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LiFePO₄/graphene as a superior cathode material for rechargeable lithium batteries: Impact of stacked graphene and unfolded graphene

Introduction

Extensive efforts have been focused on the development of alternative renewable and clean energy sources to relieve the pressure from limited fossil fuels and increasing environmental and global warming issues. Lithium ion batteries (LIBs) have been regarded as a promising energy storage system for applications in electric and hybrid electric vehicles after two decades of development. Polyanion typed cathode material LiFePO₄ (LFP) has attracted the most interest as the advanced cathode materials in LIBs because of its environmental benignity, high safety and theoretical capacity. However, the major limitation for LiFePO₄ is its intrinsically poor conductivity, which could be overcome by highly conductive hybrid structures with carbon coating or graphene incorporation [1].

In order to maximize the potential of active materials and graphene, a good combination manner between LiFePO₄ and graphene is pursued. Compared with stacked graphene, unfolded graphene possesses fewer layers and is smaller, allowing a more uniform dispersion of the LiFePO₄ precursor and a larger contact area between the graphene and the LFP active material and thereby full utilization of the unfolded graphene. In addition, unfolded graphene, which has a higher surface area than stacked graphene, provides more nucleation sites to anchor LFP nuclei, further restricting the size and agglomeration of the LFP particles. Thus, it is essentially critical to design the LiFePO₄/unfolded graphene composites, examine the performance and communicate insights into reasons for that. In particular, using X-ray absorption near edge structure (XANES) to investigate the chemical states, local chemistry environment of interested elemental and the interaction (chemical bonding) between unfolded graphene and LFP particles gleans a more complete understanding of the improved electrochemical performances.

Science

We present the use of unfolded graphene as a three-dimensional (3D) conducting network for LiFePO₄ nanoparticle growth. The facile-designed hybrids exhibit both high specific capacity and rate performances benefiting from application of the unfolded graphene matrix, which serves as a conducting 3D nano-network, enabling both Li⁺ and electrons to migrate and reach each of these LiFePO₄ particles, hence realizing the full potential of the active materials. Employing a facile method combining a sol-gel route and a solid-state reaction approach, the LiFePO₄/unfolded graphene and LiFePO₄/stacked graphene nanocomposites were obtained successfully. The compatible incorporation of LFP into well dispersed ultrathin graphene affords desirable morphology, size and distribution of the materials. Nano-sized LFP particles were dispersed uniformly and tightly anchored to the unfolded graphene network thorough strong coupling between nano-carbon materials and LFP, whereas larger sized (micro-scale) LFP particles were loosely attached on the stacked graphene. Further, the employment of unfolded graphene allows each LiFePO₄ particle attached on the 3D conducting network enables both Li ions and electrons to migrate and reach each active particle, which could greatly enhance the electronic conductivity, hence realizing the full potential of active materials. Based on the superior structure, the LiFePO₄/unfolded graphene nanocomposites after post treatment for 12 hours could reach a discharge capacity of 166.2 mA h g⁻¹ in the first cycle, which is 98% of the theoretical capacity (170 mA h g⁻¹), whereas LiFePO₄ with stacked graphene only delivers 77 mA h g⁻¹ in the 1st cycle. Moreover, no obvious decline was observed in the discharge capacity after 100 charge-discharge cycles at room temperature. For example, the discharge capacity loss was less than 1.3% over 100 cycles and the coulombic efficiency

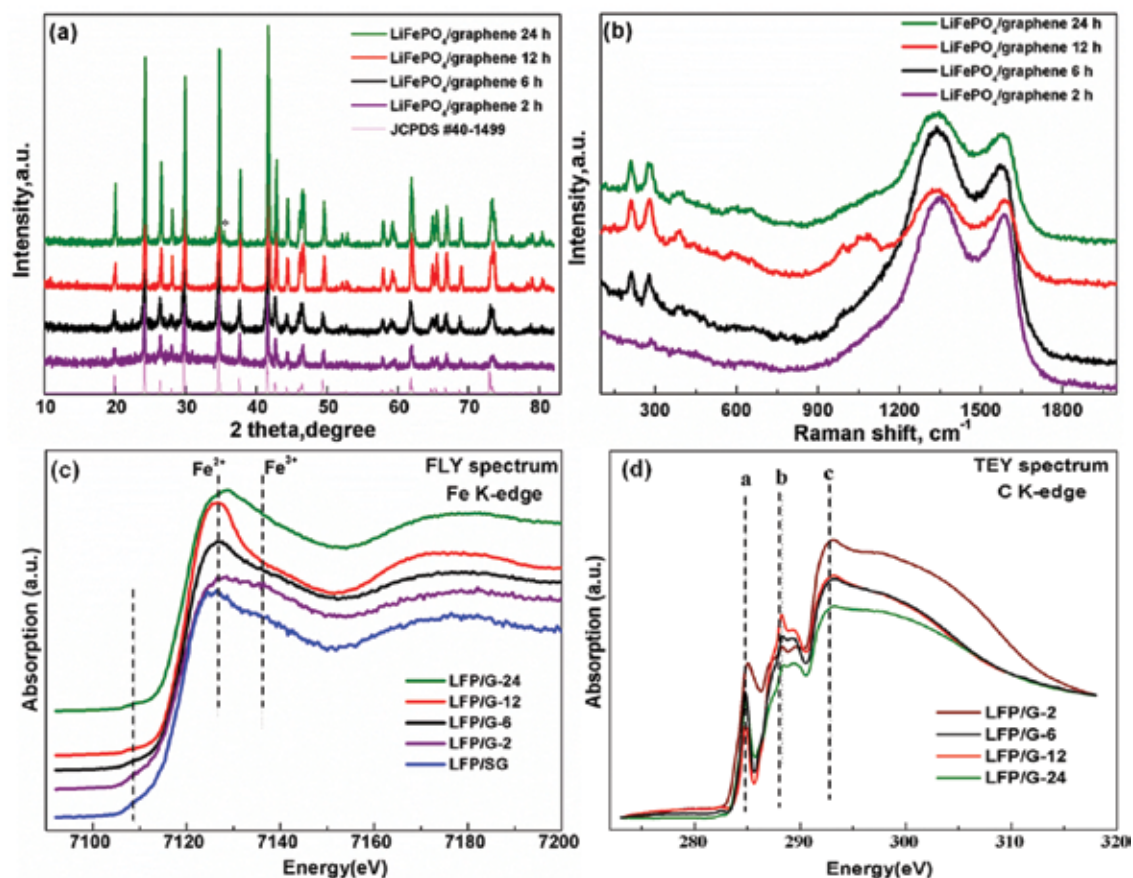


Figure 1. (a) XRD patterns, (b) Raman spectra, (c) normalized absorption of Fe K-edge and (d) C K-edge XANES spectra for LiFePO₄/unfolded graphene composites annealed at 700°C for various time.

was close to 100%. At a high current density up to 15°C (2550 mA g⁻¹), the discharge capacity remained relatively high, at 60 mA h g⁻¹. It is demonstrated that homogeneously embedded LFP nanoparticles in a superior conducting matrix can be tolerant to high charge and discharge currents, and thereby satisfying one of the mandatory electrochemical features for LIBs used in EVs and HEVs.

Various advanced characterization techniques including X-ray diffraction (XRD), Raman spectroscopy and synchrotron analysis were conducted to characterize the samples. Fe K-edge and C K-edge XANES measurements were conducted to examine the crystallinity of LiFePO₄ and chemical bonding between LiFePO₄ and unfolded graphene.

Discussion

Figure 1 (a) shows the XRD patterns of LFP/stacked graphene and different time annealed LFP/unfolded graphene from 2 h to 24 h. It is demonstrated that highly pure LFP with an orthorhombic olivine structure was successfully obtained and the crystallinity was observed to increase with the annealing time. From the Raman spectra (Figure 1 (b)), the ID/IG ratio decreases with the increase of the reaction time. A lower ID/IG ratio indicates a larger amount of graphitized carbon; i.e., the amount of graphitized carbon increases with the increasing annealing time.

Figure 1 (c) shows the Fe K-edge XANES spectra consist of two main edge jumps, the pre-edge and the main edge regions. The pre-edge peak was centered at the lower energy side of the sharply rising absorption edge (white line), corresponding to the 1s

to 3d electronic transition of Fe. For LFP/UG-2, the spectrum was broader than that of the other composites, indicating the low crystallinity of LFP/UG-2. With increasing annealing time, the spectral features became sharp, illustrating increased crystallinity of LFP/UG. The LFP/SG composites also exhibited sharp features, indicating good crystallinity. It should be noted that for LFP/UG-24 composites, the position of the Fe K-edge in the XANES spectra slightly shifted toward the higher energy side, which is related to the appearance of impurity in LFP/UG-24.

Figure 1 (d) exhibits two patterns in the C K-edge XANES spectra locating at around 285 eV and 291 eV corresponded to graphitic p* and s* transitions, respectively, which indicated that the graphitic framework existed in all of the LFP/UG nanocomposites. Therefore good electronic conductivity in LFP/UG nanocomposites

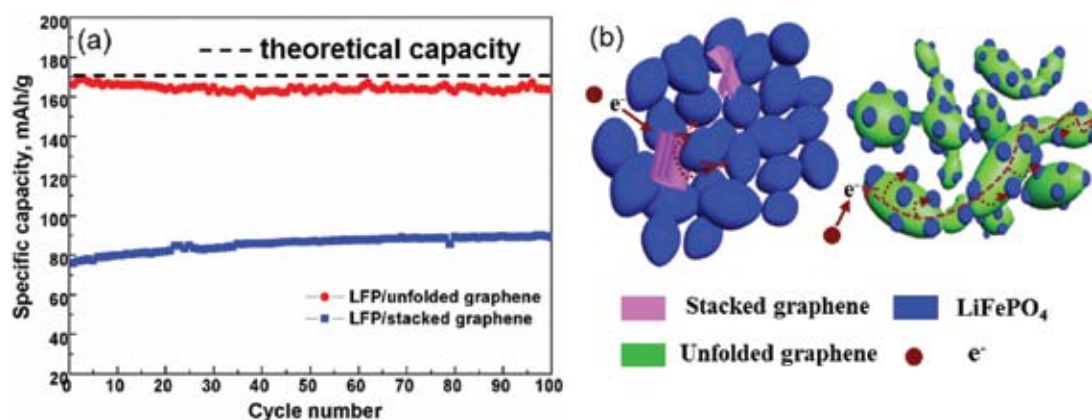


Figure 2. (a) Electrochemical performance of LiFePO₄/unfolded graphene and LiFePO₄/stacked graphene. (b) Schematic diagram to show networked structure of LiFePO₄/unfolded graphene compared with LiFePO₄/stacked graphene.

was expected. Further analysis of the XANES spectra showed several interesting features. First, p^* transition intensity for LFP/UG-12 was reduced compared with other composites. Lower intensity indicates more charge transfer from LFP to C 2p-derived p^* states in unfolded graphene, indicating stronger chemical bonding between LFP and interface of unfolded graphene. Second, the intensity of resonance at ~ 288 eV from LFP/UG-12 was stronger than the other LFP/UG composites, which is attributed to the chemical bonding between active materials and carboxylate groups. The observation in the spectra demonstrated the stronger carboxylate bonding in the LFP/UG-12 composites.

The long cycling performance of nanocomposites was investigated at a constant current density of 17 mA g^{-1} , as illustrated in Figure 2. Based on the superior structure, the LiFePO₄/unfolded graphene nanocomposites after post treatment for 12 hours could reach a discharge capacity of $166.2 \text{ mA h g}^{-1}$ in the 1st cycle, which is 98% of the theoretical capacity (170 mAh g^{-1}), and the composites display stable cycling behavior up to 100 cycles, while for LiFePO₄/stacked graphene composites with similar carbon content, it could only deliver a discharge capacity of 77 mA h g^{-1} for the first cycle.

Conclusion

In summary, a novel nanocomposite with uniformly dispersed LFP nanoparticles anchored to unfolded graphene matrix was developed for high-power electrode materials in LIBs. The use of an unfolded graphene matrix, which serves as a conducting 3D nano-network, enables both Li⁺ and electrons to migrate and reach each of LFP particles, hence realizing the full potential of the active materials. In comparison with the LFP/SG composites, the LFP/UG-12 nanocomposites delivered a much higher discharge capacity (close to the theoretical capacity) and a superior rate capability. In LFP/UG composites, the crystallinity of LFP and the chemical bonding between the LFP and unfolded graphene are improved by lengthening the annealing duration to 12 h, which can be demonstrated by the XANES spectra. The unique structure, the superior conducting properties of the graphene matrix and strong chemical interaction between LFP and the unfolded graphene enable the LFP/UG-12 nanocomposite to achieve excellent Li storage behavior. The success of this electrode design was demonstrated by the superior characteristics of the LFP/UG nanocomposite. This design could also be extended to other cathode and anode materials, which promises to promote the development of next-generation LIBs applied in EVs and HEVs with both high-power and high-energy densities.

References

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Beamline information

SXMB, SGM, XANES, Fe K-edge and C K-edge, SDD detector.