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journal homepage: www.elsevier.com/locate/elecomStructural and electrochemical investigation of $\text{Li}_2\text{MgSnO}_4$ anode for lithium batteries

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ABSTRACT

Hexagonal $\text{Li}_2\text{MgSnO}_4$ compound was synthesized at 800 °C using Urea Assisted Combustion (UAC) method and the same has been exploited as an anode material for lithium battery applications. Structural investigations through X-ray diffraction, Fourier Transform Infra Red spectroscopy and ^7Li NMR (Nuclear Magnetic Resonance spectroscopy) studies demonstrated the existence of hexagonal crystallite structure with $a = 6.10$ and $c = 9.75$. An average crystallite size of ~ 400 nm has been calculated from PXRD pattern, which was further evidenced by SEM images. An initial discharge capacity of ~ 794 mA h/g has been delivered by $\text{Li}_2\text{MgSnO}_4$ anode with an excellent capacity retention (85%) and an enhanced coulombic efficiency (97–99%). Further, the $\text{Li}_2\text{MgSnO}_4$ anode material has exhibited a steady state reversible capacity of ~ 590 mA h/g even after 30 cycles, thus qualifying the same for use in futuristic lithium battery applications.

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1. Introduction

Lithium batteries based on transition metal oxide cathodes and carbon or graphite anodes have been the choice of interest, since the commercialization of the battery technology by early 1990s [1]. However, an ever pressed demand for the electrode materials with higher reversible capacity than carbon based anode materials has stimulated researchers to explore a wide variety of alternative anode candidates for lithium-ion batteries [2]. In this regard, metals and alloys present themselves as attractive alternatives to carbon/graphite based anode materials due to their higher capacity, excellent rate capability, etc. [3]. However, the unavoidable larger volume changes of intermetallics lead to mechanical failure of the electrode, resulting in the poor cycleability of the bulk metal alloy [4].

Similarly, development of tin oxide containing glass anodes and the mechanistic investigation of tin based electroactive materials are reported to exhibit improved cycleability with a specific capacity of ~ 1800 mA h/cm³, provided the metal phase is prepared as ultra fine particulates [5]. On the other hand, the major limiting factor is the larger initial irreversible capacity loss that results from the irreversible consumption of lithium prior to lithium alloying. Therefore, in an attempt to alleviate the inherent adverse effects of both the carbon based anodes and the Sn based alloys, an alternative category Li_xMSnO_4 candidate was chosen for the present

study. Herein, Li_xMSnO_4 type of compounds with a suitable metal viz. Mg is expected to impart structural and thermal stability by way of pillaring effect [6]. Because, Mg which is known to enhance the cycleability and stability of native ABO_4 material is expected to combat the unacceptable volume changes and the consequent capacity fade problems of tin in the chosen category $\text{Li}_2\text{MgSnO}_4$ compound. In addition, the basic requirement of excess of Li related to the unacceptable irreversible capacity loss behavior is also believed to get addressed in the $\text{Li}_2\text{MgSnO}_4$ compound [7] chosen for the study. Based on these grounds, the present study was planned on the synthesis and electrochemical investigation of $\text{Li}_2\text{MgSnO}_4$ anode for possible lithium intercalation activity upon electrochemical cycling.

In short, the study has a main focus on the possibility of realizing modified structural and electrochemical properties of $\text{Li}_2\text{MgSnO}_4$ anode, especially upon extended cycling. Towards this direction, UAC method has been chosen to synthesize the title compound, based on the encouraging results of our previous studies [8].

2. Experimental

2.1. Synthesis procedure

The $\text{Li}_2\text{MgSnO}_4$ active material was synthesized by adopting Urea Assisted Combustion (UAC) method and the details pertinent to the same are described elsewhere [8]. In this regard, the actual reaction taking place in the UAC method of synthesizing $\text{Li}_2\text{MgSnO}_4$ is represented in Fig. 1.

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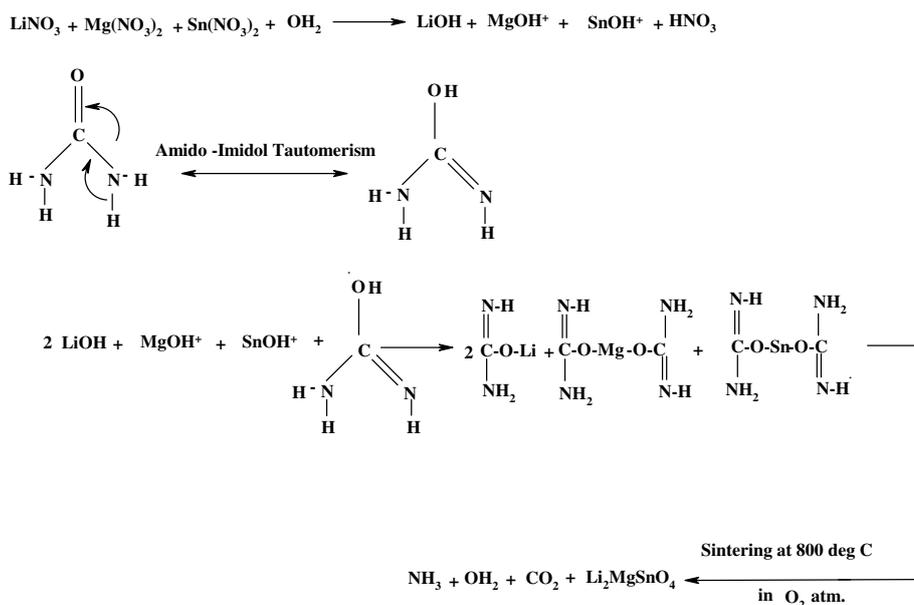


Fig. 1. Chemical reaction involved in the synthesis of $\text{Li}_2\text{MgSnO}_4$ by UAC method.

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 $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Surface morphology of the synthesized LiMnSnO_4 was investigated using Jeol S-3000 H Scanning Electron Microscope. Fourier Transform Infra Red spectroscopy (FT-IR) study was performed on a Perkin-Elmer paragon-500 FT-IR spectrophotometer using a pellet containing the mixture of KBr and the active material in the region of $400\text{--}2000 \text{ cm}^{-1}$. ^7Li NMR measurements were carried out with a Bruker MSL-400 spectrometer by employing a 5 mm Bruker VT-MAS probe operating at a ^7Li frequency of 14 MHz. Electrochemical charge–discharge study was carried out using MACCOR charge–discharge cycle life tester.

2.3. Electrode preparation and cell assembly

Details pertaining to the anode electrode preparation and the subsequent coin cell fabrication are reported already [9].

3. Results and discussion

3.1. Structural and surface morphology results

The X-ray diffraction pattern of $\text{Li}_2\text{MgSnO}_4$ compound prepared by Urea Assisted Combustion (UAC) method is shown in Fig. 2a. Existence of broad and well defined Bragg peaks demonstrates the formation of size controlled and highly crystallized $\text{Li}_2\text{MgSnO}_4$ grains. The miller indices (hkl) of all the peaks were indexed as per the JCPDS file No. 220414 that corroborates the existence of hexagonal lattice structure. The lattice parameter values calculated by least square fitting are $a = 6.10$ and $c = 9.75$. Using Scherer's formula, an average grain size of $\sim 400 \text{ nm}$ has been calculated, which is believed to be due to the exploitation of UAC method to produce ultra fine powders of $\text{Li}_2\text{MgSnO}_4$.

The powder morphology of $\text{Li}_2\text{MgSnO}_4$ material investigated using Scanning Electron Microscopy (Fig. 2b) evidences the presence of evenly distributed spherical grains with finer particle size. In general, synthesis of compounds with size reduced particles

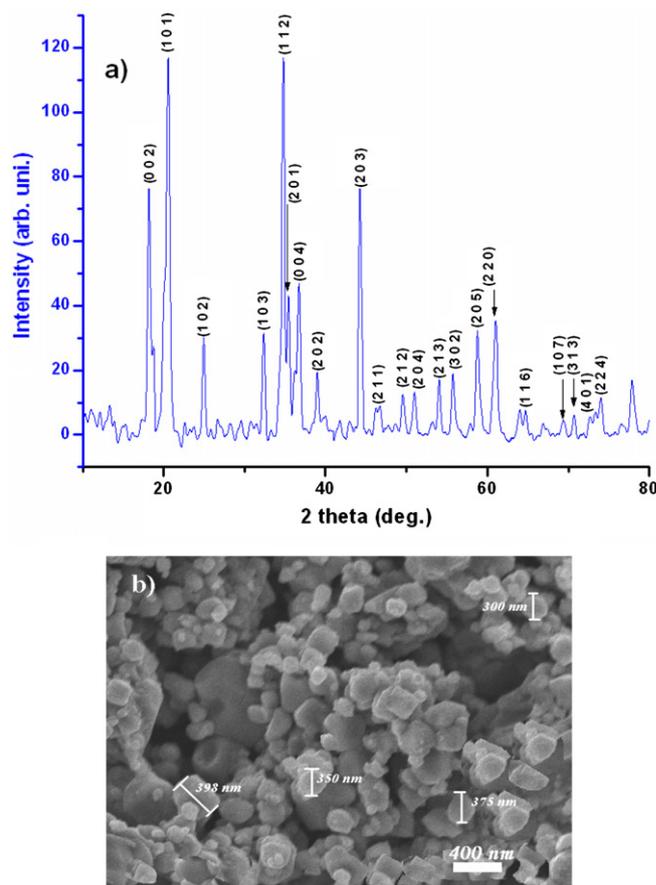


Fig. 2. (a) X-ray diffraction pattern and (b) Scanning Electron Micrograph of $\text{Li}_2\text{MgSnO}_4$.

articles or nano structured materials is possible only at temperatures below $500 \text{ }^\circ\text{C}$, regardless of the process of post grinding or the period of grinding. On the other hand, similar to our earlier report [8], an average particle size distribution of about $300\text{--}400 \text{ nm}$

is demonstrated in the present study also (Fig. 2b), which is evidenced by the XRD results as well. The presence of such kind of sub-micron sized particles exhibits the impact of UAC method in producing $\text{Li}_2\text{MgSnO}_4$ sample with preferred physical characteristics, thus indicating the possibility of realizing better electrochemical properties.

3.2. FT-IR and MAS ^7Li NMR studies

IR spectroscopy is an effective tool to detect the local cation environment of a lattice containing closely packed oxygen array. FT-IR signature of $\text{Li}_2\text{MgSnO}_4$ compound synthesized using UAC method is depicted in Fig. 3a. The vibrational frequencies at 441, 480, 1440 and 1597 cm^{-1} are attributed to the possible stretching and bending vibrational modes of Mg–O–Mg and O–Mg–O groups [10]. Similarly, the vibrational band observed at 676 cm^{-1} in Fig. 3a may be ascribed to the stretching vibration of Sn–O [8]. Since the FT-IR signals are recorded in the frequency range of 400–2000 cm^{-1} , the resonance frequencies of alkali metal cations (200–400 cm^{-1}) in their octahedral interstices (LiO_6) becomes out of scope of the present study.

The broad room temperature ^7Li NMR spectra recorded for the ^7Li nucleus ($I = 3/2$) of $\text{Li}_2\text{MgSnO}_4$ compound with a single in-

tense resonance at 0 ppm is displayed in Fig. 3b. Also, it is evident from Fig. 3b that the presence of a couple of spinning side bands is seen, due to the quadrupole broadening of the satellite lines. Since, the observation of an intense resonance at 0 ppm is the characteristic feature of a hexagonal type crystal lattice structure [11], the hexagonal crystallite structure of $\text{Li}_2\text{MgSnO}_4$ is confirmed using ^7Li NMR study, as deduced already from XRD results.

3.3. Electrochemical characterization charge–discharge studies

Generally, tin based anodes with larger particle size undergo pulverization rapidly during charge–discharge cycles due to abnormal volume expansion, resulting in a rapid drop in reversible capacity, upon cycling [12]. However, this pulverization is less extensive with the size reduced particles, and so it is postulated that electrodes with sub-micron sized particles may reduce the extent of pulverization and enhance the electrochemical behavior upon cycling [12]. In order to realize such reduced particle size only, UAC method has been deployed in the present study with a view to obtain better electrochemical properties from $\text{Li}_2\text{MgSnO}_4$ anode ultimately.

Voltage vs. capacity profile of $\text{Li}_2\text{MgSnO}_4$ anode cycled between 0–3.5 V at a constant current drain of 0.5 mA is depicted in Fig. 4a. The initial OCV of the $\text{Li}_2\text{MgSnO}_4$ anode (2.56 V) was found to rise

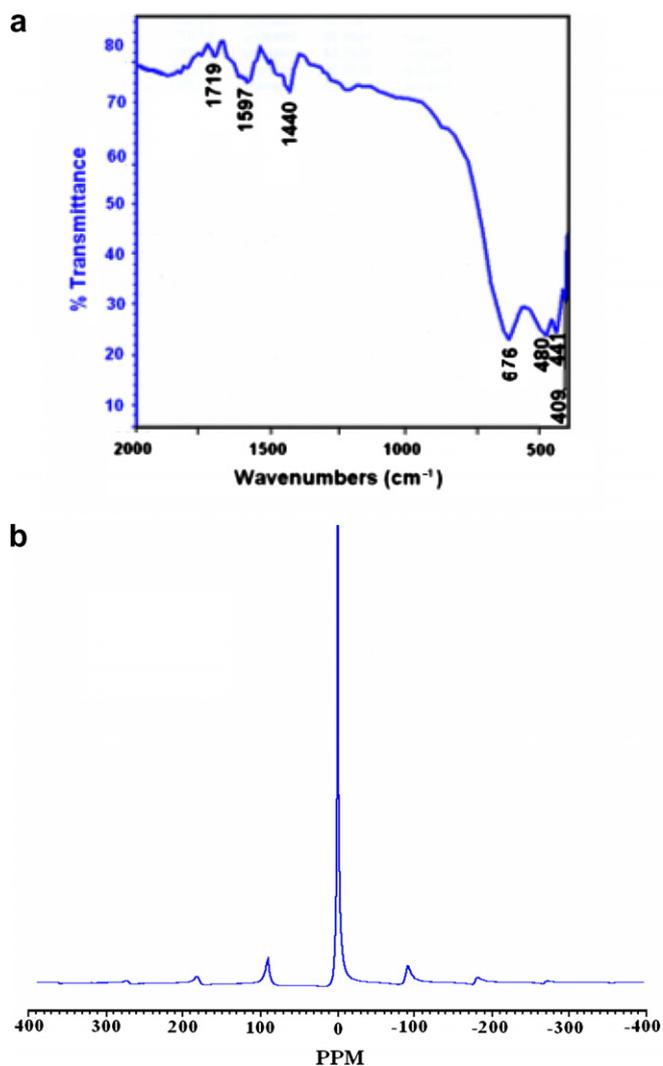


Fig. 3. (a) Room temperature FT-IR spectra and (b) MAS ^7Li NMR spectra of $\text{Li}_2\text{MgSnO}_4$.

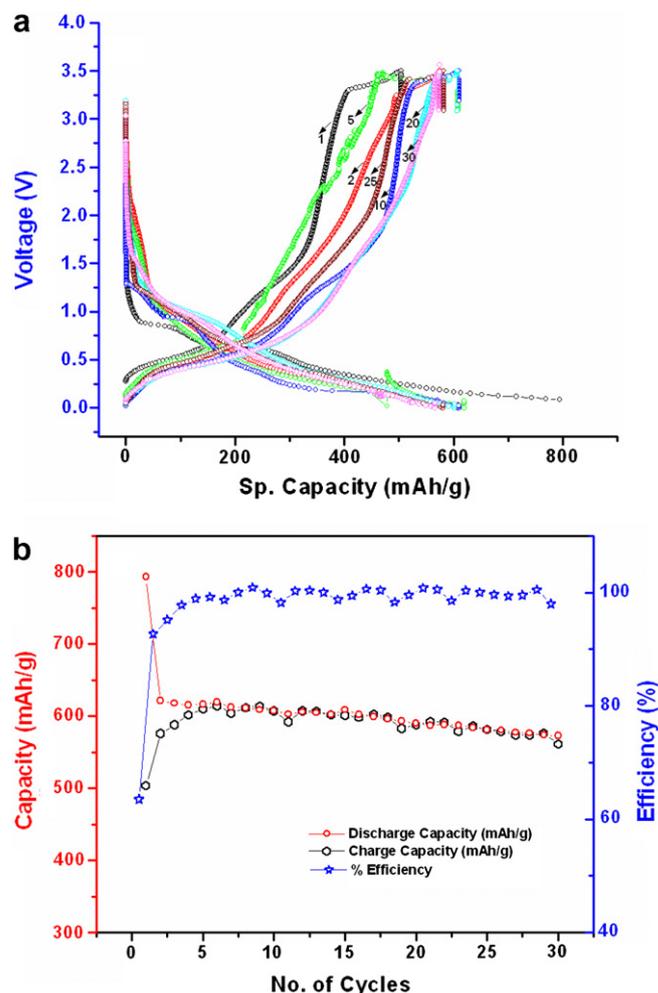


Fig. 4. (a) Voltage vs. capacity and (b) cycle life behavior of $\text{Li}_2\text{MgSnO}_4$.

to 3.18 V in the second cycle, which was raised further to the level of 3.24 V in successive cycles, as indicated in Fig. 4a. However, upon Li^+ intercalation, the potential of the $\text{Li}_2\text{MgSnO}_4$ anode dropped quickly to 1.0 V plateau region in the first cycle, which was moved further to a broader plateau around 1.2 V in the progressive cycles, due to the formation of Li_2O [13]. According to the reports of Behm and Connor et al. [14,15], the appearance of plateau region and the electrochemical behavior of Sn based oxides vary generally as a function of structure and the type of counter cation present in the matrix, respectively. As expected, the voltage vs. capacity behavior of the synthesized $\text{Li}_2\text{MgSnO}_4$ anode varies significantly from that of SnO_2 , which is an indication that the presence of excess of lithium and the Mg dopant are highly effective in addressing the irreversible capacity loss and structural stability problems of conventional anodes.

Further, it is understood from the observed specific capacity value of 794 mA h/g that a maximum utilization of ~ 7.2 lithium per formula unit is possible with the $\text{Li}_2\text{MgSnO}_4$ anode. Originally, the $\text{Li}_2\text{MgSnO}_4$ anode has displayed an initial discharge capacity (Q_{dc}) of 794 mA h/g against a charging capacity (Q_c) of 504 mA h/g, thus corresponding to an acceptable irreversible capacity loss of $\sim 20\%$ (Fig. 4b). On the other hand, the second cycle, Q_{dc} and Q_c values of $\text{Li}_2\text{MgSnO}_4$ anode were found to be 621 and 575 mA h/g, respectively, leading to an enhanced coulombic efficiency of 92.8%. Similarly, a steady state anode capacity of ~ 590 mA h/g, a value almost greater than 1.5 times than that of carbonaceous anodes with a slightly varying coulombic efficiency in the range of $\sim 90\%$ has been observed up to 30 consecutive cycles, which is the significance of the present study. In other words, despite the 20% initial irreversible capacity values, the progressive specific capacity values of $\text{Li}_2\text{MgSnO}_4$ anode was found to get stabilized upon extended cycling. Hence, it may be deduced that the $\text{Li}_2\text{MgSnO}_4$ anode of the current study has rendered apparently high specific capacity values, thus realizing the targeted aim of the study.

4. Conclusion

The physical and electrochemical behavior of a novel Sn based $\text{Li}_2\text{MgSnO}_4$ has been studied using various techniques including electrochemical charge–discharge studies. By choosing the well known combustion method with urea as the fuel (UAC method), fine internal dispersion of particles were obtained. A steady state capacity of ~ 590 mA h/g has been demonstrated by the $\text{Li}_2\text{MgSnO}_4$ anode material synthesized through the present study, thus qualifying the same as an alternative novel category anode with for use in rechargeable lithium batteries.

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