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# Improvement of electrochemical performance for $Li_3V_2(PO_4)_3/C$ electrode using $LiCoO_2$ as an additive

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ABSTRACT

A $Li_3V_2(PO_4)_3/C$ (LVP/C) electrode and a new $Li_3V_2(PO_4)_3/C$ electrode using $LiCoO_2$ as an additive (LVP/LCO/C) have been successfully fabricated and investigated via physical and electrochemical methods. Compared with the LVP/C electrode, the LVP/LCO/C electrode presents better rate capability and cyclic performance in the range 3.0–4.3 V. For the LVP/LCO/C electrode, the largest capacities of 99.3 and 68.0 mAh $g^{-1}$ are delivered at 1 and 15 C charge rates and 51 C discharge rate, respectively. 80.4% of the largest value is kept at 1 C charge and 51 C discharge rates in the 800th cycle. The excellent rate capability and cyclic performance are attributed to the small crystallite size of LVP particles, the small particles, narrow particle size distribution in the LVP/LCO/C electrode, large specific surface area and pore size, low electrical resistance for the LVP/LCO/C electrode, and the existence of the other electroactive LCO.

## 1. Introduction

In past decades, rechargeable lithium ion batteries have been rapidly developed as a portable energy storage device. Recently, they have been regarded as promising power sources for hybrid electric vehicles (HEVs) and electric vehicles (EVs) due to their high specific capacity, high power density and environment friendliness. In view of the high safety, polyanion-type materials have been discovered as potential cathode candidates for lithium ion batteries.

Among these materials, $LiFePO_4$ (LFP) and $Li_3V_2(PO_4)_3$ (LVP) are the most appealing. The olivine structure LFP has been commercialized. Nevertheless, the inherent drawbacks hinder its wide application. Compared with LFP, monoclinic LVP possesses higher ionic diffusion coefficient, discharge voltage and energy density, and better rate capability [1,2]. In the monoclinic LVP, all three lithium ions can be fully extracted from the lattice in the range 3.0–4.8 V. However, the extraction of the third lithium ion at 4.55 V is the most kinetically difficult [2]. Based on the practical use, LVP is usually cycled in the range 3.0–4.3 V, with the extraction and reinsertion of two lithium ions and corresponding to a theoretical capacity of 133 mAh $g^{-1}$.

It is well known that the low electronic conductivity and unsatisfactory rate capability restrict its practical application for LVP. Tremendous efforts have been devoted to solve these problems. The most successful strategies are coating carbon on the surface of the LVP particles [3,4], decreasing particle size [5,6] and doping with guest atoms [7,8]. Carbon coating can not only effectively improve the electronic conductivity of LVP but also suppress the LVP particle growth in the sintering process. Small particle size could decrease the lithium ions diffusion and electron-transportation distances and then is beneficial to the rate capability of the LVP. Doping with guest atoms can modify the bulk phase characteristic of the LVP that involves in the lithium ion mobility. However, the modifying methods above all focus on the preparation of the LVP material. Although doping is an effective way of improving the rate capability of LVP, the amount of the guest atom has to be strictly controlled, because the impurity can easily appear in doping [8,9]. In addition, nano-sized particles easily agglomerate together to form large particles and then worsen the electrochemical performance of LVP. Therefore, it is urgent that a simple effective method be developed to enhance the rate capability and long-term cyclic performance of LVP. To date, no studies have yet been reported on enhancing the electrochemical performance of LVP through modifying the fabrication of the LVP electrode.

Lithium cobalt oxide $LiCoO_2$ as the first generation of cathode material for commercial lithium ion batteries has been extensively researched and developed. In spite of some disadvantages, $LiCoO_2$ has still been used in commercial lithium ion batteries due to its ease of production, high electric conductivity of $10^{-2}$ S $cm^{-1}$, acceptable specific capacity, high energy density, low self-discharge and good cyclic performance [10–12].

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In the work, $LiCoO_2$ as an additive has been introduced to fabricate the LVP/LCO/C electrode. The electrochemical performance, especially at high charge–discharge rates, has been studied for the LVP/LCO/C electrode.

## 2. Experimental

The LVP/C composite material was synthesized by a sol–gel method based on composite chelating reagents using $LiOH\cdot H_2O$ (A.R.), $NH_4VO_3$ (A.R.), $NH_4H_2PO_4$ (A.R.), $C_2H_2O_4\cdot 2H_2O$ (oxalic acid, A.R.), $C_2H_5NO_2$ (glycine, A.R.) and beta-cyclodextrin as raw materials, previously reported by us [13]. The mass ratio of glycine to beta-cyclodextrin was 9:25.

The carbon content was determined by the methodology previously reported [14], and the carbon amount of the LVP/C composite material is 6.95 wt.%.

For the fabrication of the cathode electrodes, 85 wt.% active material was ball-milled with 10 wt.% acetylene black and 5 wt.% polyvinylidene difluoride (PVDF) or 82 wt.% active material was ball-milled with 3 wt.% commercial lithium cobalt oxide $LiCoO_2$

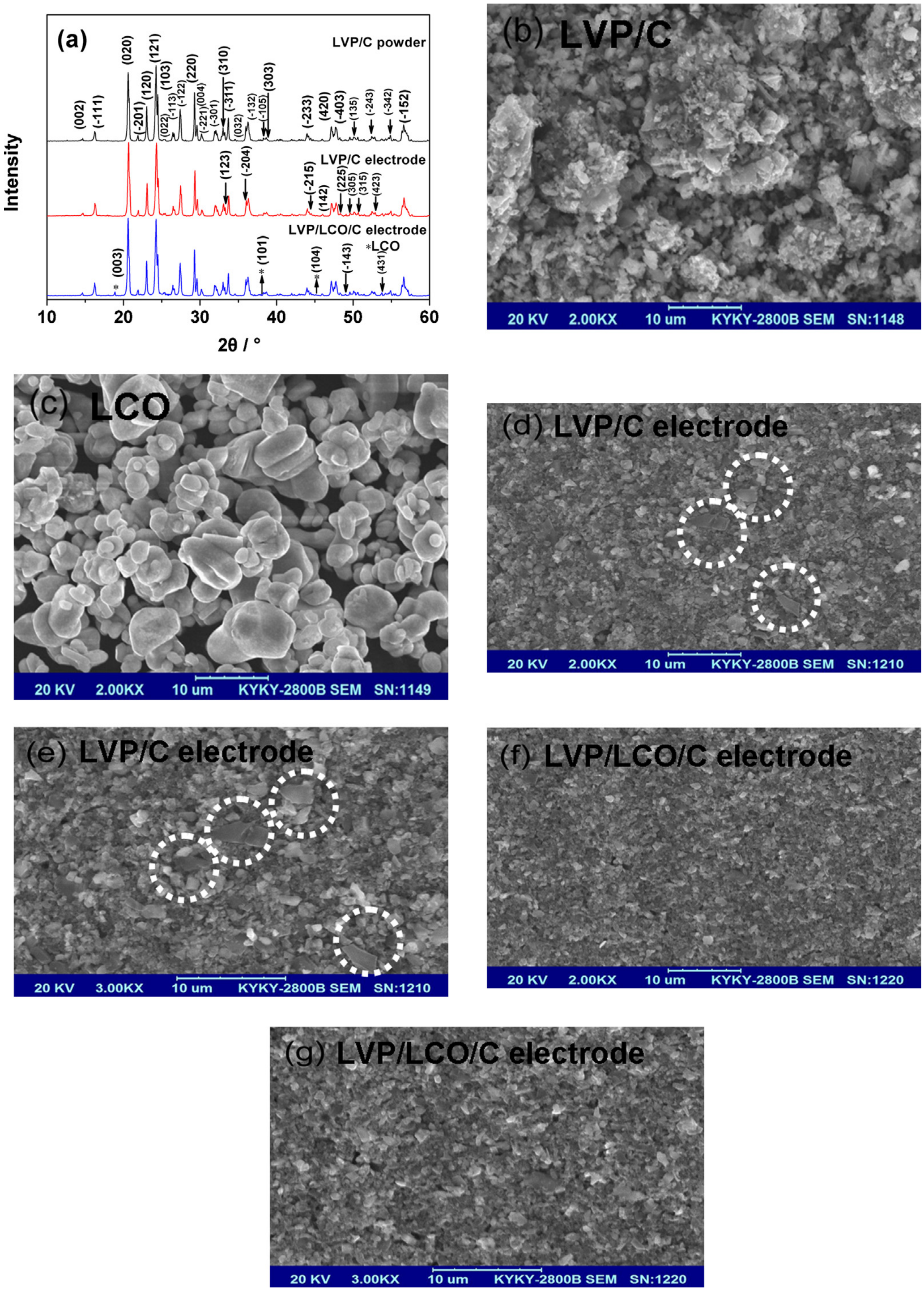

**Fig. 1.** X-ray diffraction patterns of the as-prepared $Li_3V_2(PO_4)_3$/C material, $Li_3V_2(PO_4)_3$/C and $Li_3V_2(PO_4)_3/LiCoO_2$/C electrodes (a), and SEM images of $Li_3V_2(PO_4)_3$/C material (b), commercial $LiCoO_2$ material (c), $Li_3V_2(PO_4)_3$/C electrode (d) and (e) and $Li_3V_2(PO_4)_3/LiCoO_2$/C electrode (f)–(g).