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Influence of pH value and chelating reagent on performance of $Li_3V_2(PO_4)_3$/C cathode material

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Abstract: The $Li_3V_2(PO_4)_3$/C composite cathode material was synthesized via sol−gel method using three different chelating agents (citric acid, salicylic acid and polyacrylic acid) at pH value of 3 or 7. The crystal structure, morphology, specific surface area and electrochemical performance of the prepared samples were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge/discharge test. The results show that the effects of pH value on the performance of the prepared materials are greatly related to the chelating agents. With salicylic acid or polyacrylic acid as the chelating reagent, the structure, morphology and electrochemical performance of the samples are greatly influenced by the pH values. However, the structure of the materials with citric acid as the chelating agent does not change as pH value changes, and the materials own uniform particle size distribution and good electrochemical performance. It delivers an initial discharge capacity of 113.58 mA·h/g at 10*C*, remaining as high as 108.48 mA·h/g after 900 cycles, with a capacity retention of 95.51%.

Key words: $Li_3V_2(PO_4)_3$; cathode material; sol−gel method; chelating agents; pH value

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1 Introduction

The development of new energy sources, especially the lithium-ion batteries, has attracted tremendous interest due to the depletion of fossil energy and environmental issues. Cathode material which accounts for more than 30% of the total cost is the key to the development of lithium-ion battery. Currently, $LiCoO_2$ is widely used as cathode material in commercial lithium-ion batteries, but its high cost and toxicity inhibit its use in large-scale, so more efforts have been made to study new cathode materials. $Li_3V_2(PO_4)_3$ is a high promising material proposed as a cathode for higher voltage Li-ion batteries because of its good ion mobility, high reversible capacity and high operating voltage [1,2]. The reversible cycling of all three lithium ions from $Li_3V_2(PO_4)_3$ corresponds to a high theoretical capacity of 197 mA·h/g [3,4]. Combining with its high safety, $Li_3V_2(PO_4)_3$ has been proposed to be a potential candidate of cathode materials for Li-ion batteries.

Many methods are applied to synthesizing $Li_3V_2(PO_4)_3$ cathode materials, including conventional solid-state synthesis [5−7], hydrothermal [8,9], sol−gel method [10−13], microwave solid-state synthesis method [14], and other soft chemistry methods [15−17], etc. Among them sol−gel method allows reactants to mix at the atomic or molecular level. Meanwhile, enormous advantages such as lower calcination temperature, shorter sintering time and smaller particle size are the important considerations. Thus, sol−gel method is promising to synthesize material of higher purity and smaller particle sizes.

TANG et al [18,19] reported that the conditions of solution during the sol−gel process greatly influenced the electrochemical performance of the samples. In this study, the pH value of solution was found to have great impact on the performance of the materials. Moreover, the impact factor of pH value varies with the type of chelating agents used. The physical properties and electrochemical performance of the synthesized materials were discussed in detail.

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2 Experimental

2.1 Materials and preparation

The samples were prepared by the sol−gel method. $LiOH·H_2O$ (99%), NH_4VO_3 (99%), H_3PO_4 (85%) at stoichiometric ratio were used as raw materials. Citric acid, salicylic acid and polyacrylic acid were used as carbon sources and chelating reagents. Firstly, $LiOH·H_2O$ and NH_4VO_3 were dissolved in deionized water at room temperature. H_3PO_4 and one of the chelating reagents were then added into the solution. Finally, a certain amount of $NH_3·H_2O$ was added to adjust the pH value of solution. This solution was constantly stirred at 80 °C for 2 h, and then the excess solvent was removed by vacuum distillation. The resulting gel precursor was dried in a vacuum oven at 90 °C for 15 h. After being dried, the precursors were decomposed in a tube furnace at 350 °C for 4 h, and then heated at 700 °C for 6 h under flowing argon. The final product was a black powder. The samples synthesized with citric acid, salicylic acid and polyacrylic acid under pH value of 3 were marked as A1, B1 and C1, respectively, and A2, B2 and C2, respectively for pH value of 7.

2.2 Characterization

The carbon content was verified by analytical instrument (CS-902, Wanlianda Xinke, Beijing, China). The residual carbon contents of all the samples were 2%−3% (mass fraction). The crystalline structure of each product was analyzed by X-ray diffractometer (XRD, D/max-rB, Rigaku, Cu K_α radiation) (λ=1.5046 Å) operated at 40 kV and 40 mA. The particle morphology and particle size of the $Li_3V_2(PO_4)_3$ powders were observed on a scanning electron microscope (SEM, SPA400 Seiko Instruments). The particle size distribution was estimated on a laser particle size distribution tester (JL−1155).

2.3 Electrochemical measurements

The electrochemical properties of $Li_3V_2(PO_4)_3$ were evaluated in CR2032 coin cells, which consisted of a LVP/C working electrode and a lithium foil counter electrode separated by a Celgard 2300 microporous membrane. The cathode was fabricated by pressing a mixture (in mass fraction) of 80% active material, 13% acetylene black (conducting additive) and 7% PVDF (binder) onto an Al foil. The anode was lithium foil and the electrolyte was 1 mol/L $LiPF_6$ solution in ethylene carbonate (EC):dimethyl carbonate (DMC) (1:1 in volume ratio). Galvanostatic charging/discharging tests were conducted at different current densities in the voltage range of 3.0−4.5 V with a battery test system (Neware BTS−610). Cyclic voltammetry (CV) was performed by a LK9805 electrochemical analyser between 3.0 and 4.5 V at a scanning rate of 0.1 mV/s. Electrochemical impedance spectroscopy (EIS) was conducted at a frequency range of 10 mHz−100 kHz with a vibration of 5 mV using a Zahner electrochemical work station.

3 Results and discussion

3.1 Sample characterization

Figure 1 shows the X-ray diffraction patterns of the $Li_3V_2(PO_4)_3/C$ composites synthesized with different chelating reagents under various pH values. It can be seen that at pH=3, the characteristic peaks of all the samples are sharp and without any impurity peaks. There is also no additional diffraction peak related the carbon, which can be attributed to the low content (shown in Table 1) or amorphous form. However, when pH values are adjusted to 7, the XRD patterns are different because of different chelating reagents. Compared with sample A2, there are some impurities peaks displayed on the XRD patterns of samples B2 and C2. What's more, the intensities of diffraction peaks of sample C2 are much weaker than those of the other two samples. Table 1

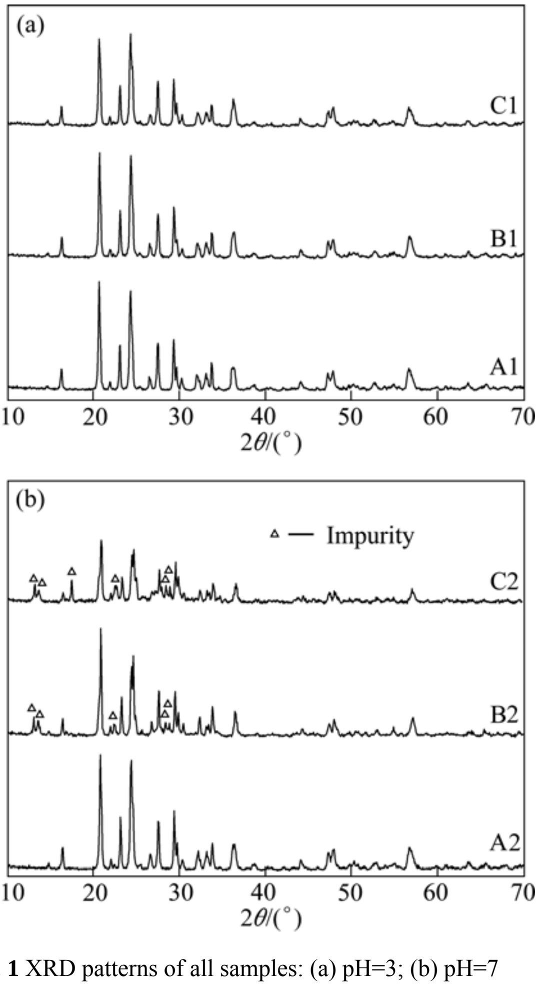

Fig. 1 XRD patterns of all samples: (a) pH=3; (b) pH=7

Table 1 Physical parameters of $Li_3V_2(PO_4)_3$/C samples

Sample	Chelating reagent	pH	Carbon content/%	Crystalline/%	Grain size/nm
A1	Citric acid	3	3.12	88.96	35.7
A2	Citric acid	7	3.06	89.78	37.0
B1	Salicylic acid	3	3.43	89.12	35.6
B2	Salicylic acid	7	3.65	79.83	37.9
C1	Polyacrylic acid	3	5.28	88.83	36.0
C2	Polyacrylic acid	7	5.39	68.83	26.9

shows the crystallinity and grain sizes of all the samples calculated by Jade 5.0 software. It can be seen that samples B2 and C2 have smaller crystallinity than the others, which corresponds to the results of characteristic peaks intensity. Sample C2 has the lowest crystallinity and the smallest grain sizes, indicating that the cell of sample C2 does not grow well, which may be quite disadvantageous to its electrochemical properties.

Figure 2 shows the SEM images of all the samples, and much difference in the morphologies with the pH value changing can be observed clearly. Samples A1 and A2 prepared with critic acid as chelating reagents have small particle size. When the pH value turns to 7, the materials have more uniform particle size distribution and small particles agglomerated. The particle size distribution for sample A2 is shown in Fig. 3. The diameters at 10%, 50%, 75% and 99% cumulative volume for the particles are 0.195, 0.528, 1.019 and 2.853 μm, and the average size 0.747 μm, which is consistent with the results of SEM. Sample B2 exhibits a similar particle shape, but a smaller particle size compared with B1. The morphology of sample C2 is different from that of sample C1. The particles are block and distributed in 2−3 μm with a smooth surface, which

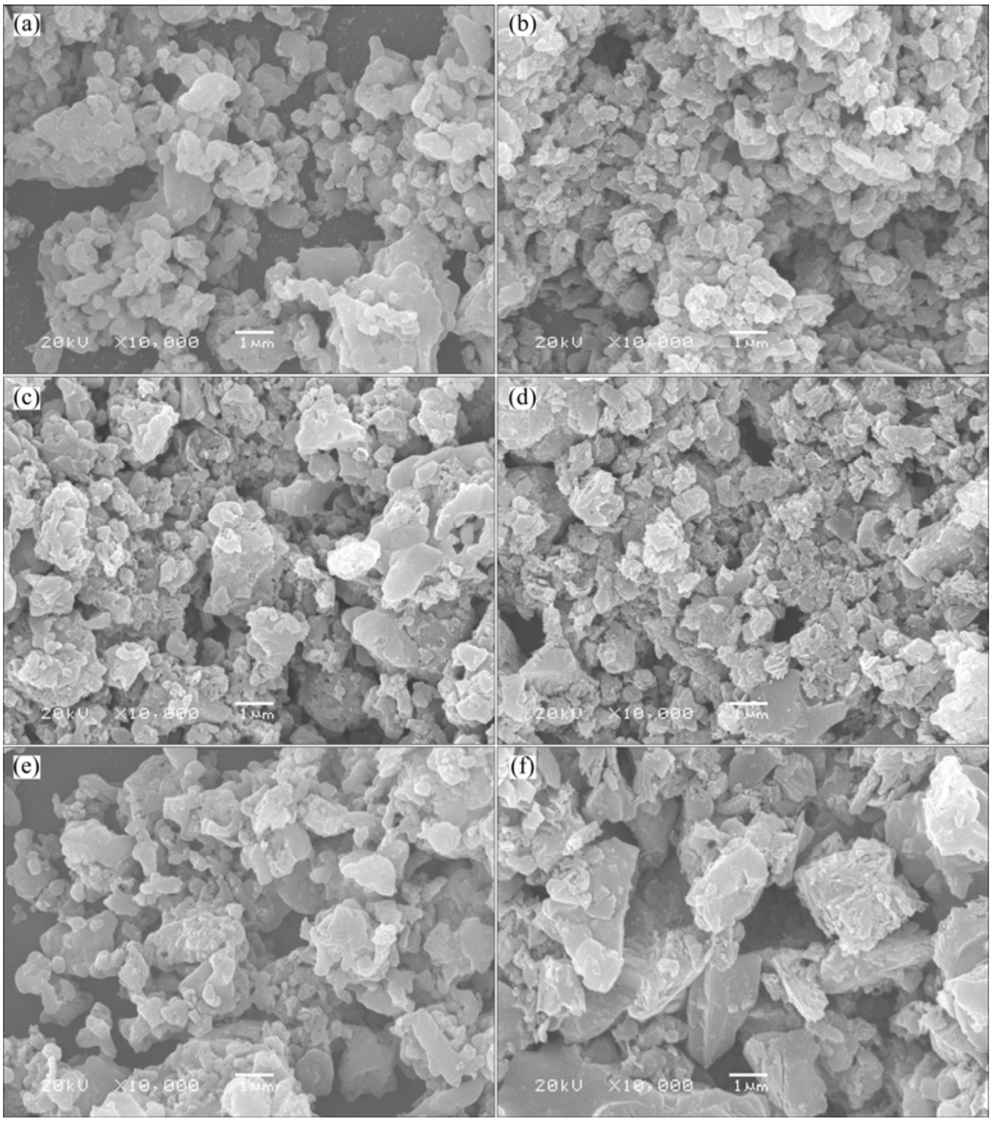

Fig. 2 SEM images of samples: (a) Sample A1; (b) Sample A2; (c) Sample B1; (d) Sample B2; (e) Sample C1; (f) Sample C2

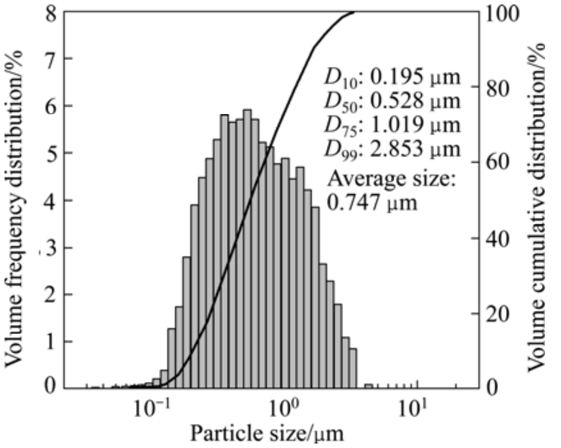

Fig. 3 Particle size distribution of sample A2

does not favour lithium-ion diffusion. The carbon content of sample C2 is as high as 5.39%, but the particles are also big. The impurities in sample C2 may be the main reason resulting in big particles.

Based on XRD and SEM results, it is obvious that the stability of chelating reagents is so much related to the pH value. Compared to salicylic acid and polyacrylic acid, critic acid has the highest stability. Since critic acid (H_3Cit) is a polybasic acid, multi-stage ionization happens according to different pH values of the solution. Therefore, the ions in the solution are various under different pH values. When the pH value is 3, the amount of H_3Cit and H_2Cit^- ions is the largest, and the chelating reactions can occur smoothly; when pH value is increased to 7, H_2Cit^- and $HCit^{2-}$ ions are dominated, which are helpful to the chelating reactions. However, the other two organic acids have weaker chelation. When pH value is as high as 7, the vanadate will separately form as precipitation and result in big particles and impurity, which may have a notable effect on the electrochemical performance of $Li_3V_2(PO_4)_3$.

3.2 Electrochemical properties

Figure 4 shows the initial discharge curves of all the samples. It can be seen that all the samples display typical voltage profiles of $Li_3V_2(PO_4)_3$ containing three discharge flat plateaus at a lower rate. However, with the increase of current density, the differences of polarization for all the samples are greater. Samples A1(pH=3) and A2 (pH=7) with critic acid as chelating reagent show lower polarization and good rate capacity (Fig. 4(a) and (b)). The two samples exhibit the similar initial discharge capacities of 123.6 mA·h/g and 121.5 mA·h/g at 0.1*C*. Sample A2 exhibits higher rate capacity. The initial discharge capacities of sample A2 at 0.1*C*, 0.2*C*, 0.5*C*, 1*C*, 3*C*, 5*C*, 10*C* and 20*C* are 121.5, 117.8, 116.7, 115.9, 114.5, 114.0, 112.7 and 110.8 mA·h/g, respectively; however, those of sample A1 are 123.6, 120.8, 117.2, 116.9, 113.2, 110.6, 104.0 and 92.9 mA·h/g, respectively. With salicylic acid as chelating reagent, the polarizations become higher, the voltage of the flat plateaus decreases fast with the increase of current density (Fig. 4(c)). Although sample B2 (pH=7) displays a higher initial discharge capacity (103.7 mA·h/g) than sample B1 (pH=3, 89.7 mA·h/g), they both exhibit bad rate capability, and the capacities at 20*C* are only about 60 mA·h/g. When using polyacrylic acid as chelating reagent, the initial discharge capacities of the two samples are lower than those of the others because the carbon content is as high as 5.3%. So, the active material in $Li_3V_2(PO_4)_3$/C composite material is lower, resulting in lower initial discharge capacity. From Fig. 4(e), it can be seen that the pH value of solution has great influence on the electrochemical properties. Sample C1 has lower polarization and the discharge capacities decrease slightly with the increase of current density; however, sample C2 displays very bad electrochemical properties, and the initial discharge capacity is as low as 67.3 mA·h/g at 0.1*C*, and only 28.5 mA·h/g under 20*C*.

Figure 5 displays the cycling performance of all the samples at different discharge rates between 3.0 and 4.5 V. As can be seen, samples A1and A2 have the best electrochemical performance. Their discharge capacities are much higher than those of the others, which maintain 94.8 and 110.8 mA·h/g at a high rate of 20*C*. Samples B1 and B2 show a severe decline in capacity during cycling, specifically sample B2. The bad rate performance of sample B2 may be attributed to its low purity. Sample C1 shows better electrochemical performance and the worst capacity happens to sample C2. Combined with the results of XRD and SEM, the low discharge capacities may be attributed to the poor crystallinity, low purity and big particle size of the sample.

Sample A2 can not only supply large capacity under high rate conditions, but also maintain good cycling stability. As shown in Fig. 6, under a high rate of 10*C*, a capacity of 113.58 mA·h/g is delivered. After 900 cycles it is also as high as 108.48 mA·h/g, with a capacity retention of 95.51%. The inset figure shows the charge/discharge curves. There are three flat plateaus on the discharge curves, which nearly keeps the same after 900 cycles. The promising electrochemical performance of the as-prepared $Li_3V_2(PO_4)_3$/C composite can be attributed to the small particle size and large specific area, which are beneficial for the lithium extraction and insertion reactions under high discharge current. According to the electrochemical performance presented above, the as-prepared $Li_3V_2(PO_4)_3$/C composite cathode material is very attractive to develop high power

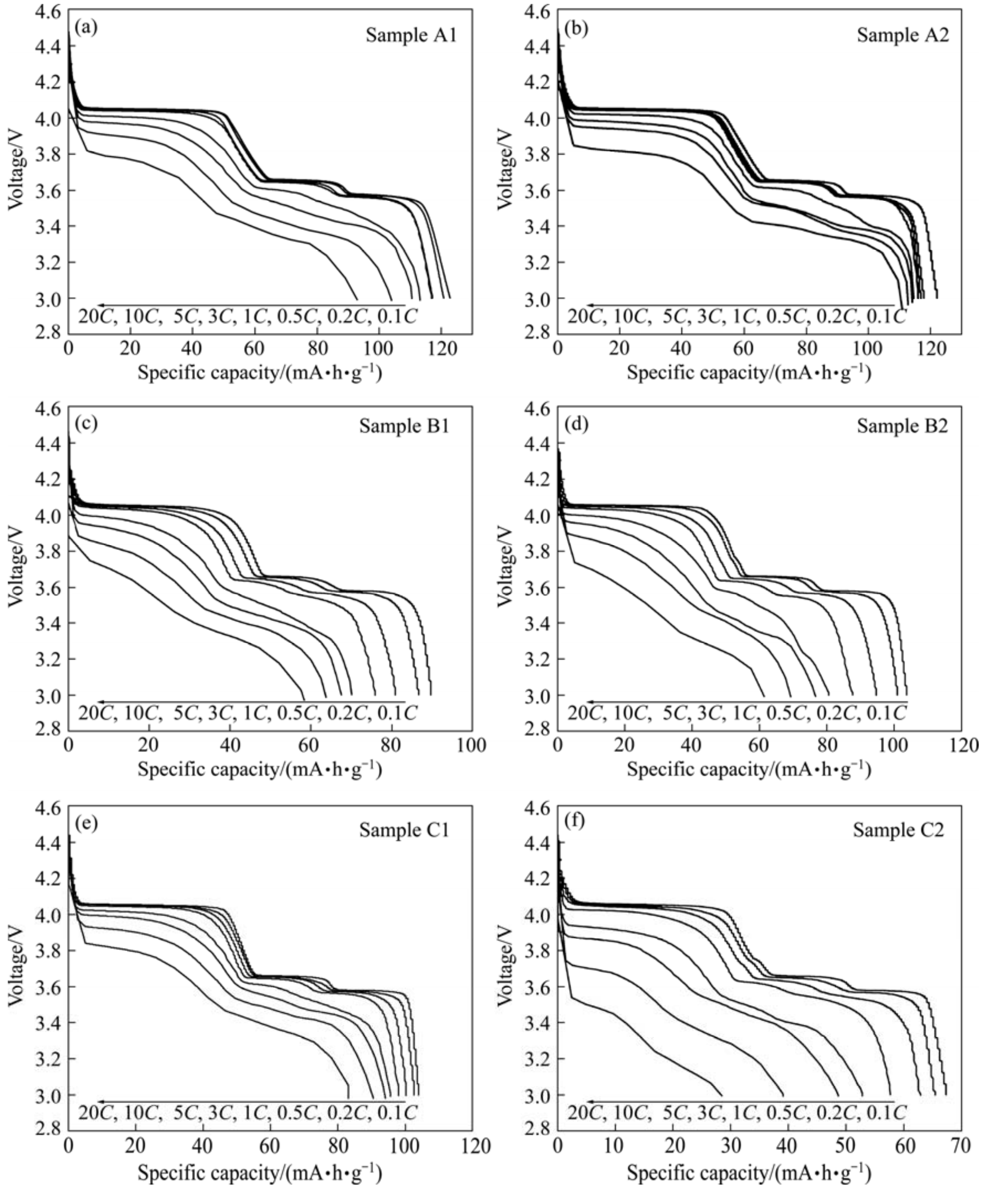

Fig. 4 Initial discharge curves of all samples at different discharge rates

lithium-ion batteries for electric vehicles (EVs) or hybrid electric vehicles (HEVs).

Figure 7 shows the CV curves of sample A2 from 3.0 V to 4.5 V at a scanning rate of 0.10 mV/s. It exhibits typical oxidative peaks near at 3.62, 3.71, and 4.12 V (vs Li/Li^+) as well as reductive peaks 3.55, 3.63, and 4.01 V (vs Li/Li^+), respectively, which correspond to the charge/discharge curves. Since only two Li^+ ions are removed, all of the three current peaks are assigned to the V^{3+}/V^{4+} redox couple. The redox peaks are sharp and the redox capacities (peak areas) ratio is close to 1, indicating a strong reversibility of the electrode reaction. In addition, the separations of redox peaks are small, and the maximum one is only 0.11 V, which also shows a good reversibility of electrode reaction, indicating that the material has good cycling performance.

Figure 8 presents the Nyquist plots of all the samples measured at the open-circuit voltage after galvanostatic charging/discharging tests at 20*C*. The spectra of samples show an intercept at high frequency, followed by a depressed semicircle in the high-middle frequency region, and a straight line in the low frequency

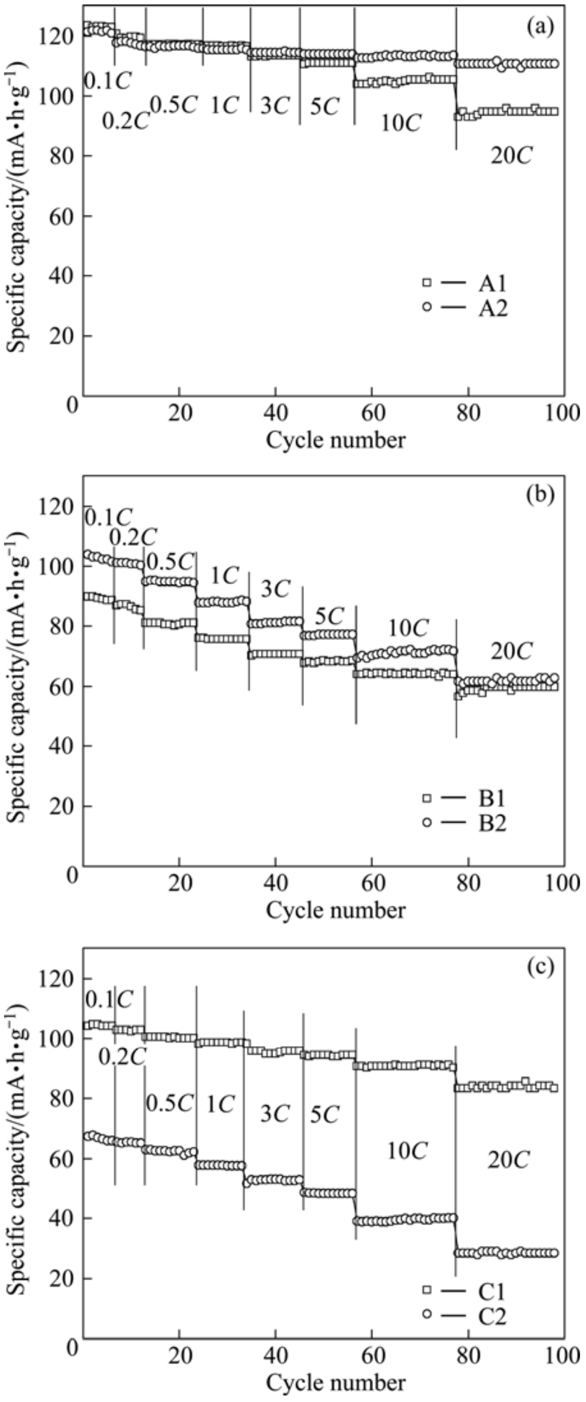

Fig. 5 Cycling performance of all samples at different discharge rates

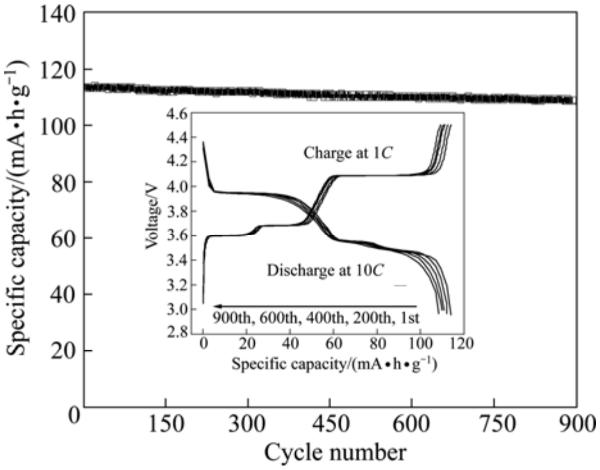

Fig. 6 Cycling performance of sample A2 at rate of 10*C*

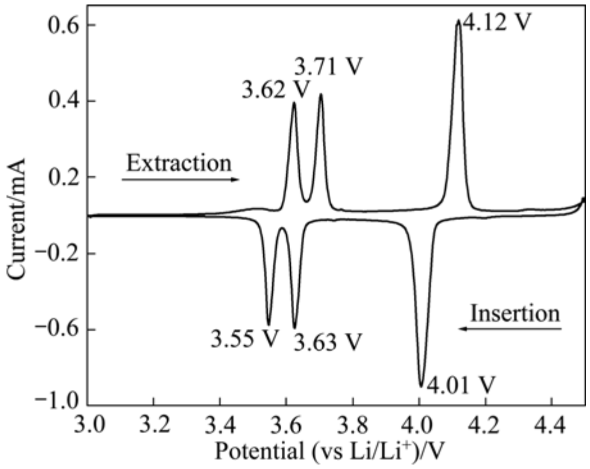

Fig. 7 Cyclic voltammograms of sample A2

region. Refinements of the diagrams were conducted by using the Zview2 program. An equivalent circuit has been built as shown in Figs. 8(a) and (b). In the circuit, the R_e represents the solution resistance of the electrolyte; R_{ct} and CPE_1 stand for the charge-transfer resistance and double-layer capacitance, respectively; *W* represents the diffusion-controlled Warburg impedance. The parameters of the equivalent circuit are shown in Table 2. It is found that the R_e is similar for all the samples at 2−5 Ω. R_{ct} values of sample A1 (66.1 Ω) and A2 (64.0 Ω) are much lower than the others after about 100 cycles, indicating that the two samples have better cycle performance. For the other samples, the R_{ct} values are much larger, especially the one has changed the pH value to 7, which may be attributed to the impurity in the materials increasing the impedance remarkably.

Table 2 Parameters obtained from equivalent circuit fitting of experiment data

Sample	R_e/Ω	R_{ct}/Ω
A1	2.5	66.1
A2	4.1	64.0
B1	2.4	184.8
B2	2.3	257.2
C1	4.5	133.8
C2	3.9	312.4

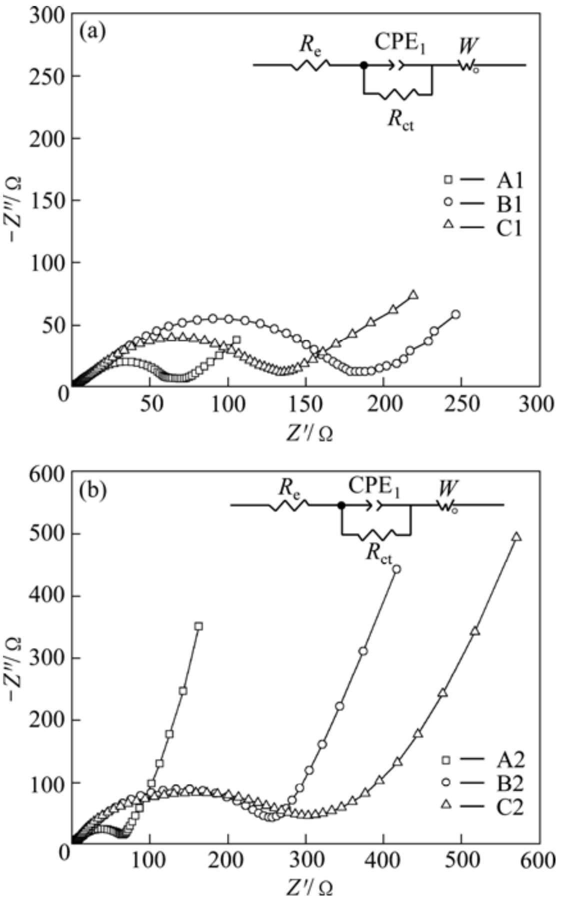

Fig. 8 EIS curves of all samples: (a) pH=3; (b) pH=7

4 Conclusions

1) $Li_3V_2(PO_4)_3/C$ composite cathode material was synthesized via sol−gel method using three different chelating reagents (citric acid, salicylic acid and polyacrylic acid) under different pH values (3, 7).

2) XRD patterns and SEM images show that increasing the pH value is good for the samples with critic acid as chelating reagents; however, when salicylic acid or polyacrylic acid is used as chelating reagent, high pH value leads to impurity and big particles.

3) Electrochemical tests indicate that the samples with critic acid as chelating reagents have better electrochemical performance than the others, especially the one with pH value of 7 demonstrated a good rate performance and a stable long-term cycling capacity of 113.58 mA·h/g with capacity retention of 95.51% at discharge rate of 10*C* up to 900 cycles.

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pH 值和螯合剂复合作用对正极材料 $Li_3V_2(PO_4)_3/C$ 性能的影响

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摘 要：使用不同的螯合剂(柠檬酸、水杨酸和聚丙烯酸)在不同的 pH 值条件下，采用溶胶−凝胶法合成 $Li_3V_2(PO_4)_3/C$ 正极材料。通过 X 射线衍射(XRD)、扫描电镜(SEM)、循环伏安(CV)、电化学阻抗谱(EIS)以及恒流充放电测试等方法, 研究材料的结构、形貌及电化学性能。结果表明，pH 值对材料性能的影响与所采用的螯合剂有很大的关系。当采用水杨酸和聚丙烯酸为螯合剂时，升高 pH 值对材料的结构、形貌和电化学性能有较大的负面影响。而采用柠檬酸为螯合剂时，材料结构无变化且颗粒分布更均匀，高倍率放电性能和循环性能也得到改善，10*C* 首次放电容量为 113.58 mA·h/g，循环 900 次后容量保持率为 95.51%。

关键词：$Li_3V_2(PO_4)_3$；正极材料；溶胶−凝胶法；螯合剂；pH 值

(Edited by Hua YANG)