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# Cation-substituted LiFePO<sub>4</sub> prepared from the FeSO<sub>4</sub>·7H<sub>2</sub>O waste slag as a potential Li battery cathode material

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# A R T I C L E I N F O

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# ABSTRACT

The purpose of this study is to utilize the huge FeSO<sub>4</sub>·7H<sub>2</sub>O waste slag produced by the titanium dioxide industry. FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O precursors are synthesized at various pH values by using the waste slag and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O as raw materials, and without any purifying process. ICP analysis confirms that the impurity content of FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O increases with the pH value. Crystalline cation-substituted LiFePO<sub>4</sub> are prepared from the FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O precursors. The cation dopants do not obviously change the structure of LiFePO<sub>4</sub>, and all the samples are single olivine-type phase and well crystallized. The lattice parameters of LiFePO<sub>4</sub> decrease with the increased dopants contents. The dopants limit the size of LiFePO<sub>4</sub> nanocrystals, LiFePO<sub>4</sub> particles agglomeration and, consequently, improve the electrochemical performance of LiFePO<sub>4</sub>. The cation-substituted LiFePO<sub>4</sub> at high current rates. The optimal pH value for synthesizing FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O from the waste slag is about 1.0, with 96.6% iron recovery. The cation-substituted LiFePO<sub>4</sub> prepared from this precursor exhibits the best electrochemical properties, which delivers a capacity of 152, 142 and 126 mAh g<sup>-1</sup> at 1C, 2C and 5C rate, respectively, and shows excellent cycling performance.

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# 1. Introduction

Titanium dioxide is widely used in the manufacture of paints, paper, varnishes, lacquer, printing inks, rubber, ceramics, food, etc. Titanium dioxide pigment is commercially manufactured by two main processes, namely the sulfate and the chloride processes. The sulfate process still produces about 50% of global production [1]. However, large quantity of FeSO<sub>4</sub>.7H<sub>2</sub>O waste slag is produced in the sulfate route, for example, to produce 1 tonne pigment from ilmenite (containing TiO<sub>2</sub>  $\sim$ 48 wt.%, FeO  $\sim$ 33 wt.%, Fe<sub>2</sub>O<sub>3</sub>  $\sim$ 6 wt.% and MgO ~6 wt.%), about 3 tonnes FeSO<sub>4</sub>·7H<sub>2</sub>O waste slag would be produced [2]. In China, about 0.6 million tonnes of TiO<sub>2</sub> pigment is manufactured each year, of which more than 90% are operated with the sulfate route [3]. According to this, it can be estimated that more than 1.62 million tonnes FeSO<sub>4</sub>·7H<sub>2</sub>O waste slag would be produced each year. Unfortunately, this waste slag is less marketable and difficult to be utilized because of its high impurity content (a typical chemical composition is shown in Table 1), which causes not only severe environmental problems but also the waste of iron resource. Therefore, the urgent need for proper utilization of waste slag has attracted great attention of the world.

The common methods for utilization of the waste slag are preparing iron oxide series productions, such as magnetic iron oxide [4], iron oxide red [5], iron oxide yellow [6], iron oxide black [7]. However, these methods are usually complicated and consist of many purifying processes, due to various impurities (i.e., Mg, Mn, Ca, Al, Ti, etc.) which are harmful to the performance of the materials. Apart from these methods, little work has been performed to utilize the FeSO<sub>4</sub>·7H<sub>2</sub>O waste slag. Therefore, a simple and effective way to utilize the waste slag should be researched urgently.

In the present study, we propose a novel, simple, low cost and effective method to utilize the waste slag. In this method, oxalic acid was selected as a precipitator and added to the solution of  $FeSO_4 \cdot 7H_2O$  waste slag. By controlling the pH value, metallic ions were precipitated selectively due to the various solubility products of metallic oxalates, then  $FeC_2O_4 \cdot 2H_2O$  with small amounts of metallic impurities (i.e., Mg, Mn, Ca and Ti) was obtained. Finally, cation-substituted LiFePO<sub>4</sub> was prepared with the as-synthesized  $FeC_2O_4 \cdot 2H_2O$  as raw material. The whole route requires no further purification, owing to some impurities (Mg, Mn and Ti, for example) could benefit the electrochemical performance of LiFePO<sub>4</sub> [8–15].

# 2. Experimental

# 2.1. Materials and preparation

 $FeC_2O_4\cdot 2H_2O$  was synthesized by a co-precipitation method with the following procedures: (1) FeSO\_4\cdot 7H\_2O waste slag (chemical composition is shown in Table 1) was dissolved in de-ionized water to obtain 0.25 M (Fe) solution, and the solution

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#### Table 1

A typical chemical composition (wt.%) of FeSO<sub>4</sub>·7H<sub>2</sub>O waste slag.

FeSO <sub>4</sub> ·7H <sub>2</sub> O	MgSO <sub>4</sub> ·7H <sub>2</sub> O	MnSO <sub>4</sub> ·5H <sub>2</sub> O	$Al_2(SO_4)_3 \cdot 18H_2O$
88.52	6.04	0.35	0.28
CaSO <sub>4</sub> ·2H <sub>2</sub> O	TiOSO <sub>4</sub>	Water insoluble	Others
0.18	0.52	3.83	0.28

#### Table 2

The initial metallic ions concentration ( $[M^{n+}]_0$ , mol L<sup>-1</sup>), solubility-product constant  $K_{sp}$  and theoretic initial precipitation pH values of the corresponding poorly soluble metallic oxalate and metallic hydroxide.

Precipitate	K <sub>sp</sub>	$[\mathbb{M}^{n^+}]_0$	Initial precipitation pH
FeC <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O	$3.2 \times 10^{-7}$ [16]	0.25	0.042
MgC <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O	$4.8 \times 10^{-6}$ [17]	0.0192	1.187
MnC <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O	1.7 × 10 <sup>-7</sup> [17]	0.0011	1.083
$CaC_2O_4 \cdot H_2O$	$4.0 \times 10^{-9}$ [16]	0.0008	0.337
Fe(OH) <sub>2</sub>	8.0 × 10 <sup>-16</sup> [16]	0.25	7.979
Mg(OH) <sub>2</sub> [fresh]	6.0 × 10 <sup>-10</sup> [16]	0.0192	7.763
Mn(OH) <sub>2</sub>	$1.9 \times 10^{-13}$ [16]	0.0011	7.288
Al(OH)3 [Al3+, 3OH-]	$1.3 \times 10^{-33}$ [16]	0.0007	2.014
Ca(OH) <sub>2</sub>	$5.5 \times 10^{-6}$ [16]	0.0008	8.244
TiO(OH) <sub>2</sub>	1.0 × 10 <sup>-29</sup> [16]	0.0026	2.905

was filtered to separate the water-insoluble; (2)  $H_2C_2O_4 \cdot 2H_2O$  was added to the solution under vigorous stirring, a yellow color precipitate formed immediately; (3) then  $NH_3 \cdot H_2O$  (2 M) was dropped slowly into the solution to control the pH at different values (i.e., 0.3, 0.7, 1.0 and 1.3, respectively). (4) After being stirred for 30 min, the precipitates were filtered, washed three times with de-ionized water and dried at  $80 \,^{\circ}C$  for 12 h in an oven, and labeled as  $A_0$ ,  $B_0$ ,  $C_0$  and  $D_0$ , according to the different pH values of 0.3, 0.7, 1.0 and 1.3, respectively.

Cation-substituted LiFePO<sub>4</sub> was synthesized by a mechanical activation process followed by high-temperature calcination. The as-prepared FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, Li<sub>2</sub>CO<sub>3</sub> and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (all chemicals of .99% purity) were weighed in the stoichiometric of LiFePO<sub>4</sub>. The ingredients were dispersed in ethanol and ground for 4 h by high energy ball milling (200 rpm) at room temperature. The as-obtained slurries were dried in an oven at 80 °C. Finally the precursors were calcinated in a tubular furnace at 650 °C for 12 h with flowing argon (99.999%) and cooled to room temperature. Thus, cation-substituted LiFePO<sub>4</sub> were obtained and labeled as A, B, C and D according to the different FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O of A<sub>0</sub>, B<sub>0</sub>, C<sub>0</sub> and D<sub>0</sub>, respectively. For comparison, a pure LiFePO<sub>4</sub> sample (labeled as P) was prepared from analytically pure FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O

#### 2.2. Characterization

The metal content of samples was analyzed using inductively coupled plasma emission spectroscopy (ICP, IRIS intrepid XSP, Thermo Electron Corporation). The SEM image and elemental mapping of the particles were observed with scanning electron microscopy (SEM, JEOL, JSM-5600LV). The powder X-ray diffraction (XRD, Rint-2000, Rigaku) using CuK $\alpha$  radiation was employed to identify the crystalline phase of the synthesized materials. XRD Rietveld refinement was performed by FULLPROF.

#### 2.3. Battery preparation and measurement

The electrochemical performance was performed using a two-electrode cointype cell (CR2025) of Li|LiPF<sub>6</sub> (EC:EMC:DMC = 1:1:1 in volume) |LiFePO<sub>4</sub>. The working cathode is composed of 80 wt.% LiFePO<sub>4</sub> powders, 10 wt.% acetylene black as conducting agent, and 10 wt.% poly (vinylidene fluoride) as binder. After being blended in *N*-methyl pyrrolidinone, the mixed slurry was spread uniformly on a thin aluminum foil and dried in vacuum for 12 h at 120 °C. A metal lithium foil was used as anode. Electrodes were punched in the form of 14 mm diameter disks, and the typical positive electrode loadings were in the range of 1.95–2 mg cm<sup>-2</sup>. A polypropylene micro-porous film was used as the separator. The assembly of the cells was carried out in a dry argon-filled glove box. The cells were charged and discharged over a voltage range of 2.5–4.1 V versus Li/Li<sup>+</sup> electrode at room temperature. Electrochemical impedance spectroscopy was carried out with a CHI660 electrochemical analyzer. The impedance spectra were measured at the stable voltage of 2.5 V, and were recorded by applying an AC voltage of 5 mV amplitude in the 1 MHz–0.01 Hz frequency range.

# 3. Results and discussion

# 3.1. FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O precursors identification

The initial metallic ions concentration, solubility-product constant  $K_{sp}$  and theoretic initial precipitation pH of the corresponding poorly soluble metallic oxalate and metallic hydroxide are shown in Table 2. The initial precipitation pH values were calculated by using the Eqs. (1) and (2), respectively, according to the solubility product principle.

$$pH = -lg \sqrt{\frac{K_{a1}K_{a2}[H_2C_2O_4]_0}{K_{sp}/[M^{2+}]_0}}$$
(1)

$$pH = 14 - \sqrt[n]{\frac{\lg K_{sp}}{[M^{n+}]_0}}$$
(2)

where M is the metal elements, *n* is the valent of M,  $K_{a1}$  and  $K_{a2}$  are the first ionization constant and second ionization constant of oxalic acid, respectively,  $[M^{n+}]_0$  is the initial metallic ions concentration, and  $[H_2C_2O_4]_0$  is the initial oxalic acid concentration (0.28 mol L<sup>-1</sup>).

In order to precipitate the metallic ions selectively, we chose the pH values of 0.3, 0.7, 1.0 and 1.3 to prepare the FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O precursors. Table 3 shows the molar ratio of the metal elements in waste slag and FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, and the iron recovery at various pH values. According to the theoretic calculations (Table 2), Mg, Mn, Ca, Al and Ti will not be deposited until the pH reaches 1.187, 1.083, 0.337, 2.014 and 2.905, respectively. However, it can be seen (Table 3) that small amounts of Mg, Mn and Ti are detected below their theoretic precipitation pH values. For example, Mg are detected in all the samples, nevertheless, the Mg/Fe values of the samples synthesized at pH  $\leq$  1.0 (sample A<sub>0</sub> 0.0020/1, B<sub>0</sub> 0.0022/1 and C<sub>0</sub> 0.0023/1) are not affected obviously by the pH values, and they are much lower than the value of the sample synthesized at pH = 1.3 (sample  $D_0 0.0082/1$ ), which indicates that the magnesium detected in sample A<sub>0</sub>, B<sub>0</sub> and C<sub>0</sub> should be owing to magnesium ions adsorbed on the FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O particles and difficult to be washed out. Likewise, a small amount of Ti in sample  $A_0$ ,  $B_0$ ,  $C_0$  and  $D_0$  (Ti/Fe 0.0018/1, 0.0020/1, 0.0021/1 and 0.0021/1, respectively) is due to the adsorption of titanium ions. However, Mn is detected in sample C<sub>0</sub>, which attributes to the pH (=1.0) is very close to the theoretic initial precipitation pH (=1.083).

It is obvious that the impurity content of  $FeC_2O_4 \cdot 2H_2O$  increases with the pH increasing from 0.3 to 1.3, corresponding, the iron recovery increases. The recovery rate of iron is 63.5%, 93.4%, 96.6% and 98.6% at pH of 0.3, 0.7, 1.0 and 1.3, respectively. The iron recovery of sample  $A_0$  is unsatisfactory though it contains the lowest impurity. When the pH is higher than 1.0, its contribution to the increase of iron recovery is limited, and the impurity content will be increased rapidly.

Fig. 1 shows the XRD patterns of  $FeC_2O_4$ ·2H<sub>2</sub>O synthesized at different pH values. As shown, all the samples are single phase

Table 3

The molar ratio of Fe, Mg, Mn, Ca, Al and Ti in FeSO<sub>4</sub>·7H<sub>2</sub>O waste slag and FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, and the iron recovery at various pH values.

Sample	Fe	Mg	Mn	Ca	Al	Ti	Fe recovery (%)
Waste slag	1	0.1122	0.0046	0.0033	0.0026	0.0102	-
$A_0 (pH = 0.3)$	1	0.0020	$\sim 0$	$\sim 0$	${\sim}0$	0.0018	63.5
$B_0 (pH = 0.7)$	1	0.0022	$\sim 0$	0.0004	${\sim}0$	0.0020	93.4
$C_0 (pH = 1.0)$	1	0.0023	0.0012	0.0009	${\sim}0$	0.0021	96.6
$D_0 (pH = 1.3)$	1	0.0082	0.0036	0.0021	${\sim}0$	0.0021	98.6



Fig. 1. XRD patterns of  $FeC_2O_4 \cdot 2H_2O$  which are labeled as  $A_0$ ,  $B_0$ ,  $C_0$  and  $D_0$ , according to different pH values 0.3, 0.7, 1.0 and 1.3, respectively.

of iron oxalate hydrate (FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O), which can be indexed to an orthorhombic system with the space group *Cccm* (JCPDS no. 22-0635). Additionally, no impurity phases are detected, which demonstrates that the adsorbed impurities are amorphous.

# 3.2. LiFePO<sub>4</sub> identification

The XRD patterns of LiFePO<sub>4</sub> samples are shown in Fig. 2(a). As shown, the diffraction lines of all samples are indexed to an orthorhombic crystal structure (triphylite, space group *Pnma*), and no impurity phases are detected. The results indicate that the metallic dopants ( $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Ti^{4+}$  and  $Ca^{2+}$ ) do not obviously change the structural characteristics of LiFePO<sub>4</sub> during heat treatment. However, the XRD peaks intensities decrease with the increased dopants contents, which reveals that the metallic cations has entered the lattices of LiFePO<sub>4</sub> crystal. Previous studies have shown that metallic ions could be doped not only in Li-site but also in Fe-site [8–15], therefore,  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Ti^{4+}$  and  $Ca^{2+}$  ions could be doped in Li-site, Fe-site or both. But in either case, it will induce the formation of cation-deficient solid solution, which can benefit the electrochemical performance of LiFePO<sub>4</sub>.

Fig. 2(a) also reveals that the diffraction peaks shift to higher degrees with the doping amount of cations. For clear observation, the peak positions of (131) planes are magnified and shown in Fig. 2(b). The XRD refinement according to the Rietveld method indicates that the lattice parameters *a*, *b* and *c* decrease with the increased impurities contents, and the results are shown in Table 4. As we all know,  $Mg^{2+}$  (0.72 Å),  $Mn^{2+}$  (0.67 Å) and  $Ti^{4+}$  (0.61 Å) ions have smaller ionic radii than both Li<sup>+</sup> (0.76 Å) and Fe<sup>2+</sup> (0.78 Å) ions, while Ca<sup>2+</sup> (1.00 Å) ion has a larger ionic radius. It can be expected that  $Mg^{2+}$ ,  $Mn^{2+}$  and  $Ti^{4+}$  doping could reduce the lattice constants of LiFePO<sub>4</sub>, while Ca<sup>2+</sup> doping could expand the lattice constants.

# Table 4

Lattice parameters and	l crystallite size	of LiFePO <sub>4</sub>	samples
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Sample	The lattice parameters				Crystallite size d <sub>131</sub> (nm)
	a (Å)	b (Å)	<i>c</i> (Å)	$V(Å^3)$	
Р	10.3201(3)	6.0091(5)	4.7018(4)	291.580(6)	44.1
А	10.3135(4)	6.0046(8)	4.6975(6)	290.909(7)	42.9
В	10.3133(5)	6.0024(7)	4.6953(9)	290.660(8)	42.0
С	10.3130(9)	6.0010(5)	4.6934(8)	290.467(9)	41.4
D	10.3122(7)	6.0003(6)	4.6928(6)	290.373(7)	40.2



**Fig. 2.** XRD patterns of LiFePO<sub>4</sub> samples (a) and magnified (1 3 1) peaks of the patterns (b), where P, A, B, C and D are synthesized from pure  $FeC_2O_4 \cdot 2H_2O$ , precursor  $A_0$ ,  $B_0$ ,  $C_0$  and  $D_0$ , respectively.

However, as a result of the cations co-doping, the lattice parameters decreased.

The crystallite size, *d*, was calculated from the X-ray line width using the Scherrer formula,  $d = 0.9\lambda/\beta_{1/2}\cos\theta$ , where  $\lambda$  is the X-ray wavelength,  $\beta_{1/2}$  is the corrected width of the main diffraction peak (1 3 1) at half height, and  $\theta$  is the diffraction angle. As shown in Table 4, the *d* value decrease with the dopants contents, indicating that the dopants limit the size of LiFePO<sub>4</sub> nanocrystals.

Fig. 3 shows the SEM images of LiFePO<sub>4</sub> samples. It is obvious that the cation-substituted samples own less agglomeration and scatter more uniform than the pure sample. This demonstrates that the metallic dopants inhibit particles to aggregate during calcinations, which is conducive to shorten the lithium-ion diffusion distance. The elements distributions of cation-substituted LiFePO<sub>4</sub> were measured by EDS. As a typical case, the EDS maps of Fe, Mg, Ca, Mn and Ti for sample C are shown in Fig. 4. As shown, the distribution areas of all the elements are homogeneous, owing to the co-precipitation, which results in the atom-scale mixed of various elements. Furthermore, Al is not detected by EDS, which is consistent with the result obtained from ICP analysis.

Fig. 5 shows the AC impedance spectra of the LiFePO<sub>4</sub> electrodes. The impedance spectra are fitted using an equivalent circuit. In the equivalent circuit,  $R_s$  and  $R_{ct}$  represent the solution resistance and charge-transfer resistance, respectively. CPE is related to the



Fig. 3. SEM images of LiFePO<sub>4</sub> samples.

double layer capacitance and passivation film capacitance. *W* represents the Warburg impedance. The parameters of the equivalent circuit are summarized in Table 5. The plot of the real axis  $Z_{re}$  versus the reciprocal square root of the lower angular frequencies  $\omega^{-0.5}$  is illustrated in Fig. 6. The straight lines are attributed to the diffusion of the lithium ions into the bulk of the electrode materials, the so-called Warburg diffusion. This relation is governed by Eq. (3) [18,19]. According to Fig. 6 and Eq. (3), the slopes of the straight

lines represent the values of Warburg impedance coefficient ( $\sigma_w$ ). The diffusion coefficient (D) of the lithium ions diffusing into the bulk electrode materials are calculated using Eq. (4) and recorded in Table 5.

$$Z_{\rm re} = R_{\rm S} + R_{\rm ct} + \sigma_{\rm W} \cdot \omega^{-0.5} \tag{3}$$

$$D = 0.5 \left(\frac{RT}{AF^2 \sigma_{\rm w}C}\right)^2 \tag{4}$$

Impedance parameters of the LiFePO<sub>4</sub> electrodes.

Sample	$R_{\rm s}\left(\Omega\right)$	$R_{\rm ct}$ ( $\Omega$ )	$\sigma_{\rm w} \left(\Omega  {\rm cm}^2/{\rm s}^{0.5} \right)$	<i>D</i> (cm <sup>2</sup> /s)	$i^0$ (mA/cm <sup>2</sup> )
Р	5.1	1228	204	$3.59\times10^{-13}$	$2.09\times10^{-5}$
Α	9.4	233	181	$4.56 \times 10^{-13}$	$1.10 imes10^{-4}$
В	4.9	157	143	$7.31 \times 10^{-13}$	$1.64\times10^{-4}$
С	4.1	146	110	$1.23 \times 10^{-12}$	$1.76\times10^{-4}$
D	5.5	434	175	$4.88\times10^{-13}$	$5.92\times10^{-5}$



Fig. 4. EDS maps of Fe, Mg, Ca, Mn and Ti for sample C.







**Fig. 6.** The relationship between  $Z_{re}$  and  $\omega^{-1/2}$  at low frequencies.

where  $R_{ct}$ , charge transfer resistance;  $R_s$ , solution resistance;  $\omega$ , angular frequency in the low frequency region; D, lithium-ion diffusion coefficient; R, the gas constant; T, the absolute temperature; F, Faraday's constant; A, the area of the electrode surface; and C, molar concentration of Li<sup>+</sup> ions.

As shown in Table 5, the cation-substituted LiFePO<sub>4</sub> exhibit much lower charge-transfer resistance than that of pure LiFePO<sub>4</sub>, indicating that cations doping can significantly increase the electrical conductivity of LiFePO<sub>4</sub>. The exchange current density  $(i^0)$  was calculated by the formula,  $i^0 = RT/nFR_{ct}$ . Cation-substituted samples show higher exchange current densities than the pure sample, and sample C shows the highest value. Also, the cation-substituted LiFePO<sub>4</sub> electrodes have better ionic conductivity than the pure LiFePO<sub>4</sub> electrode. It is reported that the lithium ions diffusivity increase with the increased parameters *b* and *c* [9,20], thus, the pure LiFePO<sub>4</sub> should possess the highest ionic conductivity. But the results show that the pure sample has the lowest value, which should be ascribed to the cation-substituted samples have smaller crystallite sizes and less particle agglomerations than the pure sample. Furthermore, sample D exhibits lower ionic conductivity than sample C. That may be owing to sample D has the lowest parameters *b* and *c*, namely has the narrowest tunnel for Li<sup>+</sup> ion across [9,20]. Sample C shows the highest electronic conductivity and ionic conductivity, indicating that an appropriate amount of cation dopant is important.

Fig. 7 displays the initial charge/discharge curves of LiFePO<sub>4</sub> samples at different *C*-rates. All the samples exhibit very long and plat plateau around 3.4 V at low current rates (0.1*C* and 0.5*C*). The sample P, A, B, C and D show a discharge capacity of 167, 165, 164, 164 and 162 mAh  $g^{-1}$  at 0.1*C* rate, respectively, which approach the theoretical capacity of 170 mAh  $g^{-1}$ . By increasing the current rate, the utilization percentage of the active material decreased along with the polarization of electrodes increased. The pure LiFePO<sub>4</sub> electrode exhibits serious polarization at 1*C*, 2*C* and 5*C* rates, and delivers a capacity of 136, 112 and 67 mAh  $g^{-1}$  at the corresponding *C*-rate. While the cation-substituted LiFePO<sub>4</sub> show smaller polarization and much better electrochemical properties. Sample A, B, C and D exhibit a capacity of 149, 150, 152 and 148 mAh  $g^{-1}$  at 1*C* rate, 139, 140, 142 and 137 mAh  $g^{-1}$  at 2*C* rate, and 123, 124, 126 and 122 mAh  $g^{-1}$  at 5*C* rate, respectively.

Cyclic stability of LiFePO<sub>4</sub> samples at room temperature is shown in Fig. 8. As shown, the capacities waved with the room tem-



Fig. 7. The initial charge/discharge curves of LiFePO<sub>4</sub> samples with different C-rates at room temperature.

perature. All the samples exhibit excellent cycling performance at low current rates (0.1*C* and 0.5*C*), and without capacity fading after 10 cycles. But at higher current rates, cation-substituted samples show much better cyclic stability than the pure LiFePO<sub>4</sub>. After 50 cycles, pure LiFePO<sub>4</sub> only retains 90.4%, 85.7% and 83.6% of its initial discharge capacity at 1*C*, 2*C* and 5*C* rate, respectively. While sample A, B, C and D maintain 100%, 100.3%, 99.5% and 98.0% of its initial discharge capacity at 1*C* rate, 98.6%, 100%, 99.3% and 94.4%

of its initial discharge capacity at 2*C* rate, and 98.4%, 99.2%, 100.1% and 92.6% of its initial discharge capacity at 5*C* rate, respectively. Cation-substituted LiFePO<sub>4</sub> exhibiting much better electrochemical properties can be attributed to: (1) cation-doping effectively restrains the LiFePO<sub>4</sub> crystals growth and inhibits the particles aggregation and, consequently, enhances the lithium-ion diffusion speed cross the LiFePO<sub>4</sub>/FePO<sub>4</sub> interface; (2) cation-doping reduces the charge transfer resistance ( $R_{ct}$ ), and thus increases the electri-



**Fig. 8.** Cycling performances of LiFePO₄ samples at different C-rates. The cells cycled 10 times at 0.1C and 0.5C, respectively, and then cycled 50 times at 1C, 2C and 5C in turn.

cal conductivity of LiFePO<sub>4</sub>. Furthermore, sample C shows the most excellent electrochemical properties, due to the highest electronic conductivity and ionic conductivity.

#### 4. Conclusions

FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O precursors are prepared from the FeSO<sub>4</sub>·7H<sub>2</sub>O waste slag, without any purifying process. ICP results show that a small amount of metallic ions precipitated into the precursors. The impurity content of FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O and the iron recovery are greatly affected by the pH value. Cation-substituted LiFePO<sub>4</sub> samples are synthesized with the as-prepared FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, and all the cation-substituted samples show excellent electrochemical properties. However, considering the best electrochemical performance of LiFePO<sub>4</sub> and the satisfactory recovery rate of iron, the optimal pH value for synthesizing FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O is about 1.0.In particular, it must be pointed out that this route is generally practical in this field, owing to the FeSO<sub>4</sub>·7H<sub>2</sub>O waste slag produced by the titanium dioxide industry possesses relatively stable impurity content. Moreover, this method can also be used for utilizing those waste slags which have lower or a little higher impurity content than the slag discussed in this paper. Based on these results, it can be concluded that this method is a simple, efficient, economical and environment-friendly way for both FeSO<sub>4</sub>.7H<sub>2</sub>O waste slag utilization and LiFePO<sub>4</sub> preparation.

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#### References

- [1] B. Liang, C. Li, C. Zhang, Y. Zhang, Hydrometallurgy 76 (2005) 173.
- M. Xu, M. Guo, J. Zhang, T. Wan, L. Kong, J. Iron Steel Res. Int. 13 (2006) 6. [2]
- C. Li, B. Liang, L. Guo, Hydrometallurgy 89 (2007) 1. [3]
- J.T. Nong, H. Huang, S.Q. Wei, Chin. Patent 200611018642.X (2007).
  C.Q. Cai, Z.Y. Zeng, Q.L. Xu, Chin. Patent 02148428.7 (2008).
- C.Q. Cai, Z.Y. Zeng, Q.L. Xu, Chin. Patent 02148429.5 (2008). [6]
- P.F. Huang, Chin. Patent 200710130428.8 (2007). [7]
- [8] J.F. Ni, H.H. Zhou, J.T. Chen, X.X. Zhang, Mater. Lett. 59 (2005) 2361.
- [9] S.-H. Wu, M.-S. Chen, C.-J. Chien, Y.-P. Fu, J. Power Sources 189 (2009) 440.
- [10] G.X. Wang, S. Bewlay, S.A. Needham, H.K. Liu, R.S. Liu, V.A. Drozd, J.-F. Lee, J.M. Chen, J. Electrochem. Soc. 153 (2006) A25.
- L. Li, X. Li, Z. Wang, L. Wu, J. Zheng, H. Guo, J. Phys. Chem. Solids 70 (2009) 238. [11]
- [12] S.Y. Chung, J.T. Bloking, Y.M. Chiang, Nat. Mater. 1 (2002) 123.
- [13] N. Meethong, Y.H. Kao, S.A. Speakman, Y.M. Chiang, Adv. Funct. Mater. 19 (2009) 1060
- [14] J. Yao, S. Bewlay, K. Konstantionv, V.A. Drozd, R.S. Liu, X.L. Wang, H.K. Liu, G.X. Wang, J. Alloys Compd. 425 (2006) 362.
- T. Nakamura, K. Sakumoto, M. Okamoto, S. Seki, Y. Kobayashi, T. Takeuchi, M. [15] Tabuchi, Y. Yamada, J. Power Sources 174 (2007) 435.
- [16] J.A. Dean (Ed.), Lange's Handbook of Chemistry, 13th ed., McGraw-Hill, New York, 1985.
- [17] D.R. Lide, Handbook of Chemistry and Physics, 78th ed., CRC Press, Boca Raton, New York, 1997-1998.
- [18] A.Y. Shenouda, K.R. Murali, J. Power Sources 176 (2008) 332.
- [19] A.Y. Shenouda, H.K. Liu, J. Alloys Compd. 477 (2009) 498.
- [20] C. Ouyang, S. Shi, Z. Wang, X. Huang, L. Chen, Phys. Rev. B 69 (2004) 104303.