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V_2O_5/Mesoporous Carbon Composite as a Cathode Material for Lithium-ion Batteries

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ABSTRACT

V_2O_5/mesoporous carbon composite has been prepared by an ultrasonically assisted method followed by a sintering process. The as-prepared V_2O_5/mesoporous carbon material containing 90 wt% V_2O_5 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 V_2O_5 nanoparticles. The improved electrochemical performance indicates that the V_2O_5/mesoporous carbon composite could be used as a promising cathode material for 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 $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, $LiMn_2O_4$, 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} cm^{-1}) and its sluggish diffusion of lithium ions ($\sim10^{-12}$ cm^2 s^{-1}) [13–16]. Moreover, phase transitions of $Li_xV_2O_5$ 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

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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

2.1. 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 N_2, 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 HNO_3 (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 H_2O_2 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.

2.2. Preparation of V_2O_5/mesoporous carbon

V_2O_5 was prepared by the sol method by stirring 0.5 g V_2O_5 powder into 50 mL H_2O_2 (30 wt%) for 24 h at room temperature [50]. Then, 0.2 g mesoporous carbon was dispersed into the V_2O_5 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 V_2O_5/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 V_2O_5 nanoparticles (denoted as V_2O_5 np), and the third portion was sintered at 300 °C for 5 h in air atmosphere (denoted as V_2O_5/mc).

2.3. Characterisation

The specific surface area (determined by the Brunauer-Emmett-Teller (BET) method) and nitrogen adsorption-adsorption isotherms of samples of mesoporous carbon and V_2O_5/mc before sintering were measured in order to observe the effects of the insertion process on the properties of the mesoporous carbon. V_2O_5/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 V_2O_5 into the mesoporous carbon was successful or not.

All the resultant products were characterised by X-ray diffraction (XRD; GBC MMA Diffractometer, Cu Kα radiation, $\lambda = 1.5406$ Å). The content of V_2O_5 in the V_2O_5/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

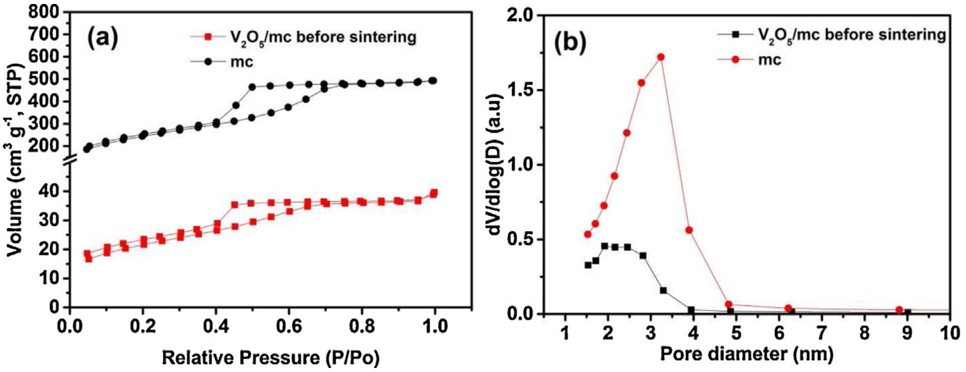

Fig. 1. (a) Nitrogen adsorption-desorption isotherms; (b) pore size distributions of mesoporous carbon (mc) and V_2O_5/mc before sintering.