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Preparation of a flower-like iron phosphate materials as novel anode for dual-ion batteries

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Abstract

Dual-ion batteries (DIBs) have exceptional advantages over other electrochemical energy storage devices. In particular, the application of graphite cathodes exhibits superior properties in cost and safety. However, such batteries still suffer from the decomposition of electrolyte under high voltage for the conditional anode electrode. At the same time, the formation SEI of anode also result in the high irreversible. In this study, a new type of anode material of FePO$_4$ is explored for possible application in DIBs. The low voltage range of FePO$_4$ is controlled by partial lithiation to improve cycle stability. The flower-like structure can reach fast transport of electron and ions for ultra-thick electrode. And, the electrochemical performance is studied in great detail under different loading masses in full batteries. Above studies confirm that FePO$_4$ could yield stable cycling of DIBs. And, it shows obvious application advantages with low cost and without resource constraints in medium and long-term development.

Key Words:

dual-ion batteries; FePO$_4$ anode; anion intercalation
1. Introduction

With the large-scale application on electric vehicle field, the blooming lithium-ion batteries (LIBs) industry has been developed to meet the continuous requirements of mass production. Currently, transition metals like nickel, cobalt and manganese become important components in cathodes of LIBs. However, these metal resources employed for cathodes are constantly depleting, severely affecting the future industrial development of LIBs. [1-5] Or, from another perspective, unstablility of cathode matrix structures might induce crystalline failure, including overcharging, over-heat, manufacture problem and various misusing. [6-10] This, in turn, would lead to thermal runaway and security issues. [11,12] Hence, resources limitation and potential social safety are the main bottlenecks for wide application of LIBs in electric vehicle field.

Faced with the large-scale application of LIBs, alternative dual-ion batteries (DIBs) are increasing explored in recent years. DIBs are promising energy-storage systems owing to their special storage mechanisms and material characteristics. [13-18] Unlike “rocking-chair structure” of LIBs, the anions like PF$_6^-$ in electrolyte are inserted into layered-graphite cathodes of DIBs while lithium ions migrate towards anode electrode during charge. [19,20] These ions will then return to the electrolyte after discharge owing to transfer of anions and cations from the electrolyte. At voltages of 5.4 or 5.5 V (vs lithium reference), graphene
layer of cathode could store large amounts of anions to form anion intercalation compounds (C(PF$_6$)$_n$). [21-24] This yields reversible capacities ranging from 130 to 150 mAh g$^{-1}$ at n=24. [25,26] It is almost the same as other cathode materials, such as LiFePO$_4$, LiCoO$_2$ or Li$_2$Mn$_2$O$_4$.

And, the graphite based-on anion intercalation can get rid of the limitation of metal matrix. Hence, usage of graphite can become a promising cathode electrode in DIBs. Currently, the development of DIBs is still limited by several technical issues, such as hard paring between graphite cathode and general anode electrode, such as graphite anode, [27-29] soft carbon or hard carbon. [30,31] The elevated voltage windows lead to oxidative decomposition and deterioration of the electrochemical performances during charge-discharge processes. Note that most current DIBs are based on ionic liquids (ILs) electrolyte. [32-35] Moreover, electrochemical process of DIBs can consume large amounts of anion and cation (Li-salt) from the electrolyte owing to the work mechanism. And, the formation-SEI consumes lithium resources at low anode potentials (≤1 V) during initial charging processes. [36,37] During reversible discharge, ion imbalances in electrolyte might yield incomplete extraction from graphite cathode (C(PF$_6$)$_n$). Therefore, the use of common anode might limit their wide applications in DIBs.

Therefore, finding suitable anode materials is important for better performance DIBs. Herein, we propose a possible anode with the
promising voltage window, that is the iron phosphate (FePO₄) material, to tentatively study its performance in DIBs. The FePO₄ is a precursor of LiFePO₄ cathode material commonly produced in industry with extremely wide range of applications and low-cost. [38-41] Lithium iron phosphate (LiFePO₄) with specific capacity of 140-150 mAh g⁻¹ and excellent reversibility widely used in vehicles batteries and large-scale energy storage systems is employed as cathode material. The stability of LiFePO₄ material is mainly due to its stable structure and inertness of Fe²⁺/Fe³⁺. [42,43] During delithiation, lithium ions in the material are extracted from the olivine crystals, changing the active material to FePO₄.

During reverse reaction, FePO₄ gradually transforms into LiFePO₄ as lithium storage precursor. Meanwhile, volume of the material will not change at this process. In addition, LiFePO₄ with redox pair of 3.3/3.4 V is commercialized, and this material can be obtained by calcination of precursor FePO₄ and lithium hydroxide at high temperature. [44,45] Some recent studies have synthesized amorphous iron phosphate with higher specific capacity as cathode material of LIBs. [46-48] Compared to olivine- LiFePO₄, amorphous LiFePO₄ possesses an amorphous structure with wide voltage window at 1.5-4 V and lithiation-delithiation curve of certain slope voltage value.

Here, the possibility of FePO₄ anode material is studied to explore in application of DIBs. The particular potential plateau of the redox pair in
FePO$_4$ anode prevents formation of SEI consuming lithium sources during first electrochemical processes. Owing to the low electronic conductivity of FePO$_4$, we applied the combination methods of sol-gel and hydrothermal to obtain flower-like FePO$_4$ materials. Through this structure, the FePO$_4$ anode ultra-thick electrode was reached to pair the graphite cathode in dual-ion batteries. [49] These yields first reversible efficiencies close to 100% to protect the stable lithium resources in electrolyte. By conversion of LiFePO$_4$ cathode, stable electrochemical performance and high voltage are obtained by pairing graphite cathode, confirming that FePO$_4$ could apply in the DIBs to obtain stable performance.

2. Experimental

2.1 Material preparation

The FePO$_4$ was synthesized by mixing FeSO$_4$ with (NH$_4$)$_2$HPO$_4$ at stoichiometric ratio of Fe/P=1. The two aqueous solutions were then mixed to obtain colloid solution. The ascorbic and PEG-400 were added into the solution. And, after addition of H$_2$O$_2$, yellow precipitate hydration precursor was obtained. The suspension solution was put into the microwave reactor at 30 min. Then, the solution was transferred to the polytetrafluoroethylene reactor in hydration hotbox overnight at 180 °C. After hydrothermal reaction, the compound was washed several times. At last, the precipitation with H$_2$O was calcined at 380 °C for 6 h in muffle furnace to obtain well-dispersed FePO$_4$. FePO$_4$ was employed as anode
during battery testing. Layered-graphite (Alfa Aesar, 325 Mesh, KS-6 99.8%) was used as cathode for intercalation host of PF$_6^-$ anions.

2.2. Electrode preparation

Graphite or FePO$_4$, polyvinylidene fluoride (PVDF) and Super-P were mixed at weight ratio of 8:1:1 in N-methyl pyrrolidinone (NMP) solvent under mechanical stirring for 12 hours. The resultant slurry was then coated onto Al-foil (for cathode/anode electrode) by an automatic coating machine. Owing to the higher voltage of anode electrode, the current foil was applied to the Al-foil. Three kinds of electrodes of different thicknesses were controlled by the thickness gauge system, including 150 μm, 300 μm, and 500 μm at the wet slurry. The use of Al-foil on both cathode and anode sides led to low-cost. The obtained electrodes were then dried under vacuum at 110°C for 6 hours to let water evaporate. Then, the thickness electrode was tested at dry state after rolling: 106 μm; 202 μm; 320 μm. The loading mass of three electrodes was 3.68 mg cm$^{-2}$, 7.24 mg cm$^{-2}$ and 12.4 mg cm$^{-2}$. The mass ratio of anode and cathode was 1.5:1; 3:1; 5:1. For cathode, layered-graphite (Alfa Aesar, 325 Mesh, natural graphite 99.8%) was used as intercalation host of PF$_6^-$ anions.

2.2 Characterization

The electrode thickness was mainly controlled by that of control mould to form coated Al-foil. Different proportions of loading masses at anode and cathode electrode were considered by controlling the coating
thickness on Al-foil. The electrodes were dried at 120 °C under vacuum for 6 h to evaporate water. The half-cells (CR 2032) were assembled in a glove box under dry Ar-atmosphere. The electrolyte of PC:EMC (3:7) solvent was employed to obtain high-performance batteries owing to its high conductivity and dielectric constant. The concentration of Li-salt was set to 1.5 M LiPF$_6$. Nitrogen adsorption–desorption isotherms were collected at 77 K on a Quantachrome (Hook, UK) instrument and used for measurements of the specific surface area (SSA) and pore-size distribution at 1–100 nm. The electrochemical characterizations were conducted by galvanostatic charge-discharge testing (LAND 2001 CT battery tester). Cyclic voltammetry (CV) was carried on an electrochemical workstation (CH660E) at different current scan rates. Scanning electron microscopy (SEM) images were obtained on XL-30 microscope (Quanta FEG, FEI, PHILIPS).

3. Results and discussion

In this study, a flower-like FePO$_4$ material was synthesized by the sol-gel and hydrothermal reaction. Owing to the low electronic conductivity of FePO$_4$, such materials can shorten the pathway of electron and ions, and the detailed process was presented in Fig. 1a. The FePO$_4$ was synthesized by mixing FeSO$_4$ with (NH$_4$)$_2$HPO$_4$ and the adding of ascorbic and PEG-400 in microwave reactor. Then, the solution was heated by hydrothermal reaction at 180 °C. At last, the precipitation was calcined at 380 °C for 6 h.
in muffle furnace to obtain well-dispersed FePO$_4$. Note that FePO$_4$ can be used as precursor for synthesis of LiFePO$_4$ with extremely low cost and simple synthesis procedure. The schematic of this material was demonstrated as shown in Fig 1b. It shows a flower-like and strange structure with regular arrangement of petal flake, which is completely different from the previous particle or core-shell material. This special structure can provide many pores and short pathways to fast transfer ions and electrons. Thus, the material includes a larger number of pores in the crimped micro-nanostructure in Fig. 2. And, the pores can absorb the electrolyte in advance and decrease the interface polarization. In such materials, the super-thickness electrode was reached by such special structure owing to the maintaining enough electrolyte value in pores. Fig. 2d show the X-ray diffraction (XRD) pattern of this material. All the peaks of FePO$_4$ structure correspond to the standard characteristic peak of FePO$_4$ [JCPDS19-0721], and it can be seen that the composite material contains the characteristic peak of FePO$_4$, such as 26.5º, 43º, 52º attributing to the phases of (002), (100) (101) (004), respectively. Particle size is mainly distributed between 100 -500 nm, and D50 is about 200 nm. These nanoscale materials can ensure electron and ion transport under coating electrode of high weight, which meets the needs of industrialization.

Figs. 2e and f shows the nitrogen adsorption-desorption curves of prepared FePO$_4$ materials. The curve demonstrates the characteristics of
type-IV and the hysteresis loop of type-H3 under high pressure, thus it indicates that there are two kinds of voids, mesopores and micropores. This is closely related to the flower-like structure of this material. Such materials demonstrate high specific surface area (~186 m² g⁻¹). Fig. 2f shows the cumulative pore volume for the Barrett-Joyner-Halenda (BJH) pore size distribution curves. As we can see that the FePO₄ presents a larger number of micropores and mesopores. There is a wider peak of pore size at 1-100 nm, which comes from the tensile strength of nitrogen desorption. This result again shows that the pore size distribution and expected characteristics are in line with the design characteristics of flower-like structure.
Fig. 1: (a) Schematic of synthesis of flower-like FePO$_4$ materials and (b) the transmission pathway of electron and ions. The special structure ensures the efficient capability under electrochemical process.

Herein, such FePO$_4$ material was used as the anode electrode to show some properties, as shown in Fig. 3a. And, it depicts the charge-discharge curves (intercalation-deintercalation) of FePO$_4$ for anode electrodes with LiPF$_6$ and PC: EMC. The FePO$_4$ material was able to intercalate lithium ions, hence their electrochemical properties as anode electrode in half-cell was measured, and the voltage ranged from 1 V to 3.8 V. The voltage presents a wide platform changes, which is different from the previous curves of LiFePO$_4$ cathode. The main reason is attributed to a similar amorphous phase structure. The FePO$_4$ materials show ideal lithium-storage capability to change to LiFePO$_4$ during charge-transfer process. To improve the stability of FePO$_4$ in full batteries, lower voltage platforms would be mandatory through partial electrochemical reaction of FePO$_4$ anode. Hence, we tailored the cut-off potential of FePO$_4$ anode to studies
the voltage and cycles curves. The charge-discharge curves and cyclic voltammetry profiles of different electrodes are shown in Figs. 3b and c. Three curves exhibit quite different charge capacities and voltage platforms under different voltage windows. In addition, these half-cells were scanned in the voltage ranges of 3.5 V, 3.0 V and 2.5 V, respectively. Similar peaks were noticed, including the reduction peak at 1.8 V and oxidation peak at 2.5 V. When voltage was cut off at 2.5 V, the electrode showed only half peak at 2.5 V indicative of incomplete electrochemical reaction and describing partial lithium insertion-extraction due to real lower voltage platform.
Fig. 2: (a) (b) SEMs, (c) TEM and XRD of flower-like FePO$_4$. (e) (f) the nitrogen adsorption-desorption curves of prepared FePO$_4$ materials.

Cycling was conducted at different voltage ranges and the results are depicted in Fig. 3d. During the different voltage range, the FePO$_4$ shows different reversible capacity and cyclic trend. At the initial stage, the charge capacity was up to 130 mAh g$^{-1}$ due to deep insertion-extraction reaction of anode materials. As electrochemical processes occurred repeatedly, the cycling capacity led to certain fading changes. After 500 cycles, this capacity loss reached 95 mAh g$^{-1}$. At voltage window of 1.0-3.0 V, the specific capacity was recorded at about 100 mAh g$^{-1}$. However, it was relatively stable to obtain reversible capacity of 95 mAh g$^{-1}$ after 500 cycles. For FePO$_4$ electrode, about 71 mAh g$^{-1}$ specific capacity was obtained at 1.0-2.5 V. Thus, the cutoff range of voltage would be associated with partial lithiation reaction of FePO$_4$. After 500 cycles, the capacity became quite stable with loss rate below 2%. For three FePO$_4$ electrode types, the coulombic efficiencies were basically above 96%. Therefore, more stable cycling performance can be obtained by controlling the upper voltage of FePO$_4$ electrode, such as the range of 1.0-2.5 V.
Fig. 3: (a) Charge and discharge curves of FePO$_4$ anode for half-cell. (b) Charge and discharge curves under different voltage window of FePO$_4$. (c) cyclic voltammetry curves of FePO$_4$ electrode at different voltage ranges of 1-2.5 V, 1-3 V, and 1-3.5 V. (d) Cycle performance of different cut-off voltage ranges of FePO$_4$ anodes.

Even if the voltage platform was decreased by the different voltage window, the FePO$_4$ still shows the voltage above 1 V, which limits the application in lithium ion batteries of high energy density owing to the voltage below 4.5 V for cathode electrode. However, as we known, the dual-ion batteries often display the quite voltage window above 5.4 V. Full batteries with high voltage will affect the electrochemical stability and increase the difficulty of electrolyte selection. It is an ideal way to reduce this effect by the anode material of the higher voltage platform. The schematic representation of DIBs is shown in Fig. 4a. Unlike “rocking-chair” of LIBs, the stored energy in DIBs was obtained by inserting anions and cations from the electrolyte on both cathode and anode at the same
time. The ions were then extracted simultaneously into the electrolyte during discharge.

Fig. 4: (a) Schematic representation of DIBs, including cathode of graphite and anode of FePO₄ materials. (b) Charge-discharge curves for graphite cathode. (c) Cyclic voltammetry curves of both electrodes (d) Schematic of super-thickness electrodes by various loading masses (anode coating weight /cathode coating weight, record as m₋/m₊) for DIBs.

Currently, layered graphite is considered as the most ideal materials with the excellent electrochemical performance. For graphite cathodes, previous studies have showed that the layered material can store anions of PF₆⁻ to form C₆(PF₆)ₙ in LiPF₆-based electrolyte. The material demonstrates excellent anion intercalation properties with voltage window above 5.4 V. However, current electrolyte systems are difficult to withstand oxidation decomposition under such voltages, causing lifetime degradation. If the maximum intercalation voltage of cathode electrode is controlled, the specific capacity will be significantly reduced. Thus, the anode of promising voltage platform is critical for the application of DIBs.
The FePO$_4$ can as host to store the dissociated Li-ions from electrolyte, mainly providing an appropriate voltage platform over 1 V (vs Li$^0$/Li$^+$).

**Fig. 4b** represents the electrochemical profile of PF$_6^-$ stored in layered graphite in LiPF$_6$ electrolyte. The reversible deintercalation of PF$_6^-$ anions were attributed to reversible capacity of 125-128 mAh g$^{-1}$ between 3.5-5.45 V. At the high voltage, the current electrolyte almost impossible to endure, such ethylene carbonate (EC), propylene carbonate (PC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC) et al. In previous studies, the ionic liquid was often used to avoid, but the using of materials have to increase cost and decrease the rate performance owing to the high viscosity of ionic liquid. Therefore, the FePO$_4$ material is used as anode to provide a rational design for complete DIBs. **Fig. 4c** display the both cyclic voltammetric (CV) curve of graphite cathode and FePO$_4$ anode at the same time. We can see the maximum voltage of 4.4 V and minimum voltage range of 1 V were shown, when the intercalation and deintercalation simultaneous for anions and caions. Due to elevated electrochemical platform of anode electrodes, the ideal voltage range was obtained to prove the feasibility of such electrochemical system of DIBs.
Fig. 5: (a) Charge-discharge curves and (b) cycling performances of different batteries assembled by various loading masses (anode coating weight /cathode coating weight, record as m⁻/m⁺) for DIBs.

For FePO₄ electrode, we prepared both thicknesses electrode of FePO₄, as shown in Fig. 4d. The excess of coating mass for anode material can achieve lower voltage platform and stable electrochemical performance. Though, super-thickness electrodes were coated by precise controlling of thickness by scraper in Fig. 4d. Three electrodes of different thickness were designed, including the loading mass ratios of anode to cathode (m⁻/m⁺) of: 1.5:1, 3:1 and 5:1.
Fig. 6: Tri-electrode curves of three types of (a) $m:m_+ = 1.5:1$; (b) $m:m_+ = 3:1$; (c) $m:m_+ = 5:1$ batteries assembled by loading mass electrodes in full DIBs: full cell voltage, positive (vs. lithium), and negative (vs. lithium).

In full batteries, the lithium extraction depth of electrodes could be achieved by adjusting loading mass of the active material in both anode and cathode electrodes. In LIBs industrial, the specific capacity of anode is always higher than that of cathode to achieve full using of cathode material and prevent lithium precipitation on anode surface. Three types of full DIBs were assembled with (-) FePO$_4$|graphite (+) at loading mass ratios of anode to cathode ($m_-/m_+$) of: 1.5:1, 3:1 and 5:1, respectively. The charge-discharge curves of full DIBs in voltage range of 1-4.5 V are shown in Fig. 5a. All charging curves showed the same trend but different voltage platforms during changing. The graphite electrode depicted higher lithiation plateau of 5:1 of full batteries. During discharge, the reversible
curves indicated the same differences of voltage, with values of 2.38, 2.61, and 3.04 V in middle capacity, respectively.

Fig. 7: (a) Charge and (b) discharge voltage platform during cycling of three DIBs types assembled with different loading masses. (c) and (d) the EIS curves of DIBs at before and after cycles.

The cycle performances of the electrodes are shown in Fig. 5b. The initial capacities of the three electrodes were estimated to 118.6, 113.2 and 105.4, respectively. Although the early stages looked similar, the characteristics gradually differed. The cycling capacity at m⁻/m⁺ =1.5/1 rapidly decreased after the first 20 cycles, and the last capacity maintained only 85 mAh g⁻¹ after 200 cycles. At the same time, the other electrodes maintained stable cyclic capacity (m⁻/m⁺=3/1 or 5/1). The constant fade rate was estimated to less than 5%. However, the capacity of m⁻/m⁺ = 5/1 electrode decayed rapidly during the initial stage and remained relatively
stable until 75 mAh g$^{-1}$ after 20 cycles. The electrode capacity still showed 68 mAh g$^{-1}$ after 200 cycles. The cyclic curves also display the stability for both samples of 1.5:1, 3:1 but the rapid fading for the 5:1 sample owing to the over thickness of FePO$_4$ electrodes.

The tri-electrode curves of different full-batteries were measured to further study the voltage changes of cathode and anode electrodes. The different electrodes included m-/m+ = 1.5/1, 3/1 and 5/1 (Fig. 6a-c). All three batteries exhibited similar charge-discharge voltage windows for the positive (vs reference electrode). The cut-off voltage of the positive electrode reached 5.52 V at mass ratio of m-/m+ = 5/1, as well as 5.45 V and 5.48 V at m-/m+ = 1.5/1 and 3/1 electrodes, respectively. The reason was attributed to insufficient amount of active materials and same specific capacity. The charge-discharge curves of the anode (vs reference electrode) appeared obviously different for these three curves. This was mainly due to different ratios employed in the three electrodes. Excess active material in full batteries might lead to partial lithium insertion, and increase in FePO$_4$ ratio relative to the cathode would rapidly decline voltage platform of the anode. Lower charging voltage platform of the anode (vs reference electrode) during discharge was also observed in full batteries, and higher voltage plateaus of full batteries were obtained in Fig. 6c.
Fig. 8: (a) Cycling performances of full batteries. (b) Charge-discharge curves at different cycles (1, 5, 50, 100, and 500 cycles) and (c) different rate cycling.

To further analyze the voltage platforms, the charge-discharge processes of three electrode types in full batteries were recorded and the results are displayed in Fig. 7a, b. The voltage platform of cathode/anode electrode (solid point) depicted certain difference. The electrode with elevated loading mass presented higher voltage platform, consistent with results of Fig. 6a-c. During cycling, the voltages platform values increased for all three batteries. Meanwhile, the battery voltage with low loading mass rose significantly according to loading mass, and voltage maintained relatively stable value. Comparison of full batteries revealed that voltage platforms of anode-reference electrode followed an opposite trend. The higher loading mass showed more stable voltage value. The reason for this
might have to do with the better reversibility of lithiation at electrodes with high loading mass owing to partial lithium intercalation. Moreover, the depth of lithium intercalation of a-FePO$_4$ anode reduced capacity retention ratio of the batteries. In Fig. 7b, the variation trend of discharge voltage platform remained similar to that of charging voltage. The enhancement in loading mass of anode could not only improve cycling performance of materials but also ensure batteries with high discharge voltages and elevated energy densities. The electrochemical impedance spectroscopy (EIS) was conducted to verify the changes at interface of electrode for DIBs in Fig. 7c and 7d. The electrode (m$_a$/m$_t$=1.5/1) shows more stable interface impedance in relative to another electrodes (3:1 and 5:1). And, the changes of electrode (3/1) can be also accepted owing to without obvious increasing of impedance. This reason is attributed to the excellent structure of flower-like to ensure enough pathway of electron and ions.

Based on batteries with different loading masses, the best ratio of anode:cathode was determined as 3:1. Fig. 8a exhibits the cycling performances of full batteries (-) FePO$_4$ || graphite (+). The batteries delivered charge capacity of 115 mAh g$^{-1}$ and discharge capacity of 105 mAh g$^{-1}$ during the starting stage. The coulombic efficiency reached only 91.3 %, and may be attributed to irreversible anion intercalation into layered graphite material (C→ C (PF$_6$)$_n$). In addition, the discharge capacity slightly increased during the 10 first cycles, and CE increased to
about 96%. This suggested that irreversible anion in intercalation compounds can be extracted into the electrolyte. During following cycles, the charge and discharge capacities remained stable without obvious decrease. After 500 cycles, high capacity still can be to obtain above 100 mAh g\(^{-1}\) with CE around 96%. The charge-discharge curves at different cycles (1, 5, 50, 100, and 500 cycles) are presented in Fig. 8b, corresponding to cycling of Fig. 7a. The capacity kept stable and charge capacity slightly reduced. The voltage plateau decreased from 1 to 500 cycles. A plateau at about 3 V appeared with obvious depression from 3 V (1 cycle) to 2.9 V (500 cycles). Over 0.1 V voltage platform fade was reflected in electrochemical performances after cycling. The voltage changes obtained during charging were larger than those recorded during discharge. This was attributed to high resistance of anion intercalation in layered-graphite. However, the capacity was not affected owing to the relatively wider charge-discharge voltage window. Fig. 8c gathers the rate capacities of full batteries under different current densities of 50, 100, 200, 500, 1000, and back to 50 mA g\(^{-1}\). The specific capacity was kept ideal under higher current densities. The capacity retention reached 92%, 88%, 84% and 76% at 100, 200, 500 and 1000 cycles, respectively. Note that the value of 50 mA g\(^{-1}\) at starting stage, and showed remarkable recovery after 50 cycles.
4. Conclusions

Based on graphite cathode, the dual-ion batteries exhibit excellent advantages in terms of high-safety and low-cost for next generation energy storage devices. However, the electrolyte is difficult to withstand oxidative decomposition above 5 V. Here, a new flower-like FePO$_4$ anode was proposed by pairing graphite-based DIBs. As precursor of LiFePO$_4$ material, FePO$_4$ showed obvious advantages in terms of structural stability and low cost, and exhibited an extended electrochemical window of 1-3.5 V. In full batteries, suitable voltage window was obtained owing to the wide 1-3.5 V voltage range. For further improving full batteries voltages, different loading mass ratios of anode/cathode were explored and 3 V was determined as best value. In addition, the electrolyte of PC-EMC solvent was selected. Overall, these findings look promising for industrial application of DIBs with low-cost and high energy density.

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