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The high electrochemical performance of $Li_3V_2(PO_4)_3$ supported by graphene and carbon-nanofibers for advanced Li-ion batteries

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ABSTRACT

The intrinsically low electronic conductivity of $Li_3V_2(PO_4)_3$ (LVP) is a major drawback to be widely used as cathode materials for Li-ion battery. In this study, we synthesized novel LVP composites combining them with carbon nanofiber (CNF) and graphene with improved electrochemical performance. The specific capacity of LVP/CNF-graphene (LVP-CG) was 207 mAh g^{-1} at 0.1C between 3.0 and 4.8 V, which is beyond the theoretical capacity of LVP (197 mAh g^{-1}). Moreover, the LVP-CG composite shows smaller particle size, high surface area, improved electronic kinetic behavior and low resistance in the LVP electrode. Our results demonstrate that novel composite with CNF and graphene can be widely used in other phosphate-based cathode materials for advanced Li-ion batteries.

1. Introduction

The green and sustainable energy power source should be developed due to the climate change concern and growing demand for energy storage. Regarding of energy and environment crisis, Li-ion batteries (LIBs) have great potential as one of the promising energy storage devices due to its high volume and gravimetric energy density [1–6]. However, there are still many issues to be resolved before the wide use of LIBs with high capacity, rate capability, and energy density. The monoclinic $Li_3V_2(PO_4)_3$ (LVP) has been considered as a promising cathode material for LIBs because of its high operating voltages, high theoretical capacity (197 mAh g^{-1} in the potential range 3.0–4.8 V), and intrinsic stability [7–10]. Owing to the inherent low electronic conductivity (about 2.3×10^{-8} cm^{-1} at room temperature) of LVP, the specific capacity could not be achieved. A lot of approaches have been pursued with metal doping [11–16], carbon coating, and smaller particle size [17–22]. Among them, carbon coating and transition metal doping are widely used to improve their electronic conductivity. As a result, the high specific capacity and cycle stability of LVP were significantly enhanced. However, these results still exhibit low specific capacity at low current rate. In addition, the carbon coating method and transition metal doping resulted in an irregular electrical conductive layer and a minimal doping effect, which can lead to less improved electrode conductivity of LVP. The high capacity and energy density of LIBs is also important in practical use. More recently, novel cathode materials of LVP have also been also proposed with hierarchical nanowire [23] and carbon matrix [24] structures and conducting polymer [25,26]. However, they did not report the specific capacity in the potential range of 3.0–4.8 V. Three lithium ions inserted/extracted from the $Li_3V_2(PO_4)_3$ lattice enable the theoretical capacity to achieve 197 mAh g^{-1} in that voltage window, which is the highest among the polyanion framework materials.

For the high electrochemical performance of LVP, electron transport and ion conductivity are very important factors for the electrode. Graphene has positive properties in energy storage devices, especially in high surface area and electronic conductivity [27–32]. However, their closed-stacking structure can prevent electron transport in the vertical direction and limit the high electrochemical performance. Therefore it should be needed in the development of an unique electrode design that allows electrons to effectively transport in graphene matrix. In addition, the introduction of surface functional groups on CNF and graphene is a promising strategy to increase the specific capacity of electrodes [33]. Previously, we reported the LVP/Ag graphene composite synthesized by a facile sol–gel route to improve the electronic conductivity of the LVP [34]. The LVP/Ag-graphene composites exhibited a reasonable discharge capacity at 0.1C and capacity retention (78%) at 0.5C in the potential range of 3.0–4.8 V. Moreover, the exceptional discharge capacity of 134 mAh g^{-1}

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was achieved at 10C, which is the highest value in graphene based LVP composites [29–32].

In our report, we developed the novel structure of LVP combined with graphene and CNF for LIBs, which is beneficial for improving high capacity and rate capability. The specific capacity LVP/CNF-graphene (LVP-CG) exhibits the specific capacity of 207 mAh g^{-1} at 0.1C between 3.0 and 4.8 V, which is beyond the theoretical capacity of LVP (197 mAh g^{-1}). The beyond specific capacity is ascribed to the favorable electron conducting property in CNF and graphene structures in the LVP-CG rather than from carbon materials.

2. Experimental

All the solvents and chemicals are commercially available and used as received unless otherwise stated.

2.1. Functionalization of CNFs and graphene powder

The functionalization of CNF was prepared by using an oxidation CNF. The CNFs were oxidized in HNO_3 (70%, J.T. Baker) solution for 2 h at 80 °C in order to make functional groups on their surface. The functionalized CNFs were washed in DI water and dried at 100 °C in the oven. The graphene powder was dispersed in aqueous KOH solution (mass ratio of KOH and graphene, 7) for 24 h. The KOH solution with graphene was filtered, washed and dried at 100 °C in the oven.

2.2. Synthesis of LVP/CNF-graphene

The LVP was synthesized through the sol–gel method by using V_2O_5, $H_2C_2O_4$, $NH_4H_2PO_4$, and Li_2CO_3, respectively. The detailed preparation method is described below. First, V_2O_5 and $H_2C_2O_4$ in a stoichiometric ratio of 1:3 were dissolved in deionized (DI) water at 80 °C until clear blue solution was formed. Oxalic acid was used not only as a reducing agent but also as a chelating agent. Second, after magnetic stirring for 1 h, the amount of stoichiometric $NH_4H_2PO_4$ and Li_2CO_3 and the solution was vigorously stirred for 1 h to form LVP precursor. Sequentially, the functionalized CNFs (100 mg) and graphene (50 mg) were mixed in DI water and then sonicated for 2 h. Third, the LVP precursor solution poured into the CNF and graphene solution and stirred by using a magnetic force stirrer for 24 h. Finally, the mixture was heated at 80 °C and the resulting slurry was dried at 100 °C, followed by sintered at 350 °C for 4 h and then 800 °C for 8 h under argon atmosphere in a tube furnace. The ramping rate was 5 °C min^{-1}. The pristine LVP and LVP-G were synthesized with same method except for graphene or CNF.

2.3. Characterization

The morphology and elements of the samples was investigated by a field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi) working at 30 kV and energy-dispersive spectrum (EDS), respectively. Transition electron microscopy (TEM) images were observed using a TF30ST at a 300 kV acceleration voltage. The powder X-ray diffraction (XRD, X-pert PRO MPD, Philips) patterns of composites were conducted with Cu Kα radiation ($\lambda = 1.5406$ Å) operating at 40 kV and 30 mA between 10° and 90° at a scan rate of 0.01°, 2θ/min. Raman measurement (NTEGRA SPECTRA, NT-MDT) was conducted with a laser wavelength of 532 nm. The carbon content of the samples was measured by a CHNS Elemental Analyzer (EA, 2400 series 2). Brunauer–Emmet–Teller measurement (BELSORP-Max, BEL JAPAN) was analyzed by adsorption of N_2 at 300 °C.

2.4. Electrochemical measurements

The electrochemical performance of the LVP/CNF-graphene was evaluated by 2032 coin cells assembled in a dry room. The electrode was prepared with active material (70%), Super P (20%), and polyvinylidene Fluoride (PVdF, 10%) as a binder. Consequently, the paste was casted onto Al foil and dried at 100 °C in the vacuum oven overnight. The Li metal was used as the counter and reference electrode. The 1 M $LiPF_6$ dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume) and polypropylene 2400 was also used as an electrolyte and a separator, respectively. Galvanostatic charge–discharge was performed in a potential range of 3.0–4.3 and 3.0–4.8 V (vs. Li^+/Li) using a battery cycler (TOCAT-3100, TOYO System). The C-rates were based on the theoretical capacity of the LVP (1C = 133 and 197 mAh g^{-1}). The cyclic voltammetry (CV) was recorded at potential range of 3.0–4.8 V at a scan rate of 0.1 mV s^{-1}. The electrochemical impedance measurement (EIS) was also conducted after the 20th charge–discharge cycle by using a Biologic VMP3 multichannel system, and the applied frequency range was from 100 kHz to 10 mHz with an amplitude of 5 mV. The typical electrode mass and thickness was about 1.1 mg cm^{-2} and 20 μm, respectively. All of the electrochemical measurement was carried out at room temperature and all capacity values were calculated based on the weight of active material of LVP.

3. Result and discussion

Fig. 1 illustrates the preparation method of LVP-CG composites. (The detailed synthesis method was described in ESI). Briefly, the

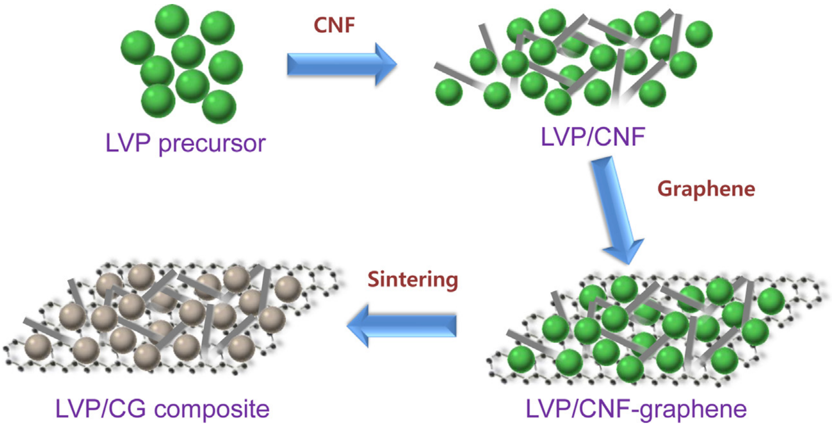

Fig. 1. Schematic of preparation steps for LVP-CG composite.