EFFECT OF THE AMOUNT OF WATER ON THE SYNTHESIS OF LiMn_2O_4 , USED AS CATHODE MATERIAL IN LITHIUM-ION BATTERIES

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ABSTRACT

LiMn_2O_4 with nanostructured morphologies possess rapid kinetics which is favorable for the intercalation of lithium ions in battery electrodes¹. In this work, we have studied the effect of varying the amount of water in the hydrothermal synthesis of nanostructured LiMn_2O_4 spinel. It was found that three distinct nanostructured morphologies of this compound are obtained when the volume of water used during the synthesis is varied. The powders were morphologically and structurally characterized using TEM, XRD, and BET yielding particle sizes ranging from 1 to 50 nm, with 90 % of the sample possessing a particle size of 21.7 nm. X-ray diffraction analysis show characteristic peaks and confirm the compound's identity and crystalline structure. Furthermore, the electrochemical behavior of this material in lithium ion batteries was studied. The results indicate that the electrochemical performance is strongly influenced by the size and shape of the $\alpha\text{-LiMn}_2\text{O}_4$ nanoparticles.

INTRODUCTION

In recent years, much research has focused on the synthesis of spinel LiMn_2O_4 as a potential candidate to replace lamellar oxides of Ni and Co which are often used as the cathode material in electronic devices such as lithium-ion batteries. Particularly interesting has been the work of the Tarascon's group using LiMn_2O_4 as cathode who reported capacity of 120 mAh when the cell were cycled at a rate of 0.1C or 0.2C in the voltage range 0.9-4.1V at temperatures of 25 and 55°C^{2,3}. The equilibrium properties of the cathode material can be affected by reduction of its size, which results in modification of the phase transformation behavior upon Li insertion/extraction. Reduction of the particle size of LiMn_2O_4 has been shown to change the mechanism of Li ion insertion from a two phase-transformation with a miscibility gap to a single-phase solid-state reaction⁴. A review about nanomaterials for rechargeable lithium batteries see ref 5.

In addition to these important features, LiMn_2O_4 with nanostructured morphologies possess rapid kinetics which are favorable for the intercalation of lithium ions in battery electrodes¹. Currently, lithium ions represent a large share in the development of electronic products, particularly in electric vehicles. However, a key problem limiting the marketing of batteries based on LiMn_2O_4 is the severe electrochemical capacity loss during cycling⁶. Two main factors are cited for causing the gradual capacity loss of LiMn_2O_4 : the Jahn-Teller distortion⁷⁻¹¹ and the dissolution of manganese to Mn^{2+} from surface particles into the electrolyte¹²⁻¹⁶.

The morphology and surface area of the particles has a profound effect on the electrochemical properties of a material. Through the synthesis of electrode materials with nanoscale dimensions, the electrochemical performance of many materials has been greatly improved¹⁷⁻²¹. In recent years, with the rapid development of nanostructure synthesis, electrode materials from mesoporous nanostructures have attracted much attention since it has been shown to provide a significant increase in rechargeable lithium ion battery performance with respect to energy density, life cycle, and speed performance²²⁻²⁹. This comes as a direct consequence of a greater specific surface area leading to a concomitant increase in current density. Moreover, the walls of the pores are much thinner which implies a shorter route for the transport of lithium ions, thereby increasing the diffusion of Li^+ ions. In addition, the pore walls can also act as a buffer layer to relieve the volume expansion of the electrode materials during lithiation/delithiation³⁰⁻³¹. The synthesis technique used in this work is complementary to ceramics, co-precipitation, freeze-drying, salts-hydrolysis, sputtering and spray pyrolysis techniques previously employed by our group in the synthesis of mixed oxides with spinel structure³³.

EXPERIMENTAL

The synthesis of ultrathin LiMn_2O_4 nanostructure particles was carried out in a two-stage synthesis. First, the $\alpha\text{-MnO}_2$ particles were synthesized. These were prepared using as precursor $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot (\text{NH}_4)_2\text{S}_2\text{O}_8$ and $(\text{NH}_4)_2\text{SO}_4$ all Aldrich reagents, mixed in a molar ratio of 2:2:1, respectively, placed within

a bomb Parr, using a solvothermal reaction at 140°C for 14 hours. The solvent used was a mixture of 40 mL octanol with x mL water, which is summarized in Table 1.

The next step in the synthesis was to obtain the LiMn_2O_4 phase using a solid state reaction between the $\alpha\text{-MnO}_2$ particles prepared in previous step, with the addition of LiOH in a molar ratio of 2:1, respectively, using ethanol as solvent. Subsequently, the precursor was heated to 400°C at a rate of 0.5°C/min, held at 400 °C for 30 min, then heated to 800°C at a rate of 5°C/min where the sample was then allowed to cool. The LiMn_2O_4 morphology was characterized by XRD, XPS, and TEM. For the electrochemical studies, the electrodes were prepared using a mixture of 80 wt% LiMn_2O_4 active material, 10 wt% conductive carbon black, and 10 wt% organic binder, PVDF. The as-prepared electrodes were tested against 2032 coin-type lithium cells. Electrochemical studies of charge/discharge were carried out in the potential range of 3.6 V to 4.5 V. In the following electrochemical results, all values are reported vs. the Li^+/Li couple.

Table1: Summary of the synthesis conditions.

x / Amount of H_2O (mL)	Symbology of samples
13.5	Li50
40.5	Li70
67.5	Li90

RESULTS AND DISCUSSION

The hydrothermal synthesis employed is based on a mixture of polar (water) and nonpolar (octanol) solvents, allowing the formation of micelles that can act as nano-reactors inside which the desired product is generated. To optimize the different experimental variables, it was first proposed to study the effect of the amount of water added to the reaction mixture on the morphology of LiMn_2O_4 nanoparticles, since the morphology directly influences the electrochemical behavior of the electrode paste. The LiMn_2O_4 nanoparticles were characterized by XRD, which produced the diffraction pattern shown in Figure 1. The diffraction pattern shows present an important background noise. Nevertheless shows the characteristic signals corresponding to planes of a spinel type structure with the cubic phase (space group Fd3m 227, No. 35-0782 JCPDS data). This was consistent for all LiMn_2O_4 samples synthesized, regardless of the volume of water used during synthesis.

The size and surface area of the particles formed were estimated using the BET method. These results are shown in Figures 2A and 2B. Figure 2A depicts the distribution curve of the particle size determined by adsorption of N_2 molecules. It was determined that 90% of LiMn_2O_4 particles have an average particle size of 21.7 nm. From the isotherm type I shown in Figure 2B, the surface area of the sample was determined to have an average value of 11.7 m^2/g . These same trends have been observed for all samples synthesized.

Fig. 1: XRD pattern of LiMn_2O_4 obtained for all samples synthesized.

Figures 3A, 3B, and 3C show TEM images obtained for samples Li50, Li70, and Li90, respectively. It can be seen that the morphology of the particles varies depending on the volume of water used during the synthesis. The sample Li50 exhibits a hexagonal laminar type morphology, whereas the Li70 sample is characterized by a mixture of hexagonal and wire-like forms. In the case of the Li90 sample, only nanowire-like structure is observed. Contrary

to the results obtained from XRD and BET analysis, where no significant discrepancies were observed as a result of the volume of water used during synthesis, a clear effect on the morphology is observed. The morphology also had a marked effect on the electrochemical behavior as shown below. The coin-type cells were cycled 200 consecutive times in a range between 3.6 V and 4.5 V versus a Li^+/Li at a capacity rate of C/5.

Fig. 2. BET analysis of LiMn_2O_4 . A) pore volume vs. pore diameter, B) volume of gas adsorbed vs. relative pressure.

Figures 4A, 4B, and 4C represent the potential response as a function of the specific capacity for samples Li50, Li70, and Li90, respectively. It can be observed during the first 10th charging cycles, a characteristic curve for the LiMn_2O_4 spinel appears which exhibits two pseudo-plateau around 3.9 V and 4.2 V. These plateaus have been assigned to the redox couple $\text{Mn}^{3+}/\text{Mn}^{4+}$. Furthermore, from Figures 4A and 4B, it can be seen that the specific capacity attains a maximum value of 7.5 mAh/g (at 4.5 V), after which it begins to decrease with cycling. This may be due to insertion/extraction process becoming less reversible, causing a polarization of the battery. This phenomenon is reflected

in Figures 4A and 4B by the increase in resistibility of the system. As a result, the amount of active material (Li^+ ion) available for transportation from one electrode to another decreases for each charge-discharge cycle. This same trend was observed for the cell prepared with Li90, with a notable difference. As shown in Figure 4C, a significant increase in specific capacity occurs during 200 cycles, reaching a specific capacity of about 200 mAh/g.

Because XRD and BET analyses yield similar conclusions in all cases, indicating an appropriate methodology for synthesis and product homogeneity, a discussion of the notable difference in the electrochemical behavior must be

centered with respect to the morphology of the active material. As mentioned, the sample Li90 was characterized principally by nanowire-like structures, which can act as a tunnel for the efficient intercalation of lithium ions. Further this should favor the diffusion compared to the other more amorphous structures.

Fig. 3: TEM imagen of α -LiMn₂O₄ as obtained from hydrothermal reaction. (A) Li50, (b) Li70 y (c) Li90.

Fig.4. Galvanostatic response of (A) Li50, (B) Li70 and (C) Li90 samples obtained at different charge cycles: (—) 1er cycle (---) 5 cycle (.....) 10 cycle (■) 50 cycle (○) 100 cycle and (▼) 200 cycle. In Figure 4d, the specific capacity obtained at 200 cycle is compared for each sample (▼) Li50, (○) Li70 and (■) Li90.

CONCLUSIONS

The present study shows a clear relationship between the amount of water added to the reaction mixture and the morphology of spinel LiMn_2O_4 powder obtained. This study also confirmed a direct correlation between the type of morphology and the oxide electrochemical properties. It was found that LiMn_2O_4 powder with nanowire morphology shows a higher specific capacity (200 *mAh/g*) than other morphologies.

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