

Electrochemical properties of carbon coated LiFePO₄ cathode materials

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Abstract

Carbon coated lithium iron phosphates were prepared by a carbon aerogel synthesis process, through which LiFePO₄ particles were embedded in amorphous carbon. The carbon coating effect can significantly enhance the electronic conductivity of LiFePO₄. The electrochemical properties of the as-prepared LiFePO₄ cathode materials were systematically characterised. The carbon coated LiFePO₄ cathode demonstrated a high capacity and stable cyclability.

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1. Introduction

Lithium-ion batteries have a great potential to be used as power sources for electric vehicles (EVs) and hybrid electric vehicles (HEVs). However, the cost, safety and environmental friendliness of cathode materials are major concerns for the applications of large-scale lithium-ion batteries due to the use of cobalt-based oxides. The discovery of polyanion compounds with the general formula Li_xM_y(XO)_z (M = transition metal; X = P, S, As, Mo or W), provides a new class of cathode materials for lithium-ion batteries [1,2]. Among them, lithium iron phosphates have attracted particular interest. LiFePO₄ has a theoretical capacity of 170 mAh g⁻¹. It is inexpensive, non-toxic and environment friendly. LiFePO₄ has an ordered olivine structure (SP: Pnma), in which FeO₆ octahedra share common corners in the bc plane. In the LiFePO₄ crystal structure, the oxygen atoms are arranged in a distorted, hexagonal close-packed arrangement, in which the lithium and iron atoms occupy octahedral sites, while the phosphorous atoms occupy tetrahedral sites. The strong P–O covalency stabilizes the anti-bonding Fe³⁺/Fe²⁺ state through the Fe–O–X inductive effect to generate high

operating potential [3–5]. Therefore, LiFePO₄ has a high lithium intercalation voltage of 3.4 V versus lithium metal. However, LiFePO₄ suffers from low electronic conductivity, limiting its capacity and rate capacity.

The electronic conductivity of lithium iron phosphates can be improved by many different material processing approaches such as reducing the crystal size of LiFePO₄ [6–9], carbon addition [10–16], metal powder addition [17,18] and doping with supervalent ions [19,20]. Therefore, the electrochemical performance of lithium iron phosphates can be significantly enhanced through the improvement of the electronic conductivity of the materials. In this investigation, we prepared carbon-included lithium iron phosphates via a carbon aerogel synthesis process, through which lithium iron phosphate and amorphous carbon formed simultaneously. The electrochemical properties of as-prepared LiFePO₄–carbon composites as cathodes in lithium-ion cells were measured via various electrochemical testing.

2. Experimental

Li(OH)·H₂O (99.9%, Aldrich), FeC₂O₄·H₂O (99%, Aldrich) and NH₄H₂PO₄ (97%, Aldrich) were used as raw

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chemicals. The stoichiometric reactants were dissolved in deionised water, in which diluted nitric acid was added to accelerate the dissolving of $\text{FeC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. A typical carbon gel was formed by mixing 0.29 M resorcinol and 0.57 M formaldehyde. The LiFePO_4 reactant solution and the carbon gel solution were mixed and the pH value was adjusted to be in the range of 6.5–7.4. Then, the mixture solution was put in an ampoule, sealed and heated on a hot plate. The temperature was maintained at 85 °C. When the solution became viscous, the ampoule was moved to an oven and kept at 85 °C for 10 h. The carbon aerogel was then formed with the reactants Li^+ , Fe^{2+} and $[\text{PO}_4]^{3-}$ dispersing inside. The gel was first decomposed at 450 °C and then sintered at 750 °C for 12 h under flowing argon to yield carbon coated LiFePO_4 . The carbon content was analysed by thermal gravimetric analysis (TGA) to be 20 wt%.

The electrochemical measurement of the synthesized lithium iron phosphates was performed by assembling CR2032 coin cells. The electrodes were made by dispersing 84 wt% active materials, 8 wt% carbon black and 8 wt% polyvinylidene fluoride (PVDF) binder in *n*-methyl pyrrolidone (NMP) solvent to form homogeneous slurry. The slurry was then spread onto an Al foil. The coated electrodes were dried in a vacuum oven under a vacuum pressure of 30 Torr at 120 °C for 12 h. The electrodes were then pressed at a pressure of 1200 kg cm^{-2} to enhance the contact between the active materials and the conductive carbons. The active material loading was about 1.5–2 mg per individual electrode. The cells were assembled in an argon filled glove-box (Mbraun, Unilab, Germany) using lithium metal foil as the counter electrode. The electrolyte was 1 M LiPF_6 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v, provided by MERCK KgaA, Germany). The cells were galvanostatically charged and discharged over a voltage range of 2.75–4.3 V. Cyclic voltammetry (CV) measurements were performed using an EG & G Scanning Potentiostat (Model 362) at a scanning rate of 0.1 mV s^{-1} .

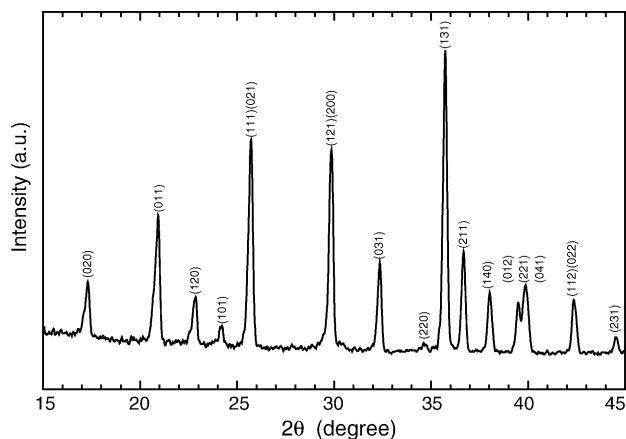


Fig. 2. X-ray diffraction pattern of LiFePO_4 .

3. Results and discussion

Under an appropriate pH environment and warm temperature, resorcinol reacts with formaldehyde to initially form chains of hydroxymethyl derivatives, which then further react with each other to form a cross-linked three-dimensional network (called R/F gel). Fig. 1 shows a schematic diagram of the reaction of resorcinol with formaldehyde. Through cross-linking, R/F carbon gel forms an interconnected bead structure [21,22]. The ingredient ions Li^+ , Fe^{2+} and $[\text{PO}_4]^{3-}$ are homogeneously distributed inside the carbon aerogel. After heat treatment at 750 °C, the carbon gel was carbonized to become amorphous carbon. Simultaneously, LiFePO_4 crystals were formed.

The X-ray diffraction pattern of LiFePO_4 is shown in Fig. 2. All diffraction peaks are indexed with an orthorhombic crystal structure (SP: Pnma). No impurity phases were detected by X-ray diffraction. Thermal gravimetric analysis (TGA) and ICP analysis have identified that approximately 20 wt% carbon is included in the LiFePO_4 . However, no diffraction line from crystalline carbon (graphite) appeared

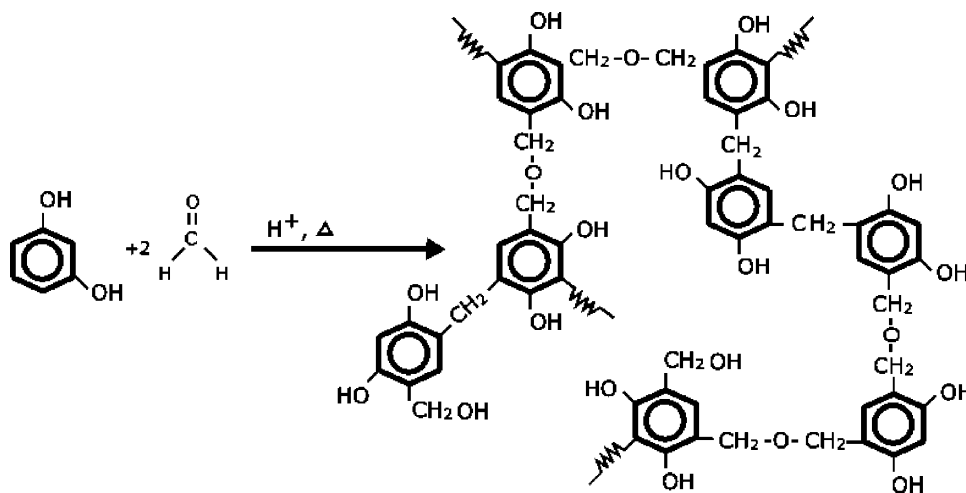


Fig. 1. A schematic diagram of the R–F gel formation.

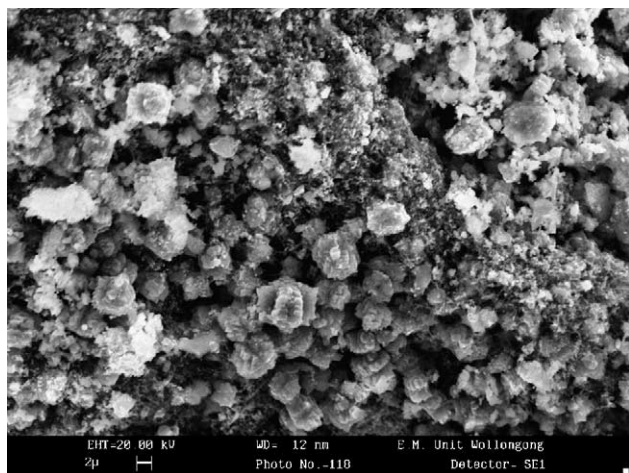


Fig. 3. SEM image of LiFePO₄ powders.

in the diffraction pattern. Therefore, we can conclude that the carbon generated from carbon gel carbonization is amorphous carbon. Fig. 3 shows a SEM image of LiFePO₄ powders. LiFePO₄ powders have a small average crystal size that is less than 1 μm . Fibrous amorphous carbons are present in the SEM photograph. These amorphous carbons can significantly enhance the electronic conductivity of LiFePO₄ materials. We pressed the as-prepared lithium iron phosphates into disk-shaped pellets. The electronic conductivity was measured by the two-point dc method. The LiFePO₄ pellets exhibit high electronic conductivity in the range of several S cm^{-1} at room temperature. The included carbons contribute to the high electronic conductivity of LiFePO₄ materials.

Cyclic voltammetry measurements were performed on LiFePO₄ electrodes using a scanning rate of 0.1 mA s^{-1} . Fig. 4 shows typical cyclic voltammograms of a LiFePO₄ electrode. During the anodic sweep, lithium ions are extracted from the LiFePO₄ structure. An oxidation peak is located at 3.51 V versus Li/Li⁺. When the potential was scanned from 4.4 to 2.5 V, a reduction peak occurred at 3.32 V, corresponding to lithium insertion into the LiFePO₄ structure. The sharp

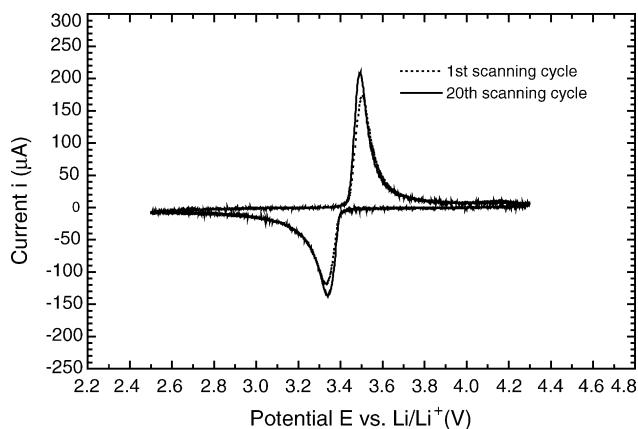


Fig. 4. Cyclic voltammograms of a LiFePO₄ electrode.

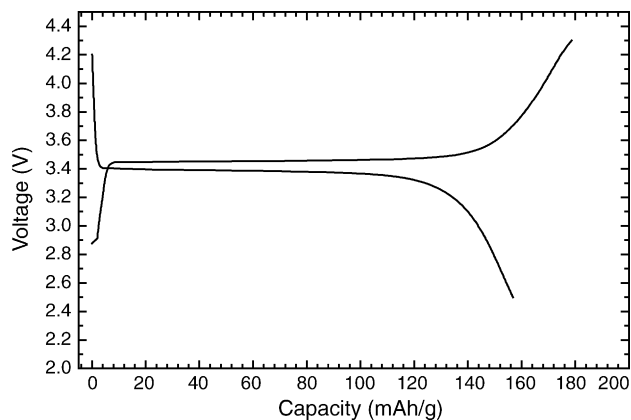


Fig. 5. Charge/discharge profiles of a LiFePO₄ electrode at the C/5 rate.

lithium insertion and extraction peaks in the CV curves indicated high reactivity of the carbon-included LiFePO₄ electrode. After 20 scanning cycles, the redox peaks remain in similar magnitude, indicating good stability of the electrode.

In order to determine the capacity and cyclability of LiFePO₄ electrode, we performed charge/discharge cycling tests on LiFePO₄ electrodes at different rates. Fig. 5 shows the charge/discharge voltage profiles in the first cycle for a LiFePO₄ electrode at the C/5 rate (0.25 mA cm^{-2}). The as-prepared LiFePO₄ electrode demonstrated a high specific discharge capacity of 159 mAh g^{-1} in the first cycle, approaching the theoretical capacity of 170 mAh g^{-1} . However, LiFePO₄ without carbon coating delivered a much lower capacity of 100 mAh g^{-1} in the first cycle [23]. The high capacity delivered by LiFePO₄ electrode should be attributed to the enhanced electronic conductivity of the materials due to carbon coating. Since the individual LiFePO₄ particles are connected by a carbon network, the active LiFePO₄ materials can be fully utilized for lithium extraction and insertion reactions. Fig. 6 shows the results of cyclability tests of LiFePO₄ electrodes at different charging and discharging rates. Although the specific capacity decreases with increasing charge/discharge rate, the capacity retention remains very good for all the different

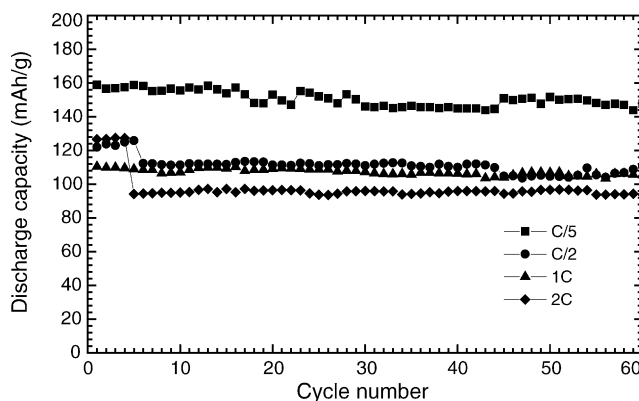


Fig. 6. Discharge capacity vs. cycle number for LiFePO₄ electrodes at different charge/discharge rates.

rates. Therefore, the carbon-included LiFePO_4 electrodes demonstrated high capacity and good cyclability.

4. Conclusions

The R/F carbon gel synthesis process has been used to prepare carbon coated LiFePO_4 . This process can produce fine LiFePO_4 embedded in amorphous carbon. The electronic conductivity of LiFePO_4 materials can be dramatically enhanced via the carbon inclusion. The cyclic voltammetry tests show the high reactivity of the as-prepared LiFePO_4 electrodes. A high capacity of 160 mAh g^{-1} at the C/5 rate has been demonstrated by the LiFePO_4 electrode. These electrodes also exhibited good cyclability at different charge/discharge rates.

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