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Improvement of the Cycle Performance of $LiNi_{0.5}Mn_{1.5}O_4$ Cathode Active Materials by *In-Situ* Coating with Poly(3,4-Ethylenedioxythiophene)

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Abstract

$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO)/poly(3,4-ethylenedioxythiophene) (PEDOT) composite cathode materials were prepared through *in-situ* polymerization of thiophene monomer (EDOT), with ammonium persulphate (APS) as oxidizing agent, p-toluenesulfonic acid (PTSA) as dopant. The morphology, amount of PEDOT coating, electrochemical properties of LNMO/PEDOT were characterized by scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and galvanostatic charge and discharge tests. The results show that the composite materials show better cycle performance than bare LNMO.

Keywords

Lithium-Ion Battery $LiNi_{0.5}Mn_{1.5}O_4$ PEDOT *In-Situ* Coating

1. Introduction

Rechargeable lithium-ion batteries are now expected to put into use in hybrid electric vehicles (HEVs) and electric vehicles (EVs) [1] [2]. Unfortunately, the specific energy density of the present commercialized lithium-ion battery can hardly meet the requirements for practical applications [3]. In the current studied cathodes for lithium-ion batteries, the $LiNi_{0.5}Mn_{1.5}O_4$ which owns high operating voltage (4.6 - 4.8 V), high theoretical capacity (147 mAh/g), high energy density (658 Wh/kg) and good thermal stability [4] [5]. However, the high operational potential will cause the reactions between electrolyte and LNMO, and form solid electrolyte interphase (SEI) layer, which will increase the cell impedance and limit lithium ion diffusion resulting in capacity decline with cycling. In addition, Mn^{3+} is apt to dissolve in the electrolyte at high potential, which leads to structural instability of electrode materials [6] [7]. PEDOT has been considered as another type of potential additive to improve the cycling stability and rate performance in lithium ion batteries due to the high electronic conductivity and stability [8] [9]. Hereupon, we have prepared LNMO with PEDOT coating that have better cycle performance through *in-situ* polymerization in an aqueous solution.

2. Experiment Section

2.1. Preparation of Material

Firstly, a certain amount of EDOT was added to the p-toluenesulfonic acid solution with continuous stirring for 2 h. Then, in protection of nitrogen, the LNMO and APS were added respectively into above solution and stirred for 12 h at 0˚C. During the synthesis process, the PEDOT layer was prepared through the oxidative polymerization of EDOT using the APS as oxidant. Finally, the powder was washed several times with distilled water and ethanol, and dried at 80˚C overnight to obtain the PEDOT/LNMO composite.

2.2. Materials Characterization

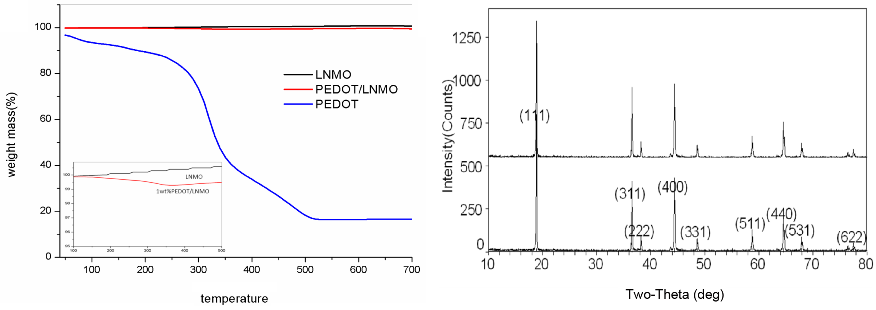
Thermogravimetric analysis (TGA, TA corporation Q60, heating rate is 10˚C/min) was used to determine the PEDOT content. The crystal structures of LNMO and PEDOT/LNMO samples were investigated by X-ray diffraction patterns (XRD, Bruk-D8X with CuKα) at a scan rate of 3˚/s from 10˚ to 90˚. The morphologies of the samples were observed by scanning electron microscopy (SEM, HITACHI S-4800), the electrochemical properties were tested by constant-current charge–discharge (LAND CT2001A) at 3 - 4.9 V.

2.3. Electrochemical Measurements

The electrochemical properties of the cathodes were tested by using CR2016 coin cells. The electrode slurries were made by fully mixing 80 wt% active material, 10 wt% super-p, and 10wt% poly-(vinylidene fluoride) (PVDF) binder in N-Methyl pyrrolidone (NMP) solvent. Lithium sheets, 1.2 M LiPF6 in 3:7 ethylene carbonate–ethyl methyl carbonate (v/v), and micro-porous polypropylene film (Celgard 2400) were used as anode, electrolyte and separator respectively. The coin cells were cycled in the voltage range between 3 V and 4.9 V at 0.2 C at room.

3. Results and Discussion

The PEDOT content in the composite was determined by thermogravimetric analysis is 1wt% [**Figure 1(a)**]. The samples were heated from 50˚C to 700˚C at a rate of 10˚C/min. The X-ray diffraction (XRD) data obtained from the bare LNMO and the LNMO-PEDOT composites are displayed in **Figure 1(b)**. The LNMO and PEDOT/LNMO materials exhibit the same characteristic $LiNi_{0.5}Mn_{1.5}O_4$ peaks that two-theta are 18.7, 36.4, 38.0, 44.2, 48.5, 58.6, 64.4 and



(a) (b)

Figure 1. TGA curves, with the inset showing an enlargement of the indicated region (a); X-ray diffraction patterns (b) of the samples.

67.7 contacted with crystal plane of (111) (311) (222) (400) (331) (511) (440) and (531) respectively. There are not obviously different in the XRD images between the bare LNMO and the PEDOT-coated LNMO composites was observed, demonstrating that the PEDOT wrapping layer does not change the spinel crystalline structure of LNMO.

Morphology of PEDOT/$LiNi_{0.5}Mn_{1.5}O_4$ and bare $LiNi_{0.5}Mn_{1.5}O_4$ was investigated by SEM in **Figure 2**. It was seen that the surface of bare LNMO material are very clean and smooth, and scanning electron micrographs show that this sample is a well-crystallized spinel in **Figure 2(a)**. By comparison, some layered material on the surface of the 1 wt% PEDOT/LNMO composite was observed [**Figure 2(b)**]. And the surface of the composite material is very rough. This indicates that a relatively uniform PEDOT layer had been coated successfully onto the outer surface of the LNMO.

Figure 3 compares the cycling performances of the bare LNMO and PEDOT/LNMO electrodes at the 0.2 C rate and room temperature (25˚C). The bare LNMO suggests a discharge capacity of 125 mAh/g at the first cycle. The discharge capacity continuously decreases and drops to 98.4 mAh/g after 100 cycles, so that only 78% capacity retention is achieved. In contrast, the discharge capacity of 1wt-PEDOT/LNMO is 114 mAh/g after 100 cycles. There is 91.2% respective capacity retention that takes on better cycle performance than bare LNMO. It was demonstrated that PEDOT is an effective additive for improving the electrochemical performance of the LNMO cathode material. The promising electro-chemical performance of PEDOT/LNMO would be ascribed to two reasons: 1) PEDOT is a conductive polymer and can work as a conductive additive, thus improving the conductivity of LNMO; 2) The dissolution of transition metals into the electrolyte can be suppressed by the PEDOT layer.

4. Conclusion

$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO)/PEDOT composite cathode materials were prepared by *in situ* polymerization. After 1 wt% PEDOT coating, spinel crystalline structure of LNMO is not changed. Discharge capacity continuously decreases and drops to 98.4 mAh/g for bare LNMO. In contrast, reversible discharge capacities of

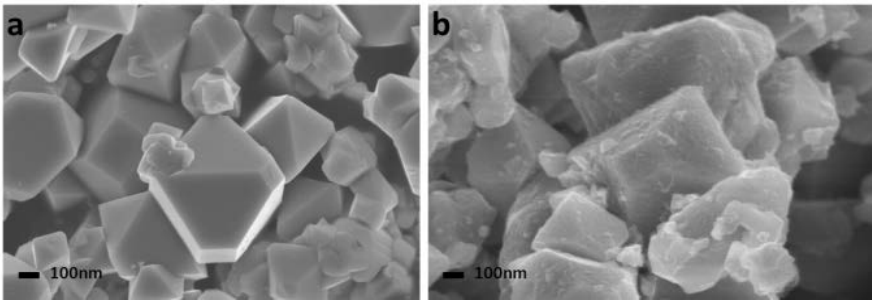


Figure 2. SEM images of bare LNMO (a) and 1 wt%-PEDOT/LNMO (b).

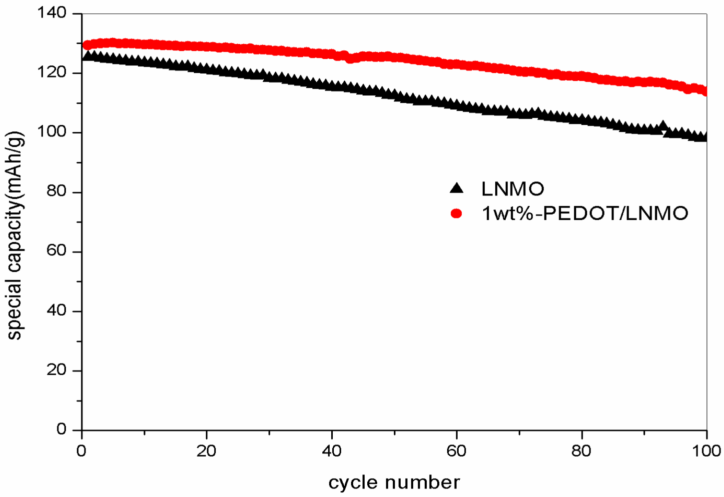


Figure 3. Cycle life of LNMO and 1wt%PEDOT/LNMO composites at the 0.2C rate.

114 mAh/g can be obtained for composite materials with 1 wt% PEDOT after 100 cycles at room temperature. It is suggested that the LNMO with 1 wt% PEDOT coating shows better cycle life than bare LNMO.

References

[1] Ouyang, L., Guo, L., Cai, W., Ye, J., Hu, R., *et al.* (2014) Facile Synthesis of Ge@FLG Composites by Plasma Assisted Ball Milling for Lithium Ion Battery Anodes. *Journal of Materials Chemistry A,* **2**, 11280-11285. https://doi.org/10.1039/C4TA01267D

[2] Oltean, V.A., Philippe, B., Renault, S., Duarte, R.F., Rensmo, H. and Brandell, D. (2016) Investigating the Interfacial Chemistry of Organic Electrodes in Li- and Na-Ion Batteries. *Chemistry of Materials,* **28**, 8742-8751. https://doi.org/10.1021/acs.chemmater.6b04086

[3] Zhang, S., Gu, H., Pan, H., Yang, S., Du, W., Li, X., Gao, M., Liu, Y., Zhu, M. and Ouyang, L. (2017) A Novel Strategy to Suppress Capacity and Voltage Fading of Li- and Mn-Rich Layered Oxide Cathode Material for Lithium-Ion Batteries. *Advanced Energy Materials,* **7**, 1339-1350. https://doi.org/10.1002/aenm.201601066

[4] Manthiram, A., Chemelewski, K. and Lee, E.S. (2014) A Perspective on the High-Voltage $LiNi_{0.5}Mn_{1.5}O_4$ Spinel Cathode for Lithium-Ion Batteries. *Energy & Environmental Science,* **7**, 1339-1350. https://doi.org/10.1039/c3ee42981d

[5] Gao, X.W., Deng, Y.F., Wexler, D., Chen, G.H., Chou, S.L., Liu, H.K., Shi, Z.C. and Wang, J.Z. (2014) Improving the Electrochemical Performance of the $LiNi_{0.5}Mn_{1.5}O_4$

Spinel by Polypyrrole Coating as a Cathode Material for the Lithium-Ion Battery. *Journal of Materials Chemistry A,* **3**, 404-411. https://doi.org/10.1039/C4TA04018J

[6] Yi, T.F., Mei, J. and Zhu, Y.R. (2016) Key Strategies for Enhancing the Cycling Stability and Rate Capacity of $LiNi_{0.5}Mn_{1.5}O_4$ as High-Voltage Cathode Materials for High Power Lithium-Ion Batteries. *Journal of Power Sources,* **316**, 85-105. https://doi.org/10.1016/j.jpowsour.2016.03.070

[7] Ma, J., Hu, P., Cui, G. and Chen, L. (2016) ChemInform Abstract: Surface and Interface Issues in Spinel $LiNi_{0.5}Mn_{1.5}O_4$: Insights into a Potential Cathode Material for High Energy Density Lithium Ion Batteries. *Cheminform,* **47**. https://doi.org/10.1002/chin.201631243

[8] Zhao, X., Mai, Y., Luo, H., Tang, D., Lee, B., Huang, C. and Zhang, L. (2014) Nano-MoS_2/Poly(3,4-Ethylenedioxythiophene): Poly(Styrenesulfonate) Composite Prepared by a Facial Dip-Coating Process for Li-Ion Battery Anode. *Applied Surface Science,* **288**, 736-741. https://doi.org/10.1016/j.apsusc.2013.10.142

[9] Wang, X., Shen, L., Li, H., Wang, J., Dou, H. and Zhang, X. (2014) PEDOT Coated $Li_4Ti_5O_{12}$ Nanorods: Soft Chemistry Approach Synthesis and Their Lithium Storage Properties. *Electrochimica Acta,* **129**, 283-289. https://doi.org/10.1016/j.electacta.2014.02.112