Co-doped lithium ironorthosilicatenano cathode materials for plug in electric vehicles

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Abstract:-*In a deal for establishing cathode material Co Doped Lithium ironorthosilicate for Electric vehicles, Co-doped nano particles were synthesized via polyol method. To identify the structural properties of Co-doped Lithium Iron silicate, they have been characterized by XRD, FTIR, SEM and RAMAN for various molar ratio of Fe and Co (0.97, 0.94 and 0.03, 0.06) respectively. From the XRD result, lattice arrangement of the doped nano particles were well defined with the space group of $Pmn2_1$ and the dopant cobalt does not affect the structure in the array of lithium ironorthosilicate. FTIR result shows bonding nature of Si-O and Fe-O in the region 584 and $860 cm^{-1}$. The SEM analysis was used to study the surface morphology. The structural and the degree of crystallinity of the material were examined by RAMAN studies.*

1.   Introduction

The establishment of Lithium-ion batteries (LIBs) technology is very essential in plug in electric vehicles, hybrid electric vehicles, space and power grid apps, due to the demand in the development of lightweight, long life, rate capability etc., The choice of future materials holds some properties like, increasing specific capacity of the cathode materials that lead to the lowering weight of the battery, abundant of consumed raw material (cathode) and paved a way to reduce the cost of the battery. These developments have also lead to recognize the best Lithium ion batteries in the universal market. The polyanion type cathode material obey the aforementioned futuristic properties (low cost, lightweight etc.,). After demonstration on reversible electrochemical activities of Lithium ion in Li_2FeSiO_4 by Nyten et al[1]; many investigations has communicated in various scientific article with the name of Lithium ironorthosilicate[2–4]. Along with some salient future, Li_2FeSiO_4 have low intrinsic electronic conductivity. In order to overcome the difficulty, considerable efforts have been made by carbon coating, particle size reduction and doping cations[5]. Cationic substitution in the well-defined network can improve the electrochemical properties of Lithium ironorthosilicate because substitution expands the cell size and cell volume. Hence cationic substitution is considered to be an effective way to modify its intrinsic properties (electronic and ionic conductivity) [6]. However, if cation could be incorporated into Lithium ironorthosilicate base; it might create vacancies at Li sites owing to charge balancing nature. Those vacancies might expect to improve the lithium ion conductivity with higher power capability. Among these, lower substitution of cation at Fe sites might enhance electrochemical performance of cathode materials via oxidation and reduction phenomenon. In this study, the effect of Cobalt substituted in the lattice of Lithium ironorthosilicatehas been investigated via polyol method. Polyol method is one the effective method to synthesis cathode material [7]. The ultimate aim of the polyol method [8] is to dissolve the salt in polyol solvent, and the thermal energy is increased sequentially to imitate   co-precipitation by hydrolysis at high temperature. Solvent is used in the method to control oxidation state of cation to improve structural perfection. Finally, nanoparticles have been obtained directly in the solvent medium, and there is no requirement ofheat treatment at high temperature. Here, dopant cobalt replaces the iron sites with mole ratio (0.03-0.97 & 0.06-0.94) in Lithium ironorthosilicate ($Li_2Fe_{1-x}Co_xSiO_4$). The investigation was followed by structural and morphological aspects with respect to the concentration of dopant.

2.   Materials and methods

The Co doped Lithium ironorthosilicate ($Li_2Fe_{1-x}Co_xSiO_4$) was prepared by polyol route. All the chemicals were directly used without further purification. The 0.03 mole of Cobalt sulfateheptahydrate, 0.97 mole of Iron (II) sulfateheptahydrate, 2 mole of Lithium acetate dihydrate and 1 mole of Tetraethoxysilane (TEOS) were separately dissolved in 30 ml of deionized water with continuous stirring. The aforementioned solution was poured sequentially in the order of iron, cobalt, TEOS and then followed by Lithium acetate in slow rate into the 100 ml of Tetraethylene glycol (TTEG). The TTEG with aqueous solution was stirred vigorously at 100℃, kept for 4 h, later,the solution washeated at high temperature in the round bottom flask capped with condenser for 20 h. Then, the solution was allowed to cool down to ambient temperature, the Co doped Lithium ironorthosilicate material was separated by centrifuging with ethanol to remove the residual polyol solvent and impurities. As a final step, the centrifuged material was dried in a vacuum oven at 150°C for 12 h.

The phase of our materials was characterized by X-ray powder diffractometer with Cu Kα radiation (PANalyticalX'pert PRO powder X-ray diffractometer). The formation of the carbon was confirmed by Micro Raman (SEKI focal). Structural bonding was explained with the help of Thermo Nicolet 380 FTIR spectrophotometer. Morphology of the sample was observed using High resolution Scanning electron microscope (ZEISS).

3. Result and discussion

Fig.1 shows the XRD patterns of the as prepared Lithium ironorthosilicate($Li_2Fe_{1-x}Co_xSiO_4$) with various mole ratios of cobalt and iron (0.03:0.97 and 0.06:0.94) via polyol route. In the structure of LFS [LiO_4], [FeO_4] and [SiO_4] tetrahedrons shares corners with each other [9]. It could be noted that the 0.03 mol of cobalt substituted by Lithium ironorthosilicate has poor crystallinity with respect to the 0.06 mol based sample. However, some low intense peaks at 2θ=16, 24 and 68° were found in minimum mol of Co doped spinel type array, which indicates that 0.03 mole ratio of cobalt substituted XRD result is similar to Lithium ironorthosilicate with aforementioned 2θ values. But it is not exactly matched with that pattern.Besides, the 0.06 mol ratio of Co substitution change the phase of the LFS which is obviously seen in fig.1 (2θ =33, 38 and 58). These phase change arises as the Cobalt ion has disturbed the lattice of LFS. For both XRD result, no peak of impurity such as Fe_3O_4, Fe_2O_3 and Li_2SiO_3 are detected. Hence, the as-synthesised samples have high purity in nature [10].

The purity of $Li_2Fe_{0.97}Co_{0.03}SiO_4$ and $Li_2Fe_{0.94}Co_{0.06}SiO_4$ is further proved by Fourier Transform infrared spectroscopy. From this study, there are two peaks at 906 and 865 cm^{-1} representing the bending modes of Si-O. The peak observed at 614 cm^{-1} corresponds to the Fe-O bending vibration. At the same time, there is no absorption peak at 780 and 110 cm^{-1} corresponding to vibration of Si-O in Li_2SiO_3 [11]. The vibration peak at 2377 and 3184 cm^{-1}is attributed to the stretching vibration of C=C and OH respectively [12, 13].

Raman spectra were examined to find the nature of carbon formed on the surface of Co doped LFS. The Raman spectra (Fig.3) of Co-LFS depict that there is no evident of peak at 1350 and 1590 cm^{-1}. The spectra confirm that carbon precursor is in amorphous phase and it could be suggested that the sample may form crystalline carbon after necessary high temperature treatment[14].

The SEM image of lithium ironorthosilicate doped with various mole ratio of Cobalt 0.03 and 0.06 were shown in Fig. 4(a, b). The morphological detail and particle size were investigated using HRSEM. From the images, it is understood that the samples doped with 0.06 mol% of Cobalt has lesser agglomeration than sample doped with 0.03 mol%. No uniform particle size is found for both the samples.

4. Conclusion

$Li_2Fe_{1-x}Co_xSiO_4$ (x = 0.03 and 0.06 mol) nanoparticles were prepared via polyol route using TTEG as a polyol solvent. The effect of Co doping into the lattice of Lithium ironorthosilicate were characterized by XRD, FTIR, micro RAMAN and SEM. Among the samples 0.03 mol of Cobalt in LFS, is found relatively matched lesser with maximum intensity peaks of LFS. The higher matching of maximum intense peaks has been revealed from the sample doped with 0.06 mol%. Hence, increasing amount of dopant material might cause the lattice imperfection of LFS. Impurities checking could be carried out by FTIR, thereare no absorption peaks at 780 and 110 cm^{-1} corresponding to vibration of Si-O in Li_2SiO_3 respectively. Disordered nature of carbon might be interpreted by Micro Raman spectra. Morphological behaviour of the as-synthesized materials was observed through SEM.

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FIGURE CAPTIONS
Figure1.XRD result of Cobalt doped LFS
**Figure 2.**FTIR spectrum of Cobalt doped LFS
Figure 3.RAMAN studies of Cobalt doped LFS
Figure 4.(a and b) SEM image of Cobalt (0.03 and 0.06) doped LFS

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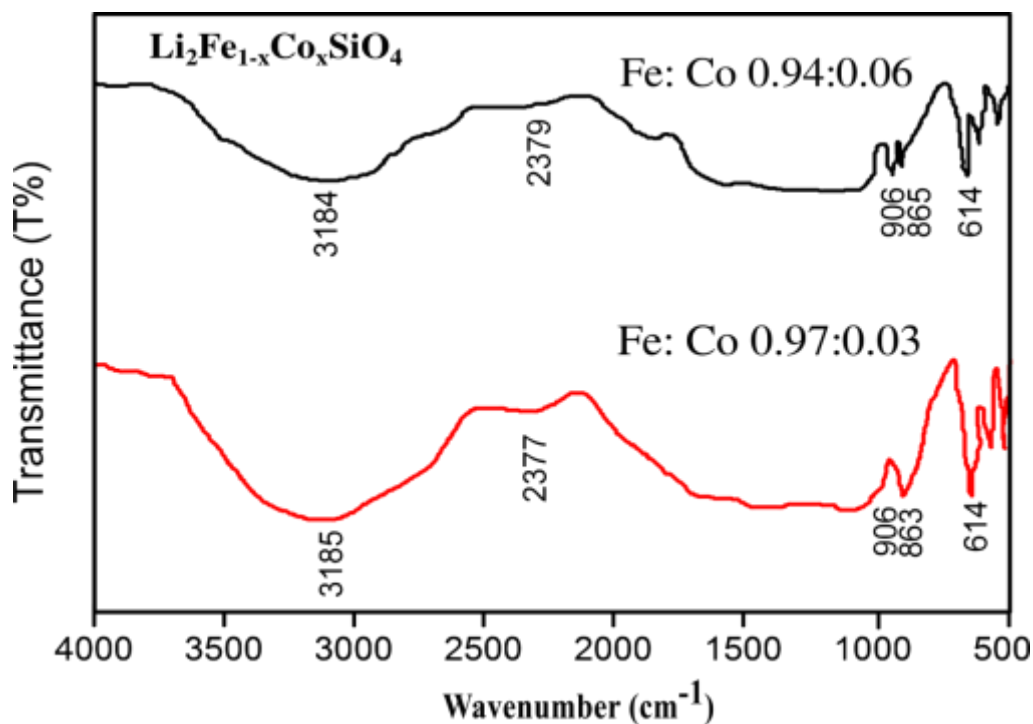
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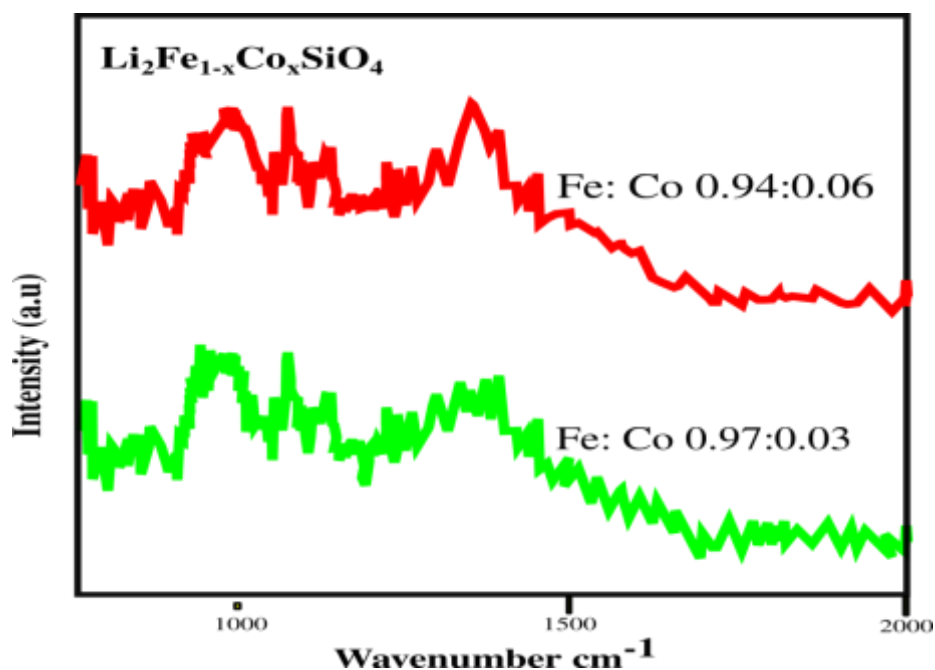
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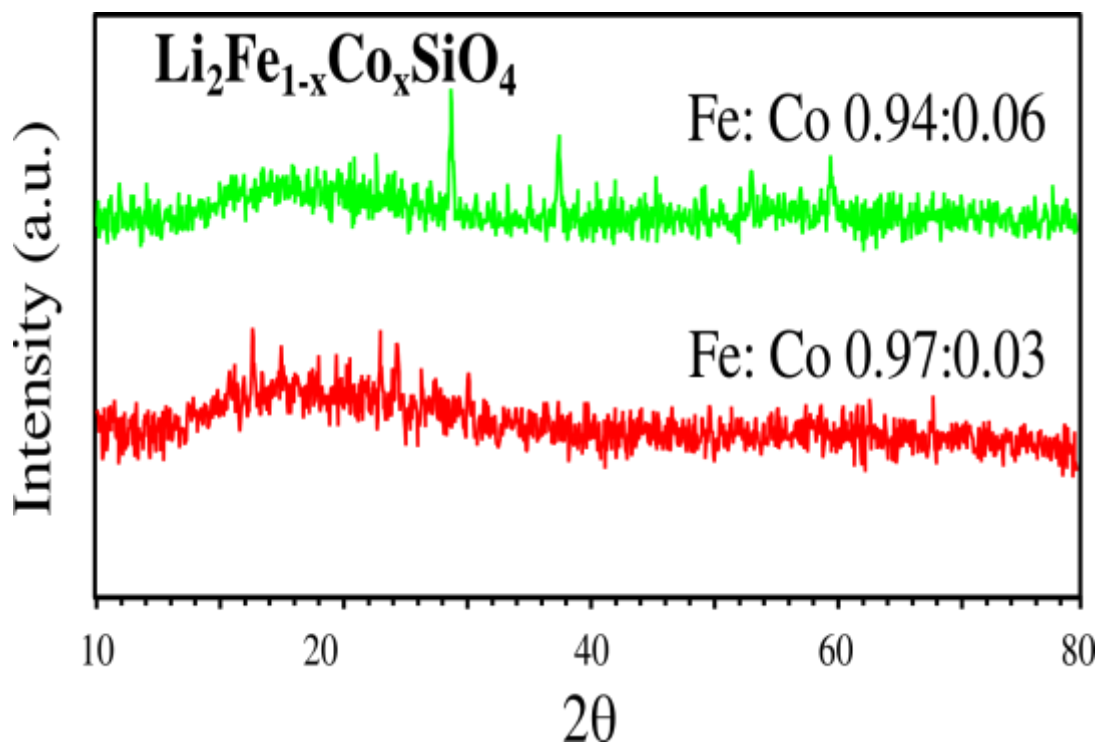
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Figure 2

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Figure 3

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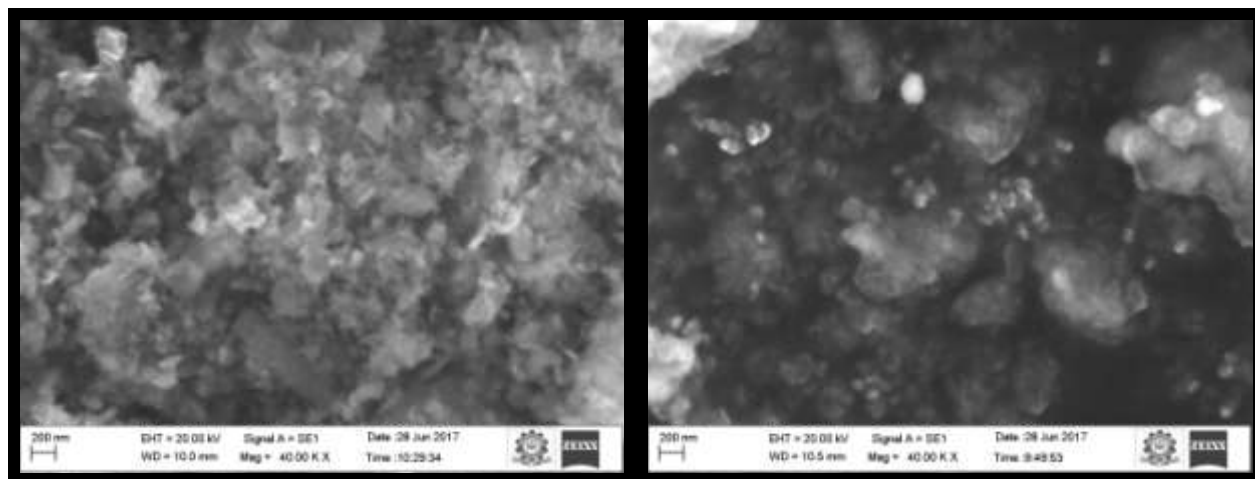**Title of the manuscript:**Co-doped lithium ironorthosilicatenanocathode materials for plug in electric vehicles

Figure 4

a)Co-0.03 in LFS   (b)Co-0.06 in LFS