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Research Paper

Encapsulation of Lithium Vanadium Phosphate in Reduced Graphene Oxide for a Lithium-ion Battery Cathode with Stable Elevated Temperature Performance

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ABSTRACT

Polyanion-type cathode materials have received considerable attention for lithium-ion battery applications because of their excellent thermal stability compared to oxide compounds. Although the incorporation of carbonaceous materials can augment the cycling performance, the role of carbon structures in lithium vanadium phosphate ($Li_3V_2(PO_4)_3$, LVP) compounds remains unclear at an elevated temperature. Herein, carbon-coated $Li_3V_2(PO_4)_3$ (C-LVP) and reduced-graphene-oxide-wrapped $Li_3V_2(PO_4)_3$ (rGO-LVP) samples are prepared, their electrochemical performance is examined at room temperature and an elevated temperature. The rGO-LVP and C-LVP samples exhibit discharge capacities of ~131 mAh g^{-1} and ~124 mAh g^{-1}, respectively, at charge and discharge rates of 10C in the range of 3.0–4.3 V at 55 °C after cycling at various rates. The capacity retentions of the rGO-LVP and C-LVP samples are ~95% and ~85%, respectively, after 150 cycles at charge and discharge rates of 1C in the range of 3.0–4.3 V at 55 °C. The excellent rate performance and cycling stability of the rGO-LVP sample are due to its capability in maintaining a low charge transfer resistance or a higher electrical conductivity and ionic conductivity as compared to the C-LVP sample during electrochemical cycling, as demonstrated by electrochemical impedance spectroscopy and cyclic voltammetry. The results have provided essential insight into designing inorganic–carbon hybrid materials for future batteries.

1. Introduction

Since lithium-ion batteries are deemed as potential energy storage systems, various types of electrode materials have attracted a great deal of attention due to their high performance and stability [1–5]. A group of metal phosphates has been found to reversibly react with lithium during the insertion into and deinsertion from their open frameworks without structural changes [6–9]. The intercalation hosts of metal phosphates are attractive because of their strong covalent bond formation in O—P—O, which is more stable than that in $LiCoO_2$, leading to good thermal and chemical stabilities [10,11]. The strong covalent P—O bonds prevent the cleavage of O_2 from the $(PO_4)^{3-}$ polyanion that can lead to the possibilities of fire and explosion in the presence of flammable organic electrolytes and the generation of heat at elevated temperatures [12]. Unlike some transition-metal (M) oxide compounds (M—O), O_2 molecules can be easily released at elevated temperatures because of their structural and phase instabilities during electrochemical operations to transform into a more stable phase. Therefore, it is particularly crucial for mobile applications such as electric vehicles, where the heat generated by the devices or instruments is the main safety concern when the battery is in use [12]. Recently, lithium vanadium phosphate ($Li_3V_2(PO_4)_3$, LVP), which has a (sodium (Na) Super Ionic Conductor) NASICON-like structure has become a prospective cathode material in lithium-ion batteries owing to its reaction potential of about 3.8 V with a high theoretical capacity of 197 mAh g^{-1} [8] and its crystal structure, which enables 3D pathways for Li^+ insertion/extraction [8,10,11,13].

Although the polyanion is sustainable at elevated temperatures, it still suffers from faster capacity fading at room temperature, as the metal from the compound dissolves kinetically and quickly into the electrolyte owing to corrosion due to hydrofluoric acid (HF) under hot and humid conditions [12,14,15], especially in mobile

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applications that operate under hot and humid weather conditions. Therefore, efforts to improve the polyanion-based LVP cathode have focused on enhancing its electronic conductivity using a carbon coating [16–18], conductive additives [19], and doping with metal ions [20,21] or anions [22]. Carbon coatings have been employed to improve the electron transport during battery cycling [16,17]. An exceptional carbon coating method using an ionic liquid as both [23,24] a carbon source and synthesis medium has achieved high rate capability, especially when coupled with a reduction in the particle size to less than 10 nm, and was embedded in a carbon matrix, which provides well-connected ultrafine particles to deliver a capacity over 100 mAh g^{-1} at 100C [23]. Doping with metal ions has been considered to increase the Li^+ diffusion channel resulting in a higher electrical conductivity [20]. Although various strategies have been explored to improve the electrochemical performance of LVP at room temperature, there is still lack of studies on the electrochemical performance at elevated temperatures in order to consider its utilization in hot weather.

When the electrodes are cycled or stored over long periods, the resistance of the electrodes increases owing to the structural changes in the materials and the formation of electronic or ionic barrier materials on the surface of the cathode materials [14,25]. Consequently, the electrodes perform poorly during electrochemical cycling, particularly when operating at elevated temperatures, where metal dissolution from the active materials and electrolyte decomposition become more serious. Kerlau and Kostecki [25] have ascribed the degradation in the electrochemical performance of $LiFePO_4$ to the carbon materials added to the electrodes or composites of the active materials, where the carbon induces the formation of inactive interfacial materials and increases the impedance of the electrodes. On the other hand, Koltypin et al. [15] have attributed the dissolution of iron from $LiFePO_4$ to HF, forming from the decomposition of $LiPF_6$, as the main factor in the degradation in the cycling stability at elevated temperatures. Surface coating techniques have been employed to address these problems by coating the active materials with a Si film [26] and ZnO [27]. Wang et al. [12] have demonstrated that a carbon coating can prevent the attack of HF and the formation of inactive materials or solid electrolyte interphase (SEI)-like layers on the surface of $LiFePO_4$. The SEI layer is typically used to describe a barrier layer on the anode and the analogous layer on the cathode is called the cathode electrolyte interface (CEI), a layer composed of LiF, $ROCO_2LI$, $ROCO_2M$, ROLi, MCO_3, Li_2CO_3, MF_2, polycarbonates, and polyethylene oxide [28–30]. Although work on coating LVP with carbon has made noteworthy progress, the problem of operating at elevated temperatures continues to present challenges. As a result, holistic improvements in these strategies remain attractive solutions in operating lithium-ion batteries above room temperature.

Recently, graphene has been used to form composites with electrode materials. Apart from the excellent electronic conductivity, graphene possesses beneficial features such as good chemical and thermal stabilities and a high surface area, flexibility, and mechanical strength [9,31,32]. Several reports have demonstrated improvements in the specific capacity and rate capability using reduced graphene oxide (rGO) as a conductive material for compositing with LVP [9,33–37]. Different carbon sources such as cetyltrimethylammonium bromide (CTAB) [38], polyvinyl alcohol (PVA) [39], citric acid [40], and sucrose [41] were also used to coat rGO-wrapped $Li_3V_2(PO_4)_3$ (rGO-LVP) composites. Here, we demonstrate the simple and effective synthesis of LVP particles wrapped with rGO (rGO-LVP) to enhance the rate capability and cycling stability at room temperature and an elevated temperature. Such a design can support a high electrical conductivity and thermal stability by rGO, as shown in Fig. 1a and b.

The main purpose of this work is to describe the effects of carbonaceous materials with different structures as conductive and protective materials when compositing with LVP to enhance the cycling performance and retain their structural stability throughout long-term cycling to maintain their excellent electronic and ionic conductivities, specifically at an elevated temperature. Both rGO-LVP and carbon-coated LVP (C-LVP) samples consisting of carbonaceous materials were expected to provide superior electrochemical performance at the beginning of the long-term cycling process and low rate performance. It was expected that the difference in electrochemical behavior of both C-LVP and rGO-LVP samples would show in longer cycling and a higher rate performance. Such differing electrochemical behaviors of C-LVP and rGO-LVP samples were described by combining various characterization tools. A significant improvement in the electrochemical performance was obtained by rGO-LVP, possibly because of its higher degree of graphitization, which has fewer active sites such as defects for side reaction products to form on the surface of carbon. The understanding of the incorporation of the type of carbon material onto the surface of LVP is crucial for obtaining the optimum electrochemical performance, which can suggest reasonable alternatives to design future materials for battery design.

2. Experimental

2.1. Preparation of functionalized graphene oxide

Graphene oxide was prepared from graphite powder (SP-1, 30 μm nominal particle size, Bay Carbon, Bay City, MI) by pre-oxidation as described by Kovtyukhova et al. followed by a modified Hummer method as described elsewhere [42,43]. First, graphite powder (2.0 g) was heated to 80 °C in a mixture of concentrated H_2SO_4 (20 mL), $K_2S_2O_8$ (1.0 g), and P_2O_5 (1.0 g) under continuous stirring. After 4.5 h, the mixture was diluted with 1 L of distilled deionized (DDI) water. The product was filtered and washed with DDI water until the pH of the filtrate became neutral. The dried and pre-oxidized graphite was dispersed in concentrated H_2SO_4 (75 mL) with dissolved $KMnO_4$ (10 g) and heated to 35 °C. After 2 h, 160 mL DDI water was added slowly to prevent overflow, while the temperature was kept below ~50 °C. It was continuously stirred for an additional 2 h, after which H_2O_2 (~30%, Sigma Aldrich) was added to the solution to terminate oxidation of graphite. It was then diluted with 500 mL DDI water. The supernatant was decanted to obtain a yellow precipitate, which was centrifuged and washed with 10% HCl a few times and followed by washing with DDI water until the pH of the solution became neutral. The centrifuged graphene oxide (GO) was re-dispersed into DDI water and sonicated to obtain ~3.5 mg/mL of GO suspension.

2.2. Preparation of rGO-LVP and carbon-coated LVP cathode materials

In a typical preparation, the GO suspension (~8 mL) was treated with ~0.4 g oxalic acid (98% $H_2C_2O_4 \cdot 2H_2O$, Junsei) at room temperature for more than 5 h under continuous stirring. Another solution containing of ~0.2334 g NH_4VO_3 (99.9%, Sigma Aldrich), ~0.1108 g Li_2CO_3 (Sigma Aldrich), 0.3454 g $NH_4H_2(PO_4)$ (Sigma Aldrich), and ~0.4 g $H_2C_2O_4$ was prepared at 80 °C by stirring till the solution turned blue in color. The two solutions were mixed together and heated at 80 °C while being constantly stirring. The mixture was heated till a thick dark-brown gel was formed, which was further heated to 200 °C to obtain a black solid. This product was ground into a powder and heat-treated at 700 °C in the presence of flowing N_2 (5 wt% H_2) for 10 hours. Carbon-coated LVP