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Synthesis of Non Precious Metals (NPM) Electrocatalysts for Higher ORR Efficiency in Fuel Cell Applications

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***Abstract*—** Pt-less electrocatalysts for the assistance in Oxygen Reduction Reaction, elucidating at the cathode of PEMFC have been widely researched. To be considered as an alternative this research work focuses two different classes of Non-Precious Group Metals (Non-PGM),carbon base supports and Metal Organic Frameworks have been synthesized and tested for ORR characteristics i.e Cobalt doped Graphitic Carbon Nitrides (Co-C_3N_4) and Zeolitic Imidazole Framework with iron as a dopant i.e Fe^{+2}. Potentiodynamic steady state convectively diffusing the reacting material within the electrolyte is employed at varying rpm to attain Linear Sweep Voltammograms at 20 $mV.s^{-1}$ in 0.1M KOH and 0.1 $HClO_4$ electrolytes are obtained at 400, 800,1200 and 1600 rpm. Charge transfer number is obtained, showing the rate determining step of the reaction kinetics of transport of ionic species in the Oxygen reduction.

***Keywords*—** Electrocatalysts , Proton Exchange Membrane Fuel Cells (PEMFCs) , Zeolitic Immidizole Frameworks (ZIF), Graphitic Carbon Nitrides, Hydrodynamic methods.

I. INTRODUCTION

Green Energy alternatives have been explored widely pertaining to mass increase in global warming, to provide secure energy shift we have various technologies available at commercial and lab scale. Fuel cell among the sustainabale solution behave like a charge generator, an electro-chemical cell, provided with two electrodes.i.e Anode and Cathode.Among various fuel cell classes, Proton exchange Membrane Fuel Cells (PEMFCs) are widely encouraged. Oxygen-Reduction Reaction (ORR) happening at cathode of low temperature Proton Exchange Membrane Fuel Cells occurs at very slow kinetics[1] than Hydrogen Reduction Reaction (HOR) at anode of the PEMFC.[2] To catalyze the ORR process Pt-based catalysts are utilized.[1,2] ORR process occurs either in a 2e- or 4e- pathway,[2,3] resulting in an undesirable intermediate peroxide in the rate determining step.4e- transfer is much desirable comparably shown by Pt/C supports.[3] Pt-based catalysts are formed by Pt-nanoparticles deposition on carbon black (Vulcan X-72) substrate commercially, known as Pt/C where Pt concentration varies while material is sintered at slow rate to fix Pt-particles on organic substrate.[4] Pt-particle inclusion as a catalyst increases capital cost by 56%, hindering commercialization economically.[5] Downsizing Pt-nanoparticles to atomic level still renders Pt-based catalyst as the best choice, reducing its capital cost.[6] Non- Precious group metals (non-PGM) used as catalytic materials to eradicate the need of platinum electrocatalysts have been reported, Transition metal doped nitrogen carbon composites (T-NC) showed promising results.[7] Pyrolyzed transition metal group, acting as ligand precursors (Fe^{+2} or Co^{+2}) on the carbonic substrate have been researched widely, higher catalytic activity can be achieved in condition while these materials exhibit efficient onset potentials in basic medium.[8]Corrosion of carbon supports suggests them to be more synthetically developed into nano porous particles. A controlled synthesis of nano-porous particles doped with mesoporous silica, aluminosilicate and crystallized particles of colloidal crystals have been considered lately for ORR applications.[9]

A new class of self-supported materials have been reported in literature, showing greater electrolytic activity for ORR applications, surface porosity, current density, stability and electron transfer efficiency.[10] Metal Organic Frameworks (MOF) represents a large variety of novel material where organic linkers are doped with metal ions, providing a flexible structure and effective substrate base template for porous carbon composites. MOF's have been widely used in catalyst applications, energy storage systems and sensors.[11] The morphology and composition greatly affects the efficiency of a catalyst material [10,11], Zeolitic imidazole Frameworks (ZIF), a subclass of MOF materials first synthesized at Argonne National Laboratory in 1950's with Co^{+2} doping act to various functional precursors based on carbon.[12]Zhang et al, stated the addition of ZIF-67 precursor attaining higher porosity of composite structure followed by pyrolyzing after adding thioacetamide. An equilibrium was achieved between dopant concentrations while maintaining impedance at minimum.[13] Papuans et. Al reported synthesizing novel materials based on ZIF including II valency ligands for ORR applications, through calcination of materials in nitrogen environment at higher temperatures. The actives sites detected by qualitative analysis showed the bonding Fe+2 within the ligand (nitrogen). Rotating disk analysis stated that charge transfer of 4e- in alkaline medium.[14]

Zhao et al, stated a state of art method for synthesizing ZIF electrocatalyst in all solid-state mixing. Iron acted as a dopant in addition to ZnO and imidazole (Im) at 200°C in a single step reaction.[15] Xia et al, reported the synthesis and thermal activation of ZIF-67, which showed increased surface area and ORR activity in HClO4.[16] ZIF precursors have been utilized to tailor nitrogen doped carbon nanotubes N-CNT's.[17] Shui et al, developed materials based acrylates doped with Fe, methyl ZIF and ZIF-8.The pyrolysis was carried out for 1hr in Argon gas at 1000°C.Ammonia was supplied at 900°C.The N-coordinated Fe+2 acted as an active site in porous channel of ligand.[18]

Carbon support based, transition metal complexes are considered Non-precious materials for ORR activity i.e, CNT's and g-C3N4 structures,[19] where N doping has been widely reported providing structural stability.[20] g-C3N4 refers to a class of structural misnomers having different chemical compositions, but the same structural linkage of the bonding atoms are known as Graphitic Carbon Nitrides. A graphitic carbon layered planar sheet structure providing greater surface porosity is formed, when N-doping occurs at higher temperatures. [20,21] N-doped precursors are pyrolyzed with carbonaceous materials developing g-C3N4 structure. A 2e-pathway is followed in these carbon support structures producing peroxide.[22] Higher electronic coupling between graphitic linkages in both acidic and basic mediums provide greater ORR abilities to carbon support catalysts. [23] Increased chemical activity dependent on transition metal doping in nano-porous structure with reasonable ORR catalytic abilities were observed.[24]

The physiochemical behavior of components forming a catalyst,formation of dense active sites along with reasonable porosity to surface area ratio determines the characteristics of the ORR catalytic behavior after pyrolysis, providing enhanced limiting currents and onset potentials. [12-24] This research explored the controlled synthesis and electrochemical activity for ORR process within the scope of Non-precious materials group, having no trace of Pt particles for Low temperature PEMFC's application.

II. MATERIAL AND METHODS

A. *Synthesizing ORR-Catalysts*

A ligand is formed in autoclave, Zn(Fe) ZIF was synthesized by one-pot hydrothermal treatment of Zinc Nitrate Hexahydrate Zn(NO3)2.6H2O(Sigma-Aldrich), FeSO4.7H2O (Sigma-Aldrich) and 2-Methylimidazole 1hr purging in Ar-environment followed by 4 days continuous drying at 140°C.Acid washing was done in 0.5M H2SO4 by centrifugation and catalyst is dried at 80°C.

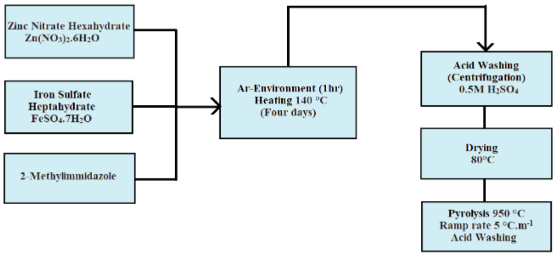

Figure 1. Flowsheet for preparing ZIF based catalyst

At ramp of 5°C/min for 1hr, carbonization in tubular furnace is done at 950 °C. The ZIF is washed to exfoliate unreacted metallic content with Sulfuric acid and dried at 80°C. Graphitic carbon nitride having g-C3N4 stoichiometry was synthesized by thermal treatment at of 1,3,5-trichloromelamine(C3N3Cl3), sodium amide (NaNH2) with induction of benzene at 220°C.While keeping 1/6 Co: N ratio, 1g of g-C3N4,0.5 g FeSO4.7H2O (Sigma-Aldrich), and 0.52g of Cobalt Chloride (Sigma-Aldrich) were added and dried at 450°C for 1 day. A brief pyrolysis was done at 600°C ,1 hr in tubular furnace at 5°C/min ramp. Washing was done by 0.5 M H2SO4 followed by drying at 80°C for 24 hrs.

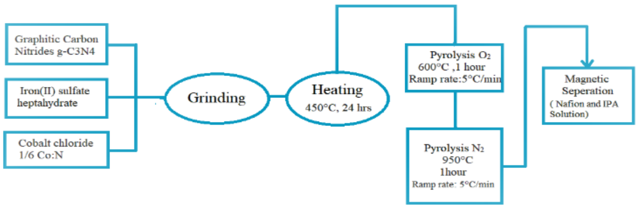

Figure 2. Preparation methodology of Graphitic carbon nitrides

B. *Material testing*

Hydrodynamic Rotating Disk Electrode technique is used to analyze the electrochemical reduction of oxygen at cathode. A 3-electrode system, providing a steady-state diffusion through rotating disk at varying rotation per minute. A dispersant formed by 24ml IPA, 5 % wt Nafion (1100 EW, Sigma-Aldrich) and DI water ((Thermo Scientific Barnstead MicroPure) was used 1ml and 4mg/ml of solid catalyst material was added to formulate ink slurry for testing. To homogenize the slurry, agitation was done followed by acoustic exposure/sonication for 30 min. Alumina polish and DI water cleaning of electrode (Dia=5mm) to render electrode surface dust free. The ink layer is dropped (~ 48µl) on Glassy carbon (GC) electrode, the hydrophilic region of electrode. A uniform layer is obtained by air-heater drying at 700 rpm. Nitrogen (99.9% pure) purging is done and Cyclic voltammograms are obtained at 400 rpm to activate the catalytic activity. CV scan was done at 50 mV.s-1 for 50 cycles, higher scan rates are used because unreacted impurities hinders the catalytic ORR activity of the material. Linear Sweep Voltammetry (LSV) scans determine reactive capacity of oxygen reduction. Electrode potential varied in electrolytic mediums, (0.9 to –1.0) vs SCE for 0.1M HCLO4 and (0.2 to-1.0) vs SCE for 0.1M KOH. A constant scan rate of 20 mV.s-1 ,while succeeding rpm to induce convective-diffusion at 400,800,1200 and 1600 rpm was maintained.

III. RESULTS AND DISCUSSION

ORR elucidates at the onset potentials, for this higher value of Onset potential are required. A reversible electrochemical equilibrium is achieved at exchange current density i.e backward and forward reaction at same potential level.[25] This parameter defines the reaction rate, depending on the active surface area of electrode. To validate the ORR, Nitrogen current values are deducted from the oxygen current value due to presence of capacitive current.[24]

Table 1, indicates the values obtained through experimentation on three electrode system, reference electrode being Calomel Electrode (Koslow Scientific) while the electrolytic medium was basic (0.1 M KOH). The efficient values of limiting current are shown by Graphitic carbon nitrides at the same conditions, while Fe-ZIF restrains from showing better performances on both onset potentials and limiting current. A reason could be the hindered active sites, not definite reactive surface area available, since morphology is yet unknown. Linear Sweep voltammograms obtain at varying torque increase in reactivity at higher rotation rates represents the convective diffusion.

TABLE 1.ORR DEFINING PARAMETERS AT ROOM TEMPERATURE 25°C

Electrocatalyst material	Onset potential (V)	Limiting current (mA.cm^{-2})
Pt/C (20% wt pt)	0.89- ~0.90	5.3
Zn(Fe)ZIF	0.65	2.7
Co-C3N4	0.74	4.5

A chemical gradient referring to the transfers of ion from active surface area towards electrolyte. Fig 3, presents LSV scan in perchloric acid, slower scan rates dissolves material in electrolyte instead of testing it gives the ORR pattern for Pt/C in acidic media, while other scans are in basic electrolyte.

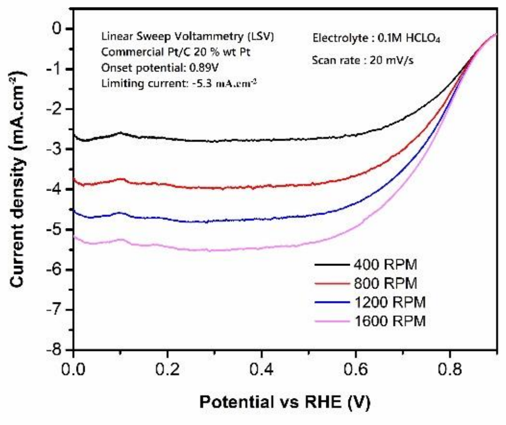

Figure 3. LSV scan (20 mv.s-1) 20% Pt on carbon black

The electrochemical analysis of Graphitic Carbon Nitrides provide an acceptable limiting current and onset potential, result showed in Fig-4 provided their layered planar structure expose active areas for reaction. A comparison analysis of Non-PGM catalyst is done in Fig.6 where Graphitic carbon nitrides show promising aspects as compared to Pt/C. Charge transfer of ionic species with respect to electrode potentials is governed by Nernst Equation,[26] when reacting species are brought to reactive surface of electrode. Where the net charge transfer is given by eq (1), ***i*** is the exchange current density (mA.cm^{-2}) and *F=96485 C.mol^{-1}* (Faraday's constant).

$$V_{net} = \frac{i}{nF} \qquad \text{eq.(1)}$$

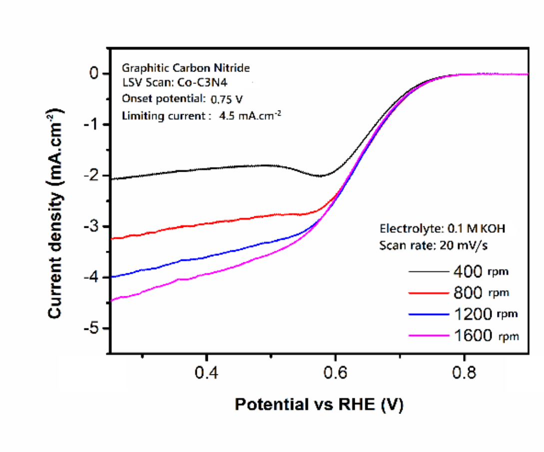

Figure 4. Linear sweep voltammogram for CoC3N4

Iron dopant ZIF catalyst shows low onset potentials ,relative to the acceptable limiting current as non precious metal catalyst. A fact to that is presence of tetrahedral structure of metal organic framework,placing one atom with thin crystalline morphology of four atoms.Fig-5 refers to LSV analysis of ZIF based catalyst formed by one pot method. Fig-6

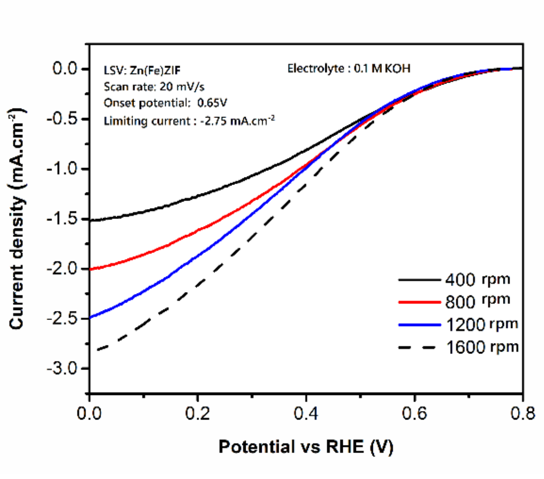

Figure 5. Linear sweep voltametery of iron doped ZIF

Higher onset potentials defines a sharp initiation of reaction, whereas there are some applications requiring lower onsets. Open circuit voltages and half wave potentials are also looked upon for characterization in potentiodynamic techniques.

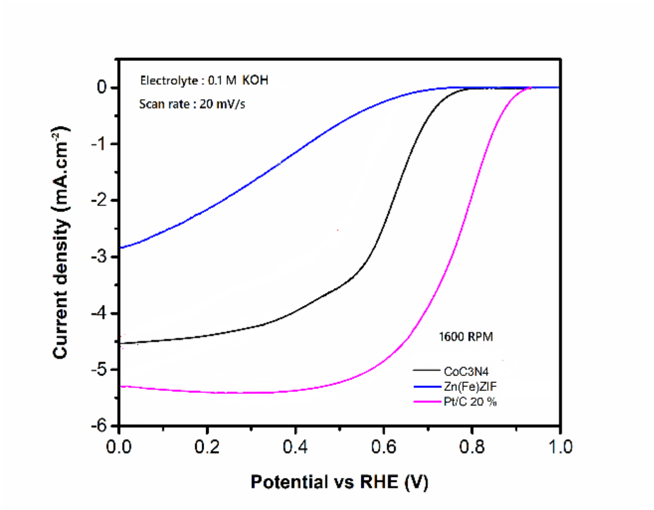

Figure 6. Performance comparison of LSV scans at 1600 RPM

Charge transportation is either by reaction taking a 2e- or a 4e- transfer, depends upon the reactivity of electrode surface. Cell potentials are higher at 2e- reaction process, but deteriorating towards membrane, on the other hand a 4e-pathway is much favorable shown by Pt/C in Figure 2 ,the Non-PGM catalysts following a 2e- transfer. Graphitic Carbon Nitrides are close to attaining a four-electron transfer, while a hindered reactivity due to unavailability of the active sites [27] can be seen in Fig-7. This parameter greatly effects the selectivity of catalyst for ORR applications as it defines the path of electrochemical kinetics highlighting the intermediate reaction that is responsible for rate. Electrolytic material in which diffusion occurs also plays a vital role in the ORR and durability of catalyst reactivity.

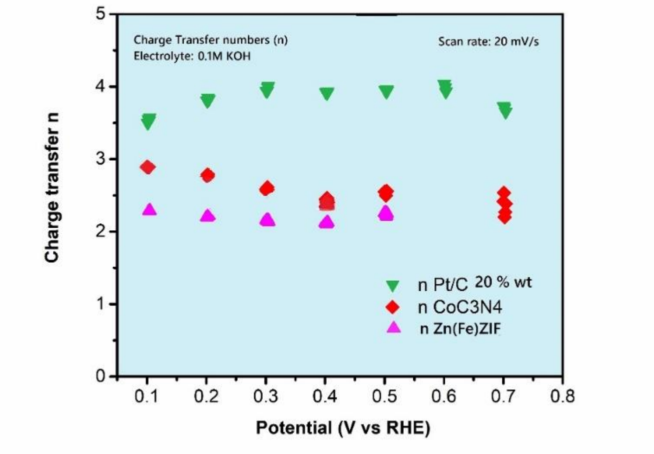

Figure 7. Charge number comparison for brtter ORR efficiencies

CONCUSLION

The research work discussed in this paper, identifies potential candidates for Oxygen-reduction reaction elucidating at the cathode of Low Temperature Proton Exchange Membrane Fuel Cells. Non-PGM catalysts provide a variety of electrocatalysts for ORR application, among them two entire different classes of Non precious metals have been synthesized in this work namely Graphitic Carbon Nitrides and Iron Zinc ZIF material. Co-C3N4 offer acceptable values of electrocatalytic limiting current due to presence of layered planar structure exposing more surface activity while showing low onset potentials. Iron Zinc ZIF shows less performance then the former catalyst, in terms of composite formation having reduced probable sites for oxygen reduction. Moreover, pyrolyzing environment contributes a lot to the morphology, there trying different gases can be beneficial to have better ORR characteristics of electrocatalysts.

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