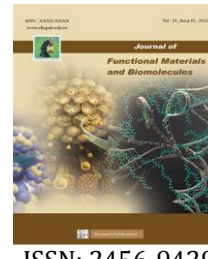




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Probing the Electrochemical Reactions in Li Battery Materials Employing Magnetization Measurements

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Abstract

We report on utilization of magnetization measurements as a tool to investigate the cathode/anode materials after they are electrochemically charged and discharged. We have performed the *ex-situ* magnetic studies on the CoFe_2O_4 electrodes after 1st discharge, 1st cycle, 20 and 30 cycles to understand the chemical reactions taking place during the electrochemical cycling. Nanocrystalline cobalt ferrite particles were synthesized by a sol-gel combustion method. CoFe_2O_4 is found to crystallize in inverse spinel structure belonging to Fd-3m space group without any impurity phase. CoFe_2O_4 electrodes were prepared with PVDF and alginate binders separately and electrochemical cycling was performed on all of them. RT magnetization measurements were carried out on the electrodes after 1st discharge, 1st cycle, 20 cycles and 30 cycles. Saturation magnetization (M_s) of pure CoFe_2O_4 powder is seen to be 77 emu/g. In the case of CoFe_2O_4 -PVDF electrodes, saturation magnetization values after 1st discharge, 1st cycle and 30 cycles are 135, 97 and 43 emu/g respectively. Saturation magnetization value of CoFe_2O_4 -alginate electrodes after 1st discharge, 1st, 20th and 30th cycles is seen to be 130, 63, 60 and 62 emu/g respectively. Obtained results indicate magnetization measurements can help to identify the chemical reactions taking place during the electrochemical cycles in the electrode materials containing magnetic elements.

Key words: Sol-gel combustion method, Magnetization measurements, Electrochemical cycling.

1 Introduction

Lithium batteries with an operating voltage of ~3.6-4 V are extensively used as a power source for portable electronic devices such as laptops, cell phones, etc [1-3]. In most of the commercial batteries, LiCoO_2 and graphite are used as a cathode and anode material respectively [4-6]. The graphite based anode material has already reached its theoretical capacity and the search for alternative anode materials has become the pressing need for several research groups. Layered two dimensional structure or 3D networks of oxides like Fe_2O_3 , TiO_2 , NiO , SnO_2 , CuO , in

which Li can intercalate reversibly into the lattice without destroying the crystal structure are extensively studied as an alternative for anode material [7-11]. In addition to that, possibilities of employing the Fe-based ferrites (NiFe_2O_4 , CoFe_2O_4 , ZnFe_2O_4 , etc.) as anode material have been explored by few research groups [12-14]. However, Capacity fading during the initial few cycles is one of the challenging problem in ferrite based anodes [12-14].

Co ferrite (CFO) is a ferromagnetic material, crystallizes in inverse spinel structure with the space group of Fd-3m [15,16]. In inverse spinel structure, oxygen ions form face centered cubic (FCC) lattice and the tetrahedral (A) sites are occupied by the Fe^{3+} ions and the octahedral sites (B) are occupied by the divalent metal ions (M^{2+}) and Fe^{3+} , in equal proportions [15, 16].

Materials with nano dimensions (nanoparticles, nanorods, nanowires) have attracted enormous attention for their enhanced electrochemical properties and interesting behaviors applied in Li battery research field [17-20]. Due to high surface area and very fast redox reactions, battery capability and other electrochemical behaviors are highly influenced by nano materials.

After the electrochemical test, finding out the structural changes in the cathode or anode material employing XRD measurements is very difficult and challenging in the battery research field due to the presence of binder materials in the electrodes. In the present case, we made an attempt to utilize the magnetization measurements as a tool to investigate the cathode/anode materials after they are electrochemically charged and discharged. We have performed the *ex-situ* magnetic studies on the electrodes after 1st discharge, 1st cycle, 20 and 30 cycles to understand the chemical reactions taking place during the electrochemical cycling. Effect of different binders (polyvinyl pyrrolidone (PVP), polyvinylidene fluoride (PVDF), poly acrylic acid (PAA) and carboxymethyl cellulose (CMC)) on electrochemical properties of electrodes have been reported by several research groups [21-23]. In the present case, we have employed PVDF and alginate binders to prepare the electrodes and made an attempt to explore the structural changes through

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magnetization studies in each electrode after the electrochemical cycling of CFO anodes. The results obtained are presented and discussed in this paper.

2 Experimental

2.1 Material synthesis

Nanocrystalline cobalt ferrite CFO particles were synthesized by a sol-gel combustion method. Ni (NO₃)₂·6H₂O, Fe (NO₃)₃·9H₂O, citric acid and urea were used as precursors to synthesize nanocrystalline CoFe₂O₄ particles. First, the stoichiometric solutions of all the required precursors were mixed with continuous stirring at RT and at 80°C to form a gel, which was then heated up to 180°C. The amorphous powders were collected and pure nano crystalline CoFe₂O₄ particles were obtained by annealing the powders at 600°C for 3 h.

2.2 Characterization

Structural characterization at room temperature (RT) was performed by obtaining the powder X-ray diffraction (XRD) patterns employing Cu-K α radiation (1.54 Å). The measurements were performed employing a PANalytical (X'pert PRO) X-ray diffractometer. Particle size and morphology analysis were characterized employing a field emission scanning electron microscope (FE-SEM Hitachi S-4800, Japan) and a transmission electron microscope with energy dispersive spectroscopy (TEM), JEOL 2010F HRTEM, Japan, with a 200 kV operating voltage. The Raman spectra of powders were recorded at RT employing a HR 800 Raman spectrophotometer (Jobin Yvon- Horiba, France) using monochromatic He-Ne LASER (632.8 nm), operating at 20 mW.

The electrochemical studies of the synthesized CoFe₂O₄ nanoparticle were analyzed in a CR2032 coin cells. The composite electrode was prepared by mixing 70 wt. % of active material with 20 wt. % Super P carbon black and 10 wt. % PVDF and sodium alginate binders in suitable solvent. The obtained slurry was coated on a piece of copper foil and cut into 12 mm diameter circular electrodes. Lithium foil was used as anode and 1 M solution of LiPF₆ in ethylene carbonate and dimethyl carbonate (1 : 1) was used as the electrolyte. Coin cells were assembled in an argon-filled dry glove box (M. O. Tech) using Whatman GF/D borosilicate glass-fiber separator. Magnetization measurement was carried out at RT employing a vibrating sample magnetometer (VSM, LakeShore 7407). After the Electrochemical cycles, materials were removed from the electrodes and the obtained powders were used for the magnetization measurements.

3. Results and Discussion

3.1 Structural characteristics and surface morphology

Figure 1 shows the Rietveld refined [24] XRD patterns of the pure CFO powders recorded at RT. CFO is found to crystallize in inverse spinel structure belonging to Fd-3m space group without any impurity phase. Rietveld refinement was carried out on the XRD data obtained at RT using the GSAS program. The wrp (weighted refined

parameter) and the χ^2 (goodness of the fit) values of the fitting are 4% and 1.00 respectively.

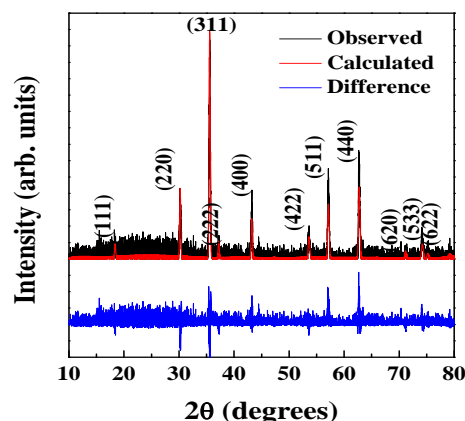


Fig1. Rietveld refined XRD pattern of CoFe₂O₄ powders. Calculated and difference curves are also shown. Formation of inverse spinel phase without any impurities is evident.

The calculated lattice constants $a=b=c$ values at RT is 13.854 Å (± 0.002 Å), which agrees well with the reported value [JCPDS Card No 22-1086] [15]. Figure 2 shows the (SEM image) morphology of the sample. It is clear that the nanocrystalline particles are uniformly distributed. The crystallite size (D) was calculated from the integral width of the diffraction lines using the well-known Scherrer's equation after background subtraction and correction for instrumental broadening. The Scherrer equation is: [25]

$$D = 0.9\lambda / \beta \cos\theta, \quad \{1\}$$

where D is the size, λ is the wavelength of the filament used in the XRD machine, β is the width of a peak at half of its intensity, and θ is the angle of the peak. The average grain sizes was found to be ~ 25 nm.

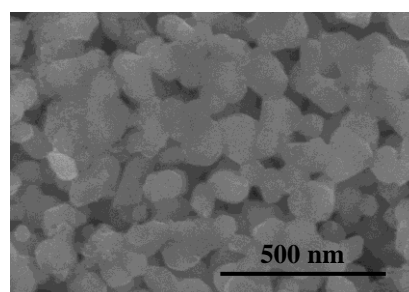


Fig 2 SEM image of CoFe₂O₄ particles. Uniform distribution of nano particles is clearly seen.

3.2. Raman spectroscopy studies

Figure 3 shows the Raman spectra of CFO powder recorded at RT. Raman spectra showed five active modes of (A_{1g} + E_g + 3F_{2g}) and the peaks were observed for CFO at 302.34 cm⁻¹, 460.38 cm⁻¹, 577.60 cm⁻¹, 615.88 cm⁻¹ and at 690.63 cm⁻¹. The peaks corresponding to the wave numbers of 660 cm⁻¹ to 720 cm⁻¹ indicate tetrahedral group and that between 460 cm⁻¹ to 660 cm⁻¹ indicate octahedral group of ferrites [26].

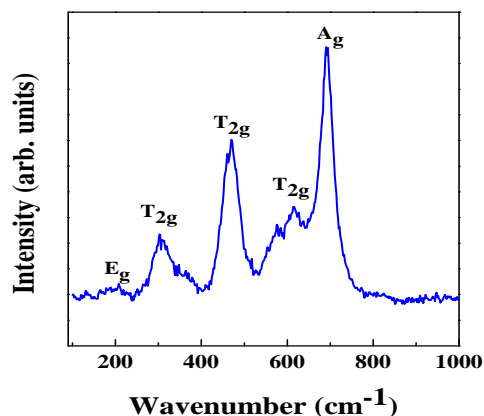


Fig 3 Room temperature Raman spectra of CoFe_2O_4 powders

3.3. Magnetic properties

CFO electrodes were prepared with PVDF and alginate binders separately and electrochemical cycling was performed on all of them. RT XRD and magnetization measurements were carried out on the electrodes after 1st discharge, 1st cycle, 20 cycles and 30 cycles.

During the 1st discharge, CFO reacts with the Li ions and convert into Co and Fe nanoparticles along with an amorphous Li_2O phase. However, in the reverse oxidation process (completion of 1st cycle), Co and Fe nanoparticles are oxidized to CoO and Fe_2O_3 phases respectively. Conversion redox mechanism may occur in the following steps [13]

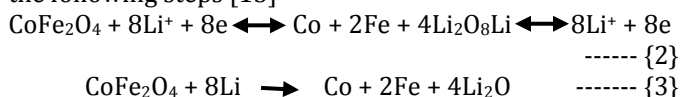


Figure 4 and 5 shows the RT magnetization curves of CFO-PVDF and CFO-alginate electrodes respectively with compared to pure CFO powders. Magnetic moment is seen to be unsaturated even at 15 kOe for all the cases and the magnetic moment at 15 kOe is represented as saturation magnetization (M_s) here after. Saturation magnetization (M_s) of pure CFO powder is seen to be 77 emu/g, which is agreeing well with the reported values indicating the formation of CFO in pure phase. In the case of CFO-PVDF electrodes, saturation magnetization values after 1st discharge, 1st cycle and 30 cycles are 135, 97 and 43 emu/g respectively (Table I).

Electrochemical cycles	Saturation magnetization M_s (emu/g)	
	CFO - PVDF	CFO - Alginate
1 st Discharge	135	130
1 st Cycle	97	63
20 cycles	-	60
30 cycles	43	62

M_s value after 1st discharge (135 emu/g) is seen to be higher than that of pure CFO powder (80 emu/g).

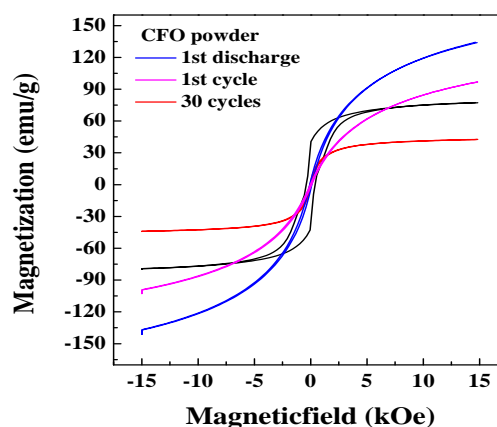
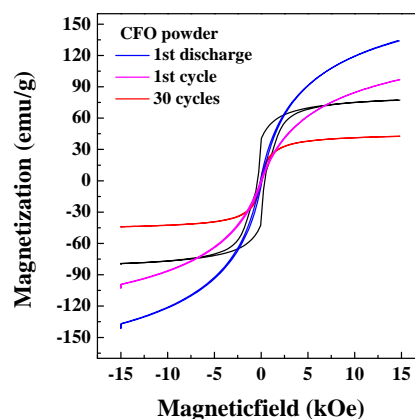


Fig 4 Room temperature magnetization curves of CFO-PVDF electrodes after 1st discharge, 1st and 30th cycles compared with the pure CFO powders. Saturation magnetization is seen to decrease with increasing cycle numbers.

M_s values after the electrochemical cycling's can be explained as follows. After the 1st discharge, nanoparticle of Fe and Co along with amorphous Li_2O is present in the electrode. Exchange interaction between the Fe and Co magnetic moments might be complicated in the disordered discharged electrode due to the presence of amorphous Li_2O . Few moments might couple parallel to each other and few might couple anti-parallel to each other. Therefore, the net magnetization is expected to be less than the sum of pure Fe and Co moments. Reported M_s values for pure Fe and Co are 221 and 162 emu/g respectively [27]. Observed M_s value after 1st discharge is seen to be in between the pure Fe and Co M_s values and higher than that of pure CFO powder (80 emu/g), clearly indicating the formation of Fe and Co nanoparticles. After the completion of 1st cycle, Fe and Co nanoparticles are oxidized to Fe_2O_3 and CoO phases respectively. Nanoparticles of Fe_2O_3 and CoO are reported to be very weak ferromagnetic materials

with feeble M_s (≈ 1 emu/g) values.^{28,29} In the present case, the M_s value after 1st cycles is seen to be higher (97 emu/g) than that of Fe_2O_3 and CoO nano particles. Lavela *et.al* [30] have reported the temperature variation of Mossbauer spectroscopy studies on $CoFe_2O_4$ electrodes after fully charged and discharged states. From the changes in the hyperfine parameters, they have observed the formation of metal particles in fully charged and discharged states with the particle size of 4.5 to 7 nm and their super paramagnetic behaviour. In the present case, nano sized metal particles of Fe and Co might not have completely converted into oxides after the completion of 1st cycle, leading to larger observed M_s value. M_s value is seen to decrease continuously with increasing electrochemical cycles and its value is seen to be 43 emu/g after 30 cycles. The weak interface and interaction between the CFO and PVDF binders with increasing number of cycles resulted in weakening the exchange interaction and continuous decrease of magnetic moments.

Figure 5 shows the magnetization curves of CFO-alginate electrodes after 1st discharge, 1st, 20th and 30th cycles. M_s value after 1st discharge is seen to be 130 emu/g, which is almost same as the CFO-PVDF electrode saturation magnetization value. The M_s value is seen to decrease to 63 emu/g after the completion of 1st cycle and almost same value with increasing the number of cycles (cycle 20 and 30). The strong bonding and stable interface between the CFO and alginate binders even after several cycles resulted in constant specific capacity and M_s values is clearly evident. Magnetization loops are seen to be very narrow after charging and discharging the electrodes. Due to the very small particle size, each particle behaves as a single domain resulted in superparamagnetic like behavior.

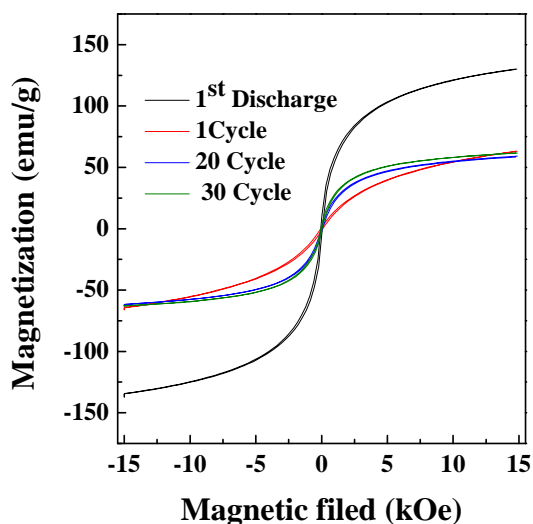


Fig 5 Room temperature magnetization curves of CFO-alginate electrodes after 1st discharge, 1st, 20th and 30th cycles compared with the pure CFO powders. Saturation magnetization is seen to be almost constant with increasing cycle numbers.

4 Conclusions

In summary, *ex-situ* magnetic studies on the $CoFe_2O_4$ electrodes after the electrochemical cycling helps to understand the chemical reactions taking place during the electrochemical cycling. Nanocrystalline $CoFe_2O_4$ particles were synthesized by a sol-gel combustion method and found to crystallize in inverse spinel structure with lattice constants $a=b=c$ values at RT is 8.354 Å (± 0.002 Å). Raman spectra showed five active modes of ($A_{1g} + E_g + 3F_{2g}$) and the peaks corresponding to the wave numbers of 660 cm^{-1} to 720 cm^{-1} indicate tetrahedral group and that between 460 cm^{-1} to 660 cm^{-1} indicate octahedral group of ferrites. $CoFe_2O_4$ electrodes were prepared with PVDF and alginate binders separately and electrochemical cycling was performed on all of them. RT magnetization measurements were carried out on the electrodes after 1st discharge, 1st cycle, 20 cycles and 30 cycles. In the case of $CoFe_2O_4$ -PVDF electrodes, saturation magnetization values after 1st discharge, 1st cycle and 30 cycles are 135, 97 and 43 emu/g respectively. Saturation magnetization value of $CoFe_2O_4$ -alginate electrodes after 1st discharge, 1st, 20th and 30th cycles is seen to be 130, 63, 60 and 62 emu/g respectively. Saturation magnetization values obtained after the electrochemical measurements helps to identify the chemical reactions taking place in the electrode materials containing magnetic elements.

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