

Synthesis and electrochemical properties of K-doped LiFePO_4/C composite as cathode material for lithium-ion batteries

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Abstract $\text{Li}_{1-x}\text{K}_x\text{FePO}_4/\text{C}$ ($x=0, 0.03, 0.05, \text{ and } 0.07$) composites were synthesized at 700°C in an argon atmosphere by carbon thermal reduction method. Based on X-ray diffraction, scanning electron microscopy, and transmission electron microscopy analysis, the composite was ultrafine sphere-like particles with $100\text{--}300\text{ nm}$ size, and the lattice structure of LiFePO_4 was not destroyed by K doping, while the lattice volume was enlarged. The electrochemical properties were investigated by four-point probe conductivity measurements, galvanostatic charge and discharge tests, cyclic voltammetry and electrochemical impedance spectroscopy. The results indicated that the capacity performance at high rate and cyclic stability were improved by doping an appropriate amount of K, which might be ascribed to the fact that the doped K ion expands Li ion diffusion pathway. Among the doped materials, the $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$ samples exhibited the best electrochemical activity, with the initial discharge capacity of 153.7 mAh g^{-1} at 0.1 C and the capacity retention rate of about 92% after 50 cycles at above 1 C , 11% higher than undoped sample. Remarkably, it still showed good cycle retention at a high current rate of 10 C .

Keywords LiFePO_4 · K-doped · Lithium-ion batteries

Introduction

LiFePO_4 is an attractive positive electrode material for lithium-ion batteries because of its low cost, non-toxicity,

large theoretical capacity (170 mAh g^{-1}) and high safety, especially thermal stability at high temperature [1–3]. Recently, the LiFePO_4 -based battery attracts attention as a power source for electric powered vehicles (EVs) and hybrid electric vehicles (HEVs) owing to its many advantages described above. However, one of the key challenges of the lithium-ion battery with LiFePO_4 to power the EV/HEV is its poor high-rate performance due to its low electronic and ionic conductivity, which cannot finish the charging process in short time and cannot meet the peak power demands for vehicular applications such as starting, accelerating, and uphill driving [4–6].

Several methods have been reported to improve its electrochemical performance, including surface coating [7, 8], minimizing the particle size [9, 10], and lattice doping [11, 12]. The last one is one of the effective approaches to improve the high-rate performance of the LiFePO_4 material. The suitable element is introduced into lattice and alternates the gap between the conduction band and valence band by changing the structure of energy gap [13], which will expand lithium ion diffusion pathway so that lithium ion can intercalate/de-intercalate easily at high current rates. Our group [14] has investigated the effects of Na doping on the electrochemical properties of LiFePO_4/C cathode material and found that the lithium ion diffusion pathway was expanded, and its electronic conductive and electrochemical performance were both improved comparing with high valance metal ions doping (such as Cr) and pure LiFePO_4 . However, Na-doped LiFePO_4/C has poor capacity retention at high rate [14]. Na and K have similar properties considering that they are located in the same main group of the periodic table of elements. Besides K ion has larger radius than Na ion. As discussed above, it's expected that K ion could be doped into the lattice of LiFePO_4 to expand diffusion pathway and provide larger space for lithium ion

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intercalation/de-intercalation, which may further improve the high-rate electrochemical activity of LiFePO_4/C .

In this paper, the K-doped LiFePO_4/C cathode material was prepared by carbon thermal reduction method. The effects of the doping amount of K on the electrochemical properties of LiFePO_4/C cathode material were investigated.

Experimental

The starting materials for synthesizing the $\text{FePO}_4/\text{polyaniline}$ (PANI) composite were $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, and aniline. In a typical synthesis, 100 mL distilled water solution containing 0.025 mol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was slowly added to 200 mL of solution containing 0.025 mol $\text{NH}_4\text{H}_2\text{PO}_4$ and 1 mL of aniline under stirring. The pH of the solution was adjusted to 2.1 by adding ammonia. The reaction mixture was ultrasonic heated for 2 h, then stirred for 8 h at room temperature. The $\text{FePO}_4/\text{PANI}$ composite was filtered and washed several times with distilled water, followed by drying in vacuum at 60 °C for 24 h. The $\text{Li}_{1-x}\text{K}_x\text{FePO}_4/\text{C}$ ($x=0, 0.03, 0.05, \text{ and } 0.07$) composites were synthesized from the prepared $\text{FePO}_4/\text{PANI}$ composite by mixing with an equimolar amount of CH_3COOLi (with respect to the amount of FePO_4 in the prepared composite), a certain amount of KNO_3 and some glucose. After mixing uniformly, the precursors were heated at 350 °C for 5 h in argon atmosphere. The precursors were then ball-milling for 6 h and finally calcined at 700 °C for 10 h in argon atmosphere to obtain the LiFePO_4/C composite.

X-ray diffraction of the product was carried on a Rigaku D/max2550VB⁺ 18 kW using graphite-monochromatized $\text{Cu K}\alpha$ radiation (40 kV, 250 mA). The morphology of the as-prepared K-doped LiFePO_4 powder was observed by a JEM-2010 transmission electron microscopy (TEM) and a JSM-6360-LV scanning electron microscopy (SEM) equipped with an energy dispersive spectrometer (EDS), respectively. The content of carbon was determined by C-S 800 infrared carbon sulfur analyzer. Electronic conductivity measurements were carried out by four-point probe method using a RTS-9 Digital Instrument.

The composite cathodes were made by dispersing 80 wt.% active material, 10 wt.% acetylene black, and 10 wt.% polyvinylidene fluoride to form a slurry. The slurry was coated onto an Al foil then pressed at 15 MPa and dried at 110 °C for 12 h in a vacuum oven. The CR2016 coin cells were assembled in an argon-filled glove box (Mbraun, Unilab, Germany) with a lithium foil as the counter electrode. The electrolyte was 1 M LiPF_6 in ethylene carbonate + dimethyl carbonate + diethyl carbonate (volume ratio of 1:1:1). The cells were galvanostatically charged and discharged between 2.5 and 4.2 V at 25 °C on the electrochemical test instrument (CT2001A, Wuhan Land Electronic Co. Ltd., China). Cyclic

voltammetry measurements were performed using electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China) at a scan rate of 0.1 mV s^{-1} between 2.5 and 4.2 V. Electrochemical impedance spectroscopy (EIS) was performed with a ZAHNER-IM6 electrochemical workstation (Germany). The sinusoidal excitation voltage applied to the cells was 5 mV with a frequency range of between 0.01 Hz and 100 kHz. All potentials are cited in this paper with respect to the reference Li^+/Li .

Results and discussion

Physical property and morphology

XRD patterns of $\text{Li}_{1-x}\text{K}_x\text{FePO}_4/\text{C}$ powders with different K-doped contents ($x=0, 0.03, 0.05, \text{ and } 0.07$) are shown in Fig. 1. The samples with K-doped contents ($x=0, 0.03$) can be indexed to an ordered olivine structure (space group *Pnma*). However, when the doping amount is too high, some impurity Fe_2P peak (mark with stars) are observed in $\text{Li}_{1-x}\text{K}_x\text{FePO}_4/\text{C}$ ($x=0.05, 0.07$) powders. And there is no evidence for the formation of crystalline or amorphous carbons. A small amount of doped K does not destruct the lattice structure of LiFePO_4 . The doping of K would be inclined to occupy Li sites because the phase of KFePO_4 is structurally analogous to LiFePO_4 and that K and Li atoms have the same outer electronic structure. The lattice parameters of all the samples calculated from the XRD patterns based on the *Pnma* space group are summarized in Table 1. The lattice parameters *b*, *c*, and *V* of the $\text{Li}_{1-x}\text{K}_x\text{FePO}_4/\text{C}$ ($x=0.03, 0.05, \text{ and } 0.07$) samples are larger than those of the LiFePO_4/C sample, which may be due to K ion ($r=1.31 \text{ \AA}$) with larger radius than that of Li ion ($r=0.68 \text{ \AA}$) occupying

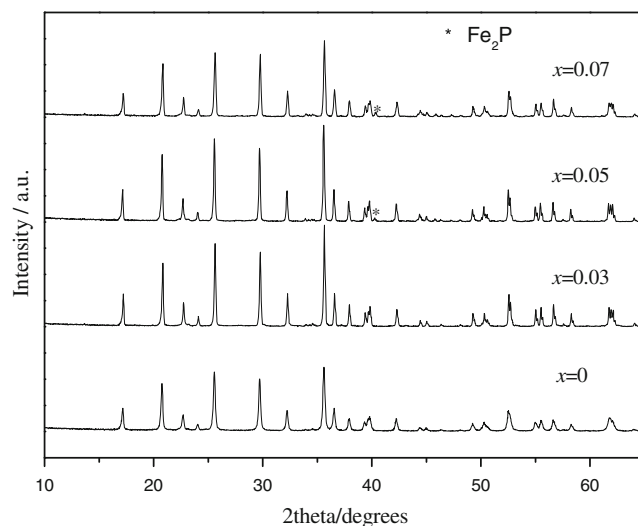


Fig. 1 XRD patterns of $\text{Li}_{1-x}\text{K}_x\text{FePO}_4/\text{C}$ ($x=0, 0.03, 0.05, \text{ and } 0.07$)

Table 1 Lattice parameters of $\text{Li}_{1-x}\text{K}_x\text{FePO}_4/\text{C}$

Sample	a (Å)	b (Å)	c (Å)	V (Å ³)
LiFePO ₄ /C	6.00809	10.32033	4.68929	290.76164
Li _{0.97} K _{0.03} FePO ₄ /C	6.00415	10.37329	4.69707	292.54662
Li _{0.95} K _{0.05} FePO ₄ /C	6.00764	10.35595	4.69297	291.97228
Li _{0.93} K _{0.07} FePO ₄ /C	6.00985	10.34612	4.68947	291.58482

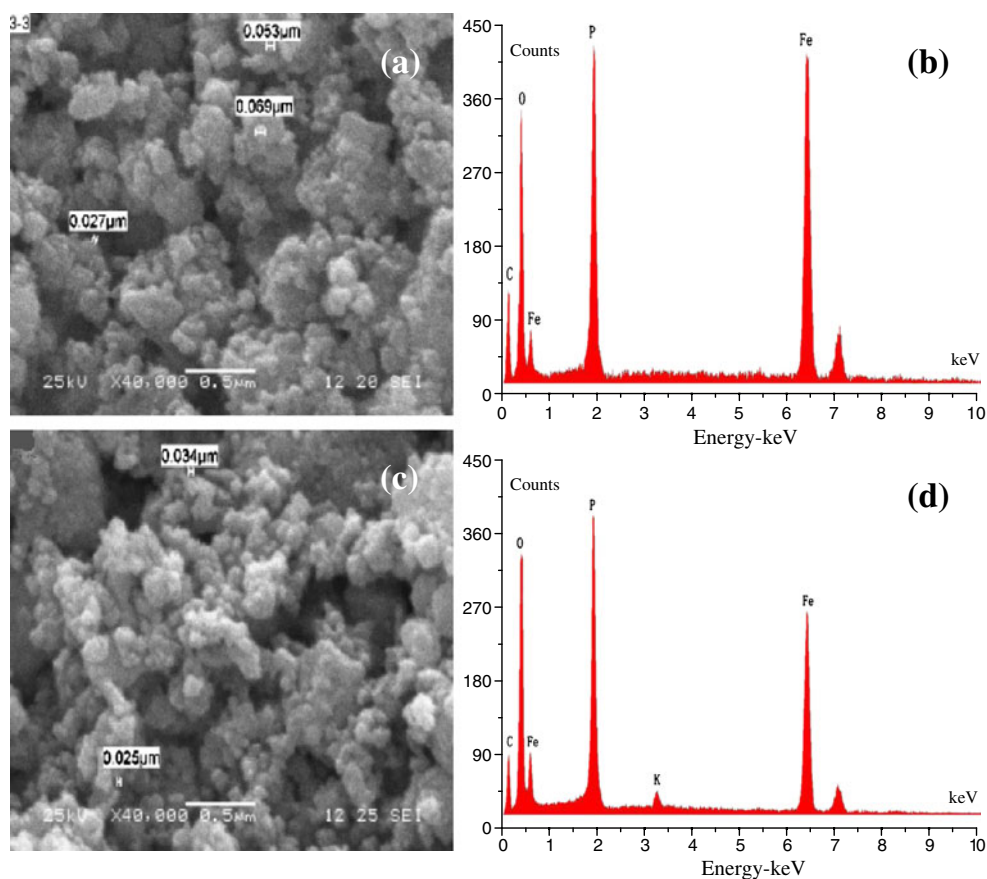
Li sites. The expansion in lattice crystal could provide more space for lithium ion intercalation/de-intercalation [15]. The lattice parameters b , c , and V of the $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$ sample are the largest among all the samples. The ratio of the lattice parameters V of $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$ against LiFePO_4/C is 1.006, which is larger than 1.004 in the Na-doped LiFePO_4/C case [14]. It demonstrates that the effect of K ion on expanding lithium ion diffusion pathway is more obvious than that of Na ion, which is agreement with larger radius of K ion [16]. While the lattice parameters a of the $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$ sample is the least, which shortens the diffusion distance of lithium ion and enhances lithium ion intercalation/de-intercalation [17].

SEM images of LiFePO_4/C (Fig. 2a) and $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$ (Fig. 2c) are shown in Fig. 2. The formation of small and nearly spherical primary particles can be observed, while

some particles agglomerated to form larger secondary particles with sizes varying in the range 100–300 nm. And the two samples have the similar particle size, indicating no influence on morphology with the K doping. However, the comparison of the EDS map of $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$ (Fig. 2d) and LiFePO_4/C (Fig. 2b) unambiguously confirm that the $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$ sample contain Fe, P, O, and C components with a trace of K, while the other does not.

Figure 3 shows the TEM image of the $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$. It can be seen that nano-carbons (marked primary particles by arrows) are wrapping and connecting particles, thereby resulting in increasing the surface electronic conductivity of LiFePO_4 crystallites and ensuring a good electric connection between the crystallites. The electronic conductivity of $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$ and undoped LiFePO_4/C are 1.01×10^{-2} and $7.28 \times 10^{-3} \text{ S cm}^{-1}$, respectively, which is measured by four-point probe method. The electronic conductivity is increased by the doped K ions in the crystal which may be attributed to the aberrance of the crystal structure [13]. Furthermore, the amount of residual carbon in $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$ and undoped LiFePO_4/C are 3.44 and 3.52 wt.%, respectively, which is measured by C-S 800 infrared carbon sulfur analyzer. It indicated that the effect of carbon coating on the electronic conductivity of the both samples could be

Fig. 2 SEM images of LiFePO_4/C (a) and $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$ (c) with corresponding EDS map (b and d)



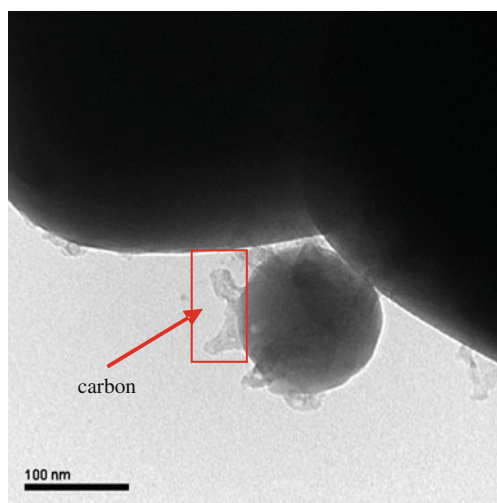


Fig. 3 TEM image of $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$

deemed to be equivalent. Compared to the sample without doping K, the larger electronic conductivity of the sample $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$ is attributed to the effect of doping K.

Electrochemical properties

Figure 4 demonstrates the initial charge/discharge curves of the $\text{Li}_{1-x}\text{K}_x\text{FePO}_4/\text{C}$ ($x=0, 0.03, 0.05, \text{ and } 0.07$) samples at 0.1 C rate between cutoff voltage 2.5 and 4.2 V. A flat and long voltage curve around 3.4 V profile indicates that the extraction and the insertion reactions of lithium ion proceed via a first-order transition between FePO_4 and LiFePO_4 [1]. The initial special discharge capacities for $\text{Li}_{1-x}\text{K}_x\text{FePO}_4/\text{C}$ samples ($x=0, 0.03, 0.05, \text{ and } 0.07$) are 158.8, 153.7, 143.7, and 139.3 mAh g^{-1} , respectively. As the K content increased, the first irreversible capacities gradually become

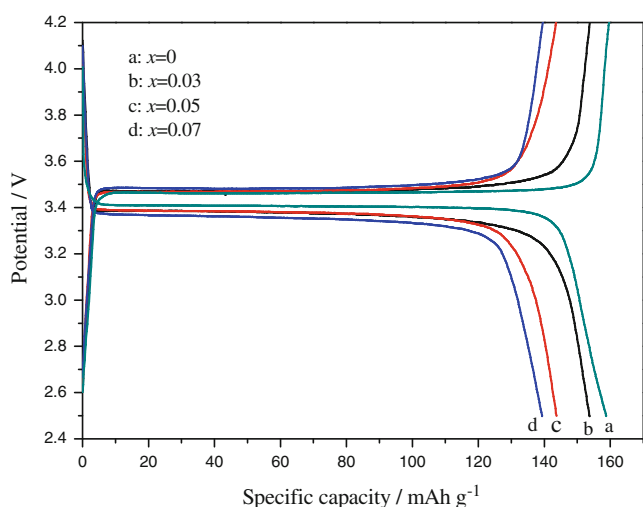


Fig. 4 Initial charge and discharge curves of $\text{Li}_{1-x}\text{K}_x\text{FePO}_4/\text{C}$ ($x=0, 0.03, 0.05, \text{ and } 0.07$) electrodes at 0.1 C

smaller due to the partial substitution of Li ion with non-active K ion [18].

Figure 5 shows the variation of the specific discharge capacity with the number of cycles. The charge/discharge current density is relatively high at the 1 C rate with a cutoff voltage of 2.5–4.2 V. The cycling retention rate of $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$ after 50 cycles is about 97% of its maximum capacity, whereas the retention rate of LiFePO_4/C is 81%. The capacity fading of the LiFePO_4/C is attributed to the slow diffusion of lithium ion and the large polarization. On the contrary, the K-doped LiFePO_4/C materials improve capacity retention without significant capacity fading. During the process of lithium ion de-intercalation, the Fe^{2+} (0.074 nm) changes to the Fe^{3+} (0.064 nm) with smaller radius which limited diffusion of lithium ions [19]. The doping K occupies Li sites and acts as a pillar to facilitate the lithium ion diffusion [19, 20]. Therefore, the improvement in cycle performance is realized by doping an appropriate amount of K.

As shown above, the $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$ sample exhibits the best electrochemical performance among the prepared $\text{Li}_{1-x}\text{K}_x\text{FePO}_4/\text{C}$ ($x=0, 0.03, 0.05, \text{ and } 0.07$) powders. Figure 6 presents the initial discharge capability of $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$ cathode materials at different rate. The $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$ sample exhibits discharge capacity of 153.7, 147.6, 141.7, 131.5, 125.2, 97, and 76.4 mAh g^{-1} as it is discharged at 0.1, 0.5, 1, 2, 3, 5, and 10 C, respectively. As the current density increases, the discharge capacity decreases due to the polarization of lithium ions diffusion and charge transfer. The cycling performance of LiFePO_4/C and $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$ at various rates is shown in Fig. 7. It is clearly showed that the $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$ presents excellent high-rate performance. Even at the high current rate of 10 C, the cell still presents a discharge

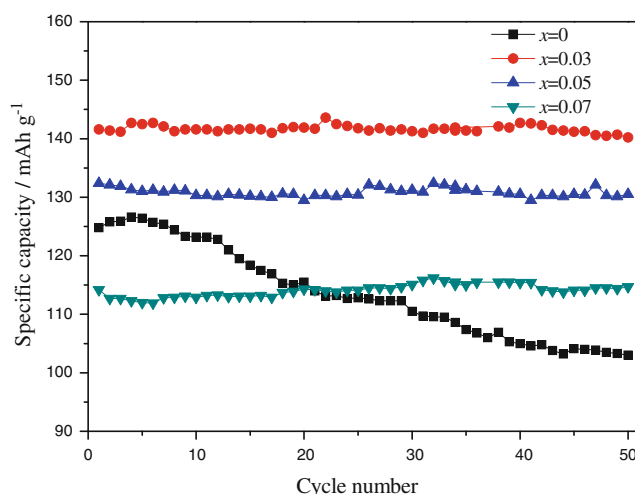


Fig. 5 Cycle performance of $\text{Li}_{1-x}\text{K}_x\text{FePO}_4/\text{C}$ ($x=0, 0.03, 0.05, \text{ and } 0.07$) electrodes at 1 C

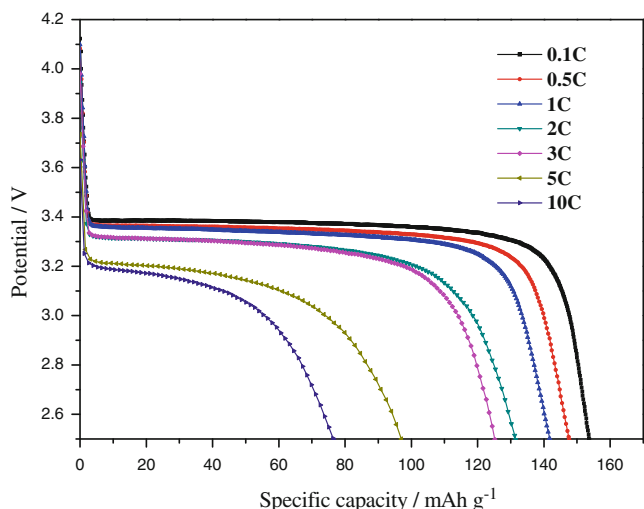


Fig. 6 Initial discharge curves of $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$ electrodes at various rates

capacity of about 70 mAh g^{-1} and exhibits quite good cycle retention. Contrarily, the LiFePO_4/C sample shows a high discharge capacity at 0.1 and 0.5 C. However, the discharge capacity sharply decreases at a rate of above 1 C. On the other hand, when 0.1 C is applied again, the discharge specific capacity of all samples recovers completely, inferring that their structures have not been broken. Thence, the capacity loss for bare LiFePO_4/C at higher charge/discharge rate is mainly caused by the low diffusion rate of lithium ions and stronger polarization [21, 22].

The different behaviors between LiFePO_4/C and $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$ are obviously associated with K doping. The doping K occupies Li sites, which decreasing lithium content. So LiFePO_4/C has a higher discharge capacity than $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$ at 0.1 and 0.5 C. The higher discharge capacity and more stable cycle life of the $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$

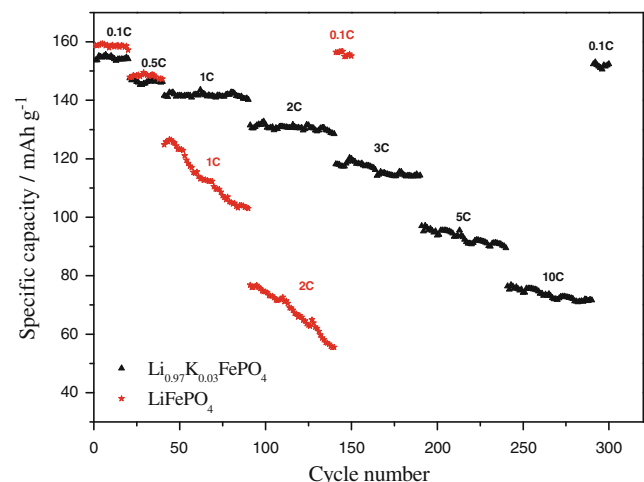


Fig. 7 Cycling performance of LiFePO_4/C and $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$ electrodes at various rates

sample at high rate are ascribed to the doping K ion to expand Li ion diffusion pathway. These results suggest that the K ions might be played a pillar in structure, which provides larger space for the movement of lithium ion. The results indicate that K-doped sample exhibits excellent high-rate electrochemical performance which may be attributed to the aberrance of the crystal structure caused by the doped K ions in the crystal.

Figure 8 shows the cyclic voltammograms (CV) curves of $\text{Li}_{1-x}\text{K}_x\text{FePO}_4/\text{C}$ samples at a scan rate of 0.1 mV s^{-1} . Each of the CV consists of an oxidation peak and a reduction peak, corresponding to the charge–discharge reaction of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple. In the CV profiles, higher peak current means better electrode reaction kinetics and consequently better rate performance of the LiFePO_4 cathode material. The $\text{Li}_{0.97}\text{K}_{0.03}\text{FePO}_4/\text{C}$ sample shows the best electrochemical behavior among all the samples, with the highest peak current and the narrowest potential margin between the anodic current peak (3.6 V) and the cathodic current peak (3.26 V). The voltage difference between oxidation and reduction potential is 0.34 V, which is the smallest among all of them. The larger voltage difference, well-defined peaks, and narrower peak separation suggest that the reversibility of the electrode reaction is improved by doping an appropriate amount of K.

In order to gain additional supporting evidence, electrochemical impedance spectroscopy was measured in the fully discharged state. Figure 9a show the Nyquist plots of $\text{Li}_{1-x}\text{K}_x\text{FePO}_4/\text{C}$ ($x=0, 0.03$) samples at an ambient temperature. Both profiles exhibit a semicircle in the high frequency region and a straight line in the low-frequency region. An intercept at the Z' axis at high frequency corresponds to the ohmic resistance (R_c), which represents the resistance of the electrolyte and electrode. The

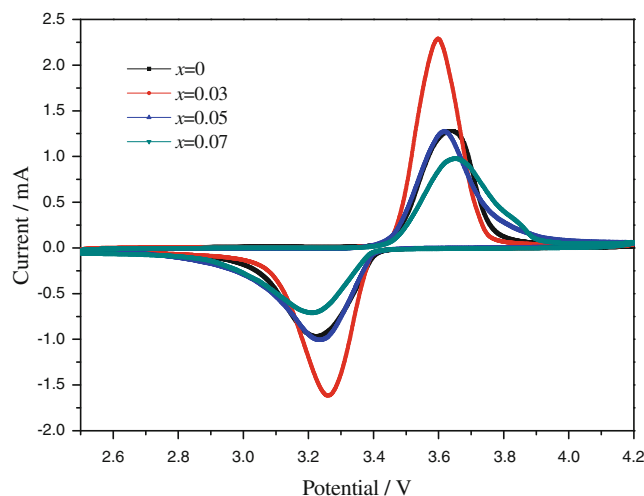


Fig. 8 Cyclic voltammograms of lithium cells with $\text{Li}_{1-x}\text{K}_x\text{FePO}_4/\text{C}$ composite, the second cycle at a scanning rate of 0.1 mV s^{-1}

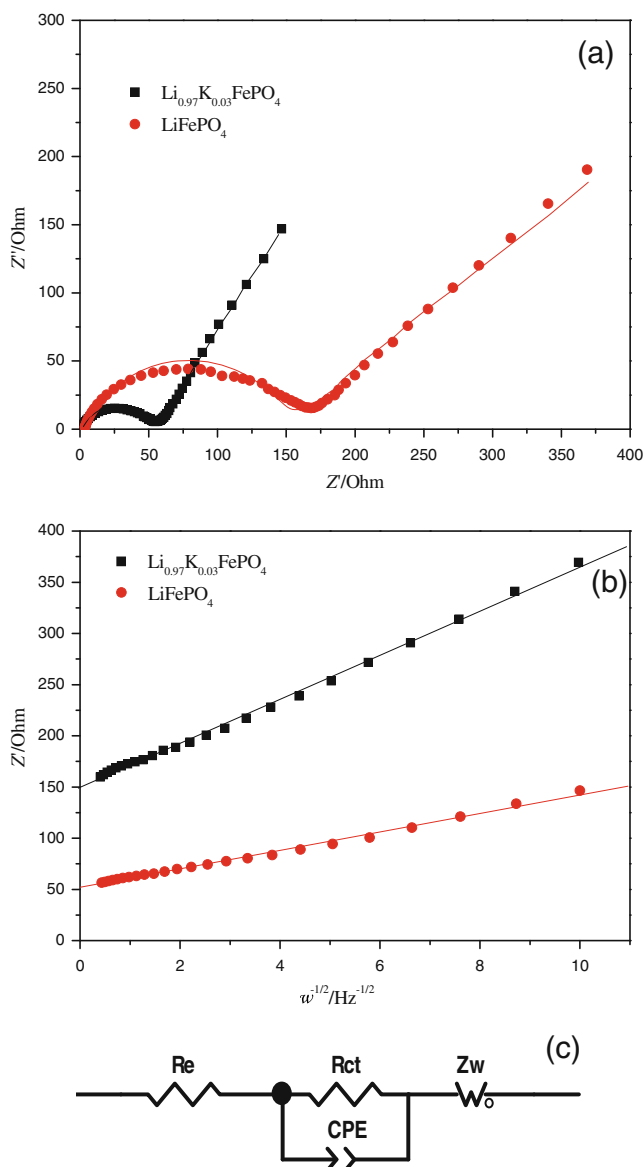


Fig. 9 EIS spectra of LiFePO₄/C and Li_{0.97}K_{0.03}FePO₄/C cathodes (a), the relationship between Z' and square root of frequency ($\omega^{-1/2}$) in the low-frequency region (b), and equivalent circuit used for fitting the experimental EIS data (c)

semicircle in the middle frequency range indicates the charge transfer resistance (R_{ct}). The straight line in low-frequency range is attributed to the diffusion of the lithium ions into the bulk of the electrode material or so-called Warburg impedance (Z_w). The lithium ion diffusion coefficients (D) of LiFePO₄/C and Li_{0.97}K_{0.03}FePO₄/C are calculated according to the following equation [23]:

$$D = R^2 T^2 / 2A^2 n^4 F^4 C^2 \sigma^2 \quad (1)$$

where R is the gas constant, T is the absolute temperature, A is the surface area of the cathode, n is the number of electrons per molecule during oxidization, F is the Faraday

constant, C is the concentration of lithium ion, and σ is the Warburg factor which has relationship with Z' :

$$Z' = R_D + R_L + \sigma \omega^{-1/2} \quad (2)$$

Figure 9b shows the relationship between Z' and square root of frequency ($\omega^{-1/2}$) in the low-frequency region. The diffusion coefficient of lithium ion is calculated based on Eqs. 1 and 2. The calculated lithium ion diffusion coefficients of LiFePO₄/C and Li_{0.97}K_{0.03}FePO₄/C are 1.20×10^{-16} and 1.14×10^{-15} cm² s⁻¹, respectively. The lithium ion diffusion coefficient is increased slightly by doping due to the pillar effect in the crystal lattice [24]. Interpretation of the impedance spectra is based on the equivalent circuit in Fig. 9c. A constant phase element CPE is placed to represent the double layer capacitance and passivation film capacitance. The charge transfer resistance (R_{ct}) of LiFePO₄/C and Li_{0.97}K_{0.03}FePO₄/C composite are 148 and 51 Ω, respectively. The charge transfer resistance (R_{ct}) is considered as Li ion transfer reaction. The charge transfer reaction is related to complex reaction process of charge transfer between the electrolyte and the active materials. The charge transfer resistance (R_{ct}) decreases due to that doping K ions expands the Li ion diffusion pathway, which can enhance the migration of Li ion at the electrode/electrolyte interface and transportation of electrons [15]. It is obvious that the lithium ion diffusion coefficient drastically increases, and the charge transfer resistance (R_{ct}) decreases when doping of a certain amount of K⁺ and therefore enhances the electrochemical activity of LiFePO₄/C composite, and this is consistent with the results in Figs. 7 and 8.

Conclusions

Olivine-type Li_{1-x}K_xFePO₄/C ($x=0, 0.03, 0.05, \text{ and } 0.07$) samples were successfully synthesized at 700 °C by carbon thermal reduction method. XRD analysis showed that no other impurities were detected in LiFePO₄/C and Li_{0.97}K_{0.03}FePO₄/C, while an impurity phase of Fe₂P existed in Li_{0.95}K_{0.05}FePO₄/C and Li_{0.93}K_{0.07}FePO₄/C. Among all the samples, the Li_{0.97}K_{0.03}FePO₄/C showed the highest discharge capacities at high-rate and stable cycle performance, which might be attributed to the fact that the doping K ion expands the lattice volume and provides more space for lithium ion intercalation/de-intercalation. And its initial discharge capacity was more than 153 mAh g⁻¹ at 0.1 C and 141 mAh g⁻¹ at 1 C. Even at high current density of 10 C, the cell still presented good cycle retention. The electronic conductivity measured by four-point probe was increased by doping an appropriate amount of K. The lithium ion diffusion coefficient and the charge transfer

resistance measured by EIS were increased and decreased by doping an appropriate amount of K. These results clearly expounded the favorable effects of doping an appropriate amount of K. K-doped LiFePO_4/C is of great potential use as cathode material for EV/HEV batteries.

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