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Electrochemical performance of patterned LiFePO4 nano-electrode with a pristine amorphous layer

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A patterned LiFePO4 nanorod with a pristine amorphous LiFePO4 surface layer was fabricated by controlling the temperature gradient from the interior to the exterior layer in high-temperature annealing process through designing hierarchical multilayer electrode structure. The three dimensional patterned LiFePO4 nanorods were prepared using tobacco mosaic virus nano-forest arrays. The results indicate that the nano-electrodes nearly reached the theoretical capacity at a very low C rate even without conductive coatings. The amorphous LiFePO4 can fast transport the Li-ion to inside crystal LiFePO4, thus enhancing the rate capability. © 2014 AIP Publishing LLC.

The olivine-type LiFePO4 has been considered as one practical choice for lithium-ion battery electrodes material due to its superior inherent merits, including low cost, environment friendliness, remarkable thermal stability, excellent long cycle ability, and high safety.1 However, the application of LiFePO4 is limited because of its poor high C rate performance, which is restricted by sluggish kinetics of electron2 and Li3 transport.3

The challenge of poor power density can be migrated when the LiFePO4 electrodes is fabricated as three-dimensional (3-D) nano-array2 and coated with a superior ionic/electronic conductor layer on LiFePO4 nano-array surface. For example, highly electronic conductive carbon was coated on the surface of LiFePO4 for improving surface conductivity.5 However, the carbon may decrease the tap density of materials6 and introduce the impurity contamination when the battery is applied in micro-electromechanical systems (MEMS).

Alternatively, highly conductive amorphous glass film was also coated to nanostructured LiFePO4 to enhance the power density. For example, as a conductive and protective layer, the amorphous conductive NiP and glassy lithium phosphate phase7 layer were coated on LiFePO4 to enhance the rate performance of LiFePO4.8 The amorphous Li3P2O7 coated on the LiFePO4 surface could improve the ionic conductivity, thus enhance rate capacity of electrodes.9 It is suggested10 that the disordered nature of the amorphous materials can also modify the surface potential of lithium to facilitate the adsorption of Li+.

However, it has been a challenge to design a robust heterogeneous surface films on the electrode that surviving in entire life of batteries even though the advantages of these surface films are well understood.11 The fabrication of amorphous binary or ternary compounds usually involved some complicated synthesis process.8–11 Since heterogeneous layer normally has different compositions with the underneath electrode, the interface between surface heterogeneous layer and cathode may withstand the inevitable thermal flux during the micro-fabrication process and subsequent charge-discharge cycle, resulting in increase of interface resistance,12 thus decrease the electrochemical properties of cathode materials.

In this Letter, the 3-D multilayer LiFePO4 nano-electrodes were prepared by using the tobacco mosaic virus (TMV1cys) as the templates. A pristine amorphous layer (PAL) of the LiFePO4 was formed on the surface of nano-LiFePO4 electrodes by designing a hierarchical architecture of multilayer LiFePO4 thin films. Since the PAL has the same composition with the electrode, thus significantly reduces the interface resistance. The effects of the pristine amorphous surface toplayer on electrochemical properties of 3-D LiFePO4 nano-electrode were systematically investigated.

The self-assembly TMV1cys was adopted as a bioinorganic template to form nano-scaled 3-D structure.14 To form an amorphous LiFePO4 layer on the crystal LiFePO4 electrode, a temperature gradient range from the interior to the outmost surface of LiFePO4 during annealing in a vacuum chamber was created by designing multilayer thin films with different thermal conductivities. Since the thermal radiation in the vacuum chamber is very weak, the temperature gradient can be created by the inside-out thermal conduction of multilayer films, which can induce a successive phase transformation in the as-prepared LiFePO4 cathodes.15

The Titanium (Ti) and Nickel (Ni) films were employed as thermal conductive layers. The Ni films were deposited on TMV1cys templates well by the electroless plating method. The highly dense Ni/TMV1cys nanorods were attached to the SS substrate in a nearly vertical manner (Fig. 1(a)). Since Ni atom could rapidly drift into the LiFePO4 film during charge-discharge cycles procedure16 reducing the electrochemical performance of LiFePO4, Ti barrier layers were...
deposited between Ni and LiFePO₄ layers for preventing the Ni diffusion. Moreover, the tensile strength of Ti (about 240 MPa (Ref. 17)) is relatively higher. The integration of Ti and Ni metal layers can also improve the electric contact of layer interfaces and the rigidity of the electrodes, which can effectively accommodate the stress/strain generated between electrode and the substrate due to the volume change of the electrodes during lithiation-delithiation process, and thus improving the stability of cathodes. The deposition of Ni, Ti, and LiFePO₄ layers in sequence can therefore form the hierarchical architecture of multilayer films with different thermal conductivities.

The magnetron sputtering deposition of LiFePO₄ on 3-D Ti/Ni/TMV substrates was conducted in base pressure of 1.5 × 10⁻⁴ Pa and working pressure of 1 Pa at a sputtering power density of 3 W/cm². The average deposition rate is 4.5 nm/min. The target-to-substrate distance is 70 mm. The surface morphology of 3-D LiFePO₄/Ti/Ni/TMV1cys electrodes is shown in Fig. 1(b). After sputtering deposition, some samples were annealed at 500 °C for either 2 h or 4 h in a vacuum furnace. The pressure of the vacuum furnace was lower than 1.0 × 10⁻³ Pa during annealing.

X-ray diffraction (XRD) measurement was employed to ascertain the crystallographic structure of the samples by a Rigaku diffractometer using Cu-Kα radiation. Mass of samples was weighed by a high precision microbalance with an accuracy of 1 μg before and after LiFePO₄ depositing. The surface morphology of nano-electrodes was observed by Field Emission Scanning Electron Microscope (FESEM). A high-resolution transmission electron microscope (HRTEM) with an energy-dispersive spectrometer (EDS) was employed to analyze the microstructures and composition of nano-electrodes. The electrochemical performance of LiFePO₄/Ti/Ni/TMV nano-electrodes was evaluated using coin cells (R2032) with lithium foil as an anode electrode and a 1M LiPF₆ solution in ethylene carbonate/diethyl carbonate (1:1 by volume) as an electrolyte.

The as-deposited LiFePO₄/Ti/Ni/TMV nanorods have an average of ~500 nm in diameter and greater than 2.5 μm in length (Fig. 1(b)). The microstructure of LiFePO₄, Ti, and Ni layers can be clearly identified by EDS line scan and TEM images as shown in Figs. 1(c) and 1(d). These results indicate that the LiFePO₄/Ti/Ni/TMV nano-electrodes were constructed.

The XRD patterns of the LiFePO₄/Ti/Ni/TMV nano-electrodes are shown in Fig. 2. The as-deposited LiFePO₄ nano-electrodes give no apparent diffraction peaks as shown in Fig. 2(a), which is in accordance with an amorphous ring in the interpolated FFT image as shown in the insetted image of Fig. 1(c). It is clear that the as-deposited nano-electrodes have amorphous structure. After annealed at 500 °C for 2 h or 4 h, all the diffraction peaks of the nano-electrodes (Figs. 2(b) and 2(c)) could be observed and the results indicate that the nano-electrodes were crystallized.

FIG. 1. (a) SEM image of Ti/Ni/TMV; (b) SEM image of as-deposited 3-D LiFePO₄/Ti/Ni/TMV; (c) TEM image of single 3-D LiFePO₄/Ti/Ni/TMV electrode and corresponding FFT (Fast Fourier Transform) figure; (d) EDS element line distribution of single electrode along the red line in (c).

FIG. 2. XRD patterns of LiFePO₄ cathodes. (a) As-deposited multi-layers; (b) annealed at 500 °C for 2 h in vacuum; (c) annealed at 500 °C for 4 h in vacuum.
(c)) can be indexed to the orthorhombic system with the Pnma space group, according to the JCPDF database. No diffraction peaks related with Ni and Ti are observed in Fig. 2 because the thickness of the metal sub layer is too thin.

Fig. 3 shows the microstructure of the annealed nanoelectrodes. As demonstrated in the FFT and TEM images (Figs. 3(a)–3(c)), a 10 nm PAL was coated on the outmost surface of the nano-electrodes that were annealed at 500 °C for 2 h. Therefore, the PAL could be grown on the outmost surface of the crystal LiFePO₄ nano-electrodes when the LiFePO₄/Ti/Ni/TMV nano-electrode was annealed at 500 °C for 2 h. However, the nano-electrodes were completely crystallized with further increasing annealing time (Figs. 3(d)–3(f)). Therefore, the PAL can be formed on the outmost surface of nano-electrodes by tuning the annealing process. This is because the heat transmission of multilayer nano-electrodes during annealing process is along the sub-layer metal (Ti and Ni) from inside to outside generate a temperature gradient ranging from the interior to the exterior layer of multilayer films. The crystallization of LiFePO₄ would start in sequence along the depth direction of the multilayer films. Therefore, the multilayer LiFePO₄/Ti/Ni/TMV nano-electrodes with either the pristine amorphous toplayer or full crystal structure (FC) layer can be obtained simply by the precise control of annealing parameters.

Fig. 4(a) shows the charge/discharge voltage profiles of LiFePO₄ nano-electrodes with the PAL and FC at 1C. As shown in Fig. 4(a), both charge and discharge profiles show reversible electrochemical reactions at voltage plateaus around 3.4 V, which are the characteristic of phase transition between FePO₄ and LiFePO₄. Without adding conducting materials, both the LiFePO₄ multilayer nano-electrodes could nearly reach the theoretical value at 0.1C as showing in Fig. 4(b). To evaluate the effects of the crystal structure of surface layer on rate performance, both LiFePO₄ nano-electrodes with crystal and amorphous surface layer were subjected to an aggressive testing protocol in which the cells were both charged and discharged at the same rate. Fig. 4(b) shows the rate capacity of the two LiFePO₄/Ti/Ni/TMV electrodes at different charge/discharge current rates from 0.1C to 10C. The capacity of both electrodes at 0.5C dropped down 14% and 18% than those of nano-electrodes at 0.1C, respectively. However, due to the fast Li-ion transport in amorphous LiFePO₄, the discharge capacity of the LiFePO₄ nano-electrodes with PAL is higher than that of the nano-electrodes with FC when the cycling is larger than 1C rate (Fig. 4(b)). Moreover, the discharge capacity of the LiFePO₄ nano-electrodes with PAL was 12.5% and 24% higher than those of the LiFePO₄ nano-electrodes with FC at 5C and 10C, respectively (Fig. 4(b)). Even after a certain number of charge/discharge cycles at 5C and 10C, the LiFePO₄ nano-electrodes with PAL had a slower capacity fading rate and a better high-rate charge-discharge cycle performance (Fig. 4(b)). This might be explained by that the PAL removes the anisotropy of the surface properties and enhances the delivery of Li⁺ to the (010) facet of LiFePO₄.
where it can be inserted. It is concluded that the limiting factor for charge/discharge is the delivery of Li$^+$ and electrons at the surface diffusion rather than bulk diffusion. Therefore, the high-rate discharge performance of the materials can be improved by coating LiFePO$_4$ with the PAL, which can eliminate the anisotropy of the surface and increase the diffusion rate of the lithium ion in electrode material surface.

In conclusion, we have prepared the 3-D LiFePO$_4$/Ti/Ni/TMV nano-electrodes. A pristine amorphous surface toplayer on 3-D LiFePO$_4$ nano-electrode was formed by one-step annealing process through designing a hierarchical architecture of multilayer thin films. The effects of PAL and FC surface layers on electrochemical performance of the LiFePO$_4$ nano-electrodes were systematically investigated. Both of the LiFePO$_4$ nano-electrodes can nearly reach the theoretical capacity at a low C rate without coating conducting materials. However, the LiFePO$_4$ cathode with PAL has a predominant rate capacity at high C rate and a slower capacity fading rate. The pristine amorphous surface structure of the nano-electrodes can significantly enhance the rate performance of the lithium-ion battery.

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