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Combustion synthesized $LiMnSnO_4$ cathode for lithium batteries

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Abstract

Novel category $LiMnSnO_4$ compound was synthesized via. Urea assisted combustion (UAC) method at 800 °C and examined for possible use as cathode material in lithium-ion batteries. The XRD (X-ray diffraction) results of $LiMnSnO_4$ sample authenticate the orthorhombic crystal structure with high degree of crystallinity. Presence of uniformly distributed nanometric grains (scanning electron microscopy) with preferred local cation environment is evident from FT IR (Fourier transform infra red spectroscopic) and ^7Li NMR (nuclear magnetic resonance spectroscopy) studies. The charge–discharge behavior of $Li/LiMnSnO_4$ cells demonstrated a specific capacity of 113 mA h/g, with an excellent capacity retention (95%) and Ah efficiency (>99%). Besides, the internal resistance of the $Li/LiMnSnO_4$ cell after 30 cycles is negligibly small, thus demonstrating good electronic conductivity and cycling stability, required for any lithium intercalating cathode material.

Keywords: $LiMnSnO_4$ cathode; MAS ^7Li NMR; Orthorhombic; Urea assisted combustion method; Lithium-ion battery

1. Introduction

Compounds that can reversibly incorporate lithium ions into their crystal structures are of interest for application as cathode materials in rechargeable lithium batteries [1]. Common cathode materials used in lithium batteries are spinel $LiMn_2O_4$ [2], layered $LiCoO_2$ [3], $LiNiO_2$ [4] and the olivine category $LiFePO_4$ [5]. Basically, the deployment of $LiMn_2O_4$ cathode in practical devices is limited, as it suffers from poor capacity retention due to Jahn-Teller distortion induced metal dissolution [2]. On the other hand, the most commonly used $LiCoO_2$ and the high capacity $LiNiO_2$ cathodes need to be addressed for their toxicity, cost and safety issues [6]. Similarly, phospho-olivines, popularly known for their low cost, nontoxicity and high inherent safety also have low electronic conductivity and slow lithium ion diffusion across the $LiFePO_4/FePO_4$ boundary problems, thus necessitates the search for newer and alternate cathode materials for lithium battery applications.

Besides olivines, it is believed that there is ample hope for $LiMSnO_4$ category compounds as possible lithium insertion electrodes [1,7], wherein report on $LiFeSnO_4$ compound alone is available in the literature till date [8]. Based on the intriguing results of such a preliminary explorative study on $LiFeSnO_4$ compound [1,8], it was decided to synthesize a related category eco-benign and economically viable $LiMnSnO_4$ compound, so as to explore the possibility of deploying the same as cathode in rechargeable lithium cells. Hence, a detailed investigation on $LiMnSnO_4$ compound has been made for the first time with a view to understand the structural and electrochemical behavior of the same for exploitation as lithium intercalating cathode material.

As is well known that the synthesis procedure adopted plays a vital role in deciding the specific capacity and capacity fade of an electrode material, Urea assisted combustion (UAC) method has been chosen for the present work, based on our earlier studies [9]. As expected, UAC method has resulted in the formation of ultra fine

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$LiMnSnO_4$ powders with desirable physical as well as electrochemical characteristics of lithium intercalating cathode material, which is the significance of present study.

2. Experimental

2.1. Synthesis procedure

The $LiMnSnO_4$ active material was synthesized by adopting Urea assisted combustion (UAC) method where stoichiometric proportions of respective high purity metal nitrate (Sigma Aldrich, India) precursors were dissolved in triple distilled water. To the homogeneous solution was added calculated quantity of urea, a popularly known combustion fuel, along with continuous stirring. The clear solution thus obtained after the addition of urea was heat treated at 120 °C for 12 h. followed by sintering at 300 °C for about 5 h. to expel carbon in the form of CO_2 that resulted from the combustion of urea. The sintered precursor obtained at this stage was ground to yield finer powder and was further heat treated at a higher temperature of 800 °C for 3 h. using an alumina crucible. Herein, both the rate of heating and cooling were maintained at 1 °C/min to avoid surface cracking of the particles and to ensure the presence of uniformly distributed particles of sub-micron size. Also, the properly controlled and duly monitored heating sequence renders improved yield (70%) of the final product without any undesirable agglomeration that takes place normally during high temperature sintering process.

2.2. Physical and electrochemical characterization

Phase characterization was done from the powder X-ray diffraction (XRD) patterns recorded on a Philips 1830 X- ray diffractometer using Ni filtered Cu Kα

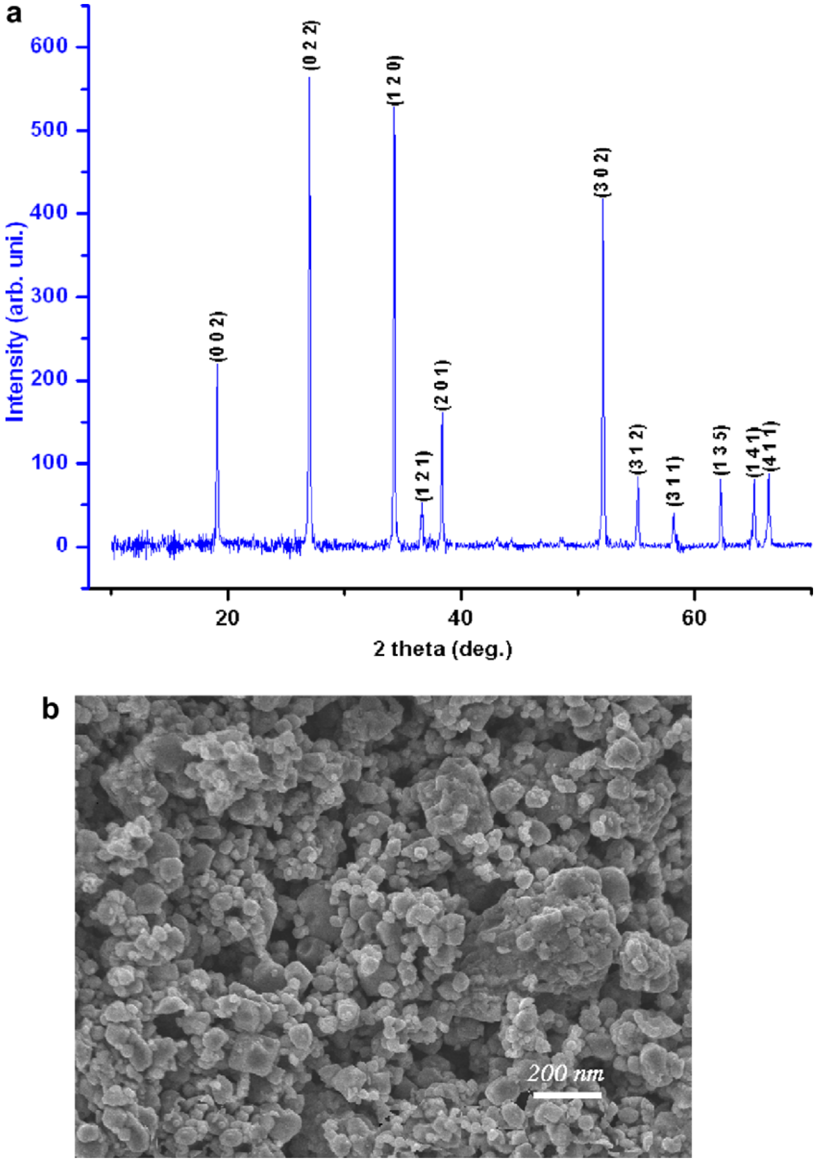

Fig. 1. (a) X-ray diffraction pattern and (b) SEM image of $LiMnSnO_4$ compound calcined at 800 °C.