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# Sonochemical assisted synthesis of $MnO_2$ nano-structure and its application in Li battery

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**Abstract:** γ-$MnO_2$ nanoparticles were synthesized by the ultrasonication irradiation of the solution prepared by mixing $MnSO_4$ and $(NH_4)_2S_2O_8$ solutions. The reaction conditions such as temperature and manganese sulphate concentration optimized to reach the smallest particle sizes and proper morphologies. The $MnO_2$ nanoparticles were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). $MnO_2$ samples prepared under optimized experimental conditions have lead particles in the range of 50-70 nm, as shown by SEM. The XRD results reveal that only γ-$MnO_2$ is formed under reaction conditions. The synthesized $MnO_2$ was used as the active cathode material in Li/$MnO_2$ battery. Discharge profiles of sonicator based cathode material and stirrer based one compared with each other and demonstrated that nanosized materials show higher capacities.

**Keywords:** Lithium battery; Nanostructure; Manganese dioxide; Ultrasonication.

## Introduction

Lithium metal is attractive as battery anode material because of its low atomic mass (6.94 amu), high electrochemical reduction potential (-3.04 V), high specific capacity (3.86 Ah/g), and good conductivity. Because of these outstanding features, enormous activity has been done by different research groups all around the world for the development of high-performance lithium batteries during the last two decades [1]. The first published interest in lithium batteries began with the work of Harris in 1958. The work eventually led to the development and commercialization of a variety of primary lithium cells during the 1970s [2]. Among the different types of lithium batteries, the primary Li/$MnO_2$ cell was one of the first Li cells to be commercialized. Since then it was a promising candidate for the demand of high specific energy and high power batteries applied in portable computers, portable power tools, and medical and industrial instruments [3].

The advantageous features of these cells include high nominal voltage (3 V), high specific energy (230 Wh/kg), high energy density (535 Wh/L), operation over a wide temperature range, superior shelf life, low cost.

Manganese dioxide can form different types of polymorphs such as α, β, γ, and δ. Among them, especially γ-$MnO_2$ has good electrochemical performances and is used in battery industries [4-6].

In this work we report on the synthesis of γ-$MnO_2$ nanoparticles by using sonochemical processing, and the characteristic of synthesized nanoparticles were investigated as cathode material in Li/$MnO_2$ primary cell.

## Experimental

*Apparatus*

A cylindrical two-walled glass cell with an interior volume of 300 ml was used for the sonication of the reaction solution. The solution temperature was kept constant by circulating water from a water bath (Optima, Tokyo, Japan). A multiwave ultrasonic generator (Sonicator-3000; Misonix, Inc., Farmingdale, NY, USA), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 600 W, was used for the ultrasonic irradiation. The ultrasonic generator automatically adjusted the power level.

*Synthesis of $MnO_2$ nanoparticles*

The redox reaction between manganese sulphate and ammonium peroxydisulphate was adopted for synthesis of γ-$MnO_2$. The oxidation proceeds in the presence of ultrasonication as follows:

$$MnSO_4 + (NH_4)_2S_2O_8 + 2H_2O \xrightarrow{)))} MnO_2 + (NH_4)_2SO_4 + 2H_2SO_4$$

100 mL of $MnSO_4$ and $(NH_4)_2S_2O_8$ solutions with definite concentrations were mixed together in reaction vessel and the solution was sonicated for 60 min. Then the solution was centrifuged at 7500 rpm for 5 min. A dark brown precipitate was obtained, washed several times with doubly distilled water and dried in an oven at 80 °C for 6 h.

The obtained powder was annealed in 350 °C in electrical furnace for 150 min to dehydrate and form HTMD (Heat Treated Manganese Dioxide).

The experiment was repeated using stirring instead of ultrasonication and the resulting precipitate was centrifuged, washed and dried, as described above.

*Sample characterization*

The crystalline phases of the synthesized samples were identified by X-ray diffraction (XRD) using Philips X'pert diffractometer) and Cu Kα radiation (k = 0.15418 nm). Morphological studies of synthesized samples were performed by SEM (Philips XL 30).

*Electrode fabrication and electrochemical measurements*

The positive electrode was fabricated by mixing the synthesized $MnO_2$ as the active cathode material, carbon active, and PTFE as binder with a weight ratio of 85:10:5. The resultant slurry was coated onto a nickel grid, pressed and then dried in the oven at 120 °C for 24 h. Cells were composed by stacking cathode against a Li foil as anode, separated by polypropylene separator soaked in electrolyte (1 M $LiClO_4$ in Propylene carbonate). Cell assembling was performed in an argon atmospheric glove box. Electrochemical impedance measurements were carried out by applying an ac signal with amplitude of 5 mV at the frequency varying from 100 kHz to 100 mHz. Data acquisition and analysis were done respectively using the electrochemical impedance software ZPlot and Zview.

The discharge experiments were examined with an Autolab-30 instrument in constant current densities, 5 and 10 $mA.cm^{-2}$ at 25 °C.

## Results and Discussion

The X-ray powder diffraction diagrams of γ-$MnO_2$ before and after heat treatment are shown in Fig. 1. As it is seemed, after heat treatment of $MnO_2$, the diffraction peaks of 2θ = 22° and 2θ = 36° disappeared and a new peak appeared around 2θ = 29°. Moreover, the peak around 2θ = 56° was clearly separated into two peaks which correspond to a transformation from the ramsdellite to the pyrolusite structure [7].

Fig. 2 shows SEM images of γ-$MnO_2$, synthesized by using stirrer. It can be seen from the pictures that the synthesized particles are aggregated and do not have a definite morphology. We investigated the effects of manganese sulphate concentration (0.05, 0.1, and 0.2 M) and temperature (40, 50, and 60 °C) on the particle size, morphology and phases of the prepared manganese dioxide. It has been found that the applied ultrasonic wave determines the particle size. Increasing the ultrasonic wave amplitude decreases the rate of particle growth [8].

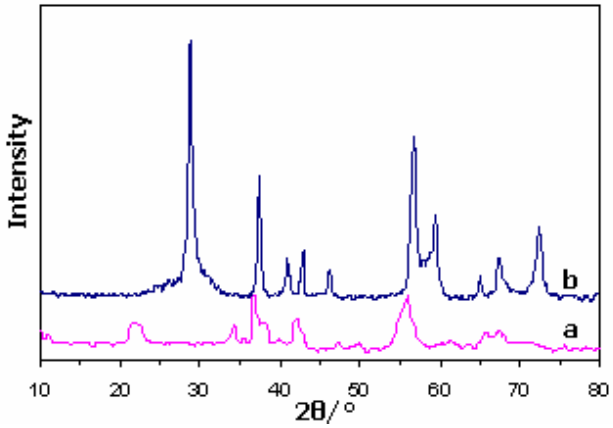


Fig. 1. X-ray powder diffraction patterns for γ-MnO2: (a) before heat treatment, (b) after heat treatment (350 °C for 150 min).

So in this work we have used constant ultrasonication power of about 60 W. In Fig. 3, the SEM pictures of Synthesized $MnO_2$ in presence of ultrasonication are shown. This sample is synthesized at 60 °C and 0.2 M concentration of manganese sulphate.

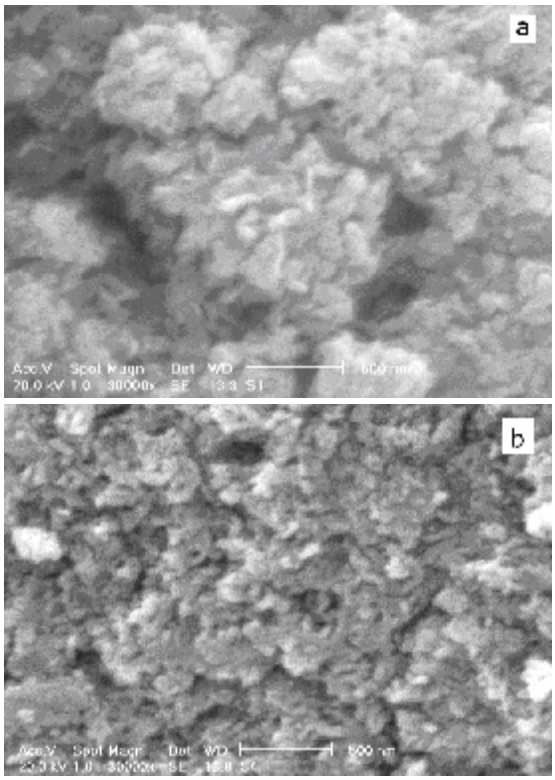


Fig. 2. SEM images of synthesized γ-$MnO_2$ by stirrer: (a) at 50 °C, (b) at 60°C.

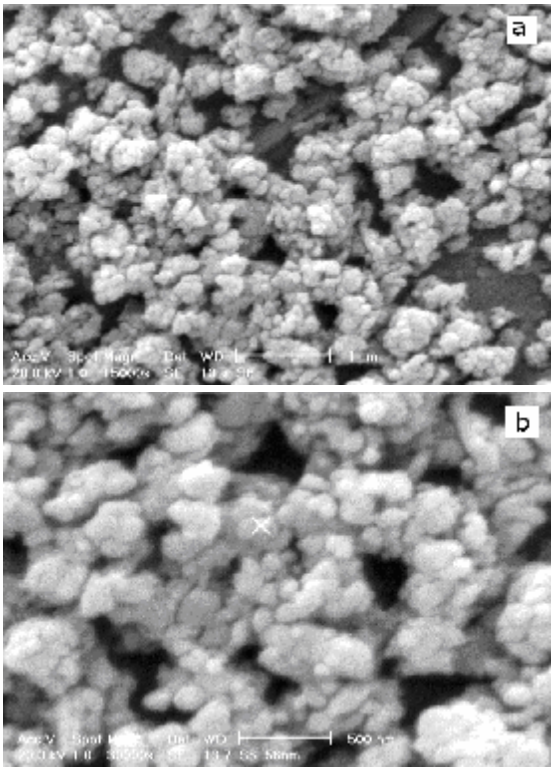


Fig. 3. SEM photographs of γ-MnO2 synthesized at 60 °C, 0.2 M MnSO4, and in presence of ultrasonication: (a) 15000x magnification, (b) 30000x magnification.

Fig. 4 shows the discharge profiles of γ-$MnO_2$, synthesized by stirrer and sonicator. As can be seen, the cell with stirrer based cathode material showed a discharge capacity of about 171.26 $mAhg^{-1}$ and the one with sonicator based cathode material showed a capacity equal to 213.48 $mAhg^{-1}$. The discharge capacity for sonicated material showed higher values compared to that of bulk γ-$MnO_2$. This is due to the large surface area of the nanosized electrode material.

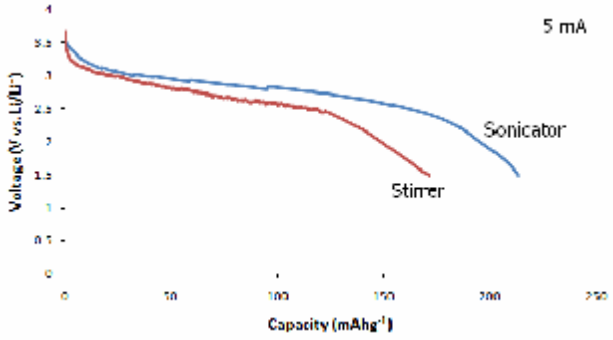


Fig. 4. Discharge profile of γ-$MnO_2$, synthesized by stirrer and sonicator at the constant current discharge of 5 mA.

Typical electrochemical impedance spectra of synthesized γ-$MnO_2$ by stirrer and sonicator at potential of OCV are shown in Fig. 5. The spectra display two arcs, one in high-frequency (HF) region which is related to solid electrolyte interface (SEI) film ($R_{SEI}$ coupled with SEI film capacitance), and the second arc in the medium-frequency (MF), corresponds to charge transfer resistance coupled with double capacitance. As it can be seen from these spectra, using the nanosized materials declined the charge transfer resistance. It can be attributed to the decreased diffusion path length due to the presence of small particles in the cathode layer, which makes it easier for Li ions to intercalate into the $MnO_2$ lattice.

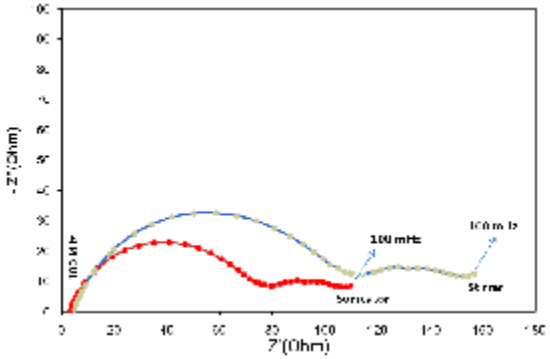

Fig. 5. Electrochemical impedance spectra of γ-$MnO_2$, synthesized by stirrer and sonicator.

## Conclusion

γ-$MnO_2$ nanoparticles are prepared by ultrasonication of reaction solution. The structure and microstructure of the nanoparticles were characterized by X-ray diffraction. The discharge profiles of sonicator based cathode material and stirrer based one were compared and demonstrated that using nanosized materials yield higher discharge capacities (213.48 $mAhg^{-1}$) and facilitate the intercalation of Li ions into $MnO_2$ lattice during the discharge cycle.

## Acknowledgment

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