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V₂O₅/mesoporous carbon composite as a cathode material for lithium-ion batteries

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V₂O₅/mesoporous carbon composite as a cathode material for lithium-ion batteries

Abstract

V₂O₅/mesoporous carbon composite has been prepared by an ultrasonically assisted method followed by a sintering process. The as-prepared V₂O₅/mesoporous carbon material containing 90 wt% V₂O₅ shows better electrochemical performance, with capacity of 163 mA h g⁻¹ after 100 cycles at the current density of 500 mA g⁻¹, as well as better charge/discharge rate capability for lithium storage than V₂O₅ nanoparticles. The improved electrochemical performance indicates that the V₂O₅/mesoporous carbon composite could be used as a promising cathode material for lithium ion batteries.

Keywords

ion, lithium, material, batteries, cathode, carbon, composite, mesoporous, v2o5

Disciplines

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V₂O₅/Mesoporous Carbon Composite as a Cathode Material for Lithium-ion Batteries

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ABSTRACT

V₂O₅/mesoporous carbon composite has been prepared by an ultrasonically assisted method followed by a sintering process. The as-prepared V₂O₅/mesoporous carbon material containing 90 wt% V₂O₅ shows better electrochemical performance, with capacity of 163 mA h g⁻¹ after 100 cycles at the current density of 500 mA g⁻¹, as well as better charge/discharge rate capability for lithium storage than V₂O₅ nanoparticles. The improved electrochemical performance indicates that the V₂O₅/mesoporous carbon composite could be used as a promising cathode material for lithium ion batteries.

Keywords: *vanadium pentoxide; mesoporous carbon; cathode; lithium ion batteries*

1. Introduction

Nowadays, rechargeable Li-ion batteries (LIBs) are extensively used in almost all types of

electronic devices, including cell phones, laptop computers, camcorders, and even electric and hybrid electric vehicles, due to their high energy and power density, high voltage, and long lifespan [1-3]. The worldwide market for lithium ion batteries is growing fast, especially for consumer products, and it will grow even more in the next decade. Frost & Sullivan, a business consulting firm, has reported that the global lithium-ion battery market in 2012 was worth \$11.7 billion, mainly for consumer applications, and this is expected to be twice as great, around \$22.5 billion, in 2016 [4].

Until now, LiCoO_2 , which was first introduced by SONY, has been the most commonly used cathode material in LIBs. Due to the toxicity, high cost, and safety issues of LiCoO_2 , however, many efforts have been made to develop other cathode materials, such as $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, LiMn_2O_4 , and LiFePO_4 [5-7]. These materials have shown significant improvements in their cycling stability and rate capability. Enhancement of their reversible lithium storage capacity has been limited, however, due to their intrinsic redox chemistry, which allows only one Li^+ insertion/extraction per formula unit. Hence, new materials need to be developed as cathode candidates with enlarged theoretical capacity through multi-electron reactions per formula unit, in order to comply with the demand for LIBs with high capacity and fast charge capability.

Among the many potential cathode candidates, vanadium pentoxide (V_2O_5) is one of the most promising due to its high energy density, abundance, low cost, and easy to synthesize [8-12]. The high theoretical capacity of V_2O_5 is especially attractive, around 294 mA h g^{-1} for the intercalation/deintercalation of two Li^+ ions between 2.0 and 4.0 V, which is much better than those of conventional cathode materials, such as LiMn_2O_4 (148 mA h g^{-1}) and LiFePO_4 (176 mA h g^{-1}). In spite of these advantages, the electrochemical performance of V_2O_5 is limited by its poor electrical conductivity (10^{-3} to $10^{-2} \text{ S cm}^{-1}$) and its sluggish diffusion of lithium ions ($\sim 10^{-12} \text{ cm}^2 \text{ s}^{-1}$) [13-16]. Moreover, phase transitions of $\text{Li}_x\text{V}_2\text{O}_5$ during the charge/discharge process often

cause structural instability and can further degrade its cycling performance [17-19]. These drawbacks have limited the practical application of this material in commercial LIBs. Several approaches have been tried to solve these issues: fabricating nanostructures, changing the pore size, and modifying the electrical conductivity with a carbon matrix [11-13, 15, 18, 20-45].

One approach to address these issues is modifying the V_2O_5 with ordered mesoporous carbon. Mesoporous carbon, which has pore sizes between 2 and 50 nm, will facilitate electrolyte diffusion into the bulk of the electrode material and hence provide fast transport channels for the conductive ions (i.e. Li^+ ions). Carbon will also provide fast electronic transport, which may enhance the overall performance of lithium ion batteries. The other properties of mesoporous carbon, such as its high thermal stability, large surface area, uniform pore diameter, high pore volume, and interconnected pore structure, also increase its potential value in lithium ion batteries [46, 47]. Some metal oxide/mesoporous carbon composites have already been synthesized, such as ones containing Sn/SnO_2 , SnO_2 , Cr_2O_3 , and TiO_2 , as electrode materials for lithium ion batteries [18-22]. V_2O_5 -mesoporous carbon composite as an electrode material for capacitors has also been reported by Yu et al. [48]. In this work, we use mesoporous carbon to prepare V_2O_5 -mesoporous carbon composite as a cathode material for LIBs. The mesoporous structure of the carbon helps the diffusion of electrolyte into the bulk of the electrode and, as a result, provides fast transport channels for Li^+ ions.

2. Experimental

Preparation of mesoporous carbon

The mesoporous carbon was synthesized in a similar way to the procedure reported by C. F. Xue et al. [49] with a slight modification. Firstly, a resol solution was prepared as the carbon precursor. Phenol (61 g) was melted at 42 °C in a flask, and 20 mL 20 wt% NaOH solution was then slowly added under stirring over a period of 20 minutes. After that, 100 mL formalin (37

wt%) was added to the solution, and the mixture was heat-treated at 70 °C for 1 h. The pH of the mixture was adjusted to 7.0 after cooling down to room temperature naturally. Water was then eliminated under vacuum at a temperature below 50 °C, and the obtained product (resol solution) was dissolved in ethanol (40 wt%).

The mesoporous-carbon-silica composite monoliths were prepared via evaporation-induced coating self-assembly (EISA). In a typical synthesis, 16 g F127 triblock copolymer was dissolved in a mixture of ethanol (82 mL) and 0.2 M HCl (10 mL), and stirred for 1 h at 40 °C. Then, the resol solution was slowly added to this solution under stirring for 10 min, followed by the addition of 20.8 g tetraethyl orthosilicate (TEOS), and stirring was continued for 2 h at ambient temperature. The obtained solution was poured onto polyurethane (PU) foam. The air bubbles inside the PU foam were eliminated by regularly squashing the foam with a glass rod during the infusion process. The infused PU foam was turned constantly for 5–8 h to vaporize the solvent. Then, the PU foam was heated at 100 °C for 20 h in an oven for further thermopolymerization. The calcination was carried out at 900 °C for 3 h under flowing N₂, with heating rates of 1 °C min⁻¹ below 600 °C and 5 °C min⁻¹ above 600 °C, so that a mesoporous composite was obtained. Then, the resultant composite was washed in boiled NaOH solution (2.5 M) to remove the silica in order to obtain mesoporous carbon. Surface modification of the mesoporous carbon was performed in the following way: 1 g mesoporous carbon was added into 100 mL HNO₃ (20 wt%) and stirred for 3 h at 80 °C. The resultant product was recovered by filtration and washed with deionized water until the filtrate pH was 7. Then, the product was added into 100 g of H₂O₂ 30 wt% solution and stirred at room temperature for 30 min, after which, the stirring was continued at 60 °C for 1 h. Finally, the product was obtained by filtration, washed thoroughly with water, and dried at 80 °C for 12 h.

Preparation of V₂O₅/mesoporous carbon

V₂O₅ was prepared by the sol method by stirring 0.5 g V₂O₅ powder into 50 mL H₂O₂ (30 wt%) for 24 h at room temperature [50]. Then, 0.2 g mesoporous carbon was dispersed into the V₂O₅ sol, and the mixture was stirred for 1 h. After that, the mixture was ultrasonicated for 3 h at room temperature. The precipitate was filtered and washed with distilled water and ethanol. Then, the solvent was removed by drying at 120 °C for 12 h. The resultant product (denoted as V₂O₅/mc before sintering) was divided into three portions: the first portion was reserved without further treatment, another portion was sintered at 550 °C in air atmosphere for 2 h with a 5 °C min⁻¹ heating rate to burn away the carbon to produce V₂O₅ nanoparticles (denoted as V₂O₅ np), and the third portion was sintered at 300 °C for 5 h in air atmosphere (denoted as V₂O₅/mc).

Characterisation

The specific surface area (determined by the Brunauer-Emmett-Teller (BET) method) and nitrogen adsorption-desorption isotherms of samples of mesoporous carbon and V₂O₅/mc before sintering were measured in order to observe the effects of the insertion process on the properties of the mesoporous carbon. V₂O₅/mc before sintering was examined by transmission electron microscopy (TEM; JEOL 2010 and JEOL ARM-200F) in order to determine whether the insertion process of V₂O₅ into the mesoporous carbon was successful or not.

All the resultant products were characterised by X-ray diffraction (XRD; GBC MMA Diffractometer, Cu K α radiation, $\lambda = 1.5406 \text{ \AA}$). The content of V₂O₅ in the V₂O₅/mc was investigated by thermogravimetric analysis (TGA; Mettler Toledo TGA/DSC1), which was taken into account in the battery testing. For electrochemical performance testing, working electrodes were prepared by mixing 85 wt% active material, 6 wt% conductive agent (carbon black, Super-P-Li), and 9 wt% polyvinylidene difluoride (PVDF) binder (Sigma-Aldrich) in N-methyl-2-pyrrolidinone (NMP) to form a homogeneous slurry. The slurry was uniformly pasted onto

aluminium foil and dried in a vacuum oven at 120 °C for 12 h. Electrochemical cells (CR2032 coin type) containing the working electrode and Li foil as the counter and reference electrode were assembled in an Ar-filled glove box (Mbraun, Unilab, USA). 1 M LiPF₆ in a 3:4:3 (v/v) mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC), with 5% fluoroethylene carbonate (FEC) additive was used as the electrolyte. The galvanostatic charge-discharge measurements were performed on a Land CT2001A battery tester.

3. Results and discussion

Fig. 1 presents the nitrogen adsorption–desorption isotherms and the pore size distribution curves of the mesoporous carbon (mc) and V₂O₅/mc composites before sintering. As can be seen in Figure 1(a), N₂ sorption isotherms of both samples show hysteresis and therefore represent type-IV behaviour, according to the IUPAC classification, indicating mesoporous structure. Fig. 1(b) reveals that the main pore size of the mesoporous carbon (mc) is about 3 nm, and the pore size decreases to 2-3 nm after insertion of V₂O₅. This is consistent with the BET surface area and total pore volume data for the mesoporous carbon and the V₂O₅/mc before sintering, as summarized in Table 1. The BET surface area (S_{BET}) of the V₂O₅/mc before sintering is decreased significantly compared to that of mesoporous carbon matrix alone, which are calculated to be 77.2 and 874 m² g⁻¹, respectively. This clearly indicates that the V₂O₅ nanoparticles have filled most of the pores in the mesoporous carbon. The total pore volumes of the mc and the V₂O₅/mc composite are 0.76 and 0.06 cm³ g⁻¹, respectively which also demonstrates that the V₂O₅ nanoparticles block the pore channels.

The TEM images and energy dispersive spectroscopy (EDS) results confirm the dispersion of the V₂O₅ particles in the pores of the mesoporous carbon. Fig. 2(a) shows the highly ordered mesoporous carbon in the mesoporous carbon sample. Scanning transmission electron microscope

(STEM) images of V_2O_5/mc before sintering are presented in Fig. 2(b) and (c), which are in bright field (BF) and annular dark field (ADF) mapping mode, respectively. Amorphous structures of carbon and lattice fringes of V_2O_5 are observed in the BF mode figure. In the ADF mapping mode, the dark contrast is from the pores of carbon without any V_2O_5 particles, while the light contrast reflects the very fine particles of V_2O_5 in the occupied pores of mesoporous carbon. The EDS spectrum in Fig. 2(d) of the area in Fig. 2(b) and (c) confirms the presence of V_2O_5 in the sample.

We have applied two strategies to prevent the coating of V_2O_5 on the carbon. Firstly, the V_2O_5 was dissolved in H_2O_2 to form a V_2O_5 sol. Secondly, due to the capillary effect of the mesopores and the applied ultrasonication, the majority of V_2O_5 can be sucked into the pores of the mesoporous carbon. BET test results have confirmed the insertion of the V_2O_5 particles into the pores of the carbon. The TEM image in Figure 2(b) shows some light contrast representing pores in the carbon and some dark contrast representing V_2O_5 in the occupied pores, confirming that our strategies have been successful.

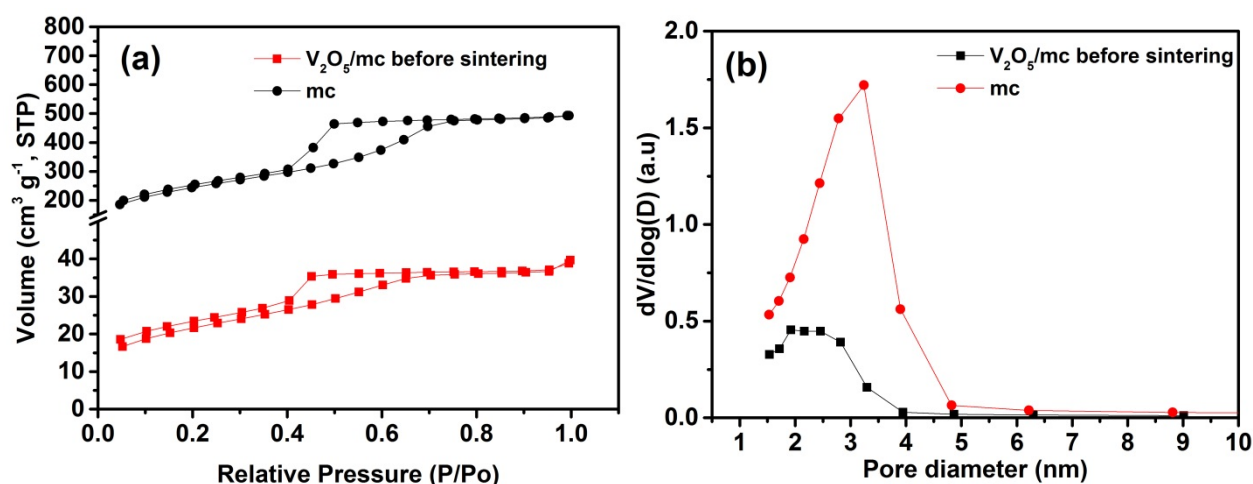


Figure 1. (a) Nitrogen adsorption-desorption isotherms; (b) pore size distributions of mesoporous carbon (mc) and V_2O_5/mc before sintering.

Table 1. BET surface area and total pore volume per gram of the mesoporous carbon and the V₂O₅/mc before sintering.

| Sample | S _{BET} (m ² g ⁻¹) | V _{pore} (cm ³ g ⁻¹) |
|--|--|--|
| Mesoporous carbon (mc) | 874 | 0.76 |
| V ₂ O ₅ /mc before sintering | 77.2 | 0.06 |

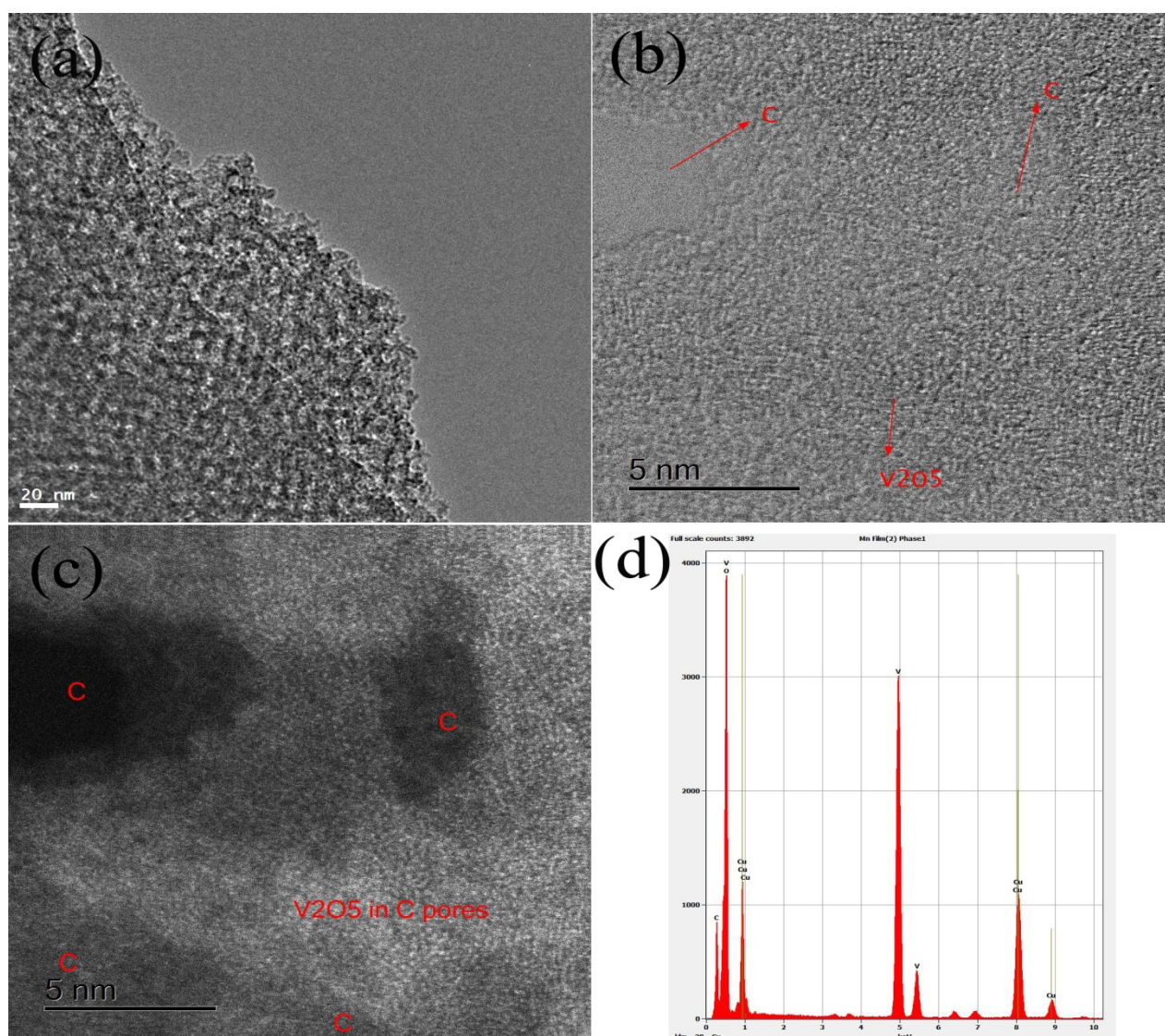
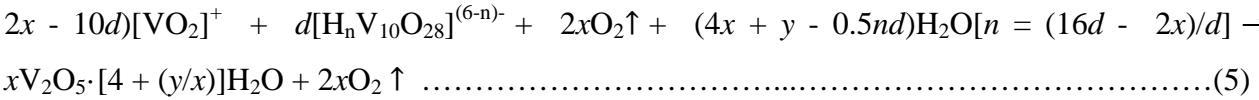
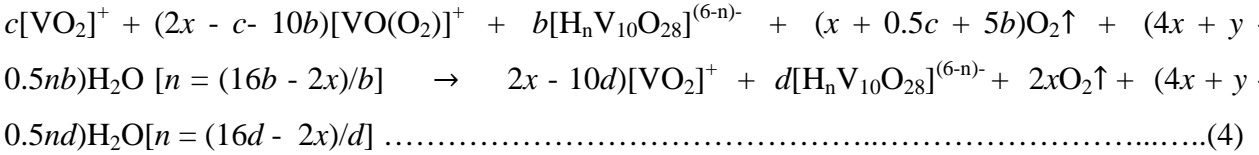
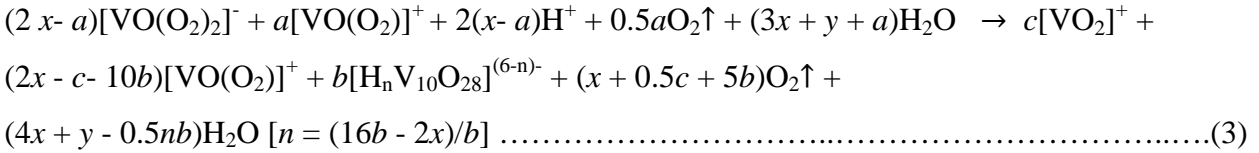
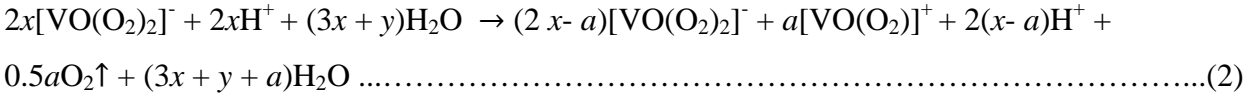
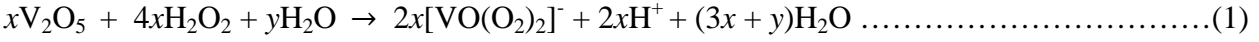


Figure 2. (a) TEM image of mesoporous carbon sample; (b) STEM image of V₂O₅/mc before sintering in BF mapping mode; (c) STEM image of V₂O₅/mc before sintering in ADF mapping mode (with dark contrast representing pores of carbon, light representing pores + V₂O₅ particles); (d) EDS spectrum of the area in (b) and (c) (with the Cu peak coming from the TEM sample holder).

The reactions of V₂O₅ powder and H₂O₂ in the order used to make V₂O₅ sol can be described by the following reactions [39]:



$xV_2O_5 \cdot [4 + (y/x)]H_2O$ represents the resulting vanadium pentoxide sol. In lithium ion battery tests, the resulting vanadium pentoxide sol sample will suffer from poor electrochemical performance due to the crystal water, and therefore, a sintering process at 300 °C for 5 h was applied to the V₂O₅/mc before sintering sample to further remove the crystal water. Fig. 3 (a) presents the XRD patterns of V₂O₅/mc, V₂O₅ np, and V₂O₅/mc before sintering. The XRD patterns of V₂O₅/mc and V₂O₅ np indicate that all the diffraction peaks are in good agreement with the standard pattern of orthorhombic V₂O₅ (space group: Pmnm (No. 59), $a = 1.1516$ nm, $b = 0.3565$ nm, $c = 0.4372$ nm, JCPDS card No. 41-1426). In contrast, the pattern of V₂O₅/mc before sintering shows two diffraction peaks at 26.2° and 51.3°. The weakness and broadness of the peaks indicate the poor crystallization and small crystallite size of the vanadium pentoxide. It can be concluded that ultrasonic treatment inhibits the aggregation of vanadium pentoxide.

The content of V₂O₅ in the V₂O₅/mc sample (after sintering) was examined by thermogravimetric analysis (TGA) in air (Figure 3 (b)). As illustrated in the Figure, the weight loss before 150 °C can be assigned to the evaporation and removal of moisture. When the heating

was continued to 550 °C, the weight loss could be determined to be carbon removal. The content of V₂O₅ in the V₂O₅/mc sample after sintering is 90 wt%, which was taken into account in the battery testing.

The rate capabilities of V₂O₅/mc and V₂O₅ np were measured at various current densities between 2 and 4 V. Figure 4(a) presents the rate capability of V₂O₅/mc, which is better than that of V₂O₅ np. The V₂O₅/mc electrode displays better performance than the V₂O₅ np electrode at all current densities. The capacities of V₂O₅/mc are 291, 265, and 247 mA g⁻¹, at current densities of 100, 250, and 500 mA g⁻¹, respectively. In contrast, the capacity of V₂O₅ np rapidly decreases as the current density is increased. It shows the capacities of 275, 235, and 182 mA g⁻¹ at current densities of 100, 250, and 500 mA g⁻¹, respectively. After a deep cycling at 5 A g⁻¹, the V₂O₅/mc electrode can almost recover its initial capacity when the current density is returned to 100 mA g⁻¹. Evidently, the V₂O₅/mc sample demonstrates higher capacity at every current density. The V₂O₅/mc electrode also shows improved rate capability performance compared with those of V₂O₅/rGO [40], V₂O₅/PEDOT/MnO₂ nanowire [41], multiwalled CNT- V₂O₅ [39], V₂O₅ nanosheet /RGO [42], and graphene nanoribbon / V₂O₅ [43], as shown in Table 2.

The cycling performances of V₂O₅/mc and V₂O₅ np samples at a current density of 500 mA g⁻¹ are shown in Figure 4(b). The capacity retention of V₂O₅/mc is considerably higher than that of V₂O₅ np. A better reversible capacity of 163 mAh g⁻¹ is maintained after 100 cycles, which represents a capacity loss of 40 %, while the capacity of V₂O₅ np electrode declines to around 50 % after 100 cycles. V₂O₅/mc with capacity of 198 mAh g⁻¹ after 50 cycles also shows comparable or better performance in comparison with several V₂O₅/carbon composites from recently published works (Table 2), for example, V₂O₅/rGO (105 mAh g⁻¹ at 5700 mA g⁻¹) [40], V₂O₅/PEDOT/MnO₂ nanowire (166 mAh g⁻¹ after 40 cycles at 50 mA g⁻¹) [41], multiwalled CNT- V₂O₅ (199 mAh g⁻¹ at 100 mA g⁻¹) [39], V₂O₅ nanosheet /RGO (150 mAh g⁻¹ at 600 mA g⁻¹) [42], and graphene nanoribbon / V₂O₅ (230 mAh g⁻¹ at 30 mA g⁻¹) [43].

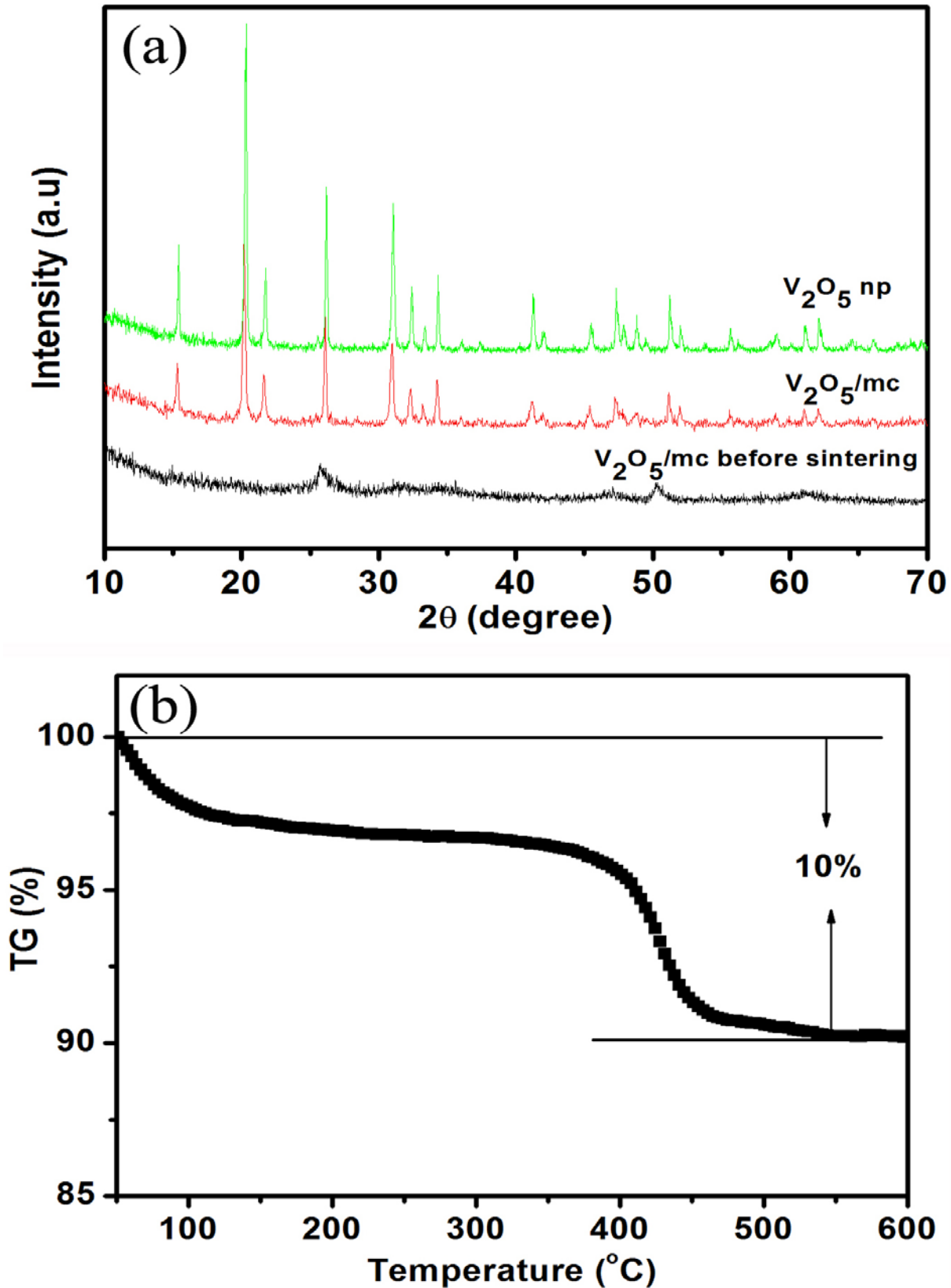


Figure 3. (a) XRD patterns of V_2O_5 nanoparticles (V_2O_5 np) and of V_2O_5 /mesoporous carbon (V_2O_5/mc) before and after sintering; (b) TGA curve of V_2O_5 /mesoporous carbon (V_2O_5/mc) after sintering

We have also synthesized a composite of V_2O_5 nanoparticles and mesoporous carbon made by simple mixing (denoted as V_2O_5/mc sm) for comparison. Its rate capability and cycling performance, as shown in Figure 4(a) and (b), are not as good as those of V_2O_5/mc produced by the ultrasonication technique. The lower rate capability and cycling performance indicate that the mesoporous structure plays an important role in Li^+ ion transport that the performance will be improved much more by the insertion of V_2O_5 particles into the pores.

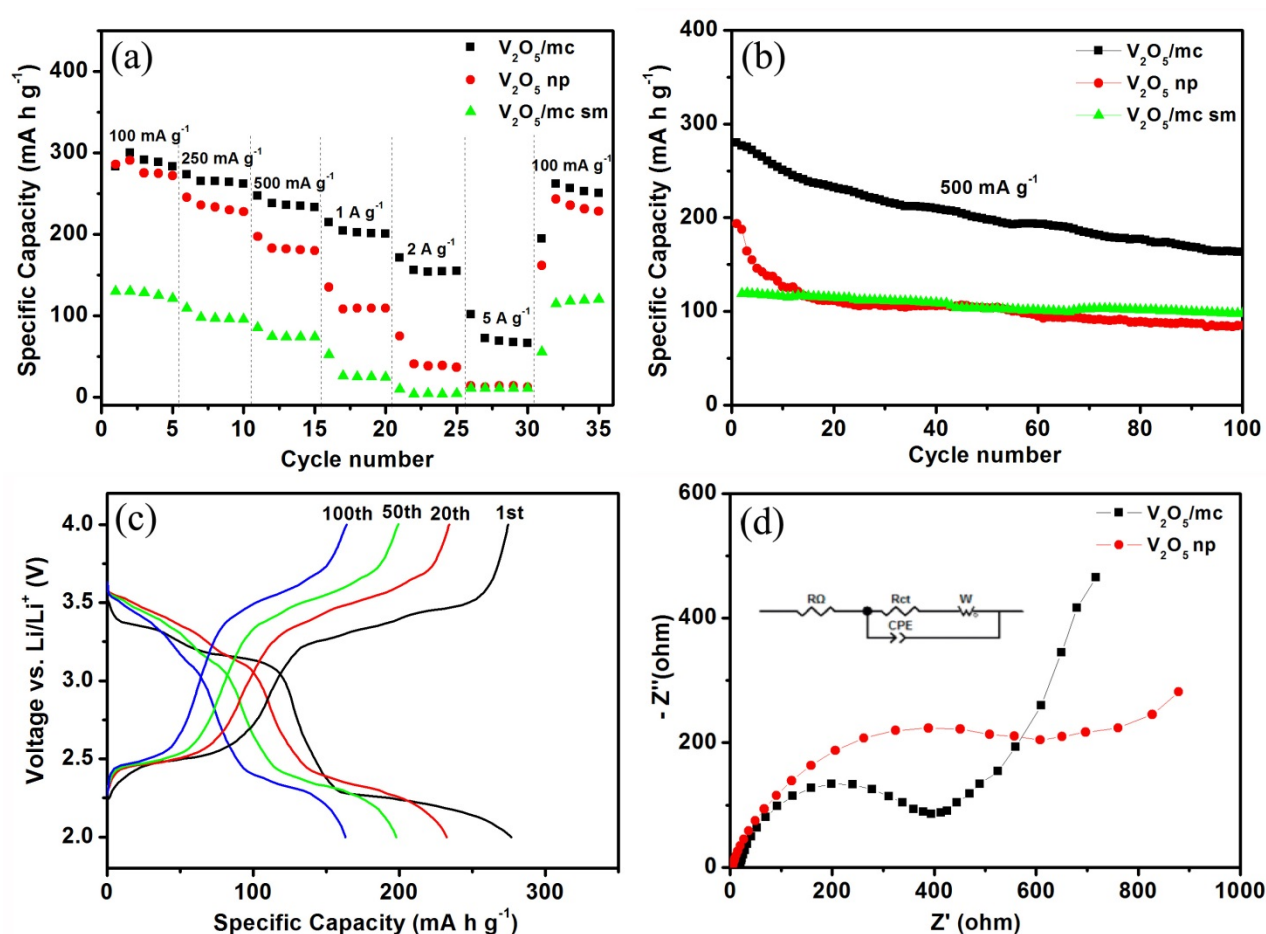


Figure 4. (a) Rate capability of V_2O_5/mc , V_2O_5 n, and V_2O_5/mc sm at various current densities; (b) cycling performance of V_2O_5/mc , V_2O_5 np, and V_2O_5/mc sm in the voltage range of 2.0–4.0 V at the current density of 500 mA g^{-1} ; (c) charge/discharge voltage profiles of V_2O_5/mc at the current density of 100 mA g^{-1} for the selected cycles indicated; (d) electrochemical impedance spectra of V_2O_5/mc and V_2O_5 np electrodes after 5 charge/discharge cycles and the equivalent circuit used to fit the impedance data (inset).

Table 2. Comparison of our and recently published works on V₂O₅/Carbon composites for lithium ion batteries.

| Electrode Description | Rate Capability | Specific Capacity after 50 cycles | Reference |
|--|--|--|-----------|
| V ₂ O ₅ /rGO | 220 mAh g ⁻¹ at 190 mA g ⁻¹ 180 mAh g ⁻¹ at 950 mA g ⁻¹ | 105 mAh g ⁻¹ at 5700 mA g ⁻¹ | [40] |
| V ₂ O ₅ /PEDOT & MnO ₂ nanowire | 164 mAh g ⁻¹ at 100 mA g ⁻¹ 48 mAh g ⁻¹ at 500 mA g ⁻¹ | 166 mAh g ⁻¹ after 40 cycles at 50 mA g ⁻¹ | [41] |
| Multiwalled CNT-V ₂ O ₅ | 250 mAh g ⁻¹ at 200 mA g ⁻¹ 221 mAh g ⁻¹ at 400 mA g ⁻¹ 193 mAh g ⁻¹ at 600 mA g ⁻¹ | 199 mAh g ⁻¹ at 100 mA g ⁻¹ | [39] |
| V ₂ O ₅ nanosheet /RGO | 200 mAh g ⁻¹ at 600 mA g ⁻¹ 138 mAh g ⁻¹ at 3000 mA g ⁻¹ | 150 mAh g ⁻¹ at 600 mA g ⁻¹ | [42] |
| Graphene nanoribbon/ V ₂ O ₅ | 200 mAh g ⁻¹ at 300 mA g ⁻¹ 165 mAh g ⁻¹ at 600 mA g ⁻¹ | 230 mAh g ⁻¹ at 30 mA g ⁻¹ | [43] |
| This work | 291 mAh g⁻¹ at 100 mA g⁻¹ 265 mAh g⁻¹ at 250 mA g⁻¹ 247 mAh g⁻¹ at 500 mA g⁻¹ | 198 mAh g⁻¹ at 500 mA g⁻¹ | |

Figure 4(c) presents charge/discharge profiles of V₂O₅/mc at a current density of 500 mA g⁻¹ in the voltage window of 2.0–4.0 V. There are three plateaus at about 3.3, 3.1, and 2.2 V in the first cycle, which can be attributed to the phase transitions during Li⁺ ion intercalation from α-Li_xV₂O₅ ($x < 0.01$) to ε-Li_xV₂O₅ ($0.35 < x < 0.7$), from ε-Li_xV₂O₅ to δ-Li_xV₂O₅ ($x < 1$), and from δ-Li_xV₂O₅ to γ-Li_xV₂O₅ ($x > 1$), respectively [39]. Three plateaus corresponding to the Li⁺ ion deintercalation processes are also occurred on the charge curve. Figure 4(d) shows the Nyquist plots of V₂O₅/mc and V₂O₅ np after five cycles. In the equivalent circuit (inset), R_{Ω} and R_{ct} reflect the ohmic resistance and the charge transfer resistance, respectively. CPE is the constant phase-angle element, involving double layer capacitance; and W is the Warburg impedance, representing the solid-state diffusion of Li⁺ ions into the bulk of the active material. The charge transfer resistance, R_{ct} , for V₂O₅/mc (397 Ω cm⁻²) is less than that for V₂O₅-np (604 Ω cm⁻²), indicating

improved charge transfer in the V_2O_5/mc electrode. The reason for the better performance of V_2O_5/mc is likely to be because the V_2O_5 is in a composite with mesoporous carbon, which can provide fast transport channels for lithium ions.

4. Conclusions

We have successfully fabricated a V_2O_5 /mesoporous carbon composite by using an ultrasound assisted method followed by sintering. The mesoporous structure of the carbon facilitates the electrolyte diffusion into the bulk of the electrode material and hence provides fast transport channels for Li^+ ions. As a cathode material for LIBs, V_2O_5 /mesoporous carbon shows better performance than V_2O_5 nanoparticles, suggesting that V_2O_5 /mesoporous carbon composite could be used as a promising cathode material for lithium ion batteries.

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