

# Electrochemical reaction mechanism in $MFe_2O_4$ ( $M = Fe, Co, Ni \& Cu$ ) conversion type negative electrode systems

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## Introduction

Nanostructured materials are widely used for enhancing power density in rechargeable lithium-ion batteries [1]. In particular, the research on electrode systems those operate through electrochemical reversible conversion mechanism have been a topic of interest due to their intrinsically higher capacity comparing to intercalation-type electrode [2,3]. Fe-containing oxides are particularly interesting as conversion-type materials since iron is cost effective and environmentally friendly. The partial substitution of Fe in the spinel structure of  $Fe_3O_4$  with other 3d-metals may influence the cation distribution in the spinel structure as well as the  $Li^+$  ion solubility in these spinel ferrites during lithiation and delithiation. This further may have impact on the phase transformations and the electrode microstructure during the conversion reaction. In the present work, a comparative study of different metal ferrites,  $MFe_2O_4$  ( $M = Fe, Co, Ni$  and  $Cu$ ) as anode materials for li-ion batteries, to elucidate the influence of partial substitution of Fe in the spinel structure with different 3d-cations, are reported.

## Synthesis: Experimental Details

Synthesis of metal ferrites were carried out by inverse co-precipitation route. Metal acetate precursors with 1:2 ratio is dissolved in doubly distilled deionized water and added to 1M of NaOH solution drop wise with vigorous stirring. The solutions were heated and kept at 80°C for one hour. The precipitates were centrifuged with deionized water and were dried at 85°C overnight. The final calcination was performed at 600°C and 800°C.

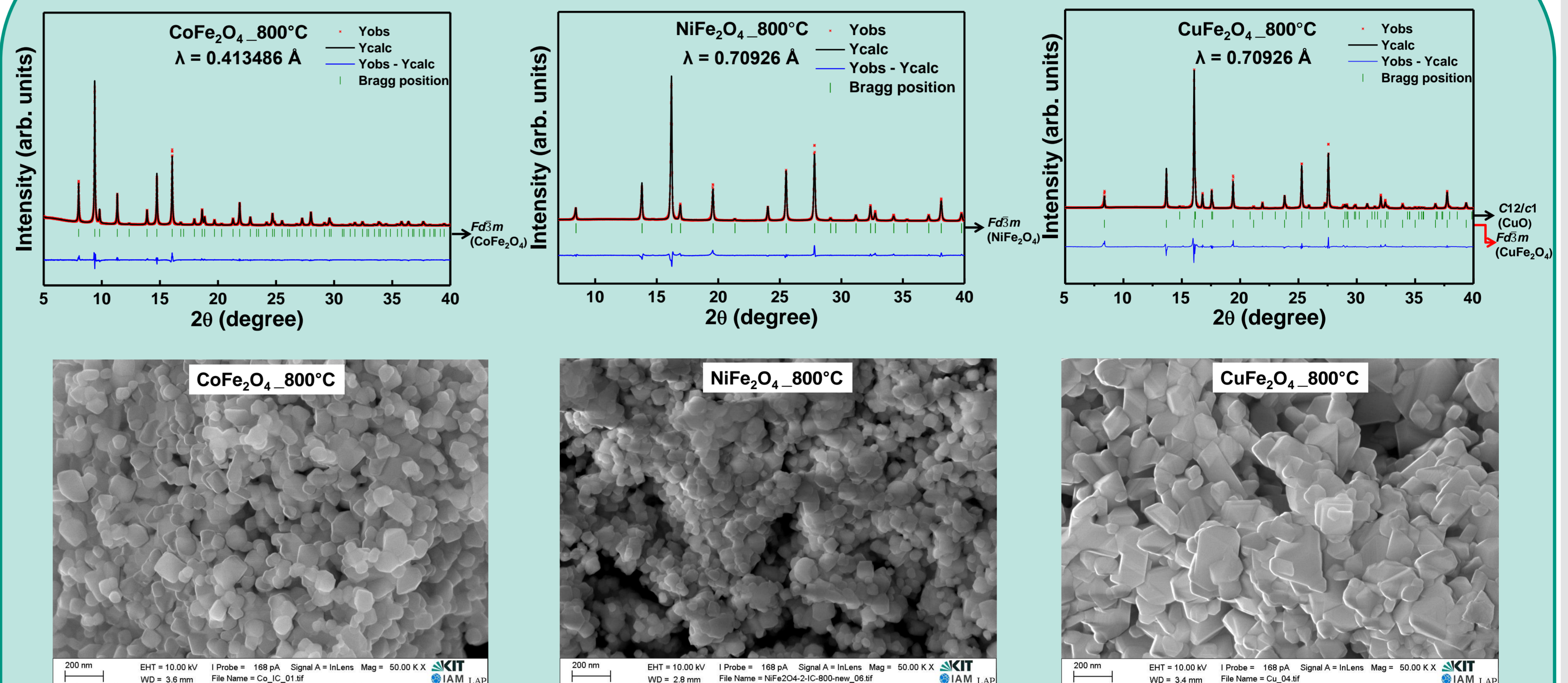
## Characterization:

*Ex situ* and *in situ* X-ray absorption spectroscopy (XAS) were carried out at the XAS beamline at ANKA, Karlsruhe. The morphology of the particles was studied with Zeiss Supra 55 Scanning Electron Microscope (SEM) with primary energy of 15 keV and in-lens detector. Structural characterization by X-ray powder diffraction (XRD) were performed in 0.5 mm  $\varnothing$  quartz capillaries at Powder Diffraction Beam Line (MSPD) at ALBA (Synchrotron radiation, energy = 30KeV,  $\lambda = 0.413486 \text{ \AA}$ ) and at KIT (Mo-K $\alpha_1$  radiation;  $\lambda = 0.70926 \text{ \AA}$ ).

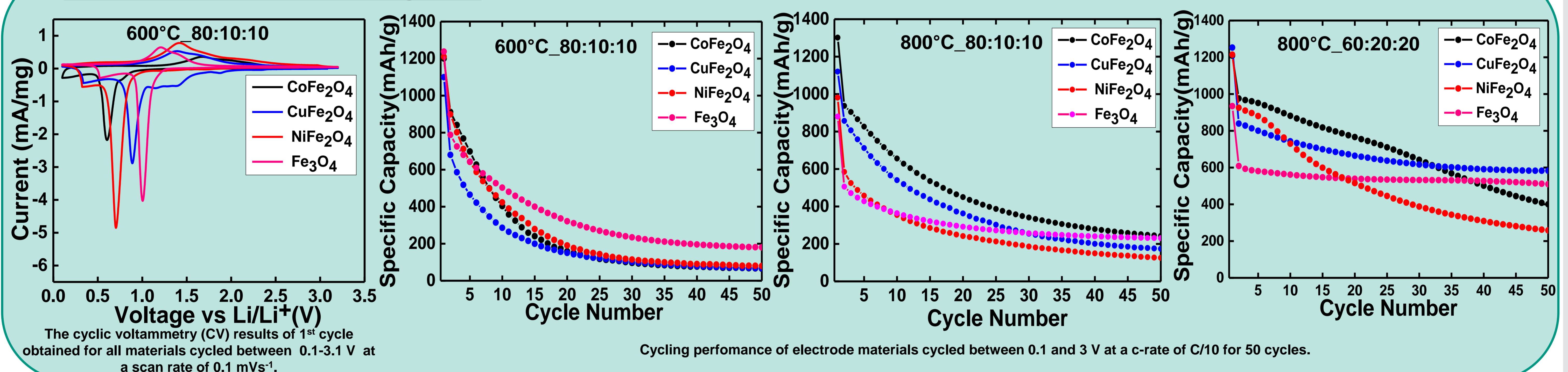
## Electrochemical experiments:

The electrode mixture was prepared by mixing active material, Super C65 C(TIMCAL) and polyvinylidene difluoride (PVdF) binder in two different ratios of 80:10:10 and 60:20:20 respectively. The mixture was coated on copper foil, dried, punched out to obtain electrodes of 1.2 cm diameter. The materials were tested in Li-half cells with LP30 (1M LiPF<sub>6</sub> in EC-DMC = 1:2) electrolyte.

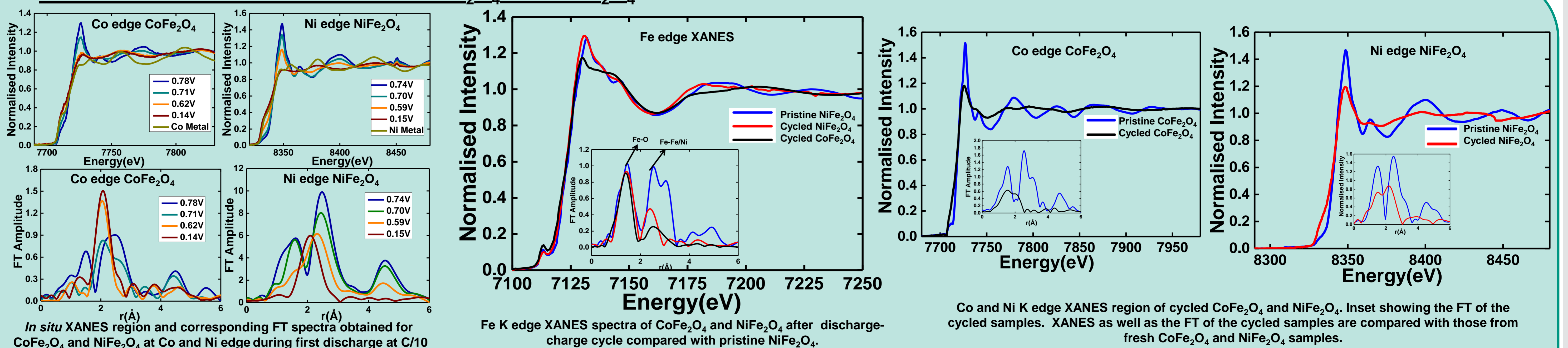
## Results: Structural and Morphological Characterization



## Results: Electrochemical Investigations



## Results: *In situ* and *ex situ* XAS of $CoFe_2O_4$ and $NiFe_2O_4$



## Conclusion and Outlook

- Ternary transition metal ferrites  $MFe_2O_4$  ( $M = Fe, Co, Ni$  and  $Cu$ ) synthesized by inverse co-precipitation were investigated as conversion electrode model systems in Li half cells.
- Annealing temperature and electrode composition has great influence on cycling stability of the materials.
- EXAFS studies reveal the reduction of ternary oxides into corresponding metallic states and subsequent transformation into metal oxides.
- As observed from EXAFS; hindered reoxidation of Co and Ni in the applied potential window could be a reason for the observed irreversible capacity loss in the first cycle for conversion materials.
- Improving the electronic conductivity by forming a conductive carbon encapsulation around the metal ferrites will contribute to better electrochemical performance[4].

## References

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- [2] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, and J.M. Tarascon, *Nature*, **407**, 496–499 (2000).
- [3] R. Adam, D. Wadewitz, W. Gruner, V. Klemm, H. Ehrenberg and D. Rafaja, *Journal of the Electrochemical Society*, **160**, A1594 (2013).
- [4] S. Peng, L. Li, and M. Srinivasan, *J. Energy Chem.*, **2014**, *23*, 301–307.