UDC 621.355+544.65

HIGH-RATE $LiMn_2O_4$ CATHODE MATERIAL FOR Li-ION BATTERIES SYNTHESIZED BY MICROWAVE-ASSISTED CITRATE METHOD

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Spinel $LiMn_2O_4$ cathode materials of high-rate electrochemical performance were successfully synthesized using a microwave-assisted citrate technique. The influence of synthesis conditions on structural and morphological characteristics of the materials obtained were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The synthesized spinels deliver specific capacity up to 97 mAh/g at the 0.5 C rate and demonstrate excellent cyclability and high-rate capability up to 40 C.

In the technology of materials for lithium ion batteries (LIBs), considerable attention is paid to transition from micro- to nanosized electrode materials, which is associated with necessity to obtain higher specific characteristics during long cycling and high-rate operation [1, 2]. It is of special importance in terms of the energy required by powerful consumers such as electric vehicles.

Spinel $LiMn_2O_4$ is a promising cathode material for using in such LIBs [1, 2]. The choice of the optimal $LiMn_2O_4$ synthesis conditions is a significant factor for achieving high electrochemical characteristics of synthesized materials.

Using microwave (MW) irradiation for the synthesis of electrode materials becomes more and more popular [3]. On the first place, this is related to high speed and energy efficiency of such a process. The minimization of the duration of heating allows for obtaining nanosized materials.

In this work, MW heating coupled with the citrate synthesis method was employed for the synthesis of $LiMn_2O_4$. The influence of the duration of MW stage on structural and morphological characteristics of the materials obtained was investigated. The suitability of this method for the synthesis of $LiMn_2O_4$ for the high-rate LIBs was shown.

Research Methodology

Solutions of lithium nitrate, manganese nitrate and citric acid of 0.5-2M concentrations mixed in the molar ratio of 1:2:6 according to the procedure described in Refs. [4-6], were used to prepare $LiMn_2O_4$.

For MW synthesis, consumer Saturn ST-MW7154 and LG MS-1949W microwave ovens were used operating at 2.45 GHz frequency with maximum output power of 700 W. The mixture of solutions in a quantity of 20-30 ml was placed in MW oven and irradiated at a power of 120-600 W for 30-35 min. The precursor obtained was ground and then subjected to heating in the MW oven for 15-20 min at maximal operating power. After that the power was reduced to 420 W and the process was continued. The temperature was measured with an infrared contactless UT303A pyrometer after switching the oven off. Then $LiMn_2O_4$ samples were annealed at 700 °C for 24 h with constant heating and cooling rates equal to 5 and 2 °C/min, respectively.

The particle size and morphology were characterized by means of scanning electron microscopy (JSM 6700F, JEOL, Japan). The phase composition and structural parameters were studied using X-ray diffraction on a DRON UM1 diffractometer with CoKα radiation.

Electrochemical investigations were performed in CR2016 coin cells with Li anode on a home-made automated workstation. The cathode slurry consisting of 80.6 % of the working material ($LiMn_2O_4$), 11.4% of a conducting additive and 8 % of a poly(vinylidene difluoride) binder was coated on an aluminum foil with a doctor blade. Celgard 2500 was employed as a separator. The 1 M solution of $LiPF_6$ in a mixture of ethylene carbonate and dimethyl carbonate taken in the 1:1 mass ratio was used as an electrolyte. Galvanostatic investigations were performed in the 3.4-4.5 V potential range at different current densities expressed in C values (1C = 148 mA/g).

Results and Discussion

The X-ray diffraction patterns of $LiMn_2O_4$ samples obtained at various duration of MW pyrolysis are shown in Fig.1. All samples are well-formed crystalline $LiMn_2O_4$ phases (JCPDS 35-0782) regardless of MW exposure duration as indicated by respective peaks. Any impurities in synthesized samples have not been detected. The morphology of the synthesized $LiMn_2O_4$ samples is shown in Fig. 2.

Shortening of the thermal treatment by the use of MW pyrolysis allows at this stage for getting weakly agglomerated particles with the average size of less than 50 nm (Fig. 2a). Further annealing during 24 h at 700 °C leads to expected enlargement of particles; their average sizes increase to 50-60 nm (Fig. 2b). There is a marked growth in the particle size of spinel to 60-80 nm with increasing of exposure of MW pyrolysis to 2 (Fig. 2c) and 4 (Fig. 2d) min, which is associated with a higher rate of crystal growth, that occurs during MW heating. Nevertheless, all synthesized $LiMn_2O_4$ samples remain weakly agglomerated, which is important in terms of obtaining high electrochemical performances.

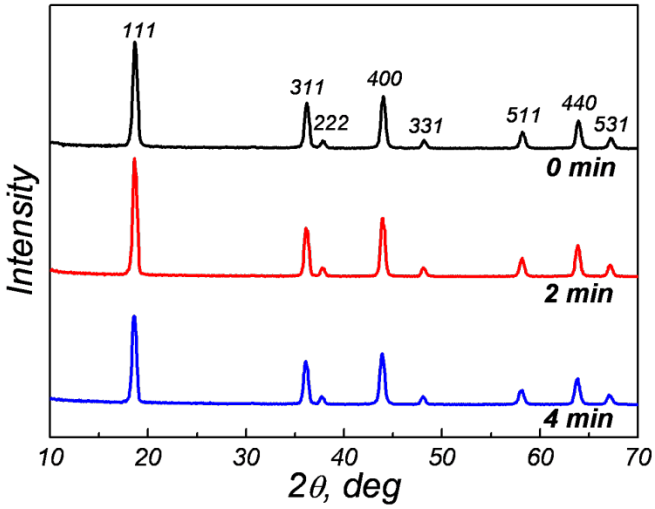

Figure 1. *XRD patterns of samples obtained at various duration of MW pyrolysis.*

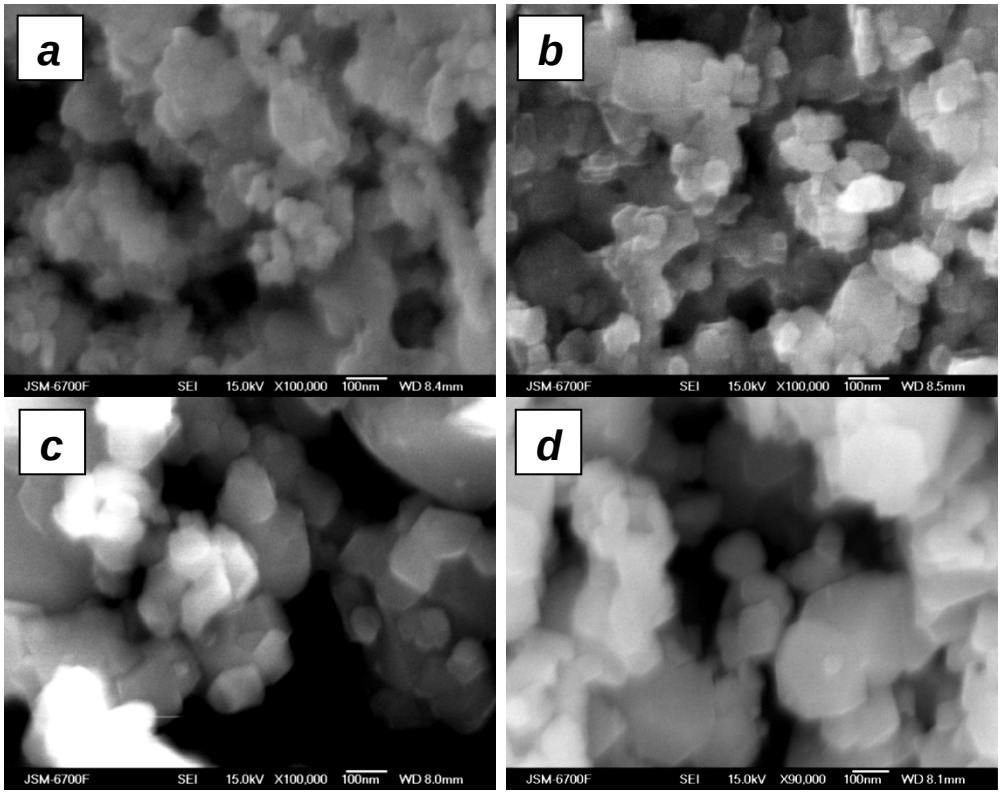

Figure 2. *SEM images of $LiMn_2O_4$ samples (a) MW treated for 15-20 min at 700 W; (b) same as (a) + annealing for 24 h; (c) same as (a) + MW treatment for 2 min at 420 W + annealing for 24 h; (d) same as (a) + MW treatment for 4 min at 420 W + annealing for 24 h.*

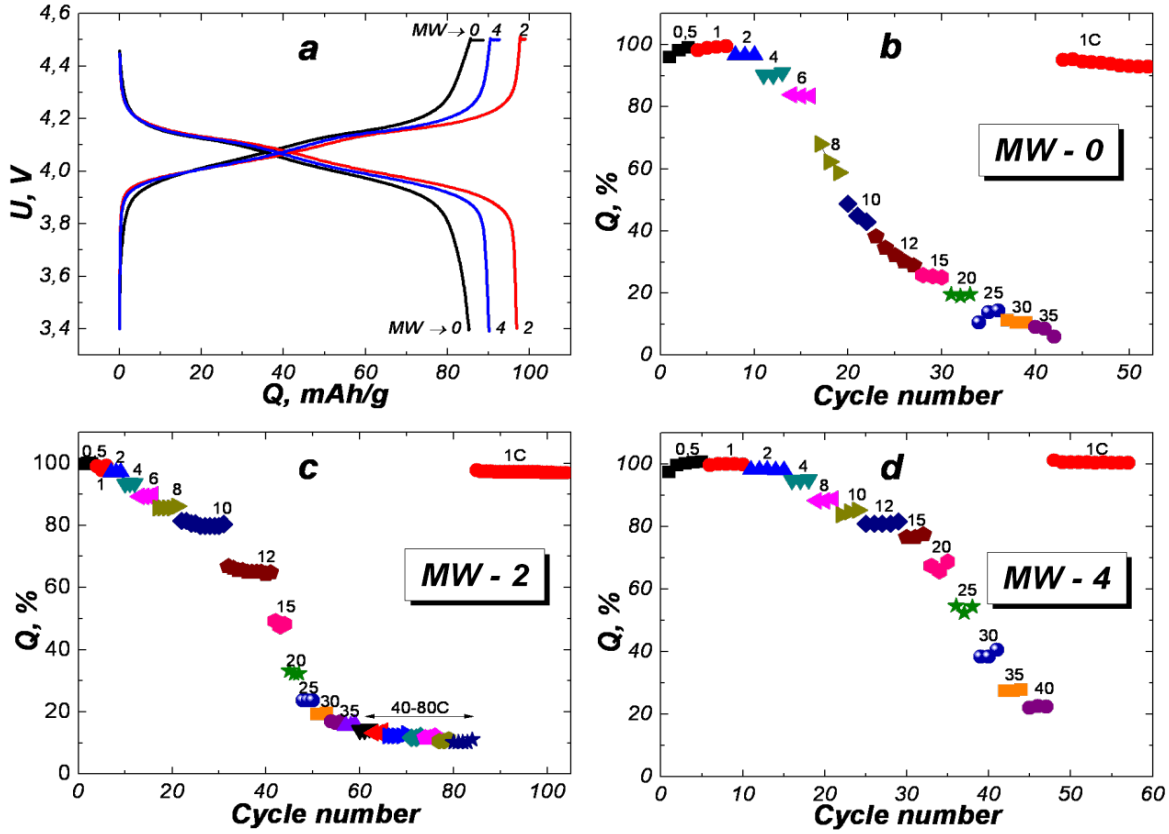

Figure 3. *Galvanostatic curves of the Li||$LiMn_2O_4$ cells on the third charge-discharge cycles at 0.5 C rate (a) and (b-d) dependences of the discharge capacity on cycle number at various current rates (charge rate of 1 C with a trickle charge at 0.1C). Numeric values mean discharge current densities in C units*

Fig. 3a shows the galvanostatic curves of the Li||$LiMn_2O_4$ cells on the third charge-discharge cycle at the minimal current load of 0.5 C. The specific discharge capacities obtained are quite low and their values are 85, 97 and 90 mAh/g for $LiMn_2O_4$ samples with MW duration of 0, 2, 4 min, respectively. However, the synthesized spinels demonstrate quite good high-rate capabilities, and the best among them is the sample with MW duration of 4 min (Fig. 3d). Its specific capacity at the 25 C rate is more than 50 % of its initial value, and upon the maximum discharge current of 40 C, the capacity equals to 22 %.

In addition, during control cycling at the 1 C current rate, this spinel demonstrate 100 % of initial specific capacity. This indicates on absence of degradation of the electrode materal and shows prospects for its application in high-power LIBs.

Conclusions

In the present paper, $LiMn_2O_4$ has been synthesized by using a microwave-assisted citrate method. It is shown that variation of the MW heating duration allows for obtaining $LiMn_2O_4$ of controllable dispersion with average particle size from 50 nm. Investigations of electrochemical characteristics show that in spite of quite low specific capacities not exceeding 97 mAh/g, the materials in question are able to sustain high current loads (up to 40 C) without degradation, which makes them promising for possible use in LIBs of new generation.

Acknowledgments

Thanks are due to Dr. S.A. Kirillov for discussions and advice.

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