Electrochimica Acta 279 (2018) 108–117

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Analysis of the effects of different carbon coating strategies on structure and electrochemical behavior of $LiCoPO_4$ material as a high-voltage cathode electrode for lithium ion batteries

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ARTICLE INFO

Article history:
Received 1 February 2018
Received in revised form
25 April 2018
Accepted 8 May 2018
Available online 14 May 2018

Keywords:
$LiCoPO_4$
High-voltage cathode
Lithium ion battery

ABSTRACT

The olivine polymorph $LiCoPO_4$ was synthesized by solvothermal and a subsequent annealing process. Carbon free, ex-situ carbon coated and in-situ carbon coated materials were prepared. With the addition of citric acid in the solvothermal reaction, a carbon layer was coated via an in-situ approach. To systematically compare the different carbon coating routes, the structure and morphology of the $LiCoPO_4$ materials were investigated by XRD, Raman, and SEM. HAADF-STEM combined with EDX was applied to analyze the homogeneity of the carbon layer and corresponding antisite defects. Electrochemical properties were analyzed by half-cells measuring cyclic-voltammograms, charge/discharge cycling behavior stability and rate-capability. It was found that the in-situ carbon coated $LiCoPO_4/C$ exhibited a superior electrochemical performance due to the relatively uniform and complete surface-layer formation. As a result, an appropriate carbon layer improves the electronic and ionic transport properties, ensures fast electron-transfer kinetics at the electrode particle surfaces and suppresses unwanted side reactions with the electrolyte.

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1. Introduction

Lithium ion batteries (LIBs) are gaining attention as the demands for more compact electronic devices with enhanced safety continue to rise [1,2]. Over the past several decades, some intercalation cathode materials have been widely investigated and even commercialized for practical applications, such as $LiCoO_2$, $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$, $LiMn_2O_4$ and $LiFePO_4$ [3]. However, these traditional materials do not meet the challenges to be applied in the field of electric vehicles (EVs), hybrid EVs (HEVs) yet due to the comparatively low energy density [4]. Since the gravimetric energy density is the product of the specific discharge capacity and average discharge voltage, it is critical to search for materials with high discharge voltage plateaus, which potentially offers an improved energy density [5,6].

The olivine-structured $LiMPO_4$ (M = Fe, Mn, Co, Ni) has attracted extensive research attention because of its high structural and thermal stability [7], and $LiCoPO_4$ is one of the most promising candidates to improve the energy density due to its high theoretical capacity (167 mAh g^{-1}) and high operating voltage (approximately 4.8 V vs. Li/Li^+) [8,9]. However, the low electronic conductivity and low Li^+ ionic conductivity related to the one-dimensional ion transport channel limit its electrochemical performance [4,10]. In addition, the irreversible decomposition reactions also contribute to low coulombic efficiency and capacity fading upon cycling [11]. Many efforts have been devoted to develop its electrochemical activity, including minimizing the particle size [12], controlling the morphology [13], doping with aliovalent metal ions [14] and coating with conductive layers [15,16]. The facile solvothermal route, as a bottom-up process, was proven to be a kinetically controlled approach for $LiCoPO_4$ [17–20]. The smaller size provides shorter electron and Li^+ diffusion paths along the b-axis inside the particle [21,22]. Also, a surface coating with pyrolytic carbon is a

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https://doi.org/10.1016/j.electacta.2018.05.067
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very effective method to reduce the irreversible capacity loss. Moreover, the deposition of carbon coatings with high temperature annealing in inert atmosphere leads to a drastic increase to about 10^4~10^5 S cm^{-1} of the electrical conductivity of $LiCoPO_4$ [23]. With respect to carbon coating, a series of factors are significant and can influence the electrochemical performance, such as the choice of carbon source, the thickness, the homogeneity and the carbon content [24,25], which are mainly dependent on the synthesis methodology. Previously, an ex-situ route by adding different carbon source to realize coating layer is very often used [12,26,27], but in many cases an inhomogeneous covering limits this method. On the other hand, in-situ coating approach is facile and can form a continuous and uniform layer, which has been reported by many authors recently [12,24,28–30]. The effectiveness of the different carbon coating strategies is still under discussion.

In this work, $LiCoPO_4$ particle were synthesized by solvothermal and a subsequent annealing process. As a common ex-situ strategy, $LiCoPO_4$/C with carbon coating layer was realized by mixing with sucrose type carbon source and following calcination. In-situ carbon coated LCP/C was synthesized by addition of citric acid, forming a homogeneous carbon layer during solvothermal reaction. A systematic investigation was performed to compare the different carbon coating strategies, including structure, morphology, homogeneity of carbon layer as well as electrochemical performance. In addition, in-situ electrochemical impedance spectroscopy was performed to analyze the origin of the sluggish kinetics of $LiCoPO_4$.

2. Experimental section

2.1. Synthesis of bare $LiCoPO_4$ and $LiCoPO_4$/C

Lithium hydroxide monohydrate ($LiOH \cdot H_2O$, 99.0%), sucrose ($C_{12}H_{22}O_{11}$, 99.5%), ethylene glycol ($C_2H_6O_2$, 99.8%) and citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$, 99.5–100.5%) were purchased from Sigma-Aldrich, cobalt (II) acetate tetrahydrate ($Co(CH_3COO)_2 \cdot 4H_2O$, 98.0–102.0%), ortho-phosphoric acid (H_3PO_4, 86%) and isopropanol (pure) were purchased from VWR chemicals. All chemical reagents were used as received. For the preparation of the precursor solution for the solvothermal reaction, 0.03 mol $Co(CH_3COO)_2 \cdot 4H_2O$ and 0.03 mol H_3PO_4 were firstly dissolved in a mixture of deionized water and ethylene glycol (1:1 vol/vol), which formed a homogenous red solution under continuous magnetically stirring. Afterwards, 0.09 mol $LiOH \cdot H_2O$ were dissolved in the water/ethylene glycol mixture solution and then added to the above solution. The Co^{2+} and PO_4^{3-} concentration in the final precursor solution was 0.1 mol L^{-1}, and the pH value was around 8.5 (*cf.* graphical abstract). The resulting mixture solution was transferred into a 500 mL Teflon-lined vessel for solvothermal reaction (Berghof GmbH, Germany). The filling ratio of the inner system was 60%, and the initial pressure was set to 20 bar by filling argon into the reactor vessel before starting. The whole reaction process was kept at 180 °C for 24 h, and afterwards the system was allowed to cool to room temperature freely. Then the obtained product was collected by centrifugation and washed with pure water and isopropanol, and dried in vacuum at 90 °C overnight. The bare $LiCoPO_4$ (LCP) powder was obtained by annealing above precursor powder at 650 °C under argon flow in a tube furnace for 5 h. For carbon coating, sucrose and the precursor powder were dissolved in pure water with a weight ratio of 3:10. The resulting slurry was continuous magnetically stirred in an oil bath at 80 °C until forming a dried mixture. The LCP/C ex-situ powder was obtained by the same annealing process. With respect to in-situ carbon coating, 0.015 mol citric acid was added in the precursor solution as a chelating agent and carbon source, and pH value decreased to around 6.5. After the same solvothermal and annealing process, LCP/C in-situ powder was obtained.

2.2. Materials characterization

The crystallinity and phase analysis was carried out by powder X-ray diffraction (XRD) measurements between 10° and 80° in Bragg-Brentano-geometry with an EMPYREAN (Panalytical, Netherlands) X-ray diffractometer with Cu-K_α radiation operating at 40 kV, 40 mA. For Rietveld refinement the FullProf Suite software was used in 'Profile Matching' configuration. As basis data for the refinement, *Pnma* space group (ICSD_87422) for $LiCoPO_4$, $Fm\overline{3}m$ space group (ICSD_76632) for Co content and $Fm\overline{3}m$ space group (ICSD_9865) for CoO content of the materials have been used, respectively. Raman spectra were recorded by a SENTERRA Raman microscope (Bruker, Germany) with an excitation wavelength of 532 nm from an argon laser source. Elemental analysis was performed by inductively coupled plasma with optical emission spectroscopy (ICP-OES) for Li, Co and P contents, respectively. Approximately 10 mg of the powder samples were dissolved in a solution mixed by 3 mL HCl, 3 mL H_2O_2 and 3 mL HNO_3, and then diluted it to 50 mL volume. For the determination, two aliquots of the sample solution obtained were diluted and analyzed. Carbon contents were analyzed by combustion analyses using a Leco CS600 instrument. Scanning electron microscopy (SEM) images were taken on a Quanta FEG 650 (FEI, USA) environmental scanning electron microscope operated at a voltage of 20 kV. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-Ray (EDX) spectroscopy experiments were carried out using an FEI Titan G2 electron microscope operated at an accelerating voltage of 200 kV and equipped with a spherical aberration corrector unit and a Super-X EDX system. The samples were prepared by dispersing powder samples in ethanol and dropping the dispersion onto a carbon coated TEM copper grid. The specific surface area was determined in Brunauer-Emmet-Teller (BET) measurements by N_2 adsorption.

2.3. Electrochemical measurements

The electrochemical performance was tested in Swagelok-type cells. The composite electrodes were prepared by mixing active materials, carbon black (Super P, Alfa-Aesar), and polyvinylidene fluoride binder (PVDF, Sigma-Aldrich) in a weight ratio of 8:1:1. The mixing process for the slurry was performed by an ARV-310 vacuum mixer (Thinky, Japan), and afterwards the slurry was tape casting onto the aluminium foil (thickness ~ 25 μm, Goodfellow, UK) by using semi-automatic film applicator ZAA 2300 (Zehntner, Switzerland). After the electrodes were dried under vacuum, an electric hot rolling press (MTI, USA) was used for the electrode densification. The assembly of the test half-cells was carried out in an argon filled glovebox, where the concentrations of water and oxygen were kept less than 0.1 ppm. Metallic lithium foil (Alfa-Aesar, Germany) was used as both counter and reference electrode. A glass fiber membrane (Whatman, UK) was served as separator. As electrolyte 1M $LiPF_6$ in a 1:1 solvent mixture of ethylenecarbonate (EC)/dimethylcarbonate (DMC) (LP30, BASF, USA) was used. Electrochemical tests were carried out at 25 °C in a climate chamber MKF120 (Binder, Germany). Galvanostatic charge/discharge tests, cyclic-voltammograms (CV), and electrochemical impedance spectroscopy (EIS) measurements were conducted by a VMP3 potentiostat (Bio-Logic, France). The charge/discharge tests were performed at different current densities between 3.5 V and 5.0 V vs. Li/Li$^+$, and the C rate performance was accomplished by galvanostatic charging and discharging at C rates between 0.1C and 5C current (1C = 166.6 mA g^{-1}) at the first cycle. CVs were measured in

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