

Optimizing the rate performance and cycle life of $\text{Li}_2\text{MTi}_3\text{O}_8$ (M=Mn, Co, Zn)/CNTs for lithium-ion battery anodes by constructing one-dimensional carbon-based hybrid structure

Mao Qian, Yakun Tang, Lang Liu*, Yue Zhang, Yang Gao, Xiaohui Li, Ting Liu

Preparation and sulfonation of polymer nanotubes: All reagents are commercially usable with AR grade and used without further purification. The detailed process of polymer nanotubes (PNTs) and SPNTs can be seen in the reported literature.^{S1}

Synthesis of CNTs with embedded $\text{Li}_2\text{MTi}_3\text{O}_8$ (M = Mn, Co, Zn,) nanoparticles: Firstly, 70 mg SPNTs was dispersed in 7 mL ethanol with ultrasound for 30 min. Secondly, 400 mg LiNO_3 was added until dissolved completely. Thirdly, 3 g TBT was added to the above solution and stirred for 12 h at room temperature to allow a saturated adsorption of gel into the walls of SPNTs. After centrifugation, the residue was dipped by tissue paper to suck excess liquid. The dried powders and 0.0002 mol $\text{M}(\text{CH}_3\text{COO})_2(\text{M} = \text{Mn, Co, Zn}) \cdot n\text{H}_2\text{O}$ were mixed and grind in an agate mortar with for 15 min at room temperature. Finally, the precursor was calcined at 700 °C for 3h in N_2 , and acquiring $\text{Li}_2\text{MTi}_3\text{O}_8$ (M= Mn, Co, Zn) nanoparticles with different particle size embedded in carbon nanotubes, named LMT/C, LCT/C and LZT/C.

Materials characterization: Physical phase of samples was tested by X-ray diffraction (XRD) of Smart Lab SE. The surface microstructure and morphology of samples were researched by HITACHI SU-4800 scanning electron microscope (SEM) and HITACHI JEM-2100 transmission electron microscope (TEM). The content of carbon was analyzed by HITACHI STA7300 thermogravimetric analysis (TGA) at a heating rate of 10°C min⁻¹ from 25 °C to 800 °C in air.

Electrochemical characterization: 2032 coin cells were employed to test electrochemical performances of the three samples, and then lithium metal was served as counter electrode. The mixture containing active materials, acetylene black and polyvinylidene fluoride with a weight ratio of 8:1:1 were dissolved in *N*-methyl-2-pyrrolidone to form slurry, which were evenly casted on copper foil and dried at 110°C one day in vacuum. And the mass loading of electrodes is 0.5-0.8 mg. Cells were assembled in an argon-filled glove box with Celgard 2325 membrane as the separator and LiPF_6 (1 M) in ethylene carbonate/diethyl carbonate (1:1 vol) as the electrolyte. Electrochemical testing and cyclic voltammetry (CV) measurement of the cells were tested between 0.01 and 3 V.

Table S1 Comparison of electrochemical performance for electrode materials

Material	Current density (A g ⁻¹)	Cycle number	Capacity (mA h g ⁻¹)	Voltage (V)	Ref.
$\text{Li}_2\text{MnTi}_3\text{O}_8/\text{C}$	0.1C	50	240	0.02-3	S2
$\text{Li}_2\text{MnTi}_3\text{O}_8/\text{C}$	2C	100	171	0.02-3	S2
$\text{Li}_2\text{ZnTi}_3\text{O}_8@\text{C}$	2	200	150	0.02-3	S3
$\text{Li}_2\text{ZnTi}_3\text{O}_8@\text{C}@La_2O_3$	2	200	180	0.02-3	S3
$\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$	0.5	600	230	0.01-3	S4
$\text{Li}_2\text{ZnTi}_{2.95}\text{Nb}_{0.05}\text{O}_8/\text{C}$	0.1C	50	248	0.05-3	S5
$\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$	0.5	600	200	0.02-3	S6
$\text{Li}_2\text{Zn}_{0.93}\text{Mo}_{0.07}\text{Ti}_3\text{O}_8@\text{G}$	2	300	210	0.02-3	S7
LZTO@RGO	1C	100	200	0.05-3	S8
$\text{Li}_2\text{ZnTi}_3\text{O}_8@\text{GNS-CNT}$	2	300	180	0.02-3	S9
$\text{Li}_2\text{ZnTi}_3\text{O}_8@\text{MWCNTs}$	5	600	180	0.05-3	S10
$\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}\&\text{N}$	1.5	400	229	0.05-3	S11
$\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{G}$	2	300	170	0.01-3	S12

References

- S1. H. J. Zhou, L. Liu, X. Wang, F. X. Liang, S. J. Bao, D. M. Lv, Y. K. Tang and D. Z. Jia, *J. Mater. Chem. A*, 2013, **1**(30), 8525.
- S2. L. Yang, X. Y. Zhang, Y. Li, F. Hao, H. S. Chen, M. Yang and D. N. Fang, *Acta*, 2015, **155**, 272-278.
- S3. Z. H. Meng, S. H. Wang, H. W. Wang, L. J. Wang and S. Wang, *RSC Adv.*, 2019, **9**(36), 20618-20623.
- S4. J. L. Qin, H. L. F. Zhu, N. Lun, Y. X. Qi and Y. J. Bai, *Carbon*, 2020, **163**, 297-307.
- S5. N. Firdous, N. Arshad and P. Norby, *Energy Fuels*, 2020, **34**, 14968-14974.
- S6. H. Yang, H. L. Zhu, Y. X. Qi, N. Lun and Y. J. Bai, *J. Mater. Sci.*, 2020, **55**, 15538-15550.

- S7. S. Wang, Y. F. Bi, L. J. Wang, Z. H. Meng and B. M. Luo, *Electrochim. Acta.*, 2019, **301**, 319-324.
- S8. S. Yildiz and H. Sahan, *J. Electrochem. Soc.*, 2019, **166**(10), A2002-A2012.
- S9. S. Wang, L. J. Wang, Z. H. Meng and R. Xun, *J. Alloys Compd.*, 2019, **774**, 581-585.
- S10. C. Y. An, C. H. Li, H. Q. Tang, T. Liu and Z. Y. Tang, *J. Alloys Compd.*, 2020, **816**, 152580.
- S11. C. Chen, Z. Y. Li, and B. M. Xu, *Mater. Chem. Phys.*, 2020, **245**, 122718.
- S12. S. Wang, L. J. Wang, Z. H. Meng and B. M. Luo, *RSC. Adv.*, 2018, **8**(55), 31628-31632.