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THE $\text{Li}_2\text{FeSiO}_4$ / C COMPOSITES OBTAINED FROM CELLULOSE GEL

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ABSTRACT

In this study, monoclinic polymorph of $\text{Li}_2\text{FeSiO}_4$ (space group $P2_1/n$) in composite with carbon has been synthesized by sol-gel method followed by rapid heating, short high-temperature delay, and subsequent quenching. Three composites were made with 3, 9 and 14 weight percent of the carbon. The effect of the carbon on structure, morphology and electrochemical performance of the prepared composites has been examined by X-ray diffractometry, scanning electron microscopy and galvanostatic cycling.

INTRODUCTION

Recently, an entirely new class of polyoxyanion cathodes based on the lithium transition-metal orthosilicates (Li_2MSiO_4 , $M = \text{Fe}$, Mn , and Co), has been attracting growing interest due to their potentially high theoretical capacities arising from the possibility of the extraction of two Li-ions per formula unit [1]. $\text{Li}_2\text{FeSiO}_4$ takes prominent position among this family of compounds due to its structural stability and natural abundance of iron. Here we report a simple method for the synthesis of $\text{Li}_2\text{FeSiO}_4/\text{C}$ composite based on a sol-gel precursor preparation, followed by short-time, high-temperature treatment. *In situ* created carbon restricts growth of $\text{Li}_2\text{FeSiO}_4$ particles and increases overall conductivity of the composite. In this work we examined how carbon content affects morphology and structure of the obtained powder and how it modifies electrochemical behavior of the $\text{Li}_2\text{FeSiO}_4$ cathode.

EXPERIMENTAL

The synthetic procedure was conducted via two steps. The first is sol-gel precursor preparation starting from Li_2CO_3 , $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS) mixed in the molar ratio of 1:1:1:1. Water-soluble methylcellulose was used as a source of carbon. Three samples were synthesized with three different concentration of methylcellulose. The motivation for the sol-gel processing lies in the fact that it provides homogenous mixing of reactants at the molecular level [2]. The second step is calcination of the dried gel precursor. The calcinations were performed at 750°C in slightly reductive atmosphere ($\text{Ar} + 5\%\text{H}_2$). During pyrolytic degradation, methylcellulose decomposes to carbon, creating at the same time more reductive environment that prevents iron oxidation and formation of Fe^{3+} sites. According to mass percentage of carbon, the samples will be noted as LFS_3%C, LFS_9%C and LFS_14%C. X-ray diffraction data were collected on a Philips PW 1050 diffractometer with $\text{Cu-K}\alpha_{1,2}$ radiation (Ni filter) at the room temperature. Measurements were done in 2θ range of 10 - 70° with step size of 0.02° and counting time of 3s per step. The carbon content in the three samples was determined thermogravimetrically to be 3, 9 and 14 mass percent of the carbon. The morphology of the synthesized powders was analyzed by FESEM (TESCAN, MIRA3 XMU) at 20 kV. The particle size analyzer (PSA) Mastersizer 2000 (Malvern Instruments Ltd., UK) was used for the determination of the particle size distribution. Electrochemical measurements were performed at VMP3 potentiostat/galvanostat at 55°C . The cell consisted of two electrodes vacuum-sealed in triplex foil (coffee bag foil). Working electrode was made from synthesized material, carbon black and polyvinylidene fluoride (PVdF, Aldrich) mixed in 75:15:10 weight percent ratio and deposited on Al foil from slurry prepared in N-methyl-2-pyrrolidone. The working electrode and the counter electrode consisting of metallic lithium were separated with a Celgard separator. 1M solution of LiPF_6 (Chemmetall) in EC/DMC (Aldrich) was used as electrolyte. Galvanostatic charge/discharge tests were performed between 2 and 4 V at different current rates.

RESULTS AND DISCUSSION

The XRD patterns of the as-prepared samples are shown in Fig. 1. The crystal system was confirmed to be monoclinic, space group $P2_1/n$. There is no evidence of a crystalline carbon, so internal carbon could be treated as a contribution to the background. The mean crystallite size was calculated using X-ray Line Profile Fitting program (XFIT) based on a fundamental parameters convolution approach to generate line profiles [3]. The mean

crystallite sizes for the three samples are displayed in Table 1. There is noticeable crystallite size decrease when the carbon content increases.

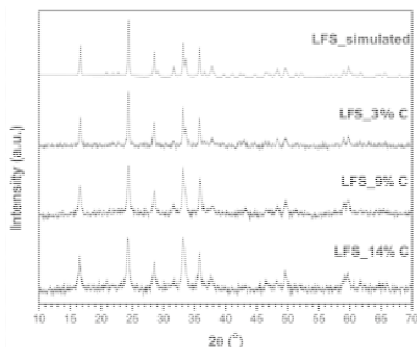


Figure 1. XRD patterns for the obtained samples and pattern simulated in $P2_1/n$.

powders with 14%C and 9%C. The particles are irregular in shape and highly agglomerated. However, the agglomeration is more pronounced in the sample with 9% of carbon. The particle size distribution curves of the powders (Fig. 2 insets) has a lognormal shape with mean particle size of 340 nm for the 14%C sample and 360 nm for the LFS_9%C sample. By comparing mean particle size with the mean crystallite size, it can be concluded that particles are polycrystalline, composed of number of crystallites.

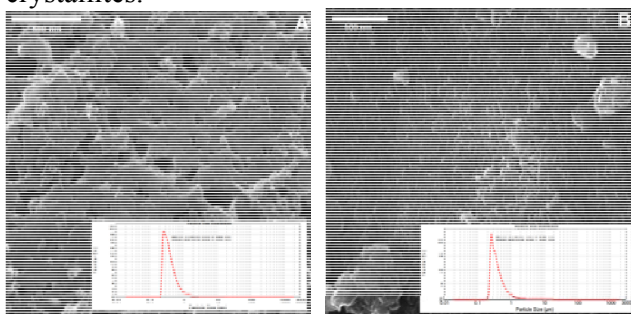


Figure 2. FESEM micrographs of the prepared powders: LFS_9%C (A) and LFS_14%C (B).

Fig. 3 shows the discharge curves and the cycling performance of the $\text{Li}_2\text{FeSiO}_4/\text{C}$ cathodes in the potential range of 2-4 V (vs. Li^+/Li) at current densities of C/10 and 1C. All samples exhibit excellent cycle stability at given voltage range. However, there exists apparent difference in specific capacity achieved between low and high carbon content samples. For the current density of C/10 the samples with 9% and 14% of carbon gave

Table 1. Calculated crystallite size.

Weight percent of carbon (%)	Crystallite size (nm)
3	30
9	18
14	15

The shape and morphology of the particles in $\text{Li}_2\text{FeSiO}_4/\text{C}$ composite samples were followed by electron microscopy measurements. Fig. 2. presents FESEM images for the

similar values of near 100 mAh/g discharge capacity. At the current density of 1C these two samples achieved two times lower but still significant value of ~50 mAh/g. This value is comparable with the value given by LFS_3%C sample at ten times lower current density.

As mentioned earlier, *in situ* made carbon prevents agglomeration and restricts $\text{Li}_2\text{FeSiO}_4$ particle growth. Access of lithium into depth of the particle is facilitated for the smaller particles (the diffusion path is shorter) leading to higher specific capacity. On the other hand, high amounts of carbon that surround the particle can block lithium diffusion, which leads to the decrease in the specific capacity. Finally, higher ratio of the carbon vs. active material leads to the decrease in energy density of the composite. Therefore, the optimal concentration of the carbon exists, above which there is no improvement in the electrochemical performance but setbacks can occur.

CONCLUSION

Monoclinic $\text{Li}_2\text{FeSiO}_4$ that crystallizes in $P2_1/n$ space group was synthesized by means of the sol-gel processing followed by quick solid-state reaction step at 750°C. The content of the *in situ* created carbon was effectively controlled throughout the synthesis procedure. The carbon in $\text{Li}_2\text{FeSiO}_4/\text{C}$ composite has multiple roles of which not all are positive. The effect of carbon on structure, morphology and electrochemistry of the $\text{Li}_2\text{FeSiO}_4$ was examined. The optimal concentration of carbon was found to be near 10% of composite weight.

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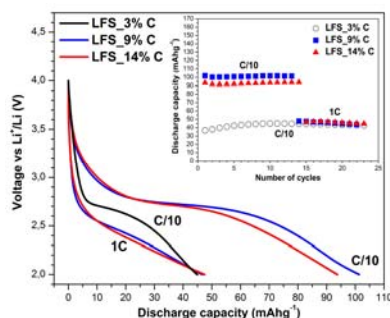


Figure 3. Discharge curves and cycling performance (inset) at C/10 and 1C