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Constructing durable carbon layer on $LiMn_{0.8}Fe_{0.2}PO_4$ with superior long-term cycling performance for lithium-ion battery

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ABSTRACT

$LiMn_{0.8}Fe_{0.2}PO_4$ is becoming one of the most promising cathode materials for lithium ion batteries. However, the capacity suffers from a loss during long-term cycling, which is directly associated with Mn dissolution due to the disproportionation reaction of Mn^{3+}. Here, we report a chemical vapor deposition (CVD) approach to modify $LiMn_{0.8}Fe_{0.2}PO_4$ particles with carbon so as to minimize Mn dissolution from cathode. The deposited carbon layer not only protects $LiMn_{0.8}Fe_{0.2}PO_4$ cathode from electrolyte corrosion, but also enhances the electronic/ionic conductivity owing to its higher graphitize degree. As a consequence, the electrochemical performances have a significant improvement. The capacity retention achieves 96% after 450 cycles at 1 C at room temperature (25 °C). Even at elevated temperature (55 °C), the capacity retention also reaches at 97 % after 50 cycles at 1 C rate, which is much higher than that of untreated sample (89%). Hence, the cathode material based on $LiMn_{0.8}Fe_{0.2}PO_4$ encapsulated with durable carbon by CVD method represents a promising strategy for developing its long-term cycling performance through suppressing Manganese dissolution.

1. Introduction

It is a well-known challenge for developing energy storage and conversion systems to meet the demands for rapid consumption of fossil fuels and raising environmental concerns. The electrochemical systems can provide clean and efficient routs for energy storage and conversion, such as lithium-ion batteries, fuel cells and super capacitors [1–3]. Because of its high energy density, wide range of application and long cycle life, lithium-ion batteries are recognized as one of the most appropriate and promising energy-storage systems. They are also being pursued intensively for transporting applications, including hydric electric vehicles, plug-in electric vehicles and pure electric vehicles [4–6]. However, current lithium ion batteries does not fulfill many of the performances and safety requirements for further application, and therefore safer and more reliable high performances batteries are being actively pursued to develop [7–9].

In general, the cathode material is regarded as the determining component of a lithium battery. In 1997, Goodenough and coworkers discovered the olivine type cathode material $LiMPO_4$ (M = Fe, Mn, Co and Ni), which has been extensively studied owing to its low cost, environmental friendliness and superior thermal stability [10–12]. Among these compounds, $LiMnPO_4$ cathode material is now admitted as one of the most promising candidate for advanced batteries, because of its higher operating voltage (4.1 V vs. Li^+/Li°) compare to $LiFePO_4$ (3.4 V vs. Li^+/Li°). More importantly, this operating voltage is within the stable working potential window of well-known carbonate ester-based electrolytes [13–16]. However, the poor cycling performance of this material, particularly at elevated temperature, limits its wide application for lithium ion batteries. Previous researches confirmed that the capacity fading of $LiMnPO_4$ cells was directly associated with the Manganese dissolution from the interface of cathode/electrolyte due to the Manganese (III) disproportionation. Then, the subsequent compounds deposit on the anode, which is of great damage to SEI. This is the main cause for the cell impedance increase [17–21]. Many of researches reported that these Mn based cathode materials were prone to arise Mn dissolution at high temperature, which results in serious capacity fading [22–24]. Jo et al. reported that $LiMnPO_4/C$ only retained 58% of its initial capacity after 40 cycles at elevated temperature (60 °C) [19]. Damen et al. also showed that the capacity retention of $LiMnPO_4/C$ was only around 75% after 50 cycles at 50 °C with the initial capacity of $120\,mA\,h\,g^{-1}$ [25]. To address this issue, a variety of methods, such as surface coating, caption doping, were attempted or combined in most case to suppress the Manganese dissolution

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from $LiMnPO_4$ so as to overcome the capacity fade, thereby enhancing the cycling performance of cell [26–28]. Previously, many researches have been reported that Fe doping can effectively minimize the Mn dissolution and even improve the electronic/ionic conductivity of the material [29–34].

On the other hand, surface coating is an available approach that has been widely used to enhance the electrochemical performance of $LiMnPO_4$ [35–37]. The surface coating layer can prevent direct contact between the electrolyte and $LiMnPO_4$ owing to its strong resistance against to hydrogen fluoride attack from the electrolytes [18]. Carbon coating is recognized as a very practical and commonly used way for improving electrochemical performance [15]. At present, there are two main carbon coating methods: one is the conventional method by mixing organic substances with cathode material followed by annealing and the other is chemical vapor deposition (CVD). In general, CVD, that contained vapor flows across the particle to deposited carbon on its surface, is recognized as a simple and effective way that can be capable of realizing uniform carbon coating [38,39]. Recently, Tian et al. proposed a method of CVD to coat carbon on the $LiFePO_4$ particle using the solid glucose as carbon source [40]. The cathode exhibited a good electrochemical performance owing to the well uniform and high quality coated carbon layer that can enhance the electronic conductivity and improve its stability. Belharouak et al. introduced an inexpensive and easy carbon coating technique of CVD for the $LiFePO_4$ material which delivered 140 mA h g^{-1} at room temperature [41]. This result is due to the fact that the process of gas decomposition allows for carbon to deposit in the pores of the particle resulting in a better conducting network formation within the particle. Also, Nan et al. prepared Li_2S spheres with three size through a normal method and then coated with carbon by CVD, which showed an excellent cycling performance, because the durable carbon shell protected S from dissolution as polysulfides and thus alleviated capacity fading [42]. Therefore, this effective, safe, and controllable carbon coating method of CVD is highly desired on $LiMn_{0.8}Fe_{0.2}PO_4$ cathode material. Additionally, the availability of conductive and protective carbon not only improves its cycling performance by suppressing Mn dissolution, but also enhances its rate capability through enhancing electronic/ionic conductivity, which consequently makes it far more promising to explore high power $LiMn_{0.8}Fe_{0.2}PO_4$ for further application.

Herein, we propose a two-step carbon coating method. The precursor obtained by spray dry method was annealed under high temperature. Then, the particles were coated with durable carbon layer through the CVD method, as illustrated in Fig. 1. The uniform and high quality carbon coated by CVD can protect the bulk $LiMn_{0.8}Fe_{0.2}PO_4$ material from electrolyte corrosion. Thereby, it can minimize the Mn dissolution and suppresses capacity fading effectively during long-term cycling. Moreover, the graphitization degree of carbon for the modification sample is higher than that of the unmodified sample. This illustrates that the electronic/ionic conductivity of treated sample is higher than that of the untreated sample. As a consequence, the electrochemical performance shows an increase in terms of cycling and rate performance.

2. Experimental

2.1. Preparation Samples

The $LiMn_{0.8}Fe_{0.2}PO_4$ particle was synthesized by a CVD assisted two-step coating method. The precursor was prepared by spray dry method. The $LiOH{\cdot}H_2O$, $MnCO_3$, $FeC_2O_4{\cdot}2H_2O$ and $NH_4H_2PO_4$ were mixed in an aqueous solution with 10 wt.% glucose under vigorously stirring in a molar ratio of 1:0.8:0.2:1 to form slurry with the solid content of 30 wt.%. The mixture was then spray dried at 120 °C and the as collected brownish powder was calcined at 650 °C for 8 h with the heating rate of 5 °C/min in an Ar atmosphere, and the obtained composites are donated as LMFP. Then, the prepared particles were placed in the center of the quartz tube furnace that was heated from room temperature to 650 °C and maintained 8 min in flowing H_2/C_2H_2 with a flow rate of 15 cm^3 min^{-1} and 20 cm^3 min^{-1}, respectively. The resulting sample is designed as C-LMFP.

2.2. Characterization

The crystalline structures were characterized by X-ray powder diffraction (XRD, Bruker AXS, D8-Advance) that utilized Cu-Kα radiation (λ_1 = 1.54056 Å, λ_2 = 1.54439 Å). Data were collected over the 2θ range from 10° to 70° with a scan rate of 0.0067° S^{-1} at ambient temperature. The morphology was analyzed by a Hitachi S-4800 field emission scanning-electron microscope (SEM) and the surface microstructure was carried out by HRTEM of FEI Tecnai F20 operated at 200 kV. Raman spectra were obtained using a Raman spectrometer (Renishaw in Via Reflex) coupled with microscope in a reflectance mode with a 532 nm excitation laser source. The carbon content was measured by an organic element analyzer (PE 2400 II).

2.3. Electrochemical measurements

The cathode electrodes were prepared by slurry with a mixture of 80 wt.% the active materials, 15 wt.% Super P carbon, and 5 wt.% polyvinylidene fluoride binder, which were dissolved in N-methyl-2-pyrrolidone. The resultant slurry was coated onto an Al foil, and then dried at 80 °C for 12 h. The thickness was about 25 μm, and accordingly, the loading density of the electrode was 2.5–3.5 mg cm^{-2}. The 2032-type coin cell was assembled in an argon-filled glove box with lithium metal as anode and Celgard 2502 as the separator. The electrolyte consists of 1 M $LiPF_6$ which dissolved in ethylene carbonate and dimethyl carbonate with 3: 7 volume ratios (Zhangjiagang Guotai-Huarong New Chemical Materials *Co.*

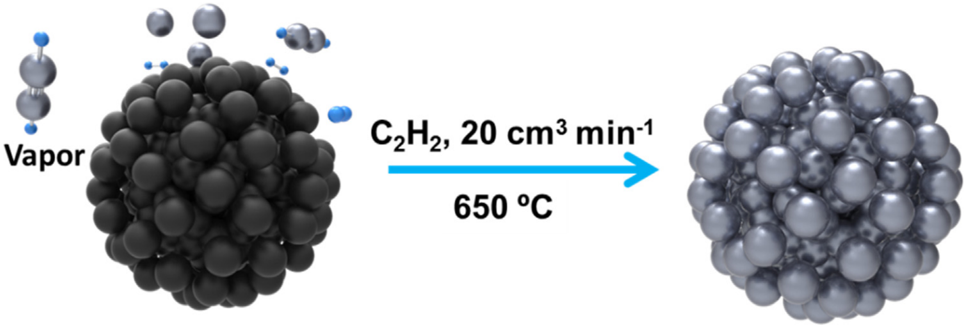

Fig. 1. Schematic illustration of formation procedure for durable carbon coating C-LMFP.