

Effect Of MWCNT On Prepared Cathode Material $(\text{Li}_2\text{Mn}_x\text{Fe}_{1-x}\text{SiO}_4)$ For Energy Storage Applications

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Abstract. The electrode material $\text{Li}_2\text{MnFeSiO}_4$ was successfully synthesized by standard sol-gel method and further modified with multiwalled carbon nano tube (MWCNT) to achieve better electrochemical properties. Our strategy helps us to improve the performance and storage capacity as compared with the bared material. This novel composite structure constructs an efficient cation (Li^+) and electron channel which significantly enhance the Li^+ ion diffusion coefficient and reduced charge transfer resistance. Hence leads to high conductivity and specific capacity. Characterization technique like Field emission scanning electron microscopy (FESEM) has been used to confirm its morphology, structure and particle size which comes out to be of the order of ~ 20 to 30 nm. Lesser particle size reveals better electrochemical properties. Electrical conductivity ($\sim 10^{-5} \text{ Scm}^{-1}$) of MWCNT doped oxide cathode materials was recorded using ac impedance spectroscopy technique which reflects tenfold increment when compared with pure oxide cathode materials. Cyclic voltametry analysis has been done to calculate specific capacity and potential window of materials with and without CNTs. The results obtained from different techniques are well correlated and suitable for energy storage applications.

INTRODUCTION

Energy demand and supply has always been one of the crucial factor for the evolution of civilization. Due to finiteness of fossil fuels, concern of scientific communities over energy storage devices is reasonable and appreciable. In this context, an electrochemical energy storage device such as Li^+ batteries plays an important role in efficient use of renewable energy. To make Li^+ batteries more greener and sustainable source of energy, research is directed to increase its energy density, lower its cost and improve its safety. Also as reported by Taracson *et al* ,to improve the energy density of battery by 57 % , cathode capacity needs to be doubled where as anode needs to have enhanced capacity by 10 times to improve its energy density by 47%. So selection of good cathode material is very important in order to improve the efficiency of Li ion battery [1]. In the development of cathode material, a branch of polyanion compounds Lithium transition metal orthosilicates has gained much attention due to their high theoretical capacity. From the reports of Nyten *et.al* $\text{Li}_2\text{FeSiO}_4$ shows excellent cyclic stability and electrochemical activity. However its poor rate capability which results from its low electronic conductivity inhibits its further use for commercial purpose.

Conductivity can be improved by using following means: (1). Conductive coating (2). Particle size reduction (3). Supervalent and Isovalent cation doping. Supervalent or isovalent cation doping is often employed to improve the electrochemical performance of $\text{Li}_2\text{FeSiO}_4$. In this paper, we reported the doping of Mn^{2+} in $\text{Li}_2\text{FeSiO}_4$ Since Mn^{2+} can go from 2^+ to 4^+ . When Fe^{2+} is substituted by these divalent cation, the possibility of more than one electron reaction is function of redox properties of substituent divalent cation[2].

Further in order to improve its electronic conductivity, MWCNT are used to make composite with prepared cathode material $\text{Li}_2\text{MnFeSiO}_4$. Recently Carbon Nano tubes with its unique properties (High specific area, High electronic conductivity and stable one dimensional structure) have been considered as an excellent conductive framework material for lithium ion batteries [3]. Huang *et.al* reported CNTs modified $\text{Li}_2\text{FeSiO}_4/\text{C}$ synthesized by solid state reaction [4]. Also Peng *et.al* synthesized nano $\text{Li}_2\text{FeSiO}_4/\text{C}/\text{CNT}$ by Sol -Gel method and composite can reversibly extract more than one Li^+ and exhibit favorable electrochemical performance [5].

In this study, we successfully synthesize a novel composite $\text{Li}_2\text{Mn}_x\text{Fe}_{1-x}\text{SiO}_4$ /MWCNT by using Sol-Gel method. Field Emission scanning electron microscopy (FESEM) reveals the surface morphology of the material sample. Impedance spectroscopy has been characterized for the estimation of electrical conductivity, which is estimated in the order of 10^{-3} with CNT.

EXPERIMENTAL

Synthesis of $\text{Li}_2\text{Mn}_x\text{Fe}_{1-x}\text{SiO}_4$

Standard Sol Gel Method is used for the preparation of $\text{Li}_2\text{Mn}_x\text{Fe}_{1-x}\text{SiO}_4$. Stoichiometric amounts of Li_2CO_3 , MnO_2 , Fe_2O_3 , and SiO_2 are used as precursors. Above mentioned precursors get hydrolyzed to form a solution. Formed solution was magnetically stirred continuously for 12 hrs. Further evaporation of solvent was done continues stirring at 80°C . With continues heating and stirring, a dry gel is formed. This dry Gel is further ground to powder. Finally cathode material was sintered by first heating at 350°C for 2 hrs and second heating at 900°C for 12 hrs. Prepared cathode material is labeled as LMFS.

Synthesis of $\text{Li}_2\text{Mn}_x\text{Fe}_{1-x}\text{SiO}_4$ /MWCNT

Further to improve the particle –particle connectivity, composite of $\text{Li}_2\text{MnFeSiO}_4$ /Multi walled carbon nano tube (MWCNT) was prepared via solution method. Stoichiometric amount of MWCNT was well dispersed in solution containing 10 ml distilled water and 10 ml acetonitrile through sonication. Then the active material ($\text{Li}_2\text{MnFeSiO}_4$) was added in sequence and finally 0.5 ml of hydrazine was added. As obtained solution was refluxed at 80°C for two hrs with stirring to obtain $\text{Li}_2\text{MnFeSiO}_4$ /MWCNT composite. This mentioned procedure was further followed to prepare samples with 3,6,12 wt percent of MWCNT. These prepared samples are labeled as LMFS-C3 , LMFS-C6 and LMFS-C12 respectively. The synthesis route was adopted here based on reported literature and modified as per our requirement by changing calcinations temperature and reaction time [6]. Morphology and Particle size was observed by FESEM (card Ziess,Merlin Compact). Electrical conductivity and cyclic voltametry were performed by using electrochemical analyser (model:CH-760).

RESULTS AND DISCUSSION

FESEM Observations

As field emission scanning electron microscope (FESEM) is very powerful tool to get surface morphology and topology of the prepared materials. High magnification attainable combined with large depth of field makes FESEM an outstanding diagnostic system. Figure1(a) , clearly shows the spherical shape of particles .Very homogeneous topology was observed in case of $\text{Li}_2\text{Mn}_x\text{Fe}_{1-x}\text{SiO}_4$. Also particle size was calculated using software (image j) , which comes out to be of order of 27 nm. This particle size is much improved size if compared with $\text{Li}_2\text{FeSiO}_4$ and $\text{Li}_2\text{MnSiO}_4$. Figure1: (b) ,(c),(d) clearly shows the uniform distribution of multi walled carbon nano tubes over the surface of cathode material .This uniform distribution of CNT's results in improved conductivity which enhances the electrochemical performance. Also particle size calculated by software 'image j' is found to be 24.2 nm & 22.3 nm for samples LMFS- C3 & LMFS-C6 respectively. Average particle size distribution plot is also shown in the figure. From graphs it is concluded that particle size get reduced on addition of carbon nano tube. As it is reported in literature that material with lesser particle size reveals good electrochemical properties [7,8]. Thus improved electrochemical properties of cathode material are expected with addition of MWCNT. The possible reason behind improved properties is reduction of path length for Li^+ ions [3]. A smaller particle size could reduce the internal stress because the binding force of the particles may increase with the relative area of grain boundaries. Figure 1(d) clearly shows the homogeneous distribution of CNTs over the surface. This three dimensional network formed by CNTs favors the fast electron transfer.

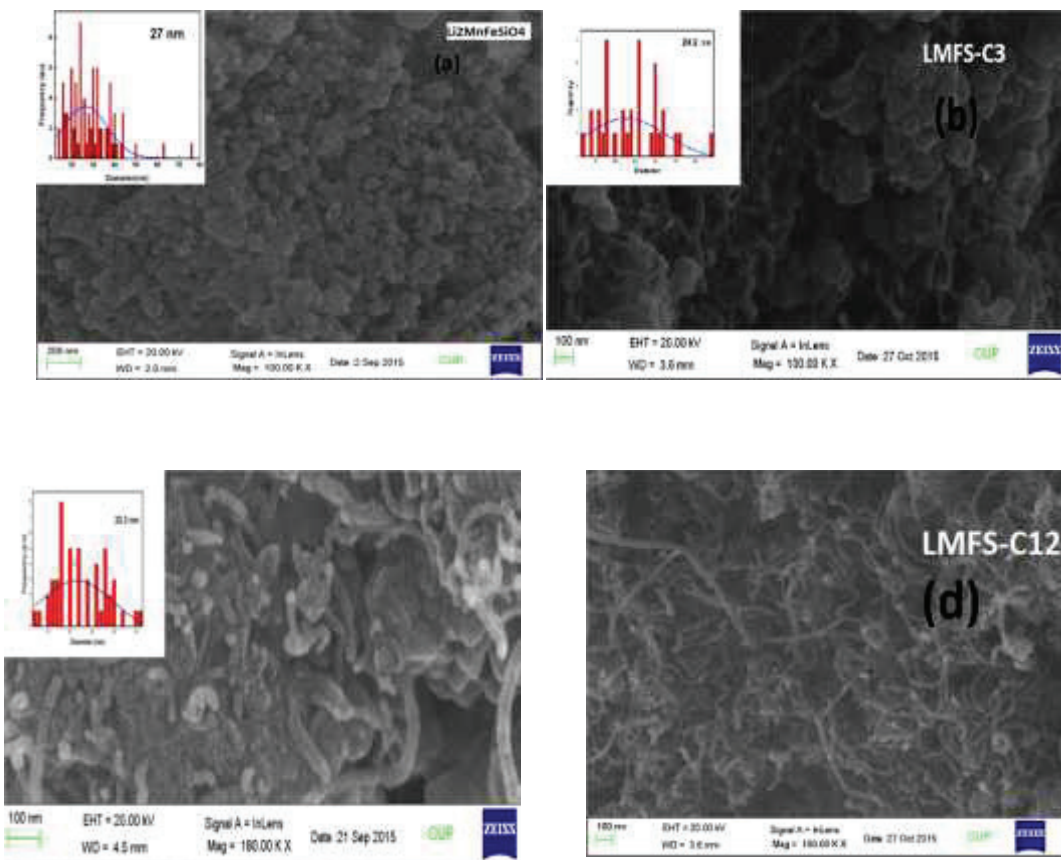
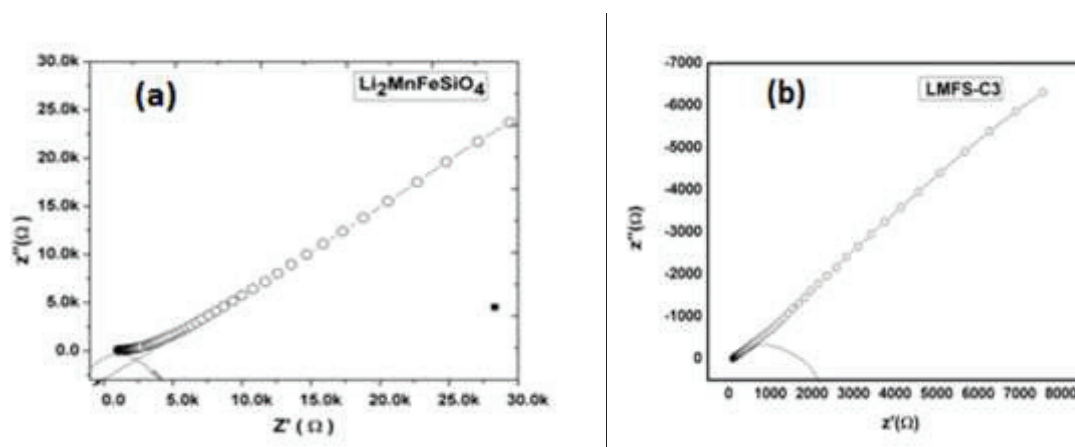


FIGURE 1: FESEM images of prepared samples; (a)- LMFS, (b)-LMFS-C3 , (c)-LMFS-C6 ,(d)- LMFS-C12

Electrochemical Analysis

A.C impedance measurements of cathode materials were carried out in the frequency range from 10 MHz to 1MHz at the input a.c signal level of 10 mV. Impedance spectrum is comprised of a small semicircle at high frequency and sharp spike at low frequency (FIG2(a)).



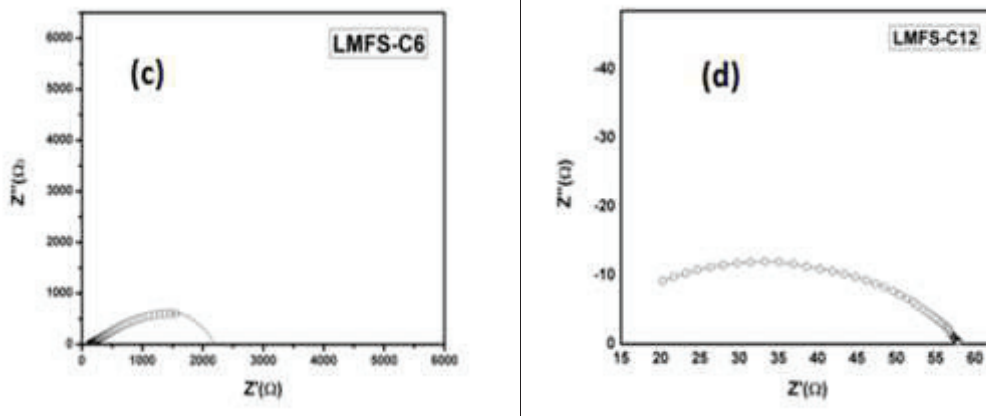


FIGURE 2: Nyquist plot of prepared samples;(a)- LMFS, (b)-LMFS-C3 , (c)-LMFS-C6 ,(d)- LMFS-C12

Small semicircle contribution is due to the bulk response of the cathode material where as lower frequency spike is due to electrode electrolyte interface. Bulk resistance of cathode material is estimated by extrapolating the semicircle and cut on the real axis[9]. Lower frequency spike clearly shows the capacitive behavior of the material. Electrical conductivity of cathode material is calculated using formula $\sigma = \frac{1 \times L}{R_b \times A}$, where symbols have their usual meanings.

From Fig.2(a), bulk resistance of LMFS, LMFS-C3,LMFS-C6 ,LMFSC-12 are estimated by extrapolating the semicircle and cut on the real axis. Estimated values of bulk resistance are 2787k ohm, 2200 k ohm, 2160 k ohm ,59 k ohm respectively. Conductivity calculated from bulk resistances are of the order of 4.881×10^{-5} , 6.184×10^{-5} , 6.2988×10^{-5} , 2.306×10^{-3} for LMFS,LMFS-C3,LMFS-C6 &LMFS-C12 respectively. The specific capacitance has been calculated for different scan rates using the formula; $C = -(\omega Z'')^{-1}$ where $\omega (=2\pi f)$ is angular frequency and Z'' is the imaginary part of the total complex impedance. An increased value of conductivity on addition of carbon nano tubes (CNT) is due to increase in particle-particle connectivity. Calculated values of specific capacitances for ,LMFS-C3,LMFS-C6,LMFS-C12 are 3.0956F,3.80F&6.33F respectively.

CONCLUSION

In summary spherical $\text{Li}_2\text{MnFeSiO}_4/\text{MWCNT}$ composite with excellent rate performance was successfully synthesized by Sol-Gel method followed by solution method to make composite with MWCNT. Excellent electrochemical properties are caused by the unique composite structure. The nano sized $\text{Li}_2\text{MnFeSiO}_4/\text{MWCNT}$ provide short path ways for Li^+ diffusion and CNT's network facilitates electron transport and avoids agglomeration of $\text{Li}_2\text{MnFeSiO}_4$. Our Results suggests that CNT play a profound part to increase electrochemical efficiency. Prepared composite will have important application for energy storage and conversion in Li ion batteries.

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