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 Fe3O4 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 process. This may further impact on the phase transformations and the electrode microstructure during the conversion reaction. In the present work, a comparative study of different metal ferrites, MFe2O4 (M = Fe, Co, Ni & 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:

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

Results: Structural and Morphological Characterization

Experimental Details

Synthesis of NiFe2O4 was carried out by reverse co-precipitation route. Metal acetate precursors with 1:2 ratio is dissolved in doubly distilled deionized water and added to 1 M NaOH solution drop wise with vigorous stirring. The solutions were heated and kept at 85°C for one hour. The precipitates were centrifuged and deionized water and 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) performed in 0.5 mm quartz capillaries at Powder Diffraction Beam Line (MSPDF) at ALSB (Sorbonne radiation, energy = 300 KeV, λ = 0.413486 Å) and at KIT (MoKα, radiation, λ = 0.70925 Å).

Electrochemical experiments:

The electrode mixture was prepared by mixing active material, Super C65 (TMCAL) 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 electrodes were tested in Li half-cell with LiPF6 in EC/DMC - 1:1 electrolyte.

Results: Electrochemical Investigations

The cyclic voltammetry (CV) of all samples was recorded at a scan rate of 0.1 mV/s.

Results: In situ and ex situ XAS of CoFe2O4 and NiFe2O4

Co and Ni K-edge XAS region and corresponding FT spectra obtained for CoFe2O4 and NiFe2O4 after discharge-charge cycle with pristine NiFe2O4.

References