



Li-ion batteries from LiFePO₄ cathode and anatase/graphene composite anode for stationary energy storage

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ABSTRACT

Li-ion batteries made from LiFePO₄ cathode and anatase TiO₂/graphene composite anode were investigated for potential application in stationary energy storage. Fine-structured LiFePO₄ was synthesized by a novel molten surfactant approach whereas anatase TiO₂/graphene nanocomposite was prepared via self-assembly method. The full cell that operated at 1.6 V demonstrated negligible fade even after more than 700 cycles at measured 1 C rate. While with relative lower energy density than traditional Li-ion chemistries interested for vehicle applications, the Li-ion batteries based on LiFePO₄/TiO₂ combination potentially offers long life and low cost, along with safety, all which are critical to the stationary applications.

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1. Introduction

Concerns over the use of fossil fuels and the environmental consequence of their use, coupled with the trend of carbon monetization, have spurred great interest in renewable energy from sources such as wind and solar. The power from the intermittent renewable sources is however varied and uncontrolled. Electrical energy storage is considered an effective, clean way to smooth out the intermittency and make dispatchable of the renewable energy. One potential technology is to use Li-ion batteries that have gained great success in mobile electronics and been the leading technology extensively developed for vehicle applications [1,2]. Without volume and weight constraints, the renewable integration and grid applications may not require energy/power densities as high as that for electronic and vehicle applications. Instead, as utility assets, the electrical energy storage devices emphasize more on life and cost, along with safety. Of particular interests are the Li-ion chemistries that are made from electrode materials of reasonable cost and excellent structural and chemical stability, as well as low heat generation, during Li-extraction/insertion. As an example,

we have studied Li-ion batteries with LiFePO₄ cathode and anatase TiO₂ based anodes.

For cathode, we choose LiFePO₄ because of its stability, low-cost and environmental friendliness. While having a lower voltage vs. Li of 3.45 V, than many other cathode compositions, LiFePO₄ shows flat discharge/charge curves during two-phase Li-extraction/insertion process and excellent cycling stability due to its unique ordered olivine structure [2–7]. Similarly, titanium oxide based materials including TiO₂-polymorphs and Li₄Ti₅O₁₂ exhibit a relative high voltage vs. Li (1–2 V), [3,8–10] but have open structures that allow Li-insertion/extraction without much structural straining, thus potentially a long cycle life. In addition, the relative high voltage vs. Li of the TiO₂-base anodes helps to avoid SEI layer formation, making the battery much safer than the graphite anodes used commercially. Previously, spinel Li₄Ti₅O₁₂ and TiO₂ (B) have been used as stable anode [11–13]. However, the anode materials require additional step to synthesize starting from TiO₂ materials. Direct use of TiO₂ would be a low-cost and efficient way to make full-cell battery for stationary energy storage. One of disadvantage of TiO₂ includes low conductivity and therefore slow electrochemical kinetics. Recently, we have demonstrated hybrid TiO₂-graphene nanostructures which combine nanostructured TiO₂ with highly conductive graphene showing enhanced electron transport and Li-ion insertion/extraction kinetics [9].

In this study, we demonstrate the full cell Li-ion battery using LiFePO₄ cathode and anatase TiO₂/graphene anode. The LiFePO₄-anatase

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TiO₂/graphene cells are evaluated for electrochemical performance and the details are discussed.

2. Experimental

Fine-structured LiFePO₄ was synthesized using LiCOOCH₃·2H₂O (reagent grade, Sigma), FeC₂O₄·2H₂O (99%, Aldrich), NH₄H₂PO₄ (99.999%, Sigma–Aldrich), oleic acid (FCC, FG, Aldrich) and paraffin wax (ASTM D 87, mp. 53–57 °C, Aldrich). NH₄H₂PO₄ was milled with oleic acid for 1 h using high energy mechanical mill (HEMM, SPEX 8000M) in a stainless steel vial and balls. After paraffin wax was added and milled for 30 min, iron oxalate was added and milled for 10 min. Finally, Li acetate was added and milled for 10 min. The overall molar ratio is Li:Fe:P:oleic acid = 1:1:1:1 with paraffin addition twice the weight of oleic acid. The precursor paste was dried in oven at 110 °C for 30 min followed by heat-treatment in tube furnace at 500 °C for 8 h under UHP-3%H₂/97%Ar gas flow with ramping rate of 5 °C/min. After LiFePO₄ was synthesized, 10% carbon black by weight was added and milled in planetary mill for 4 h (Retsch 100CM) at 400 rpm. X-ray diffraction (XRD) pattern (Philips Xpert) was obtained using CuKα (1.54 Å) radiation. Microstructure of LiFePO₄ was analyzed by a field-emission scanning electron microscope (FESEM, FEI Nova 600). Anatase TiO₂/graphene composite (2.5 wt.% graphene) was obtained by self-assembly approach described in our previous publication [9]. Of the 13 mg functionalized graphene sheets (FGSs), and 0.6 mL of sodium dodecyl sulfate (SDS) aqueous solution (0.5 mol/L) were mixed by sonication. A 25 mL of TiCl₃ (0.12 mol/L) aqueous solution was added into as-prepared SDS–FGS dispersions while stirring, followed by 5 mL of 0.6 M Na₂SO₄ and 2.5 mL of H₂O₂ (1 wt.%) dropwise addition. Deionized water was further added under stirring to make total volume of 80 mL which was further stirred in a sealed polypropylene flask at 90 °C for 16 h. The final precipitates were separated by centrifuge and washed with deionized water and ethanol three times. The product was then dried in a vacuum oven at 70 °C overnight and calcined in air at 400 °C for 2 h [9].

For electrochemical evaluations, the cathode and anode comprised of active material, Super P and poly(vinylidene fluoride)

(PVDF) binder were dispersed in *N*-methylpyrrolidone (NMP) solution in a weight ratio of 80:10:10 for the anatase TiO₂/graphene anode and 90:3:7 for LiFePO₄/C cathode, respectively. Both cathode and anode slurries were then coated on an Al foil. The performance of LiFePO₄ and anatase TiO₂/graphene electrodes were evaluated, both in half and full 2325 coin cells (National Research Council, Canada) in 1 M LiPF₆ in EC/DMC (2:1) (ethyl carbonate/dimethyl carbonate) electrolyte at room temperature, using an Arbin Battery Tester (Model BT-2000, Arbin Instruments, College Station, TX, USA). The half-cells using Li as anode were tested between 4.3 and 2 V for LiFePO₄ and 3–1 V for anatase TiO₂/graphene at various C rate currents based on the theoretical capacity of 170 mAh/g for both cathode and anode whereas the full cell was tested in 1 C_m (measured C rate) rate. Due to the initial irreversible loss observed for anatase TiO₂/graphene anode, LiFePO₄ loading was 2.4 mg/cm² and 1.1 mg/cm² for anatase TiO₂/graphene in full cells and tested between 2.5 and 1 V where energy and power density was calculated based on the anode weight which is the limiting electrode.

3. Results and discussion

LiFePO₄ was synthesized using molten surfactant approach shown in Fig. 1 where nano-sized LiFePO₄ has been synthesized during the heat-treatment mimicking micelle or hydrothermal approach but with well crystallized particles. The X-ray diffraction analysis (Fig. 1) of LiFePO₄ shows lattice parameters of $a = 10.329 \text{ \AA}$, $b = 6.005 \text{ \AA}$, $c = 4.691 \text{ \AA}$ (R_p : 2.31, R_{wp} : 3.06, R_{exp} : 2.93) obtained via Rietveld refinement that matched closely to the ideally crystallized LiFePO₄ (JCPDS 81-1173, *Pnma*(62), $a = 10.33 \text{ \AA}$, $b = 6.010 \text{ \AA}$, $c = 4.692 \text{ \AA}$). The crystallite size was determined to be ~50 nm from the X-ray analysis; primary particle size ranges from 100 to 200 nm from FESEM observation. Anatase TiO₂/graphene composite show anatase TiO₂ nanoparticles (<20 nm) coated on graphene sheets where details are described in our previous publication [9].

The synthesized anatase TiO₂/graphene, LiFePO₄ and full-cell configuration have been tested at various C rates as shown in Fig. 2(a–e). As shown in Fig. 2(a and d), anatase TiO₂/graphene

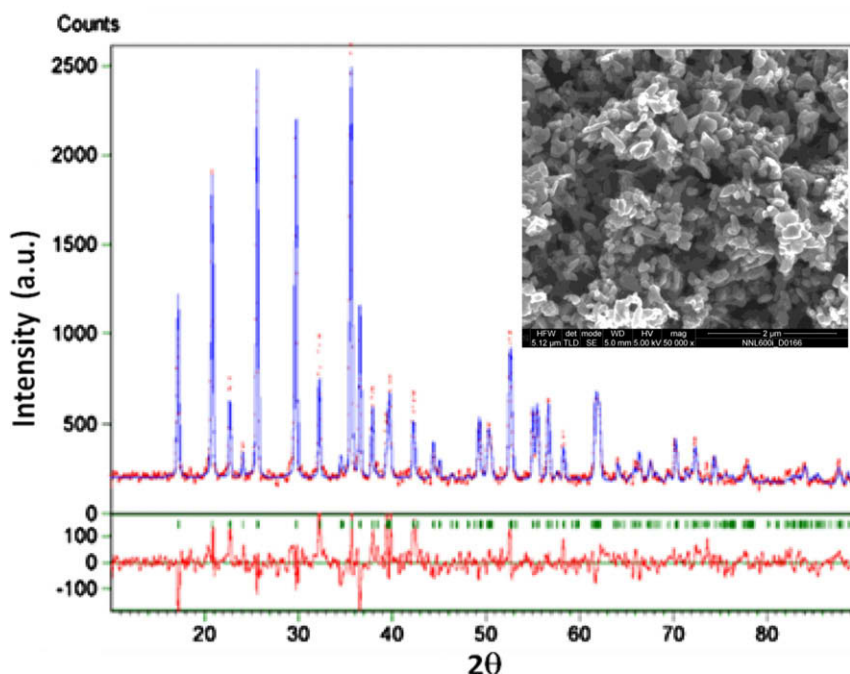


Fig. 1. XRD pattern and FESEM image of nanostructured LiFePO₄.

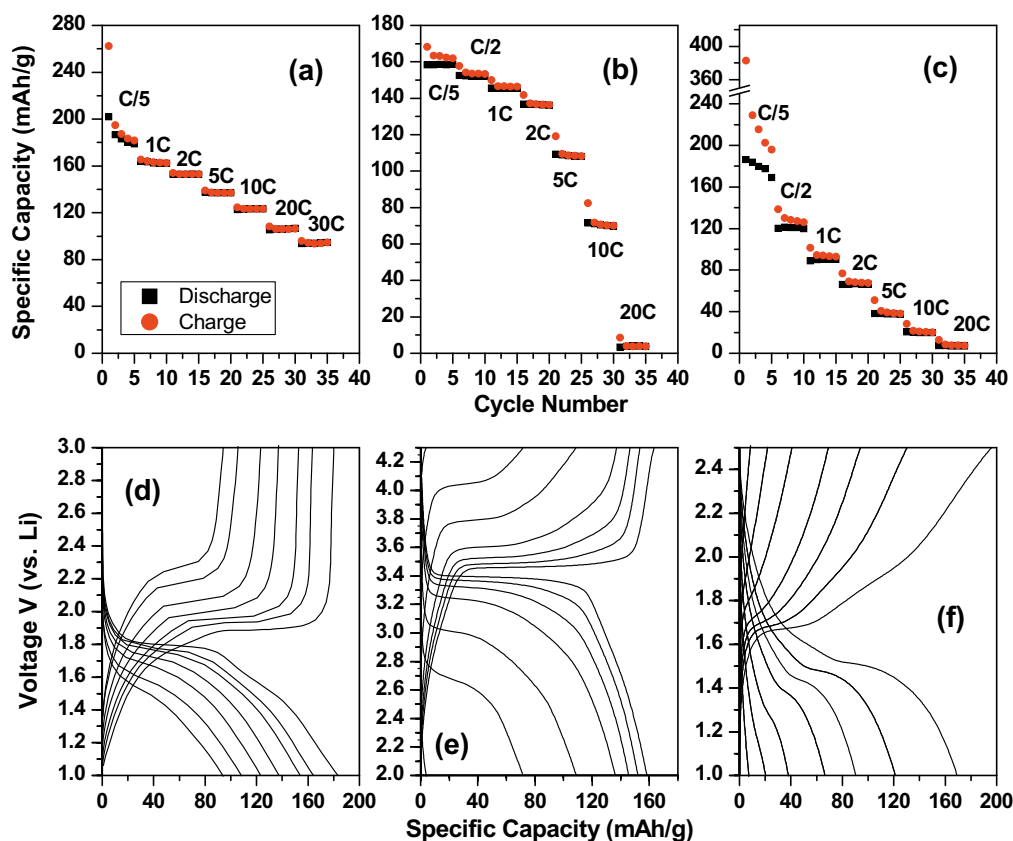


Fig. 2. Electrochemical cycling at various C rates for (a) anatase TiO₂/graphene, (b) LiFePO₄, (c) LiFePO₄-anatase TiO₂/graphene and voltage profiles of charge/discharge at various C rates for (d) anatase TiO₂/graphene, (e) LiFePO₄ and (f) LiFePO₄-anatase TiO₂/graphene.

electrodes demonstrates flat voltage curves at 1.84 V, indicating a classical two-phase electrochemical reaction process of the Li-insertion/extraction. Diffusion of Li-ions in anatase TiO₂ framework is known to accompany symmetry transformations between *I*₄/amd and orthorhombic *Pmn*2₁ when $x = 0.5$ (Li_xTiO₂), resulting in a net increase of ~4 vol.% of the unit cell leading to capacity fade. Hence, for bulk anatase TiO₂, $x = 0.5$ is often considered as the maximum electrochemical insertion of Li. However, the reduction in particle size into nano-regime (<100 nm) alternates the two-phase equilibrium phenomenon in the bulk to more of solid solution like Li uptake at the surface thus leading to increased capacity over 0.5 Li per unit formula [8]. As shown in Fig. 2(a), nano-sized anatase TiO₂/graphene composite gives more than 175 mAh/g (>0.5 Li) at C/5 rate and demonstrates good cycling capability. The anatase TiO₂/graphene also exhibited much higher rate response than that of LiFePO₄, reaching 90 mAh/g at 30 C (equivalent of measured 60 C_m rate). The LiFePO₄ electrode is characterized by a flat potential at around 3.45 V vs. Li from two-phase Li-extraction/insertion with specific capacity of 110 and 71 mAh/g at 5C and 10C (equivalent 8 C_m and 24 C_m rate), respectively. The rate capacity of the full cell (Fig. 2(c)) is lower than both cathode and anode half-cells due to the lower electronic and ionic conductivity of both cathode and anode compared to Li metal used in half-cells. Based on capacity limiting electrode, anatase TiO₂/graphene, the LiFePO₄-anatase TiO₂/graphene full cell delivered ~120 mAh/g at C/2 rate based on anode weight. The irreversible capacity loss during first cycle was 23% for anatase TiO₂/graphene anode in half-cell and 52% in full cell. Nano-sized TiO₂ usually show 20–50% irreversible loss during first cycle [8]. This is probably due to high surface area created by nano-sized TiO₂ and graphene which also shows Li-ion

storage characteristic [8,14,15]. In full cell, electrode material balance leads to changes in voltage profile of each cathode and anode and can affect the degree of irreversible loss since initial operating voltage starts from 0.2 V (OCV) followed by continuous cycling between 1 and 2.5 V. More detailed study will be conducted on the origin of irreversible loss in nano-sized TiO₂ during initial cycle.

Enhancing rate performance is vital not only for achieving higher power but also for minimizing polarization from internal resistance where the latter lead to exothermic irreversible heat generation $Q_{irr} = I\eta t + I^2 R t$ (I : current, η : absolute value of electrode polarization, R : Ohmic resistance, t : time) which plays critical role in heat management required for scaled up systems. Such heat control can extend the cycle life of Li-ion battery [16].

Fig. 3(a) shows dq/dv peaks of all electrodes tested at C/5 rate where full-cell potential of 1.6 V matches the voltage difference between cathode and anode peaks. Ragone plot of all three cells based on active material weight are compared in Fig. 3(b), the energy density of the full cell is limited by the anatase TiO₂/graphene due to the same specific capacity but lower voltage compared to LiFePO₄ whereas the power density is limited by the LiFePO₄ cathode. The full-cell power density of 4.5 kW/kg and energy density of 263 Wh/kg based on capacity limiting anatase TiO₂/graphene anode weight lies within these two limitations with LiFePO₄ cathode limiting the rate, which is opposite to conventional Li-ion batteries using graphite anode.

The cycling performance of the full-cell battery at 1 C_m rate shown in Fig. 3(c) indicates almost no fade even after 700 cycles with coulombic efficiency reaching 100% over the entire cycling test except for the initial few cycles where irreversible loss has been observed. The results confirm the ideal reversibility of the Li-ion batteries

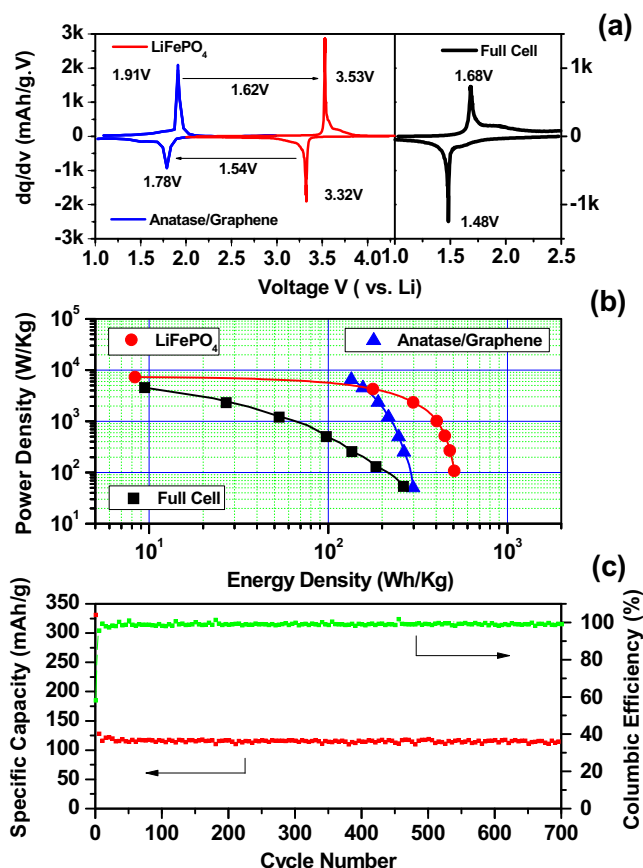


Fig. 3. (a) dq/dv peaks, (b) Ragone plot comparison of LiFePO₄, anatase TiO₂/graphene and LiFePO₄-anatase TiO₂/graphene full cell and (c) cycling performance of full cell at 1 C_m rate.

based on a combination of LiFePO₄-anatase TiO₂/graphene and the absence of losses due to parasitic processes, such as the electrolyte decomposition.

4. Conclusions

With emphasis on long life and low cost, along with safety, for the stationary applications, batteries of LiFePO₄ cathode and anatase/graphene composite anode have been characterized individually to better performance by minimizing the internal resistance

and irreversible heat generation. While with relative low energy density, the unique Li-ion cells made from LiFePO₄ cathode and anatase/graphene electrodes demonstrated negligible degradation after 700 cycles at 1 C_m rate. The excellent cycling performance makes the Li-ion battery a promising storage technology for stationary energy storage or in particular in community storage (<100 KWhs). More optimized battery design and larger scale cell test will be further studied. Also, reversible and irreversible heat generation of all electrode materials and full cell, which is crucial for stationary Li-ion batteries, will be reported in subsequent publication.

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