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Optimization of concentration of MWCNT in terms of performance of prepared novel cathode material for energy storage

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ABSTRACT

The successful synthesis of a novel cathode material $Li_2MnFeSiO_4$ (LMFS) was done using the standard Sol-Gel technique. To improve the electrical conductivity of cathode material different concentration (wt/wt) of MWCNT are incorporated into LMFS generating composite $Li_2MnFeSiO_4$/MWCNT via solution method. In order to achieve better electron passage to particle–particle boundaries, MWCNT is considered as one of the ideals and appropriate conductive additive. The $Li_2MnFeSiO_4$ nanoparticles are dispersed homogeneously in CNT's network and assembled as micro-sized porous spherical particles. Such special composite structure constructs an efficient Li^+ and electron channel, which significantly enhance the Li-ion diffusion coefficient and reduced the charge transfer resistance, hence may lead to high electrical conductivity. Carbon nano tube not only deposited on the surface, but also provide the interconnected network. This continuous conductive network enhances the electronic conductivity of the insertion/de-insertion cycles. Complex impedance spectroscopy (EIS) is used to estimate the electrical conductivity of prepared samples. The $Li_2MnFeSiO_4$/MWCNT with 12 wt% of CNT delivers highest electrical conductivity (i.e. $\sim10^{-3}$ Scm^{-1}) which is at par with desire for the energy storage applications.

Keywords: Cathode Material, MWCNT, Electronic Conductivity Li- ion battery.

INTRODUCTION

Energy demand and supply have always been one of the crucial factors for the evolution of civilization. Energy in the form of electricity is produced from solar, wind, nuclear power, burning fossilfuels, etc. However, production of electricity from renewable sources like solar and wind need a storage device for their effective usage during depletion time. In this context, electrochemical energy storage devices such as batteries plays an important role in the efficient use of renewable energy. The battery is a collective arrangement of electrical cells that stores and produces electricity by chemical reaction; storage and release is realized by electrons and ions.[1]

Since the first report from A. Nyténand co-workers,[2] lithium metal silicate (Li_2MSiO_4) has attracted enormous attention from the researchers due to its high theoretical capacity (166 $mAhg^{-1}$ for one Li-ion and 332 $mAhg^{-1}$ for two Li-ion per formula unit), high safety and environmental compatibility.[3] Meanwhile, Silicon is the most abundant and inexpensive element on earth. All these features make it as a promising cathode material for large-scale long-life energy storage batteries. Apart from this advantageous factor, the inherent property of silicate material that they have low electronic conductivity brings big obstacle to its practical application. To improve its electrochemical performance, many strategies such as coating with an electronic conductive material,[4,5] doping the host framework with isovalent ions[6,7] and decreasing the size of Li_2MSiO_4 crystallites into a nanometer level[8] have been tried to overcome its drawbacks by various researchers. Among all these methods, synthesizing a composite of Li_2FeSiO_4 nanoparticles with a conductive carbon layer is one of the effective way to increase the electronic conductivity and to facilitate the Li-ion transfer. Recently MWCNTs are found to be one of the best conductive additives for cathode material to make it practically useful. The unique combination of physical and chemical properties of MWCNTs makes it potentially useful instead of other traditionally available coating materials.[9,10]

Special composite structure with the use of MWCNTs provides the efficient way for lithium ions to diffuse. In this work Sol Gel technique has been used to prepare the sample.

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Further Electrochemical impedance spectroscopy is used to measure the estimated value of electronic conductivity. In this paper we optimize the concentration of MWCNT which is useful for practical applications of cathode material inlithium ion batteries and super capacitors.

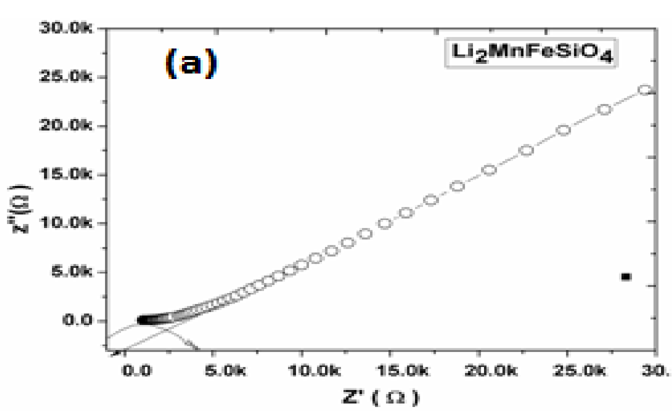
EXPERIMENTAL

Synthesis of $Li_2Mn_xFe_{1-x}SiO_4$

Standard Sol Gel Method is used for the preparation of $Li_2Mn_xFe_{1-x}SiO_4$. 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 the solvent was done via continues stirring and heating at 80˚C to form a dry gel. The obtained dry Gel is further ground to powder. Now, powdered cathode material was sintered by first heating at 350˚C for 2 hours. Again sample is ground to a more fine powder with mortar and pestle. This will help to achieve better homogeneity in its morphology. Further, in order to attain more crystalline/sintered structure, second heating at 900˚C for 12 hours has been done. The prepared cathode material is labeled as LMFS.

Synthesis of $Li_2Mn_xFe_{1-x}SiO_4$/MWCNT

Further to improve the particle–particle connectivity, a composite of $Li_2MnFeSiO_4$/Multi walled carbon nano tube (MWCNT) has been prepared via solution method. A stoichiometric amount of MWCNT is well dispersed in a solution containing 10 ml distilled water and 10 ml acetonitrile through sonication, then the active material ($Li_2MnFeSiO_4$) was added in sequence and finally 0.5 ml of hydrazine is added. As obtained solution was refluxed at 80˚C for two hours with stirring to obtain a $Li_2MnFeSiO_4$/MWCNT composite. This mentioned procedure is further followed to prepare samples with 3,6,12,15 weight percent of MWCNT. These prepared samples are labeled as LMFS-C3, LMFS-C6, LMFS-C12 and LMFS-C15 respectively. The synthesis route adopted here is based on reported literature and modified as per our requirement by changing calcinations temperature and reaction time.[11] Electrical conductivity analysis has been performed by using electrochemical work station (model:CH-760).



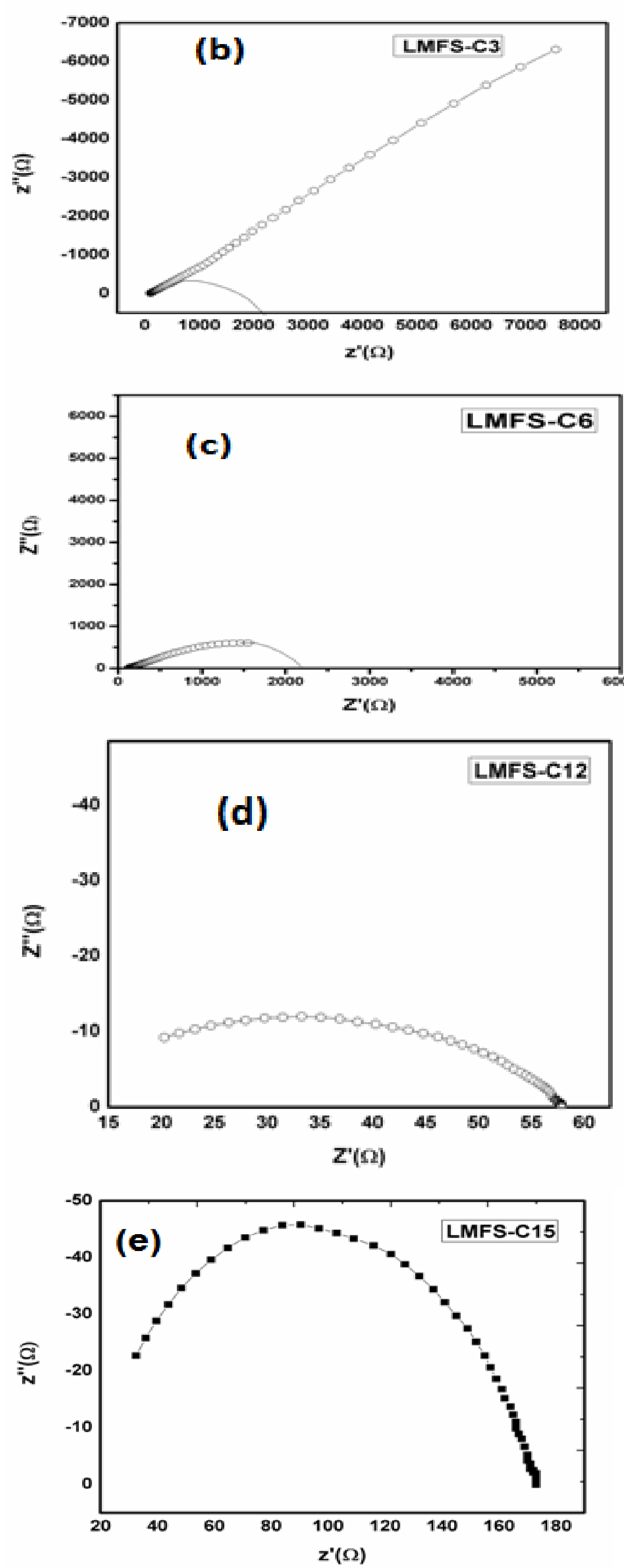


Figure 1. Nyquist Plot for Prepared Samples (a) LMFS, (b) LMFS-C3, (c) LMFS-C6, (d) LMFS-C12, (e) LMFS-C15

RESULT AND DISCUSSION

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 a sharp spike at low frequency (Figure 1(a)).[12]

Small semicircle contribution is due to the bulk response of the cathode material whereas lower frequency spike is due to electrode electrolyte interface.[13] Bulk resistance of cathode material is estimated by extrapolating the semicircle which cut on the real axis.[14-18] Lower frequency spike clearly shows the capacitive behavior of the material. Electrical conductivity of cathode material is calculated using formula;

$$\sigma = \frac{1}{R_b}\frac{\ell}{A}$$

Where, R_b= Bulk Resistance of prepared materials,
ℓ= Thickness of electrode material
A = Contact Area

Table 1. Calculated electronic conductivity of prepared samples.

S. No	Conc. of MWCNT	Bulk Resistance	Conductivity(Scm^{-1})
1	0	2787	4.881×10^{-5}
2	3	2200	6.184×10^{-5}
3	6	2160	6.2988×10^{-5}
4	12	59	2.306×10^{-3}
5	15	178	7.643×10^{-4}

From Nyquist's plot it is revealed that conductivity improves with the addition of MWCNT. The result shows that the charge transfer resistance of MWCNT free $Li_2MnFeSiO_4$ is much larger than the modified ones, that effectively proves that MWCNT coating is very effective in improving the electronic conductivity of orthosilicate materials. As MWCNT helps to improve particle-particle connectivity, thus increases lithium ion diffusion rate. Special composite structure constructs an efficient Li-ion and electron channel, which significantly enhance the Li-ion diffusion rate and reduced the charge transfer resistance, hence may lead to high electrical conductivity.[19-21] Carbon nano tube not only deposited on the surface, but also provide the interconnected network. Further if we notice the LMFS-C15, Conductivity of prepared materials decreases. Possible reason is agglomeration of particles with the addition of MWCNT. More over once Li-ions gets the resistance free clear path for intercalation phenomenon; further addition of MWCNT is not going to further increase conductivity.[22-25] Agglomeration of cathode material is expected to provide obstacles (resistance) for lithium ion diffusion. Moreover main challenge is to use maximum lithium available in the material.[26-27] By providing conductive channel to lithium ions, we are able to overcome this challenge. Similar strategy has been opted while selecting the material as well. As in $Li_2MnFeSiO_4$, two lithium ions are available for intercalation which is twice as that of conventionaly used materials like $LiMO_2$.[28-32] As maximum conductivity has been noticed for 12 weight percent of MWCNT concentration. So 12 weight percent can be optimized concentration to use this cathode material in Li-ion battery and supercapacitors.

CONCLUSIONS

As a result, synthesis of $Li_2MnFeSiO_4$/MWCNT nanocomposite electrodes provided high efficient cathode material and MWCNT. Lower conductivity of orthosilicate materials is inherent property. However we can not change inherent characteristic of any material but we can improve that property to use that material for its practical utilization. In this present work, we have used MWCNT as conductive additive with $Li_2MnFeSiO_4$ and also optimized concentration of MWCNT which is required for its desired application. 12 weight percent concentration of MWCNT with $Li_2MnFeSiO_4$ is the optimized concencentration. Our study showed that prepared nanocomposites can be good candidates for application as cathode electrodes for lithium-ion batteries by using low-cost and practical sol–gel method.

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