Supporting information

Plasma-enhanced Low-temperature Solid-state Synthesis of Spinel LiMn₂O₄ with Superior Performance for Lithium-ion Batteries

Qianqian Jiang^a, Zhaoling Ma^b, Han Zhang^{a,*} and Shuangyin Wang^{b,*}

 ^a SZU-NUS Collaborative Innovation Center for Optoelectronic Science and Technology, Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China
^b State Key Laboratory of Chem/Bio-Sensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082, P. R. China
Corresponding Email: <u>hzhang@szu.edu.cn</u> (H. Zhang); <u>shuangyinwang@hnu.edu.cn</u> (S. Wang)

Experimental

Material synthesis. Lithium hydroxide selected as a lithium source and chemical manganese dioxide (CMD) as a manganese source with a stoichiometric molar ratio of 1:2 are mixed, then ball-milled for 2 h. CMD is prepared through a redox process using KMnO₄ and MnCl₂·4H₂O as reactants. Mn⁷⁺ in KMnO₄ is reduced, while Mn²⁺ is oxidized to Mn⁴⁺ in MnO₂ and no additional oxidants or reducing agents are added in this process. The mixture is introduced into the plasma-enhanced tube furnace. Plasma is generated by an RF power supply at 13.56 MHz, and the applied RF power is set at 200 W and the temperature of the tube furnace is set at 500 °C. The flow rate of oxygen is set at 3 sccm and the total pressure in the chamber is kept at 66 Pa. The reaction takes about 20, 30, and 40 mins, respectively. The spinel LiMn₂O₄ synthesized by the above process is referred as PLA-LMO-20, PLA-LMO-30, and PLA-LMO-40, respectively. For comparison, the conventional spinel LiMn₂O₄ was also prepared by the conventional annealing method at 800°C for 4 h, and the resultant sample is referred to LMO-40.

Characterization: X-ray diffraction was used to characterize the resultant samples. XRD analyses were executed on a Siemens D500 diffractometer with a Cu K α source (40 kV, 200 mA); scan range from 10° to 80°. The morphology and particle sizes of the samples were characterized by the TEM (100CX-II made by JEOL, Tokyo, Japan). The morphology was characterized by SEM (Hitach S-4800, Japan). The particle size distribution of the as-obtained samples in the SEM images was analyzed using software ImageJ 1.46 (National Institutes of Health, USA). Cyclic voltammetry (CV, AUT85794, Netherland) experiments were conducted from 3.0 to 4.5 V at a scan rate of 0.1 mV/s.

Electrochemical measurements: The electrochemical characterization of the synthesized powder was performed into coin-type cell (CR2032) using lithium as counter-electrode in the glove box. For the fabrication of the electrode, $LiMn_2O_4$ was mixed with conductive acetylene black and polyvinylidene

fluoride (PVdF) binder. The electrode was composed of 80 wt% active material, 10 wt% polyvinylidene fluoride binder, and 10 wt% Super P carbon black, and N-methyl-2-pyrrolidone (NMP) was used as the solvent. After coating the mixed slurry onto Al foil, the electrode was dried at 120°C for 12 h and then roll-pressed. The electrolyte consists of $1.0 \text{ mol} \cdot \text{L}^{-1} \text{LiPF}_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) in a 1:1 (w/w) ratio. All cells were fabricated identically and initially cycled at 0.2 C.

Fig. S1 shows the X-ray diffraction (XRD) patterns of PLA-LMO-20, PLA-LMO-30, and PLA-LMO-40. In the XRD patterns of PLA-LMO-20 in Fig.S1a, the main peaks were attributed to the spinel type structure of the LiMn₂O₄, while little MnO₂ signals were also detected indicating that longer time (30 mins) is necessary to completely converse the mixture to the final product, LiMn₂O₄. Moreover, MnO₂ diffraction peaks could be seen from Fig.S1 (a). The diffraction peaks of the sample b and c at 18.66°, 36.30°, 38.06°, 38.06°, 44.1°, 48.3°, 58.21°, 63.80° and 67.38° were indexed to the the formation of spinel LiMn₂O₄ and those were close to those reported in the JCPDS dates (JCPDS No.35-0782), which indicates all the diffraction peaks of the two XRD patterns can been indexed to a pure phase centered cubic which is in good agreement with that reported previously ¹⁻³, thus demonstrating the high purity and good crystallinity of the as-synthesized spinel LiMn₂O₄ with the plasma time 30 min and the tube furnace temperature 500 °C which is lower than those reported with conventional thermal annealing method^{4, 5}. In order to determine the appropriate plasma time, the other physical and electrochemical characterization are investigated.



Fig. S1 XRD patterns of LiMn₂O₄ with different plasma treatment times

From Fig. S2, lots of small polyhedral particles were received, which indicated the shape of the spinel LiMn₂O₄. Although this product of the sample PLA-LMO-20 had much smaller particle size was about 380 nm, some quasi-spherical particles could also be observed in Fig.S2a. When the plasma time was 30 min, almost all the particles with the morphology of polyhedral particles were synthesized with the particle size about 400 nm. It illustrated the spinel LiMn₂O₄ powder was produced under this plasma time with high purity. With prolonged plasma time, it appeared the aggregation between the LiMn₂O₄ particles occurred with slightly larger particle size (Fig.S2c). Based on the SEM and XRD analysis, it seems that the spinel LiMn₂O₄ product synthesized with the reaction time of 30 mins has the best quality. Therefore, the LiMn₂O₄ powders produced by the plasma-enhanced low temperature method with narrow size distribution and uniform morphology are expected to achieve better electrochemical performance in batteries.



Fig. S2 SEM photographs of LiMn₂O₄ from different plasma times

The particle size distribution of the as-obtained samples in the SEM images was further analyzed using software ImageJ as shown in Fig. S3. The average particle size of sample PLA-LMO-30 was 400 nm. The proper particle size of the sample PLA-LMO-30 would contribute to good electrochemical properties ^{6,7}. PLA-LMO-30 exhibited particle size of 300-500 nm with distribution rate about 95.91%. As for LMO-4h, only 55% of the particles displayed within the range of 400-600 nm in size. The rest particles were too small or too large, which decreased the electrochemical performance of the synthesized LiMn₂O₄ samples. Compared the particle size distribution of the two sample it was found that the plasma-enhanced low-temperature solid-state approach could not only synthesize the spinel LiMn₂O₄, but also the products have the uniform particle size, which is of great importance to the electrochemical performance of the material.



Fig. S3 Particle size distribution of the synthesized LiMn₂O₄ samples: (a) PLA-LMO-30, (b) LMO-4h

The typical TEM images (Fig.S4) of all the $LiMn_2O_4$ synthesized by the plasma enhanced strategy showed that the products were the uniform distribution of spinel particles. But from the typical TEM image (Fig. S4a) of $LiMn_2O_4$ synthesized with the plasma time of 20 min, we could see the morphology of partial particles with the spherical morphology, which suggested there still might be some raw material (MnO₂) in the product as detected by the XRD pattern (Fig S1). We could clearly see that the morphology of the particle PLA-LMO-30 was polyhedral, which indicated the pure spinel $LiMn_2O_4$ was synthesized. With the increase of the plasma time, the values of average particle sizes became large and agglomerates slightly. At the same time, the size of the particle became larger. The average particle size of PLA-LMO-20 was 380 nm, when plasma time extended to 30 min, the size was 400 nm. When the time was increased to 30 min, the size was 650 nm.



Fig. 4S Transmission electron microscope (TEM) images (a, b and c) of LiMn₂O₄ from different plasma time: a) PLA-LMO-20, b) PLA-LMO-30, c) PLA-LMO-40

The initial discharge and cycling performance tests for LiMn₂O₄ samples were plotted as shown in Fig. S5a. The Fig. S5a showed the initial discharge curves of LiMn₂O₄ from different plasma times. The sample PLA-LMO-30 had the highest initial discharge capacity of 129.8 mAh/g compare with the other two samples, which indicated the high first discharge capacity of LiMn₂O₄ might due to the more synthesize spinel LiMn₂O₄ with the appropriate plasma time. The initial discharge of PLA-LMO-20 is 110.6 mAh/g. When extended the plasma time to 40 min, the initial discharge capacity for the LiMn₂O₄ decreased into 115.5 mAh/g, At the same time, the consequence of the initial discharge was consistent to the SEM result that too long plasma time would lead to the agitation of the sample which was bad for the electrochemical performance of material. In order to further confirm the best plasma treatment time, the material was synthesized with the plasma time of 60 min. The initial discharge of this sample was showing in Fig.5Sa, which only had the initial discharge of 96.3 mAh·g⁻¹, which was much lower than that of sample PLA-LMO-30. This result illustrated that prolong the plasma treatment time was not only bad for the electrochemical performance of material, but also leaded to much energy consumption.

The discharge cycle performance of the three samples was shown in Fig. S5b. Capacity fading was observed after several charge/discharge cycles in three cases, but the retention of the discharge for the sample with the plasma time of 30 min was better than any other samples. It could be seen from Fig.4B that sample PLA-LMO-30 showed an average capacity loss of 0.059 mAh/g per cycle, in other words, after 100 charge/discharge cycles, the discharge capacity of it maintained 95.46% of its initial capacity. However, the sample with the plasma time of 20 and 40 could only respectively contain 73.16 % and 83.46% after 100 cycles of their initial discharge capacities. These results clearly indicated that the LiMn₂O₄ obtained with the plasma time of 40 min could be used as a promising cathode material in lithium ion batteries.



Fig. S5 Electrochemical performance of the samples with different plasma treatment times: (a) Initial discharge curves at 0.2 C the voltage range of 3.0 - 4.3 V; (b) Cycling performance at 0.2 C with 100 cycles

The corresponding data obtained from the CV curves (Fig.4a) were listed in Table S1. The two oxidation potentials were recognized by E_{O1} and E_{O2} whereas the two reduction potentials were identified by E_{R1} and E_{R2} . The separation of peak potentials for PLA-LMO-30 (0.09/0.10 V) were much smaller than that of LMO-4h (0.16/0.13 V), which indicated that the polarization of PLA-LMO-30 was smaller than that of LMO-4h and lithium inserting reaction in PLA-LMO-30 was in a more equilibrium state and behaved more like a Nernst system. Compared to LMO-4h, this feature put PLA-LMO-30 in a better position as the positive electrode material for a better cycling performance.

| Samples | Potential Values/mV | | | | | | | |
|------------|---------------------|-----------------|-----------------|-----------------|------|-------------|--|--|
| _ | E ₀₁ | E _{O2} | E _{R1} | E _{R2} | ΔΕ1 | $\Delta E2$ | | |
| PLA-LMO-30 | 4.09 | 4.18 | 4.00 | 4.08 | 0.09 | 0.10 | | |
| LMO-4h | 4.08 | 4.20 | 3.92 | 4.07 | 0.16 | 0.13 | | |

Table S1 Data of the electrochemical parameters obtained from CV curves at a scan rate of 0.1 mV/s.

Note: E_{O1} and E_{O2} represent two oxidation potentials, and E_{R1} and E_{R2} represent two reduction potentials. Potentials vs. (Li/Li⁺)/mV.



Fig. S6 Mn 2p XPS core peaks of (a) sample LMO-4h; (b) PLA-LMO-20

In to order confirm the presence of Mn in the two sample synthesized from different methods, XPS core peak were shown in Figure S6. The results were fitted by XPS Peaking Fitting 4.1 software. The two samples were divided into four peaks, and each spectrum was deconvoluted based on MnO_2 and Mn_2O_3 spectral lines, which is consistent with those reported in the literature ⁸. For the two sample, the separation of observed binding energies between the $Mn2p_{3/2}$ and $Mn2p_{1/2}$ is ~ 11.6 eV which was in good agreement with published data ⁹. However, the observed binding energies of the $Mn2p_{3/2}$ in sample PLA-LMO-30 was 642.48 eV, which was a little larger that that of sample LMO-4h (642.31 eV). This results was in good consist with the XRD data suggesting the decrease in the lattice parameters and the stable structure.

The electrochemical performance for spinel $LiMn_2O_4$ from literature were shown in Table S2. From the data on the table, we can clearly find that the electrochemical performance is superior to that samples synthesized from different methods, indicating the plasma-enhanced low-temperature solid-state approach is excellent in synthesizing spinel $LiMn_2O_4$ than the others.

Table S2. Representative electrochemical performance for LiMn₂O₄ spinel from literature. *not mentioned

| Method | Best Reaction | Initial | Cut off | Capacity | Refs |
|---------------------------------------|--|-----------|------------|-------------------|---------------------|
| | Temperature and time | Discharge | condition | retention (%) | |
| | | (mAh/g) | (V) | | |
| Solid State | 750 ℃ 24 h | 115.2 | 3.0 - 4.3 | About 86.28 | 2002-8 |
| Reaction | | | | | |
| Solid State | 500 °C 6 h, | 122.8 | 3.2 - 4.3 | 94.54 (10cycles) | 2013-9 |
| Reaction with γ - | 900 ℃ 15 h | | | | |
| Mn ₃ O ₄ as the | | | | | |
| precursor | | | | | |
| Combustion | 800 °C 24 h | 127.9 | 3.3 - 4.35 | About 77.01 | 1999- ¹⁰ |
| Solid-phase | 1100 °C 5 h (Mn ₃ O ₄), | 127.1 | 3.4 - 4.3 | 89.142 (10 | 2014-11 |
| Reaction from | 500 °C 6 h, | | | cycles) | |
| porous spherical | 800 °C 24 h | | | | |
| Mn ₃ O ₄ | | | | | |
| Solid State | 800 °C 12 h | 112.9 | 3.2 - 4.25 | 93.27 (10 cycles) | 2015-12 |
| Reaction with | | | | | |
| industrial grade | | | | | |
| Mn ₃ O ₄ | | | | | |
| Sol-gel | 750 ℃ 120 h | 122.6 | 3.5 - 4.5 | * | 2000-13 |
| Hydrothermal | 700 ℃ 8 h | 93.5 | * | * | 2013-14 |
| Reaction | | | | | |
| Self-combustion | 400 ℃ 1 h | 116 | 3.0 - 4.2 | 81.29 | 2004-15 |
| Reaction | 800 °C 2h | | | | |
| (SCR) | | | | | |
| Facile | 750 ℃ 10 h. | 128 | 3.3 - 4.35 | * | 2013-16 |
| Topochemical | | | | | |
| Route | | | | | |

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