Design of non-precious cobalt oxide based electrocatalysts

Final Technical Report

CSIR Scheme No: 01(2813)/14/EMR-II

Submitted by

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FORM-F

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

Human Resource Development Group
(Extra Mural Research Division)
CSIR Complex, Library Avenue, Pusa, New Delhi – 110012

PROFORMA FOR PREPARING FINAL TECHNICAL REPORT

(Five copies of the report must be submitted immediately after completion of the research scheme)

1. Title of the scheme

Design of non-precious cobalt oxide based electrocatalysts	Scheme No.: 01(2813)/14/EMR-II Date of Commencement : 15/01/2015 dd/mm/yy Date of termination : 31/01/2018 dd/mm/yy

2. Name and address of Principal Investigator

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3. Name of Sponsoring laboratory of CSIR (If applicable)

NA

4. Total grant sanctioned and expenditure during the entire tenure

	Amount Sanctioned	Expenditure
Staff	NA	NA
Contingency	[50,000 + 1,94,902 + 2,02,429 + 1,66,596 + 32 (Interest)] = 6,13,959	[49,929 + 3,96,968 + 1,66,596] = 6,13,493
Equipment	NA	NA
Total	6,13,959	6,13,493

5. Equipment(s) purchased out of CSIR grant NIL

Name	Cost
NA	NA

6. Research fellows associated with scheme NIL

Name& Designation	Date of Joining	Date of leaving
NA	NA	NA

7. Name(s) of the fellow(s) who received Ph.D. by working in the scheme, along with the Title(s) of thesis: NA

8. List of research papers published/communicated, based on the research work done under the scheme (Name(s) of author(s), Title, Journal, Volume number, Year and Pages should be given for each paper published and a copy of each of them should be enclosed; reprints/copies of papers appearing after submission of FTR should also be sent to CSIR): First and acknowledgment page of each article is enclosed.

S No	Authors	Title of the paper	Name of the Journal	Volume	Pages	Year
1	K.K. Hazarika, C. Goswami, H. Saikia, B.J. Borah, P. Bharali	Cubic Mn_2O_3 nanoparticles on carbon as bifunctional electrocatalyst for oxygen reduction and oxygen evolution reactions	Molecular Catalysis	451	153-160	2018
2	C. Goswami, K.K. Hazarika, P. Bharali	Transition metal oxide nanocatalysts for oxygen reduction reaction	Material Science for Energy Technologies	1	117-128	2018
3	P. Deka, B.J. Borah, H. Saikia, P. Bharali	Cu-based nanoparticles as emerging environmental catalysts	The Chemical Record	18	1-13	2018

4	B.J. Borah, A. Mahanta, M. Mondal, H. Gogoi, Y. Yamada, P. Bharali	Cobalt-copper nanoparticles catalyzed selective oxidation reactions: Efficient catalysis at room temperature	ChemistrySelect	3	9826-9832	2018
5	H. Saikia, B.J. Borah, Y. Yamada, P. Bharali	Enhanced catalytic activity of CuPd alloy nanoparticles towards reduction of nitroaromatics and hexavalent chromium	Journal of Colloid and Interface Science	486	46-57	2017
6	H. Saikia, B.J. Borah, P. Bharali	Room temperature reduction of nitroaromatics using Pd nanoparticles stabilized on nano-CeO_2	ChemistrySelect	2	10524-10530	2017
7	H. Saikia, K.K. Hazarika, B. Chutia, B. Choudhury, P. Bharali	A simple chemical route toward high surface area CeO_2 nanoparticles displaying remarkable radical scavenging activity	ChemistrySelect	2	3369-3375	2017
8	H. Saikia, R. Duarah, P. Sudarsanam, S.K. Bhargava, P. Bharali	PdCu nanoparticles stabilized on porous CeO_2 for catalytic degradation of azo dyes: Structural characterization and kinetic studies	ChemistrySelect	2	2123-2130	2017
9	P. Deka, P. Sarmah, R.C. Deka, P. Bharali	Hetero-nanostructured Ni/α-Mn_2O_3 as highly active catalyst for aqueous phase reduction reactions	ChemistrySelect	1	4726-4735	2016
10	P. Deka, A. Hazarika, R.C. Deka, P. Bharali	Influence of CuO morphology on enhanced catalytic degradation of methylene blue and methyl orange	RSC Advances	6	95292 - 95305	2016

11	P. Deka, R. Choudhury, R.C. Deka, P. Bharali	Influence of Ni on enhanced catalytic activity of Cu/Co_3O_4 towards reduction of nitroaromatic compounds: studies on the reduction kinetics	RSC Advances	6	71517 – 71528	2016
12	P. Deka, R.C. Deka, P. Bharali	Porous CuO nanostructure as reusable catalyst for oxidative degradation of organic water pollutants	New Journal of Chemistry	40	348-357	2016
13	C. Goswami, B. Chutia, P. Bharali	Metal and Metal Oxide-Based Nanomaterials for Electrochemical Applications ISBN: 978-3-030-04473-2	In Emerging Nanostructured Materials for Energy and Environmental Science (Springer)	Ch. 12	499-530	2019*
14	B.J. Borah, M. Mondal, P. Bharali	Palladium-based Hybrid Nanocatalysts: Application toward Reduction Reactions ISBN: 978-0-12-814134-2	In Noble Metal-Metal Oxide Hybrid Nanoparticles: Fundamentals and Applications (Elsevier)	Ch. 27	565-583	2019*

* Book chapters published.

9. Details of new apparatus or equipment designed or constructed during the investigation:

No instrument was designed.

10. The likely impact of the completed work on the scientific/technological potential in the country (this may be attached as Enclosure-I):

Enclosed separately in Enclosure I

11. Is the research work done of some industrial or agricultural importance and whether patent(s) should be taken? Yes/No; if yes, what action has been/should be taken:

The work has industrial importance from viewpoint of development of alternative energy devices, e.g. the reaction carried out in the current project will facilitate the development of electrocatalysts which in turn boost fuel cell efficiency. However, no patent was filed till date.

12. How has the research work complemented the work of CSIR Laboratory that sponsored your scheme?

    This scheme was supported by CSIR, New Delhi and has direct relevance to the goal of CSIR in the development of materials for energy. CSIR-NCL, Pune and CSIR-CECRI, Karaikudi are two CSIR laboratories where research are being carried out in the field to develop materials for fuel cell reactions, with special reference to oxygen reduction reaction. The research conducted under this scheme would add basic understanding of materials development and reaction methodologies to the existing knowledge.

13. Detailed account of the work carried out in terms of the objective(s) of the project and how for they have been achieved; results and discussion should be presented in the manner of a scientific paper/project report in about 5000 words; and this should be submitted as Enclosure-II to this report.

    Enclosed separately in Enclosure II

14. An abstract of research achievements in about 200-500 words, suitable for publication.

    As proposed in the original objective of the project we successfully synthesized various compositions of Co-Fe and Co-Cu binary oxides and applied as efficient electrocatalysts for oxygen reduction reaction (ORR) in the alkaline medium. Depending on the morphology and composition of various binary oxides, we obtained remarkable activity towards ORR and selectivity to OH^-. The synthesized electrocatalysts are characterized by multi-technique approach by utilizing wide spectroscopic and microscopic methods. The binary Co-Cu and Co-Fe oxide electrocatalysts exhibit superior ORR activity via 4e pathway in comparison to benchmark Pt/C electrocatalyst. The superiority of synthesized electrocatalysts is evaluated based on early onset potential for ORR and high current density in electrochemical measurements.

15. Mention here whether or not the unspent grant has been refunded to CSIR:

    The unspent balance has been refunded in the form of demand draft along with this report.

12/2/19

Date: 12/02/2019

Signature of PI

Note: Final Technical Report is expected to be self-contained complete report of the work done.
Please do not leave any column unanswered.

Enclosure I

CSIR Scheme No: 01(2813)/14/EMR-II

CSIR Scheme Title: Design of non-precious cobalt oxide based electrocatalysts

Increasing energy demands have stimulated intense research on alternative energy conversion and storage systems with high efficiency, low cost and environmental benignity. A significant amount of research is being conducted on fuel cells as a clean, alternative energy source. Fuel cells are electrochemical devices that directly convert chemical energy into electrical energy with high efficiency and low emission of pollutants. Oxygen reduction reaction (ORR) is one of the most important fundamental reactions occurring on the cathode catalytic surface of hydrogen fuel cells. At present, the most effective cathode electrocatalyst is composed of platinum metal or its alloys on carbon black, as it supports the four electron reduction of oxygen at relatively low overpotentials. However, the slow kinetics of the ORR even on Pt catalysts is among the most limiting factors in the energy conversion efficiency of fuel cells. On the other hand, Pt is an expensive metal with low abundance. Hence, alternative non-platinum based electrocatalysts for the cathodic ORR is very crucial for practical application of fuel cells.

In the current project work we developed Co-based non-precious electrocatalysts for ORR in alkaline medium. It is observed that Co-Fe and Co-Cu based binary electrocatalysts show superior efficiency for ORR in comparison to the pristine Co-oxides. The mass specific activity is relatively better in comparison to the benchmark Pt/C electrocatalyst. The research finding in this project enriched the basic understanding in the development of non-precious metal oxide electrocalaysts for ORR. Moreover, the catalysts are very selective towards 4e pathway towards OH^- in alkaline medium. These data would facilitate designing newer electrocalaysts for exploitation in fuel cell ORR process.

Enclosure II

CSIR Scheme No: 01(2813)/14/EMR-II

CSIR Scheme Title: Design of non-precious cobalt oxide based electrocatalysts

Objectives of original proposal

(i) Synthesis of shape, size and composition controlled cobalt oxide, iron oxide, copper oxide and Co-M composite oxide (M = Fe and Cu) nanostructures by modified surfactant assisted/surfactant-free hydrothermal and solvothermal techniques.

(ii) Evaluation of synthesized cobalt oxide, iron oxide and copper oxides for ORR by cyclic voltammetry and other electrochemical techniques in alkaline media.

(iii) To investigate the impact of Fe and Cu on the ORR activity of cobalt oxide with various shape, size and composition in alkaline media.

(iv) Thorough structural characterization of synthesized cobalt oxide, iron oxide, copper oxide and Co-M composite oxide (M = Fe and Cu) nanostructures by various spectroscopic and microscopic techniques.

(v) In depth quantitative evaluation of the electrocatalytic activities and kinetics of ORR with the help Rotating-disk electrode (RDE) measurements is targeted.

(vi) Influence of carbon support is aimed to investigate on the performance of catalysts for ORR.

Experimental Section

Hydrothermal synthesis of Cu, Co, Fe oxides and their mixed oxides

$CuCl_2\cdot 2H_2O$, $CoCl_2.6H_2O$ and $FeCl_3.6H_2O$ salts of desired amounts were initially dissolved in 40 mL of distilled water. Then urea solution was prepared by dissolving 2.40 g of urea in 40 mL of distilled water and added to the homogeneous mixture from a burette drop wise and stirred for 30 min. The resulting solution is transferred to a 150 mL teflon-lined stainless steel autoclave which was then kept in an oven maintained at a temperature of 120 °C for 6 h. After 6 h, it was allowed to cool for 15 h. It was then filtered and washed with distilled water and finally with absolute ethanol and dried at 50 °C. The precursor was then calcined in a muffle furnace at 450 °C for 4 h. The various compositions of Co, Cu and Fe mixed oxides were synthesized employing the following precursors with different concentrations as shown below in Table 1.

Table 1: Amount of $CoCl_2.6H_2O$, $FeCl_3.6H_2O$ and $CuCl_2{\cdot}2H_2O$ employed for synthesis of Co, Cu and Fe mixed oxides

Serial number	$Co(NO)_3.6H_2O$(g)	$FeCl_3.6H_2O$(g)	$CuCl_2{\cdot}2H_2O$(g)	Mole Ratio	Base(g)
1	0.9517	_	_	1:0	2.40
2	0.2855	0.7568	0.4773	3:7	2.40
3	0.4758	0.5406	0.3409	1:1	2.40
4	0.6662	0.3244	0.2046	7:3	2.40
5	_	1.0812	0.6819	0:1	2.40

Carbon supported Co,Cu and Fe mixed oxide preparation

Certain amount of different compositions of Co, Cu and Fe mixed oxides and carbon are groud for about half an hour using mortar and pestle. After that the mixture is sonicated with ethanol (as a solvent) for half an hour. Then the sonicated mixture was allowed to first air dry and then kept in an oven at a temperature of 50℃ to get the resulting carbon supported oxides.

Characterization

The Powder X-ray diffraction (XRD) patterns of the samples were carried out on a Bruker AXS Model D8 focus instrument using nickel-filtered CuK_α (0.15418 nm) radiation source at the 2θ between 10° and 80°, the scan rate was $0.05°s^{-1}$. TEM and HR-TEM investigations were carried on a FEI-Technai (G2 20 S-TWIN) instrument equipped with a slow-scan CCD camera and at an accelerating voltage of 200 kV. Energy-dispersive X-ray spectroscopy (EDS) elemental mapping were performed on a "JEOL, JSM Model 6390 LV" scanning electron microscope operated at 15 kV. The loading of NCs on the carbon support was determined by Thermo gravimetric analyser (model TGA-50, Shimadzu). The flow rate of air atmosphere for the analysis was maintained at 30 mL/min and heating rate at 10 °C/min up to 700 °C. Raman spectra were recorded using a laser micro-Raman system (make: Horiba Jobin Vyon, model: LabRam HR) at room temperature on 488 nm excitation wavelength. The Brunauer-Emmett-Teller (BET) surface areas were determined by N_2 physisorption using a Quantachrome Instruments (Model: NOVA1000e).

Electrochemical Characterizations

The electrocatalytic oxygen reduction reaction (ORR) was measured using the freshly prepared catalysts by following the typical procedure. In brief, glassy carbon (GC) electrode (3 mm diameter) was polished with 0.005-µm Al_2O_3 powder. A standard suspension of the carbon-supported catalysts was prepared by adding 5 mg of fresh catalyst to 0.5 mL 2-Propanol, deionized water, and 0.5% Nafion solution respectively. The resultant mixture was sonicated for 30 min until it became a uniform dark ink. Then, 5 µL of the suspension was quantitatively transferred to the surface of the polished GC electrode. The electrode coated with a thin film of the ink was dried at 35°C under N_2 atmosphere for 6 h. The modified GC electrode was inserted into an electrochemical cell and used as the cell's working electrode. The cell included two additional electrodes: a reference electrode Ag/AgCl, saturated KCl, (Metrohm) as the reference electrode, and a platinum wire (Metrohm) and a counter electrode (Pt). Cyclic voltammetry (CV) was performed using a microcomputer-controlled electrochemical analyzer (Metrohm Autolab PGSTAT204 instrument) at room temperature. The cyclic voltammetry (CV) was measured in high purity N_2 and O_2 saturated (0.1 M KOH) solution with scan rate 50 mVs^{-1}. Rotating disk electrode (RDE) measurements were conducted in O_2-saturated 0.1 M KOH. Oxygen was continuously purged for at least 30 min before measurement, to ensure the saturation of the electrolyte with O_2 and then blanketing the solution with an O_2 atmosphere during the entire experiment and all experiments were performed at room temperature. For comparison, a commercial 20 wt % Pt/C (Alfa Aesar) was measured under the same conditions.

Results and discussion

X-ray diffraction (XRD) study: Figure 1 presents the XRD profiles of the various Co-Cu and Co-Fe composition mixed oxides. In the Figure 1a the diffraction peaks are observed at 2θ = 18.63°, 30.77°, 36.37°, 44.36°, 55.31°, 58.98° and 64.73° which could be assigned to (111), (220), (311), (400), (422), (511) and (440) reflections, respectively for the cubic spinel Co_3O_4 phase (JCPDS card no. 65-3103) and also the diffraction peaks are observed at 2θ = 32.54°, 35.53°, 38.69°, 48.77°, 53.49°, 58.25°, 61.57°, 65.84 and 67.89° which could be assigned to (110), (-110), (111), (-202), (020), (202), (-113), (022) and (113) reflections, respectively for monoclinic end centered CuO phase (JCPDS card no. 89-5895). Similarly, in Figure 1b diffraction peaks are observed at 2θ = 32.43°, 35.08°, 40.19°, 48.86°, 53.49°, 57.03°, 61.88°and 63.57° which could be assigned to (211), (110), (222), (220), (321), (332), (310) and (121) reflections, respectively for the α-Fe_2O_3 phase (JCPDS card no. 85-0987).

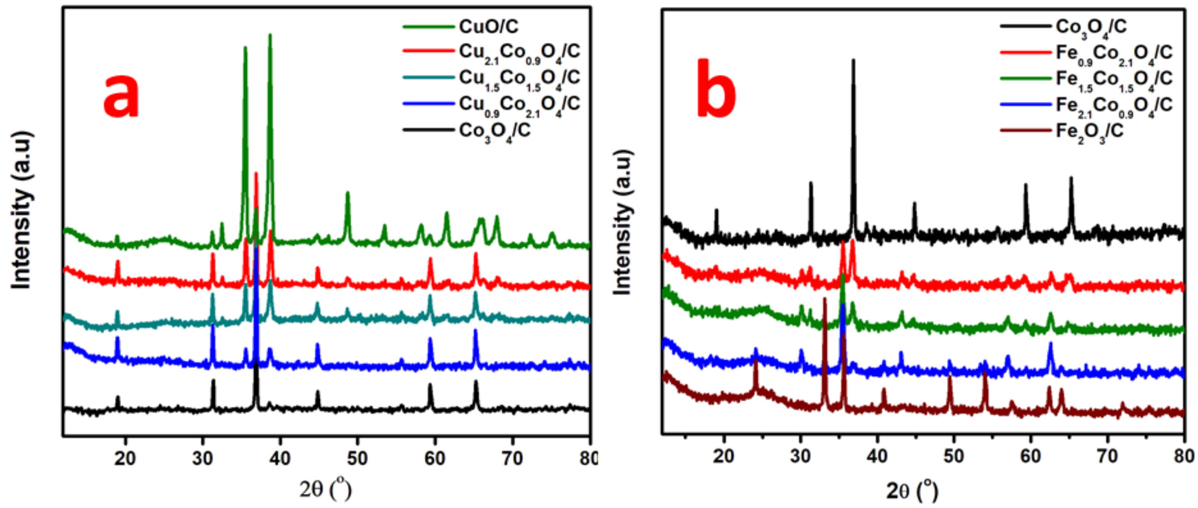

Figure 1: XRD patterns of the (a) Co-Cu/C and (b) Co-Fe/C mixed oxides of various compositions.

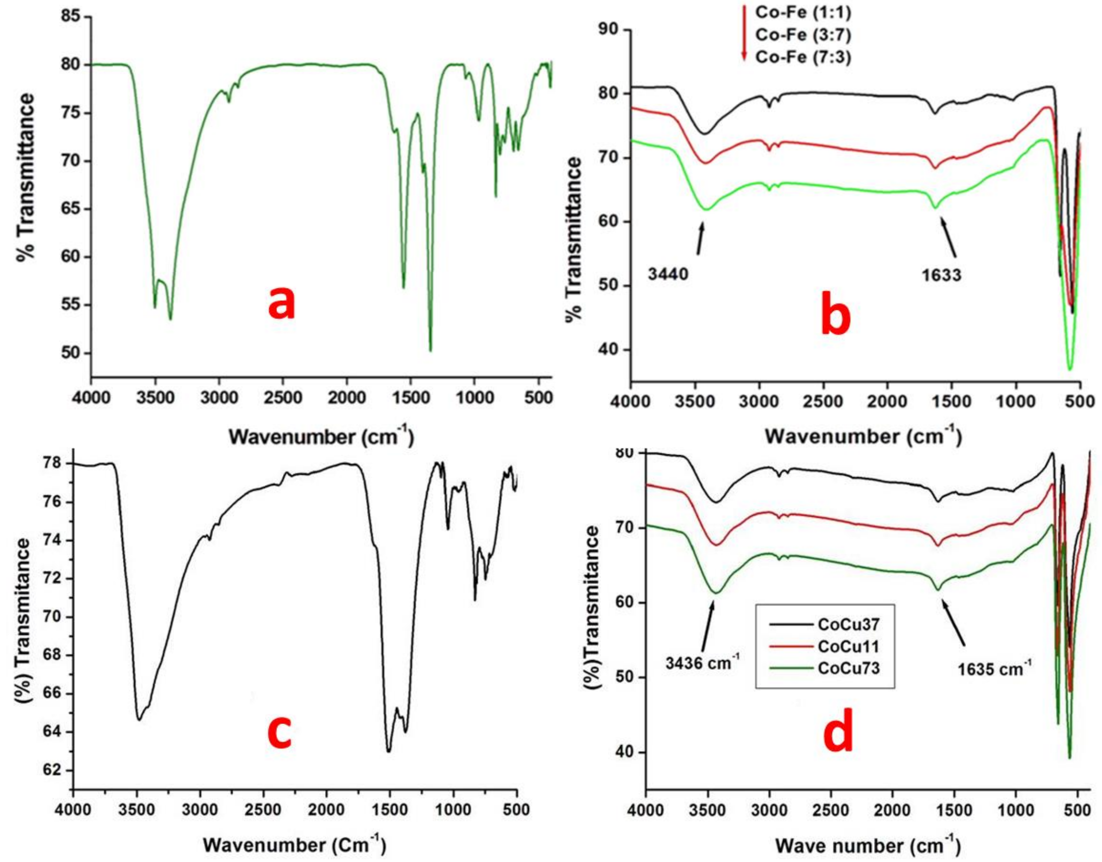

Figure 2: FT-IR spectra of the (a, c) uncalcined Co-Fe (1:1), Co-Cu (1:1) and (b, d) calcined Co-Fe, Co-Cu mixed oxide of composition (1:0), (1:1) and (0:1), respectively.

Fourier transform infra-red (FTIR) analysis: FTIR spectra of the Co-Fe and Co-Cu mixed oxides sample before and after calcination are presented in Figure 2 respectively. The FTIR study of the Co-Fe oxides before calcination show different wavenumbers where three bands observed in the lower mid-infrared 400–900 cm^{-1} range (Figure 2a). The bands were observed at wavenumbers near 424.3, 750.6 and 835.6 cm^{-1}. The band at 424.3 cm^{-1} is for Fe–O bond vibration modes. While the other two bands at 750.6 and 835.6 cm^{-1} are ascribed to the Co–O–H vibration modes with a relatively small vibration of H-bond. The FTIR spectra of the sample after calcination show two distinct bands in the lower mid-infrared 500–700 cm^{-1} range originating from the stretching vibrations of the metal-oxygen bond (Figure 2b). The first band at 547.9 cm^{-1} is associated with the Fe-O vibrations. The second band at 667.6 cm^{-1} is attributed to the ABO_3 vibrations, where A and B denotes the metal ions in a tetrahedral position. The bands were observed at wavenumbers 547.9 and 667.6 cm^{-1} for all the Co-Fe mixed oxide samples.

The FTIR spectra of the mixed oxides before calcination show different wavenumbers, where three bands observed in the range of 400–900 cm^{-1} (Figure 2c). The bands were observed at wavenumbers *ca.* 507, 747 and 839 cm^{-1}. The band below 600 cm^{-1} i.e. at 507 cm^{-1} is for Cu−O bond vibrational modes. While the other two bands 747 and 839 cm^{-1} for Co–O–H vibration modes. The FTIR study of the sample after calcinations show two distinctive bands in the lower mid-infrared 500–700 cm^{-1} range originating from the stretching vibrations of the metal-oxygen bond (Figure 2d). The first band at 579 cm^{-1} is associated with the Cu-O vibrations. The second band at 666 cm^{-1} is attributed to the ABO_3 vibrations, where A denotes the metal ions in a tetrahedral position. The bands were observed at wave numbers at 579 and 666 cm^{-1} for all the Co-Cu mixed oxide samples . Again, the strong peaks at around 3500 cm^{-1} for all the oxide samples are assigned to the stretching vibration of the ‒OH group of molecular water and of hydrogen-bound O‒H groups, noting that the peak at 1620‒1640 cm^{-1} is due to the bending mode of water molecules. Again, All the samples show bands near 3400 cm^{-1} and 1630 cm^{-1} which are attributed to O–H stretching and bending, respectively due to physisorbed water molecules.

SEM and TEM analysis: The surface topography and morphology details of the catalysts have been studied by combined SEM and TEM imaging. Figure 3a,b,c presents the SEM images of Co, Cu and Fe oxide before calcination. From the figures it is observed that Co- oxide and Cu-oxide precursors form rod like and cube like structures, respectively while agglomeration of particles can be seen in Fe-oxide. But after calcination (Figure 3d, e, f) the morphology is changed up to some extent and shows aggregation of small particles for all the oxide samples. Figure 3g, h shows the SEM images of the Co-Fe (1:1) oxide and Co-Cu (1:1) oxide sample.

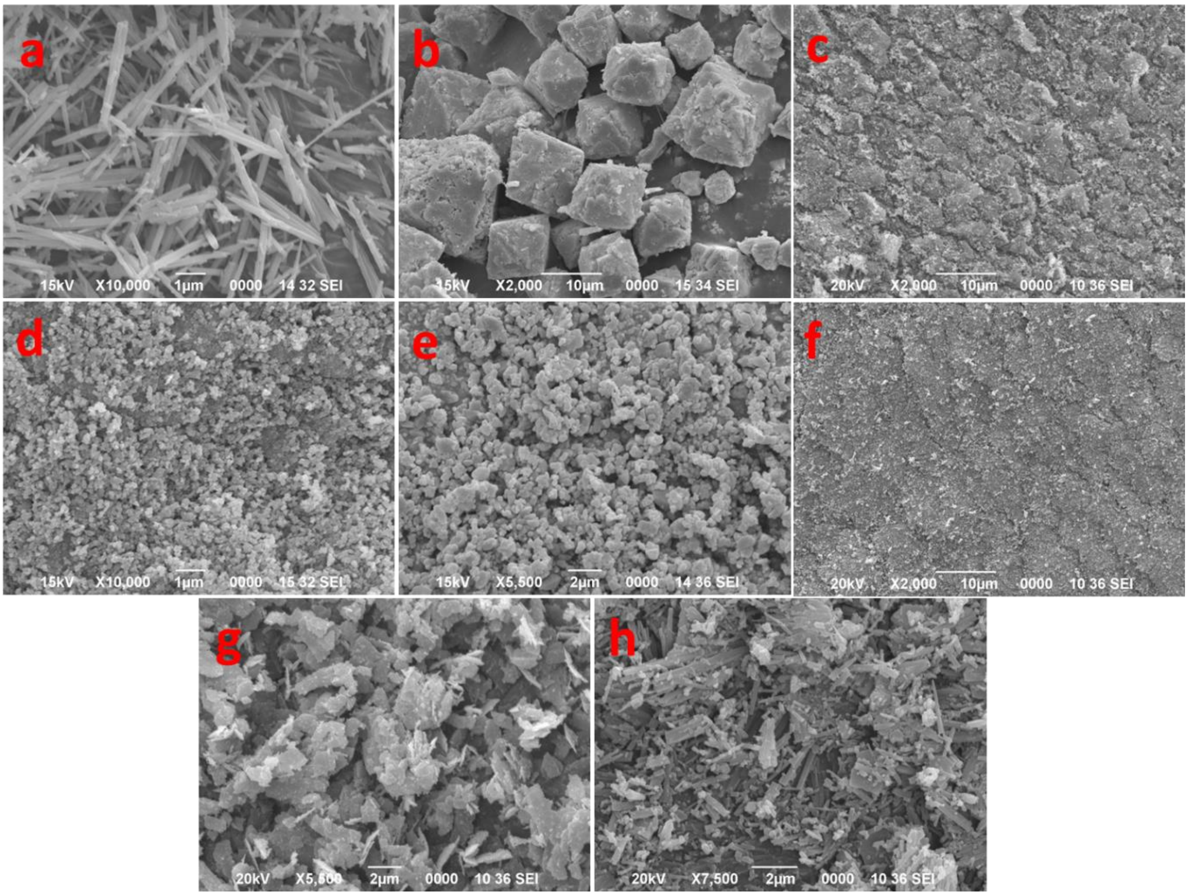

Figure 3: SEM images of (a, d) Co_3O_4 (b, e) CuO, (c, f) α-Fe_2O_3 before and after calcination and (g, h) SEM images of Co-Fe (1:1) and Co-Cu (1:1) mixed oxide before calcination.

The surface topography and morphology details of the catalysts have been studied by TEM imaging. The TEM images of carbon supported Co-Cu (1:1) and Co-Fe (1:1) oxides are depicted in Figure 4a, b. From the figure it is seen that the particles are well distributed on to the carbon support.

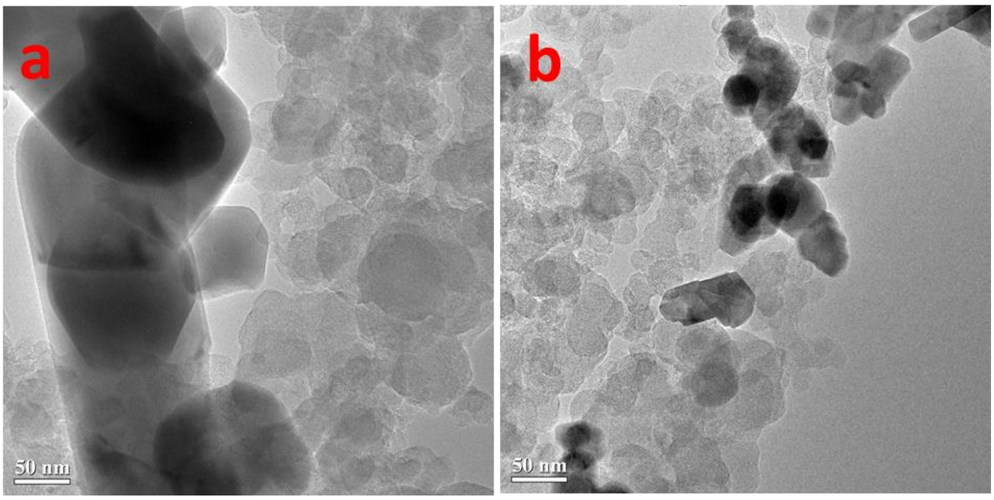

Figure 4: TEM images of (a) Co-Cu/C (1:1), (b) Co-Fe/C mixed oxides.

Raman Analysis: Figure 5 shows the Raman spectra of carbon supported Co-Cu/C (1:1) mixed oxide. The spectrum reveals 3 vibrational modes. The three Raman modes are at about 704, 1356 and 1625 cm^{-1}. The vibration mode at 704 cm^{-1} is the A_{1g}, which is the characteristic pick for Co- oxide. Peaks at 1356 and 1625 cm^{-1} are attributed to D (due to the presence of disorder in sp^2-hybridized carbon systems) and G (arises from stretching of C-C bond) bands of carbonaceous materials.

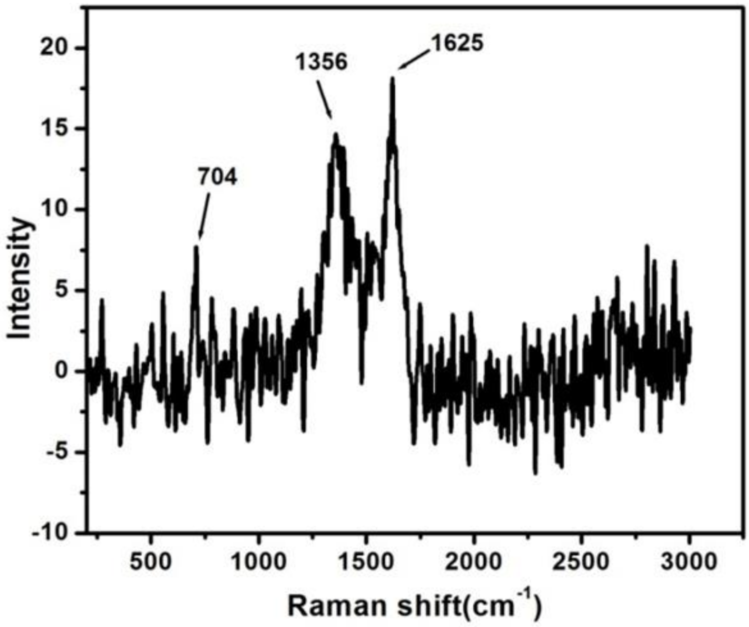

Figure 5: Raman Spectra of Co-Cu/C (1:1) mixed oxides.

BET surface area analyses

Table 2 Textural properties of Co_3O_4, CuO and α-Fe_2O_3 obtained by means of N_2 adsorption-desorption analysis

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore radius (nm)
Co_3O_4	68	0.06	1.6
CuO	10	0.01	1.7
α-Fe_2O_3	85	0.58	1.6

Electrocatalytic activity

A series of experiments were performed to investigate the ORR activity of the as-prepared carbon supported oxide samples. The electrochemical measurements were carried out with an Autolab PGSTAT 204 workstation (Metrohm, The Netherlands). The experiments were performed in a three electrode electrochemical cells with Pt wire as counter electrode, a freshly polished GC electrode as the working electrode and Ag/AgCl as reference electrode. All the experiments were recorded at room temperature. To assess the ORR catalytic activity, the nanocatalysts were first loaded on to glassy carbon electrode then the electrocatalytic activity of the carbon supported Co-oxide, Cu-oxide, Fe-oxide and their mixed oxides of different compositions for ORR was characterized by cyclic voltammetry (CV) in 0.1 M KOH in N_2 and O_2 saturated environment. In the N_2 saturated solution, the voltammograms of all the nanocatalysts were featureless but on the other hand ORR activity was observed in the O_2 saturated solution of KOH. All the nanocatalysts displayed a well-defined ORR reduction peak versus Ag/AgCl.

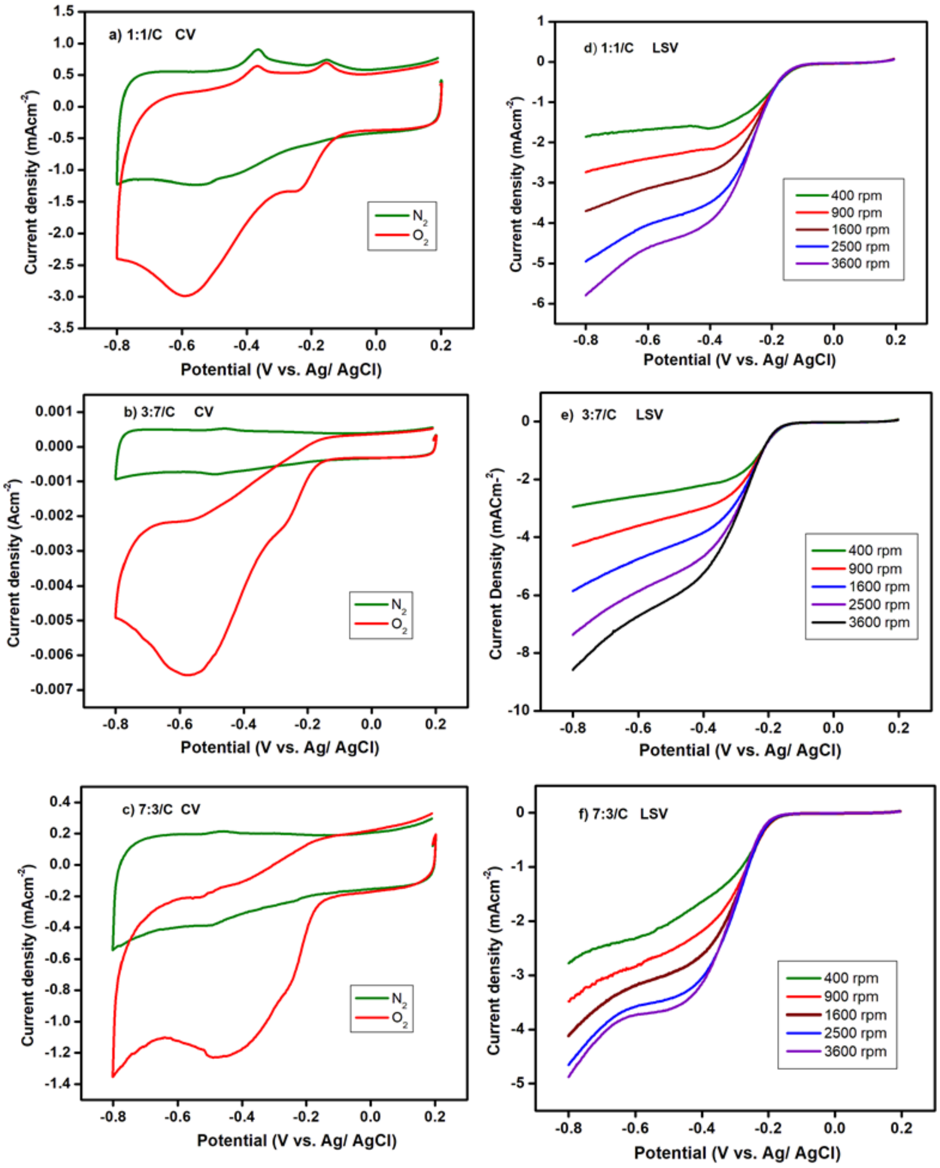

Figure 6: CV curves in O_2-saturated and N_2-saturated 0.1 M KOH (a-c, left panel) and linear sweep voltammograms in O_2-saturated 0.1 M KOH (d-f, right panel) @10 mV/s scan rate at different rotation over carbon supported Co/Fe hybrid oxides.

The ORR onset potential and peak potential of carbon supported Co-Fe mixed oxide was –0.15 V and –0.56 V, respectively, against the Ag/AgCl electrode. Linear sweeping voltammetry (LSV) was also investigated in an O_2 saturated 0.1 M KOH solution at different rotation rate of 400, 900, 1600, 2500 and 3600 rpm.

Rotating disk electrode (RDE) measurements are performed to determine the ORR pathways catalyzed by carbon supported Co-Fe hybrid oxides. Linear sweep voltammetry (LSV) was investigated in 0.1 M KOH. The CV curves along with the LSVs of carbon supported Co/Fe hybrid oxides on glassy carbon electrodes in O_2-saturated 0.1 M KOH are shown in Figure 6.

Based on these ORR polarization curves, the number of electron transferred (n) in ORR is calculated according to Koutecky-Levich equation.

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\,\omega^{0.5}} \quad \text{----------->} \quad (1)$$

$$B = 0.62\ nF\ (Do_2)^{2/3} \vartheta^{-1/6}\ Co_2 \quad \text{-------->} \quad (2)$$

Where j is the current density, j_k is the kinetic current density, ω is the rotating rate of the electrode and B is the slope that could be obtained from the Koutecky-Levich plots. F is the Faraday constant (96500 C mol^{-1}), Do_2 is the diffusion co-efficient of O_2 in 0.1 M KOH (2.0 X 10^{-5} cm^2 s^{-1}), ϑ is the kinetic viscosity (0.01 cm^2 s^{-1}), Co_2 is the bulk concentration of O_2 (1.2 X 10^{-6}mol cm^{-3}) and the value of n represents the number of transferred electron in the ORR process.

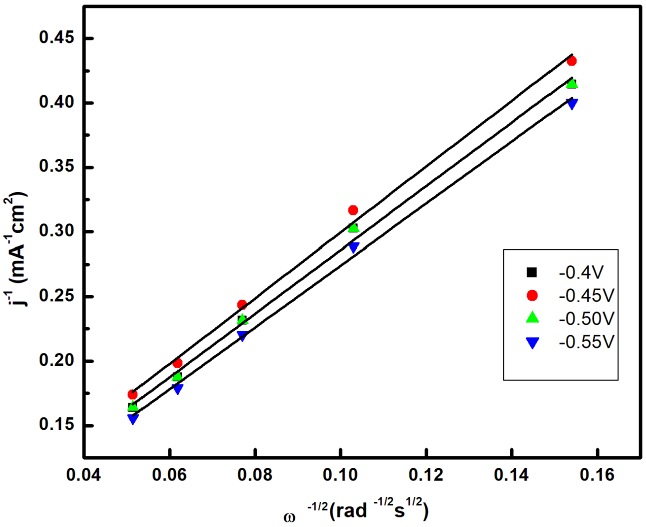

Figure 7: Koutecky–Levich (K-L) plots for carbon supported Co/Fe (3:7) hybrid oxide at –0.40 V, –0.45 V, –0.50 V and –0.55 V.

The parallel fitting lines of the Koutecky− Levich plots at different potentials have presented in Figure 7 which suggest first-order reaction kinetics for the oxygen reduction reaction. The average electron transfer number is found to be 3.9 from -0.5 to -0.65 V for the 3:7 Co/Fe/C oxide catalyst, which indicate that the ORR catalyzed by 3:7 carbon supported Co/Fe/C oxide catalyst, was mainly through the four electron (4 e) pathway.

The electrocatalytic activity of the carbon supported Co-oxide, Cu-oxide and Co-Cu mixed oxides of different compositions for ORR was characterized by cyclic voltammetry (CV) in 0.1 M KOH in N_2 and O_2 saturated environment. In the N_2 saturated solution, the voltammograms of all the nanocatalysts were featureless but on the other hand ORR activity was observed in the O_2 saturated solution of KOH. All the nanocatalysts displayed a well-defined ORR reduction peak versus Ag/AgCl.

Rotating disk electrode (RDE) measurements are performed to determine the ORR pathways catalyzed by carbon supported Co-Cu hybrid oxides. Linear sweep voltammetry (LSV) was investigated in 0.1 M KOH at different rotation rate of 400, 900, 1600, 2500 and 3600 rpm.

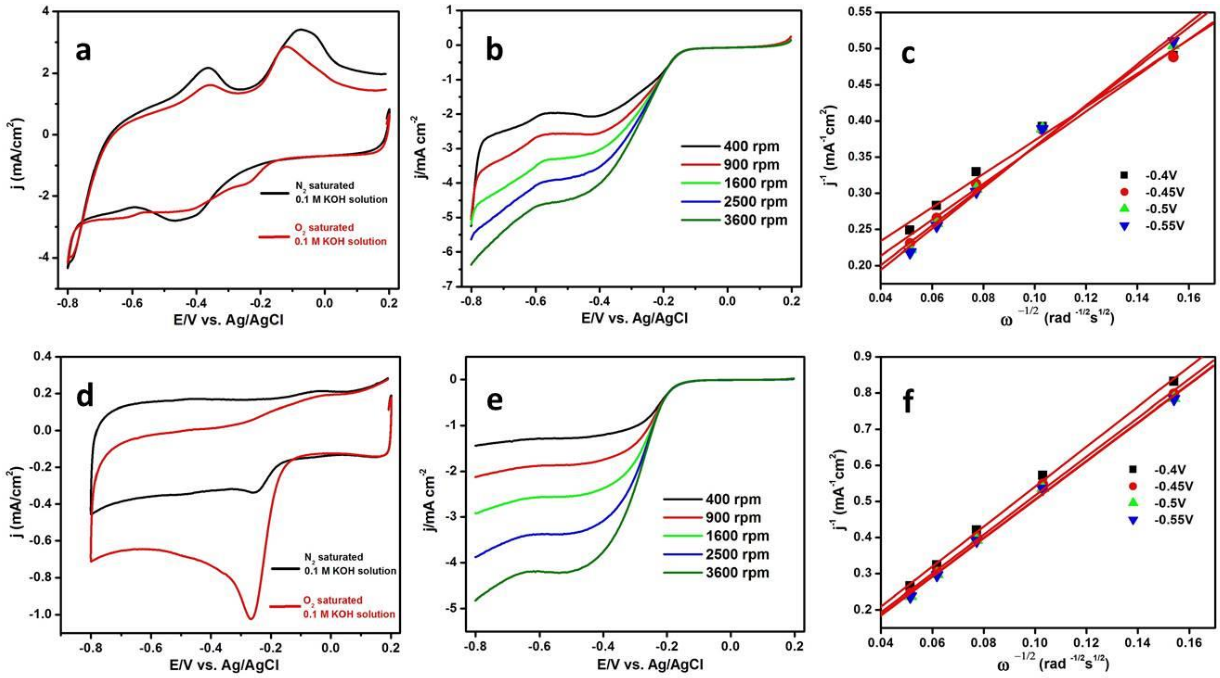

Figure 8: (a), (d) CV curves of C/Cu-oxide and C/Co oxides on glassy carbon electrode in N_2 and O_2 -saturated 0.1 M KOH. (b), (e) ORR polarization curves of C/Cu-oxide and C/Co oxides in O_2 -saturated 0.1 M KOH at different rotation rates, (c), (f) the Koutecky-Levich plots of j^{-1} vs. $\omega^{-1/2}$ at different potential for C/Cu & C/Co oxide.

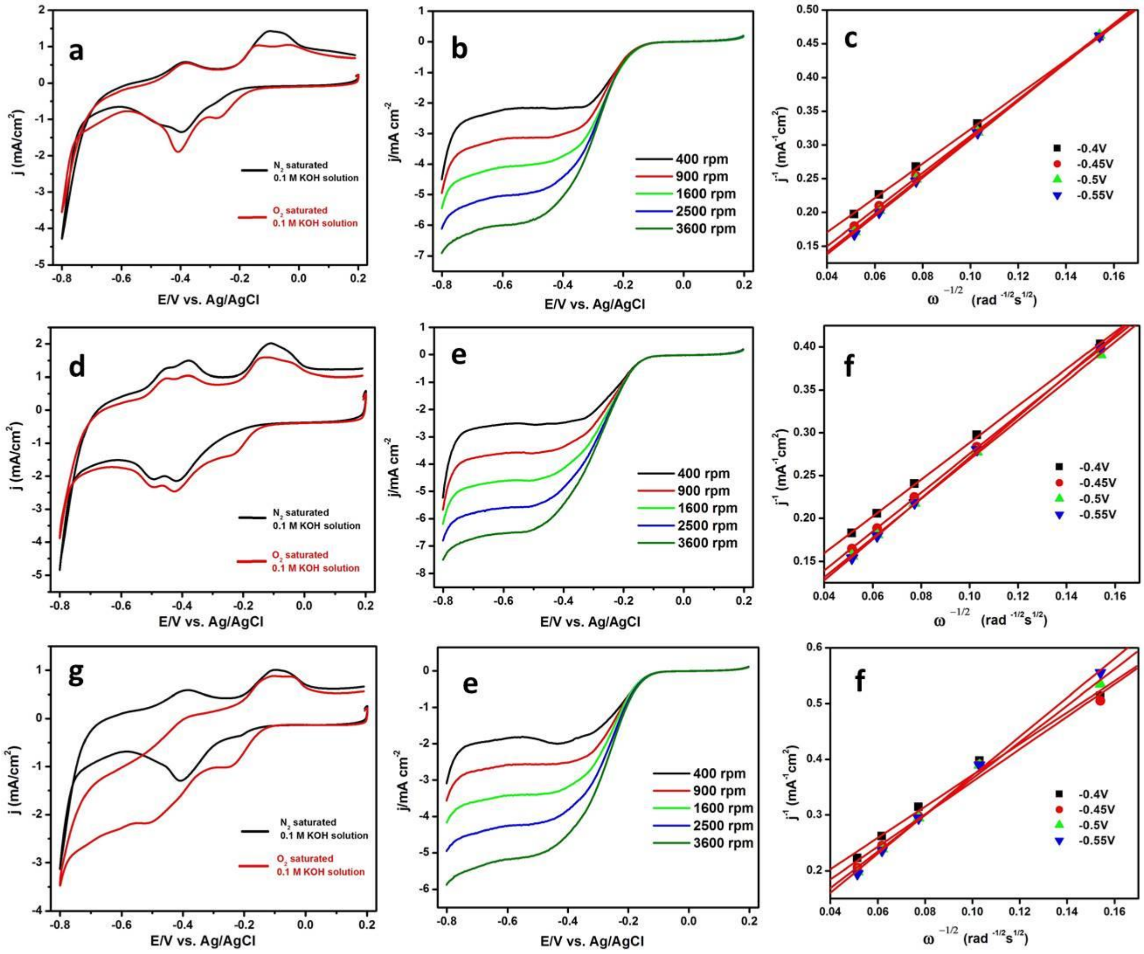

Figure 9: (a), (d), (g) CV curves of C/Co-Cu mixed oxides on glassy carbon electrode in N_2 and O_2 -saturated 0.1 M KOH. (b), (e), (h) ORR polarization curves of C/Co-Cu mixed oxides in O_2 -saturated 0.1 M KOH at different rotation rates, (c), (f), (i) the Koutecky-Levich plots of j^{-1} vs. $\omega^{-1/2}$ at different potential for C/Co-Cu mixed oxides of compositions (7:3), (1:1) and (3:7).

Table 3: The average electron transfer number at different potentials

SL No	Carbon supported oxide nanocatalysts	No of average electron count at different potentials			
		-0.4V	0.45V	-0.5V	-0.55V
1	C/Co-Oxide	1.6	1.7	1.72	1.73
2	C/Co-Cu (7-3)	3.26	3.14	2.8	2.62
3	C/Co-Cu (1-1)	4.26	4.05	4.0	3.84
4	C/Co-Cu (3-7)	3.59	3.37	3.25	3.23
5	C/Cu-Oxide	3.95	3.67	3.35	3.23

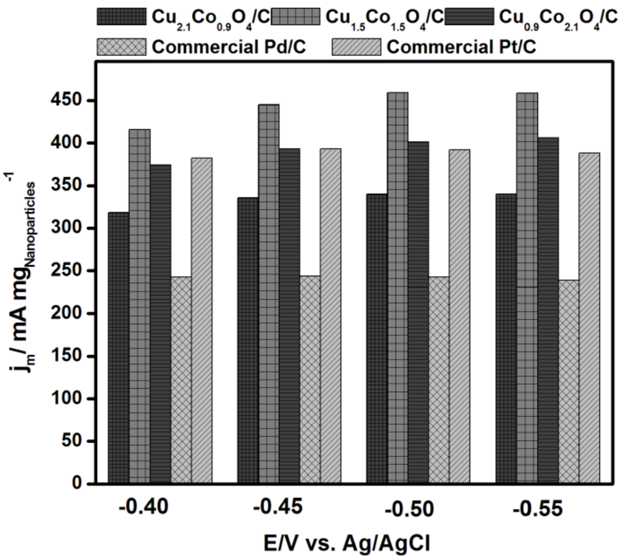

Figure 10: Mass specific activities of carbon supported mixed oxides under different potentials.

The parallel fitting lines of the Koutecky− Levich plots at different potentials suggest first-order reaction kinetics. The average electron transfer number was ≈1.7 and 3.3 from -0.4 to -0.55 V for the carbon supported Co-oxide and Cu-oxide catalyst, and was ≈4.1 from-0.4 to -0.55 V for the carbon supported Co-Cu (1:1) oxide mixture. The electron transfer number (n) obtained from the Koutecky− Levich plots based on the RDE measurements was consistent with RDE result, indicating that the ORR catalyzed by carbon supported Co-Cu (1:1) oxide was mainly through the four electron (4 e) pathway. The mass specific activities were calculated at potentials -0.40 V, -0.45 V, -0.50 V and -0.55 V for the carbon supported mixed oxide nanocatalysts and compared with the available commercial Pd/C and Pt/C. Figure 10 shows the plot of mass specific activities of the oxide nanocatalysts at different potential from which it can be seen that the synthesized carbon supported oxide nanocatalysts shows much higher electrocatalytic activity toward ORR.

FORM-L
UTILISATION CERTIFICATE

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
Human Resource Development Group
CSIR Complex, Library Avenue, Pusa, New Delhi – 110012

CSIR-HRDG Scheme No. **01(2813)/14/EMR-II**

S.No.	Particulars	Letter No. /Bank Transaction ID Nos. & Date	Amount
1	Grants received from CSIR during the year 2017-2018 (up to 31.01.2018)	**P17091814036506 dated 18/09/2017**	**1,66,596**
2	Unspent balance of previous year	-	**452**
3	Interest earned/accrued on CSIR grant	-	**14**
		Total	**1,67,062**

1. Certified that out of Rs. 1,66,596 (Rupees One Lakh Sixty Six Thousand Five Hundred and Ninety Six) of grant-in-aid released by Extramural Research (EMR) Division of HRDG (CSIR) vide letter No./Bank Transaction ID Nos. P17091814036506 dated 18/09/2017 as given in the margin during the year 2017-2018 and Rs. 14 earned/accrued as interest from bank on grants released by CSIR and Rs. Rs. 452 on account of unspent balance of the previous year, a sum of Rs. 1,66,596 has been utilized for the purpose for which it was sanctioned and that the balance of Rs. 466 remaining unutilized at the end of the year has been surrendered to EMR, HRDG (CSIR) (vide letter No. ____________, DD/Cheque No. 568145 dated 24/12/18)/ will be adjusted towards the grant-in-aid payable during the next year.

2. Certified that I have satisfied myself that the conditions on which the grants-in-aid was sanctioned have been duly fulfilled/are being fulfilled and that I have exercised the following checks to see that the money was actually utilized for the purpose for which it was sanctioned. The detail expenditure incurred during the year is shown in the enclosed "Statement of Accounts (Receipt & Payment)".

01-06-18

(Kinds of checks exercised)

1. Vouchers and Statement of Accounts
2. Grant-in-Aid
3. Expenditure Register
4. Bank statements for accrual interest
5.
6.

Signature of Authorised Officer 06/06/18
with Date& Seal
Joint Registrar
Tezpur University

Countersigned by Registrar/Dean/Director
Of the institute with Date & Seal
Registrar
Tezpur University

The Utilization certificate and statement should be signed by Head of the Finance & Accounts and countersigned by Registrar/Dean/Director of the University/Institute.

SESHAASAI(C) / CTS-2010

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कोड क्र /CODE No: 00195
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मांगड्राफ्ट
DEMAND DRAFT

Key: TULDAS
Sr. No: 857691

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मांगे जानेपर EMR ,HRDG (CSIR) ** या उनके आदेश पर
ON DEMAND PAY ______________________________________ OR ORDER

रुपये **RUPEES** Four Hundred and Sixty Six Only

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IOI 000494568145
Name of Applicant

Key: TULDAS Sr. No: 857691
TEZPUR UNIVERSITY R& D

AMOUNT BELOW 467(4/3)

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प्राधिकृत हस्ताक्षरकर्ता
AUTHORISED SIGNATORY

शाखा प्रबंधक
BRANCH MANAGER

कम्प्यूटर द्वारा मुद्रित होने पर ही वैध
VALID ONLY IF COMPUTER PRINTED

केवल 3 महीने के लिए वैध
VALID FOR 3 MONTHS ONLY

₹1,50,000/- एवं अधिक के लिखत दो अधिकारियों द्वारा हस्ताक्षरित होने पर ही वैध है।
INSTRUMENTS FOR ₹ 1,50,000/- & ABOVE ARE NOT VALID UNLESS SIGNED BY TWO OFFICERS

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Abdul Hannan
H - 1021

FORM-E

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

Human Resource Development Group
CSIR Complex, Library Avenue, Pusa, New Delhi – 110012

(Fifteen copies are to be submitted)

1. Title of the Scheme: Design of non-precious cobalt oxide based electrocatalysts	Financial year for which renewals requested : 2017-2018 (up to 31.08.18) Scheme number: 01(2813)/14/EMR-II
2. Name & Address of PI: Dr. Pankaj Bharali Department of Chemical Sciences Tezpur University Tezpur, Napaam-784 028, Assam, INDIA E-mail: pankajb@tezu.ernet.in	Date of Commencement: dd/mm/yy 15/01/2015
3. Name of Sponsoring CSIR Laboratory (if applicable): NA	

4. JRF/SRF/RA associated with the project: NIL

Name& Designation	Date of Joining	Date of leaving

5. Details of Equipment Purchased: NIL

Name of Equipment	Cost	Supplier	Date of purchase/ placing order for each item of equipment
Note: The equipment grant once fixed cannot be enhanced. PIs are advised to give authenticated estimates of the cost of equipment. Equipment should invariably be purchased within 3 months from the date of receipt of the grant and/or sanction letter.			

6. Grants received, and expenditure made in Rupees.

	1st Year 15th January 2015 to 31st March 2015	2nd Year 1st April 2015 to 31st March 2016	3rd Year 1st April 2016 to 31st March 2017	4th Year 1st April 2017 to 31st January 2018
JRF/SRF/RA	NIL	NA	NA	NA
Sanctioned	NA	NA	NA	NA
Received				
Expenditure				
CONTINGENCY	50000	200000	200000	NA
Sanctioned	50000	1,94,902	2,02,429	NA
Received	50000	NIL	3,97,331	
Expenditure	49929	NA	3,96,968	
EQUIPMENT	NIL	NA	NA	NA
Sanctioned	NA	NA	NA	NA
Received				
Expenditure				

7. Amount saved (if any) from the last year's grant

Staff	Contingency	Equipment
NIL	71 (Rupees Seventy one only)	NIL

8. Date on which scheme will complete its normal tenure of 12/24/**36** months ___31/01/2018_____.

Whether extension beyond normal tenure has been requested. Yes /**No**.

If yes, give _______ months ________ (dd/mm/yy) justification.

(Extension beyond normal tenure should be requested at the Project Monitoring Session/one year before end of normal tenure.)

Note: If yes, justification for extension and programme of work to be completed. Also mention as to why the work could not be completed as per the original plan.

9. Constraints (if any) faced in the progress of work and suggestions to overcome them. No

10. Any deviation from original plan with its nature and cause. Yes

There was minor deviation on the application of the synthesized CuO and Co_3O_4 nanostructures. As proposed these metal oxides are targeted for ORR, however, due to unavailability of instrumental facilities, i.e. electrochemical workstation with rotating disk electrode, we have employed the synthesized metal oxides for degradation of organic pollutants.

11. List of publication giving full bibliographic details accrued from this project (copies of the paper (s) should be enclosed).

i) P. Deka, R. Choudhury, R. C. Deka, **P. Bharali**, Influence of Ni on enhanced catalytic activity of Cu/Co_3O_4 towards reduction of nitroaromatic compounds: studies on the reduction kinetics, **RSC Advances, 6 (2016) 71517 – 71528.**
ii) P. Deka, R.C. Deka, **P. Bharali**, Porous CuO nanostructure as reusable catalyst for oxidative degradation of organic water pollutants, **New Journal of Chemistry, 40 (2016) 348 – 357.**
iii) P. Deka, A. Hazarika, R.C. Deka, **P. Bharali**, Influence of CuO morphology on enhanced catalytic degradation of methylene blue and methyl orange, **RSC Advances, 6 (2016) 95292 – 95305**.

12. Summary of work done (200 words).

(i) Survey of literature and procurement of chemicals/ accessories
As proposed in the time table of the original project we have carried out extensive survey of literature.

(ii) Synthesis of carbon supported cobalt-copper mixed oxides of various compositions
Cobalt-copper mixed oxides of various compositions were synthesized by hydrothermal route and characterized by FTIR, Raman, SEM, TEM, XRD, and BET surface area methods.

(iii) Electrode fabrication and evaluation of ORR activity
ORR activity was evaluated using RDE-CV, LSV experiments for the synthesized samples in 0.1 M KOH.

13. Proposed programme of work for the next year (1000 words).

It is proposed to carry out the following works during the next year:

(i) Synthesis and characterization of Co-Fe composite oxides with different Co/Fe compositions
Co-Fe composite oxides with varying Co/Fe compositions will be synthesized by adopting optimized synthetic routes of single metal oxides to fabricate identical morphologies of composite oxides.

(ii) Electrode fabrication and evaluation of ORR activity

The working electrodes will be fabricated by using the ink prepared by ultrasonically dispersing the catalyst (single as well as Cu-Fe composite metal oxide) powders in distilled water/Nafion solution and optimize the electrode fabrication conditions. Further ORR activity will be evaluated for the fabricated electrodes in suitable electrolytes in alkaline medium.

14. Detailed Annual Progress Report enlisting the objectives in beginning briefly (upto five pages maximum).

Objectives of original proposal:

- (i) Synthesis of shape, size and composition controlled cobalt oxide, iron oxide, copper oxide and Co-M composite oxide (M = Fe and Cu) nanostructures by modified surfactant assisted/surfactant-free hydrothermal and solvothermal techniques.
- (ii) Evaluation of synthesized cobalt oxide, iron oxide and copper oxides for ORR by cyclic voltammetry and other electrochemical techniques in alkaline media.
- (iii) To investigate the impact of Fe and Cu on the ORR activity of cobalt oxide with various shape, size and composition in alkaline media.
- (iv) Thorough structural characterization of synthesized cobalt oxide, iron oxide, copper oxide and Co-M composite oxide (M = Fe and Cu) nanostructures by various spectroscopic and microscopic techniques.
- (v) In depth quantitative evaluation of the electrocatalytic activities and kinetics of ORR with the help Rotating-disk electrode (RDE) measurements is targeted.
- (vi) Influence of carbon support is aimed to investigate on the performance of catalysts for ORR.

Hydrothermal synthesis of Cu-Co mixed oxides

$CuCl_2 \cdot 2H_2O$ and $CoCl_2.6H_2O$ salts of desired amounts were initially dissolved in 40 mL of distilled water. Then urea solution was prepared by dissolving 2.40 g of urea in 40 mL of distilled water and added to the homogeneous mixture from a burette drop wise and stirred for 30 min. The resulting solution is transferred to a 150 mL teflon-lined stainless steel autoclave which was then kept in an oven maintained at a temperature of 120 °C for 6 h. After 6 h, it was allowed to cool for 15 h. It was then filtered and washed with distilled water and finally with absolute ethanol and dried at 50 °C. The precursor was then calcined in a muffle furnace at 450 °C for 4 h. The various compositions of Co-Cu mixed oxides were synthesized employing the following precursors with different concentrations as shown below in Table 1.

Table 1: Amount of $CoCl_2.6H_2O$ and $CuCl_2 \cdot 2H_2O$ employed for synthesis of Co-Cu mixed oxides

Serial number	$Co(NO)_3.6H_2O$ (g)	$CuCl_2 \cdot 2H_2O$ (g)	Mole Ratio	Base (g)
1	0.9517	_	1:0	2.40
2	0.2855	0.4773	3:7	2.40
3	0.4758	0.3409	1:1	2.40
4	0.6662	0.2046	7:3	2.40
5	_	0.6819	0:1	2.40

Carbon supported Co-Cu mixed oxide preparation

Certain amount of different compositions of Co-Cu mixed oxides and carbon are grind for about half an hour using mortar and pestle. After that the mixture is sonicated with ethanol (as a solvent) for half an hour. Then the sonicated mixture was allowed to first air dry and then kept in an oven at a temperature of 50℃.

X-ray diffraction (XRD) study: Figure 1 presents the XRD profiles of the various Co-Cu composition mixed oxides. In the Figure 2 the diffraction peaks are observed at 2θ = 18.63°, 30.77°, 36.37°, 44.36°, 55.31°, 58.98° and 64.73° which could be assigned to (111), (220), (311), (400), (422), (511) and (440) reflections, respectively for the cubic spinel Co_3O_4 phase (JCPDS card no. 65-3103) and also the diffraction peaks are observed at 2θ = 32.54°, 35.53°, 38.69°, 48.77°, 53.49°, 58.25°, 61.57°, 65.84 and 67.89° which could be assigned to (110), (-110), (111), (-202), (020), (202), (-113), (022) and (113) reflections, respectively for monoclinic end centered CuO phase (JCPDS card no. 89-5895).

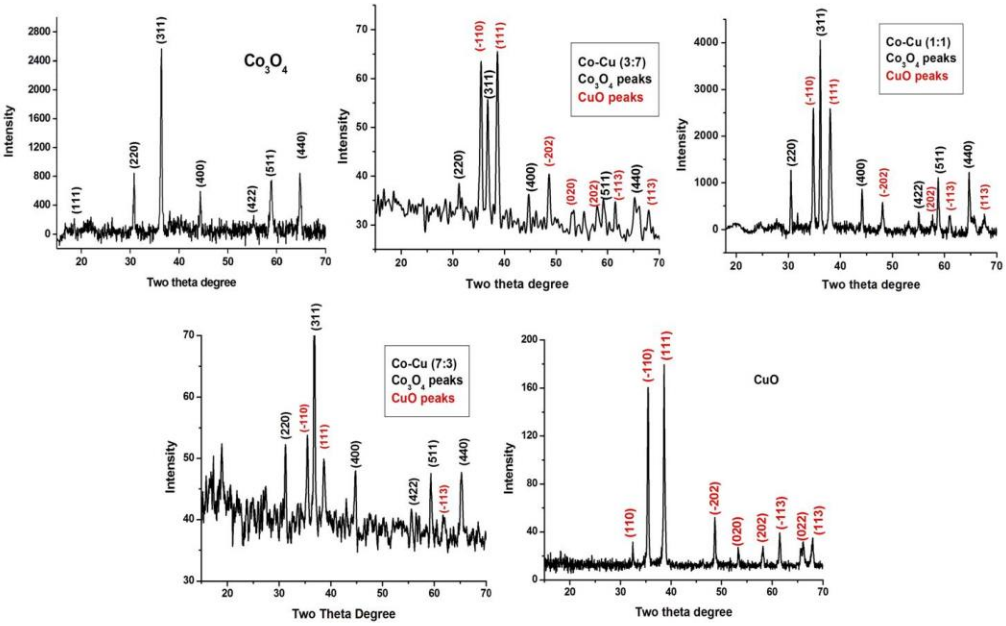

Figure 1: XRD pattern of the Co-Cu mixed oxides of various compositions.

SEM and TEM analysis: The surface topography and morphology details of the catalysts have been studied by combined SEM and TEM imaging. Figure 2a,c presents the SEM images of Co and Cu oxide before calcination. From the figures it is observed that Co- oxide and Cu-oxide precursors form rod like and cube like structures, respectively. But after calcination (Figure 2b,d) the morphology is changed up to some extent and shows aggregation of small particles. The TEM images of Co-Cu (1:1) oxides are depicted in Figure 2e,f. It can be seen from the figure that the mixed oxides are polycrystalline in nature and particles under self-assembly to form chain like structure.

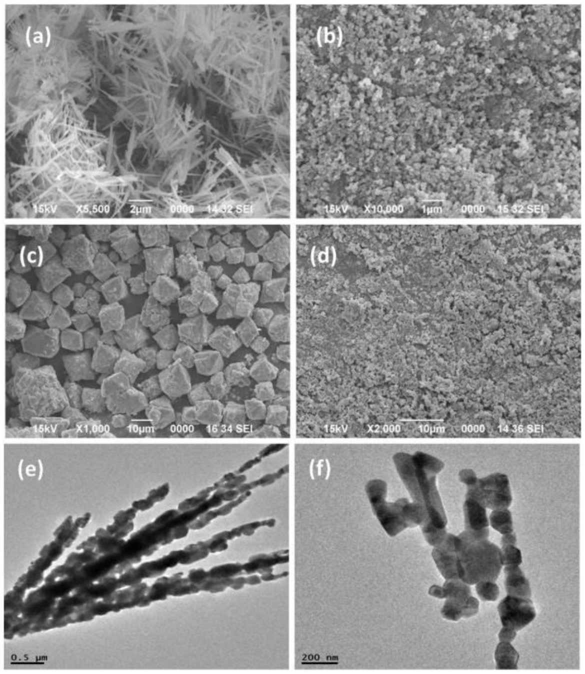

Figure 2: SEM images of (a, b) Co_3O_4 (c, d) CuO before and after calcination and TEM images of (e,f) Co-Cu (1:1) mixed oxides.

Electrochemical measurement: The electro catalytic activity of carbon supported Co, Cu-oxide and Co-Cu mixed oxides for ORR was first characterized by cyclic voltammetry (CV) in 0.1 M KOH on a glassy carbon electrode vs the Ag/AgCl electrode.

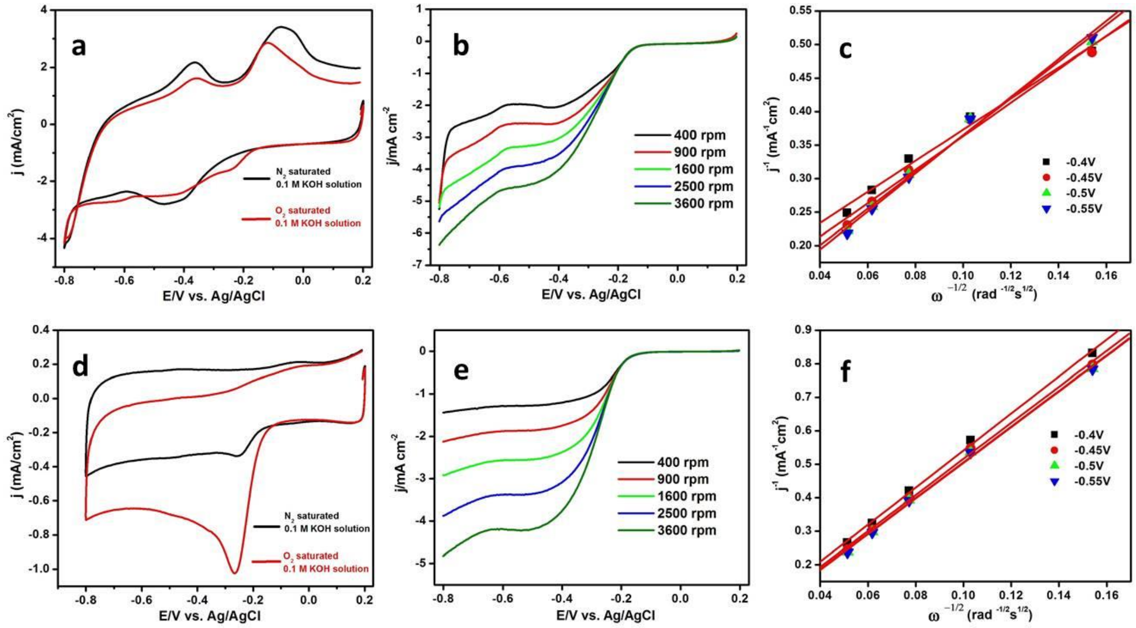

Figure 3: (a), (d) CV curves of C/Cu-oxide and C/Co oxides on glassy carbon electrode in N_2 and O_2 -saturated 0.1 M KOH. (b), (e) ORR polarization curves of C/Cu-oxide and C/Co oxides in O_2 -saturated 0.1 M KOH at different rotation rates, (c), (f) the Koutecky-Levich plots of j^{-1} vs. $\omega^{-1/2}$ at different potential for C/Cu & C/Co oxide.

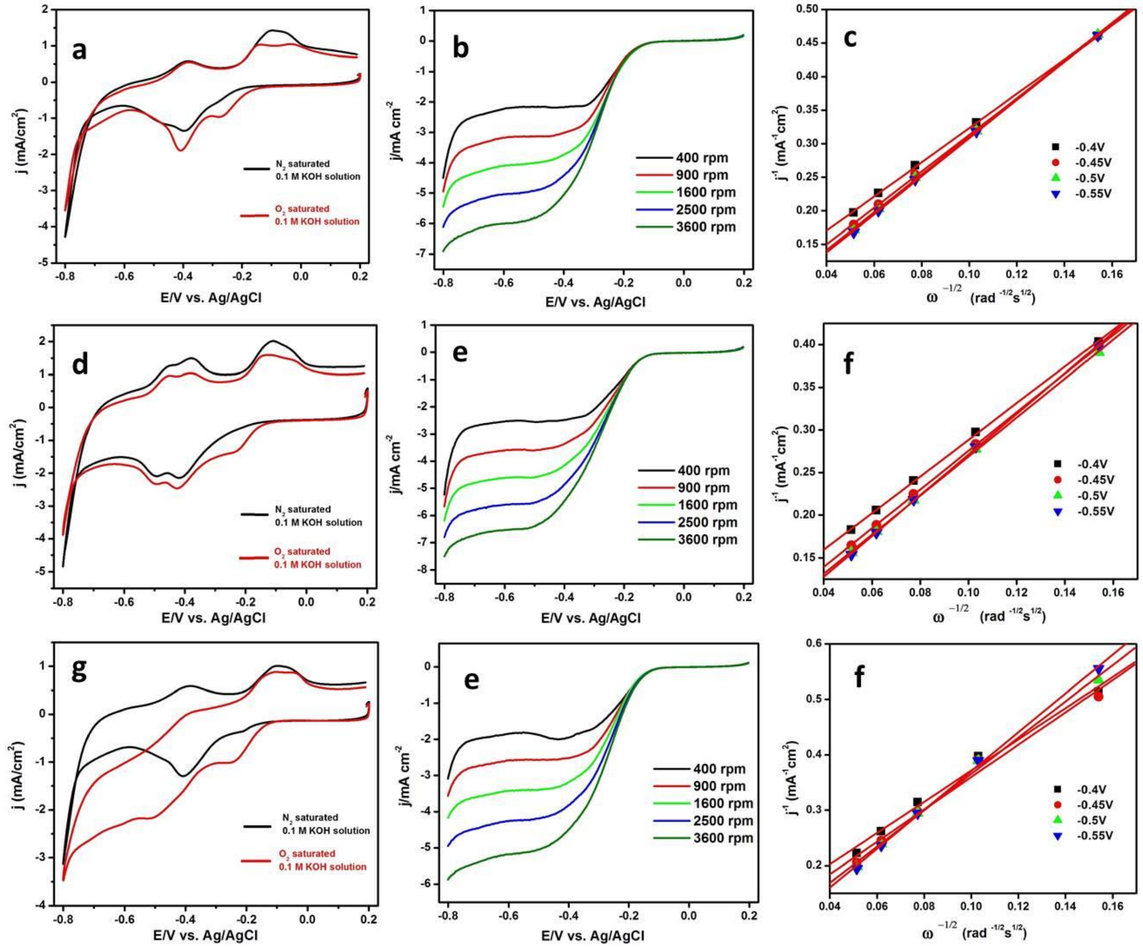

Figure 4: (a), (d), (g) CV curves of C/Co-Cu mixed oxides on glassy carbon electrode in N_2 and O_2 -saturated 0.1 M KOH. (b), (e), (h) ORR polarization curves of C/Co-Cu mixed oxides in O_2 -saturated 0.1 M KOH at different rotation rates, (c), (f), (i) the Koutecky-Levich plots of j^{-1} vs. $\omega^{-1/2}$ at different potential for C/Co-Cu mixed oxides of compositions (7:3), (1:1) and (3:7).

Table 1: The average electron transfer number at different potentials

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5	C/Cu-Oxide	3.95	3.67	3.35	3.23

Rotating disk electrode (RDE) measurements were performed to determine the ORR pathways catalyzed by Co-oxide, Cu-oxide and Co-Cu mixed oxide. Linear sweeping voltammetry (LSV) was recorded at different rotation rates using 0.1 M KOH.

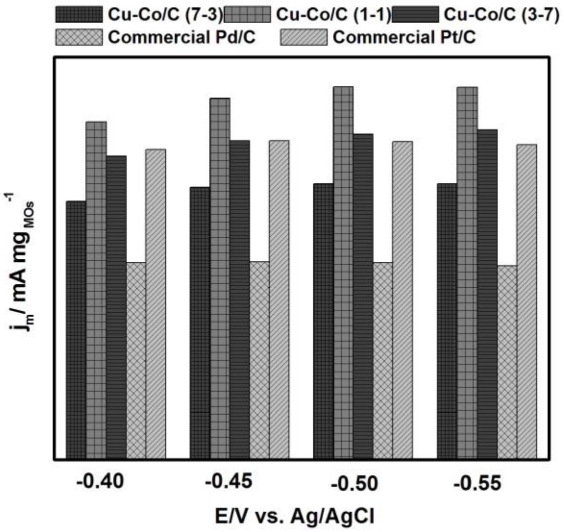

Figure 5: Mass specific activities of carbon supported mixed oxides under different potentials.

The parallel fitting lines of the Koutecky− Levich plots at different potentials suggest first-order reaction kinetics. The average electron transfer number was ≈1.7 and 3.3 from -0.4 to -0.55 V for the carbon supported Co-oxide and Cu-oxide catalyst, and was ≈4.1 from-0.4 to -0.55 V for the carbon supported Co-Cu (1:1) oxide mixture. The electron transfer number (n) obtained from the Koutecky−Levich plots based on the RDE measurements was consistent with RDE result, indicating that the ORR catalyzed by carbon supported Co-Cu (1:1) oxide was mainly through the four electron (4 e) pathway. The mass specific activities were calculated at potentials -0.40 V, -0.45 V, -0.50 V and -0.55 V for the carbon supported mixed oxide nanocatalysts and compared with the available commercial Pd/C and Pt/C. Figure 5 shows the plot of mass specific activities of the oxide nanocatalysts at different potential from which it can be seen that the synthesized carbon supported oxide nanocatalysts shows much higher electrocatalytic activity toward ORR.

Signature of PI
Date: 15/07/2017

Note: No column should be left blank; write not applicable (NA) wherever applicable.