

Carbon and spinel LiMn_2O_4 hierarchical structures for high rate Li-ion batteries

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The introduction of the first commercially produced Li-ion battery by Sony in 1990 sparked a period of unprecedented growth in the consumer electronics industry [1,2]. Now, with increasing efforts to move away from fossil-fuel-derived energy sources, a substantial amount of current research is focused on the development of an electrified transportation fleet. Unfortunately, existent battery technologies are unable to provide the necessary performance for electric vehicles and plug-in hybrid electric vehicles at a competitive cost [3]. The cost and performance metrics of current Li-ion batteries are mainly determined by the positive electrode materials.

For the last two decades, there are a lot of studies have been done to develop low cost, environmental friendly facile fabrication process for the preparation of high performance nanostructured electrode materials and to fully understand the influence factors on the electrochemical performance in the application of lithium ion batteries [4-6]. Spinel LiMn_2O_4 based cathode electrode materials are one of the most promising alternative cathode materials for Li-ion power batteries, which is due to the advantages such as low cost, good environmental compatibility, and good thermal stability. Spinel LiMn_2O_4 has a cubic structure with the space group of $Fd3m$ symmetry in which lithium and manganese ions occupy tetrahedral (8a) sites and octahedral (16d) sites, respectively, within a cubic close-packed oxygen array with oxygen ions in 32e sites. In addition, it has been reported that the charged LiMn_2O_4 material shows obviously higher thermal stability in the electrolyte at high temperature than LiCoO_2 and LiNiO_2 . The good thermal stability of spinel LiMn_2O_4 is beneficial for its use in high power batteries [7]. Although many reports revealed that the LiMn_2O_4 based electrodes offer a potentially attractive alternative to the presently commercialized LiCoO_2 , there are still some issues prohibiting LiMn_2O_4 from commercialization is its severe capacity and cycling performance fading during cycling [8, 9]. Capacity fading mechanisms of spinel LiMn_2O_4 electrodes may be summarized as follows; (i) phase transition from cubic to tetragonal phase upon 3 V cycling, (ii) micro-crack formation on the surface of the cathode material after electrochemical cycling, (iii) formation of a surface electrolyte interface (SEI layer) on the surface of the electrodes after electrochemical cycling and (iv) formation of oxygen vacancies due to the dissolution of manganese in the electrolyte. As it is well known from the literature data, the cations applied in substitution are mostly based on monovalent, divalent and trivalent metal ions which could increase the average oxidation state of Mn ions and suppress the Jahn Teller effect, resulting in better cycling performance compared with pristine LiMn_2O_4 in the 4 V region. Substituting Mn with other metal ions has been used as an important approach to improve cycling performance of spinel materials. Multiple dopants including inactive ions such as Mg, Al, and Zn, first row transition metal ions such as Ti, Cr, Fe, Co, Ni, and Cu and rare earth metal ions such as Nd and La have been extensively investigated [10-21].

Another way to improve the electrochemical performance of the LiMn_2O_4 based cathode material is to modify the cathode surface with materials inert against the electrolyte. Surface modification with several metal oxide structures such as Al_2O_3 , ZnO, ZrO_2 , CeO_2 , show lower capacity fading in the first cycle and higher discharge capacity than pristine samples [22-25]. In recent studies, AlF_3 and CaF_2 are also considered as one of the most promising coating materials to improve electrochemical performance of LiMn_2O_4 based cathode since it is believed to suppress HF corrosion during charging and discharging

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processes. Although these strategies usually cause decrease in capacity via lengthening the pathways of Li^+ ions during charging and discharging processes, surface modifications were shown to substantially improve the cyclability performance of batteries by suppressing the HF corrosions. On the other hand, the reduction of particle size is a promising strategy since it can alleviate these detrimental effects (except for the case of dissolution of Mn) and also improve the electrochemical performance of LiMn_2O_4 [26-27].

Nanostructuring battery electrode materials have been shown to enhance power performance due to the large surface-to-volume ratio that allows for a large electrode-electrolyte contact area. Nanowires or nanorods are particularly attractive. Recently we have demonstrated examples of using Si and Ge nanowires as ultrahigh capacity anode materials [28,29]. The nanowire or nanorod morphology not only has a large surface-to-volume ratio but also provides efficient one-dimensional electron transport pathways and facile strain relaxation during battery charge and discharge.

In this review, a systematic study has been explored in order to understand the surface modification and carbon reinforcing on the electrochemical properties of LiMn_2O_4 cathode electrodes. The synthesis of carbon- LiMn_2O_4 electrodes with sol-gel, sputter deposition, vacuum filtration and microwave hydrothermal carbonization techniques are studied in detail. The electrochemical features are discussed in the core-shell and co-axial structured negative electrodes in the half-cells. Studies are concentrated on the nanocomposite structures of carbon coated silicon nanoparticles reinforced with carbon, carbon nanotubes and graphene.

References

- [1] Andreasen, Ashworth, Remo and Koer, International Journal of Hydrogen Energy, **33**,7137 (2008).
- [2] Garcia, Lins, Taro, Matencio, Domingues and dos Santos, International Journal of Hydrogen Energy, **37**, 16795 (2012).
- [3] Oumellal, Zaidi, Bonnet, Cuevas, Latroche, Zhang, Bobet, Rougier and Aymard, International Journal of Hydrogen Energy, **37**, 7831 (2012).
- [4] Shaik, Rudramoorthy, Neelakrishnan, Varman, Arjunan, Energy, **36**, 1623 (2011).
- [5] Etacheri, Marom, Elazari, Salitra, Aurbach, Energy Environmental Science, **4**, 3243 (2011).
- [6] Jarvis, Deng, Allard, Manthiram, Ferreira, Chemistry of Materials, **23**, 3614 (2011).
- [7] Haijun and Haoshen, The Journal of Physical Chemistry Letters, **4**, 1268 (2013).
- [8] Arumugam and Kalaigan, Thin Solid Films, **520**, 338 (2011).
- [9] Liu, Guo, Li and Wang, Advanced Materials Research, **347-353**, 1395 (2012).
- [10] Kim, Lee, Kim, Huh, Lee and Kim, Ultrasonics Sonochemistry, **19**, 627 (2012).
- [11] Changju, Hongyeol, Dongwook, Jongsik, Eun and Jung, Journal of Power Sources;244:214 (2013).
- [12] Hiroaki, Kota, Sou, Kyungsu, Sangryun, Jaemin, Masaaki and Ryoji, Journal of Power Sources, **246**, 365 (2014).
- [13] Wei, Neeraj, Vanessa, Je and Shehuang, Journal of Power Sources, **246**, 464 (2014).
- [14] Sanjay and Bharat, Journal of Power Sources, **246**, 219 (2014).
- [15] Sihui, Jiong, Xiaobiao, Yixiao, Zhengliang, Wen, Min, Jihui and Yong, Journal of Power Sources, **245**, 570 (2014).
- [16] Xianyan, Mimi, Hongli, Changwei, Lili and Junming, Vacuum, **99**, 49

- (2014).
- [17] Zhihua, Liqiu, Keyan, Dongfeng, Journal of Alloys and Compounds, **580**, 592 (2013).
- [18] Ke, Fei, Guorong, Zhong, Yanbing and Kwang, Journal of Power Sources, **244**, 29 (2013).
- [19] Je, Wei and Shehuang, Journal of Power Sources, **244**, 35 (2013).
- [20] Toyoki, Masahiro and Hironori Journal of Power Sources, **244**, 544 (2013).
- [21] Cui, Xin, Zhen, Zhi and Dao, Electrochimica Acta **111**, 192 (2013).
- [22] Ouyang, Zeng, Sljivancanin and Baldereschi, The Journal of Physical Chemistry C, **114**, 4756 (2010).
- [23] Haowen, Cuixia, Zong and Keli, Materials Chemistry and Physics, **101**, 276 (2007).
- [24] Sunhye and Jaephil Electrochemistry Communications, **10**, 1478 (2008).
- [25] Hyung, Nan and Keon, Electrochimica Acta, **52**, 3236 (2007).
- [26] Haowen and Dingguo, Russian Journal of Electrochemistry, **45**, 762 (2009).
- [27] Xiaoyu, Jali, Tao and Aishui, Electrochimica Acta, **109**, 52 (2013).
- [28] Chan, Peng, Liu, McIlwrath, Zhang, Huggins and Cui, Nat. Nanotechnology, **3**, 31 (2008).
- [29] Chan, Zhang and Cui, Nano Letters, **8**, 307 (2008).