Effect of Ru Doping on the Properties of LiFePO$_4$/C Cathode Materials for Lithium-Ion Batteries

Yuan Gao,* Kun Xiong, Haidong Zhang, and Bingfeng Zhu*

ABSTRACT: Doping of metals is highly effective in improving electrochemical performance of lithium iron phosphate. Here, based on a first-principles calculation result that Ru doping at the Fe sites has positive effects on promoting the ability of electron and Li$^+$ transmission by reducing the lattice parameter and band gap, as well as the increase in Fermi energy, we constructed Ru-doped LiFe$_{1-x}$Ru$_x$PO$_4$/C through the sol–gel preparation technology as cathode materials for Li-ion batteries. As a result, LFP-1 ($x = 0.01$) delivers excellent specific capacities of 162.6 and 110.6 mA h g$^{-1}$ under 0.1 and 10 C, respectively. At the same time, LFP-1 emerges with excellent cycling performance, with a capacity retention of up to 95.6% after 300 cycles at 5 C. Ru doping is beneficial for improving the lithium diffusion coefficient and electrical conductivity, therefore strongly increasing electrochemical performance. This work represents a significant addition to exploring a new class of lithium iron phosphates with excellent performance in new energy storage and transition systems.

1. INTRODUCTION

In recent years, lithium iron phosphate (LiFePO$_4$) has become the highly anticipated commercial positive materials for Li-ion batteries because of a reasonable energy value, low price, high safety, and nontoxic elements.$^{1-5}$ Unfortunately, the inferior electronic conductivity and poor lithium-ion transmission capability strongly impede the commercial development for a high-energy-density battery.$^{6-8}$ Researchers have carried out various aspects of work to solve these hard problems.$^9-18$ In these modification methods, improving the intrinsic conductivity of LiFePO$_4$ is still the key problem. The doping of metals is highly effective in improving the intrinsic conductivity of LiFePO$_4$.

The electronic conductivity of LiFePO$_4$ is closely related to its microstructure and electronic energy. DFT calculations have made some progress, such as investigating the electronic structure, band structure, surface, and lattice dynamics of cathode materials.$^{22-25}$ Ban et al.$^{26}$ carried out systematic theoretical calculation and experimental research on LiFePO$_4$, which proved that donor–acceptor charge compensation codoping can significantly improve the material rate capability. Studies reported that the band gap energy can be reduced by doping metal elements to occupy iron or lithium sites, which can effectively enhance the conductivity of LiFePO$_4$. At present, research studies on the doping mechanism mainly focus on the doping of Co$^{2+}$, Zr$^{4+}$, Nb$^{5+}$, Cr$^{3+}$, etc. Due to the similar electronic structure and ionic radius, Ru doping is more likely to occupy the iron site, and the Ru heteroatom substitutes for Fe, in which case, Fe or Li vacancies will be formed in the LiFePO$_4$ lattice to supplement the charge after doping, but the mechanism of high-conductivity Ru doping of LiFePO$_4$ is rarely reported.

In this paper, we first calculated the local crystallographic structure and electronic structure of LiFe$_{1-x}$Ru$_x$PO$_4$/C with Ru substituted for Fe by first-principles DFT and then analyzed the effects of Ru doping on the cell parameters, energy band structures, and density of states of LiFePO$_4$ and proposed the change in the mechanism of the conductivity. Above all, our research results proved that raised electronic conductivity and the lithium diffusion coefficient are achieved with Ru doping, thus improving the poor rate performance of LiFePO$_4$ cathode materials in strong current density.

2. RESULTS AND DISCUSSION

2.1. First-Principles Calculations of LiFe$_{1-x}$Ru$_x$PO$_4$

Power. Lattice parameters and Fermi energies of optimized LiFe$_{1-x}$Ru$_x$PO$_4$ ($x = 0, 0.01, 0.02, 0.05$) from the first-principles calculations are shown in Table 1. It can be seen...
Table 1. Unit Cell Parameter and Fermi Energies of Optimized LiFe$_{1-x}$RuPO$_4$

| model | $a$ (Å) | $b$ (Å) | $c$ (Å) | $V$ ($Å^3$) | Fermi energy (eV) |
|-------|---------|---------|---------|-------------|------------------|
| LFP-0 | 10.1283 | 5.9958  | 4.6941  | 285.06      | 3.37             |
| LFP-1 | 10.0508 | 5.9621  | 4.6999  | 281.64      | 3.52             |
| LFP-2 | 9.9921  | 5.9145  | 4.7108  | 278.40      | 3.47             |
| LFP-5 | 9.9833  | 5.8345  | 4.7178  | 274.80      | 3.33             |

Separate phase, resulting in the declined electrochemical properties. In addition, as shown in the inset of Figure 1, the peak position moves to a high angle direction regularly, in pace with the increasing doping amount, which indicates a contraction of the unit cell volume. The experimental results are in agreement with the theoretical calculation. It also suggests that Ru doping tends to replace Fe in LiFePO$_4$.

Figure 2 shows the band structures of doped and undoped LiFePO$_4$ which are along the high symmetry point across the first Brillouin zone. Pure LiFePO$_4$ has a high band gap energy of 0.771 eV. The whole energy band is also in the high-energy position. Therefore, LiFePO$_4$ possesses low conductivity. Theoretical analysis indicates that Ru doping is effective in reducing the band gap. The decrease in the band gap of LFP-5 ($x = 0.05$) is obvious, which is 0.582 eV. The smaller band gap implies higher electrical conductivity, and Ru doping can effectively improve the electronic conductivity of LiFePO$_4$ composite cathode materials.

For clarifying the principle of Ru doping affecting the band structure, the theoretical calculation results of density of states (DOS) of LiFe$_{1-x}$RuPO$_4$ ($x = 0, 0.01, 0.02,$ and $0.05$) samples are discussed and shown in Figure 3. Since the electronic states around the Fermi level have great influence on the electron transfer process, the DOS near the Fermi level has attracted much attention. It is found that the total density of states (TDOS) of cathode materials close to the Fermi level improves with the increase in the Ru doping content, and the peak of the density of states moves toward the low-energy direction, indicating that the band gap decreases after doping. As we know, the Ru 4$d^7$ orbit is near the Fermi level, and Ru 4$d^7$ also affects the electronic states of LiFe$_{1-x}$RuPO$_4$ materials just like Fe 3$d^6$, which strengthen the peak intensity of LiFe$_{1-x}$RuPO$_4$ near the Fermi level. Results of DOS theoretical calculation prove that the band gap energy of LiFe$_{1-x}$RuPO$_4$ can be greatly reduced by Ru doping, which leads to the improvement of conductivity of LiFe$_{1-x}$RuPO$_4$.

2.2. Electrochemical Measurements. Under guidance of theoretical calculation results, electrochemical properties of Ru-doped samples between 4.2 and 2.5 V at 0.1 C were investigated, and test results are shown in Figure 4a. Compared with the LiFePO$_4$/C, Ru doping of LiFe$_{1-x}$RuPO$_4$/C exhibits a higher discharge capacity at the first charge discharge. The LFP-1 ($x = 0.01$) cathode delivers a specific discharge capacity of 162.6 mAh g$^{-1}$ and discharge plateaus, suggesting the lower polarization and an excellent electrochemical reversibility of the electrode. With the increasing Ru doping amount, discharge capacities of LFP-2 ($x = 0.02$) and LFP-5 ($x = 0.05$) are reduced to 156 and 144 mAh g$^{-1}$, respectively, and discharge plateaus decline.

Figure 4b displays cyclic reversibility of LiFe$_{1-x}$RuPO$_4$/C electrodes at various rates. All Ru-doped samples show a better rate capability and good cycling characteristics, with no significant decrease in capacity. Apparently, LFP-1 ($x = 0.01$) shows an outstanding specific capacity and rate capability. LFP-1 delivers specific discharge capacities of 162.6, 145.5, 132.4, 120.0, and 110.6 mAh g$^{-1}$ under different current densities (0.1, 1, 2, 5, and 10 C). After 15 times of charging-discharging, the capacity fading of LFP-1 is very small, and the capacity retention is still higher than 97% at a high rate.

On the contrary, the LFP-0 electrode displays inferior rate performances, and discharge capacities decrease sharply to 75 mAh g$^{-1}$ under 10 C. In addition, the as-prepared LFP-1 ($x =
0.01) cathode also displayed a satisfactory cycle life. Figure 5 shows that the LFP-1 (x = 0.01) cathode still retained 95.6% of its initial capacity after 300 cycles at 5 C. Combined with the previous theoretical calculation, we believe outstanding rate
capabilities and cycle performance of LFP-1 are attributed to proper heteroatom Ru doping in LiFePO₄, consistent with our theoretical understanding described above.

To further investigate the effect of Ru doping on the Li-ion diffusion coefficient of LiFePO₄ electrode materials, electrochemical impedance spectra of the assembled half cells were measured. The equivalent circuit and Nyquist diagram of LiFe₁₋ₓRuₓPO₄/C composite cathode materials after 3 cycles under full charge are presented in Figure 6a. All the curves are composed of two parts, one is a semicircle in high-frequency regions, and the other is inclined lines in low-frequency regions, corresponding to the double-layer response at the electrode interface and the diffusion of lithium ions in the solid phase. The Ohmic resistance (Rₑ), constant-phase element (Cᵦ), charge transfer (Rₓ), and the Warburg impedance (Zₓ) constitute an equivalent circuit pattern. The relationship graph between Z’ and ω⁻¹/² shows a slope of σ linear relationship in Figure 6b.

The lithium diffusion coefficient (Dₓ⁺) of the LiFePO₄ electrode material is counted based on the following formulas (eqs 1 and 2).

\[
D_{Li}^+ = \frac{R^2T^2}{2A^2n^2F^2C_{Li}} \frac{2}{\sigma^2}
\]  

(1)

\[
Z' = R_e + R_x + \sigma \omega^{-1/2}
\]  

(2)

Table 2 shows EIS results of the LiFe₁₋ₓRuₓPO₄/C with different Ru amounts after 3 cycles. The diffusion coefficients of lithium ions (Dₓ⁺) of samples are 3.64 × 10⁻¹², 1.11 × 10⁻¹¹, 8.64 × 10⁻¹², and 6.08 × 10⁻¹² cm² s⁻¹ separately. Apparently, Ru-doped samples have a higher lithium-ion diffusion coefficient. LFP-1 (x = 0.01) exhibits the highest Li⁺ diffusion coefficient (1.11 × 10⁻¹¹ cm² s⁻¹) and the lowest
charge transfer resistance (58.40 Ω) at the same temperature. The EIS results clearly indicate that appropriate Ru doping can enhance Li\(^+\) mobility in the bulk of the olivine structure and reduce the resistance in the cathode electrolyte interface, resulting in improved electrochemical activity of LiFePO\(_4\). When the doping amount of Ru is further increased, Ru will occupy both Li and Fe sites, which will block the Li\(^+\) diffusion channel.

2.3. SEM, Element Mapping, and XPS Analysis. Morphologies of LFP-0 and LFP-1 were characterized using a field emission scanning electron microscope (FE-SEM). The powder is composed of small secondary particles with regular dispersion. It is interesting to notice that LFP-1 powders (Figure 7b,d) show uniform submicrometer-sized smaller primary nanoparticles (50–200 nm) connected to each other to compose a porous structure with less aggregates than LFP-0 powders (Figure 7a,c). This may be attributed to the fact that Ru doping can promote the nucleation process and effectively inhibit the particle growth at high temperature.\(^{34,35}\) The finer particle size and better dispersion can reduce the diffusion path of Li\(^+\) and provide a larger surface for Li\(^+\) extraction/insertion, resulting in its enhanced diffusion speed. The energy-dispersive

### Table 2. EIS Results and \(D_{\text{Li}^+}\) of LiFe\(_{1-x}\)Ru\(_x\)PO\(_4\)/C (\(x = 0, 0.01, 0.02, \) and 0.05) Electrodes

| sample | \(R_\Omega (\Omega)\) | \(R_{ct} (\Omega)\) | \(\sigma (s \text{ cm}^{-1})\) | \(D_{\text{Li}^+} (\text{cm}^2 \text{s}^{-1})\) |
|--------|----------------------|---------------------|---------------------|----------------------|
| LFP-0  | 0.51                 | 161.87              | 53.25               | 3.64 \times 10^{-12} |
| LFP-1  | 0.55                 | 58.40               | 30.47               | 1.11 \times 10^{-11} |
| LFP-2  | 0.58                 | 70.26               | 34.57               | 8.64 \times 10^{-12} |
| LFP-5  | 0.63                 | 92.93               | 41.21               | 6.08 \times 10^{-12} |

![Figure 7. SEM images of LFP-0 (a,c) and LFP-1 (b,d) and (e,f) EDX elemental mapping images of Fe and Ru.](https://doi.org/10.1021/acsomega.1c00595)
X-ray (EDX) elemental mapping images of LFP-1 are shown in Figure 7e,f. The results indicate that Fe and Ru elements have monotonous dispersion, and Ru was doped into the lattice of bulk materials.

In order to better understand the valence of Ru, LFP-1 was characterized by XPS, and the results are shown in Figure 8. Figure 8a shows the survey scan of the LFP-1 depicting the presence of the expected core levels of Li 1s, Fe 2p, Ru 3d, P 2p, C 1s, and O 1s. As seen in Figure 8b, the high-resolution Ru 3d XPS spectrum shows that the spin–orbit is divided into 3d5/2 and 3d3/2 peaks, although it is hard to discriminate the Ru 3d peak from the carbon peak. The centers of the two split peaks are 280.7 and 284.4 eV, corresponding to Ru 3d5/2 and Ru 3d3/2, respectively. According to previous research,36 it can be inferred that Ru has +4 valence. Figure 8c shows the Fe 2p spectra, and as a result of the spin–orbit coupling, the spectrum of Fe 2p is divided into two peaks, corresponding to Fe 2p3/2 and Fe 2p1/2.37 One peak is Fe 2p3/2, which is composed of the main peak of 709.8 eV and a satellite peak of 714.7 eV. The other peak is Fe 2p1/2, which is composed of the main peak of 724 eV and a satellite peak of 727.4 eV.38 According to the XPS results, it can be inferred that Fe exists in LFP-1 with +2 valence.38 The Ru4+ heteroatom substitutes for Fe2+, in which case, Fe or Li vacancies will be formed in the LiFePO4 lattice to supplement the charge after doping. Charge compensation might promote the ability of Li+ transmission in the bulk phase and improve the electrochemical performance of LiFePO4.

3. EXPERIMENTAL SECTION

3.1. Calculation Methods. In the theoretical calculations, the first-principles calculation, which is based on density functional theory (DFT), was run in the CASTEP of Materials Studio software 8.0 using an ultrasoft pseudopotential (USPP) method.39 In terms of the electronic exchange-correlation functional, Fe d orbitals are modified by GGA+U (U = 4.6 eV, J = 0), which makes the calculated band gap of LiFePO4 consistent with the experimental value.40 An appropriate k-point mesh (3×3×3) was chosen to ensure that the total energies converge within 1.0 × 10−4 eV·atom−1. Three hundred electronvolts was chosen as the cutoff energy.

LiFePO4 is a typical olivine-type structure, and the cell parameters of LiFePO4 are a = 10.3297 Å, b = 6.0115 Å, c = 4.7017 Å, and α = β = γ = 90°.41,42 After optimizing the structure of LiFePO4, a bulk model of Ru-doped LiFePO4 is shown in Figure 9.

3.2. Synthesis. Ru-doped LiFe1−xRu xPO4/C (x = 0, 0.01, 0.02, and 0.05) were synthesized by a sol–gel preparation route from a mixture of stoichiometric amounts of reagents CH3CO2Li·2H2O, Fe(NO3)3·9H2O, H3PO4, RuCl3, and citric acid. The synthesis details of Ru-doped LiFePO4/C are similar to those of our previous studies.43 LiFe1−xRu xPO4/C samples are named as LFP-0 (x = 0), LFP-1 (x = 0.01), LFP-2 (x = 0.02), and LFP-5 (x = 0.05).

3.3. Materials Characterization. X-ray diffraction (XRD, MO3xHF22, MacScience, Japan) was employed to characterize the crystal structure of LiFe1−xRu xPO4/C under the conditions of Cu Kα radiation and a speed of 1 °C/min. A scanning electron microscope (SEM, Zeiss SIGMA 500, Germany) was used for analysis of material morphology. X-ray

Figure 8. (a) Survey X-ray photoelectron spectra for LFP-1 as well as the deconvoluted peaks of (b) Ru 3d and (c) Fe 2p.
photoelectron spectroscopy (XPS; Thermo VG Scientific Co., Ltd.) was applied to analyze the valence states of elements in the LiFe\(_{1-x}\)Ru\(_x\)PO\(_4\)/C.

3.4. Electrochemical Measurements. The charge and discharge performances were tested using a Neware BTS-SV3A automatic battery tester between 2.5 and 4.2 V (vs Li /Li\(^+\)). An electrochemical workstation (Solartron, 1287+1260) was employed to perform electrochemical impedance spectroscopy (EIS) at the potential amplitude of 5 mV and the frequency range of 10\(^{-2}\)–10\(^{4}\) Hz.

For electrochemical characterization, cathodes of 85 wt % LiFe\(_{1-x}\)Ru\(_x\)PO\(_4\)/C, 6 wt % ethyne black, and a 9 wt % PVDF binder distributed throughout N-methylpyrrolidone were made and coated on an Al substrate current collector. Cathodes were dried in vacuum at 80 °C for 24 h. CR2016-type coin cells were packaged in an Ar glovebox. A lithium metal was used as a counter electrode, LiPF\(_6\) in a mixture solvent (DMC:EC = 1:1) was used as a diaphragm.

4. CONCLUSIONS

In this study, with united use of the first-principles theoretical calculation method, experiments, and characterization, the results suggested that ruthenium doping occupying iron sites leads to a significantly improved lithium diffusion coefficient and electrical conductivity, therefore strongly increasing electrochemical performance. LFP-1 (x = 0.01) delivers excellent specific capacities of 162.6 and 110.6 mA h g\(^{-1}\) at 0.1 and 10 C and at the same time displays good cycle life. Ru doping will affect the electronic structure of LiFePO\(_4\) resulting in the shortening of Li\(^+\) diffusion distance, the increase in Fermi energy, and the reduction in the band gap. In addition, it is also conducive to promote electron and Li\(^+\) transport. Such a concept of doping substitution can be extended to optimize the specific capacity and rate capability of other materials with poor conductivity.

AUTHOR INFORMATION

Corresponding Authors

Yuan Gao – School of Environment and Resources, Engineering Research Center for Waste Oil Recovery Technology and Equipment of Ministry of Education, Chongqing Technology and Business University, Chongqing 400067, People’s Republic of China; Email: gaogone113117@ctbu.edu.cn

Bingfeng Zhu – The First Affiliated Hospital of Chongqing Medical and Pharmaceutical College, Chongqing 400040, People’s Republic of China; Email: 2621266253@qq.com

Authors

Kun Xiong – School of Environment and Resources, Engineering Research Center for Waste Oil Recovery Technology and Equipment of Ministry of Education, Chongqing Technology and Business University, Chongqing 400067, People’s Republic of China; orcid.org/0000-0002-0625-7195

Haidong Zhang – School of Environment and Resources, Engineering Research Center for Waste Oil Recovery Technology and Equipment of Ministry of Education, Chongqing Technology and Business University, Chongqing 400067, People’s Republic of China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c00595

Author Contributions

This manuscript contains works and contributions of all the authors. All authors have read the full text and agreed to publish the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was funded by the Scientific and Technological Projects from Chongqing Education Commission (KJQN2019008832), the School Science Fund Projects from Chongqing Technology and Business University (1856022), and the Research platform open project of Chongqing Technology and Business University (KFJJ2019086).

REFERENCES

(1) Padhi, A. K.; Nanjundaswamy, K. S.; Goodenough, J. B. Phospho-olivines as positive-electrode materials for rechargeable lithium batteries. J. Electrochem. Soc. 1997, 144, 1188–1194.

(2) Alias, N.; Mohamad, A. A. Advances of aqueous rechargeable lithium-ion battery: a Review. J. Power Sources 2015, 274, 237–251.

(3) Chung, S.-Y.; Bloking, J. T.; Chiang, Y.-M. Electronically conductive phospho-olivines as lithium storage electrodes. Nat. Mater. 2002, 1, 123–128.

(4) Armand, M.; Tarascon, J. M. Building better batteries. Nature 2008, 451, 652–657.

(5) Huang, S.; Ren, J.; Liu, R.; Bai, Y.; Li, X.; Huang, Y.; Yue, M.; He, X.; Yuan, G. Enhanced electrochemical properties of LiFePO\(_4\) cathode using waterborne lithiated ionomer binder in Li-ion batteries with low amount. ACS Sustainable Chem. Eng. 2018, 6, 12650–12657.

(6) Sun, X.; Li, J.; Shi, C.; Wang, Z.; Liu, E.; He, C.; Du, X.; Zhao, N. Enhanced electrochemical performance of LiFePO\(_4\) cathode with in-situ chemical vapor deposition synthesized carbon nanotubes as conductor. J. Power Sources 2012, 220, 264–268.

(7) Gowmeni, S.; Basak, P. Swapping conventional salts with an entrapped lithiated anionic polymer: fast single-ion conduction and electrolyte feasibility in LiFePO\(_4\)/Li batteries. J. Mater. Chem. A 2017, 5, 12202–12215.

(8) Guo, X.; Lan, T.; Zhang, L.; Tan, J.; Feng, X.; Chen, L. Y. A stable filamentous coaxial microelectrode for Li-ion batteries: a case of olivine LiFePO\(_4\). Chem. Commun. 2019, 55, 3529–3531.

(9) Saikia, D.; Deka, J. R.; Chou, C. J.; Lin, C. H.; Yang, Y. C.; Kao, H. M. Encapsulation of LiFePO\(_4\) Nanoparticles into 3D Inter-penetrating Ordered Mesoporous Carbon as a High-Performance Cathode for Lithium-Ion Batteries Exceeding Theoretical Capacity. ACS Appl. Energy Mater. 2019, 2, 1121–1133.

Figure 9. Cell structure model of Ru-doped LiFePO\(_4\).
(10) Tian, H.; Zhao, X.; Zhang, J.; Li, M.; Lu, H. LiFePO4 Anchored on Pristine Graphene for Ultrafast Lithium Battery. ACS Appl. Energy Mater. 2018, 1, 3497–3504.

(11) Paolella, A.; Bertoni, G.; Hovington, P.; Feng, Z.; Flacau, R.; Prato, M.; Colombo, M.; Marras, S.; Manza, L.; Turner, S.; Van Tendeloo, G.; Guerh, A.; Demopoulos, G. P.; Zaghib, K. Cation Exchange mediated elimination of the Fe-antisites in the hydrothermal synthesis of LiFePO4. Nano Energy 2015, 16, 256–267.

(12) Gao, C.; Zhou, J.; Liu, G.; Wang, L. Synthesis of F-doped LiFePO4/C cathode materials for high performance lithium-ion batteries using co-precipitation method with hydrofluoric acid source. J. Alloys Compd. 2017, 727, 501–513.

(13) Yang, W.; Chen, Y.; Peng, X.; Lin, Y.; Li, J.; Hong, Z.; Xu, G.; Huang, Z. Enhanced electrochemical performances of Cu/CuO composite decorated LiFePO4 through a facile magnetron sputtering. ACS Appl. Energy Mater. 2019, 2, 4652–4663.

(14) Yang, C.-C.; Hsu, Y.-H.; Shih, J.-Y.; Wu, Y.-S.; Karuppiah, C.; Liou, T.-H.; Lue, S. J. Preparation of 3D micro/mesoporous LiFePO4 composite wrapping with porous graphene oxide for high-power lithium ion battery. Electrochim. Acta 2017, 258, 773–785.

(15) Wang, C.; Guo, Z.; Shen, W.; Xu, Q.; Liu, H.; Wang, Y. B-doped carbon coating improves the electrochemical performance of electrode materials for Li-ion batteries. Adv. Funct. Mater. 2014, 24, 5511–5521.

(16) Nan, C.; Lu, J.; Li, L.; Li, L.; Peng, Q.; Li, Y. Size and shape control of LiFePO4 nanocrystals for better lithium ion battery cathode materials. Nano Res. 2013, 6, 469–477.

(17) Di Leccce, D.; Gancitano, V.; Hassoun, J. Investigation of Mn and Fe substitution effects on the characteristics of high-Voltage LiCo0.8Mn0.18Fe0.02O2 cathodes prepared by Sol–gel route. ACS Sustainable Chem. Eng. 2020, 8, 278–289.

(18) Lv, Y.; J.; Huang, B.; Tan, J. X.; Jiang, S. Q.; Zhang, S. F.; Wen, Y. X. Enhanced low temperature electrochemical performances of LiFePO4/C by V and P co-doping. Mater. Lett. 2018, 229, 349–352.

(19) Shi, S.; Liu, L.; Wang, D.; s.; Wang, Z.; Chen, L.; Huang, X. First-principles investigation of the structural magnetic, and electronic properties of olivine LiFePO4. Phys. Rev. B 2005, 71, 144404–195112.

(20) Yan, Z.; Huang, D.; Lai, J.; Chu, Y.; Zheng, F.; Cai, Y.; Pan, Q.; Wang, H.; Huang, Y.; Li, Q. Nickel catalyzed graphitized carbon coated LiFe1-xNixPO4 composites as cathode material for high-performance lithium-ion batteries. Electrochim. Acta 2020, 353, 136565.

(21) Zhang, Y.; Alarco, J. A.; Nerkar, J. Y.; Best, A. S.; Snook, G. A.; Talbot, P. C.; Cowie, B. C. C. Observation of Preferential Cation Exchange on Pristine Graphene for Ultrafast Lithium Battery. Adv. Funct. Mater. 2012, 229, 349–352.

(22) Wang, L.; Zhou, F.; Meng, Y.-S.; Ceder, G. First-principles study of surface properties of LiFePO4: Surface energy, structure, Wulf shape, and surface redox potential. Phys. Rev. B 2007, 76, 165435–165440.

(23) Nanda, J.; Martha, S. K.; Porter, W. D.; Wang, H.; Dudney, N. J.; Rabin, M. D.; Siegel, D. J. Thermophysical properties of LiFePO4 cathodes with carbonized pitch coatings and organic binders: Experiments and first-principles modeling. J. Power Sources 2014, 251, 8–13.

(24) Kou, X.-J.; Je, H.; Zhu, C.-B.; Rolfe, P. First-principles study of the chemical bonding and conduction behavior of LiFePO4. Chem. Phys. 2015, 446, 1–6.

(25) Fang, C.-M.; Wijs, G.-A.; Loong, C.-K. Lattice and local-mode vibrations in anhydrous and protonized LiMn2O4 spinels from first-principles theory. J. Mater. Chem. 2017, 17, 4908–4913.

(26) Ban, C.; Yin, W.-J.; Tang, H.; Wei, S.-H.; Yan, Y.; Dillon, A. C. A novel Codoping approach for enhancing the performance of LiFePO4 cathodes. Adv. Energy Mater. 2012, 2, 1028–1032.

(27) Chen, T. C.; Lin, R. H. Effects of Metal doping on properties of LiFePO4 cathode material by First-Principle calculation. Int. J. Mater. Eng. 2015, 5, 121–124.

(28) Zhang, D.; Zhang, P.; Yi, J.; Yuan, Q.; Jiang, J.; Xu, Q.; Luo, Z.; Ren, X. XRD simulation study of doped LiFePO4. J. Alloys Compd. 2011, 509, 1206–1210.

(29) Yin, X.; Huang, K.; Liu, S.; Wang, H.; Wang, H. Preparation and characterization of Na-doped LiFePO4/C composites as cathode materials for lithium-ion batteries. J. Power Sources 2010, 195, 4308–4312.

(30) Shi, S.; Ouyang, C.; Lei, M.; Tang, W. Effect of Mg-doping on the structural and electronic properties of LiCoO2: A first-principles investigation. J. Power Sources 2007, 171, 908–912.

(31) Liao, X.-Z.; Ma, Z.-F.; Gong, Q.; He, Y.-S.; Pei, L.; Zeng, L.-J. Low-temperature performance of LiFePO4/C cathode in a quaternary carbonate-based electrolyte. Electrochem. Commun. 2008, 10, 691–694.

(32) Bard, A. J.; Faulkner, L. R. Electrochemical methods: Fundamentals and applications; Wiley: New York, 1980; pp. 231–265.

(33) Shu, H.; Wang, X.; Wu, Q.; Liu, L.; Li, J.; Wang, X.; Yang, S.; Ju, B.; Yang, X.; Zhang, X.; Wang, Y.; Wei, Q.; Hu, B.; Liao, Y.; Jiang, H. The effect of ammonia concentration on the morphology and electrochemical properties of LiFePO4 synthesized by ammonia assisted hydrothermal route. Electrochem. Acta 2012, 76, 120–129.

(34) Hu, Y.; Yao, J.; Zhao, Z.; Zhu, M.; Li, Y.; Jin, H.; Zhao, H.; Wang, J. ZnO-doped LiFePO4 cathode material for lithium-ion battery fabricated by hydrothermal method. Mater. Chem. Phys. 2013, 141, 835–841.

(35) Dominko, R.; Bele, M.; Gaberscek, M.; Remskar, M.; Hanzel, D.; Goupil, J. M.; Pejovnik, S.; Jannik, M. Porous olivine composites synthesized by sol-gel technique. J. Power Sources 2006, 153, 274–280.

(36) Kim, K. H.; Kim, K. S.; Kim, G. P.; Baek, S. H. Electropolyposition of mesoporous ruthenium oxide using an aqueous mixture of CTAB and SDS as a templating agent. Curr. Appl. Phys. 2012, 12, 36–39.

(37) Bhuvaneswari, M. S.; Bramnik, N. N.; Ensling, D.; Ehrenberg, H.; Jaegermann, W. Synthesis and characterization of carbon nanofiber/LiFePO4 composites for Li ion batteries. J. Power Sources 2006, 150, 553–560.

(38) Castro, L.; Dedryvere, R.; el Khalifi, M.; Lippens, P.-E.; Bréger, J.; Tessier, C.; Gonbeau, D. The spin-polarized electronic structure of LiFePO4 and FePO4 evidenced by in-Lab XPS. J. Phys. Chem. C 2010, 114, 17995–18000.

(39) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. Atoms, molecules, solids, and surfaces: applications of the generalized gradient approximation for exchange and correlation. Phys. Rev. B 1992, 46, 6671–6687.

(40) Zhang, H.; Tang, Y.; Shen, J.; Xin, X.; Cui, L.; Chen, L.; Ouyang, C.; Shi, S.; Chen, L. Antisite defects and Mg doping in LiFePO4: a first-principles investigation. Appl. Phys. A: Mater. Sci. Process. 2011, 104, 529–537.

(41) Koh, W. Nobel Lecture: Electronic structure of matter-wave functions and density functions. Rev. Mod. Phys. 1999, 71, 1253–1266.

(42) Andersson, A. S.; Kalska, B.; Hägström, L.; Thomas, J. O. Lithium extraction/insertion in LiFePO4: an X-ray diffraction and Mossbauer spectroscopy study. Solid State Ionics 2000, 130, 41–52.

(43) Gao, Y.; Li, L.; Peng, H.; Wei, Z.-D. Surfactant-assisted Sol–Gel synthesis of nanostructured Ruthenium-doped Lithium Iron Phosphate as a cathode for Lithium-ion batteries. ChemElectroChem 2014, 12, 2146–2152.