Oxygen reduction reaction catalyzed by Ni-doped $CoFe_2O_4$/C nanoparticles in alkaline media.

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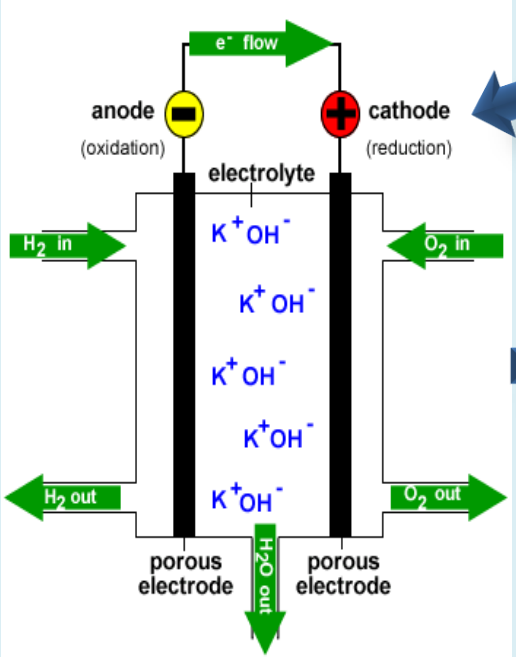
Introduction

Oxygen reduction reaction



Scheme 1. Fuel cell basic operation.

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)**

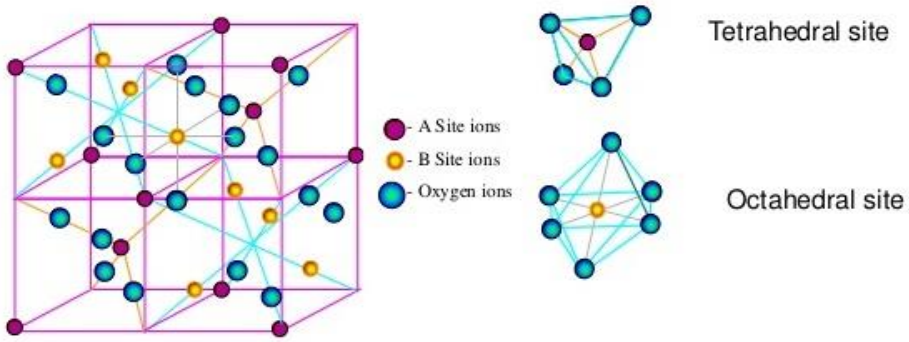


Figure 1. Typical spinel structure.

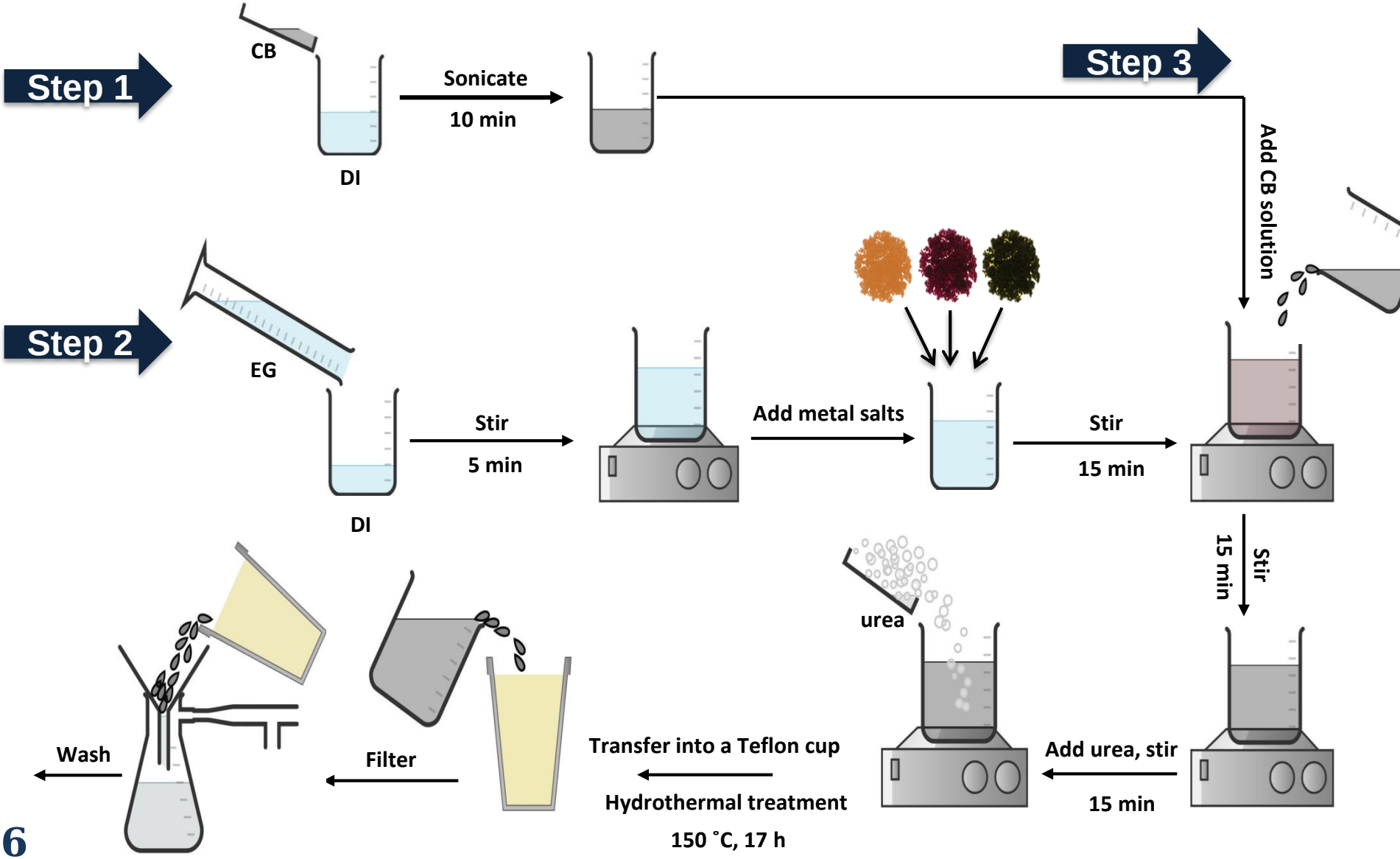
Aims and Objectives

The main aim of this work was to synthesize carbon-supported $CoFe_{2-x}Ni_xO_4$ nanoparticles with high catalytic activity for ORR in alkaline media.

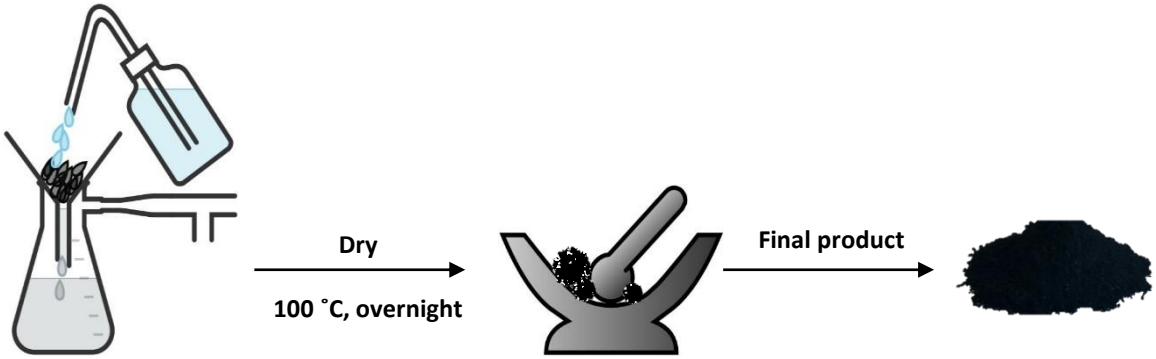
The objectives were thus to:

- Synthesize $CoFe_{2-x}Ni_xO4$ (x = 0, 0.25, 0.5 and 0.75) electrocatalysts through a 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 the LSV technique.

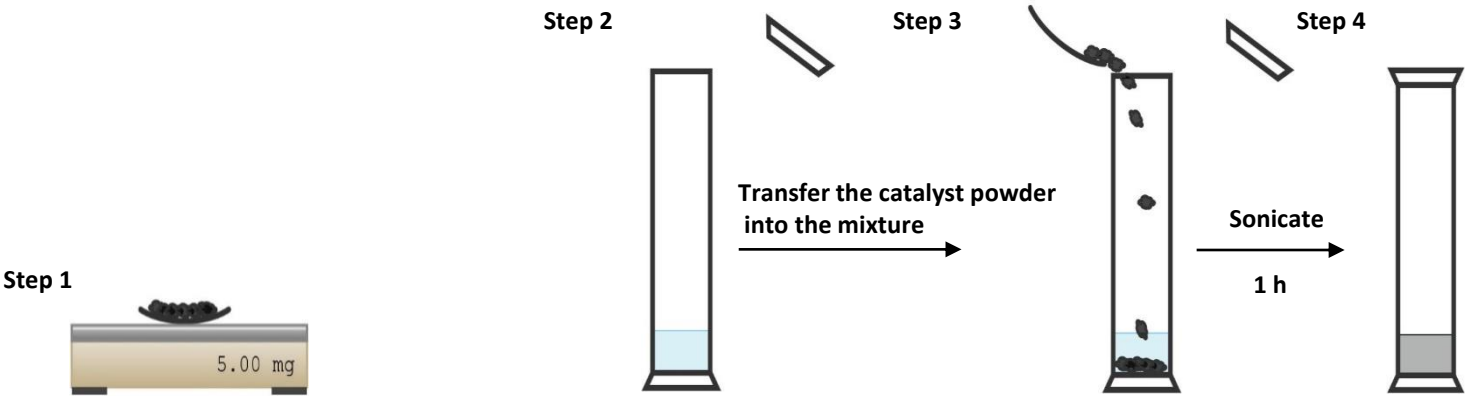
Methodology



Methodology Cont…



Ink preparation



XRD Measurements

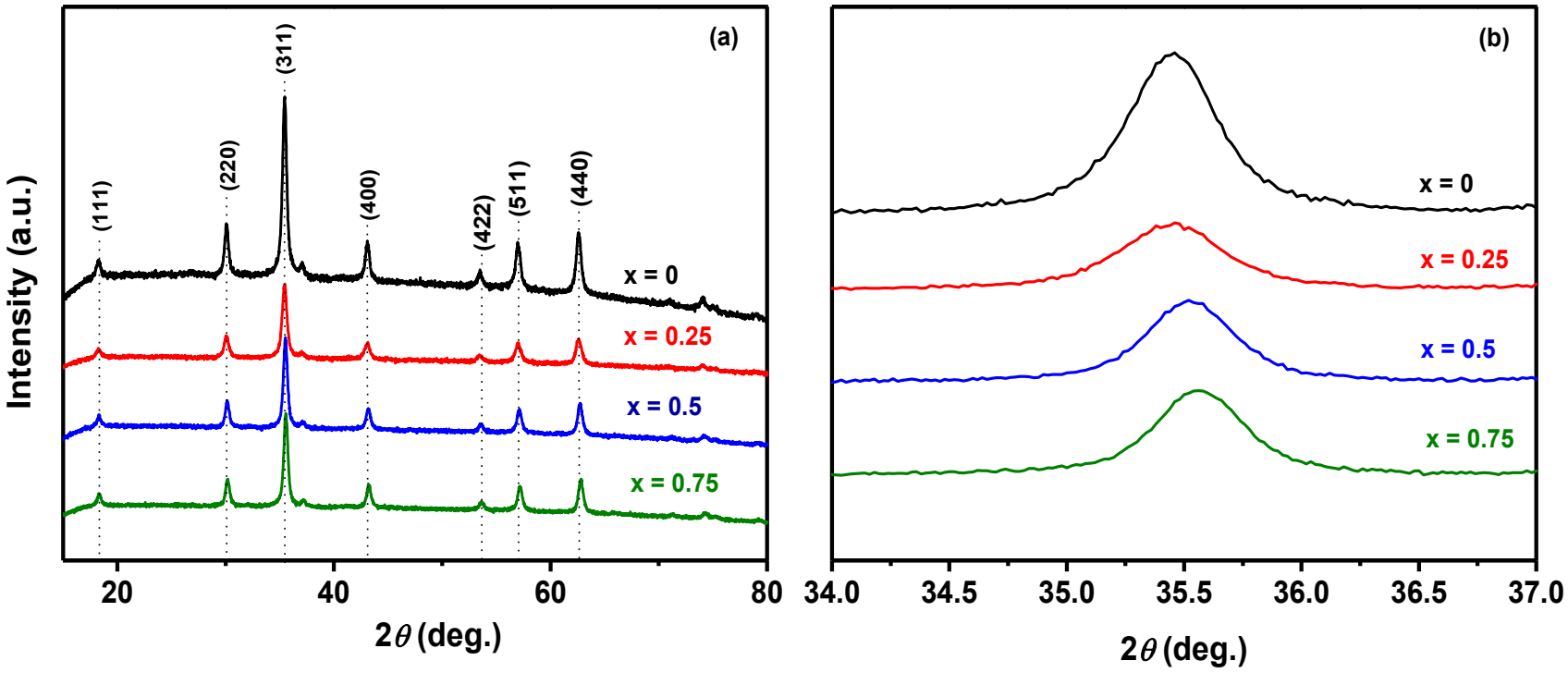


Figure 2. (a) X-ray diffraction patterns of $CoFe_{2-x}Ni_xO_4/C$ (x = 0, 0.25, 0.5 and 0.75), (b) the partially enlarged XRD patterns indicating the (311) peaks.

XRD measurements Cont…

Table 1 XRD crystallite sizes of $CoFe_{2-x}Ni_xO_4/C$ (x = 0, 0.25, 0.5 and 0.75) calculated from the (311) diffraction peak using Scherrer's equation.

Sample (x)	Crystallite size *D* (nm)
0	28.56
0.25	15.20
0.5	14.14
0.75	12.54

FTIR analysis

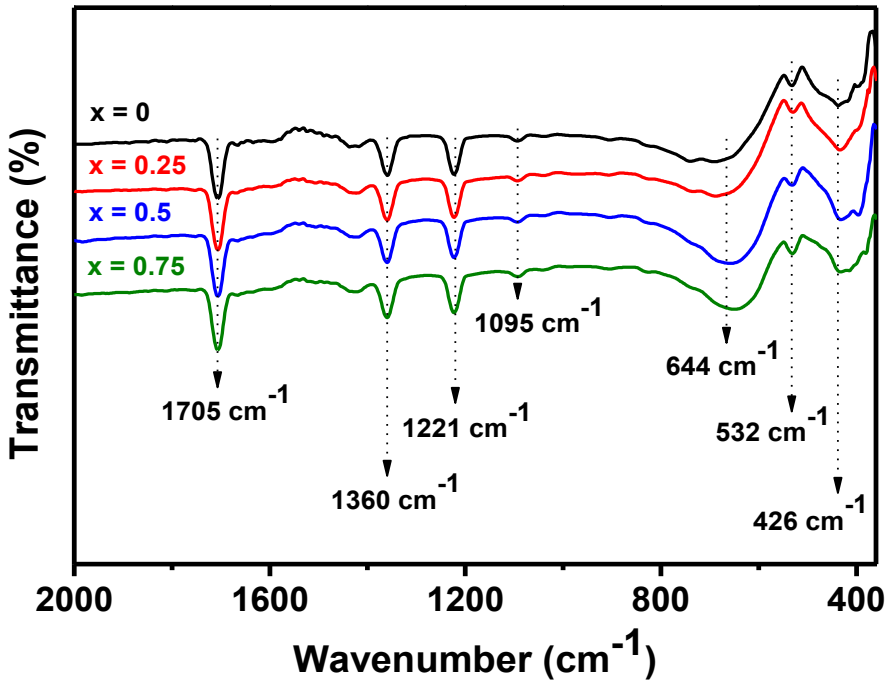


Figure 3. FTIR spectra of $CoFe_{2-x}Ni_xO_4/C$ (x = 0, 0.25, 0.5 and 0.75) samples.

TEM and SAED analysis

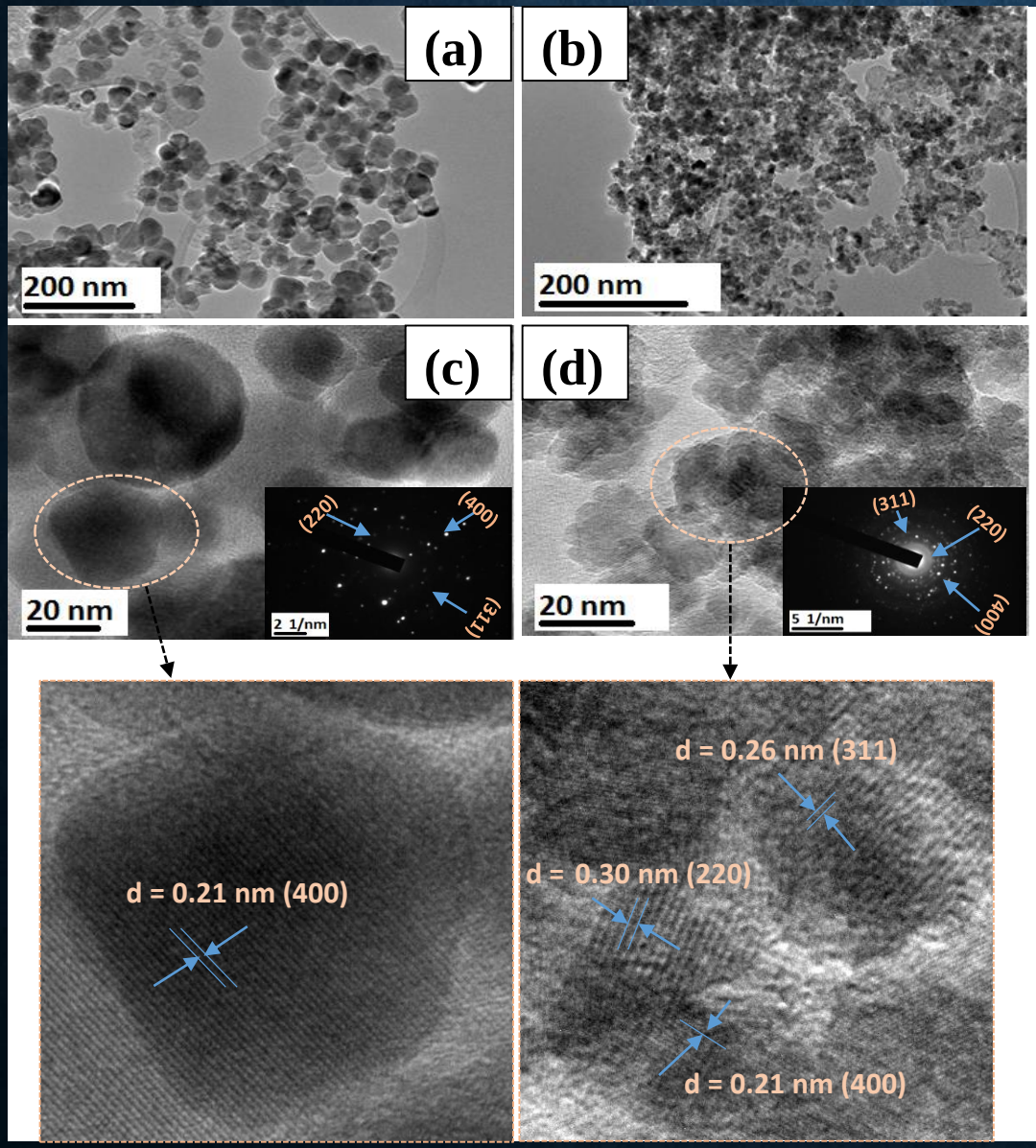


Figure 4. (a, b) Low magnification TEM images of (a) x = 0 and (b) x = 0.75. (c, d) High magnification TEM images of (c) x = 0 and (d) x = 0.75. inserts: corresponding SAED patterns.

Elemental mapping and EDX analysis

A $CoFe_2O_4/C$

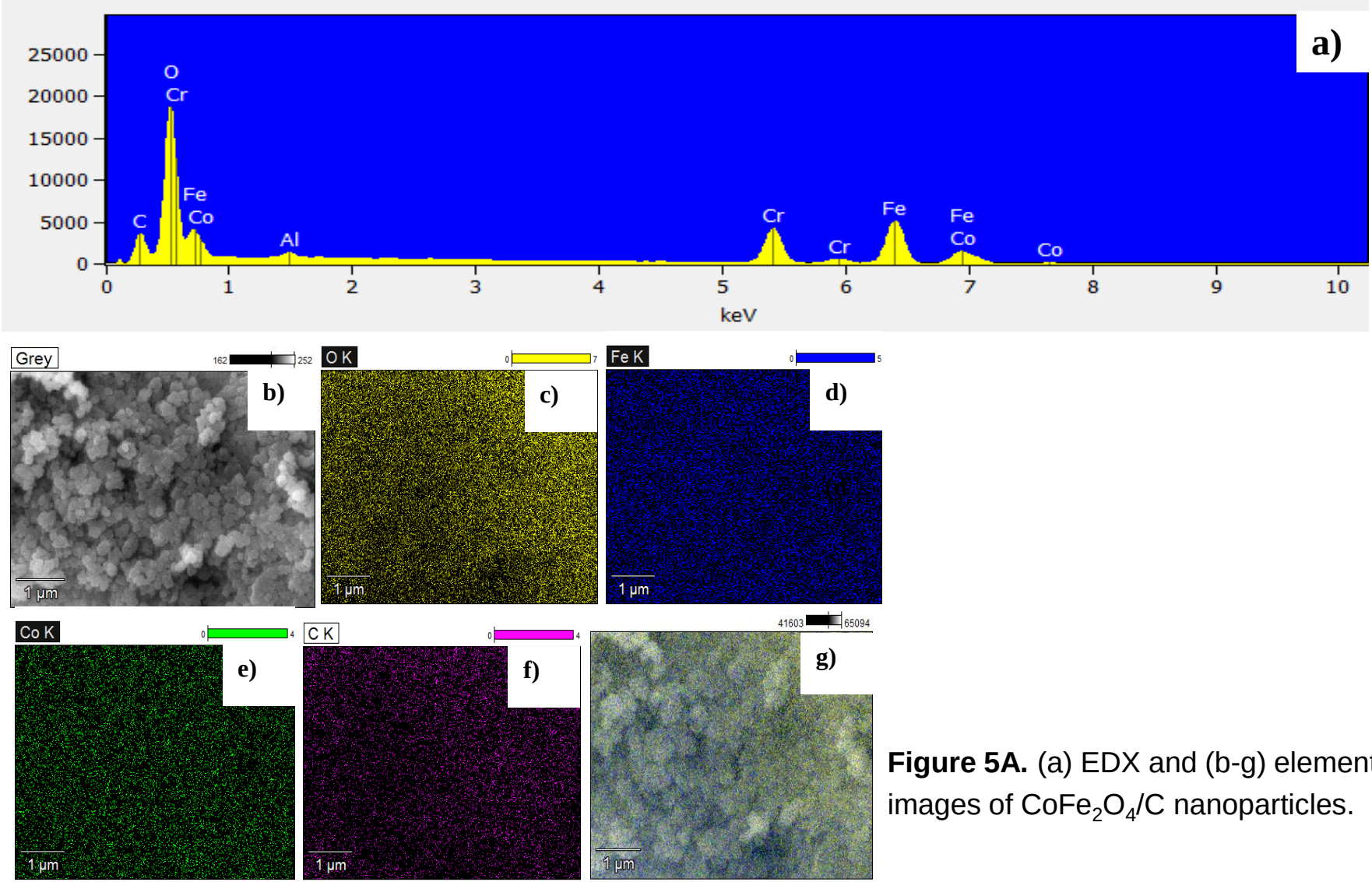
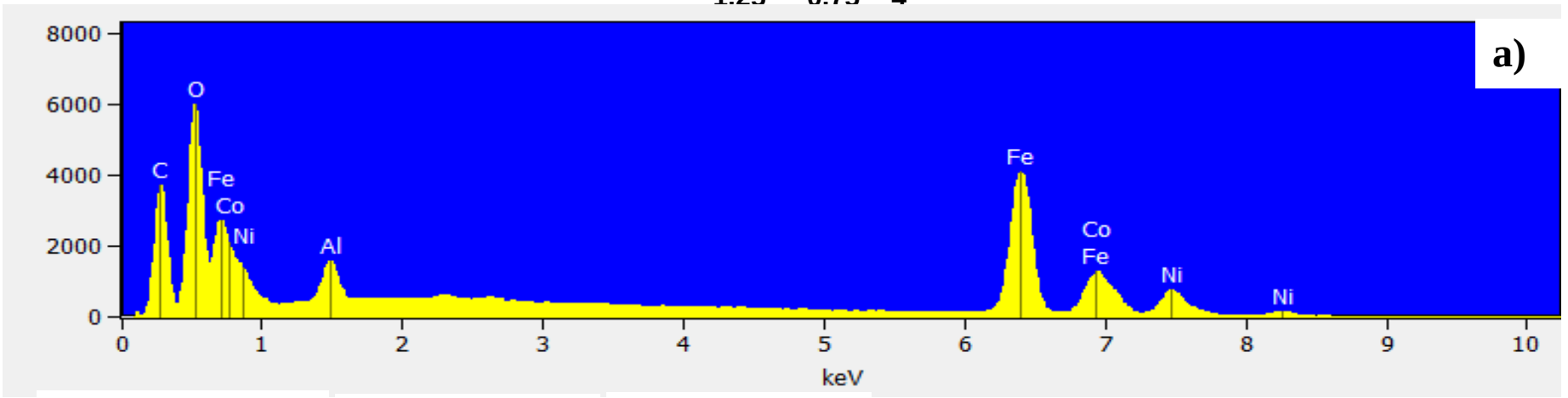


Figure 5A. (a) EDX and (b-g) elemental images of $CoFe_2O_4/C$ nanoparticles.

Elemental mapping and EDX analysis Cont…

B

$CoFe_{1.25}Ni_{0.75}O_4/C$



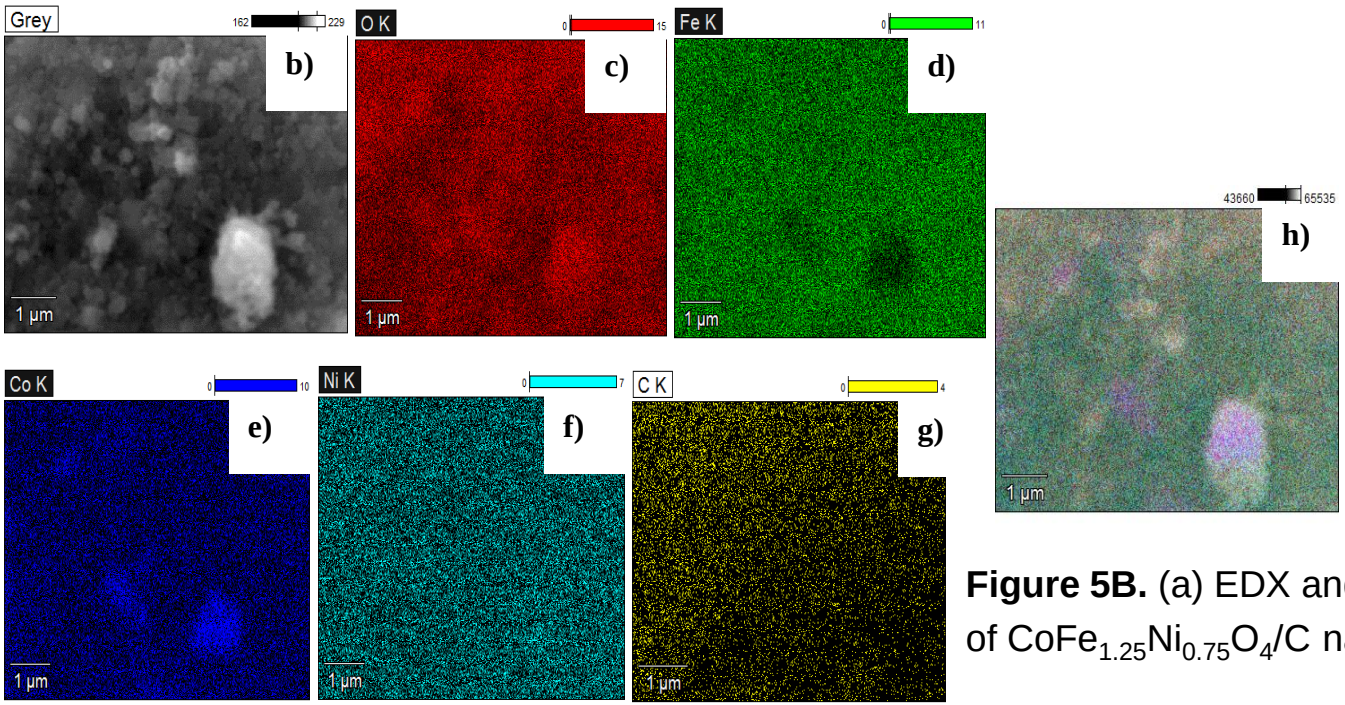


Figure 5B. (a) EDX and (b-h) elemental images of $CoFe_{1.25}Ni_{0.75}O_4/C$ nanoparticles.

Electrochemical measurements

Linear sweep voltammetry

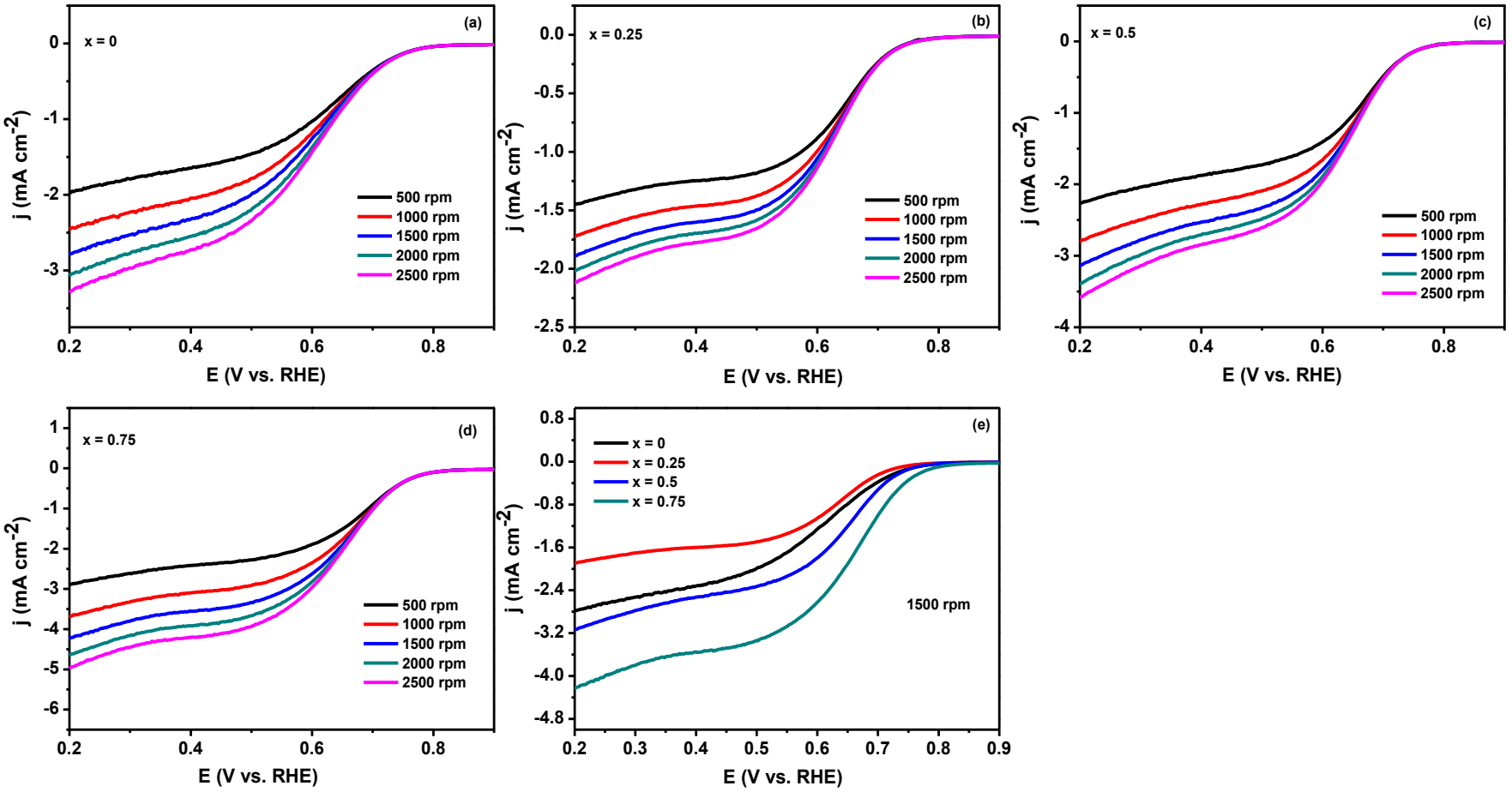


Figure 6. (a-d) LSV curves of $CoFe_{2-x}Ni_xO_4$/C catalysts. (e) Comparison of the LSV curves at 1500 rpm.

Electrochemical measurements Cont…

Kouteckey-Levich (K-L) plots Analysis

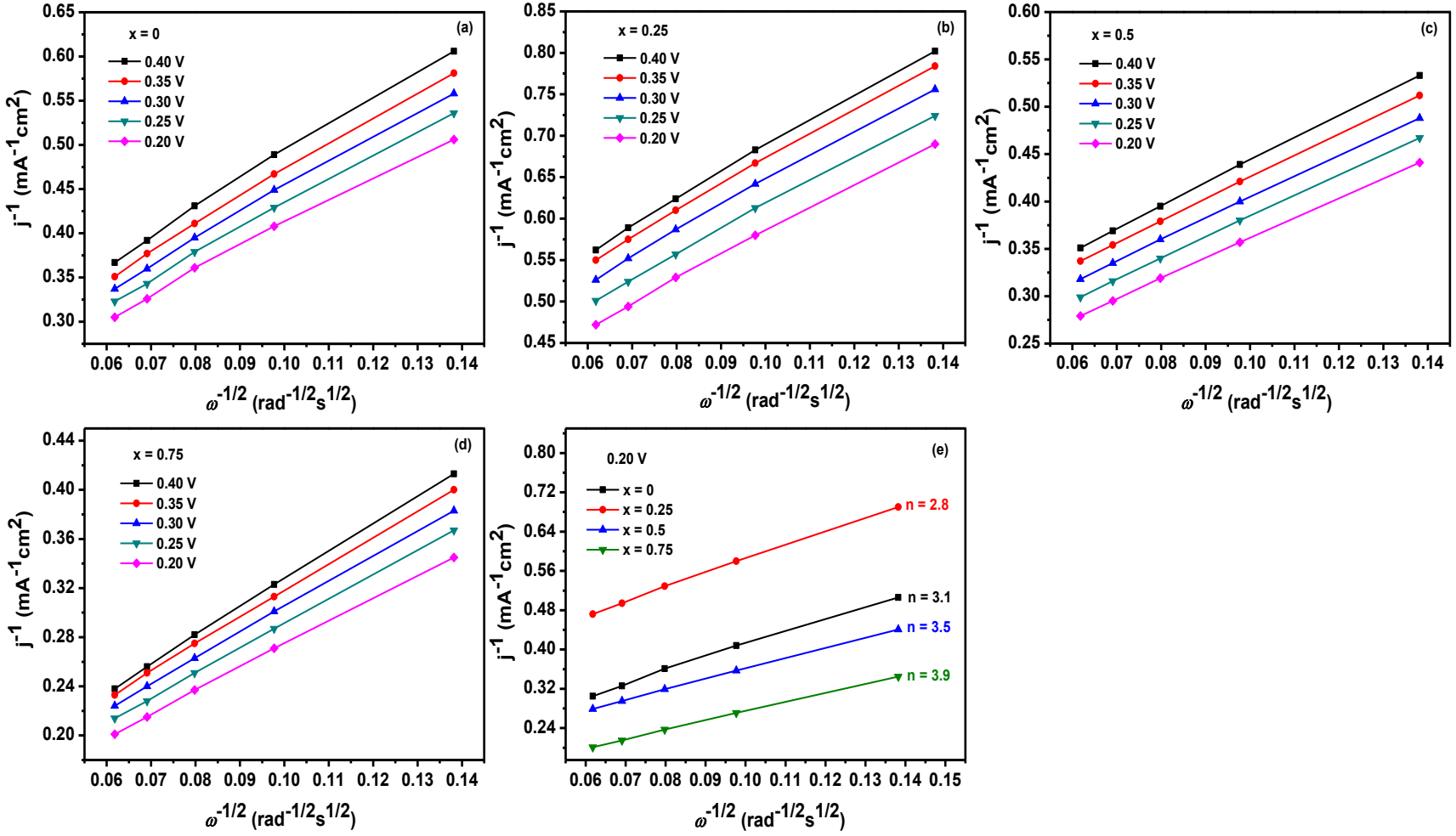


Figure 7. (a-d) K-L plots of $CoFe_{2-x}Ni_xO_4$/C catalysts. (e) Comparison of calculated *n*-values based on RDE data at 0.20 V.

Conclusions

- All the $CoFe_{2-x}Ni_xO_4/C$ (x = 0, 0.25, 0.5 and 0.75) catalysts were successfully synthesized through a hydrothermal method;

- The samples are single-phase spinel compounds with the XRD crystallite sizes of 28.56, 15.20, 14.14 and 12.54 nm for x = 0, 0.25, 0.5 and 0.75, respectively.

- Among the $CoFe_{2-x}Ni_xO_4/C$ (x = 0, 0.25, 0.5 and 0.75) catalysts, the x = 0.75 exhibited the best ORR activity. The catalytic activity increases in the order: x = 0.25< 0 < 0.5 < 0.75.

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

References

1. Bhujun, B.; Tan, M.T.; Shanmugam, A.S. Study of mixed ternary transition metal ferrites as potential electrodes for supercapacitor applications. *Results Phys*. **2017**, 7, 345-353.
2. He, H-Y. Structural and magnetic property of $Co_{1-x}Ni_xFe_2O_4$ nanoparticles synthesized by hydrothermal method. *Int. J. Appl. Ceram. Technol*. **2014**, 11, 626-636.
3. Wang, Y.; Liu, Q.; Zhang, L.; Hu, T.; Liu, W.; Liu, N.; Du, F.; Li, Q.; Wang, Y. One-pot synthesis of Ag-$CoFe_2O_4$/C as efficient catalyst for oxygen reduction in alkaline media. *Int. J. Hydrog. Energy* **2016**, 41, 22547-22553.
4. Xu, Y.; Bian, W.; Wu, J.; Tian, J-H.; Yang, R. Preparation and electrocatalytic activity of 3D hierarchical porous spinel $CoFe_2O_4$ hollow nanospheres as efficient catalyst for oxygen reduction reaction and oxygen evolution reaction. *Electrochim. Acta* **2015**, 151, 276-283.
5. Omelyanchik, A.; Singh, G.; Volochaev, M.; Sokolovc, A.; Rodionova, V.; Peddis, D. Tunable magnetic properties of Ni-doped $CoFe_2O_4$ nanoparticles prepared by the sol–gel citrate self-combustion method. *J. Magn. Magn. Mater*. **2019**, 476, 387-391.
6. Torkian, S.; Ghasemi, A.; Razavi, R.S. Cation distribution and magnetic analysis of wideband microwave absorptive $Co_xNi_{1-x}Fe_2O_4$ ferrites. *Ceram. Int*. **2017**, 43, 6987-6995.
7. Dang, Z-M.; Wang, L.; Zhang, L-P. Surface functionalization of multiwalled carbon nanotube with trifluorophenyl. *J. Nanomater*. **2006**, Article ID 83583, 1-5.

References Cont…

8. Rana, S.; Philip, J.; Raj. Micelle based synthesis of cobalt ferrite nanoparticles and its characterization using Fourier Transform Infrared Transmission Spectrometry and Thermogravimetry. *Mater. Chem. Phys.* **2010**, 124, 264-269.
9. Wang, L.; Meng, H.; Shen, P.K.; Bianchini, C.; Vizza, F.; Wei, Z. In situ FTIR spectroelectrochemical study on the mechanism of ethylene glycol electrocatalytic oxidation at a Pd electrode. *Phys. Chem. Chem. Phys* **2011**, 13, 2667–2673.
10. Boobalan, T.; Suriyanarayanan, N.; Pavithradevi, S. Structural, magnetic and dielectric properties of nanocrystalline cobalt ferrite by wet hydroxyl chemical route. *Mat. Sci. Semicon. Proc.* **2013**, 16, 1695-1700.
11. Habibi, M.H.; Parhizkar, H.J. FTIR and UV-vis diffuse reflectance spectroscopy studies of the wet chemical (WC) route synthesized nano-structure $CoFe_2O_4$ from $CoCl_2$ and $FeCl_3$. *Spectrochim. Acta A* **2014**, 127, 102-106.
12. Adeela, N.; Maaz, K.; Khan, U.; Karim, S.; Nisar, A.; Ahmad, M.; Ali, G.; Han, X.F.; Duan, J.L.; Liu, J.; Influence of manganese substitution on structural and magnetic properties of $CoFe_2O_4$ nanoparticles. *J. Alloys Compd*. **2015**, 639, 533, 540.
13. Ati, A.A.; Othaman, Z.; Samavati, A. Influence of cobalt on structural and magnetic properties of nickel ferrite nanoparticles. *J. Mol. Struct*. **2013**, 1052, 177-182.

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Thank You