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SYNTHESIS AND STUDIES ON LITHIUM IRON ORTHOSILICATE CATHODE MATERIALS VIA MODIFIED SOL-GEL METHOD

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ABSTRACT- Recently, Li_2MSiO_4 (M=Fe, Mn, Co) have received much interest as cathode materials for Li-ion batteries with high theoretical capacities and thermal stability. In this article, Li_2FeSiO_4 composites were synthesized by modified sol-gel methods with acetic acid used as reagent. Herein, effects of various preparation procedures on the structural properties of Li_2FeSiO_4 were studied. The materials were characterized by X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Raman analysis. From the XRD patterns it is observed that some impurities are presented such as Li_2SiO_3 and Fe_2O_3. The functional group vibrations and molecular structure were confirmed by FTIR and RAMAN analysis.

Keywords- [Cathode materials, Li-ion batteries, Li_2FeSiO_4]

1. INTRODUCTION

In recent years, the rechargeable lithium-ion batteries have become remarkably an important candidate in portable electronics, electric vehicles and hybrid electric vehicles [1-3]. As an important component of lithium-ion batteries, cathode materials play a decisive role in the determination of energy density, safety and life cycle of Li-ion batteries. Therefore, the existence of these cathode materials is still being a demand due to various factors such as eco-friendly, low cost and especially high-energy density and high safety [4-6].On the development of cathode materials, polyanion compounds with $(XO_4)^{n-}$ groups is considered to be one of the most capable cathode materials for LIBs which has attracted much courtesy as they are cost efficient and high safety, compared with commonly used transition metal oxides, such as $LiMn_2O_4$, $LiCoO_2$ and $LiNi_{1-x}Co_xO_2$[7,8]. Polyanion system based phosphate materials, particularly $LiFePO_4$ has attracte attention and has been studied extensively [9, 10].More recently, a new class of polyanion-type cathodes based on the orthosilicates, Li_2MSiO_4 ($M=Mn^{2+}$, Fe^{2+}, Co^{2+}) has been proposed as a promising cathode material for rechargeable lithium-ion batteries. As a member of Li_2MSiO_4, Li_2FeSiO_4 has much higher theoretical

capacity (~330 mAh g^{-1} by the utilization of two lithium ions per formula unit) than that of $LiFePO_4$ (170 mAh g^{-1}) and high thermal stability through strong Si-O bonding. In addition, these cathode materials contain iron and silicon being the utmost abundant, non-toxic and cheap constituent elements [11-15]. However, Li_2FeSiO_4 suffers from poor rate capability, low electronic conductivity and poor ionic mobility, which brings big complications to its practical applications. To overcome these obstacles various techniques such as coating with electronic conductive material, the metallic ion doping in Si sites and the particle size reduction have been applied to the orthosilicate materials. Among these tactics, reducing the particle size is an effective way to enhance the characteristics of the cathode materials [16-19]. To date, numerous methods such as solid state reaction [20], sol-gel [21] and hydrothermal [22] have been successfully adopted for the synthesis of Li_2FeSiO_4 materials. Among these methods, sol-gel method stays to be one of the powerful solution synthetic methods, as it can greatly improve the homogeneity of the precursor. This method consumes an effective way of mixing the starting materials by solution process at a molecular-level [23, 24]. In this paper, the Li_2FeSiO_4 materials were prepared using modified sol-gel method of varying the preparation procedures. The prepared composites were investigated in detail for its physical properties using XRD, FT-IR and Raman analysis.

2. MATETERIALS AND METHODS

Synthesis of Li_2FeSiO_4 Lithium acetate dihydrate, Iron (II) oxalate dihydrate and Tetraethoxysilane (TEOS) were used to prepare the Li_2FeSiO_4 by modified sol-gel methods.

Method 1- A water-ethanol solution of TEOS was mixed with a stoichiometric amount of Lithium acetate and iron oxalate. Then the mixture was subjected to magnetic stirring where the acetic acid solution was added as a catalyst. Then the solution was heated at 80°C under magnetic stirring to evaporate the solvents gradually. After the solvents were evaporated, the resulting dry gel was grounded and calcined at 650°C for 10h under Ar atmosphere. Finally the Li_2FeSiO_4 composites were obtained and this sample was labeled as M-1.

Method 2- The ethanol solution of iron oxalate was taken into the beaker-1 and TEOS was dropwise added to the solution. The ethanol solution of Lithium acetate was taken into the beaker-2. Adding, second solution (beaker-2) drop wise to the first solution (beaker-1) containing iron oxalate. The solution was stirred under magnetic stirring, the deionized water and acetic acid was added drop wise. Finally stirred and calcined in the same manner as in method-1. The final composite was labeled as M-2. Characterization of Li_2FeSiO_4 crystal structure of the prepared materials was identified by powder X-ray diffraction (PANalytical XPERT-PRO with Cu Kα radiation) analysis in the range of 2θ=10-80°. The functional group vibrations were analyzed by FT-IR spectrophotometer (Thermo Nicolet 380 Instrument Corporation) using KBr pellets and Raman spectrometer (STR 500 Laser Raman spectrometer, SEKI, Japan).

3. RESULTS AND DISCUSSION

X-ray diffraction

The crystal structure of the prepared Li_2FeSiO_4 composite was examined by X-ray diffraction (XRD) analysis. Fig.1 represents the XRD patterns of the as-synthesized samples M-1 and M-2. It is well known that Li_2FeSiO_4 has mainly three different polymorphs, such as $Pmn2_1$, $P2_1/n$ and Pmnb, stable at low, intermediate and high temperatures respectively. The XRD patterns of present samples can be identified as an

orthorhombic structure with space group of $Pmn2_1$. Some crystallized impurity peaks were detected for both samples like Li_2SiO_3 and Fe_2O_3. Of these, two samples (M-1 & M-2) second sample (M-2) sample possess good crystallinity. In both materials the precursor was calcined at 650°C for 10 h under inert atmosphere, because these higher temperatures (600 – 800°C) are usually reported in the literature for obtaining Li_2FeSiO_4 [17].

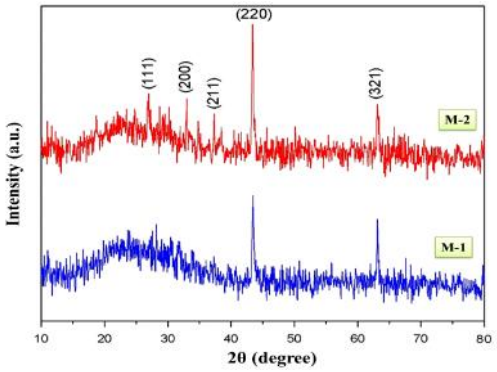

Figure 1- XRD patterns of as-prepared samples M-1 and M-2

6. FT-IR ANALYSIS

Fourier Transform Infrared Spectroscopy (FT-IR) can show additional structure information of as-prepared Li_2FeSiO_4 phase. Fig.2 shows the FT-IR spectra of the prepared samples M-1 and M-2. The infrared bands at 961 and 866 cm^{-1} can be contributed to the stretching modes of Si-O bonds in SiO_4 tetrahedra. The peak at 1087 cm^{-1} can be ascribed to the Si-O vibrations in Li_2SiO_3, and the bands at 1463 and 1506 cm^{-1} correspond to C-O vibrations in Li_2CO_3 owing to exposure in air [25]. The bands at 965 and 961 cm^{-1} can be ascribed to the C-H bending and 2926 cm^{-1} is C-H stretching. The O-H stretching is appearing in the region 3500 – 3100 cm^{-1}.

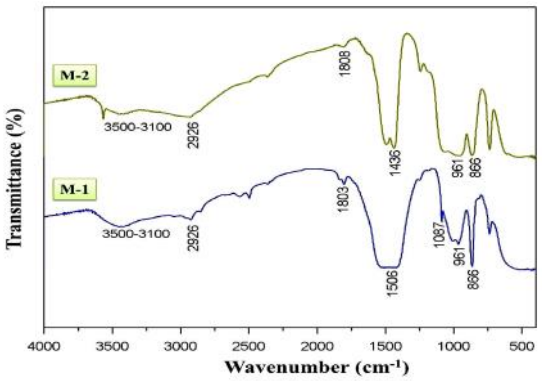

Figure 2- FTIR spectra of as-prepared samples M-1 and M-2

5. RAMAN ANALYSIS

Raman spectroscopy is used to observe the vibrational, rotational and other low-frequency modes in a Li_2FeSiO_4 composite. Fig.3 shows the Raman spectra of the as-prepared samples M-1 and M-2 in the range of 0 to 2000 cm^{-1}. The Raman bands appeared in the range of around 400 ~ 700 cm^{-1} belongs to Fe-O vibrations [26]. In the present materials no carbon source was used as a starting material, but the D band is appearing in the range of nearby 1300 cm^{-1}due to the effect of calcination temperature.

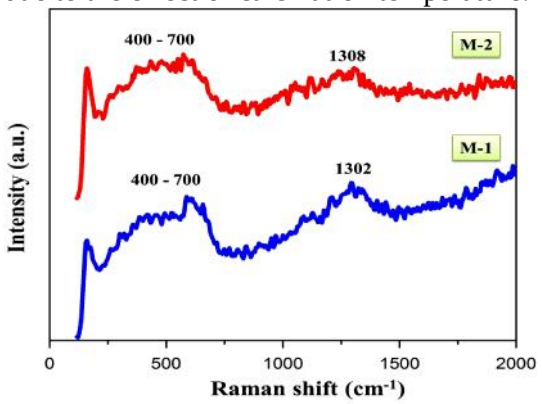

Figure 3- Raman spectra of as-prepared samples M-1 and M-2

CONCLUSION

An attempt has been made to synthesis lithium iron orthosilicate using modified sol-gel method of varying the preparation procedure. Both the samples have

been characterized for structural analyses using XRD, FTIR and Raman. From XRD pattern all the prepared materials were indexed to the orthorhombic structure with space group of $Pmn2_1$. Some impurities are present in this pattern like Li_2SiO_3 and Fe_2O_3. From FT-IR analysis the functional group vibrations have been studied and confirm the presence of Li_2SiO_3 impurity. Raman analysis provides information about the molecular structure of the prepared materials. In a comparison of two methods, the second method (M-2) is considered to be the best for obtaining a good structure. Therefore, the present study concludes that the preparation procedure plays a vital role in the synthesis of Li_2FeSiO_4 materials.

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