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Electrochemical properties of $LiAl_xFe_{1-3x/2}PO_4/C$ prepared by a solution method

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ABSTRACT

Olivine compounds $LiAl_xFe_{1-3x/2}PO_4/C$ [$x = 0, 0.01, 0.02, 0.04, 0.06, 0.12$] were prepared via an easy solution method and electrochemical properties were examined by means of X-ray diffraction, cyclic voltammetry, and charge–discharge tests. The results indicate that Al^{3+} does not affect the olivine structure of the cathode but considerably improves its initial capacity and cycle performance. Among the Al^{3+}-substitution powders, $LiAl_{0.01}Fe_{0.985}PO_4/C$ shows the best electrochemical performance. It shows initial specific discharge capacities of 157.67 and 126.65 mA hg^{-1} with C rates of 0.5 C and 5 C, respectively, which is ascribed to the enhancement of the electronic conductivity by Al^{3+}-substitution and carbon coating.

1. Introduction

Olivine structure $LiFePO_4$, has been considered a promising cathode material for lithium ion batteries following its description by Goodenough and co-workers in 1997 [1,2]. Despite its high theoretical capacity (170 mA hg^{-1}) [2], high potential (3.4 V versus Li/Li^+) [3], low cost, low toxicity [4] and excellent thermal stability [5,6], its practical use is limited by the low electronic conductivity and lithium-ion diffusivity. Many approaches have been developed to overcome this problem such as particle optimization [3], introducing conductive layer coating like carbon [7], and metal doping [8,9]. Although minimizing the particle size of $LiFePO_4$ can improve the cycle performance [10], it causes less packing of the electrochemically active particles. Carbon coating is a common way to overcome the limited rate capacity because the dispersed carbon can provide pathways for electron transferring, resulting in improvement of the conductivity and electrochemical properties [11–13]. However, the carbon coating leads to a loss in energy density due to the electrochemical inertness of the carbon; it also doesn't help the intrinsic electronic conductivity or chemical diffusion coefficient of lithium within the crystal [14]. Luckily, a lot of experimental investigations have reported different kinds of doping, for example, the Li-sites of $LiFePO_4$ are doped with Mg, Ti, Zr, Cr, Nb and Mo, was a feasible way to enhance the intrinsic conductivity [8,15–19]. The Fe-site doping weakens the Li–O interaction, resulting in high ionic mobility and diffusion coefficiency [20–24]. Recent researches have suggested that substitution of small fraction of Fe in $LiFePO_4$ by V, Ni, Co, Mg, and Zn can improve the electrochemical behavior of $LiFePO_4$ by increasing the intrinsic electronic conductivity of $LiFePO_4$ [8,22,25,26]. In addition, recently wet methods that can offer many advantages such as better homogeneity, regular morphology, and submicron sized particles are used [27–29].

On the basis of previous studies, a series of $LiAl_xFe_{1-3x/2}PO_4/C$ [$x = 0, 0.01, 0.02, 0.04, 0.06, 0.12$] cathode materials were synthesized with an easy solution process in which formation of conductive carbons and cation-substitution were achieved simultaneously. In addition low-cost $Fe(NO_3)_3$ was selected as iron source instead of expensive Fe^{2+} compound and sucrose was adopted as reductive agent and carbon source. The electrochemical properties of the synthesized composite powders were discussed in this work and the emphasis of the current investigation was to study the effect of Al^{3+}-substitution on capacity retention and cycle stability.

2. Experimental

$LiAl_xFe_{1-3x/2}PO_4/C$ [$x = 0, 0.01, 0.02, 0.04, 0.06, 0.12$] powders were prepared using a solution method. $Fe(NO_3)_3{\cdot}9H_2O$ (Tianjing Chemicals, 98.5%), $NH_4H_2PO_4$ (Tianjing Chemicals, 99%), $LiNO_3$ (Tianjing Chemicals, 96.6%), and $Al(NO_3)_3$ (Tianjing Chemicals, 99%) were used as reactants. The stoichiometric reactants were dissolved in a distilled water and ethanol mixture. After the reactants were mixed, adequate amount of sucrose was added into

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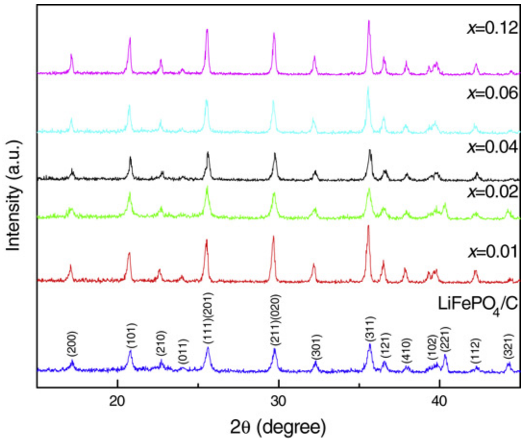

Fig. 1. XRD patterns of $LiAl_xFe_{1-3x/2}PO_4/C$ powders.

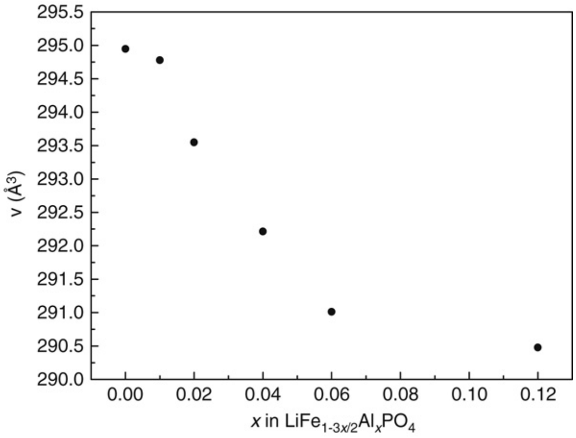

Fig. 2. Variation of unit cell volume as a function of Al contents in $LiAl_xFe_{1-3x/2}PO_4/C$.

the solution. The solution was heated and maintained at 80 °C under vigorous stirring until a viscous gel was formed. The as-formed gel was calcined at 500 °C for 1 h, further sintered at 700 °C for 10 h in an argon atmosphere, finally cooled to room temperature.

The crystalline phases of $LiAl_xFe_{1-3x/2}PO_4/C$ was identified with X-ray diffraction (XRD, Rigaku D/MAX-RC) with Cu Kα radiation ($\lambda = 1.5405$ Å, 45.0 kV, 50.0 mA). Elemental compositions of these samples (Fe, Al) were determined by ICP (Perkin-Elmer optima 5300 DV). The morphology of particle was observed with a scanning electron microscope (SEM, S-4800, Hitachi). The particles size analysis was determined by the Zetasizer (3000HS, Marlven, UK).

The electrodes were prepared by spreading the cathode slurry (75 wt% of the active material, 10 wt% of polyvinylidene fluoride (PVDF) in N-methyl pyrrolidone (NMP), and 15 wt% of carbon black) onto an aluminum foil followed by drying in vacuum at 120 °C for 12 h. A typical electrode disk contains 2.5–3.5 mg active material. The cells (CR2025) were assembled in an argon filled glove-box using lithium metal foil as the counter electrode. The electrolyte was 1.0 mol dm^{-3} $LiPF_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DEC) (1:1, v/v).

The cells were galvanostatically charged and discharged over a voltage range of 2.3–4.5 V at different rates. Cyclic voltammetry measurements were performed using a CHI660B electrochemical working station at a scanning rate of 0.1 mV s^{-1}. The C rate was calculated from the weight and theoretical capacity of $LiFePO_4$.

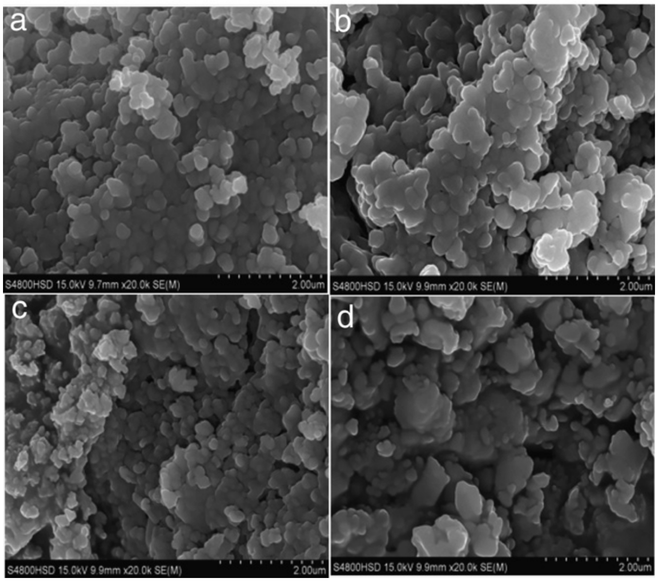

Fig. 3. Scanning electron micrographs for $LiAl_xFe_{1-3x/2}PO_4/C$ powders: (a) $x = 0.01$, (b) $x = 0.06$ (c) $x = 0.12$ (d) $x = 0$.

3. Results and discussion

3.1. Crystalline structure analysis

From the ICP results, the ratio of Fe, Al of $LiAl_xFe_{1-3x/2}PO_4/C$ ($x = 0.02, 0.12$) is 0.98:0.02 and 0.88:0.12, equal to the expectable value. Fig. 1 shows the x-ray diffraction patterns of the $LiAl_xFe_{1-3x/2}PO_4/C$ [$x = 0, 0.01, 0.02, 0.04, 0.06, 0.12$] powders. All samples exhibit single phase of $LiFePO_4$ with an ordered olivine structure indexed to the orthorhombic *Pnma* space group. The intensity of the diffraction peaks is enhanced and becomes slightly acute after substitution especially $x = 0.01, 0.06$ and 0.12. The change of the unit cell volumes as a function of x (Al content) in $LiAl_xFe_{1-3x/2}PO_4/C$ is presented in Fig. 2. As x increases, the unit cell volume decreases with Al^{3+} substitution according to Vegard's law. The decrease is because the ionic size of Al^{3+} (0.535 Å) is smaller than that of Fe^{2+} (0.78 Å). These indicate that Al^{3+} was successfully introduced into $LiFePO_4$ matrix structure and the incorporation of Al^{3+} did not alter the $LiFePO_4$ structure but slightly decreased unit cell volume. The carbon is in amorphous form, as there are no additional peaks on the XRD patterns belonging to its crystal modification, it is believed that the effect of carbon coating has restricted the undesirable conversion of iron and hence resulted in the phase pure formation of samples.

3.2. Microstructure of the powders

The effect of Al^{3+}-substitution on the particles size and morphology of $LiFePO_4/C$ powders have been investigated by SEM. Fig. 3 shows the SEM images of the cathode surface with various Al^{3+} contents. All prepared samples have a spherical shape. The morphology of pure $LiFePO_4/C$ powders shows heavy agglomeration compared to Al^{3+}-substitution powders. It is found that the Al^{3+}-substitution did not influence powder morphology, but with increasing Al^{3+} content, the particles size tends to growth slightly. The Al^{3+}-substitution powders are consisted of non-uniform particles with the size ranged between 200 and 400 nm which is smaller than the $LiFePO_4/C$ powders. When the substitution amount of Al^{3+} increases to 0.12, the morphology of the sample shows slightly particle- agglomerated. But a similar size distribution and morphology are observed regardless of