

Electrocatalytic performance of Co-doped NiFe₂O₄/C nanoparticles towards oxygen reduction reaction in alkaline media.

Mphoma S Matseke,^{a, b} Haitao Zheng^a and Kaushik Mallick^b

^aEnergy Centre, Council for Scientific and Industrial Research (CSIR), P O Box 395, Pretoria, 0001

^bDepartment of Chemistry, University of Johannesburg, P.O.Box 524, Aucklandpark, 2006

e-mail: MMatseke@csir.co.za

Introduction

Spinel metal oxides with the general formula of AB₂O₄ (Figure 1) have attracted a lot of attention over the past few decades as promising cathode materials for oxygen reduction reaction (ORR) in fuel cells [1] [2] [3] [4]. This is due to their changeable valence states, good catalytic activity and electrochemical stability [1] [2] [4].

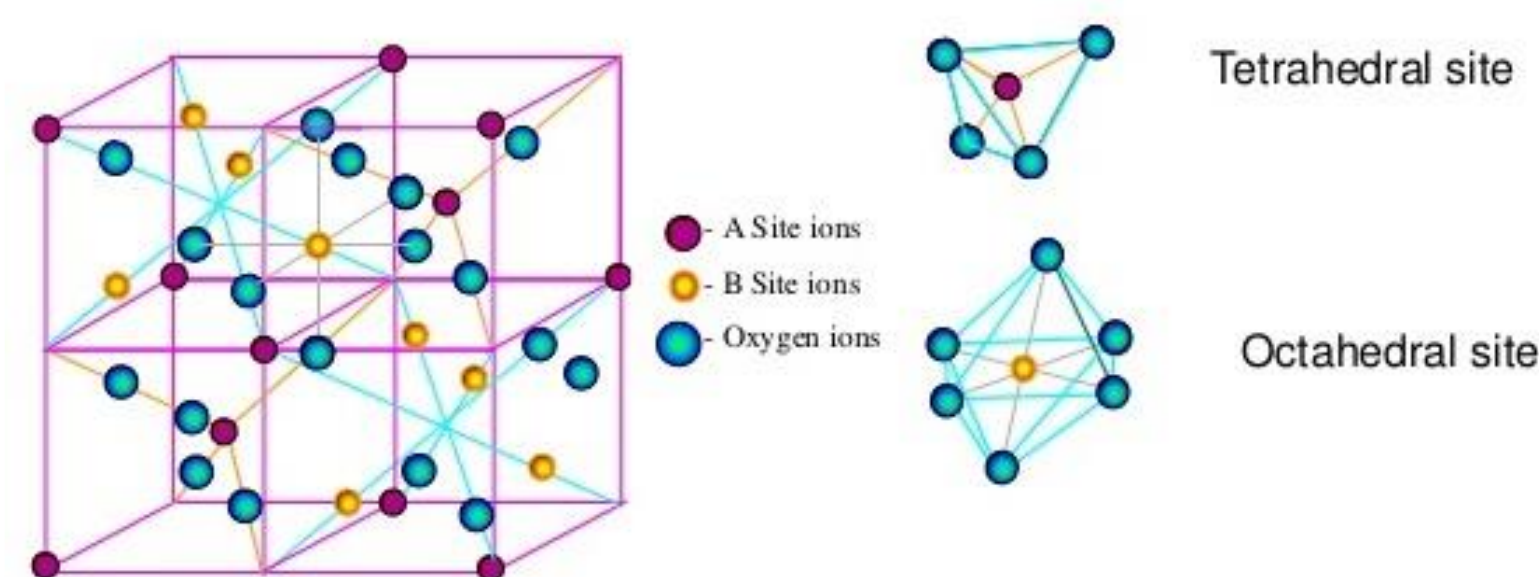


Figure 1. Typical spinel structure.

Problem Statement

Pt and Pt-based catalysts are the best ORR catalysts for many energy conversion and storage devices such as fuel cells and metal-air batteries. However, the rareness and expensive nature of Pt hamper the large scale production and commercialization of these devices. Therefore abundant, cheaper and effective catalysts have to be developed in order to replace Pt.

Aims and Objectives

The main aim of this work was to synthesize carbon-supported NiFe_{2-x}Co_xO₄ nanoparticles with high catalytic activity for ORR in alkaline media.

The objectives were therefore to:

- Synthesize NiFe_{2-x}Co_xO₄/C (x = 0, 0.25, 0.5 and 0.75) samples through a hydrothermal method;
- Employ the XRD, XPS, TEM and SAED techniques to analyze the physical properties of the synthesized samples;
- Investigate the electrochemical performances of the synthesized samples towards ORR in O₂-saturated 0.1 M KOH electrolyte through the use of the linear sweep voltammetry (LSV) technique.

Methodology

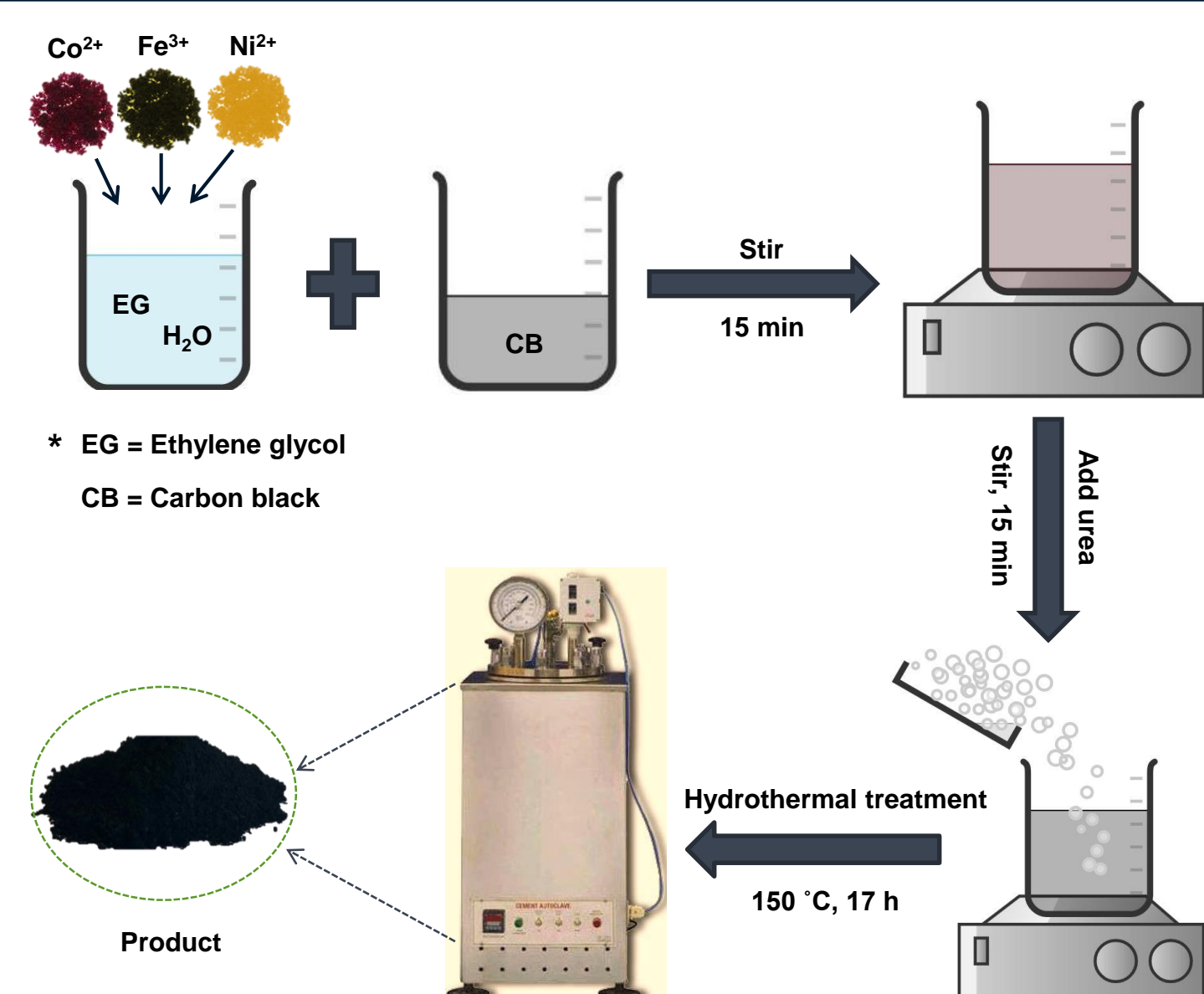


Figure 2. A hydrothermal synthesis of samples.

Results

Physical Characterization

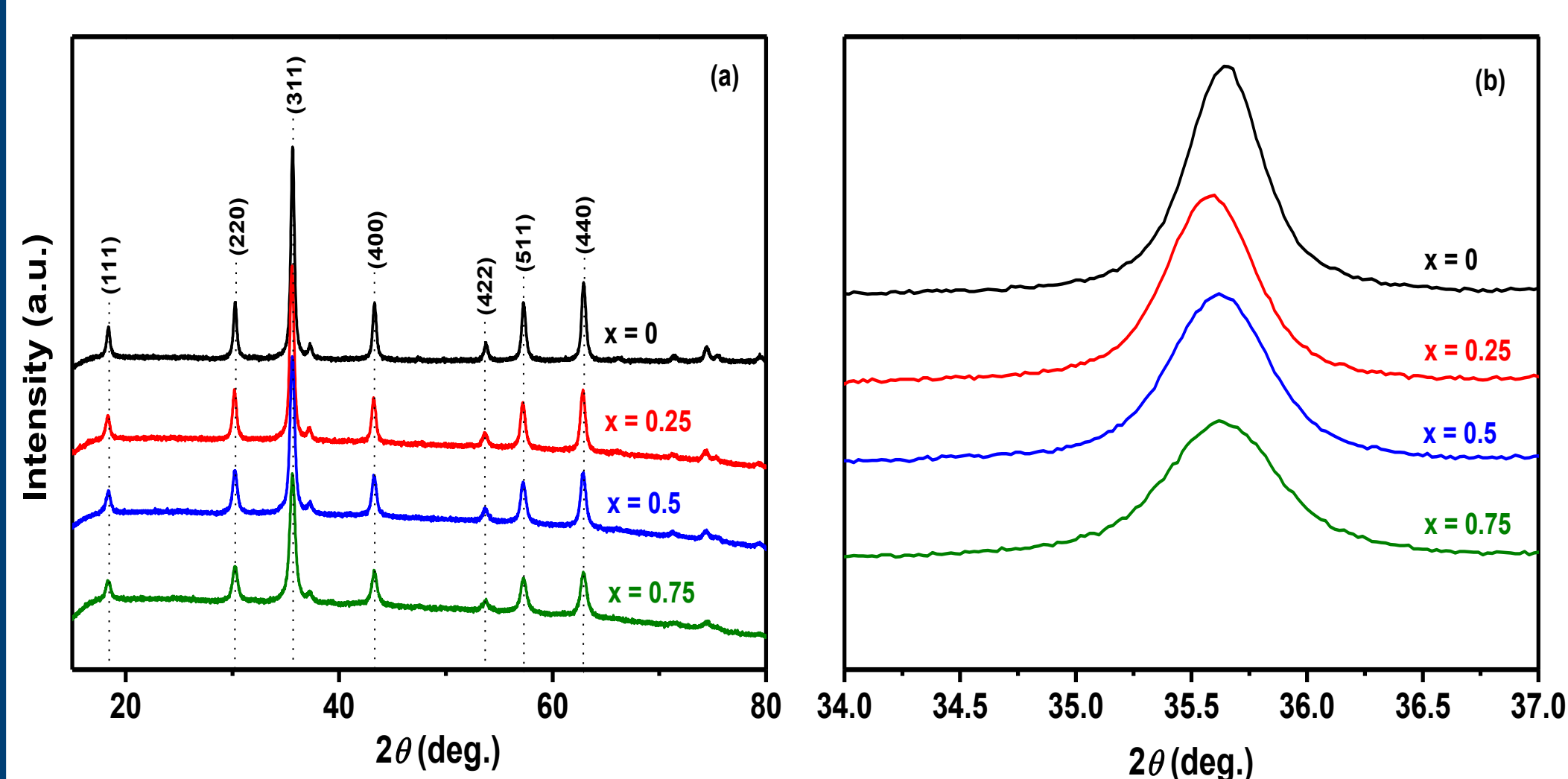


Figure 3. (a) X-ray diffraction patterns of NiFe_{2-x}Co_xO₄/C (x = 0, 0.25, 0.5 and 0.75), (b) the partially enlarged XRD patterns indicating the (311) peaks.

Table 1 Crystallite sizes *D* calculated with Scherrer's equation on the (311) diffraction peak, *d*-spacing (*d*) and lattice parameter (*a*) of NiFe_{2-x}Co_xO₄/C (x = 0, 0.25, 0.5 and 0.75) samples.

Sample (x)	Crystallite size <i>D</i> (nm)	2θ (deg.)	<i>d</i> -spacing (nm)	Lattice parameter <i>a</i> (Å)
0	23.99	35.62	0.252 ± 0.0000	8.357 ± 0.0009
0.25	19.76	35.55	0.252 ± 0.0005	8.374 ± 0.0005
0.5	17.28	35.60	0.252 ± 0.0002	8.364 ± 0.0005
0.75	15.09	35.60	0.252 ± 0.0002	8.364 ± 0.0005

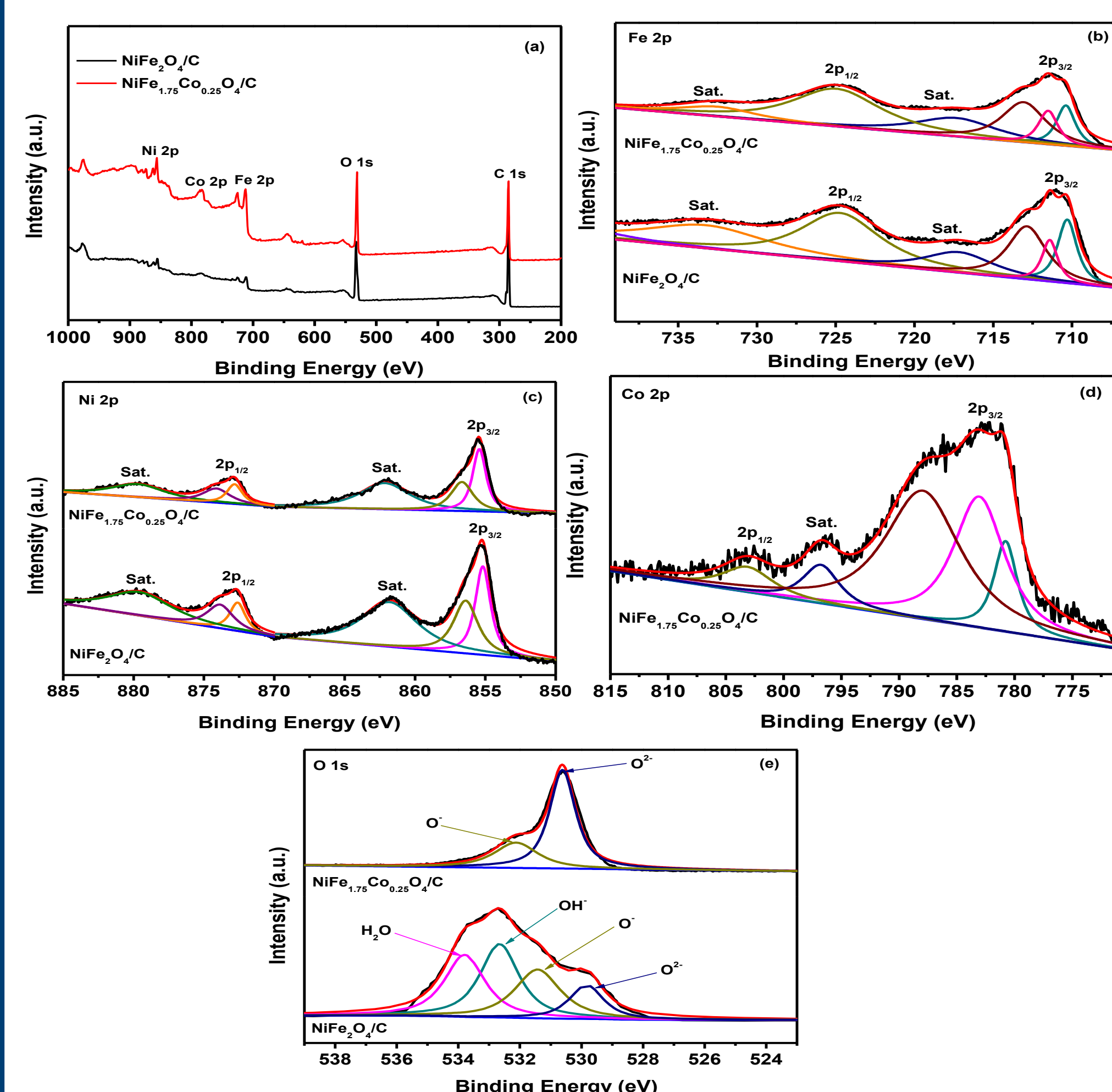


Figure 4. XPS spectra of (a) whole range, (b) Fe 2p, (c) Ni 2p, (d) Co 2p and (e) O 1s of the NiFe₂O₄/C and NiFe_{1.75}Co_{0.25}O₄/C samples.

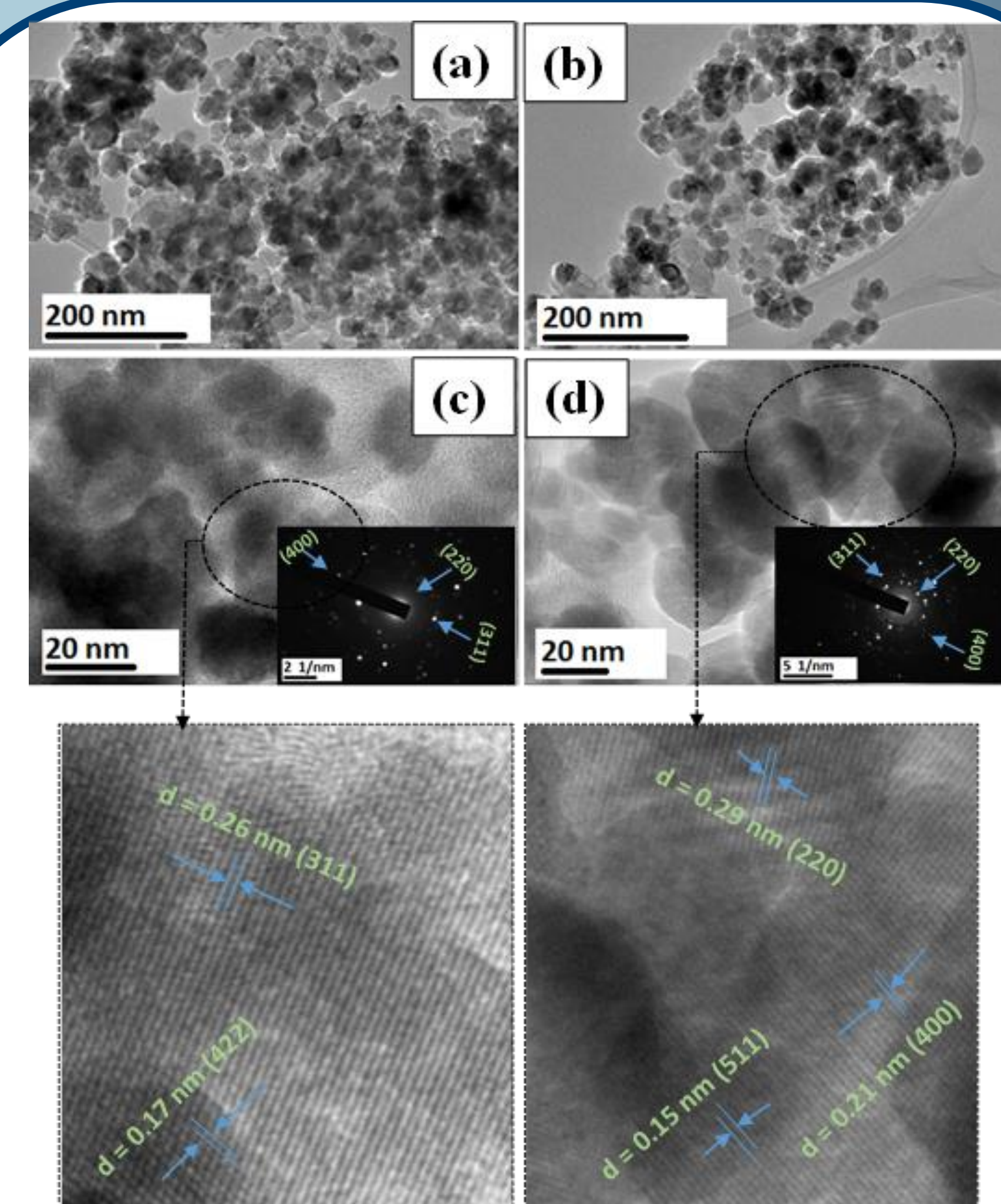


Figure 5. (a, b) TEM images of (a) NiFe₂O₄/C and (b) NiFe_{1.75}Co_{0.25}O₄/C samples. (c, d) HRTEM images of (c) NiFe₂O₄/C and (d) NiFe_{1.75}Co_{0.25}O₄/C samples, inserts: corresponding SAED patterns.

Electrochemical Characterization

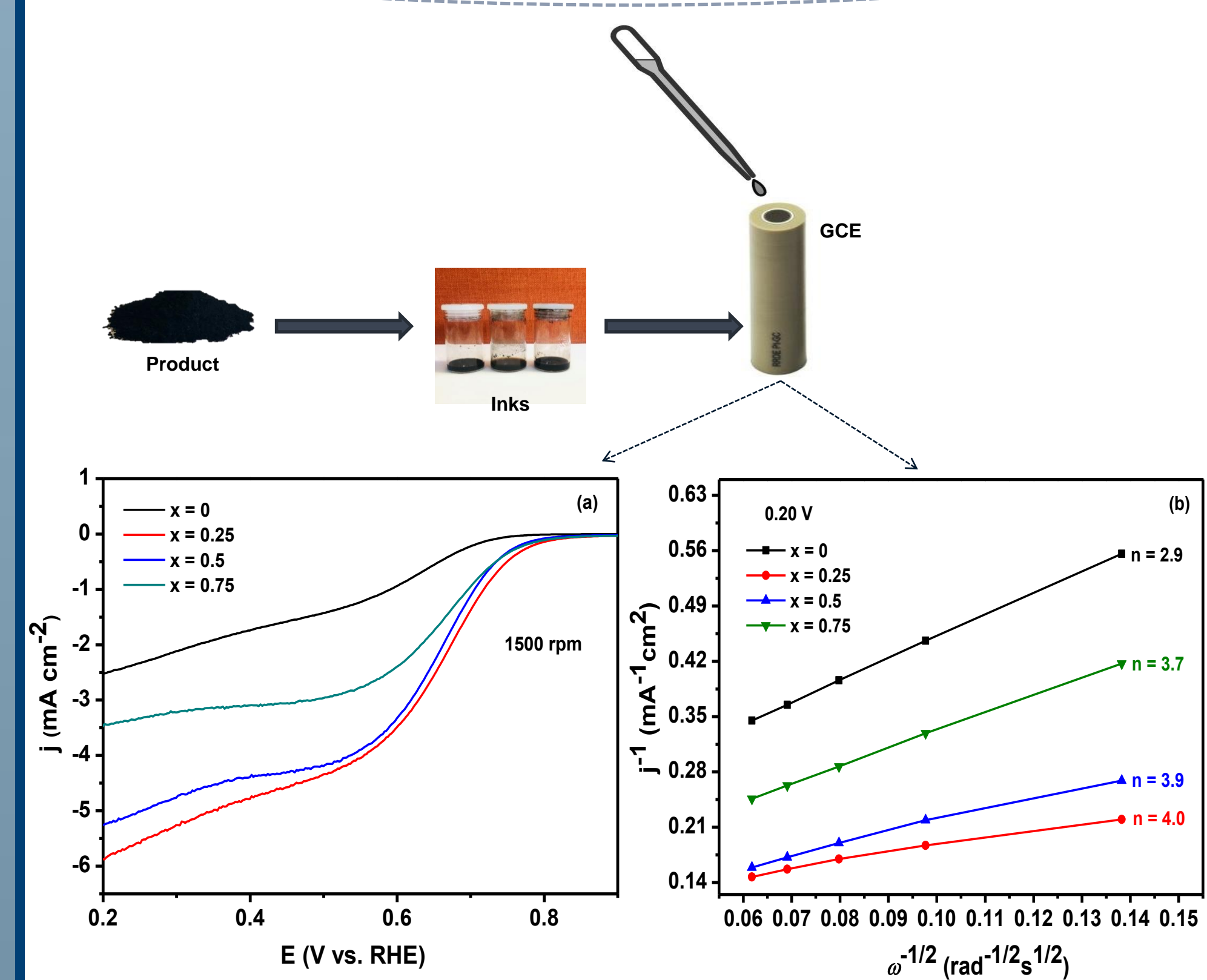


Figure 6. (a) LSV curves of NiFe_{2-x}Co_xO₄/C (x = 0, 0.25, 0.5 and 0.75) samples in O₂-saturated 0.1 M KOH solution at a scan rate of 5 mV s⁻¹ and a rotation rate of 1500 rpm. (b) K-L plots showing the electron transfer numbers (*n*) of the samples at a fixed potential of 0.20 V.

Conclusions

All NiFe_{2-x}Co_xO₄/C (x = 0, 0.25, 0.5 and 0.75) samples were successfully synthesized through a hydrothermal method. The ORR catalytic activity of the samples increases in the order: x = 0 < 0.75 < 0.5 < 0.25. Therefore, NiFe_{2-x}Co_xO₄/C nanoparticles could be potential cathode materials for ORR in alkaline fuel cells.

References

- [1] Naik, K.M and Sampath, S, *Electrochim. Acta*, 2018, **292**, 268-275.
- [2] Yan, W; Cao, X; Tian, J; Jin, C; Ke, K and Yang, R, *Carbon*, 2016, **99**, 195-202.
- [3] Liu, S; Yan, W; Cao, X; Zhou, Z and Yang, R, *Int. J. Hydrogen Energy*, 2016, **41**, 5351-5360.
- [4] Zhao, X; Fu, Y; Wang, J; Xu, Y; Tian, J-H and Yang, R, *Electrochim. Acta*, 2016, **201**, 172-178.

Acknowledgements

The authors of this work would like to thank the National Research Foundation (NRF) and the Council for Scientific and Industrial Research (CSIR) for financial support.