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Electrochemical Performance of LiV_3O_8/PPy Composite Materials Synthesized by the Non-water System

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Abstract: LiV_3O_8/polypyrrole (PPy) composite materials were prepared by an oxidative polymerization of pyrrole monomer on the surface of LiV_3O_8 using ethanol as a medium, $FeCl_3$ as an oxidant, benzene sulfonic acid sodium salt as a dopant. The crystal structures and microstructures of LiV_3O_8/PPy were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscopy (TEM). The electrochemical properties of the composites were investigated with galvanostatic charge-discharge test, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The results indicate that 10 nm pyrrole is uniformly polymerized around the LiV_3O_8, and the PPy-coating does not alter the crystal structure of the LiV_3O_8. LiV_3O_8/PPy composite material containing 6% PPy (LVP6) exhibits perfect electrochemical properties, whose first discharge capacity reaches a high specific discharge capacity of 274 mAh/g and maintains a stable capacity of 239.4 mAh/g within 100 cycles at the charge-discharge rate of 0.1 C and in the voltage range of 1.8～4.0 V, and the capacity retention is 87.4%. But the pure LiV_3O_8 shows that the first discharge capacity is 227.4 mAh/g and the discharge capacity is 160.1 mAh/g after 100 cycles, the capacity retention is only about 70.4%. LiV_3O_8/PPy composite materials exhibit better cycling performance than the pure LiV_3O_8.

Key words: LiV_3O_8; polypyrrole; coating; cathode material

Among the studied cathode materials, Lithium trivanadates (LiV_3O_8) has attracted more and more attention because of its layered structure, high energy density (730 Wh/kg), low cost, pollution-free and so on[1-3]. LiV_3O_8 is expected to become a new promising cathode material for rechargeable lithium batteries. Vanadium resources are very abundant in our country; however, vanadium and its compounds are mainly used in the steel industry as a catalyst, and its added value is too low. The utilization of LiV_3O_8 as a cathode material, will enhance the value of vanadium resources and promote the development of lithium ion battery industry. LiV_3O_8 has its own shortcomings, such as weak electron transport capacity and lower Li^+ diffusion coefficient[4,5]. The study shows that ion doping and polymer coating are effective ways to improve its electrochemical properties[5-9]. Madhuryya Deka et al.[6] synthesized LiV_3O_8/PMMA by a solid-state reaction, and the study shows that PMMA inserted into layered LiV_3O_8, provided a suitable two-dimensional path for Li^+ diffusion, improved the two-dimensional path for Li^+ diffusion, improved the ionic conductivity, and thus overall electrochemical performance.

It is generally known that polypyrrole (PPy) exhibits high conductivity of 100~102 S/cm, and other advantages, such as facile preparation, high conductivity, environmental friendliness and outstanding structural stability. Many studies showed that when $LiFePO_4$-PPy[10], LiV_3O_8-PPy[11] and $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$-PPy[12] composite cathode materials had been synthesized, the electrochemical properties of composite materials improved substantially.

Although LiV_3O_8 coated PPy as composite cathode material has been reported, Liu et al.[11] synthesized nano PPy-LiV_3O_8 composite by low temperature in-situ oxidation polymerization, and used it as cathode material in aqueous rechargeable lithium battery. The initial discharge capacity of this composite is 108 mAh/g under a current density of 125 mAh/cm^2, the capacity fading is 16% after 10th cycle, while the initial discharge of pure LiV_3O_8 is only 75 mAh/g. In this work, the LiV_3O_8-PPy composite was prepared by chemical oxidation in aqueous solutions, and shows that the synthesis of polypyrrole in aqueous solutions causes side reactions leading to the decrease of the conductivity of polypyrrole. However, the research result of the composite cathode material in non aqueous system has not been reported yet. In the previous work, we carried out a large number of studies on the composite of conductive polymer and various lithium battery cathode mate-

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rials[13-15]. Based on this work, through the use of ethanol as solvent, pyrrole (Py) as monomer, $FeCl_3$ as oxidant, benzene sulfonic acid sodium salt (TsONa) as the dopant, the LiV_3O_8/PPy composite material was prepared by in-situ polymerization, and its electrochemical performance was improved significantly.

1 Experimental

1.1 Preparation of LiV_3O_8/PPy composite

Applying a stoichiometric ratio of about Li:V:Citric acid=1:3:4, LiV_3O_8 was prepared from a mixture of NH_4VO_3, $CH_3COOLi \cdot 2H_2O$ with citric acid as chelon. These materials were then dissolved into distilled water and stirred at 80 ℃ until a blue gel was formed. The gel was dried in a vacuum oven at 100 ℃ for 12 h and then calcined in air at 550 ℃ for 12 h (heating rate of 5 ℃/min) with natural cooling to room temperature, and then the synthesized LiV_3O_8 product was obtained.

The synthesized LiV_3O_8 and doping agent TsONa were added in 100 mL ethanol, and then stoichiometric amount of pyrrole monomers and oxidant $FeCl_3$ were added in with 1:2:3 molar ratio of Py:TsONa:$FeCl_3$. The mixture was stirred in an ice bath for 4 h with nitrogen as protecting gas. The precipitate was obtained after the completion of the reaction. The precipitate was filtered, washed thoroughly with distilled water until the neutral filtrate was obtained, then dried under vacuum at 80 ℃ for 20 h, and the product LiV_3O_8/PPy composite was finally obtained. To differentiate the different ratio of PPy (including 0, 2%, 4%, 6% and 8%), we marked the LiV_3O_8/PPy composite as LVP0, LVP2, LVP4, LVP6 and LVP8.

1.2 Characterization

X-ray diffraction (XRD. Bruker D8 Advance, Germany) analysis of the obtained materials were investigated using monochromatic Cu Kα radiation source in the 2θ range 10 °~70 ° at 40 kV, 40 mA, with a scan rate of 3 °/min. The morphology were observed by scan electron microscope (SEM. S-3400N, Japan) and transmission electron microscopy (TEM. JEM 2100, Japan). Thermogravimetric analysis (TGA. TGA Q-50, USA) was carried out in air and the samples were heated from room temperature to 550 ℃, at a scan rate of 10 ℃/min.

1.3 Electrochemical measurements

The composite cathode was prepared by the synthesized LiV_3O_8/PPy, acetylene black and polyvinylidene (PVDF) in a mass ratio of 85:10:5 onto an aluminum foil with N-methyl pyrrolidone (NMP) as solvent to form a homogeneous slurry, which was then spread onto aluminum foil. The coated electrodes were dried in a vacuum oven at 85 ℃ for 8 h and then pressed into 15 mm wafers. Electrochemical characterization of the materials was tested in cells with metallic lithium as the negative electrode and a liquid electrolyte (1 mol/L $LiPF_6$ dissolved in a volume ratio of 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC)), Celgard2400 as membrane. The coin cells were assembled in an argon-filled dry box (UNILab2000, MBRAUN). Electrochemical capacity were measured on LAND-2001A systems with galvanostatic charge-discharge in the voltage range of 1.8~4.0 V at different rate. Cyclic voltammograms (CV) (scan rate: 0.1 mV/s, 1.8~4.0 V) and electrochemical impedance spectroscopy (EIS) tests (open circuit potential, amplitude 0.1 mV, 10^5 to 10^{-2} Hz) were performed with a CHI 660A electrochemical work station (CH Instrument, USA). All the tests were performed at room temperature.

2 Results and discussion

2.1 Structure and morphological characterization

Fig.1 shows the XRD patterns of LiV_3O_8/PPy composite. All the peaks in Fig.1 are similar and can be well indexed to a monoclinic structure with the space group P21/m. Most of samples are well matched with the standard JCPDS data (PDF card #72-1193)[16], which indicates the structure of LiV_3O_8 does not change after PPy is coated. The crystal plane index of typical diffraction peak at 2θ of 14 ° can be identified as (100). However, all of the samples also show a small impurity peak at 2θ of 12.3 °, which can be attributed to $Li_{0.3}V_2O_5$ (PDF card #18-0755)[17]. The intensities (100) vary with the amount of polypyrrole coated. A high intensity (100) line means crystallization is better and surface spacing of (100) is smaller, less conducive to the diffusion of Li^+. With the amount of PPy coated increasing, the diffraction peak of (100) of the LiV_3O_8/PPy composite decreases, because the LiV_3O_8 coating of amorphous polypyrrole reduces the crystallinity of cathode materials. In this study, the LVP6 shows the lowest intensities (100), which is best for lithium ion insertion/extraction in cathode material.

Fig.2 is a group of SEM images of LiV_3O_8/PPy composite, which shows that the surface of the LiV_3O_8 material particles is coated by PPy, and the LiV_3O_8 particles are interconnected. It is found that PPy has a great effect on agglomeration of LiV_3O_8 material powders, the LiV_3O_8 material has a higher aggregation property with increased PPy content. The aggregation of material is detrimental for lithium ion insertion/extraction in

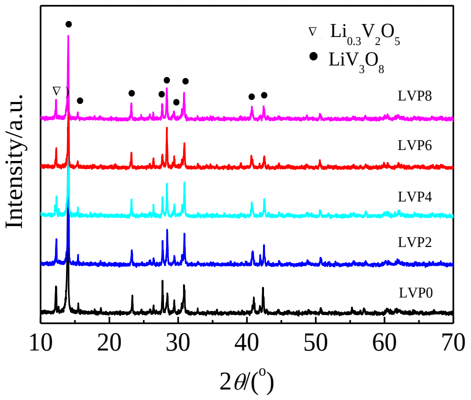

Fig.1 XRD patterns of LiV_3O_8/PPy with different contents of Polypyrrole

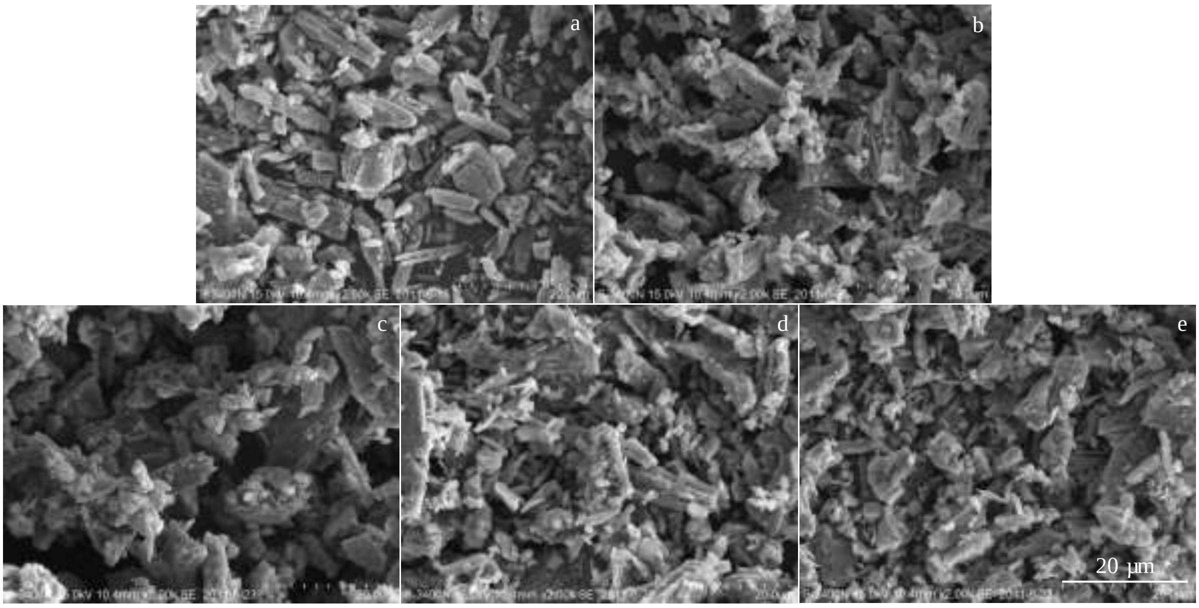

Fig.2 SEM images of LiV_3O_8/PPy with different contents of polypyrrole: (a) LVP0, (b) LVP2, (c) LVP4, (d) LVP6, and (e) LVP8

cathode material. According to the TEM photograph of LVP6 (Fig.3), there are some black and white stripes in the material, representing the layered structure of LiV_3O_8[11]. In the LVP6 nanocomposite (Fig.3b), it can be clearly seen that the surface of the LiV_3O_8 cathode materials are covered with a PPy layer of a uniform thickness of about 10 nm.

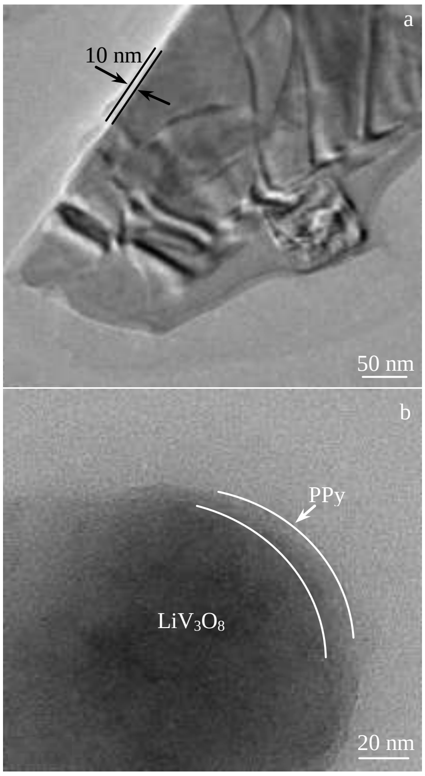

Fig.3 TEM images of LiV_3O_8/PPy composite cathode material containing 6% PPy

To estimate the amount of polypyrrole in the LVP6 composite, TGA analysis was carried out in an air atmosphere. Fig. 4 shows the TGA analysis curves of the LVP6 composite and PPy powders. It can be found that PPy powder demonstrates a mass loss of 49.4% at 500 ℃. The mass loss of LVP6 is 3.1%, pure LiV_3O_8 has almost no mass loss at 500 ℃[18]. Hence, the approximate amount of PPy in the LVP6 is calculated to be 6.3 wt%.

2.2 Electrochemical properties

Fig.5 is the cycle performance of LiV_3O_8/PPy with different contents of pyrrole under 0.1 C charge/discharge rate. It indicates that the electrochemical property of LiV_3O_8 cathode material is obviously improved due to the coating of pyrrole. As can be seen from Fig.5, the initial discharge capacity of LVP0, LVP2, LVP4, LVP6, LVP8 is 227.4, 239.1, 257.1, 274, 203.8 mAh/g, respectively. After 100 times cycle the discharge capacity remain 160.1, 196.2, 211.9, 239.4, 171.3

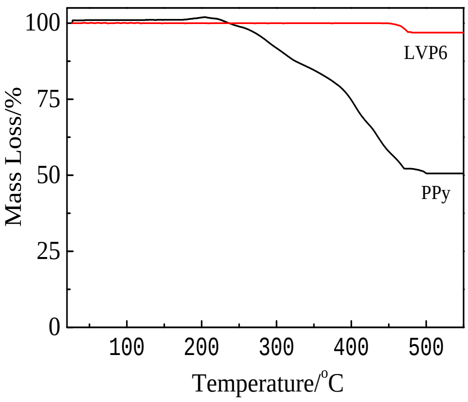

Fig.4 TGA curves of the PPy powder and LVP6

mAh/g, respectively. The capacity retention is 70.4%, 82.1%, 82.4%, 87.4%, 84.1%, respectively. The result indicates that LiV_3O_8/PPy composites prepared in ethanol liquid have a capacity retention rate above 80% after 100 times cycle. When the content of pyrrole is 6%, the initial discharge capacity of cathode material is as high as 274 mAh/g, the capacity retention rate remain 87.4% after 100 times cycle, and the capacity decay rate is less than 0.13%. Because PPy has the advantage of higher electronic conductivity and tackiness, it is used as binder and conductive agent in the cathode material. With the increasing content of PPy, the initial discharge capacity of LiV_3O_8/PPy improves gradually. But when the content of PPy is above 8%, the discharge capacity of LiV_3O_8/PPy drops, because the theory capacity of PPy is 72 mAh/g.

Fig.6 shows the initial discharge curves of LiV_3O_8/PPy composite cathode materials at 0.1 C. There are several charge/discharge plateaus in the voltage profiles whose shapes are similar to each other, and they correspond to the extraction/insertion of the Li^+ in the layered materials and are in agreement with other reports[19]. The results show that the PPy-coating does not change the charging and discharging process of LiV_3O_8.

Fig.7 shows the cyclic voltammetry curves of LiV_3O_8/PPy composite cathode materials under the scan rate of 0.1 mV/s and the sweep voltage rage from 1.8 to 4.0 V. The results indicates that the structure of the LiV_3O_8/PPy does not change compared with the LiV_3O_8 composites materials, because the oxidation and reduction peaks of the LiV_3O_8/PPy and LiV_3O_8 composites materials are similar. There are four reduction peaks at 2.52, 2.75, 2.82, 3.69 V and the oxidation peaks at 3.63, 2.80, 2.72, 2.63, 2.52 V (vs. Li/Li^+) in Fig.7 which correspond to the embedding and extracting of Li^+[20]. When the content of PPy is 6%, the peak area is the biggest and the difference between oxidation and reduction peaks voltage is the smallest, indicating an optimum electrochemical performance.

EIS was employed to further investigate the electrochemical reaction kinetics of different electrodes. The Nyquist plots and the fitting data plot for LiV_3O_8/PPy with different contents of polypyrrole at the open voltage of 2.7 (±0.3) V are shown in Fig.8. The semicircle appearing in the high frequency range is assigned to the charge-transfer resistance occurring between active materials and liquid electrolyte. The straight line is attributed to the diffusion of lithium ions into electrode materials. As shown in Fig.8, when the content of PPy is 6%, the

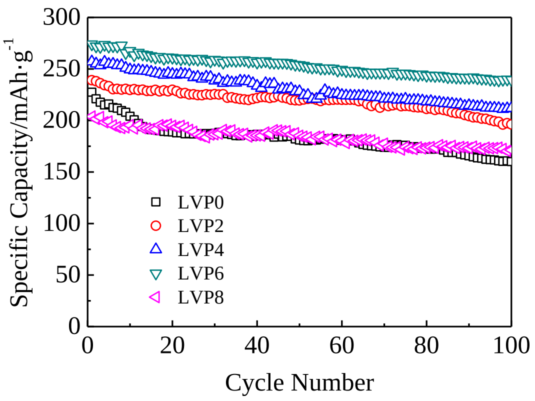

Fig.5 Cycle performance of LiV_3O_8/PPy with different contents of polypyrrole

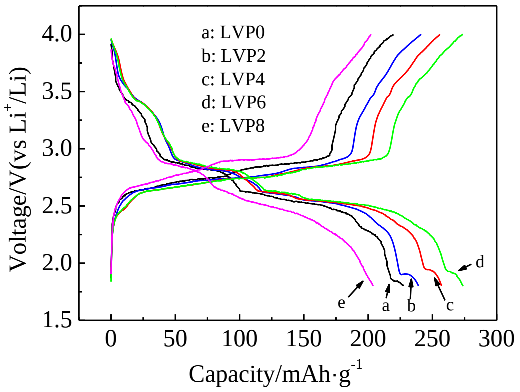

Fig.6 Initial charge-discharge curves of LiV_3O_8/PPy with different contents of polypyrrole

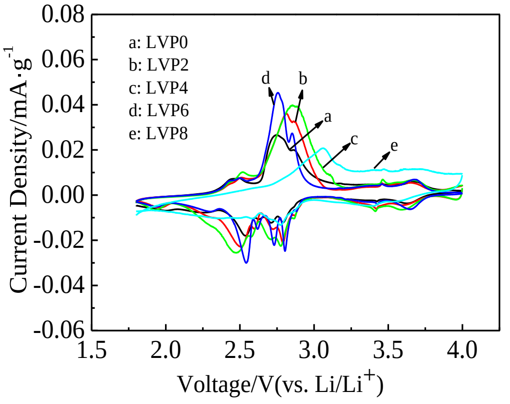

Fig.7 Cyclic voltammograms of LiV_3O_8/PPy with different contents of polypyrrole

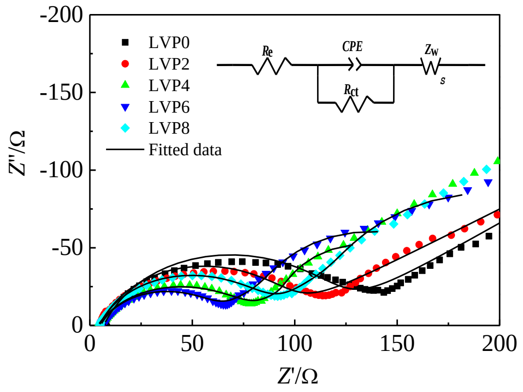

Fig.8 Nyquist and the fitting data plots for LiV_3O_8/PPy with different contents of polypyrrole

semicircle for LiV_3O_8/PPy is smallest, suggesting a lower charge-transfer resistance in the former electrode due to the introduction of a highly-conductive carbon coating layer.

3 Conclusion

1) A LiV_3O_8/PPy composite cathode material is prepared by in-situ polymerization combined with oxidation process in a non water system. PPy is coated on the surface of LiV_3O_8 particles evenly.

2) With the adding of PPy, LiV_3O_8 particles became loose, resulting in a charge transfer impedance and Warburg impedance drop.

3) When PPy content is 6%, the composites show the best electrochemistry performance, with initial discharge capacity as high as 274 mAh/g, after 100 times cycle discharge capacity of 239.4 mAh/g under 0.1 C rate and discharge capacity retention rate of LiV_3O_8/PPy at 87.4%.

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非水体系中钒酸锂/聚吡咯复合正极材料的制备及性能研究

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摘　要：采用乙醇作为介质，$FeCl_3$为氧化剂，对甲苯磺酸钠为掺杂剂，通过吡咯单体在钒酸锂表面的氧化聚合制备出了钒酸锂/聚吡咯(LiV_3O_8/PPy)复合材料。采用X射线衍射(XRD)、扫描电镜(SEM)、透射电镜(TEM)对复合材料的结构与形貌进行表征。用恒流充放电测试、循环伏安(CV)和交流阻抗(EIS)等研究了聚吡咯包覆量对材料电化学性能的影响。结果表明：在钒酸锂表面均匀地包覆了一层厚度约10 nm的聚吡咯，并没有改变钒酸锂的晶型结构。当聚吡咯包覆量为6% 时，复合材料的电化学性能最好，在0.1 C充放电倍率下，首次放电比容量为274 mAh/g，循环100次后样品的放电比容量为239.4 mAh/g，容量保持率为87.4%，而未包覆PPy的LiV_3O_8，其首次放电比容量为227.4 mAh/g，循环100次后样品的放电比容量为160.1 mAh/g，容量保持率仅为70.4%。LiV_3O_8/PPy复合正极材料的电化学性能得到了明显提高。

关键词：钒酸锂；聚吡咯；包覆；正极材料

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