Development of Novel Cathode Materials Based on MWCNT for Energy Storage/Conversion Devices

Shruti Agnihotri, Sangeeta Rattan and A.L. Sharma

Abstract In Chap. 1, already available technology for energy storage solutions like capacitors, lead acid batteries, compressed air energy storage, flywheels has been discussed in order to compare their energy and power densities. Emphasis has been laid on Rechargeable Lithium ion Battery (Li-ion). Various materials which are already explored and used as cathode of battery has also been discussed with their merits and demerits. Further introduction of prepared orthosilicate material with used conductive additive Multiwalled carbon nano tube (MWCNT) has also given. In Chap. 2, methodology used to prepare respective $Li_2MnFeSiO_4$ material and its composite with MWCNT has been discussed in detail. Further, in order to validate its electrochemical application, different steps of cell assembly of Lithium half cell fabrication has also been discussed. Chapter 3 comprises of results obtained using standard Field emission scanning electron microscope (FESEM). Effect of used MWCNT on its morphology has been discussed in this chapter. A.C Impedance spectroscopy has been used to study variation in conductivity with respect to bared material. Possible reasons for increased conductivity with morphology has also been discussed in discussion. Chapter 4 includes conclusions drawn from mentioned results. This chapter summarizes measured conductivity values with different concentrations of MWCNT. Improved conductivity with respect to bared orthosilicate material has been pointed in this chapter.

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1 Introduction

Energy demand and supply has always been one of the crucial factors for the evolution of civilization. Besides (green) energy production, storage of energy in any form is a serious issue. The possibility to collect the excess energy and having it available when energy shortage occurs are important tasks. Some technologies are already present in the market since many years. Examples of energy storage solutions are: **capacitors**, which store and release electrical energy; **lead-acid batteries**, which store chemical energy and convert it into electrical energy, e.g., to start car engines; **compressed air energy storage (CAES)**, in which air is compressed and stored in caves underground and, when required, its mechanical energy is used in turbines, to produce electricity; **superconducting magnetic energy storage systems (SMES),** which store energy in a form of a current owing inside a superconducting coil; **Flywheels**, which store energy as momentum in a rotating wheel. Different storage devices, visualized according to their power and the time required to deliver the energy [1]. A Ragone plot for different electrochemical devices can compare energy and power densities. Each device occupies a certain area, giving information not only on the performances, but also on the time in which the energy and power are delivered. The region between fuel cells and capacitors in Fig. 1 is occupied by rechargeable batteries. In this respect, rechargeable batteries are one of the most promising devices suitable for medium-sized applications, i.e., delivering a high amount of energy in a few hours. In this context, electrochemical energy storage devices such as batteries play an important role in the efficient use of renewable energy. Battery is a collective arrangement of electrical cells that stores and produces electricity by chemical reaction Li ion batteries have gained the considerable interest in recent years interms of high specific capacity, energy density, power density, cell voltage [2].

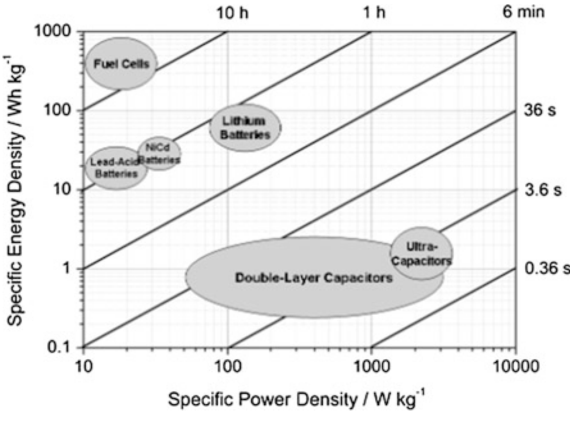

Fig. 1 Ragone plot for different energy storage devices

1.1 Basics of Lithium Ion Batteries

Li-ion batteries almost full the requirements for (hybrid) electric vehicles and, therefore, many industries and research groups are interested in these devices. Their great performances are based on the use of Li-ions, which are shuttled between the positive and the negative electrodes through the electrolyte. The use of Li-ions is appealing because lithium is the lightest metal on earth (m.w. = 6.941 g mol, density = 0.534 gcm^{-3} and as also the highest absolute electrochemical potential [3]. These properties are then responsible for high gravimetric energy density for li ion batteries. A Li ion battery consists of three main components, positive and negative electrode separated by a separator dipped in electrolyte. Negative electrode is normally an electron donor group which is electropositive in nature like lithium metal [4]. Positive electrode is normally an electron acceptor which is strongly electronegative. During discharge process, the negative electrode electrochemically oxidized and releases electron. This electron moves through outer circuit to the positive electrode which accepts electron.

In batteries the electrode itself takes part in chemical reaction. Consequently, the chemistry associated with electrode-electrolyte interface determine the battery performance. Thus performance of lithium ion battery crucially depends on the nature of electrode material used. Consequently, the research is focused on finding materials able to exchange a large amount of Li ions. Double-layer charge storage in a super capacitor is a surface process and hence surface characteristics of the electrodes greatly influence the capacitance of a super capacitor. Similarly, the open circuit voltage, energy density, power density, cyclability and self life of a lithium polymer cell also depend on electrode material properties. In general, electrode should have the following properties; (i) high electronic conductivity (ii) high surface area (iii) high temperature stability (iv) controlled pore structure (v) low equivalent series resistance (ESR) and (vi) relatively low cost (cost effective) (vii) High electronic conductivity [5]. Out of the aforementioned properties, foremost properties for improving the performance of Li ion battery are the development of suitable low cost, safety and high energy density cathode materials Recently, a new group of polyanion material Li_2MSiO_4 has been demonstrated as a promising candidate of Li ion insertion cathode material. Especially Li_2MnSiO_4 shows high theoretical capacity of 334 $mAhg^{-1}$. This is key feature of ortho silicate where two electron redox processes has been occurring. In Li_2MSiO_4 more than one Li ion per formula extraction is possible which significantly increases its experimental specific capacity and electrochemical performance.

1.2 Carbon Nano Tubes

CNTs have excellent mechanical, electrical, and chemical properties due to their light weight and perfect connection in their hexagon structure. In recent years, with the progress in the research on CNTs and nano materials, the prospect of wide application of CNTs is emerging, because of its excellent electrochemical properties [10^{-6} Sm^{-1} at 300 K for singlewalled CNTs (SWCNTs) and >10^{-5} Sm^{-1} for multiwalled nanotubes (MWCNTs)], low density, high rigidity, and high tensile strength. As our selected cathode material $Li_2Mn_{0.5}Fe_{0.5}SiO_4$ suffers from Low electronic conductivity. Use of CNTs is beneficial interms to improve this intrinsic property. It has been claimed in literature that the enhanced electrochemical activity can be achieved by few factors like (1) providing proper channels for electron and ions to react inside the material (by nanostructuring process) and (2) conductive coating on electrode material, which would benefit the electron transfer to the adjacent particles, thereby making electronic bridge between them and hence reducing grain boundary impedance for mass and electron transfer [6].

In the present report, $Li_2Mn_xFe_{1-x}SiO_4$ is prepared using standard Sol Gel technique and substitution of manganese place of iron (Fe) takes place. As polyanion materials $Li_2MnFeSiO_4$ suffers from poor electronic conductivity. To improve the conductivity of oxide materials, further modification by making its composite with Carbon nano tube. Field Emission scanning electron microscopy (FESEM) reveals the homogeneous topology of the materials sample. Impedance spectroscopy has been characterized for the estimation of electrical conductivity.

2 Experimental

2.1 Synthesis of $Li_2MnFeSiO_4$

Standard Sol Gel Method is used for the preparation of $Li_2MnFeSiO_4$. Stoichiometric amounts of Lithium carbonate (Li_2CO_3), Iron oxide (Fe_2O_3), Manganese Oxide (MnO_2), Silicon dioxide(SiO_2), Citric acid are used as precursors. Above mentioned precursors get hydrolyzed to form a solution. Formed solution was magnetically stirred continuously for 12 h. 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 h and second heating at 900 °C for 12 h. Prepared cathode material is labeled as LMFS.

2.2 Synthesis of $Li_2MnFeSiO_4$/MWCNT

Further to improve the particle–particle connectivity, composite of $Li_2MnFeSiO_4$/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 ($Li_2MnFeSiO_4$) was added in sequence and finally 0.5 ml of hydrazine was added. As obtained solution was refluxed at 80 °C for 2 h with stirring to obtain $Li_2MnFeSiO_4$/MWCNT composite. This mentioned procedure was further followed to prepare samples with 6 and 9 wt% of MWCNT. These prepared samples are labeled as LMFS-C6 and LMFS-C9 respectively.

2.3 Lithium Half-Cell Fabrication

Electrochemical characterizations were performed using two- electrode coin cells. The positive electrodes were prepared by dispersing 80 wt% active material powder, 10 wt% carbon black and 10 wt% polyvinylidenefluoride (PVDF) in *N*-methyl pyrroli- dinone (NMP) to form a slurry mixture. Then the slurry was deposited on the current collectors of aluminum foils by a blade and cut into circular discs as the cathode. The electrode was dried under vacuum at 105 °C for 20 h and then assembled into cells [7]. The specific capacity of the cathode material is calculated with the mass of $Li_2MnFeSiO_4$/MWCNT, not including the carbon content. Copper foil was used as the negative electrode. The electrolyte was $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) solvents and micro porous polypropylene film as the separator. Electrochemical impedance spectroscopy EIS) was performed to measure electronic conductivity.

2.4 Material Characterization

FESEM The field emission scanning electron microscopy (FESEM) analysis was performed using Card Ziess Merlin Compact to investigate the morphology of prepared samples. In FESEM Electrons are liberated from a field emission source and accelerated in a high electrical field gradient. Within the high vacuum column these so-called primary electrons are focussed and deflected by electronic lenses to produce a narrow scan beam that bombards the object. As a result secondary electrons are emitted from each spot on the object. The angle and velocity of these secondary electrons relates to the surface structure of the object. A detector catches the secondary electrons and produces an electronic signal. This signal is amplified and transformed to a video scan-image that can be seen on a monitor or to a digital image that can be saved and processed further.

A.C. Impedance Spectroscopy Electrochemical Impedance Spectroscopy or EIS is a powerful technique for the characterization of electrochemical systems. The promise of EIS is that, with a single experimental procedure encompassing a sufficiently broad range of frequencies, the influence of the governing physical and chemical phenomena may be isolated and distinguished at a given applied potential. Electrical conductivity of prepared samples is measured by electrochemical analyzer (model: CH-760).

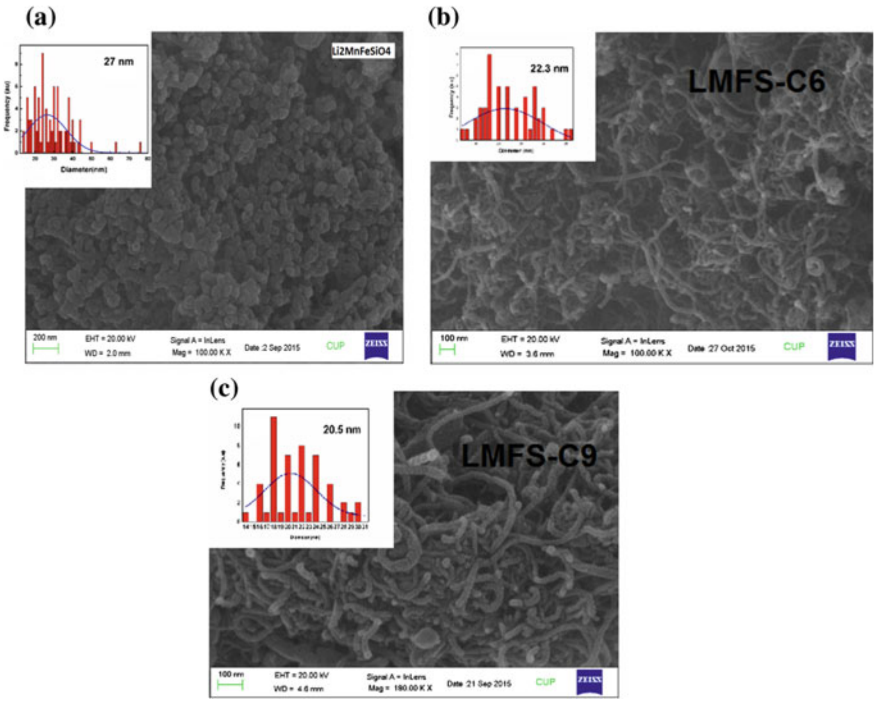

Fig. 2 FESEM images of prepared samples **a** LMFS **b** LMFS-C6 **c** LMFS-C9

3 Results and Discussion

A major aspect of our research was synthesizing the cathode, consisting of $Li_2Fe_{0.5}Mn_{0.5}SiO_4$ and Multiwalled carbon nano tube. It was important to characterize the cathode materials using FESEM in order to determine the average particle size and the distribution of particle size.

3.1 FESEM Analysis

FESEM is very powerful tool in order to get the surface morphology/topology in a very fine way. The high magnifications attainable combined with a large depth of field makes FESEM an outstanding diagnostic system for micro fabrication. Figure 2 shows the Field emission electron microscopy (FESEM) image of the prepared cathode materials. The obtained image of the FESEM clearly depicts the homogeneous distribution of the materials sample all over the sample. A small particle size could reduce the internal stress, because the binding force between particles may increase with the relative area of the grain boundaries. The particle size was measured from the software 'ImageJ' and the particle size was found to be of the order of ~27 nm (Fig. 2) for LMFS. This particle size is improved size as compared with Li_2FeSiO_4 and Li_2MnSiO_4. It is reported in literature that material with lesser particle size reveals better electrochemical properties due to reduction of path length of Li^+ ions.

Further particle size also decreases on addition of MWCNT. From Fig. 2b, c it is revealed that all the CNTs are evenly adhered to the surface of the $Li_2MnFeSiO_4$/MWCNTs micro- spheres which is highly beneficial for network formation for smooth ion transference. All the samples show a narrow particle size distribution, but the CNT-free $Li_2MnFeSiO_4$ sample exhibits larger geometric mean diameter, one possible reason is that the small precursor particles aggregate during the sintering process without added MWCNT. It is reported that samples with a smaller particle diameter reveal better electro-chemical performance, which reduces the path length of Li+ions. The $Li_2MnFeSiO_4$/MWCNT composites exhibit small particle diameter and porous structure, which facilitates to improve the electrochemical property in the electrode. Key point for expectation of improved electronic conductivity is that coating layer of MWCNT prevents the surface area of the $Li_2MnFeSiO_4$ in direct contact with the electrolyte, which is able to inhibit side

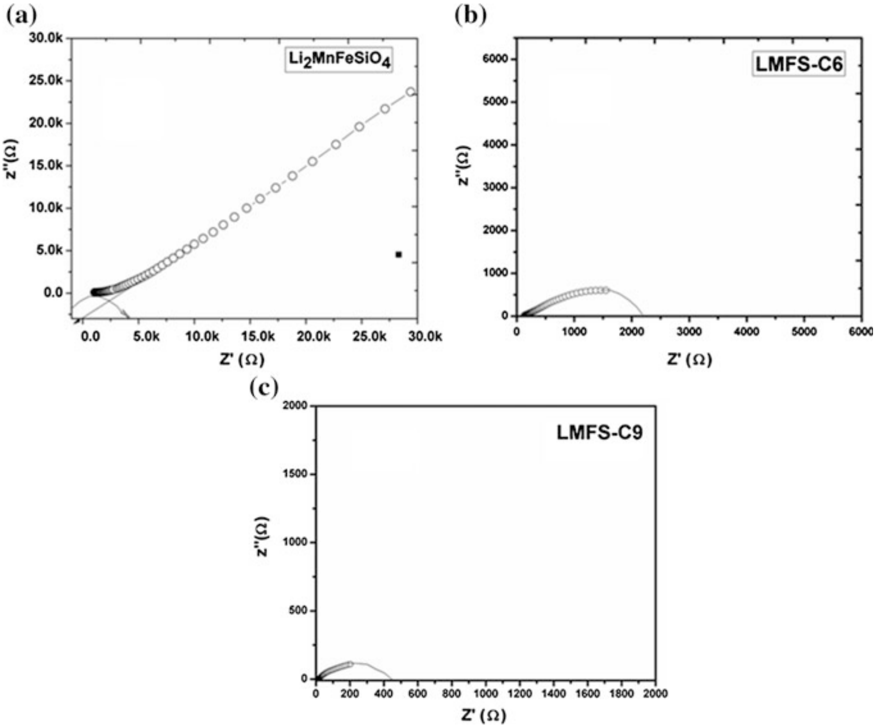

Fig. 3 Nyquist plots **a** LMFS, **b** LMFS-C6, **c** LMFS-C9

Table 1 Representing increase in electronic conductivity with MWCNT

Sample	Thickness (cm)	Contact area (cm^2)	Bulk resistance (Ω)	Electric conductivity (Scm^{-1})
LMFS	0.2	1.47	2787	4.881×10^{-5}
LMFS-C6	0.2	1.47	2160	6.29×10^{-5}
LMFS-C9	0.2	1.47	497	2.73×10^{-4}

reactions between the active material and electrolyte so as to extend the service life of the batteries [8].

3.2 A.C Impedance Spectroscopy

The A.C impedance measurement of the cathode material was carried out in the frequency range from 10 to 1 MHz at a input A.C signal level of 10 mV. The impedance spectrum is comprised of a small semicircle at high frequency is followed by sharp spike at lower frequency (Fig. 3). The small semicircle contribution is due the bulk response of the cathode materials whereas the lower frequency spike is due to the electrode electrolyte interface. The bulk resistance of the cathode materials is estimated by extrapolating the semicircle and cut on real axis, which comes out of order of ~2787 Ω, ~2160 Ω and ~497 Ω for LMFS, LMFS-C6 and LMFS-C9 respectively.

The lower frequency spike clearly shows the capacitive behavior of the cathode materials. The electrical conductivity of the cathode material is estimated by the formula: $\sigma_{dc} = \frac{1}{R_b}\frac{\ell}{A}$ where, symbols have their usual meanings. The electrical conductivity has been calculated for LMFS, LMFS-C6 and LMFS-C9 comes out to be of order of $\sim 4.881 \times 10^{-5}$ and 6.29×10^{-6} and $2.73 \times 10^{-4} S\ cm^{-1}$ respectively (Table 1).

4 Conclusion and Future Scope

In summary, sphere $Li_2MnFeSiO_4$/MWCNT composite with improved electronic conductivity was successfully synthesized via standard sol-gel method followed by solution method. Improved electronic conductivity of modified cathode material is caused by the unique composite structure. The nanosized $Li_2MnFeSiO_4$ provides short path- ways for the Li^+ diffusion and the CNTs network facilitates electron transport and avoids agglomeration of $Li_2MnFeSiO_4$ particles. Prepared composite cathode material overcome the drawback of $Li_2MnFeSiO_4$ cathode material by improving its electronic conductivity. We have observed the enhanced electronic conductivity of $Li_2MnFeSiO_4$/MWCNTs material due to better fueling of electrons at particle-particle interface. In the present case, nano dimension along with MWCNT additive helps in improving the desire kinetic behavior as lithium-ion battery cathode. More over particle size can also be optimized by utilizing a more effective mechanical processing method to crush the cathode, such as use of a ball-milling machine rather than use of a mortar and pestle. We believe that continued research on lithium silicates is both necessary and viable for the future of electronics.

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