# Ni-doped $CoFe_2O_4$/C nanoparticles as efficient catalysts for ORR in alkaline media.

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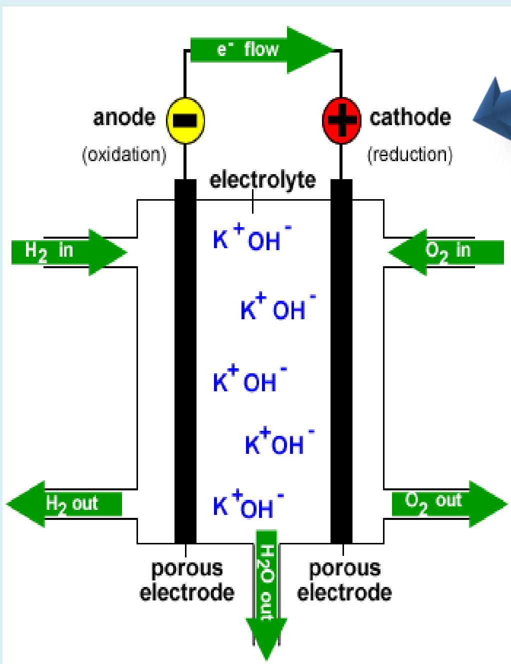
# Introduction

## Oxygen reduction reaction

Fuel cells




### Reaction pathways in alkaline media

1. $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
   (4e⁻ reduction pathway)

1. $O_2 + H_2O + 2e- \rightarrow HO_2^- + OH$
   $H_2O + HO^- + 2e^- \rightarrow 3OH^-$
   (2e⁻ reduction pathway)

# Introduction Cont…

## Spinel ferrites

- Spinel ferrites are compounds with general formula of **$A[B_2]O_4$**.

  Where A = Divalent metal ions (**$Fe^{2+}$**, **$Co^{2+}$**, **$Ni^{2+}$**, etc.)
  B = Trivalent metal ions (**$Fe^{3+}$**)

- They have cubic close packings of **$O^{2-}$** ions.

- They are made up of two types of sites: Tetrahedral sites **(A-sites)**
  Octahedral sites **(B-sites)**

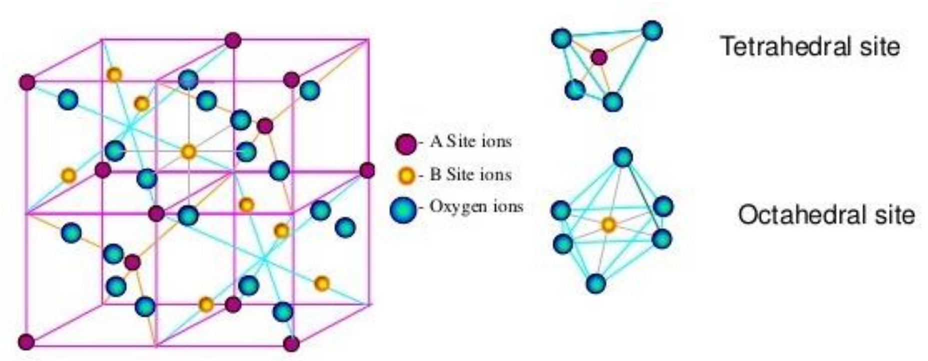



**Figure 1.** Typical spinel structure.

# Introduction Cont…

## Classification of spinels

- Normal spinel structure : δ = 1; $\mathbf{M^{2+}[Fe^{3+}]O_4^{2-}}$ ; e.g. $ZnFe_2O_4$
- Inverse spinel structure : δ = 0; $\mathbf{Fe^{3+}[M^{2+}\boldsymbol{Fe}^{3+}]\boldsymbol{O}_4^{2-}}$; e.g. $CoFe_2O_4$ $NiFe_2O_4$
- Mixed spinel structure : 0 < δ < 1; $\mathbf{M_{1-\delta}^{2+}Fe_{\delta}^{3+}[M_{\delta}^{2+}Fe_{2-\delta}^{3+}]\boldsymbol{O}_4^{2-}}$; e.g. $MnFe_2O_4$

## Why spinel ferrites?

Because of their controllable composition, structural robustness, low cost, accessibility, ease and mode of synthesis, desirable activity and environmental friendliness.

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# Aims and Objectives

The main aim of this work was to synthesize carbon-supported $Ni_xCo_{1-x}Fe_2O_4$ nanoparticles with high catalytic activity for ORR in alkaline media.

The objectives were thus to:

- Synthesize $Ni_xCo_{1-x}Fe_2O_4$ (x = 0, 0.25, 0.5, 0.75 and 1) electrocatalysts through the hydrothermal method;
- Employ the XRD, FTIR, HRTEM, EDX and SAED techniques to characterize the synthesized catalysts;
- Investigate the electrochemical performances of the synthesized catalysts for ORR in $O_2$-saturated 0.1 M KOH electrolyte through the use of CV and LSV the techniques.

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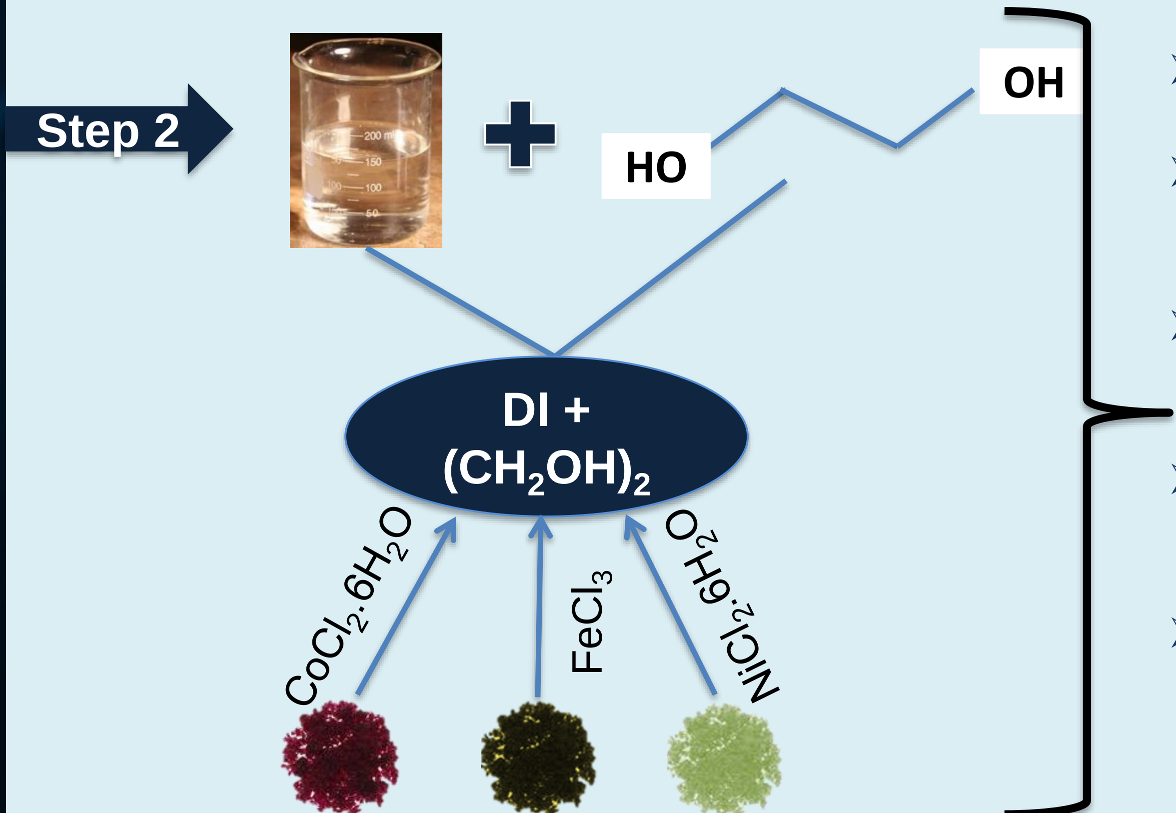
# Methodology


- Stir for 15 min.
- Add the CB solution and stir for 15 min.
- Add urea and stir for additional 15 min.
- Transfer the mixture into a Teflon cup.
- Subjection to hydrothermal reaction at 150 ºC for 17 h.

# XRD Measurements

$$d = \frac{\lambda}{2Sin\theta}\text{.................................}(1)$$

$$a = d\sqrt{(h)^2+(k)^2+(l)^2}\text{................}(2)$$

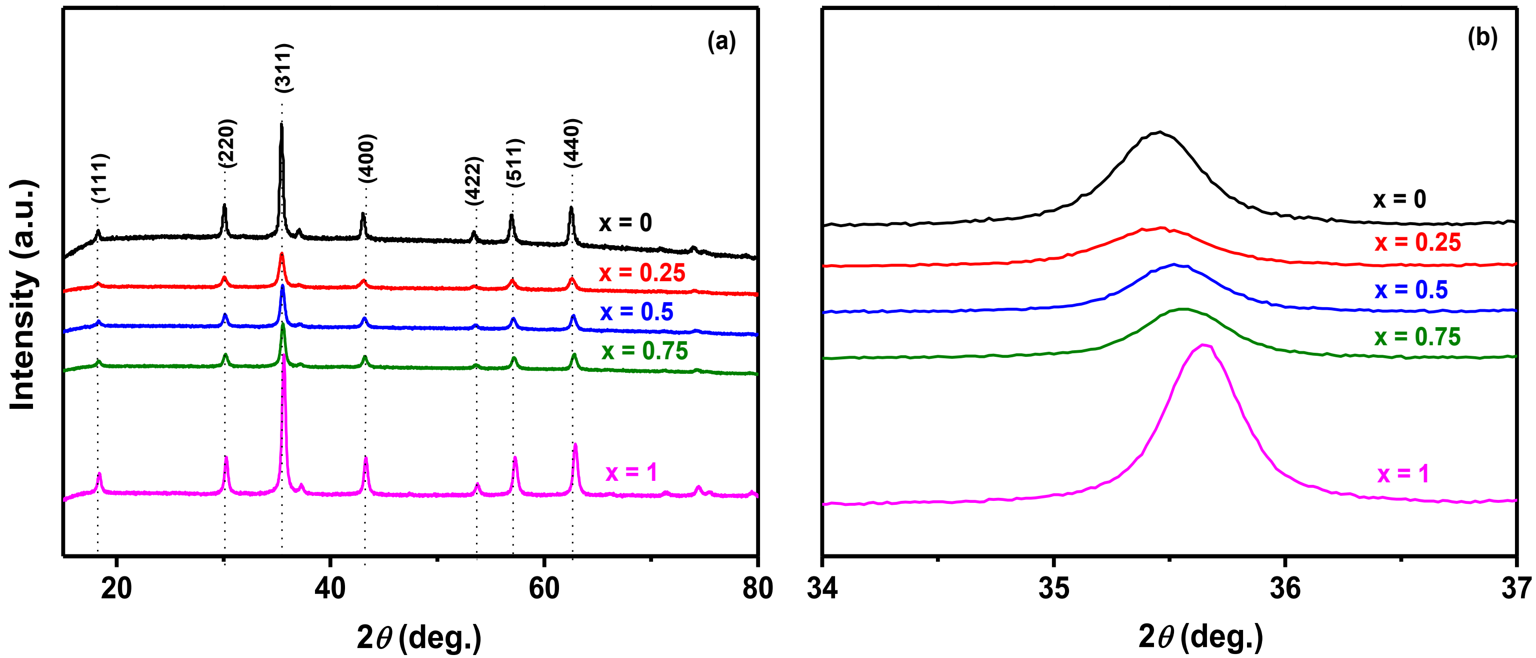



**Figure 2.** (a) (X-ray diffraction patterns of $Ni_xCo_{1-x}Fe_2O_4/C$ (x = 0, 0.25, 0.5, 0.75 and 1), (b) the partially enlarged XRD patterns indicating the (311) peaks.

# XRD Measurements Cont…

**Table 1** XRD data of $Ni_xCo_{1-x}Fe_2O_4/C$ (x = 0, 0.1, 0.25, 0.5, 0.75 and 1) calculated from the (311) diffraction peak.

| Sample (x) | Crystallite size *D* (nm) | 2*θ* (deg.) | *d*-spacing (nm) | Lattice parameter *a* (Å) |
|---|---|---|---|---|
| 0 | 28.56 | 35.50 | 0.252 ± 0.0009 | 8.387 ± 0.0007 |
| 0.25 | 17.09 | 35.43 | 0.253 ± 0.0004 | 8.404 ± 0.0003 |
| 0.5 | 20.57 | 35.49 | 0.252 ± 0.0009 | 8.387 ± 0.0007 |
| 0.75 | 20.58 | 35.53 | 0.252 ± 0.0007 | 8.381 ± 0.0001 |
| 1 | 23.99 | 35.62 | 0.252 ± 0.0000 | 8.357 ± 0.0009 |

# FTIR Analysis

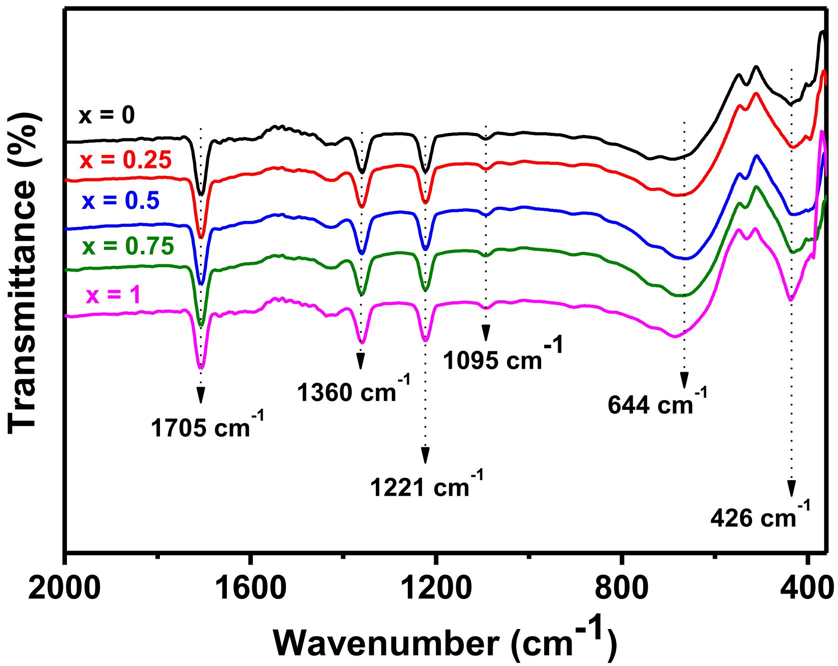



**Table 2** Assignment of FTIR spectra and variation of higher ($v_1$) and lower ($v_2$) bands with an increase in the $Ni^{2+}$ concentration.

| Sample (x) | $\upsilon_1$ ($cm^{-1}$) | $\upsilon_2$ ($cm^{-1}$) |
|---|---|---|
| 0 | 644.22 | 426.27 |
| 0.25 | 638.44 | 432.05 |
| 0.5 | 640.37 | 430.12 |
| 0.75 | 663.51 | 433.84 |
| 1 | 671.22 | 437.84 |

**Figure 3.** FTIR spectra of $Ni_xCo_{1-x}Fe_2O_4$/C (x = 0, 0.25, 0.5, 0.75 and 1) samples.

# TEM and SAED Analysis

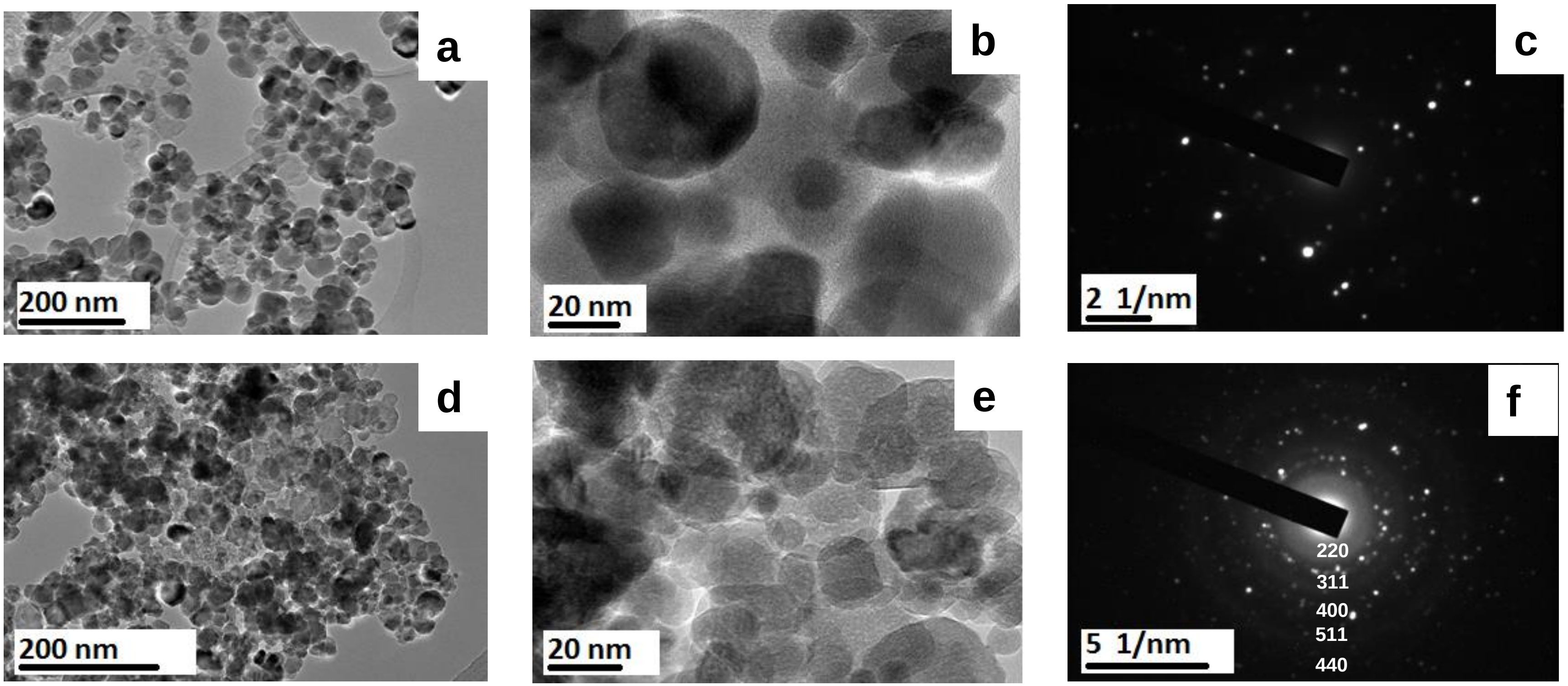
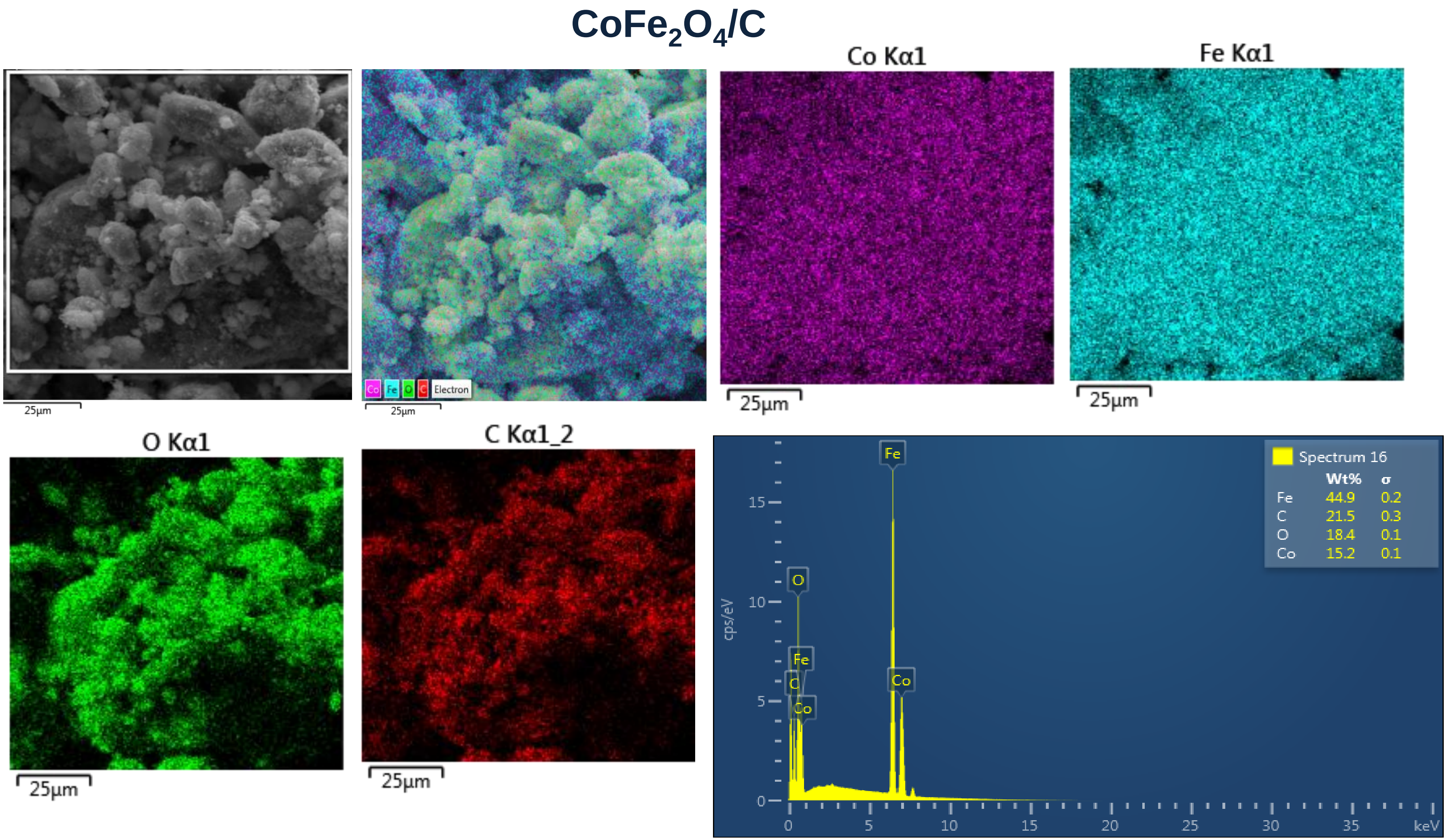



**Figure 4.** (a, b)TEM images of $CoFe_2O_4$/C. (d, e) TEM images of $Ni_{0.75}Co_{0.25}Fe_2O_4$/C. (c, f) SAED patterns of $CoFe_2O_4$/C (c) and $Ni_{0.75}Co_{0.25}Fe_2O_4$/C (f).

# Elemental mapping and EDX Analysis



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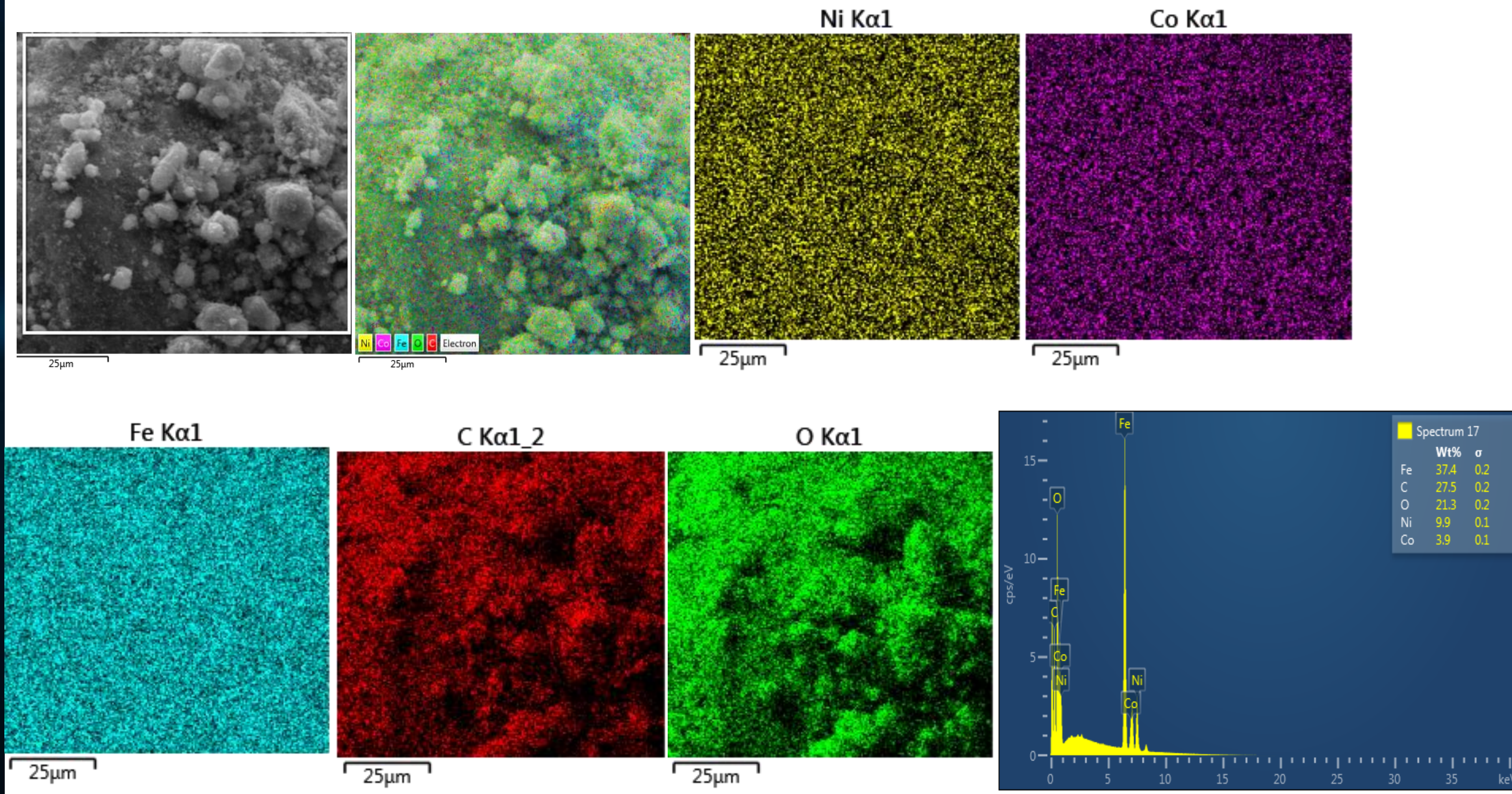
# Elemental mapping and EDX Analysis Cont…

## $Ni_{0.75}Co_{0.25}Fe_2O_4/C$



# Electrochemical measurements Cont…

## Linear sweep voltammetry

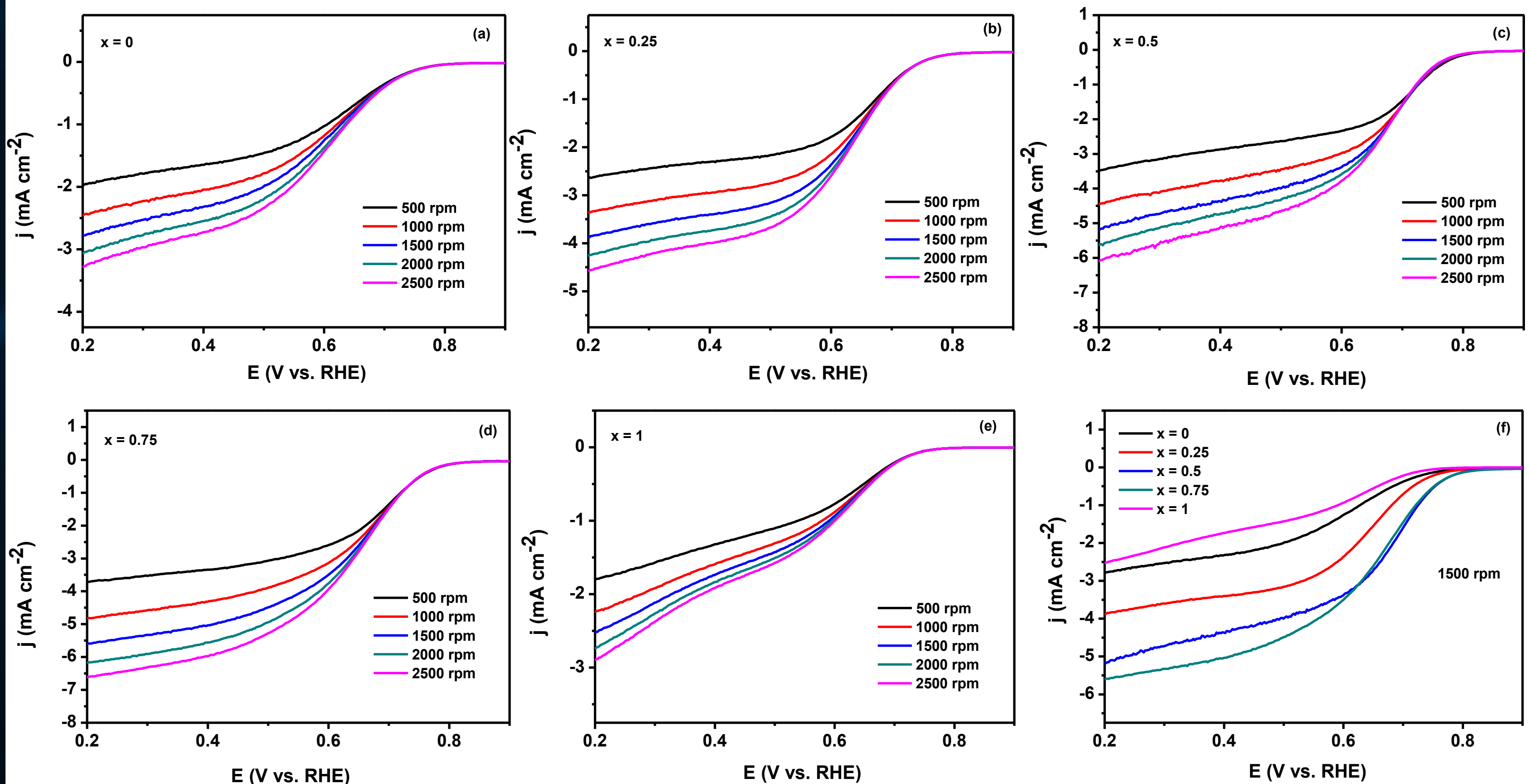



**Figure 7.** (a-e) LVS curves of $Ni_xCo_{1-x}Fe_2O_4$/C catalysts. (f) Comparison of the LSV curves at 1500 rpm.

# Electrochemical measurements

## Cyclic Voltammetry

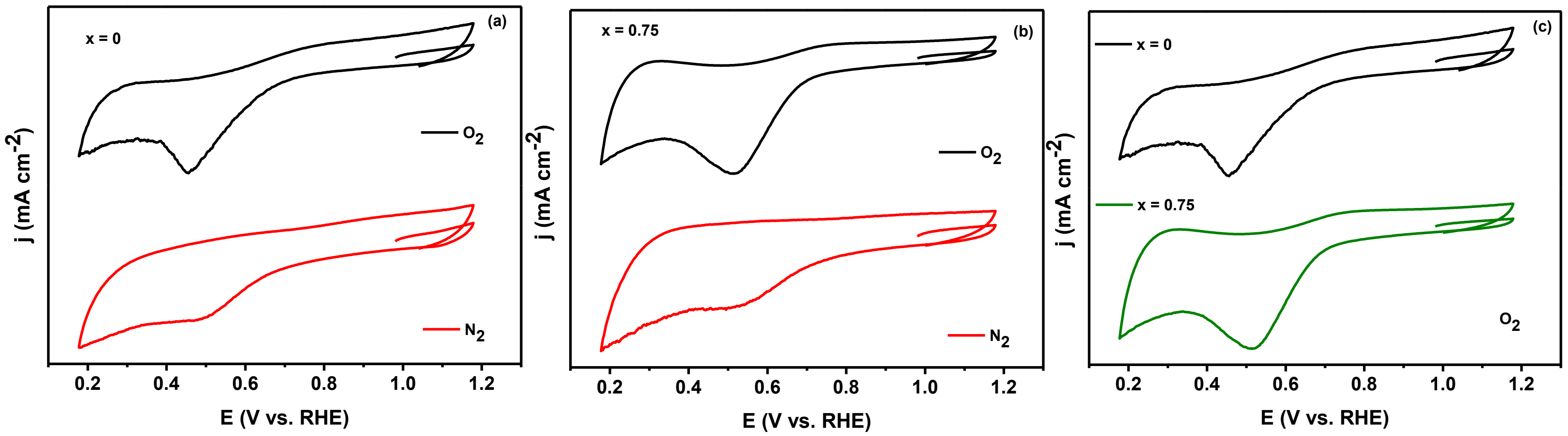



**Figure 8.** (a, b) CVs for $Ni_xCo_{1-x}Fe_2O_4$/C (x = 0 and 0.75) in $O_2$- and $N_2$-saturated 0.1 M KOH solution and a scan rate of 50 mV/s. (c) Comparison of CVs for $Ni_xCo_{1-x}Fe_2O_4$/C (x = 0 and 0.75) in $O_2$-saturated solution.

# Electrochemical measurements Cont…

## Kouteckey-Levich (K-L) plots Analysis

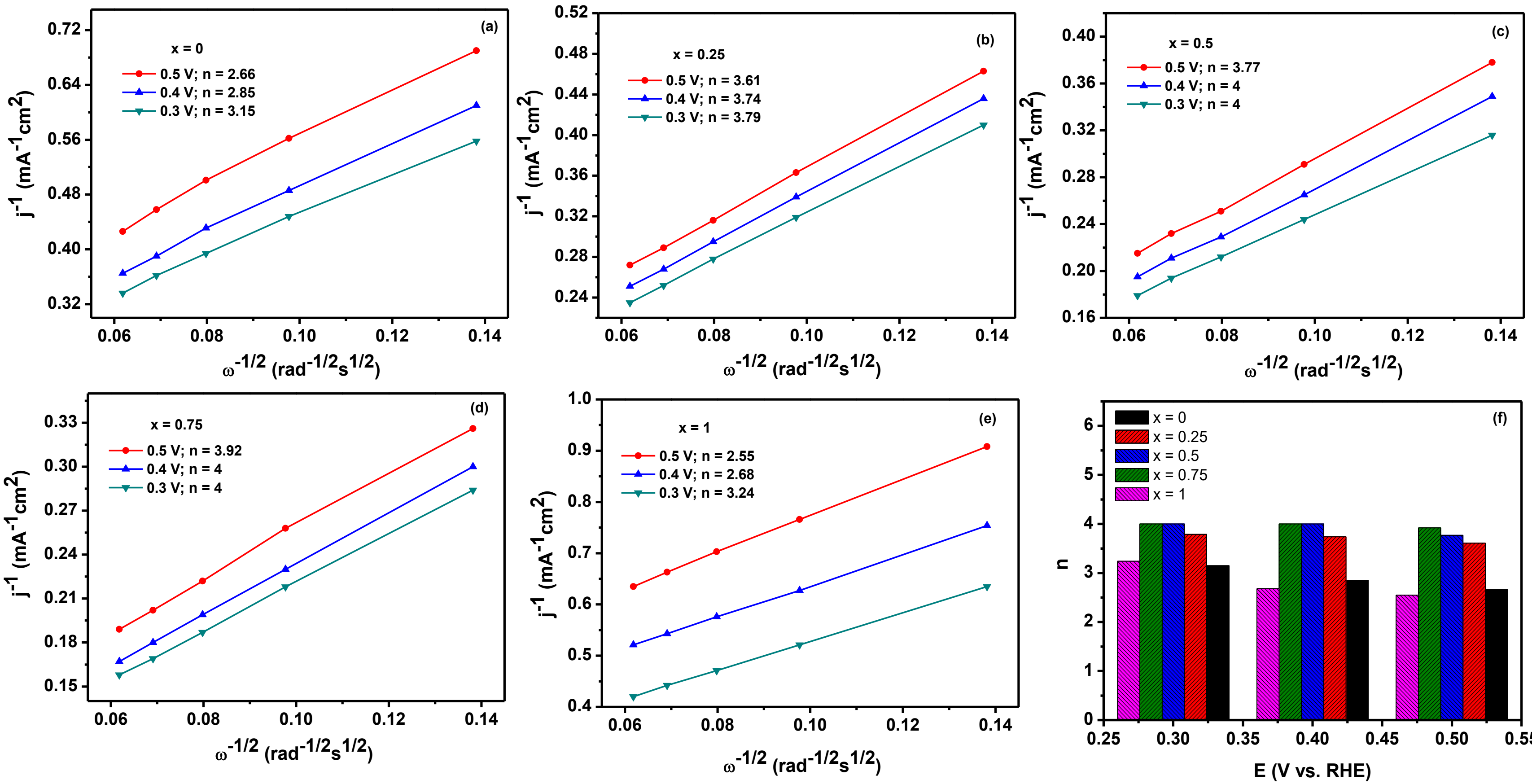



**Figure 9.** (a-e) K-L plots of $Ni_xCo_{1-x}Fe_2O_4$/C catalysts. (f) Calculated *n*-values based on RDE data.

# Electrochemical measurements Cont…

## Tafel plot Analysis

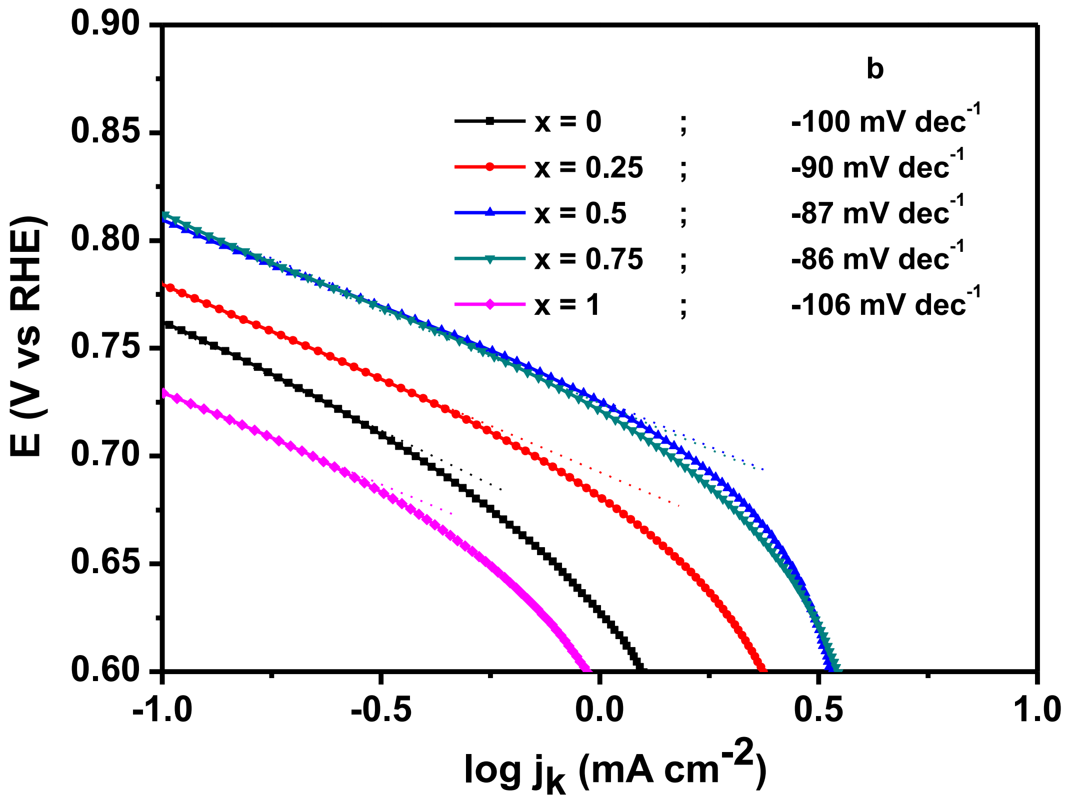



**Figure 10.** Tafel plots of $Ni_xCo_{1-x}Fe_2O_4/C$ catalysts at 1500 rpm.

# Conclusions

- All the $Ni_xCo_{1-x}Fe_2O_4/C$ (x = 0, 0.25, 0.5, 0.75 and 1) catalysts were successfully synthesized through the hydrothermal method;

- The samples are single-phase spinel compounds with the XRD crystallite sizes of 28.56, 17.09, 20.57, 20.58 and 23.99 nm for x = 0, 0.25, 0.5, 0.75 and 1, respectively.

- Partially doping $CoFe_2O_4/C$ with Ni causes a reduction in the lattice parameter (*a*).

- Among the $Ni_xCo_{1-x}Fe_2O_4/C$ (x = 0, 0.25, 0.5, 0.75 and 1) catalysts, the x = 0.75 exhibited the best ORR activity. The catalytic activity increases in the order: x = 1< 0 < 0.25 < 0.5 < 0.75.

- Ni-doped $CoFe_2O_4/C$ nanoparticles synthesized through the hydrothermal method at a low temperature could be potential cathode materials for ORR in alkaline fuel cells.

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# Thank You

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