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Nitish Kumar

FOR SUCCESSFULLY PARTICIPATING IN

SERB Sponsored

Training and Skill Internship (VRITIKA)

On

"Development of Non-Platinum-Based Oxygen Reduction Catalysts for Microbial Fuel Cells"

Duration: 1st June 2022 to 26th July 2022

Organized by

CIPET: SARP – Advanced Polymer Design and Development Research Laboratory (APDDRL), Bengaluru

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VRITIKA INTERNSHIP REPORT

ON

"Development of Non-Platinum-Based Oxygen Reduction Catalyst for Microbial Fuel-cell"

(Under the ACCELERATE VIGYAN Scheme – a SERB Initiative)

CIPET: SARP- Advanced Polymer Design and Development Research Laboratory (APDDRL), Bengaluru.

Supervised by: Dr. Kingshuk Dutta

Submitted by: Nitish Kumar

Date of Submission: 09/09/2022

OBJECTIVE:

1. To synthesise low-cost alternative cathode catalyst for microbial fuel cells. Such as; Nickel based, Cobalt based, Cerium based.

2. To develop conducting support material (Polyaniline, Polypyrole, Co-polymer) for uniform dispersion, distribution and functioning of the develop catalyst.

3. To characterize the catalyst and catalyst support by FTIR, Optical Microscope, Electrochemistry.

4. To Utilise the develop catalyst and catalyst support in the cathod microbial fuel cell and check their cell performance.

BACKGROUND:

A microbial fuel cell (MFC) is a device that converts chemical energy to electrical energy by the action of micro-organisms. These electrochemical cells are constructed using either a bioanode and/or a biocathode. Most MFCs contain a membrane to separate the compartments of the anode (where oxidation takes place) and the cathode (where reduction takes place). The electrons produced during oxidation are transferred directly to an electrode or to a redox mediator species. The electron flux is moved to the cathode. The charge balance of the system is maintained by ionic movement inside the cell, usually across an ionic membrane. Most MFCs use an organic electron donor that is oxidized to produce CO_2, protons, and electrons. Other electron donors have been reported, such as sulfur compounds or hydrogen. The cathode reaction uses a variety of electron acceptors, most often oxygen (O_2). The idea of using microbes to produce electricity was conceived in the early twentieth century. Michael Cressé Potter initiated the subject in 1911. Potter managed to generate electricity from *Saccharomyces cerevisiae*, but the work received little coverage. In 1931, Barnett Cohen created microbial half fuel cells that, when connected in series, were capable of producing over 35 volts with only a current of 2 milliamps. A study by DelDuca et al. used hydrogen produced by the fermentation of glucose by *Clostridium butyricum* as the reactant at the anode of a hydrogen and air fuel cell. Though the cell functioned, it was unreliable owing to the unstable nature of hydrogen production by the micro-organisms. This issue was resolved

by Suzuki et al. in 1976, who produced a successful MFC design a year later. In the late 1970s, little was understood about how microbial fuel cells functioned. The concept was studied by Robin M. Allen and later by H. Peter Bennetto. People saw the fuel cell as a possible method for the generation of electricity for developing countries.

Cathode material and cathode catalyst play an essential role in increasing the power density of MFCs. The ORR should be performed efficiently and durably by the cathode electrocatalyst. The cathodic ORR can be a direct four-electron transfer in which O_2 is reduced to H_2O, or a two-electron process in which H_2O_2 is generated as the formal product. The sort of reduction process that happens at the cathode is heavily determined by the type of electrocatalyst utilized. In general, noble metal electrocatalyst follows a dominant, direct four-electron process ; whereas, non-noble metal electrocatalyst follows either a direct four-electron process or a mixed two and four-electron process. An ideal ORR catalyst must fulfil the following requirements: i) high catalytic activity, ii) high stability, iii) high selectivity, iv) resistance to poisoning, and v) cost-effectiveness.The ORR catalyst's catalytic activity is determined by its morphology, electrochemical surface area, electronic conductivity, and porosit.

Cost are considerably impacted by high platinum cathode loading. For this reason, we enhanced catalyst and support materials as well as binder design have been developed.

Literature Review:

1.JOURNAL

Nickel nanocatalysts supported on sulfonated polyaniline: Potential toward methanol oxidation and as anode materials for DMFCs DOI: 10.1039/c5ta01837d| Published in Royal Society of Chemistry

2.Original Research Paper

Nanostructured Polyaniline: An Efficient Support Matrix for Platinum-Ruthenium Anode Catalyst in Direct Methanol Fuel Cell

19 June 2018| **https://doi.org/10.1002/fuce.201700201** | Published in fuel cell

3. PAPER

Nanorods of cerium oxide as an improved electrocatalyst for enhanced oxygen reduction in single-chambered microbial biofuel cell

13 January 2020 | https://doi.org/10.1088/2053-1591/ab653e | published in material research express

4.JOURNAL

Polymer electrolyte membrane with high selectivity ratio for direct methanol fuel cells: A preliminary study based on blends of partially sulfonated polymers polyaniline and PVdF-co-HFP 14 January

5. Material and Synthesis

5.1 Synthesis of Cerium Oxide (CeO2)

Material: Cerium Sulphate ($Ce(SO_4)_2$), Sodium Hydroxide (NaOH), Sodium Borohydride ($NaBH_4$), isopropanol, Distilled Water(DI).

Procedure:

1) Firstly, 1g of Ce (SO4)2 (yellow colour powder) was ultrasonicated dispersed in the mixture of 1:1 isopropanol and distilled water.
2) The solution of 1M NaOH was prepared
   Molecular weight of NaOH= 40g/mol

   40 ⟶ 1000ml

   x ⟶ 10ml

   x = 0.4g

   so, to prepare 1M NaOH 0.4g was added in 10ml DI

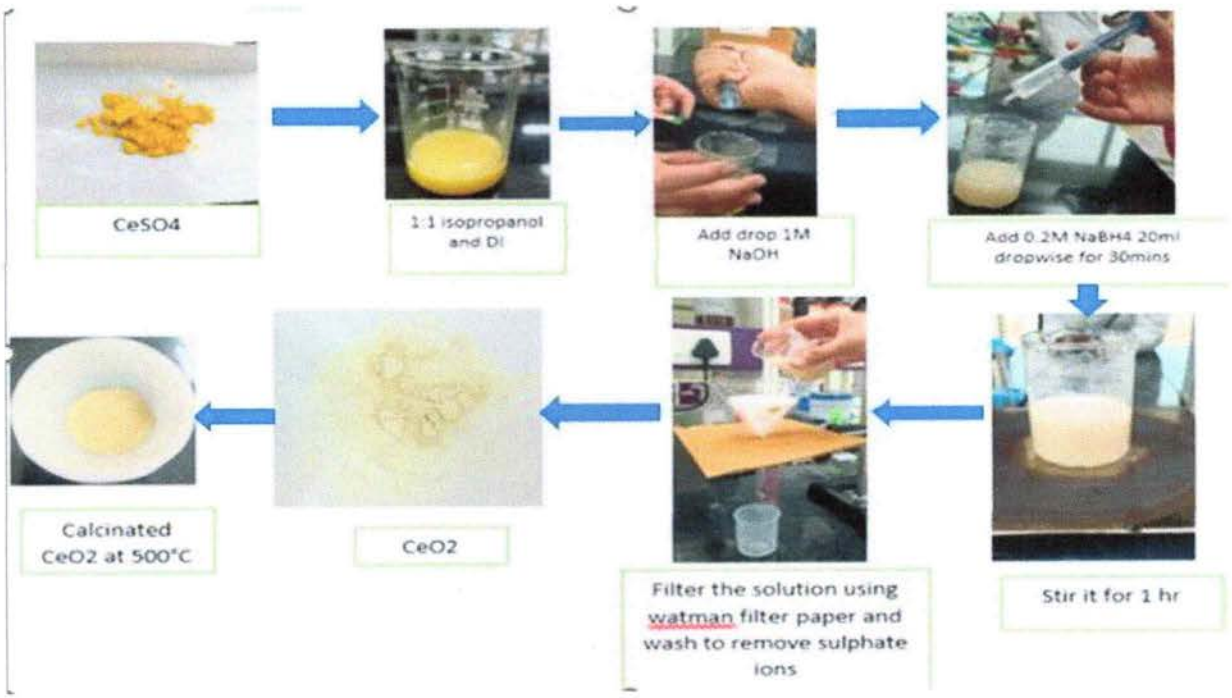
   This solution was added dropwise till pH reaches 8.
3) Then 0.2M NaBH4 solution in 20ml DI was prepared and added dropwise for 30mins.
   Molecular weight of NaBH4 = 37.83g/mol

   37.83 ⟶ 1000ml

   X ⟶ 20ml

   X = 0.7566g

   But we need prepare 0.2M
   For 0.2M 0.7566*0.2= 0.151g
   So, to prepare 0.2M NaBH4 0.151g was added in 20ml DI
4) The resultant solution was kept for stirring 1hr
5) Then the solution was filtered using filter paper and washed 7to 8 times to remove sulphate ions.
6) Then the sample was dried at 25°C for 12hr in vacuum oven (Cream color)
7) \Then calcinated CeO2 at 500°C (Light yellow



5.2 Synthesis of Polyaniline

Material: Aniline, Ammonium Persulphate (APS), HCl, DI.

Procedure:

1) Firstly, 6ml of HCl (2M) was added in 100ml of DI

2) Then 0.1M of Aniline was added in above solution and stirred properly. (Monomer solution)

Molecular weight of Aniline = 93.13g/mol

Density of Aniline = 1.02g/cm3

Volume = mass/density = 93.13/1.02 = 91.30 ml

91.30ml ⟶ 10000ml

X ⟶ 100ml

X = 0.9130ml

So, to prepare 0.1M Aniline 0.9130ml is added 100ml monomer solution

3) 0.1M of Ammonium Persulphate (APS) was added to monomer solution.

Molecular weight of APS = 228.18g/mol

228.18 ⟶ 1M

X ⟶ 0.1M

X = 22.818g for 1000ml

So for 100ml, we will require,

22.818 ⟶ 1000ml

X ⟶ 100ml

X = 2.2818g

So, to prepare 0.1 M APS 2.2818g is added in 100ml monomer solution

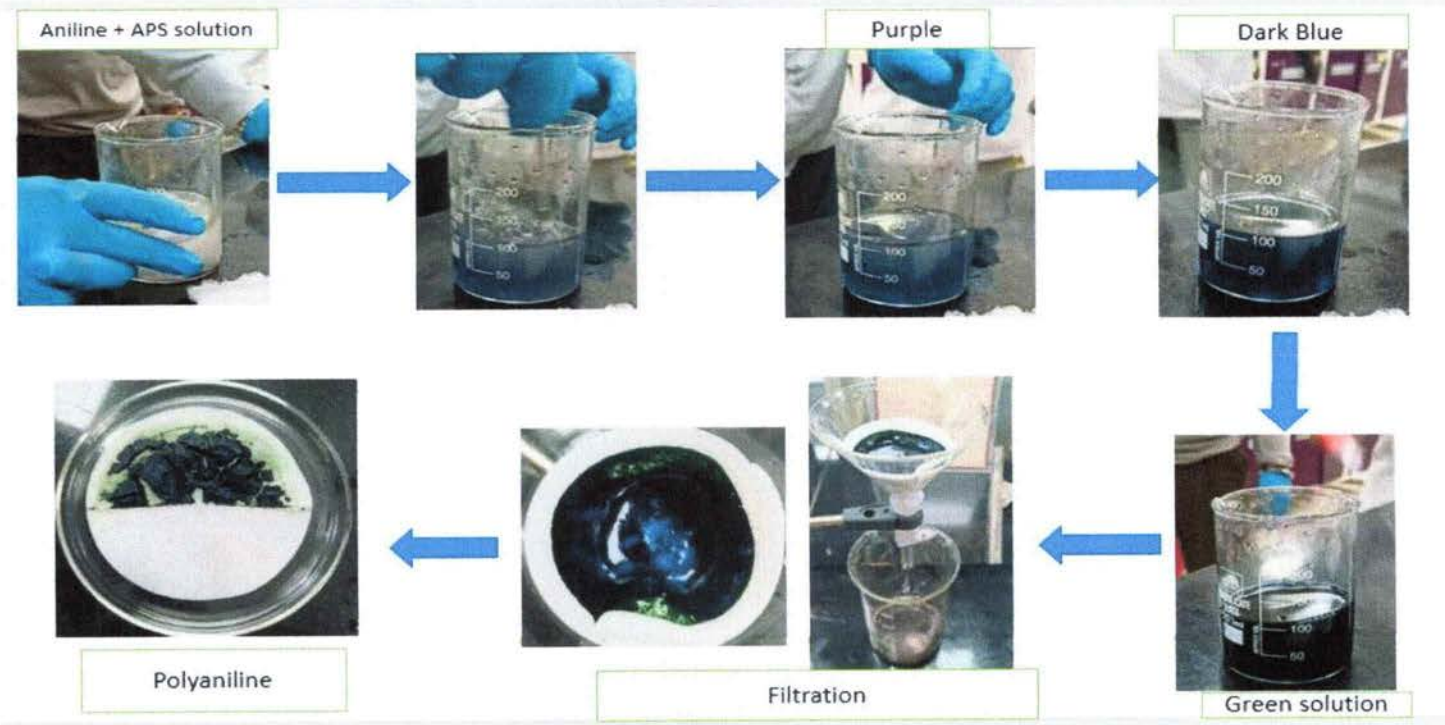
4) The solution was mixed manually for polymerization process to start

The solution color changes from Brown to purple to dark blue to green

5) The solution was kept overnight to complete the polymerization process

6) Then solution was filtered using filter paper and washed two to three times

7) Later the filtrate was kept for drying at room temperature. (Green Color)



5.3 Synthesis of Proton Exchange Membrane

Material: Cellulose Acetate, Polyvinyl Acetate, Acetic Acid, Distilled water

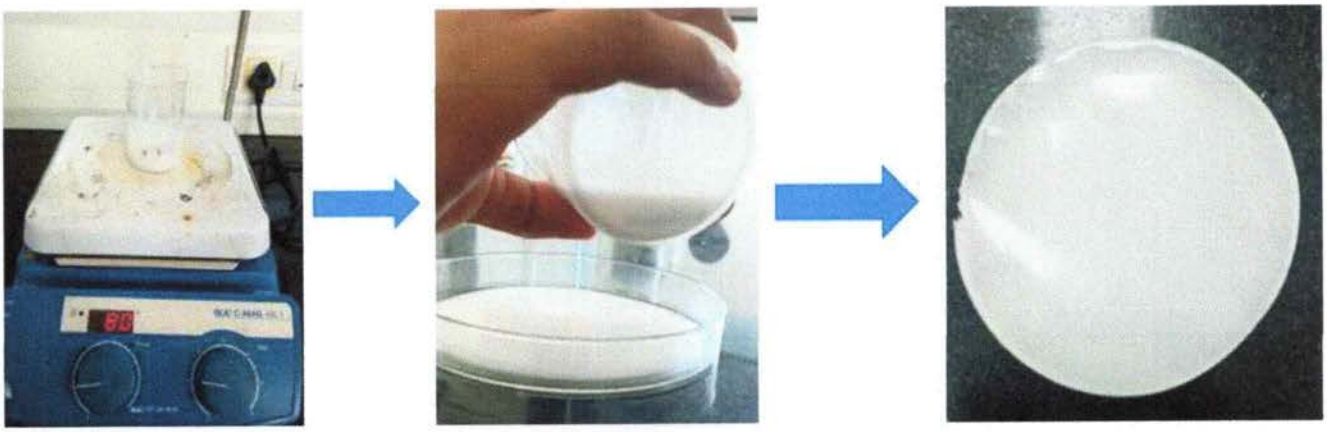
Procedure:

Total weight 3 gram in 30ml Acetic Acid solvent

80% CA (Cellulose Acetate) =2.4 g — 18ml of Acetic Acid

20% PVA (polyvinyl Acetate) = 0.6g — 12ml of distilled water

All are mixed together and kept at 60°C for 24 hr. A thick solution was formed after stirring for 24 hr which was then poured in Petri dish and kept to dry for 24hr under room condition. (White color).



CA + PVA + Acetic Acid + DI

Membrane

5.4 Synthesis of Poly pyrrole

Material: Pyrrole, Ammonium persulphate (APS), HCl, Distilled Water.

Procedure:

1) Firstly, 6ml of HCl (2M) was added in 100ml of DI

2) Then 0.1M of Pyrrole was added in above solution and stirred properly. (Monomer solution)

Molecular weight of Pyrrole = 67.09g/mol

Density of Pyrrole = 0.966g/cm3

Volume = mass/density = 67.09/0.966 = 69.45ml

69.45ml ⟶ 10000ml

X ⟶ 100ml

X = 0.69ml

So, to prepare 0.1M Pyrrole 0.690ml is added 100ml monomer solution

3) 0.1M of Ammonium Persulphate (APS) was added to monomer solution.

Molecular weight of APS = 228.18g/mol

228.18 ⟶ 1M

X ⟶ 0.1M

X = 22.818g for 1000ml

So for 100ml, we will require,

22.818 ⟶ 1000ml

X ⟶ 100ml

X = 2.2818g

So, to prepare 0.1 M APS 2.2818g is added in 100ml monomer solution

4) The solution was mixed manually for polymerization process to start.

5) The solution was kept overnight to complete the polymerization process

6) Than solution was filtered using filter paper and washed two to three times

7) Later the filtrate was kept for drying at room temperature.(Black Color)

Pyrrole+ APS solution

Filtration

Poly Pyrrole

5.5 Synthesis of Copolymer

Material: Aniline, pyrrole, Ammonium Persulphate (APS), HCl, DI.

Procedure:

1) Firstly, 6ml of HCl (2M) was added in 100ml of DI

2) Then 0.1M of Aniline was added in above solution and stirred properly. (Monomer solution)

Molecular weight of Aniline = 93.13g/mol

Density of Aniline = 1.02g/cm3

Volume = mass/density = 93.13/1.02 = 91.30ml

91.30ml ⟶ 10000ml

X ⟶ 100ml

X = 0.9130ml

So, to prepare 0.1M Aniline 0.9130ml is added 100ml monomer solution

3) Then 0.1M of Pyrrole was added in above solution and stirred properly. (Monomer solution)

Molecular weight of Pyrrole = 67.09g/mol

Density of Pyrrole = 0.966g/cm3

X = 45.636g for 1000ml

So for 100ml, we will require,

45.636 ⟶ 1000ml

X ⟶ 100ml

X = 4.5636g

So, to prepare 0.1 M APS 4.5636g is added in 100ml monomer solution

5) The solution was mixed manually for polymerization process to start

6) The solution was kept overnight to complete the polymerization process

7) Than solution was filtered using filter paper and washed two to three times

8) Later the filtrate was kept for drying at room temperature. (Black Color)

5.6 Synthesis of cobalt oxide:

Materials: Sodium hydroxide pallets, sodium borohydride, cobalt nitrate hexahydrate, deionized water

Procedure:

1). Firstly, 1 gm of $Co(NO_3)_2.6H_2O$ is added in 10 ml of DI

2). Then this solution kept for stirring for 30minutes at 75 -80 °C.

3). Preparation of 0.8M of sodium borohydride solution

Molecular weight of $NaBH_4$ = 37.83 g/mol

37.83 g/mol ⟶ 1M

x ⟶ 0.8M

x = 30.264gm

30.264 ⟶ 1000 ml

x ⟶ 50ml

x = 1.5132 gm

So, to prepare 0.8M sodium borohydride 1.5132 gm is added 50ml of Deionized water (Solution A)

4). Preparation of 0.8M of sodium hydroxide solution

Molecular weight of NaOH = 40 g/mol

40g/mol ⟶ 1M

x ⟶ 0.8M

x = 32 gm

32gm ⟶ 1000ml

x ⟶ 20ml

x = 0.64 gm

So, to prepare 0.8M sodium hydroxide 0.64 gm is added 20ml of Deionized water (Solution B)

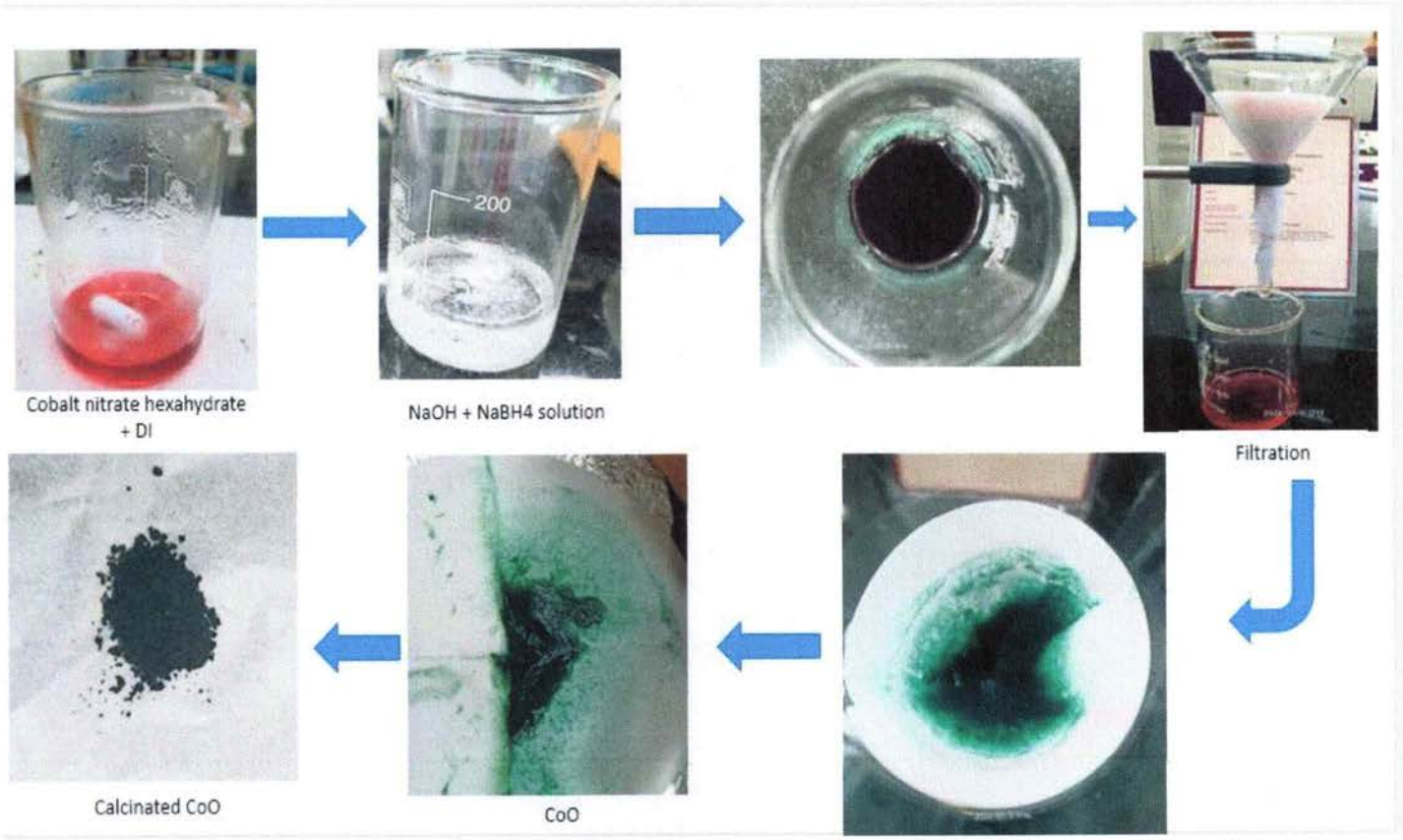
5). Now, both the solution(A + B) were mixed and than added dropwise in the solution of $Co(NO_3)_2.6H_2O$ till pH reaches to 11.1

6). This solution was kept undisturbed for 30 minutes

7). Than, solution was filtered using filter paper and washed two to three times to remove nitrate ions

8). Finally, it was kept for drying at 40 °C under hot air vacuum.(Green color)

9). The finally product was calcinated at 600°C (Black color)



5.7 Synthesis of Nickel oxide

Materials: Nickel Nitrate Hexahydrate, Sodium Hydroxide, Sodium Borohydride, Isopropanol, Distilled Water.

Procedure:

1) Firstly, we prepared 1:1 solution of isopropanol(10ml) and DI (10ml) respectively
2) Now 1gm of NiCl2.6H2O is added in this solution
3) Then solution is kept for ultrasonication for 30 minutes at room temperature.
4) Preparation of 1M of sodium hydroxide solution

Molecular weight of NaOH = 40 g/mol

40 g/mol ⟶ 1000ml

x ⟶ 10ml

x = 0.4 gm

So, to prepare 1M sodium hydroxide 0.4 gm is added 10ml of Deionized water

5) This solution added dropwise till pH reaches to 8
6) Preparation of 0.2M of sodium borohydride solution

Molecular weight of NaBH4 = 37.83 g/mol

37.83 g/mol ⟶ 1000 ml

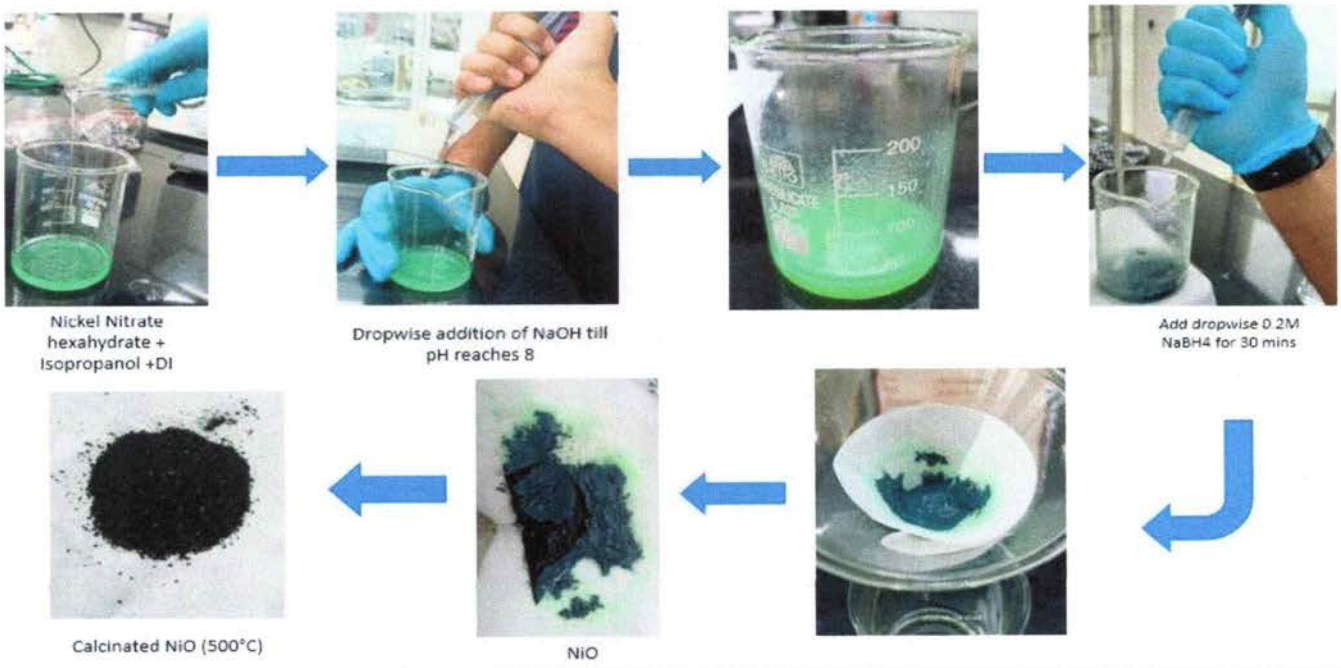
x ⟶ 20ml

x = 0.7566 gm for 1M

and for 0.2M, 0.151 gm of NaBH4 is required in 20ml of DI

7) This solution added dropwise in the above solution for 30minutes under constant stirring
   above solution left for stirring for 1 hours
8) Finally the solution filtered and washed 3 to 4 times with DI
9) The filtrate was dried at room temperature for 24 hr. (Green color)

The dried sample

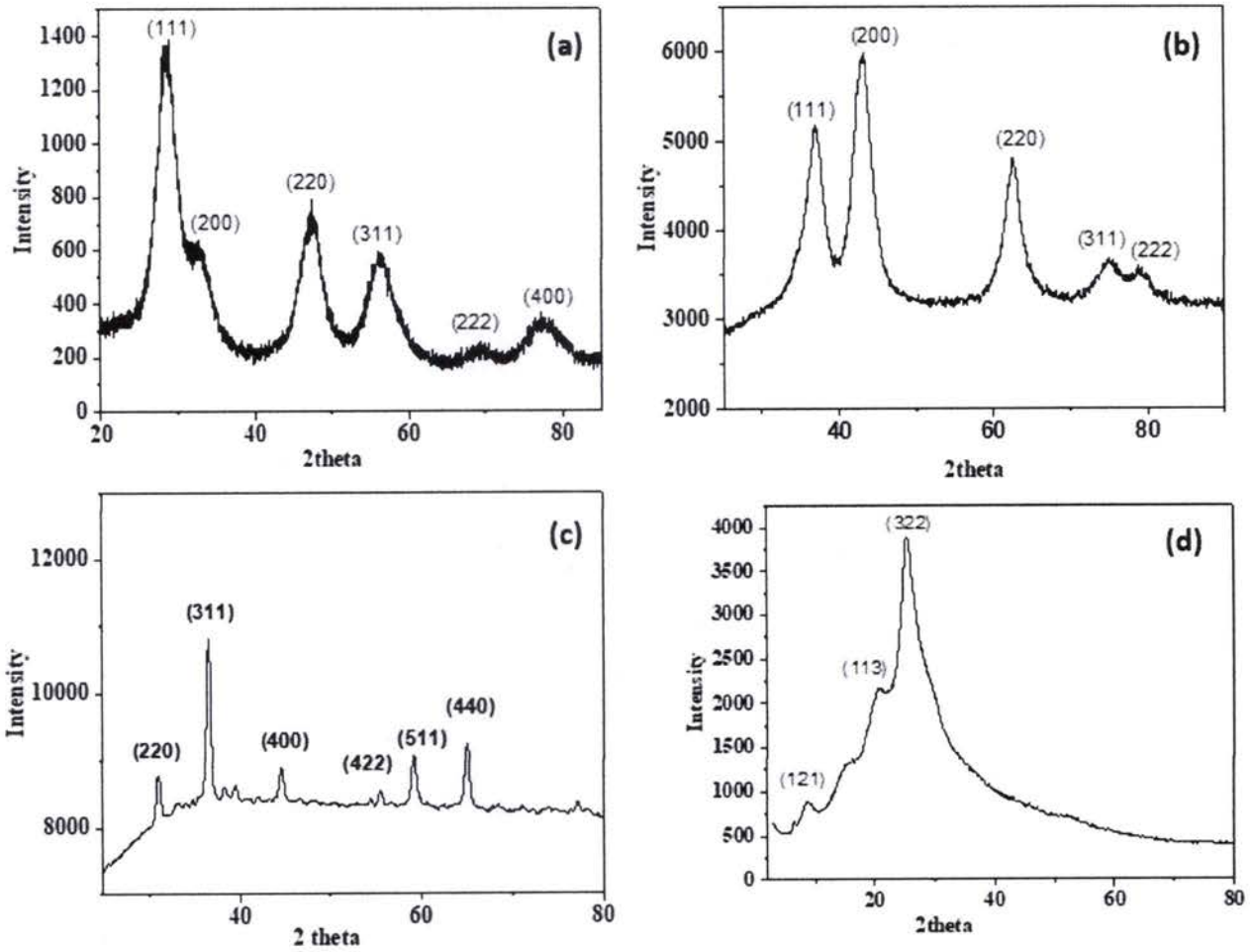


6. Results and Discussion

6.1 Physical Characterization

6.1.1 XRD analysis

The XRD patterns obtained for the CeO2 NRs and the Pt NPs are shown in figure 1. The diffraction peaks obtained for the CeO2 NRs at 2θ values of 29.33°, 34.13° and 56.18°represent the (111), (200) and (311) planes of CeO2. Further, the strong diffraction peaks obtained for the NiO at 2θ values of 36.82°, 42.86°, 62.62°, 75.1°, 79.04° correspond to the (111), (200), (220), (311), (222) facets, for CoO at 2θ values of 30.98°, 36.62°, 44.58°, 55.68°, 59.32°,65.18 corresponds to (220), (311), (400), (422), (511), (440); Polyaniline (PANI) at 2θ values at 8.46°, 20.56°, 25.22° corresponds to (1210, (113), (322); for Polypyrrole the 2θ will be 25.78° corresponds to (104).



(e)

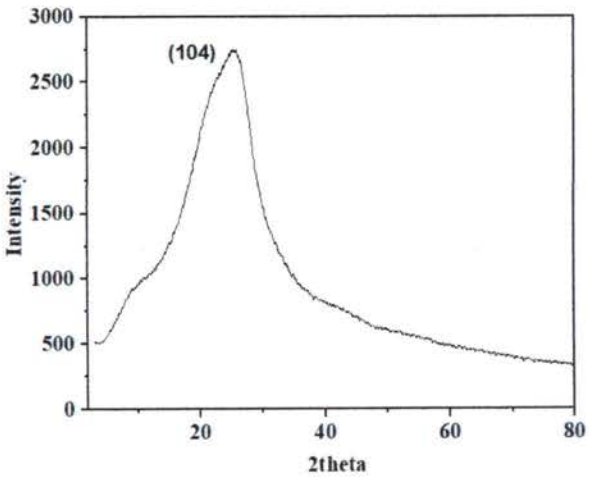
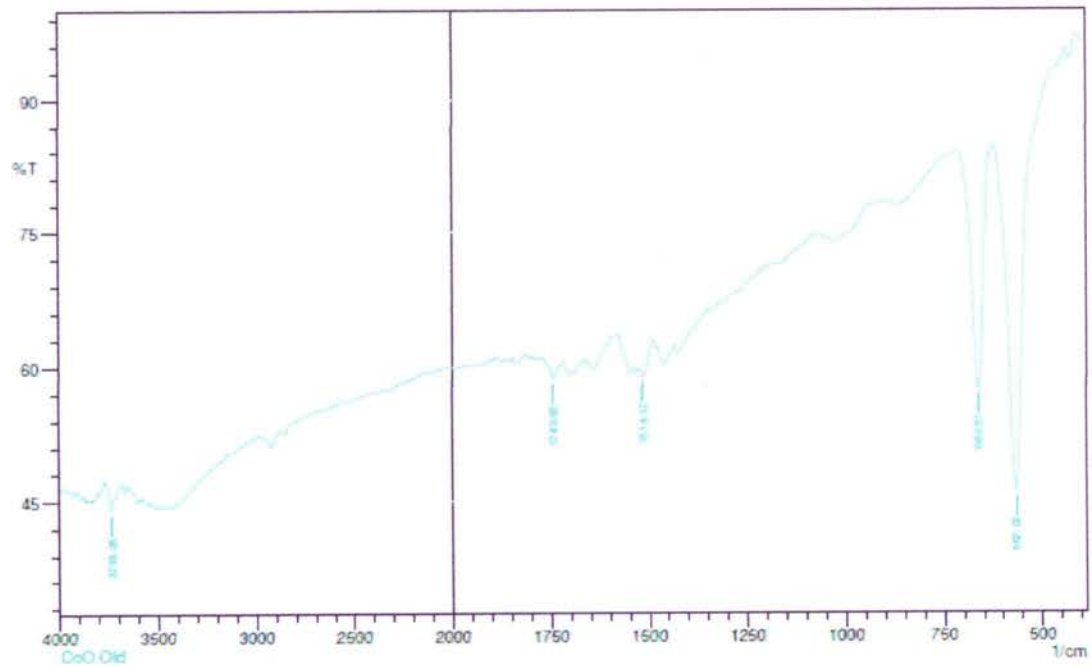


Fig. 1. XRDs spectra for ; (a) CeO_2, (b) NiO, (c) CoO, (d) PANI

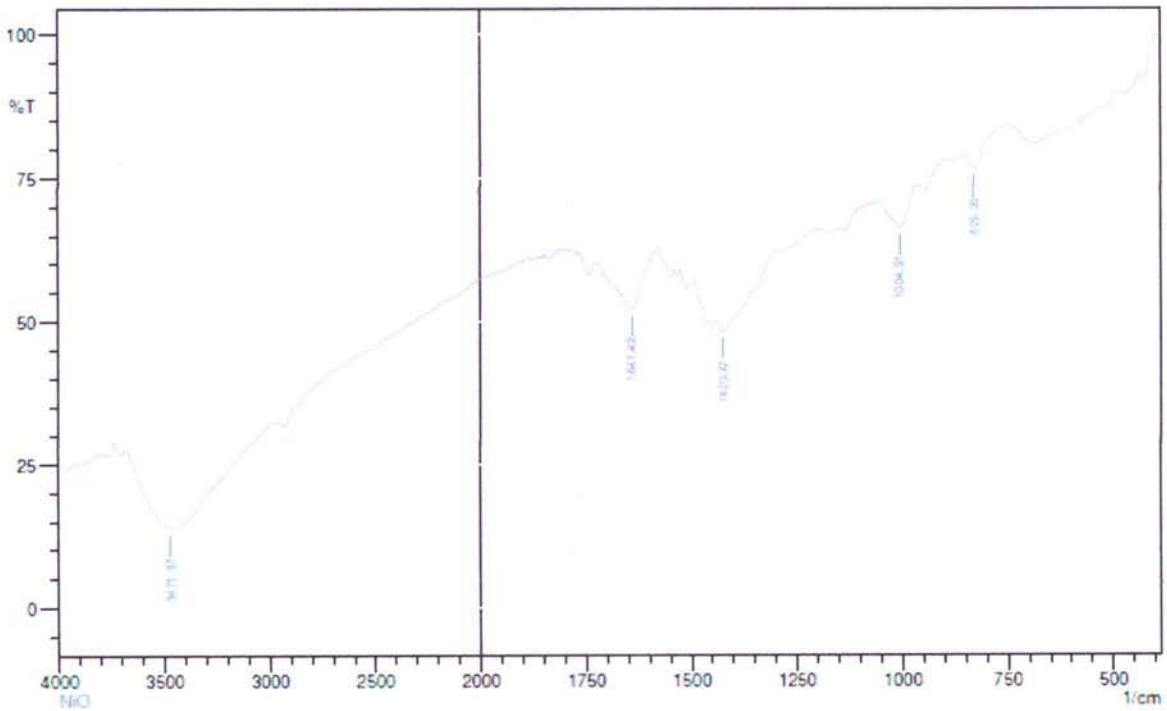
6.1.2 FTIR analyses

FTIR spectra for CoO, NiO, PANI and Poly-pyrrole are shown in figure

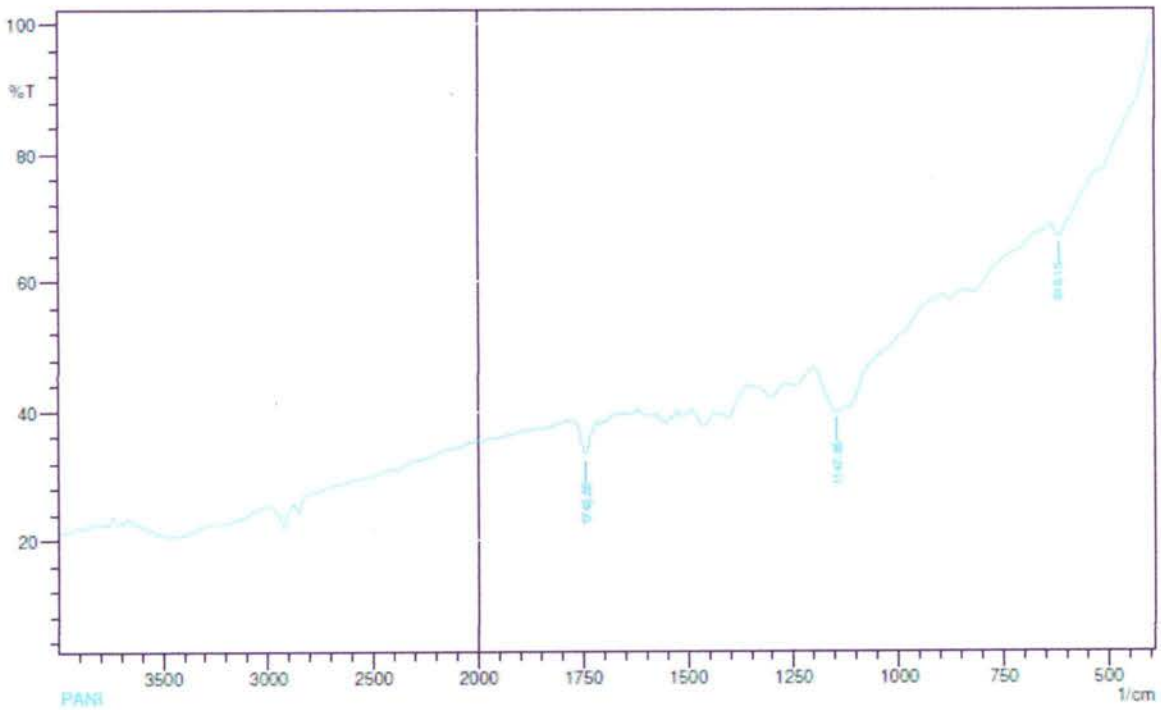
(a)



(b)


100
%T
75
50
25
0
4000
3500
3000
2500
2000
1750
1500
1250
1000
750
500
1/cm
NiO

(c)


100
%T
80
60
40
20
3500
3000
2500
2000
1750
1500
1250
1000
750
500
1/cm
PANI

(d)

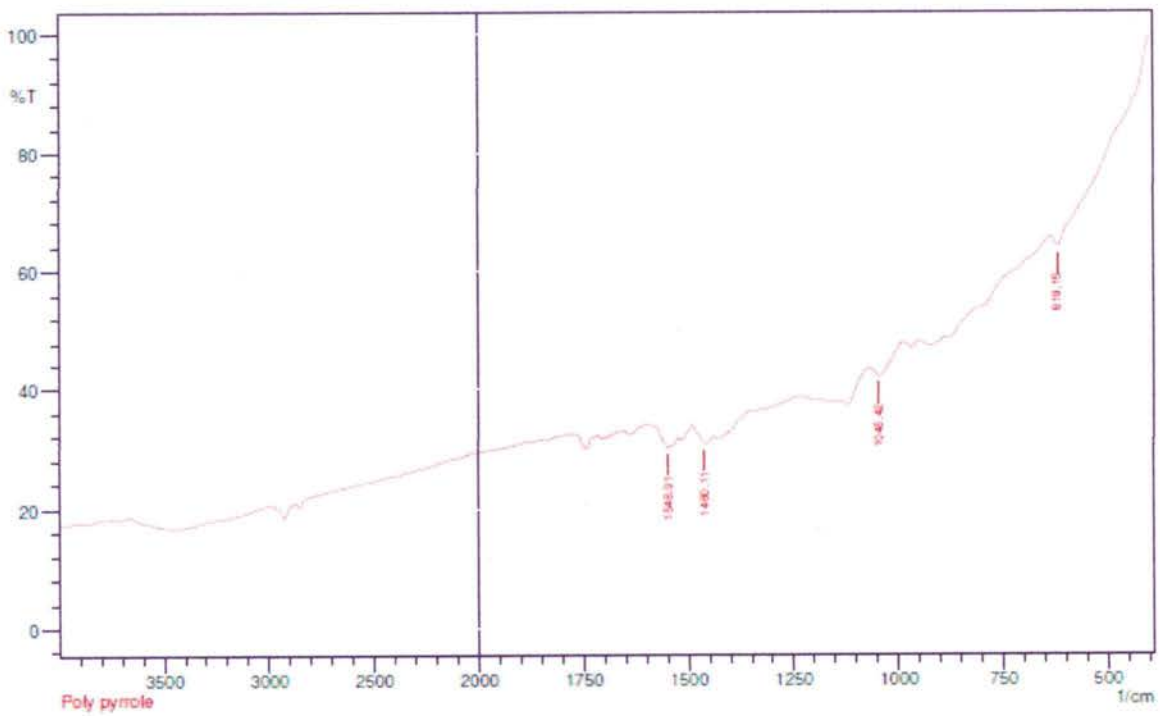


Fig. 2.; FTIR spectra for (a) CoO, (b) NiO, (c) PANI, (d) Polypyrrole

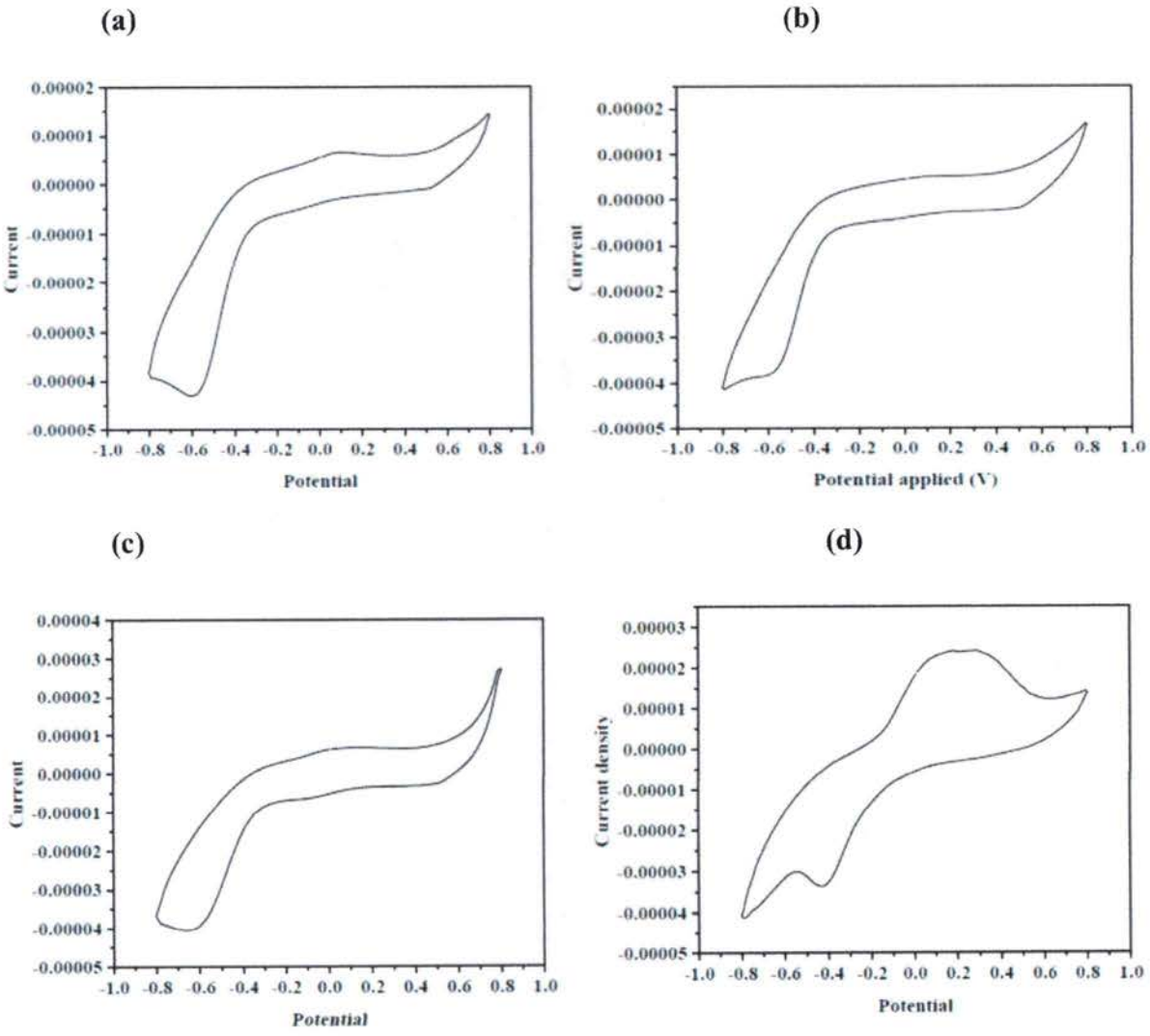
6.2 Electrochemical Characterization

Cyclic voltammetric (CV) and Electrochemical Impedance Spectroscopy (EIS) analyses of the prepared catalyst-coated electrodes were carried out at room temperature. The tests were performed in a glass cell, fitted with a conventional three-electrode assembly; where, the prepared glassy carbon electrode as the working electrode, a Pt wire was employed as the auxiliary electrode and Ag/AgCl performed the role of the reference electrode. Cyclic voltammograms were recorded in O_2 saturated 0.1 M phosphate

buffer solutions, within the potential range of −0.8 V to +0.8 V and at a scan rate of 50 mVs^{-1}

6.2.1 Cyclic Voltammetry

For the purpose of determining the ORR catalytic activities of the prepared and purchased electrocatalysts, CV analyses in the three electrode system. Figures 2(a) and (b) present the CV curves (representing the 1st steady cycle) of the synthesized NPs, the synthesized CoO and NiO in O_2 saturated 0.1 M phosphate buffer solution respectively.



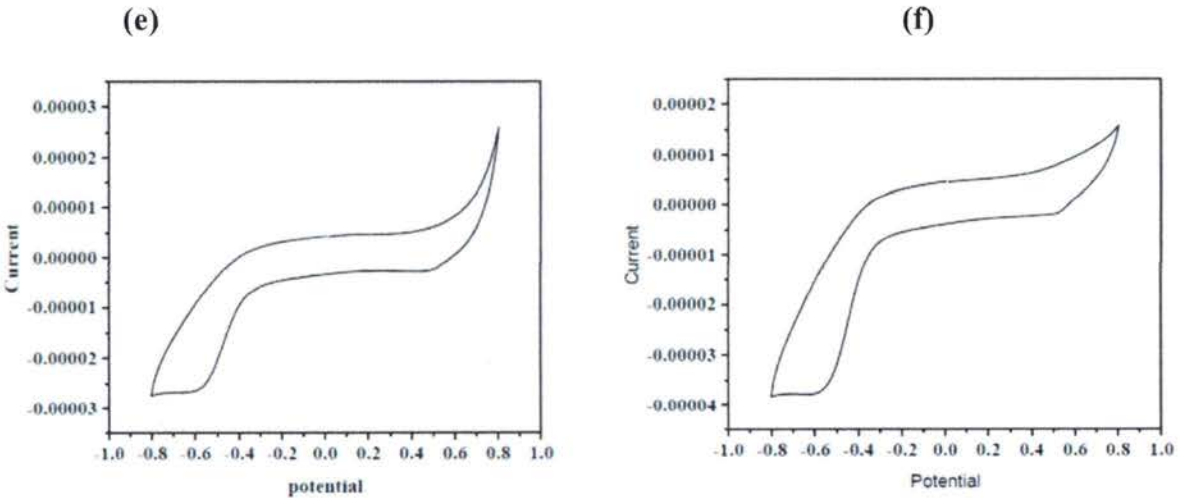
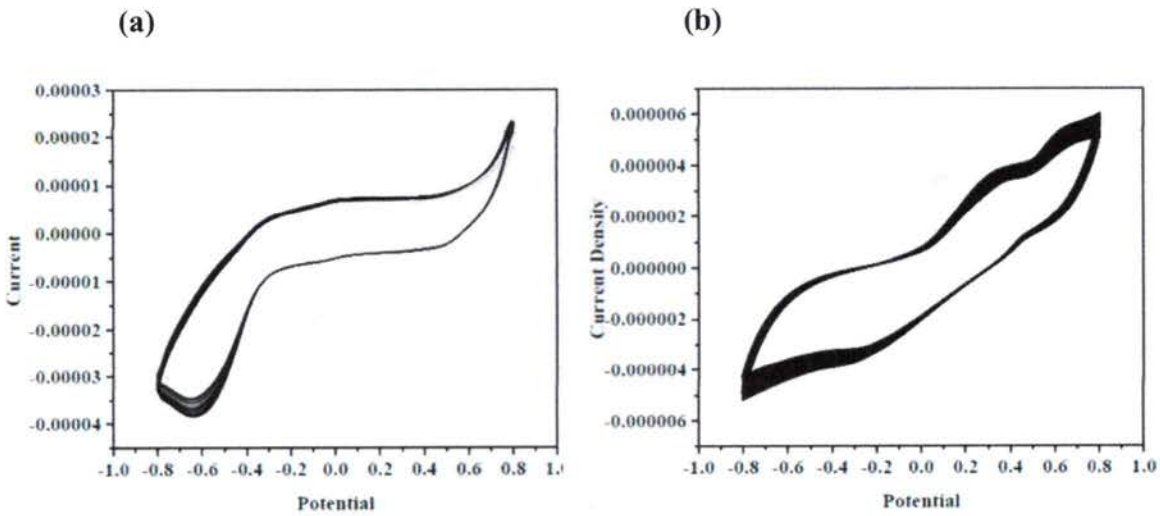


Fig. 3; cyclic voltammetry for (a) CoO-copolymer, (b) NiO-copolymer, (c) CoO-PANI, (d) NiO-PANI, (e) CoO-Polypyrole (f) NiO-polypyrole.

6.2.2 Cyclic Stability

Cyclic stability for 100 cycles are shown in Fig. 3



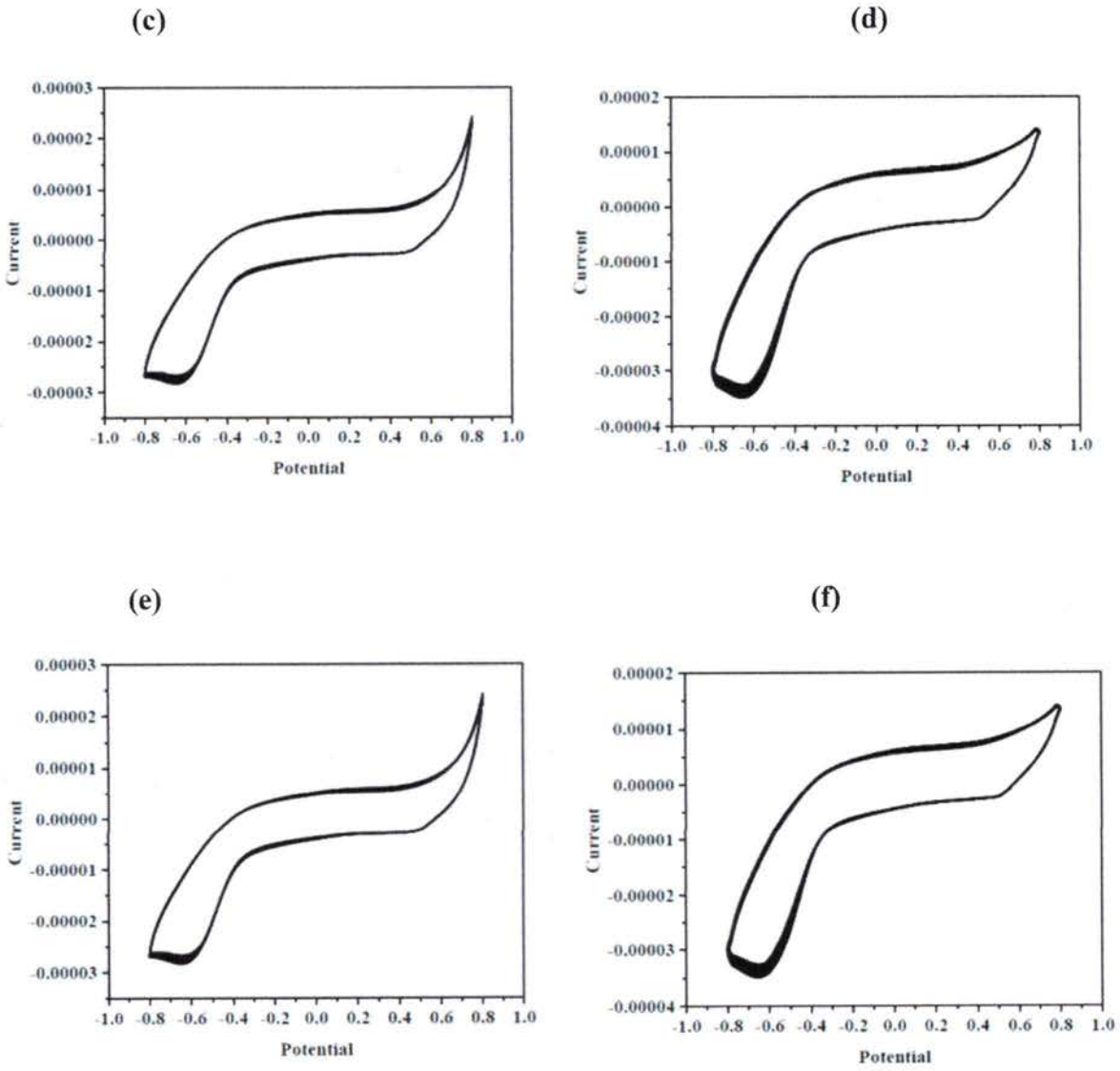


Fig. 4; cyclic Stability for 100 cycles (a) CoO-copolymer, (b) NiO-copolymer, (c) CoO-PANI, (d) NiO-PANI, (e) CoO-Polypyrole (f) NiO-polypyrole

6.2.3 Electrochemical Impedance Spectroscopy

Nyquist plots, obtained for the synthesized CoO and NiO in O_2 saturated 0.1 M phosphate buffer solutions at room temprature are presented in figure 6(b).

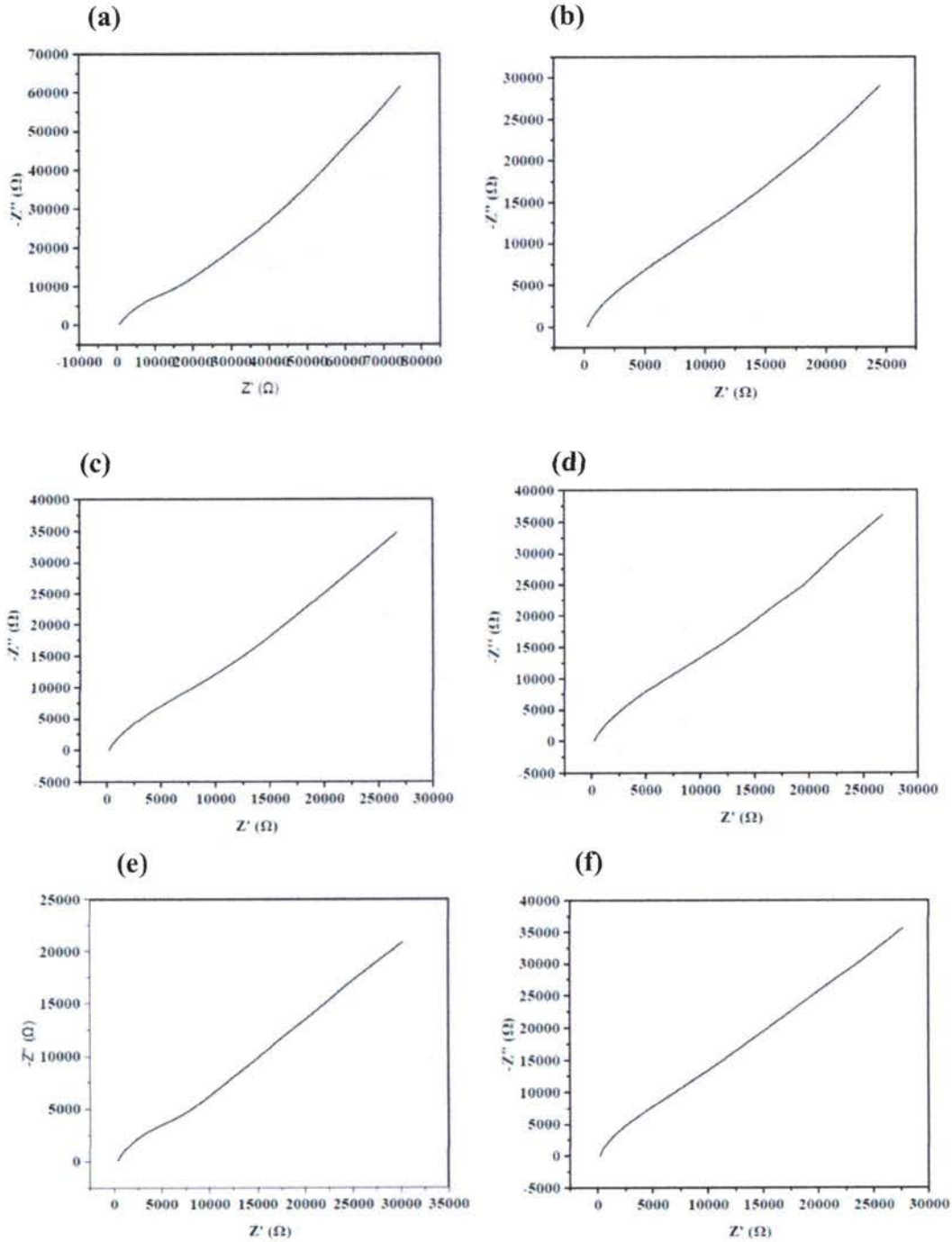


Fig. 5; Electrochemical Impedance Spectroscopyfor (a) CoO-copolymer, (b) NiO-copolymer, (c) CoO-PANI, (d) NiO-PANI, (e) CoO-Polypyrole (f) NiO-polypyrole

Weekly report:

Sr. no	week	Work done
1	Week1	Writing of review Paper
2	Week2	Synthesis of Proton Exchange Membrane(PEM) Characterization of PEM (Raman, XRD) % Swelling Ratio % Water Uptake Surface Resistivity Volume Resistivity
3	Week3	Proton Conductivity of PEM Ion Exchange Capacity of PEM Synthesis of Cerium Oxide(CeO2) Characterization of Ceo2 (Raman, FTIR, XRD, Optical Microscopy, Particle Size Analyser)
4	Week4	MFC Cell Preparation Preparation of Binder. Testing MFC using CeO2 as a catalyst. Preparation of Polyaniline(PANI)
5	Week5	Characterization of PANI (Raman, FTIR, XRD, Optical Microscopy) Industrial Visit (PIPE COMPANY) Preparation of NiO Characterization of NiO (Raman, FTIR, XRD, Optical Microscopy)
6	Week6	Preparation of CoO Characterization of CoO (Raman, FTIR, XRD, Optical Microscopy)
7	Week7	Preparation of Polypyrole Characterization Polypyrole (Raman, FTIR, XRD, Optical Microscopy)
8	Week8	Preparation of Copolymer Characterization of PANI (Raman, FTIR, XRD, Optical Microscopy) Preparation of Electrode for MFC testing Preparation of Hallow Fibre Membrane.

7. Future Scope

1.The great advantage of MFC is the direct conversion of organic waste into electricity. In future MFC can be linked to municipal waste steams or source of agricultural and animal waste providing a sustainable system for water treatment and energy production.

2.In Future MFC can be used in power environmental sensors. Environmental sensors help in understanding the eco-system. But so far powering these sensors in regular period of time is difficult, especially in deep water system. MFC is proved to be more useful in this kind of areas.