^c	1.50 ^b
<i>N-Co₁₀₀-CA-1000</i>	1.03 ^a	0.97 ^b	18.3 ^c	0.54 ^b

^a by CHN Elemental Analysis, ^b by XPS, ^c by TGA, NA: Not Available

The surface compositions of Co and N were also analyzed by XPS and the result are tabulated in **Table 4.2** in terms of wt % with the data obtained from CHN-Elemental analysis to compare the bulk and surface composition of the samples.

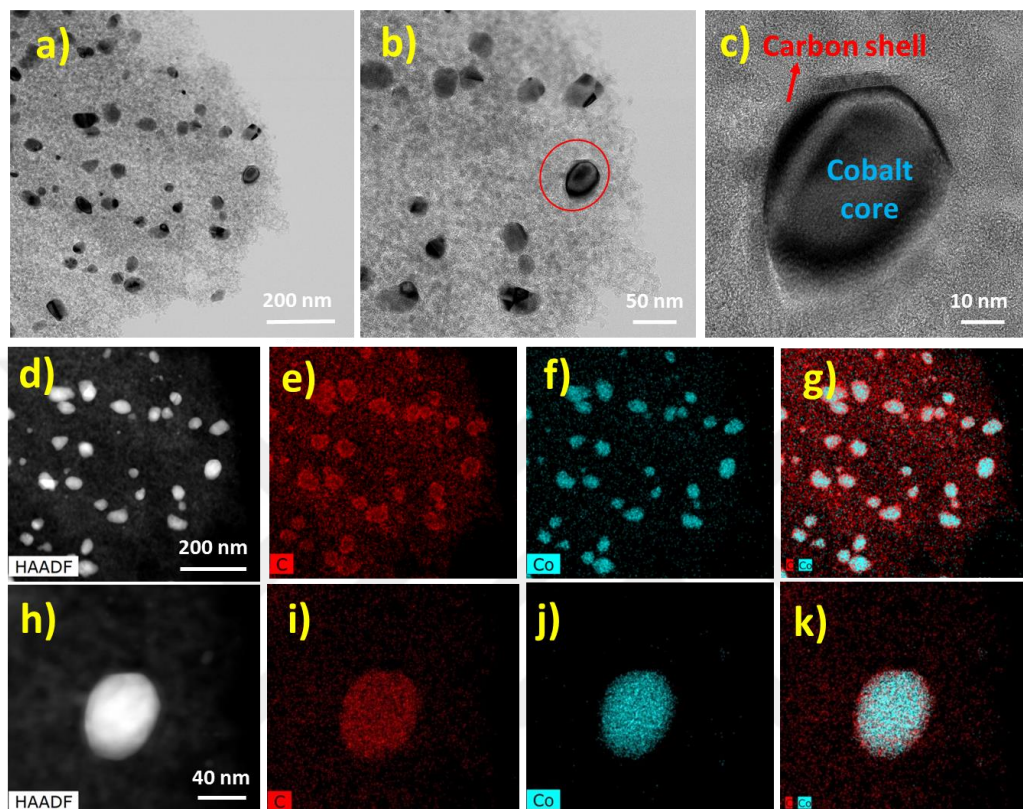


Figure 4.2 TEM Images of N-Co₁₀₀-CA-800 After Acid Treatment (a-c). HAADF-STEM image of N-Co₁₀₀-CA-800 After Acid Treatment in 200 nm(d) and 40 nm (h) Scales and Their Corresponding C and Co Elemental Mapping in 200 nm (e-g) and in 40 nm (i-j) Scales

As shown in **Table 4.2**, the surface (1.82, 1.39, 0.97 wt%) and bulk (1.90, 1.52, 1.03 wt%) nitrogen content of the samples pyrolyzed at 800, 900 and 1000 °C, respectively, are similar; this indicates that the N is distributed evenly throughout the catalyst. These data are in agreement with the N maps given in **Figure 4.1-n,t,z**. The cobalt compositions obtained from TGA and XPS showed huge differences. This is because the XPS signals of Co 2p come from only the top 1.5–2 nm on the surfaces of the catalysts [42]; and it only gives the surface cobalt fraction while TGA displays the bulk cobalt content in the

sample. Although the bulk Co compositions of the samples pyrolyzed at different temperatures were very close to one another, the surface cobalt compositions of the samples pyrolyzed at 700, 800, 900 and 1000 °C decreased in the following order of ~5.8, 3.6, 1.5, 0.5 wt%, respectively. Since no core-shell structure formed at 700 °C, the sample pyrolyzed at this temperature had the highest surface Co content. The decrease in the surface Co fraction at higher pyrolysis temperatures could be due to the increasing Co nanoparticle size.

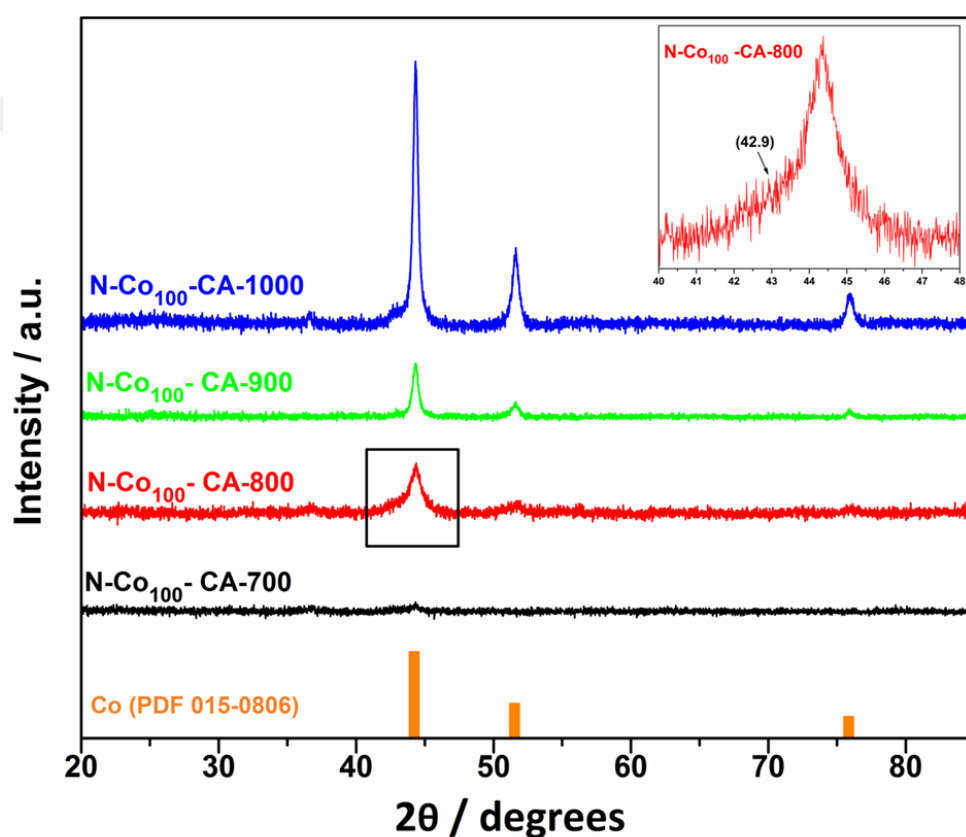


Figure 4.3 XRD Patterns of N-Co₁₀₀-CA-YYY Where YYY Indicates the Pyrolysis Temperature Under NH₃ Flow. (Inset shows the close-up pattern of rectangular area)

Figure 4.3 shows the XRD patterns of the samples which were pyrolyzed at different pyrolysis temperatures under NH₃ flow. At 700 °C, a very small diffraction signal centered around $2\theta=44.3$ is observed, which indicates that the Co nanoparticle/cluster size is at the limit of XRD detection. Figure 3 shows peaks at $2\theta=\sim 44.3^\circ$, $\sim 51.5^\circ$ and $\sim 75.9^\circ$ for N-Co₁₀₀-CA-800 which are assigned to the {111}, {200}, and {220} reflections of

face centered cubic (FCC) Co nanocrystals, respectively (PDF 15-0806). The peak at $2\theta=44.3$ appeared with a shoulder at $2\theta\sim 42.9$ indicated by the black arrow in the inset of **Figure 4.3** which was attributed to the {111} plane of Co_2N (PDF 06-0647) by Qian et al. r, however, based on its small intensity it is hard to make this assignment here. Moreover, no evidence was observed for the formation of any cobalt carbide phases.

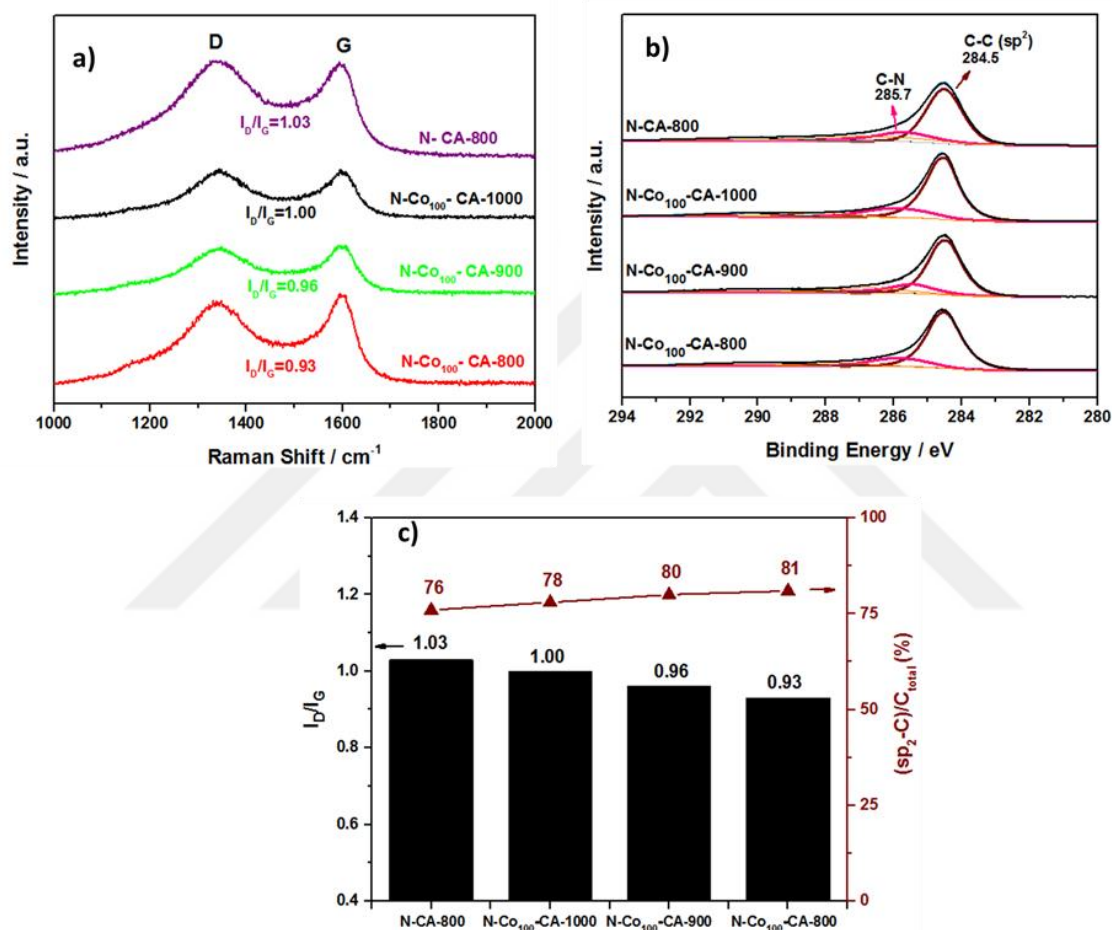


Figure 4.4 a) Raman Shifts b) High Resolution C1s Spectra of the Samples Pyrolyzed in Different Temperatures c) Intensity Ratio of the D to G Bands of the Samples(left axes) and Ratio of sp^2 Bonded Carbon Atoms to Total Carbon (right axes)

Raman microscopy revealed the D and G bands of graphitic carbon at 1357 and 1580 cm^{-1} , respectively (**Figure 4.4-a**). The D band corresponds to the diamond-like carbon structure (sp^3 bonded carbon) while the G band is due to the presence of sp^2 -bonded carbon atoms in a two-dimensional hexagonal graphitic layers [118].

The C1s spectra of the samples pyrolyzed at different temperatures (**Figure 4.4-b**) showed two distinct peaks with maximums at ~ 284.5 and 285.7 eV. The peak at ~ 284.5 eV is due to the carbon atoms that neighbor other carbon atoms in sp^2 binding environment (C–C sp^2)[82]. The peak at the higher binding energy (i.e. ~ 285.7 eV) represents the carbon atoms that are bound to more electronegative species; thus, this peak can be assigned to sp^2 carbon bound to nitrogen (N–C sp^2)[42, 82]. Thus, the C1s spectrum reveals N-functionalized carbon where the nitrogen atoms are anchored within a carbon backbone with a graphitic structure. However, we did not observe any peak at lower binding energies (~ 283 eV) which are typical for carbon atoms bound in carbide-like species [119], indicating that there are little or no cobalt carbide species in the catalysts; this is in agreement with the results obtained from XRD measurements.

Furthermore, the intensity ratio of the D to G bands is usually employed to determine the extent of graphitization. A lower I_D/I_G value is associated with a higher degree of graphitization [31]. As given in **Figure 4.4-c**, the I_D/I_G value of N-Co₁₀₀-CA-800 (0.93) compared to that of N-CA-800 (1.03) suggests that Co promotes the graphitization most probably in a catalytic manner. As the pyrolysis temperature increased, the Raman peaks became broader and the I_D/I_G value increased which indicates a lower degree of graphitization. This is probably due to the interaction of NH₃ with the surface which results in the etching of carbon aerogel. The Raman spectroscopy results are also consistent with C1s spectra of the samples where the ratio of sp^2 bonded carbon atoms to total carbon decreases with increasing pyrolysis temperature indicating lower graphitization degree (**Figure 4.4-b&c**). Moreover, an I_D/I_G ratio near one indicates low crystallinity and highly disordered nature of carbon while a value close to zero indicates high crystallinity [120]. Therefore, in **Figure 4.3**, none of the samples displayed a diffraction peak centered around 25.21° which corresponds to the graphitic (002) reflection, which is consistent with the I_D/I_G values of 0.93, 0.96 and 1.00 for the samples pyrolyzed at 800, 900 and 1000 $^\circ\text{C}$, respectively.

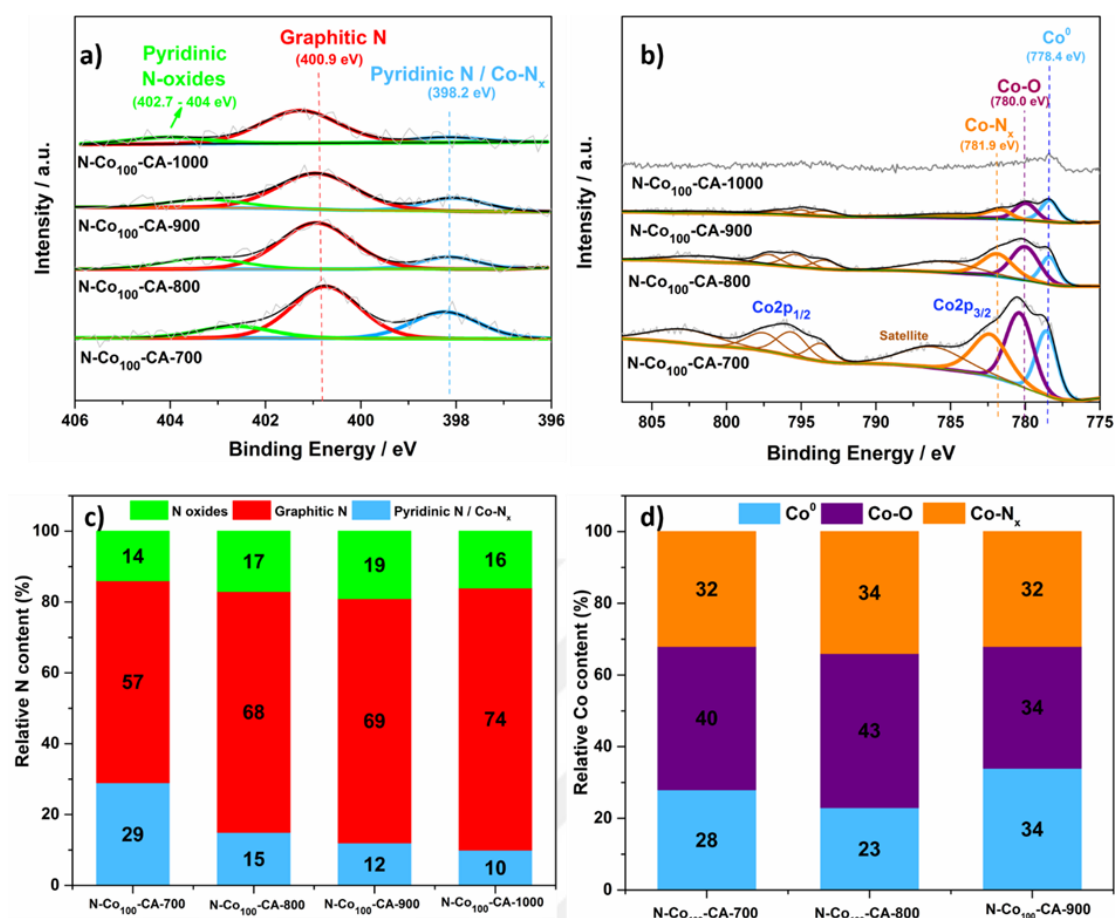


Figure 4.5 High-Resolution a) N1s b) Co2p XPS Spectra of N-Co₁₀₀-CA-YYY (YYY indicates the pyrolysis temperature under NH₃ flow) With Corresponding Relative Percentages of c) Different N Sites d) Different Co Sites

XPS was used to investigate the surface speciation. **Figure 4.5** shows the high resolution of N1s and Co2p XPS spectra of the samples pyrolyzed at different temperatures under NH₃ flow along with their fitting components. The N1s spectra of catalysts prepared at different pyrolysis temperatures (**Figure 4.5-a**) can be divided into three peaks centered at ~398.2, ~400.9, and in the peak in the range of 402.7-404 eV, which are attributed to pyridinic N (398.5 ± 0.3) [121], graphitic N (401 ± 0.3 eV) [121], and N-oxides of pyridinic N (402-405 eV) [122], respectively. It should be noted that the peak centered at ~398.2 eV might also include a contribution from nitrogen bound to the metal (Co-N_x). However, due to the little difference between the binding energy of Co-N_x and pyridinic N, it is difficult to differentiate them quantitatively using XPS [35]. Since high-resolution XPS spectrum of Co2p_{3/2} suggested the existence of Co-N_x (**Figure 4.5-b**), the peak

around 398.2 eV which appeared in N1s spectra can be considered to be a mixture of Co-N_x and pyridinic N species. The similar assignment of Co-N_x and pyridinic N species in N1s spectra was also found in the literature [123, 124]. As the pyrolysis temperature increased from 700 to 1000 °C, the graphitic N fraction increased from 57 % to 74 %, while the pyridinic N fraction decreased from 29% to 10% due to the transformation of pyridine-like N to graphite-like N species at higher pyrolysis temperatures [39]. The peak center of graphitic N species shifted to a slightly higher binding energy value (~401.2 eV) which indicates a slight shift in the electronic environment of the species. Moreover, as pyrolysis temperature increases from 700 to 1000 °C, the peak center of the pyridinic N-oxide species shifted to higher binding energy values (from 402.7 to 404 eV) which is indicative of a higher degree of oxidation at higher pyrolysis temperatures. **Figure 4.5-c** displays the high resolution Co2p spectra of the samples and their fitting components. The high resolution Co 2p spectra of the samples revealed distinct Co2p_{3/2} and Co2p_{1/2} features. The spectra of N-Co₁₀₀-CA-1000 (~ 0.19 at%) had a high noise to signal ratio due to its low cobalt content, and therefore was not deconvoluted. Co2p_{3/2} spectrum of the samples were deconvoluted into three peaks with peak maximums at ~778.4, ~780.0 and ~781.9 eV. Since both 2p_{1/2} and 2p_{3/2} components provide the same chemical information, the curve fittings were only performed for the higher intensity 2p_{3/2} components for quantitative analysis. Peaks with binding energies greater than 785 eV are not included to the curve fitting ratios due to shake-up components. The peaks located at ~778.4 eV, 780.0 ~781.9 eV were assigned to metallic cobalt [82, 125], oxo-cobalt species [125, 126] and Co-N_x species [125, 127], respectively. **Figure 4.5-d** displays the relative percentages of different cobalt sites. There is no direct correlation between pyrolysis temperature and the relative content of different Co sites indicated in **Figure 4.5-d**.

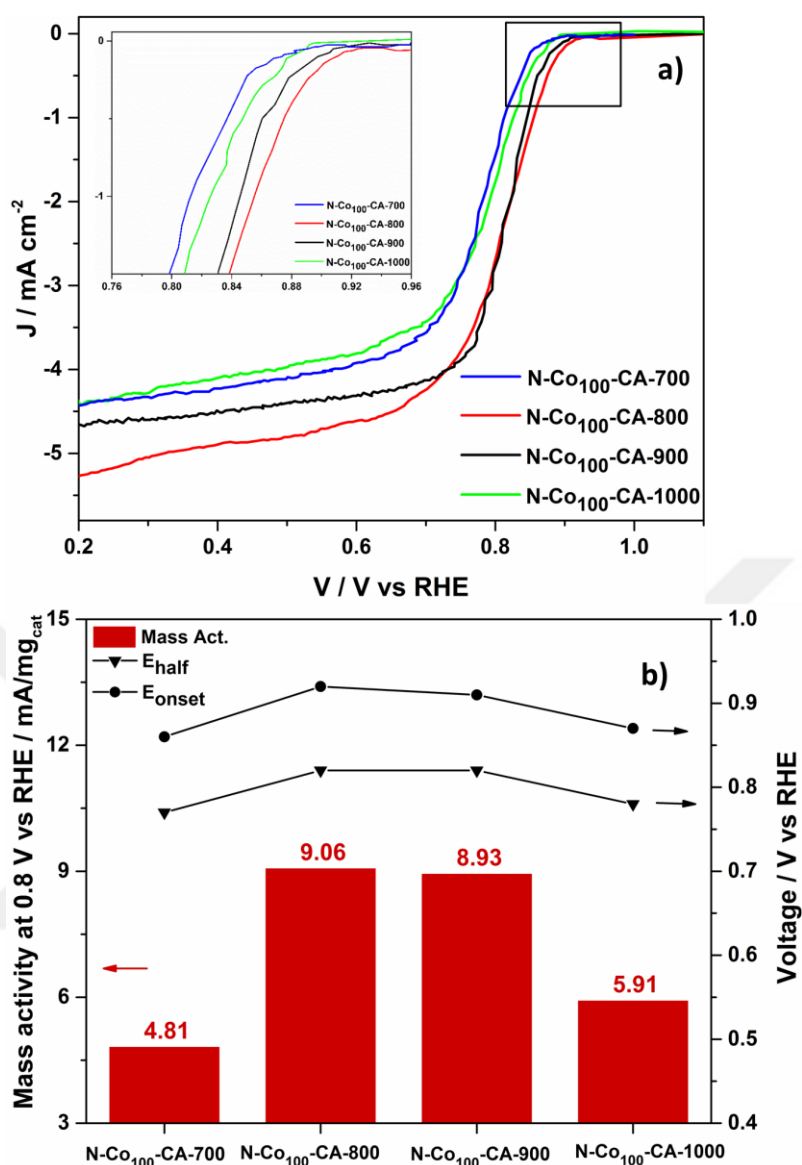


Figure 4.6 a) LSV Curves of N-Co₁₀₀-CA-YYY Where, YYY=700,800,900,1000 °C in O₂ Saturated 0.1 M KOH at 1600 rpm, 5 mV s⁻¹ b) Dependence of E_{onset} , E_{half} , and J_K (at 0.8 V vs RHE) of Catalysts on the Pyrolysis Temperature

To understand the effect of pyrolysis temperature on the ORR activity of the N-Co_{xxx}-CA-YYY catalysts, rotating-disk electrode (RDE) measurements were performed in O₂ saturated 0.1 M KOH solution. **Figure 4.6-a** shows the polarization curves of the samples pyrolyzed in NH₃ at different temperatures. As indicated in **Figure 4.6-b**, the catalysts synthesized at 800°C exhibit the highest catalytic activity based on E_{onset} , E_{half} values and

the magnitude of the mass activity at 0.8 V vs RHE; this is presumably due to the high relative content of graphitic N species (68%, **c.f. Figure 4.5-c**) which was suggested to play an important role in ORR electrocatalysis based on RDE, XPS and XAS measurements [39, 76, 128, 129]. As the pyrolysis temperature was increased from 800 to 1000 °C, the mass activity decreased (**Figure 4.6-b**) although the relative graphitic N content in the samples slightly increased (**c.f. Figure 4.5-c**). This could be due to the lower degree of graphitization observed at higher pyrolysis temperatures (**c.f. Fig. 3.4-a**) that is also consistent with decrease in the ratio of sp²-Carbon in the catalysts as shown in **c.f. Figure 4.4-c**. The degree of graphitization in the catalyst is also an important property for an electrocatalyst since it affects the electrical conductivity of the sample. The lower mass activity of the sample pyrolyzed in 700 °C can be also attributed to its relatively low carbon content (**c.f. Table 3.1**), which corresponds to the incomplete carbonization and thus to a low electrical conductivity for this sample. Moreover, we note that the lower catalytic activity of the catalysts that were prepared at 900 and 1000 °C may also be due to the lower surface areas of these samples (607 and 593 m²/g, respectively) compared to the one prepared at 800 °C (638 m²/g) because a low surface area will correspond to reduced access for O₂ molecules to the catalyst surface. However, this difference is probably within our standard deviation in surface area measurements. Various Co species including Co-O [81], Co-N_x [42, 43] and/or metallic Co [78] have been suggested as active sites for the ORR based on XPS analysis. However, since no correlation was observed between the percentages of the cobalt related sites (**c.f. Figure 4.5-d** and the mass activities of the samples prepared at different pyrolysis temperatures (**Figure 4.6-b**), there is no evidence for the role of such sites on the basis of the data obtained from these samples.

4.1.2 Effect of Cobalt Loading

The effect of cobalt and nitrogen content in the N-Co_{xxx}-CA-800 catalyst towards the ORR was also investigated. The elemental compositions of the N-Co_{xxx}-CA-800 samples, where xxx denotes the initial precursor amount used during SCD, are given in **Table 3.3**.

Table 4.3 Textural Properties and Elemental Composition of Samples Having Different Cobalt Loadings

Sample	C (wt%)	N (wt%)	Co (wt%)	S_{BET} ($m^2 g^{-1}$)	$D_{avar.}$ (nm)	V_{pore} ($cm^3 g^{-1}$)	V_{micro} ($cm^3 g^{-1}$)
N-Co ₅₀ -CA-800	81.7 ^a	1.7 ^a	8.4 ^a	655	17.2	2.4	0.10
N-Co ₇₅ -CA-800	77.5 ^a	1.6 ^a	14.9 ^a	633	17.5	2.3	0.10
N-Co ₁₀₀ -CA-800	78.8 ^a	1.9 ^a	17.9 ^b	638	19.2	2.4	0.11
N-Co ₁₅₀ -CA-800	70.9 ^a	1.5 ^a	23.7 ^b	NA	NA	NA	NA

^a by CHN elemental analysis, ^b by TGA, NA: Not Available

The data in **Table 4.3** showed that an increase in the initial cobalt precursor amount has very little effect on the nitrogen content, while the Co content correlates with the initial precursor amount. Increasing the initial Co(acac)₃ amount from 50 to 150 mg resulted in the increase of the final Co loading from 8.4 wt. % to 23.7 wt. %.

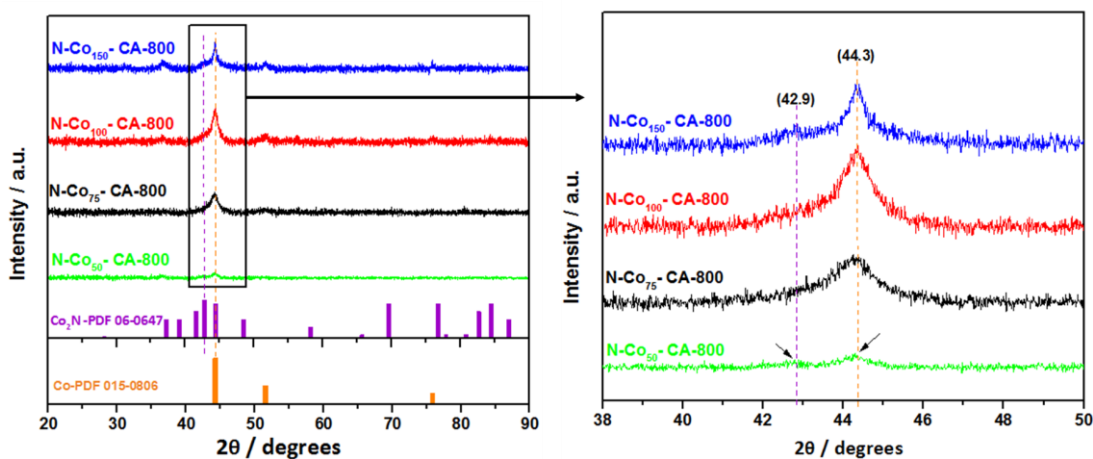


Figure 4.7 XRD Patterns of N-Co_{xxx}-CA-800 Where xxx Indicates the Initial Precursor Amount Used During SCD (close-up pattern of rectangular area is given in the figure at the right hand side)

Figure 4.7 displays the XRD pattern of the family of N-Co_{xxx}-CA-800 catalysts. As cobalt loading increases, the peaks appeared at 44.3° , which is assigned to the {111} plane of Co according to PDF 15-0806, become sharper and this indicates higher particle sizes at higher cobalt loadings as expected. The shoulders around 42.9° that are observed in close up pattern were attributed to the {111} plane of Co₂N (PDF 06-0647) by Qian et al. [42].

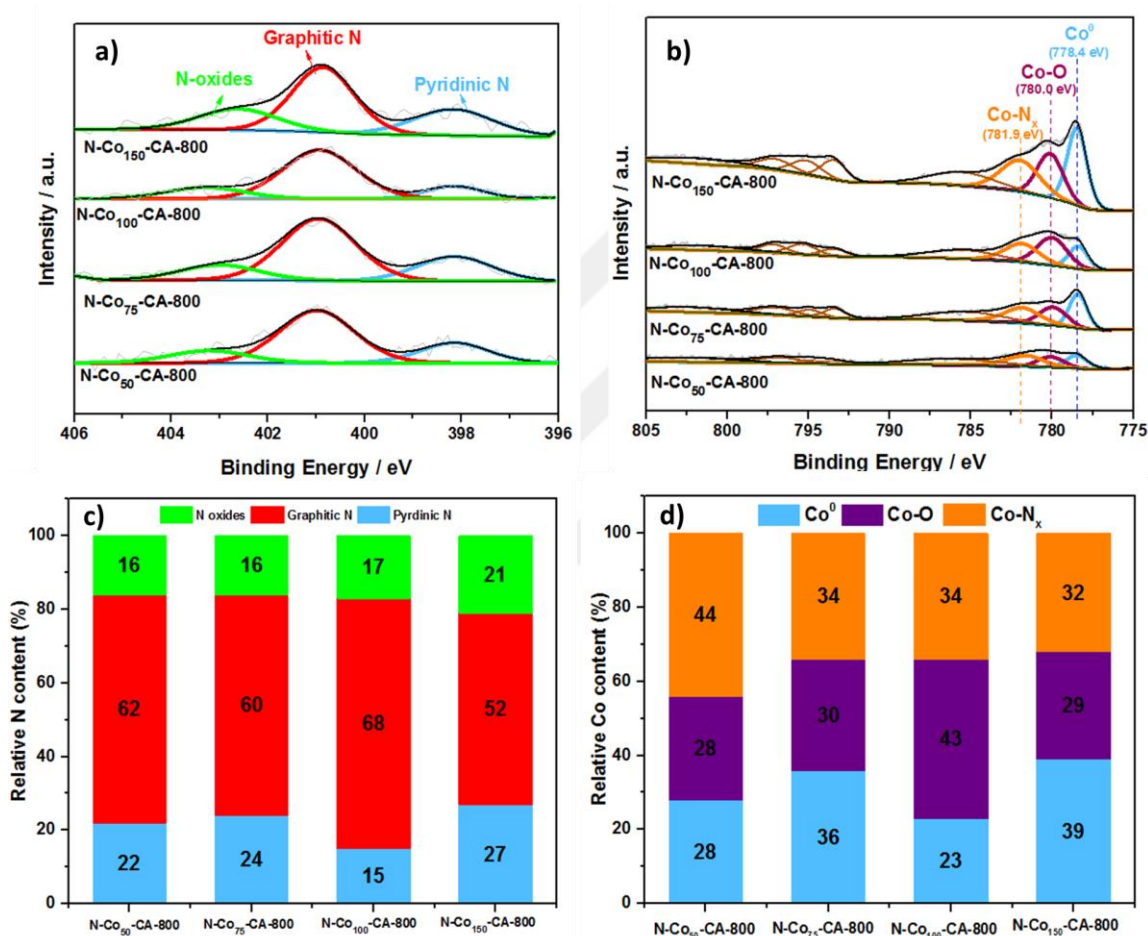


Figure 4.8 High Resolution a) N1s b) Co2p Spectra of the Family of N-Co_{xxx}-CA-800 Catalysts and Relative Percentages of c) Different N Sites d) Different Co Sites

The high resolution N1s and Co2p spectra of the samples are given in **Figure 4.8**. Changing cobalt loading did not affect the percentages of N-sites notably as shown in **Figure 4.8-b**. N-Co₁₀₀-CA-800 has the greatest graphitic N fraction (68%) and lowest pyridinic N fraction (15%) among all set. Increasing the Co loading to 23.7 wt% (N-

Co₁₅₀-CA-800) caused the decrease in the graphitic N sites to 52% as indicated in **Figure 4.8-b**. **Figure 4.8-c** shows the Co2p spectra of the samples prepared having different Co compositions and their deconvoluted components. Altering the Co content did not affect the peak positions of any sites. Relative Co contents of different Co sites were given in **Figure 4.8-d** and no direct correlation was obtained between cobalt loading and percentages of the cobalt sites.

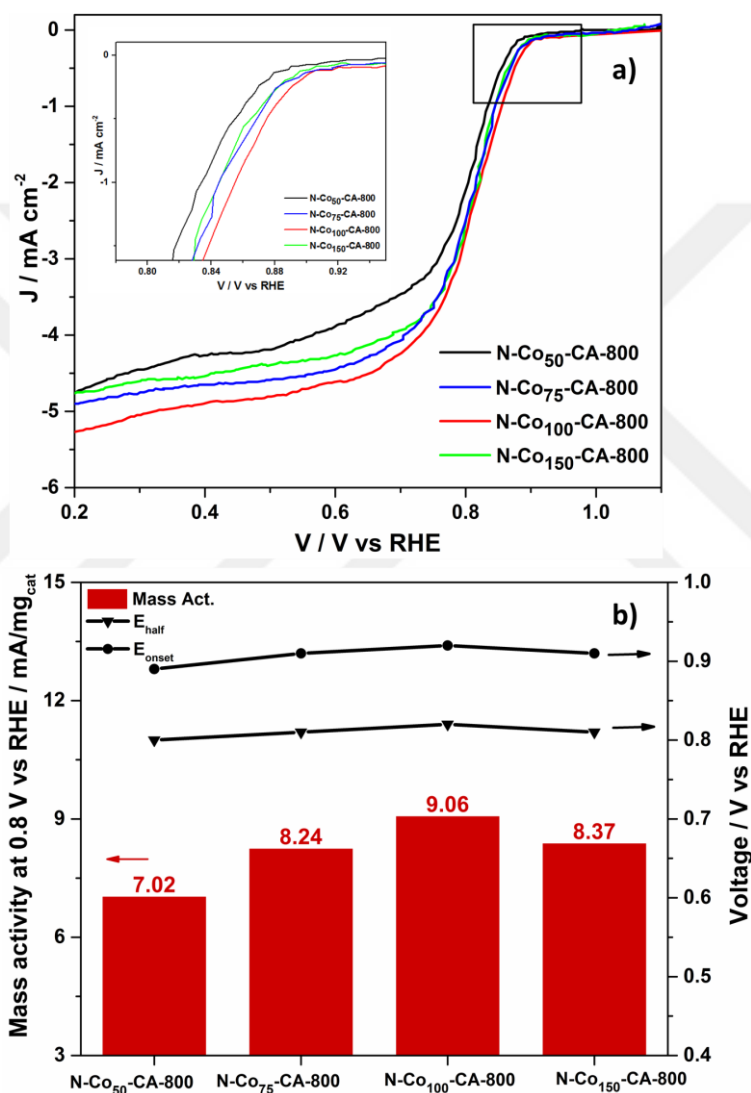


Figure 4.9 a) LSV Curves of the Family of N-Co_{xxx}-CA-800 Catalysts in O₂ Saturated 0.1 M KOH at 1600 rpm, 5 mV s⁻¹ b) Dependence of E_{onset}, E_{half}, and Mass Activity (at 0.8 V vs RHE) of Catalysts on the Cobalt Loading

Figure 4.9-a displays the ORR curves of the samples having different cobalt contents. As the cobalt content increased from 8.4 wt.% (N-Co₅₀-CA-800) to 17.9 wt. % (N-Co₁₀₀-CA-800), the mass activity also increased from 7.02 to 9.06 mA/mg_{cat}, respectively, while a further increase in the Co wt.% to 23.7 wt.% (N-Co₁₅₀-CA-800) resulted in a decrease in the mass activity to 8.37 mA/mg_{cat} (**Figure 4.9-b**). This shows that may be an optimum in Co content associated with the ORR activity even though the changes were not very pronounced.

4.1.3 Effect of Presence of Cobalt and Nitrogen

We also synthesized samples without nitrogen (Co₁₀₀-CA-800) and without cobalt (N-CA-800) to investigate the effect of cobalt and nitrogen on ORR activity.

Table 4.4 Textural Properties and Elemental Composition of Samples without Co and without N

Sample	C (wt%)	N (wt%)	Co (wt%)	S_{BET} $(m^2 g^{-1})$	$D_{avar.}$ (nm)	V_{pore} $(cm^3 g^{-1})$	V_{micro} $(cm^3 g^{-1})$
Co ₁₀₀ -CA-800	77.7 ^a	-	17.0 ^b	661	14.8	2.5	0.11
N-Co ₁₀₀ -CA-800	78.1 ^a	1.90 ^a	17.9 ^b	638	19.2	2.3	0.11
N-CA-800	78.5 ^a	4.30 ^a	-	892	16.2	3.6	0.20

^a by CHN elemental analysis, ^b by TGA

The textural properties and the elemental compositions of the samples are given in **Table 4.4**. There was no significant difference between surface areas (661 m²/g for Co₁₀₀-CA-800, 638 m²/g for N-Co₁₀₀-CA-800) and cobalt loadings of Co₁₀₀-CA-800 and N-Co₁₀₀-CA-800 catalysts whereas surface area of N-CA-800 (892 m²/g) was much greater.

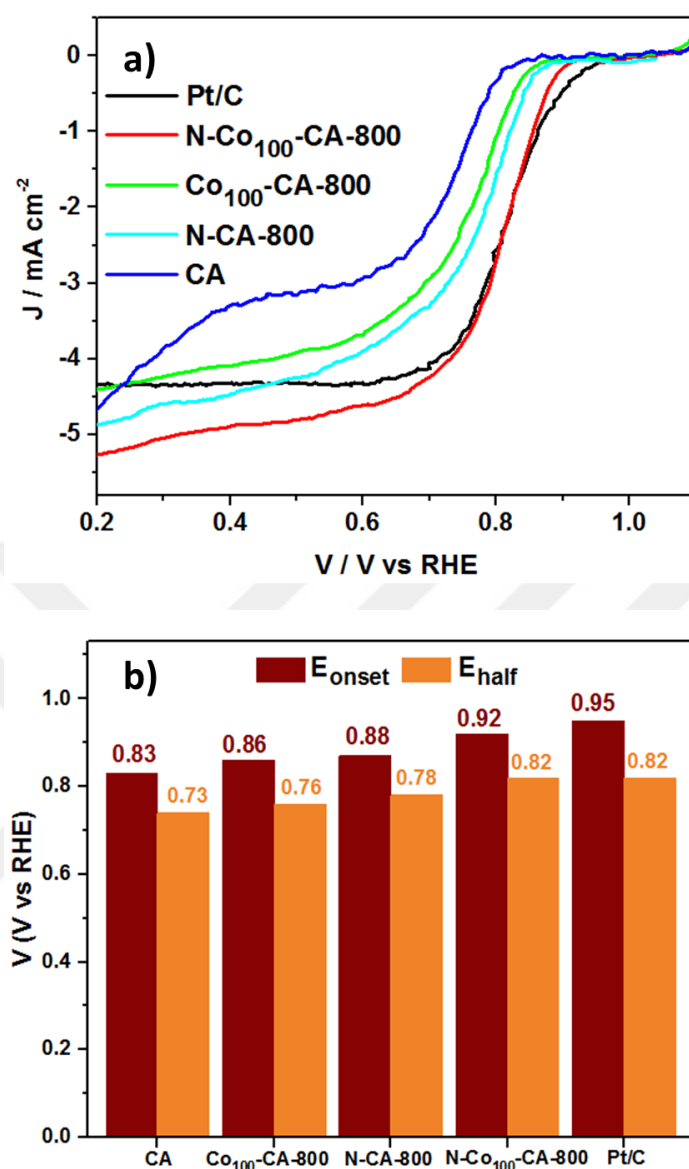


Figure 4.10 a) RDE Curves of CA, N-CA-800, Co₁₀₀-CA-800, N-Co₁₀₀-CA-800 and Pt/C at 1600 rpm and 5 mV s⁻¹ in 0.1 M KOH Solution. (Catalyst loadings of synthesized catalysts were 0.3 mg_{cat}/cm² while for Pt/C, loading was 20 μg_{Pt}/cm²)
 b) Their ORR Onset Potential (E_{onset} , defined as the potential when the cathodic current reaches 0.1 mA/cm²) and the Half-wave Potential (E_{half}) Values

Figure 4.10-a displays the RDE curves of the CA, N-CA, Co-CA and N-Co-CA samples in O₂ saturated 0.1 M KOH solution at 1600 rpm with a scan rate of 5 mV/s. The onset potential (where the cathodic current reaches 0.1 mA/ cm²) of the N-Co₁₀₀-CA-800

catalyst (0.92V vs RHE) was higher than that of N-CA-800 (0.88 V vs RHE) and Co₁₀₀-CA-800 (0.86 V vs RHE) as indicated in **Figure 4.10-b**. The onset potential of N-Co₁₀₀-CA-800 was close to that of commercial Pt/C catalyst (0.95 V vs RHE) in alkaline media, which demonstrates a promising ORR activity.

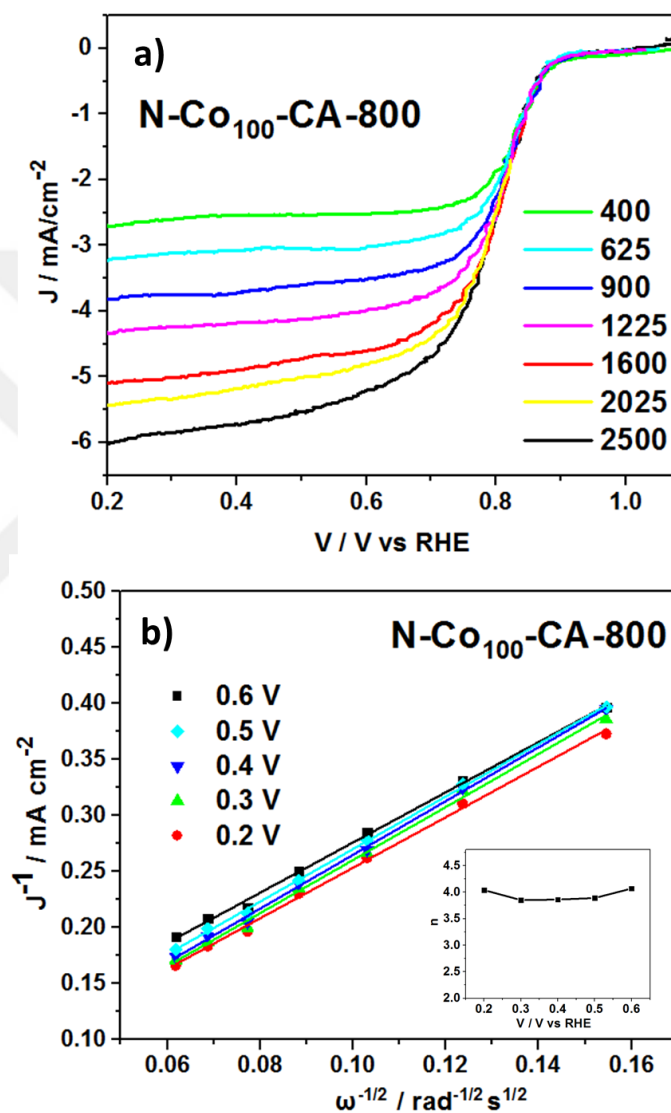


Figure 4.11 a) Polarization Curves of N-Co₁₀₀-CA-800 at Different Rotating Speeds. b) Koutecky–Levich Plots of N-Co₁₀₀-CA-800 at Different Electrode Potentials Obtained from (a). The Inset Shows the Dependence of Electron Transfer Numbers (n) on the Potential

RDE tests were further performed with rotation speeds ranging from 400 to 2500 rpm to examine the reaction kinetics for all of the studied catalysts (**Figure 4.11-a, Figure A.3**). As rotating speed increases, the limiting current density increases, which indicates a reduced diffusion length at higher speeds. The corresponding Koutecky–Levich (K–L) plots of the N-Co₁₀₀-CA-800 within the potential range from 0.2 to 0.6 V vs. RHE are given in **Figure 4.11-b**. At all potentials, the K-L Plots of N-Co₁₀₀-CA-800 show good linearity with stable slopes, suggesting first order reaction kinetics towards ORR with respect to the concentration of dissolved oxygen.

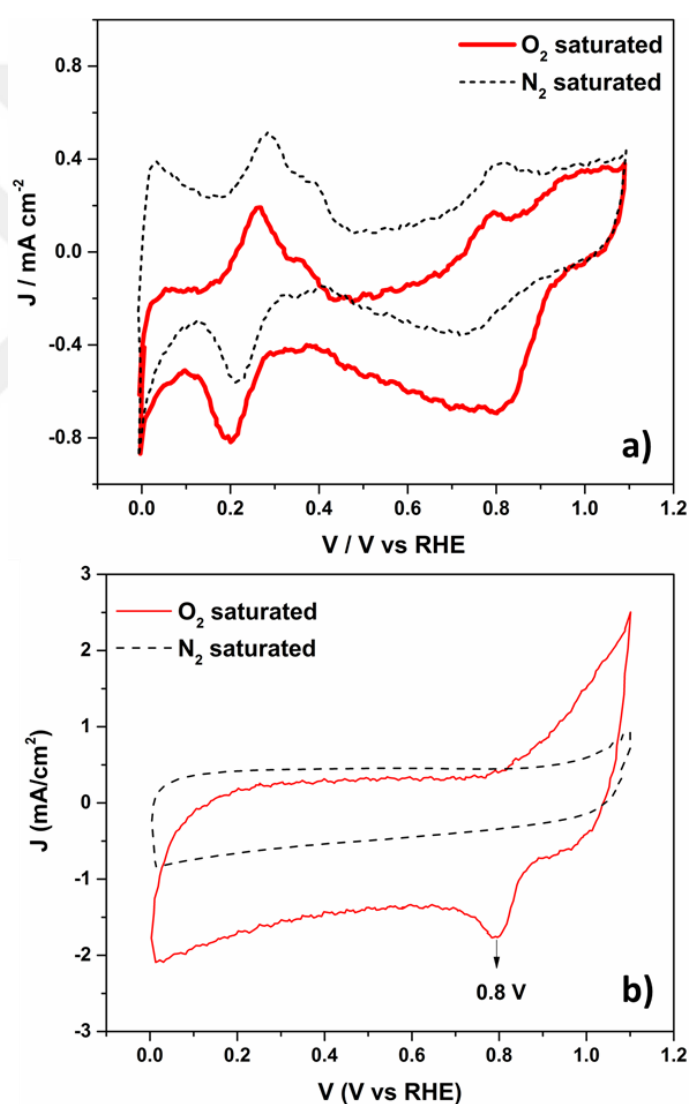


Figure 4.12 a) CVs of a) Pt/C (%20) b) N-Co₁₀₀-CA-800 in O₂-or N₂-saturated 0.1 M KOH Solutions

Figure 4.12 displays the CV curves of both Pt/C (20%) and N-Co100-CA-800 in both N₂ and O₂ saturated electrolyte. The CV results also indicate that a well-defined cathodic peak for O₂ reduction is observed at 0.8 V (vs RHE) for N-Co100-CA-800 catalyst, which is similar to that observed in the O₂ saturated CV of Pt/C (**Figure 4.12-a&b**). This reveals that the N-Co100-CA-800 catalyst exhibits pronounced electrocatalytic activity toward the ORR, while it shows a featureless quasi-rectangular voltammogram in an N₂ saturated solution.

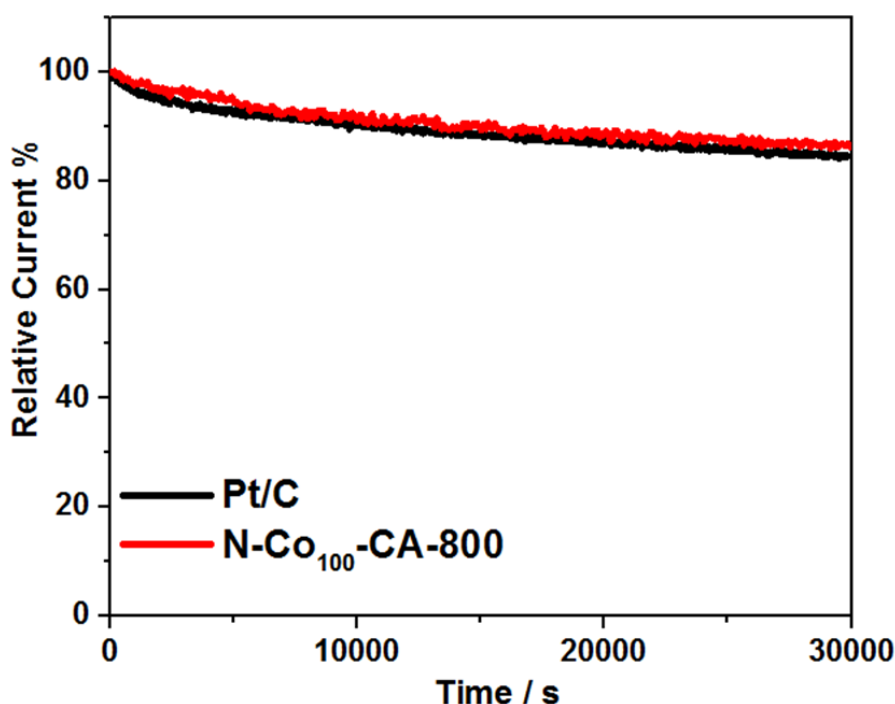


Figure 4.13 Normalized *i*-*t* Chronoamperometric Responses of N-Co₁₀₀-CA-800 and Pt/C at 0.6 V versus RHE in O₂-saturated 0.1 M KOH at a Rotating Rate of 1600 rpm

Durability is also of great significance for practical utilization of an electrocatalyst. In addition to its high catalytic activity for ORR, N-Co₁₀₀-CA-800 also exhibited good stability for ORR. As presented in **Figure 4.13**, the chronoamperomogram of the N-Co₁₀₀-CA-800 showed negligible performance attenuation after nearly 8 hours of continuous operation at 0.6 V vs. RHE, which is similar to but slightly better than the performance of commercial Pt/C in continuous operation. This demonstrates the good stability of Co- N-Co₁₀₀-CA-800 towards ORR.

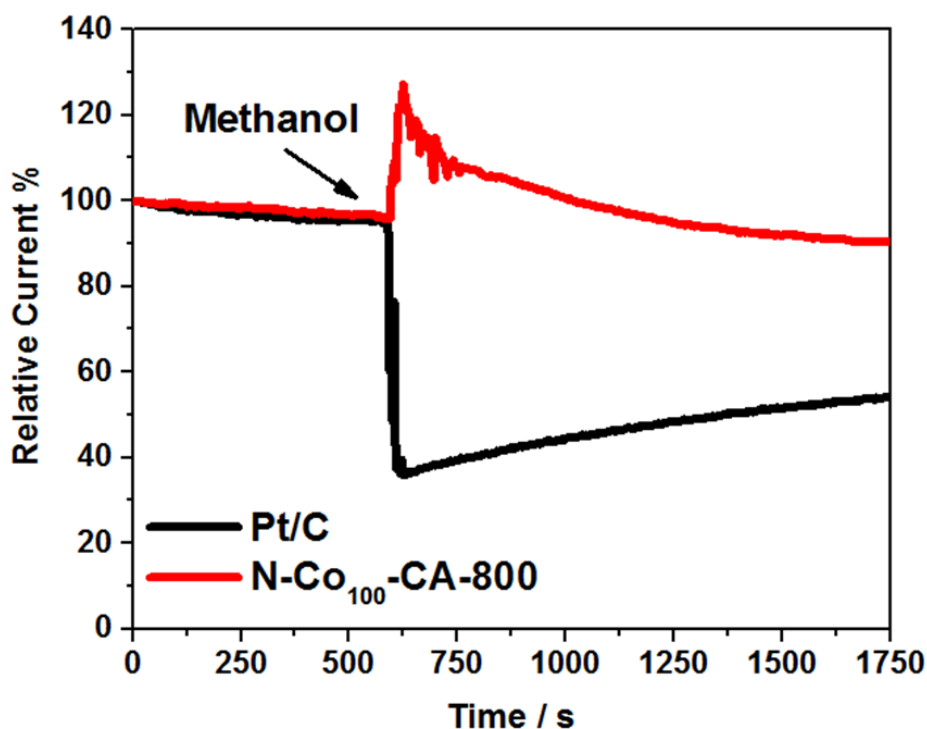


Figure 4.14 Normalized i - t Chronoamperometric Responses of N-Co₁₀₀-CA-800 and Pt/C at 0.6 V vs RHE in O₂-saturated 0.1 M KOH Solution in the Presence of Methanol. (The arrow indicate the point at which 50 ml methanol is added into the 150 ml O₂-saturated 0.1 M KOH solution (at 600 s))

The robustness of the ORR catalysts is also an important parameter in real world applications. Thus, ORR catalysts must show a tolerance to contaminant poisoning (such as methanol) during electrochemical operation. Since Pt is known to be vulnerable to methanol poisoning, an immediate drop in the relative current is observed for Pt/C in O₂-saturated KOH solution with the addition of methanol at the 600 s of the chronoamperometric experiment as illustrated in **Figure 4.14**. The relative current then slowly started to increase and reached a value ~50 % lower (at $t=1750$ s) than the relative current value before the addition of methanol. On the other hand, the addition of methanol resulted in a sudden increase of the relative current for Co- N-Co₁₀₀-CA-800 due to methanol oxidation which was followed by a slow decrease in the relative current which eventually reached the value before the addition of methanol (at $t=1750$ s). This indicates the remarkable tolerance of Co- N-Co₁₀₀-CA-800 to methanol poisoning.

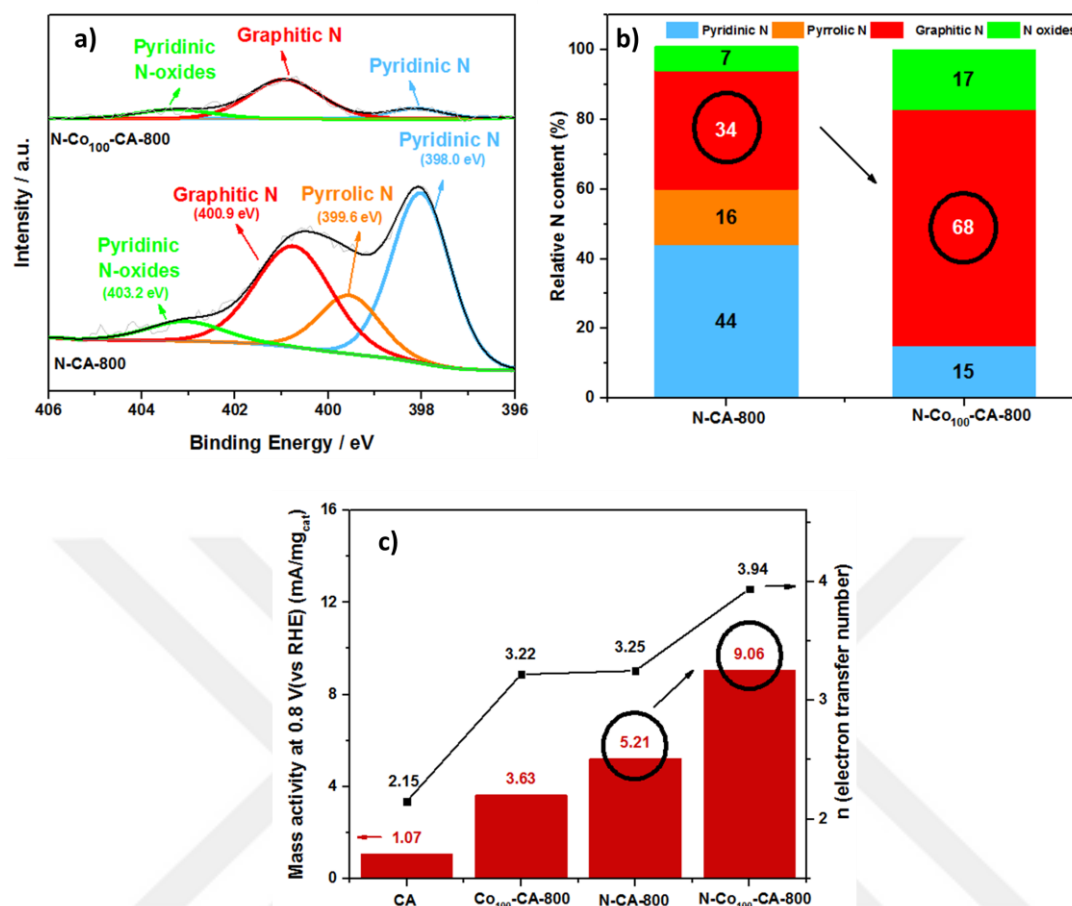


Figure 4.15 High-Resolution XPS Spectra of a) N1s Spectra of N-CA-800 and N-Co₁₀₀-CA-800 and b) Their Relative N Content (%). c) The number of Electrons Transferred (n) Calculated at 0.5 V vs RHE and the Mass Activity (J_K at 0.8 V vs RHE) of the Samples

The surface speciation in N-Co₁₀₀-CA-800, Co₁₀₀-CA-800 and N-CA-800 were investigated using XPS to elucidate the active site(s) associated with the ORR. **Figure 4.15-a** displays the high resolution N1s spectra of N-CA-800 and N-Co₁₀₀-CA-800 and **Figure 4.15-b** shows their relative N contents. Although the bulk nitrogen content of N-CA-800 (4.30 wt%) was much higher than that of N-Co₁₀₀-CA-800 (1.90 wt%)(c.f. **Table 4.4**), the activity of N-CA-800 was much lower. This indicates that N doping position and its local chemical environment are the parameters which strongly affect the ORR activity rather than bulk N loading [28]. While pyrrolic N sites at 399.6 eV [29] appeared in the spectra from N-CA-800, they were absent in the N-Co₁₀₀-CA-800. Instead, the

percentage of graphitic N sites was doubled in N-Co₁₀₀-CA-800 (68%) as compared to N-CA-800 (34%), which was correlated with nearly doubled mass activity of N-Co₁₀₀-CA-800 from 5.21 to 9.06 mA/mg_{cat} (at 0.8 V vs RHE) as indicated in **Figure 4.15-c**. It seems that the presence of cobalt promoted the formation of graphitic N centers, which is in accordance with some of the studies literature [130] and the graphitic N sites play an important role in ORR electrocatalysis [80]. It is fair to say that the percentage of pyridinic N-oxides was also increased in N-Co₁₀₀-CA-800 sample compared to the N-CA-800 sample. Therefore, their possible contribution to the catalytic activity cannot easily be overruled. **Figure 4.15-c** also displays the electron transfer number (*n*), which is obtained from the analysis of the slope of the K-L plots at 0.5 V vs RHE. With the addition of cobalt, the electron transfer number of the catalyst increased from 3.25 (N-CA-800) to 3.94 (N-Co₁₀₀-CA-800) which indicates that the presence of cobalt in N-doped catalyst is crucial to promote a four electron pathway for the ORR.

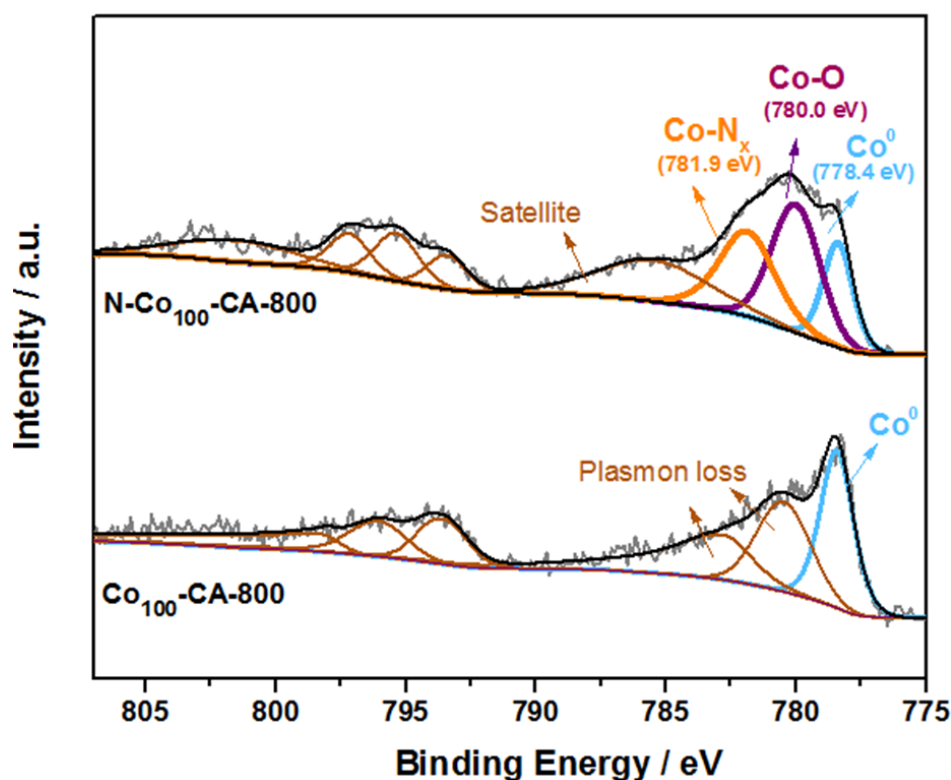


Figure 4.16 Co₂p Spectra of Co₁₀₀-CA-800 and N-Co₁₀₀-CA-800

Figure 4.16 shows the Co2p spectra of Co₁₀₀-CA-800 and N-Co₁₀₀-CA-800. The Co2p_{3/2} spectra of Co₁₀₀-CA-800 are fitted with an asymmetric main peak at ~778.4 eV and two plasmon loss peaks at ~2.5eV and ~4.9 eV above the main peak, which correspond to the typical spectral features for metallic cobalt [126]. The peak with a higher binding energy is assigned as a plasmon loss in Co₁₀₀-CA-800; this was not attributed to Co-O species since the spectrum from this sample did not show any satellite features around 786 eV which is associated with oxides [126]. While the Co₁₀₀-CA-800 had only metallic cobalt sites, N-Co₁₀₀-CA-800 manifested a broader photoelectron hump between 777 and 785 eV which was deconvoluted into three peaks centered at 778.4 eV, 780.0 eV and 781.9 eV which were assigned to metallic cobalt, Co-O and Co-N_x species, respectively (**Figure 4.16**). Since the X-ray diffraction did not show any unambiguous evidence for the presence of Co-O and N-Co_x species, they are believed to exist in highly dispersed form in the N-Co₁₀₀-CA-800 or in crystalline form smaller than the detection limit of the XRD. Along these lines, the lower activity of Co-CA-800 as compared to N-Co₁₀₀-CA-800 implies that the sites other than metallic cobalt are responsible for the higher ORR activity.

4.1.4 Effect of Nitrogen Source

The elemental composition (wt%) of the U-RFAs prepared with different U:F ratios are given in **Table 4.5**. As U:F ratio decreases, N content in the organic aerogel decreased as expected.

Table 4.5 Elemental Results of Different U-RFAs Obtained by CHN Analysis

Sample	U:F	N	C	H
U-RFA ₁	1:20	1.9	57.0	4.5
U-RFA ₂	1:10	3.2	58.4	4.6
U-RFA ₃	1:5	3.9	57.2	4.7
U-RFA ₄	1:3	4.2	59.8	5.1

After Co was loaded on U-RFA₂ and U-RFA₄ by SCD, they were pyrolyzed under N₂ flow at 800 °C, and Co₁₀₀-UCA₂-800 and Co₁₀₀-UCA₄-800 are obtained, respectively. The EDX results of these samples in terms of both at% and wt% are given in **Table 4.6**. Co₁₀₀-UCA₄-800 had higher relative N, Co and O content while its relative C content was lower compared to Co₁₀₀-UCA₂-800.

Table 4.6 EDX Results of Co₁₀₀-UCA₂-800 and Co₁₀₀-UCA₄-800

	Co ₁₀₀ -UCA ₂ -800		Co ₁₀₀ -UCA ₄ -800	
	norm. wt%	norm. at%	norm. wt%	norm. at%
C	88.21	95.74	80.39	91.49
N	0.58	0.54	0.83	0.81
O	2.08	1.69	5.38	4.60
Co	9.12	2.02	13.40	3.11

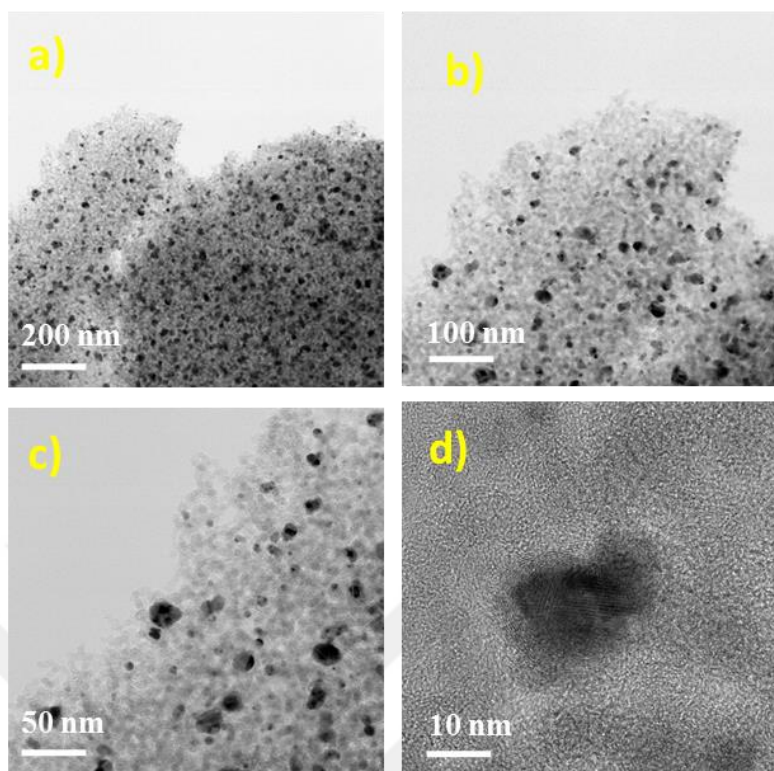


Figure 4.17 TEM Images of $\text{Co}_{100}\text{-UCA}_2\text{-800}$ in Different Magnifications

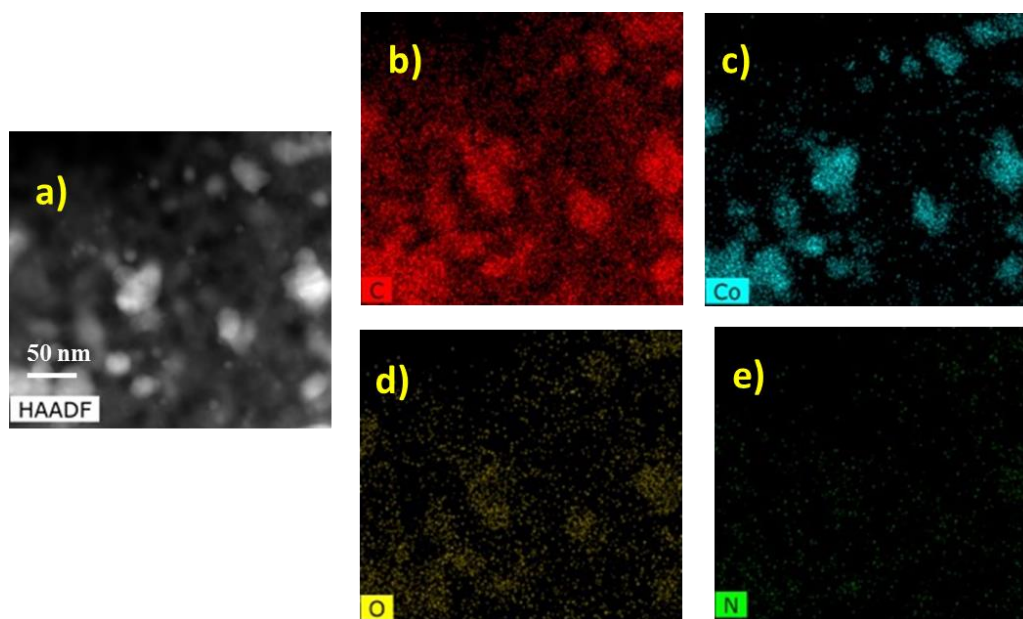


Figure 4.18 HAADF-STEM Image and Its Corresponding Elemental C, Co, O, N Mapping of $\text{Co}_{100}\text{-UCA}_2\text{-800}$

Figure 4.17 displays the TEM images of Co₁₀₀-UCA₂-800 in different scales. Co nanoparticles in the range of 10- 30 nm distributed on the carbon support can be seen in **Figure 4.17**. No core-shell structure was observed in this sample. **Figure 4.18** shows the HAADF-STEM image of Co₁₀₀-UCA₂-800 catalyst, and its corresponding elemental C, Co, O, N mapping. N atoms were homogenously distributed through the sample as shown in **Figure 4.18-e**. O atoms were also homogenously distributed through the sample but it was hard to distinguish whether the O signals observed in **Figure 4.18-d** comes from the carbon support or the cobalt oxides in the carbon support (if there is any) by just looking the **Figure 4.18**.

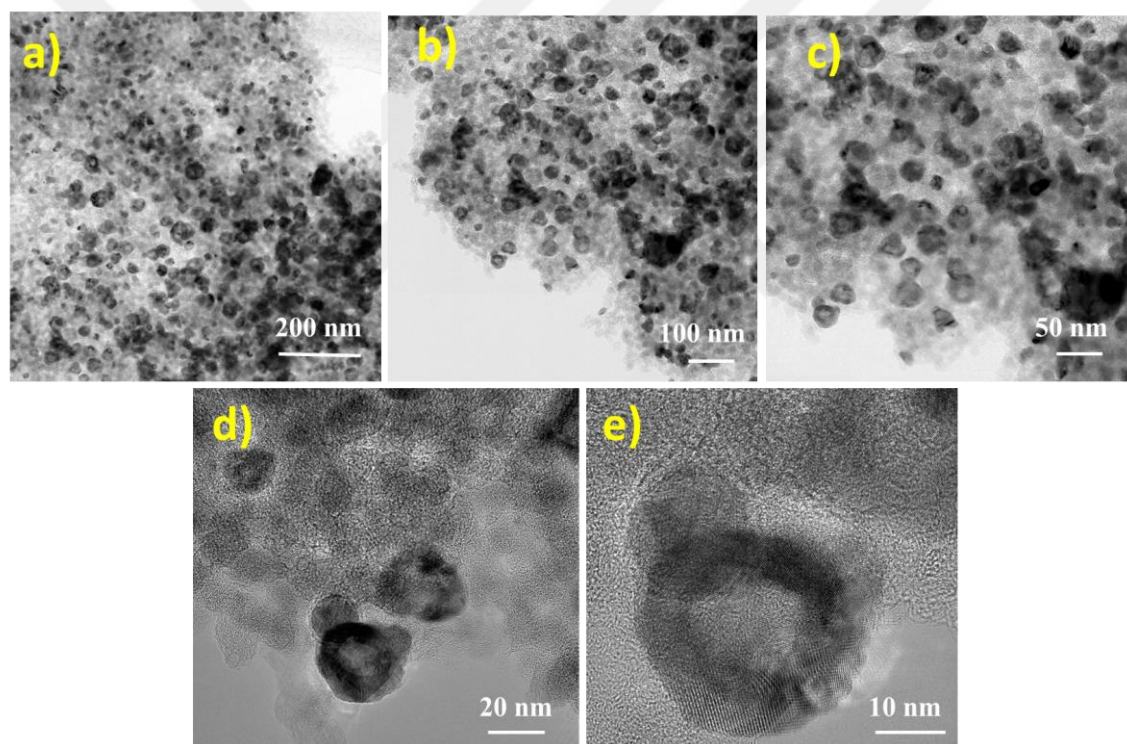


Figure 4.19 TEM Images of Co₁₀₀-UCA₄-800 in Different Magnifications

Figure 4.19 displays the TEM images of Co₁₀₀-UCA₄-800 in different scales. Co nanoparticles are thinner around central part, and they seem to be hollow (or donut shape) (**Figure 4.19-d&e**). The donut-shape of the nps can be seen more clearly in bright field and HAADF image of the sample (**Figure 4.20 a&b**).

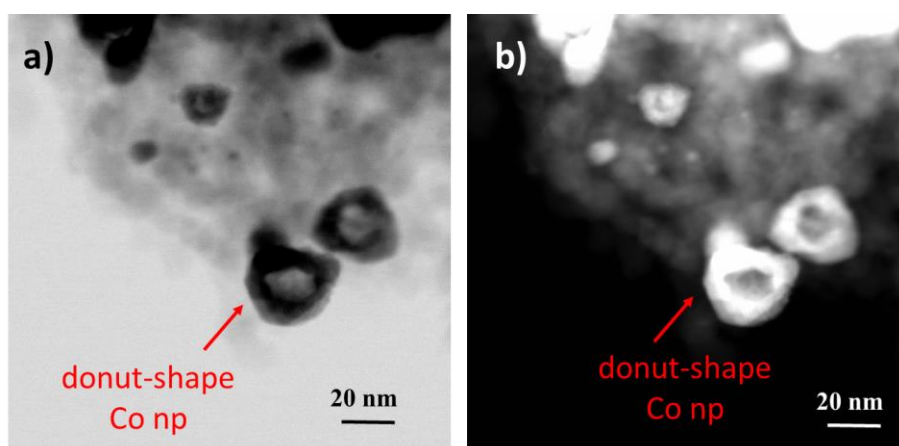


Figure 4.20 a) Bright Field Image b) HAADF Image of $\text{Co}_{100}\text{-UCA}_{4-800}$

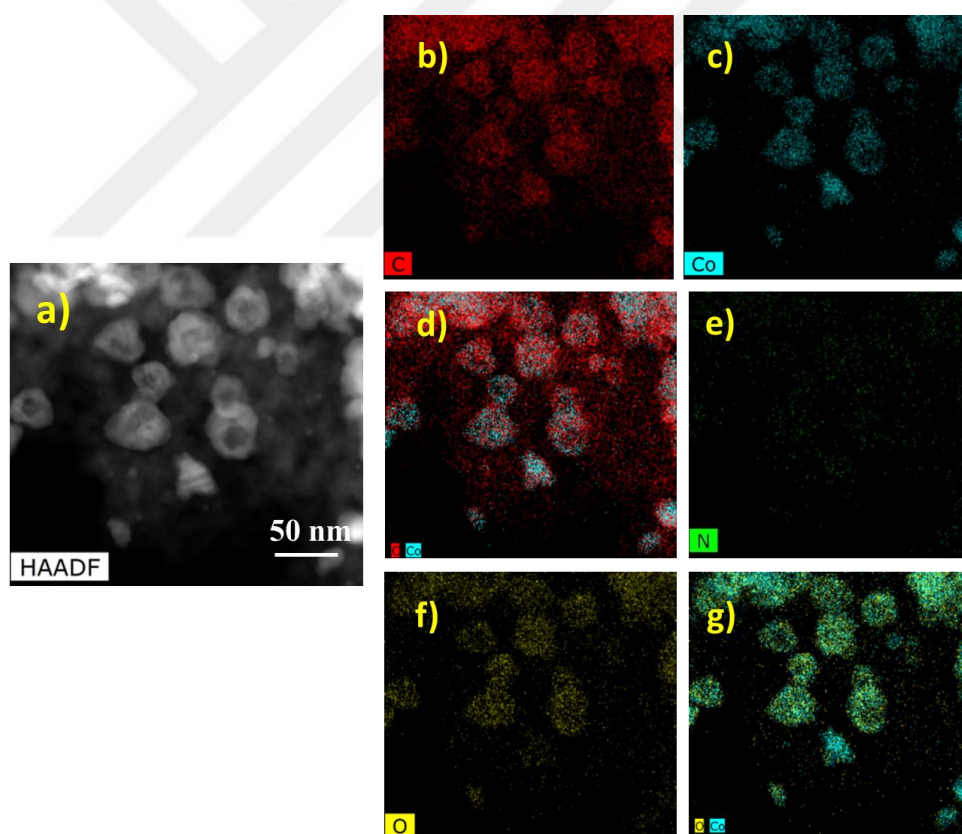


Figure 4.21 HAADF-STEM Image and Its Corresponding Elemental C, Co,O,N Mapping of $\text{Co}_{100}\text{-UCA}_{4-800}$

Figure 4.21 shows HAADF-STEM image of Co₁₀₀-UCA₄-800 and the corresponding elemental C, Co, O, N mapping. N atoms are seen homogenously distributed through the sample as shown in **Figure 4.21-e**. The O, Co and Co-O mappings given in **Figure 4.21-c,f,g** indicate the presence of some cobalt oxides in the sample.

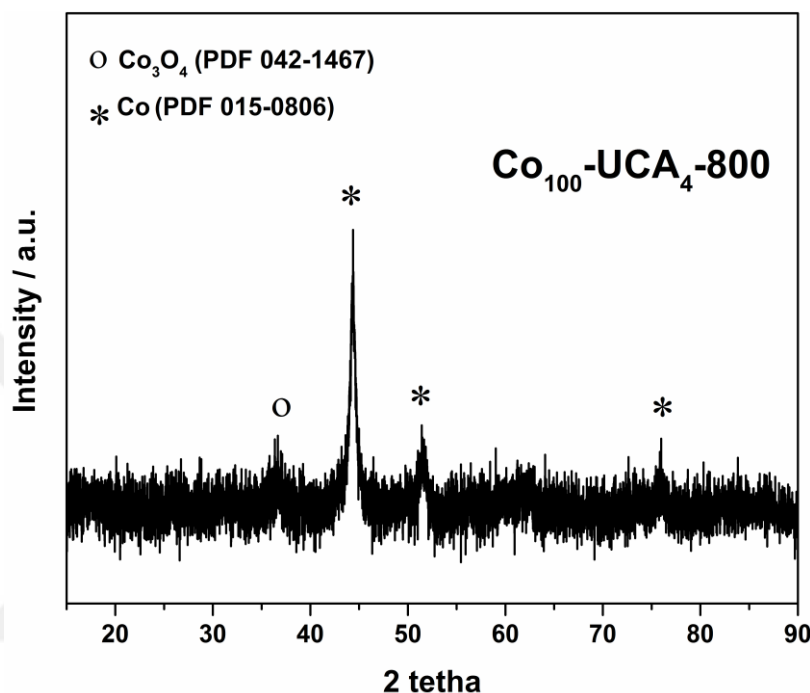


Figure 4.22 XRD Pattern of Co₁₀₀-UCA₄-800

In the XRD pattern of Co₁₀₀-UCA₄-800 (**Figure 4.22**), the peaks at $2\theta \sim 44.3^\circ$, $\sim 51.5^\circ$ and $\sim 75.9^\circ$ displays the presence of cubic (FCC) Co nanocrystals (PDF 15-0806). Moreover, a small peak at $2\theta \sim 36.7^\circ$ is assigned to {311} reflection of cubic Co₃O₄ nanocrystals (PDF 042-1467). This indicates the presence of small size crystalline Co₃O₄ nanoparticles in Co₁₀₀-UCA₄-800 catalyst.

To understand the effect of nitrogen source on the ORR activity, RDE measurements were performed in the same conditions with the previous sections, and the polarization curves of the samples are given in **Figure 4.23-a**. As indicated in **Figure 4.23-b**, both Co₁₀₀-UCA₂-800 and Co₁₀₀-UCA₄-800 exhibited much lower catalytic activity compared to N-Co₁₀₀-CA-800 based on E_{onset} , E_{half} and mass activity. This shows

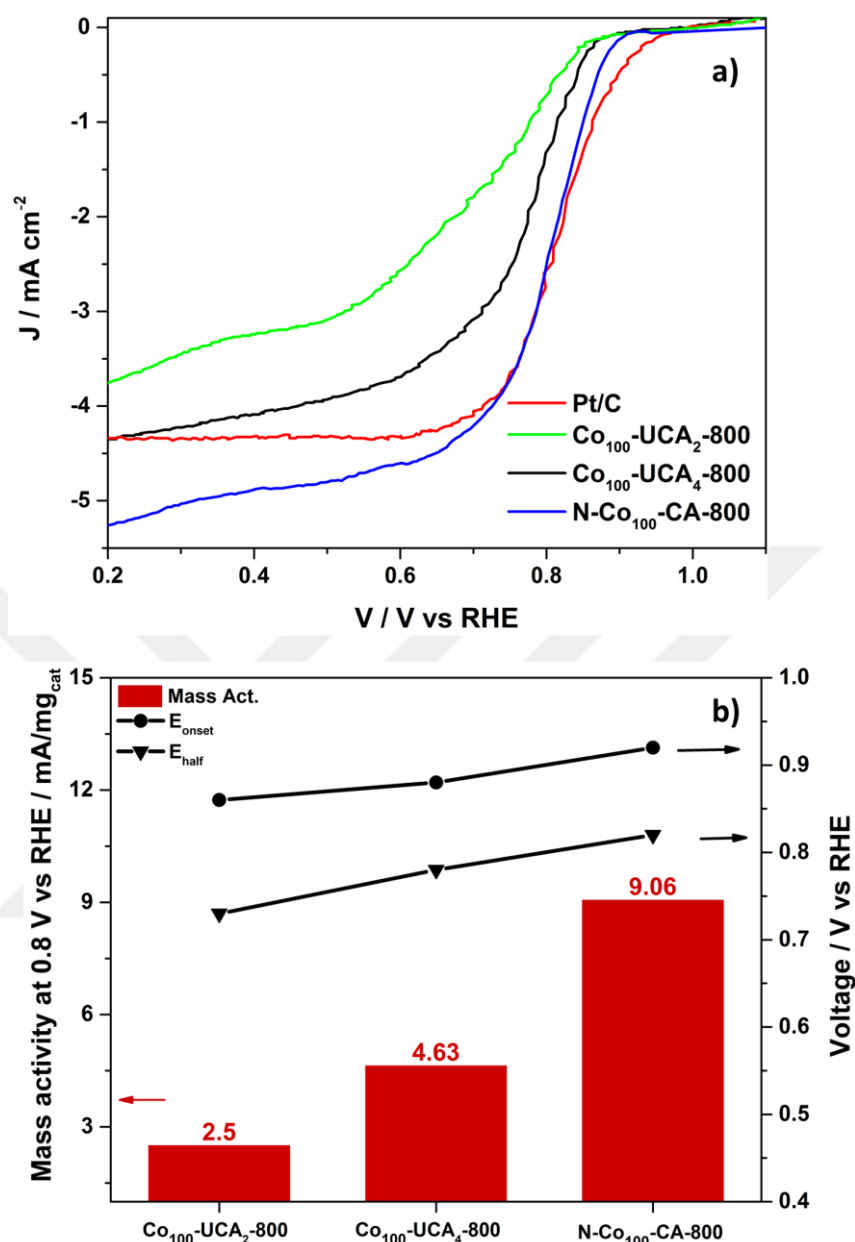


Figure 4.23 a) LSV Curves of Co₁₀₀-UCA₂-800, Co₁₀₀-UCA₄-800 and N-Co₁₀₀-CA-800 Catalysts in O₂ Saturated 0.1 M KOH at 1600 rpm, 5 mV s⁻¹ and b) Their Corresponding E_{onset}, E_{half}, and Mass Activity (at 0.8 V vs RHE)

that the N source and the addition technique of N atom into the catalyst structure significantly affect the ORR activity. One possible reason for higher activity of N-Co₁₀₀-CA-800 is that NH₃ is a more suitable N source to create active sites on carbon network for ORR compared to urea. The other reason might be the addition way of N atoms to the

carbon network. For example, some studies revealed that the presence of cobalt catalyze the formation of catalytically active C-N sites for ORR, rather than being involved as active sites [130], which can also explain the greater activity of N-Co₁₀₀-CA-800 catalyst in our case. In N-Co₁₀₀-CA-800 catalyst N atoms were doped into carbon network after Co loading, and in that way, Co might help to form catalytically active structures in this sample. However, in Co₁₀₀-UCA_α-800 samples, N content was provided by adding urea into the organic aerogel at the initial step before Co loading. Thus, Co could not contribute to the formation of catalytically active C-N structures in this samples, which resulted in low ORR activity in Co₁₀₀-UCA_α-800 samples.



4.2 Investigation of various surface species with post acid-base treatments

As we have shown, there is a mixture of various species including carbon shell covered metallic Co nanoparticles, Co-O, Co-N_x, along with graphitic and pyridinic-N species which are possible candidates as active sites in N-Co₁₀₀-CA-800. In order to further investigate the nature of the active sites and spectator species, we performed various base/acid treatments on the N-Co₁₀₀-CA-800. By carefully manipulating the order of these base and/or acid treatments some of the species mentioned above were removed and after each treatment, XPS, TEM and XRD were performed along with RDE for analysis.

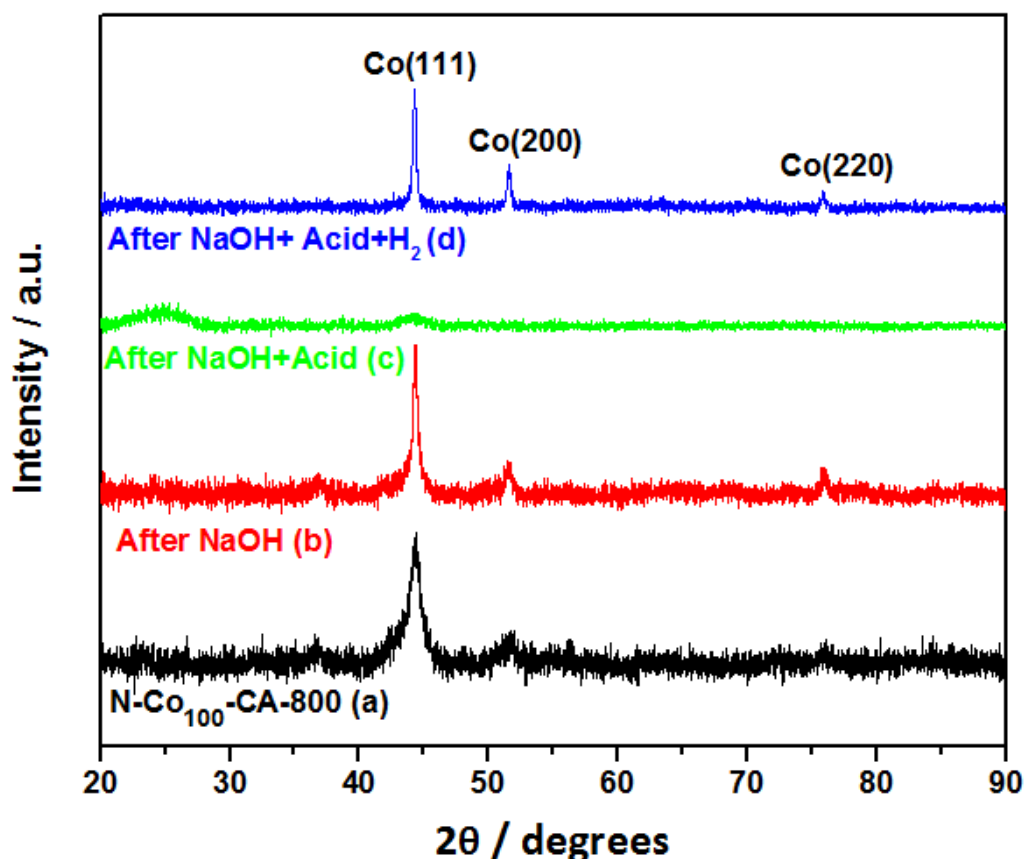


Figure 4.24 XRD Patterns of N-Co₁₀₀-CA-800 After Each Treatment

Figure 4.24 displays the XRD pattern of the N-Co₁₀₀-CA-800 after the treatments.

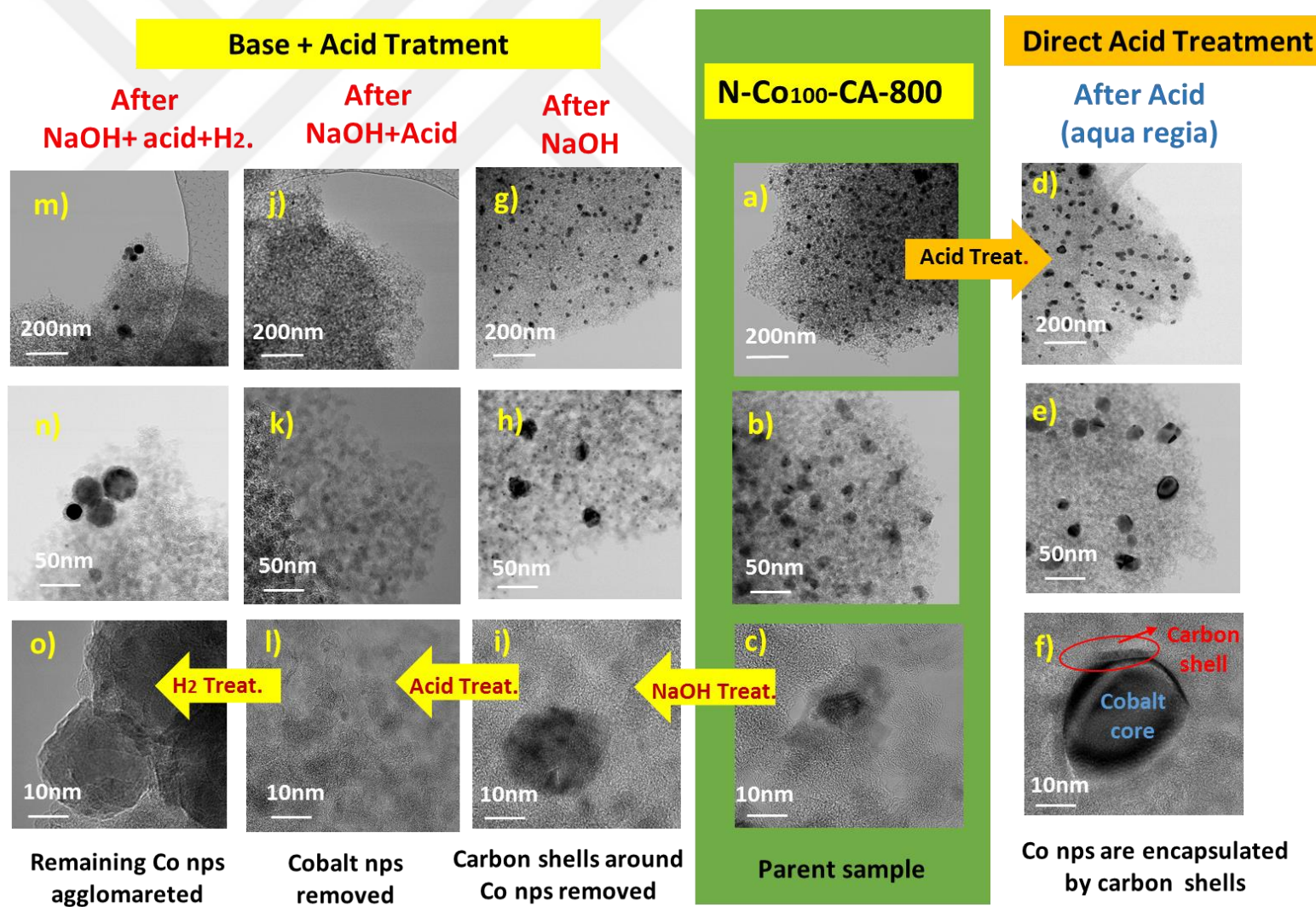
Figure 4.25 TEM Images of N-Co₁₀₀-CA-800 at Various Magnifications After Direct Acid Treatment and After NaOH+acid Treatment.

Figure 4.25 shows the TEM images of the parent N-Co₁₀₀-CA-800 at different magnifications and after each treatment. After direct acid (aqua regia) treatment, the catalyst still had plenty of cobalt nanoparticles (**Figure 4.2** and **Figure 4.25-d&e**), which were encapsulated by carbon shells (**Figure 4.2** and **Figure 4.25f**). Since the nanoparticles covered by carbon shells could not be removed by direct acid treatment, carbon etching was carried out using NaOH (17.5 M) to remove the carbon shell around the nanoparticles in order to expose the metal particles to the subsequent aqua regia treatment, thus to achieve a more efficient cobalt removing. Chemical activation with hydroxide compounds such as KOH and NaOH is a well-known method to activate the carbon material and similar base treatments to remove the carbon shells around the metal nanoparticles can be found in the literature [40]. As indicated in **Figure 4.25-i**, the carbon layer that covers cobalt metal nanoparticles is completely removed after NaOH treatment while the cobalt nanoparticles still exist as shown by XRD (**Figure 4.24**). Thus, cobalt metal particles in NaOH treated N-Co₁₀₀-CA-800 would be removed easily by subsequent acid treatment. As indicated by **Figure 4.25-j,k,l**, almost all cobalt nanoparticles were removed by the base+acid treatment which was again in agreement with the XRD results (**Figure 4.24-c**). In **Figure 4.24-c**, only a broad diffraction signal with small intensity centered around $2\theta = 44.3^\circ$ was observed after base+acid treatment indicative of small Co clusters. Subsequent to the base+acid treatment, the catalyst was treated with H₂ (10% balanced with N₂) at 800 °C for 2h as the last step since the acid washing step (subsequent to NaOH treatment) may result in the blockage of the active sites with oxygen containing functional groups introduced by the acid (H₂SO₄ or HNO₃) [28]. After H₂ treatment, pronounced FCC Co peaks were once again observed in the XRD data (**Figure 4.24-d**); this could correspond to the agglomeration of the residual Co nanoparticles into larger clusters as suggested by TEM images such as **Figure 4.25-n**.

Table 4.7 Surface Elemental Composition of N-Co₁₀₀-CA-800 After Each Treatment

	C (at%)	O (at%)	Co (at%)	N (at%)
<i>N-Co₁₀₀-CA-800 (*)</i>	93.27	4.19	0.91	1.27
<i>(*) After NaOH Treat.</i>	93.64	3.89	0.75	1.70
<i>(*) After NaOH+Acid</i>	89.22	8.33	0.20	2.24
<i>(*) After NaOH+Acid+H₂</i>	93.50	5.37	0.19	0.94
<i>N-CA-800</i>	91.89	3.08	-	5.02

Table 4.8 Catalytic Properties and Relative Compositions of Surface Species After Each Treatment

	E_{onset} (Vvs RHE)	E_{half} (V vs RHE)	Mass act. (mA/mg_{cat})	Pyridinic N (%)	Graphitic N (%)	Pyridinic N oxides (%)	Nitrate (%)	Co⁰ (%)	Co-O (%)	Co-N (%)
<i>N-Co₁₀₀-CA-800 (*)</i>	0.92	0.82	9.06	15'	68	17	0	22	43	34
<i>(*) After NaOH Treat.</i>	0.91	0.81	8.89	18'	69	12	0	42	31	27
<i>(*) After NaOH+Acid</i>	0.89	0.80	6.51	23	50	8	18	NA	NA	NA
<i>(*) After NaOH+Acid+H₂</i>	0.91	0.81	9.00	27	64	9	0	NA	NA	NA

^cThe value includes contribution of Co-N_x species

Table 4.7 shows the elemental surface composition of the samples after each treatment. The values were obtained from XPS in terms of at%. As indicated in **Table 4.7**, the NaOH treatment did not affect the surface composition of the catalyst notably. For example, the relative C and N contents remained almost the same while the surface Co content decreases from 0.91 at% to 0.75 at%.

Table 4.8 displays the catalytic properties and the relative percentages of N and Co species after each treatment.

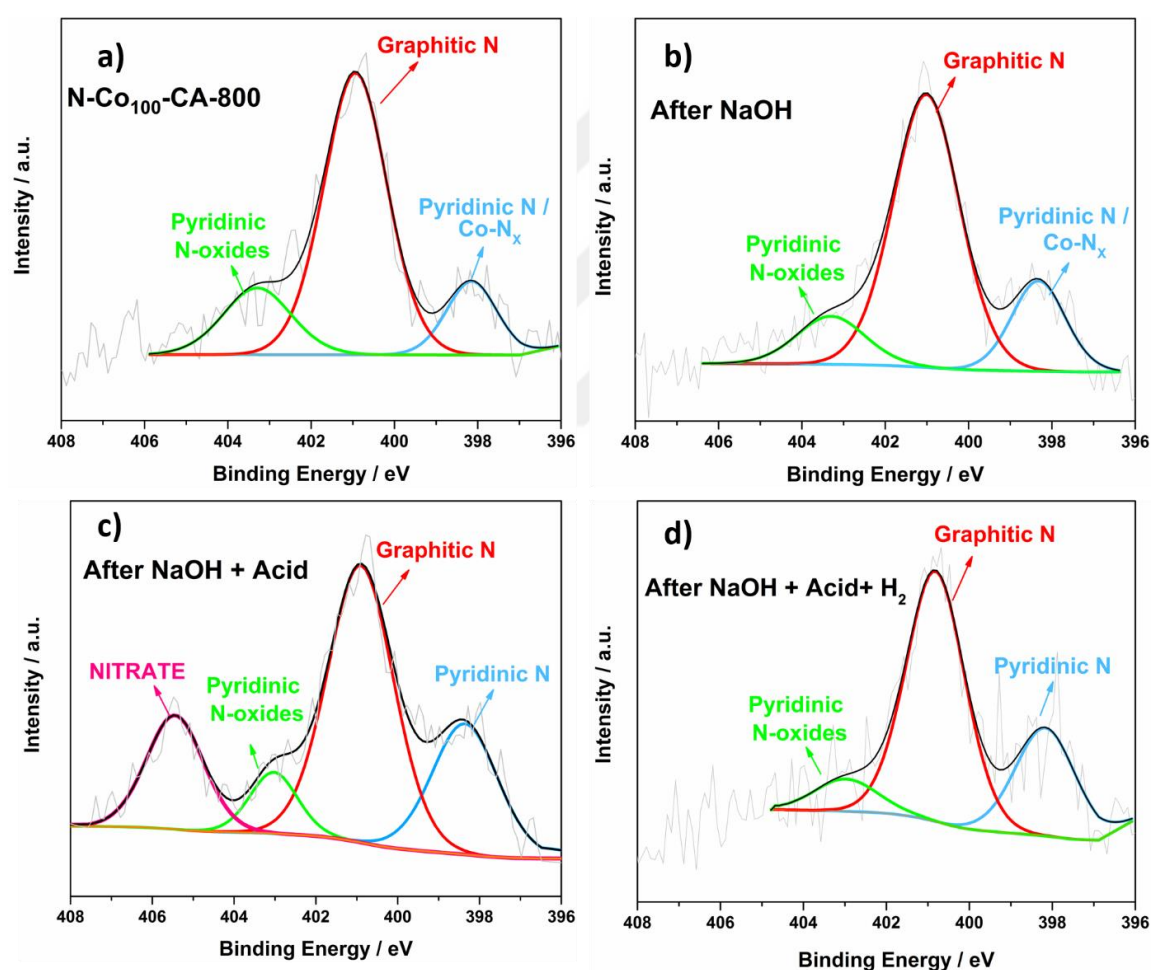


Figure 4.26 High Resolution N1s Spectra of **a)** N-Co₁₀₀-CA-800 **b)** After NaOH Treatment **c)** After NaOH+Acid Treatment **d)** After NaOH+Acid+H₂ Treatment

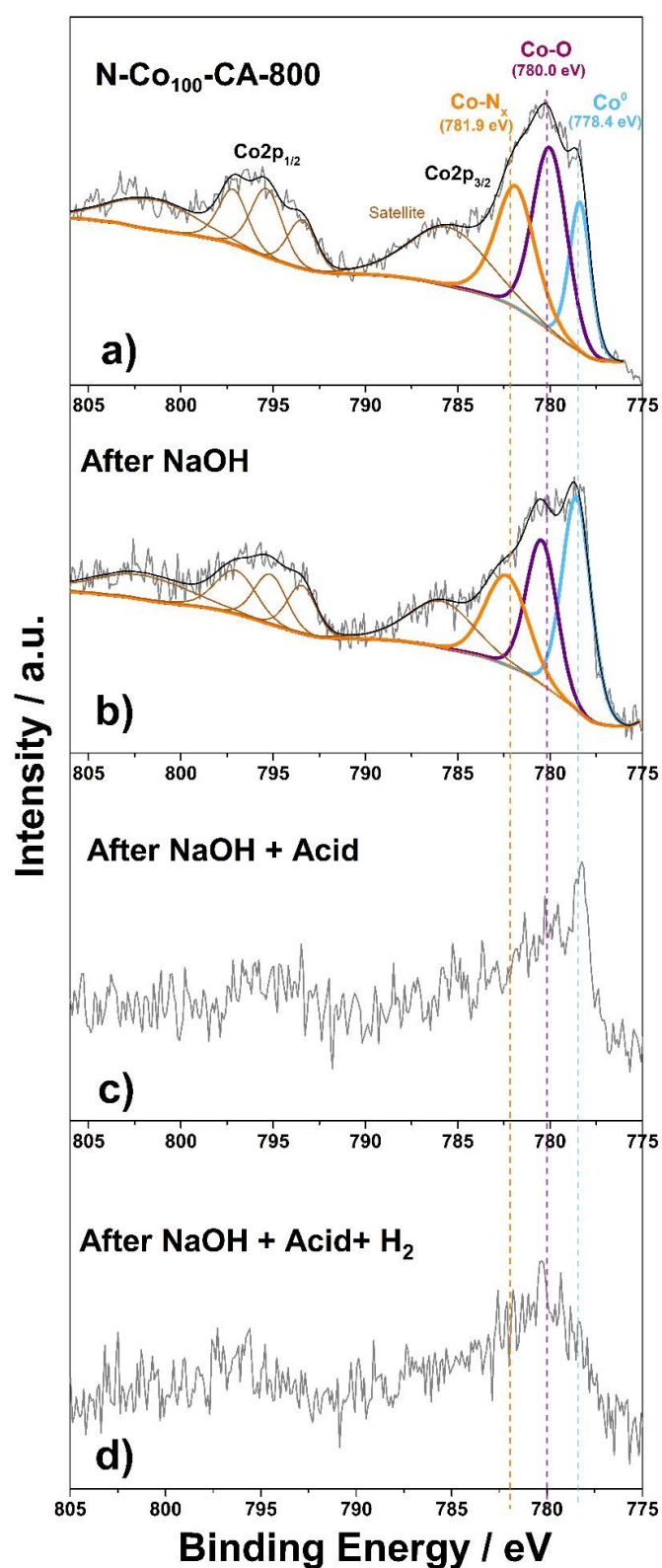


Figure 4.27 High Resolution Co₂p Spectra of **a)** N-Co₁₀₀-CA-800 **b)** After NaOH Treatment **c)** After NaOH+Acid Treatment **d)** After NaOH+Acid+ H₂ Treatment

Figure 4.26 and **Figure 4.27** show the high resolution N1s and Co2p XPS spectra, respectively, of the samples after each treatment. After NaOH treatment, since the Co2p_{3/2} spectra of the sample revealed the existence of Co-N_x species (**Figure 4.27-a**), the peak ~398.2eV in the N1s spectra of sample (**Figure 26-b**) should also include the contribution of Co-N_x species. Due to the relatively low amount of cobalt on the surface (~0.2 at. %) after base+acid and base+acid+H₂ treatments, their respective Co2p core level spectrum are very noisy as shown in **Figure 4.27-c&d**. Thus, deconvolution into separate peaks was not performed.

Table 4.8 contains the values for the relative percentages of N and Co species after each treatment together with the values for E_{onset}, E_{half}, and the mass activity of the samples obtained from the ORR curves (**Figure 4.28**). While NaOH treatment caused a decrease in the relative content of Co-O and Co-N_x sites in the catalyst by around 25% as compared to N-Co₁₀₀-CA-800 (from 43% to 31% for Co-O, and from 34% to 25 % for Co-N_x), only an insignificant decrease in the mass activity of the catalyst (~2%) (from 9.06 to 8.89 mA/mg_{cat}) was observed after NaOH treatment. This suggests that the Co-O and /or Co-N_x are most probably spectator species. When the NaOH treatment was followed by acid (aqua regia) treatment, bulk Co content significantly decreased (**Figure 4.25-j, k, l**) and the surface Co content of the catalyst decreased from 0.75 at. % to 0.19 at.% while relative N content notably increased from 1.70 to 2.24 at% (**Table 4.7**). This higher relative N content of the sample is due to the incorporation of nitrate species as observed by the XPS with a peak appeared at ~405.5 eV in the N1s spectra (**Figure 4.26-c**); these species probably originated from the HNO₃ during the acid treatment and blocked the active sites on the catalyst. Therefore, the mass activity of the sample after the acid treatment decreased from 8.89 to 6.56 mA/mg_{cat}, which correlated with the decrease in the relative percentage of graphitic N sites in the catalyst which dropped from 69% to 50% after base+acid treatment. Although peak fitting was not be carried out for the Co2p spectra of this sample due to the low cobalt and the low signal to noise ratio (**Figure 4. 27-c**), the Co2p_{3/2} spectra displayed a typical asymmetric shape for metallic cobalt with the peak appeared around 778.4 eV [126]. This indicated that there was only a very small proportion of metallic cobalt on the surface of this sample, with very small particle sizes as indicated by the XRD data (**Figure 4.24-c**). Nearly all of the cobalt (but

not all) was removed from the sample after base+acid treatment but its mass activity (6.56 mA/mg_{cat}) was still higher than that of the N-CA-800 (5.21 mA/mg_{cat}, **c.f. Figure 4.15-c**). This suggests that Co nanoparticles may also have some role in the ORR. After the final H₂ treatment, the mass activity of the catalyst was recovered, presumably because all the NO₃ species that had blocked the active sites had been removed. The disappearance of the peak around 405.5 eV in the N1s spectra of the sample supports this interpretation (**Figure 4.26-d**). The recovered mass activity is also in agreement with the recovered relative percentage of graphitic N sites, which again indicates that the enhanced activity of the N-Co₁₀₀-CA-800 catalyst resulting mainly from the presence of graphitic N sites rather than from other species. Although the relative Co content of the base+acid+H₂ treated sample is significantly lower than the that of N-Co₁₀₀-CA-800, their electrocatalytic properties are very similar which suggests that most of the –if not all– cobalt are spectators in ORR catalysis and serve only to promote graphitic-N formation. The relative percentages of the pyridinic-N and pyridinic N-oxides site did not correlate with the changes in the ORR activity upon various base/acid/H₂ treatments (**Table 4.8**) and therefore they are most probably spectators as well.

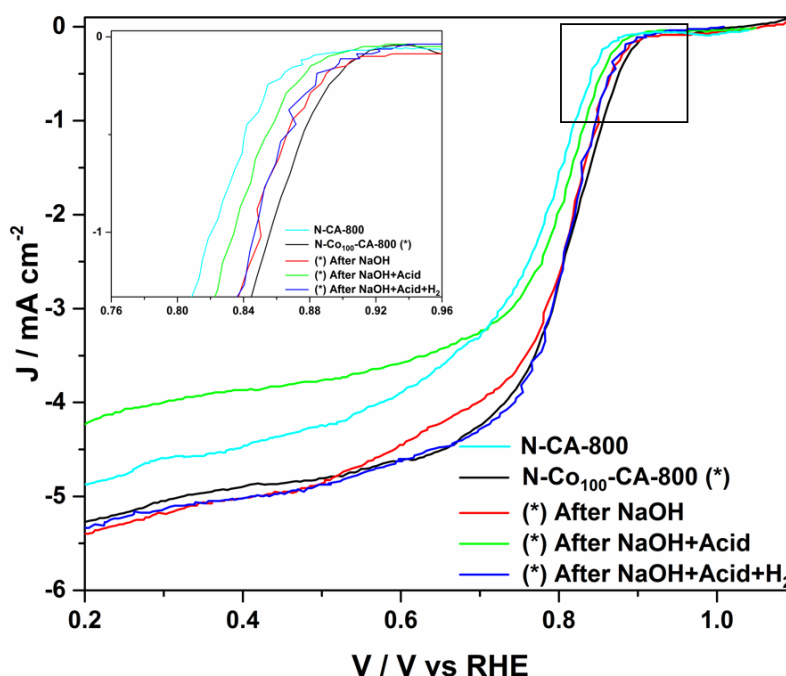


Figure 4.28 ORR Curves of N-CA-800, N-Co₁₀₀-CA-800 (abbreviated by (*)) and N-Co₁₀₀-CA-800(*) After Various Treatments

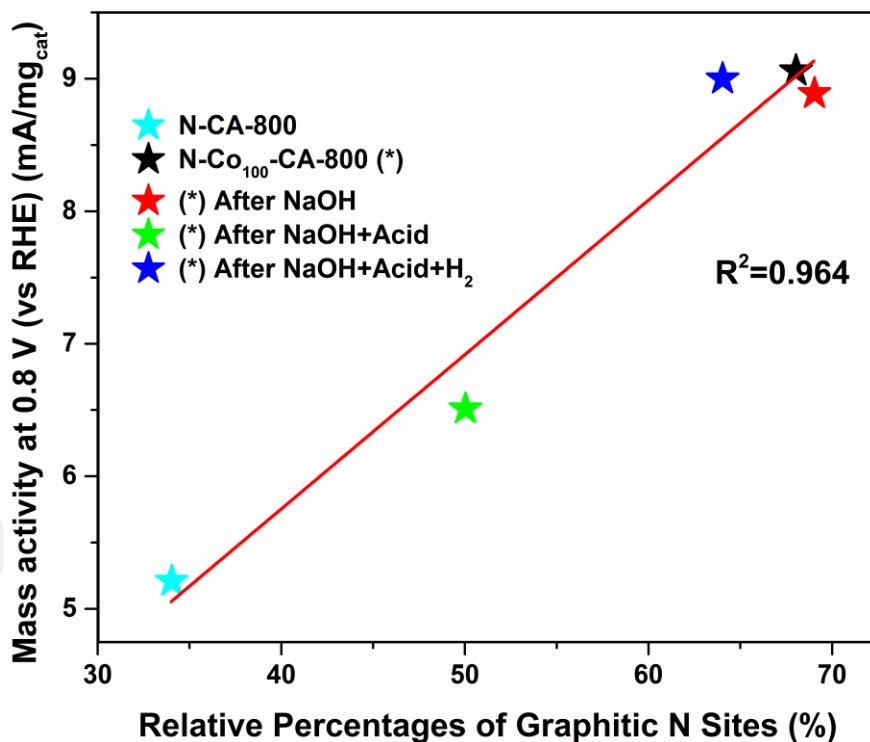


Figure 4.29 The Variation of the Mass Activity with Relative Percentages of Graphitic-N Sites in Various Samples

To confirm whether the activity recovery after H₂ treatment was due to the presence of new active sites which were created during the previously mentioned treatments, same procedure of Base+Acid+H₂ treatment was performed on the N-CA-800 catalysts. The ORR curves of N-CA-800 catalyst before and after treatments were given in **Figure A.4** and they showed that there is no notable difference between the activity of N-CA-800 before and after treatments. This indicates that the enhanced ORR activity is associated with the high fraction of graphitic-N sites, whose formation is promoted by Co. Therefore, the activity recovery of N-Co-CA-800 after H₂ treatment (**Figure 4.28**) was not due to new sites created during these treatments but due to the reduction of nitrate species interacting with H₂ and freeing the active graphitic-N sites. **Figure 4.29** shows the variation of the mass activity as a function of the relative percentages of the graphitic-N sites. Here, with increasing graphitic-N percentage, a linear increase is observed in the mass activity with $R^2 = 0.964$. This correlation strongly suggests the active site nature of

the graphitic-N species. Previous studies suggested that since the graphitic N sites impact the overall electron distribution on carbon they are mainly governing the activation energy mainly. Therefore, they might have the main role to determine the onset potential and catalytic activity towards ORR[28].

Similar to our findings, Zhang et. al. [79] also attributed the high ORR activity of such catalysts to the N-doped carbons rather than Co-N species based on the electrochemical measurements and X-ray absorption spectroscopy results. Although they proposed that encased Co nanoparticles in N doped carbon sheets mainly govern the ORR activity by considering their DFT calculations, our results unambiguously confirm that the Co only catalyzes the formation of C-N active sites rather than being involved in the reaction by itself.

On the contrary, there are some reports which suggest that the main active site in Co-containing catalysts are Co-N_x species,[42, 43, 82] although the theoretical calculations employing density functional theory (DFT) revealed that the stable Co-N centers catalyze only the 2e⁻ reduction of O₂ due to its weak interaction with peroxide[45]. Therefore, the Co-N site does not promote the complete ORR by itself, and ORR proceeds instead by a 2x2e⁻ dual-site mechanism in the presence of Co-N sites, with further reduction of peroxide occurring at some other active sites. Therefore, most probably, the reports proposing the Co-N_x species as the main active sites overlooked the significance of other N-related species in the catalyst, which would actually make the reaction proceed through a 4e⁻ pathway as shown in this work.

Consequently, for alkaline medium, we suggested the main active sites in N-Co-C catalyst as graphitic N sites by establishing a strong correlation between graphitic N site (%) and ORR activity (mA/mg_{cat}) by carefully manipulating the species in the catalyst with different treatments. With these treatments, it is also revealed that cobalt only promotes the formation of active sites (graphitic N) while it does not contribute the ORR activity by itself. Although there are also some reports proposing the main active site in Co containing catalysts as Co-N_x species[42, 43, 82], the theoretical calculations employing density functional theory (DFT) revealed that the stable Co-N centers catalyze only the 2e⁻ reduction of O₂ due to weak interaction with peroxide [45]. Therefore, Co-N

site does not promote complete ORR by itself. This suggests $2x2e^-$ dual-site ORR mechanism in the presence of Co-N sites, so that further reduction of peroxide on Co containing catalyst can occur at some other active sites. Therefore, most probably, the reports proposing the Co-N_x species as main active sites overlooked the significance of other N-related species in the catalyst, which would actually proceed the reaction mechanism to $4e^-$ pathway towards ORR.

In order to evaluate the ORR performance of the present catalyst, it is crucial to compare its electrocatalytic and structural properties with the other reported N-doped Co carbon catalysts in the literature. In **Table 4.9**, recently published N-doped cobalt carbon catalysts are listed with their corresponding properties and ORR activities in alkaline medium. The results indicate that the N-Co₁₀₀-CA-800 displayed the highest pore volume among other catalyst with the high surface area. Since the catalyst loading of the catalyst in the **Table 4.9** varies, it is much better to compare the ORR performances of the catalysts based on their mass activities rather than their E_{onset} and E_{half} ., but the mass activities of the many catalyst in the list are not available. Nevertheless, the E_{onset} and E_{half} values of the N-Co₁₀₀-CA-800 catalyst are in the range of reported values, and among other CA derived N-doped Co catalyst, it displayed similar or greater ORR performances. This indicates that N-Co₁₀₀-CA-800 is a promising catalyst for ORR, and the present method could potentially be used for fabricating other Pt-free CA derived materials with the superior actives.

Moreover, although the mass activity and surface area of the MOF derived catalyst (1393,7 m²/g and 14.2 mA/mg_{cat}, respectively) seems slightly higher than that of N-Co₁₀₀-CA-800 (638 m²/g and 9.06 mA/mg_{cat}, respectively.), it is possible to synthesize CA derived catalysts having higher activities and the surface areas by tuning their tunable properties during synthesis. It should be also noted that manufacturing the CAs would be much cheaper compared to fabricating MOFs to make the ORR based energy conversion and storage devices commercially available.

Table 4. 9 Summary of Recent N-doped Cobalt Carbon Catalysts and Their Corresponding ORR Performance in Alkaline Medium

Catalyst	S _{BET} (m ² g ⁻¹)	V _{pore} (cm ³ g ⁻¹)	Loading (mg cm ⁻²)	E _{onset} (V vs RHE)	E _{half-wave} (V vs RHE)	Mass Activity at 0.8 V vs RHE (mA mg _{cat} ⁻¹)	n	Reference
Co-N-CA	1383	1.69	0.2	0.835 ^a	0.779 ^a	NA	3.8-4.0	[90] Small 2014 , 10, 21, 4352–4361
Co-NCA4	316	0.228	0.2	0.839 ^b	0.799 ^b	14.4 ^c	3.9-4.0	[50] ChemElectro-Chem 2015 , 2, 2079 – 2088
Co-N-OMMC-0.6	635	1.65	0.22	NA	0.83	NA	3.9	[29] App. Cat. B: Envir., 2016 , 193, 1-8
Co ₁₅ -N-C ₈₀₀	470	NA	0.49	0.97	0.82	8.25	3.96	[42] ACS App. Metar. and Interfaces, 2016 , 8, 32875
N-Carbon nanotube frameworks(NCNTFs)	513	1.16	0.20	0.97	0.87	NA	3.97	[131] Nature Energy 2016 , 1

Catalyst	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{pore} ($\text{cm}^3 \text{g}^{-1}$)	Loading (mA cm^{-2})	E_{onset} (V vs RHE)	$E_{\text{half-wave}}$ (V vs RHE)	Mass Activity at 0.8 V vs RHE ($\text{mA mg}_{\text{cat}}^{-1}$)	n	Reference
CoSAs/N-C(900) (MOF derived)	1393.7	NA	0.408	0.982	0.881	14.2	3.8 - 4.0	[43] Angew. Chem. Int. Ed., 2016 , 55,10800
Co-NC	233	NA	0.21	NA	0.83	NA	3.72	[132] Angew. Chem. Int. Ed., 2016 ,55,4087
Co/NSCNT	NA	NA	0.2	0.90	0.80	NA	3.94	[133] ACS, Sustainable Chem. Energy 2017 ,5,3973
Co-NHC-900	1204	NA	0.3	NA	0.85	NA	4.0	[79] ACS App. Metar. & Inter. 2017 ,9
Co ₃ O ₄ @N-GCFs	NA	NA	0.2	0.90	NA	NA	3.9	[31] Small 2018 , 14,11
N-Co ₁₀₀ -CA-800	638	2.31	0.3	0.92	0.82	9.06	3.94	This work

^a the given value in the paper is converted to RHE by $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.197 + 0.059\text{pH}$

^b the given value in the paper is converted to RHE by $E(\text{RHE}) = E(\text{SCE}) + 0.242 + 0.059\text{pH}$

^c the value reported at -0.2 V vs SCE, which equals ~ 0.81 V vs RHE, NA: not available

Chapter 5

CONCLUSIONS AND FUTURE WORK

A new highly active family of N-Co-CA electrocatalysts were synthesized by scCO_2 assisted technique combined with NH_3 treatment. The N-Co₁₀₀-CA-800 catalyst displayed the onset potential of 0.92 V vs RHE which was very close to that of a commercial 20% Pt/C catalyst (0.95 V vs RHE) in 0.1 M KOH solution. Also, both catalysts exhibited the same half wave potentials (0.82 V vs RHE) in alkaline medium.

In the first part of the study, the effect of various parameters on ORR activity and catalyst properties were investigated. The pyrolysis temperature was varied between 700 °C-1000 °C, and the sample pyrolyzed in 800 °C displayed maximum mass activity (9.06 $\text{mA/mg}_{\text{cat}}$ at 0.8 V vs RHE). The TEM images displayed the presence of Co nanoparticles encapsulated by carbon shells in the samples pyrolyzed at 800°C to 1000 °C, and core-shell structure became more distinct as pyrolysis temperature increases. Moreover, the effect of Co content on ORR activity was examined by changing the amount of cobalt precursor between 50-150 mg during SCD, which resulted in 8.4 wt% to 23.7 wt% Co loadings in the samples, respectively. Although the changes in the ORR activity of the samples having different Co contents are not very pronounced, an optimum in Co loading associated with the ORR activity was detected where the Co content is 17.9 wt%. The roles of the Co and N doping in enhancing the activities of the N-Co-CA catalysts were also investigated. The N-Co₁₀₀-CA-800 (9.06 $\text{mA/mg}_{\text{cat}}$) exhibited nearly double the mass activity of N-CA-800 (5.21 $\text{mA/mg}_{\text{cat}}$) at 0.8 V vs RHE. The former catalyst displayed the 4e^- reaction pathway for ORR along with a superior methanol tolerance as compared to commercial 20 wt% Pt/C catalyst in alkaline media. Additionally, the effect of N source on ORR activity was studied by using urea instead of NH_3 gas as nitrogen source. In this set, the catalysts were prepared by adding urea to the initial solution in different

urea(U):formaldehyde(F) ratios. The one prepared with the U:F ratio of 1:3 exhibited the existence of donut-shape Co nanoparticles. All samples prepared with urea were displayed lower mass activity compared to the samples prepared via NH_3 treatment because presumably presence of Co catalyzes the formation catalytically active C-N structures for ORR in N-Co₁₀₀-CA-800 catalyst during NH_3 treatment.

In the second part, the chemical nature of the active sites in N-Co-CA catalyst for the ORR was investigated by modifying the surface of the catalyst via post base/acid/ H_2 treatments. In that way, we selectively removed the spectator Co species and/or blocked the graphitic-N active sites with nitrates. RDE voltammetry results and XPS data suggested that the formation of graphitic-N sites was promoted by the presence of Co species. Moreover, a strong correlation was found between mass activity and the relative percentages of graphitic-N species on the surface based on RDE and XPS measurements. The results revealed that the presence of Co during the synthesis is crucial to obtain enhanced activities although it does not contribute the ORR activity by itself as active site.

The superior electrocatalytic performance of N-Co₁₀₀-CA-800 in alkaline medium indicates that it is a promising candidate for the applications such as: alkaline metal–air batteries, alkaline hydrogen fuel cells, and alkaline direct alcohol fuel cells. Therefore, as next step, it should be tested in these devices to provide more insights into its catalytic performance for a real operation.

Moreover, the present method could potentially be used for fabricating other transition-metal-nitrogen doped carbon aerogel materials with activities superior to Pt/C. In this method, the active sites were created during the complex transformation of an organic aerogel to a carbon aerogel in the presence of cobalt by ammonia as the source of nitrogen and pyrolysis medium. Therefore, the catalytic performance of the present catalyst could be enhanced by controlling the formation of active sites via varying the synthesis parameters (i.e. tuning properties of the aerogels, changing the nitrogen content and/or using different metal precursor during SCD). Furthermore, characterizing the catalyst with more advanced spectroscopic techniques such as XAS, EXAFS etc. could provide more information about the chemical nature of active sites in such catalyst.

In the light of all results, the present technique to prepare transition-metal-nitrogen doped carbon aerogel could aid in development of novel Pt-free ORR electrocatalysts and could enable widespread use of ORR based energy conversion and storage devices.



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APPENDIX-A

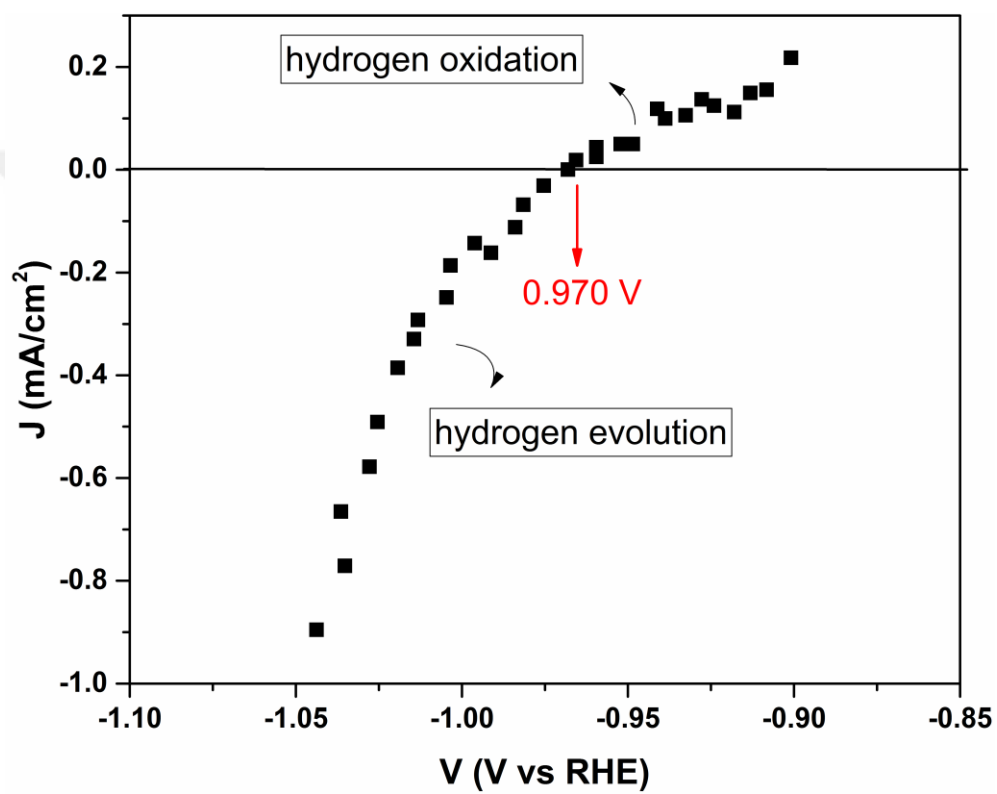


Figure A. 1 Ag/AgCl Reference Electrode Calibration.

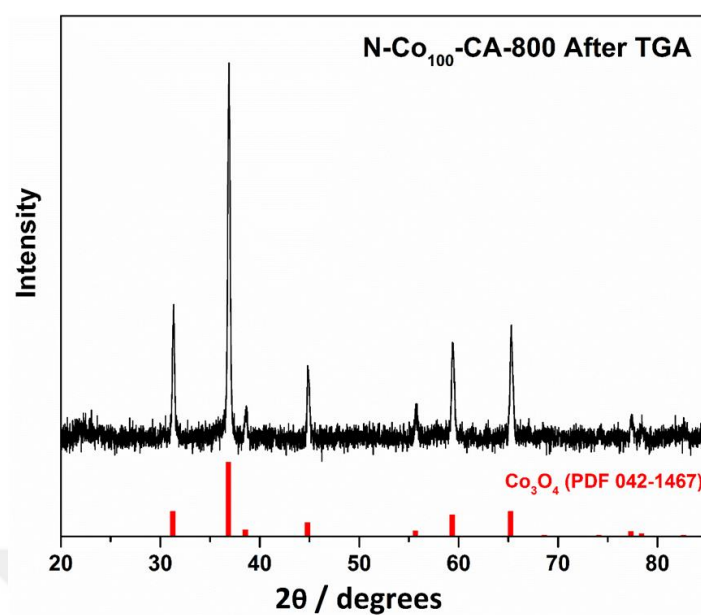


Figure A. 2 XRD Pattern of N-Co₁₀₀-CA-800 After TGA Measurement

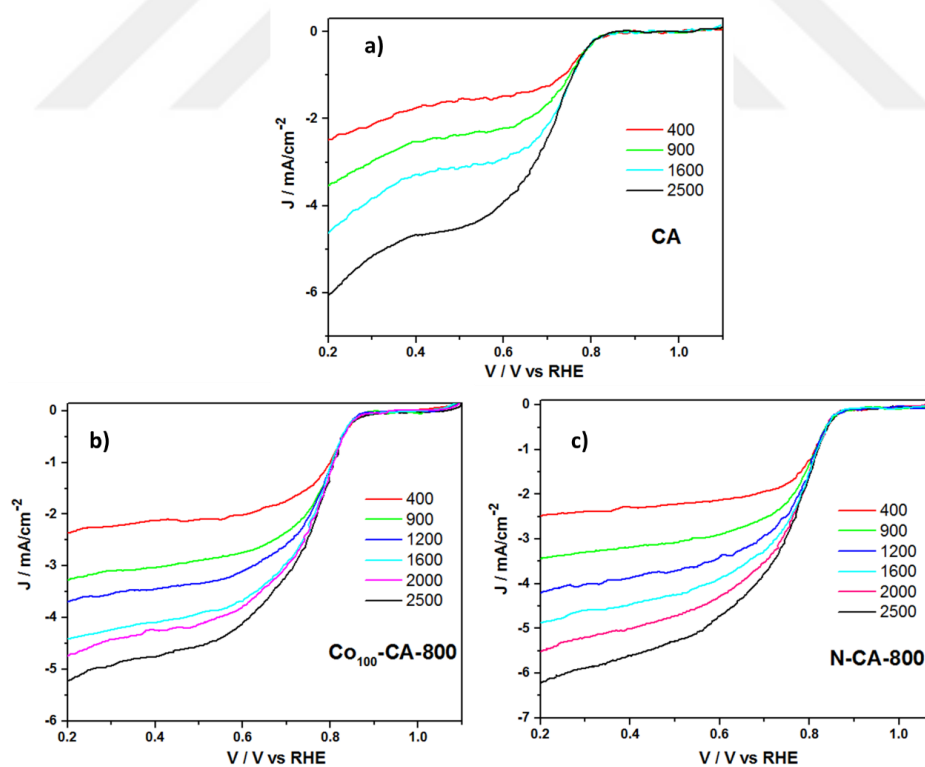


Figure A. 3 Polarization Curves of a) CA b) Co₁₀₀-CA-800 d) N-CA-800 at Different Rotating Speeds

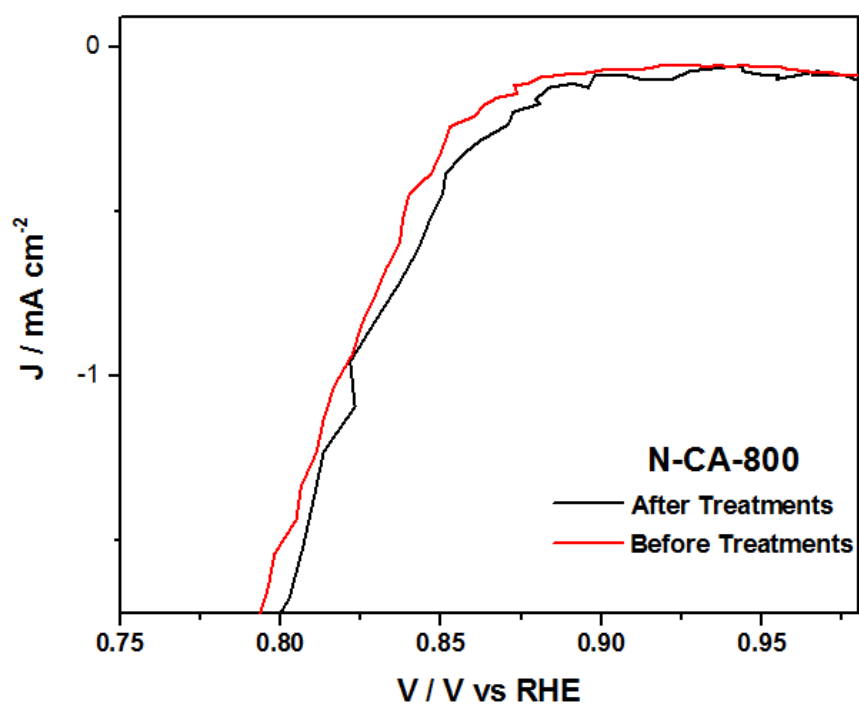


Figure A. 4 ORR of N-CA-800 Before and After NaOH+Acid+H₂ Treatments