Hierarchical LiFe$_{0.98}$M$_{0.02}$PO$_4$/C (M$^{II}$=Ni, Mn, Mg) composites via co-doping for lithium ion batteries

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Abstract. Hierarchical LiFe$_{0.98}$M$_{0.02}$PO$_4$/C (M$^{II}$=Ni, Mn, Mg) composites via co-doping with a variety of cations synthesized through carbothermal reduction assisted with spray pyrolysis are first studied. The physicochemical properties are characterized by X-ray diffraction (XRD), Elemental analyzer, Raman spectroscopy measurements, Field-emission scanning electron microscope (FE-SEM) and High-resolution transmission electron microscope (HR-TEM). The electrochemical performance is characterized via galvanostatic charge/discharge tests, Cyclic voltammetry (CV) test and Electrochemical impedance spectroscopy (EIS) measurement. The results show that successful co-doping with different substitution portfolios can stabilize the crystal structure. What’s more, trace ions incorporated into LiFePO$_4$ can also serve as catalyst for graphitization and crystal growth. Especially, among all the co-doped LiFe$_{0.98}$M$_{0.02}$PO$_4$/C (M$^{II}$=Ni, Mn, Mg) composites, LiFe$_{0.98}$Ni$_{0.01}$Mn$_{0.01}$PO$_4$/C exhibits the most outstanding electrochemical activities. The LiFe$_{0.98}$Ni$_{0.01}$Mn$_{0.01}$PO$_4$/C composite displays a high discharge capacity of ~135 mAh/g at 1 C with the capacity retention close to 95% after 100 cycles. The much more excellent ratability and superior cyclability of LiFe$_{0.98}$Ni$_{0.01}$Mn$_{0.01}$PO$_4$/C might be ascribed to the synergistic effect of vicariant lithium phosphates, that is, LiFePO$_4$, LiNiPO$_4$ and LiMnPO$_4$.

1. Introduction
Nowadays, to accommodate the imperative need of energy storage and conversion systems in portable electronics and automotive fields, many researchers have pursued to fabricate energy materials exhibiting favorable electrochemical properties [1, 2]. Since the olivine LiFePO$_4$ was first reported by Goodenough and his co-workers in 1997 [3], olivine-structured lithium-transition metal-phosphates, LiMPO$_4$ (M=Fe, Ni, Co, and Mn) has brought extensive interests over the past decades in view of their admirable theoretical capacity and environmentally friendliness [4-7].

Meanwhile, many striking strengths [8-10] such as stable voltage platform, potentially low cost, good thermal stability, desirable environmentally friendliness, alongside safety concern, undisputedly, make LiFePO$_4$ to be one of the most promising candidates for the next generation of lithium ion batteries. Nevertheless, as typically believed, its poor electronic conductivity ($\sim 10^{-9}$-$10^{-10}$ $\Omega^{-1}$cm$^{-1}$) [11],...
slow ionic diffusion (~10^{-14}-10^{-15} \text{ cm}^2/\text{s}) [12], and low working voltage (~3.5 V) [13] have hampered its high rate applications. Up to now, tremendous efforts have been devoted to address these problems including: 1) surface modification by coating ion-conductive layers [14, 15] and electron-conductive layers [15-16]; 2) bulk doping foreign atoms in the site of Li, Fe, P or O [17-19]; 3) morphology manipulation [20]; 4) structure optimization [21]. In general, it’s found that bulk doping leading to lattice distortion can increase electronic conductivity and lithium mobility effectively. Miscellaneous achievement on co-doping recently has been achieved. Ban et al. [17] fabricated Si-F co-doped LiFePO_4 and came up with its mechanism of donor-acceptor charge-compensating. Huang et al. [22] prepared magnesium and fluorine co-doped LiFe_{0.92}Mg_{0.08}(PO_4)_{0.99}F_{0.03}/C composite yielding 121 mAh/g at 0.1 C under the temperature of −20°C. However, among abovementioned examples concerning co-doping with a certain kind of cation and anion, there remain rare reports on co-doping with a variety of cations or anions.

As a consequence, we carried out our work to investigate the effect of substitution portfolios related to a variety of cations on electrochemical properties of LiFePO_4/C materials. Herein, LiFe_{0.98}M^{\text{II}}_{0.02}PO_4/C (M^{\text{II}}=\text{Ni, Mn, Mg}) composites via co-doping is synthesized through carbothermal reduction assisted with spray pyrolysis followed by a comprehensive investigation upon electrochemical performance and physicochemical properties.

2. Experimental

2.1. Preparation of electrode materials

Fig. 1 shows a brief schematic representation of proposed LiFe_{0.98}Ni_{0.01}Mn_{0.01}PO_4/C composite synthesis route and detailed experimental procedures are also given as follows. In a typical synthesis, a stoichiometric mixture of lithium dihydrophosphate (LiH_2PO_4, A.R, China Lithium, Shanghai), ferric oxide (Fe_2O_3, A.R, Aladdin Chemistry Co. Ltd., Shanghai), the desired amount of citric acid (C_6H_8O_7·H_2O, A.R, Shanghai Lingfeng Chemical Reagent Co. Ltd.), nickel acetate tetrahydrate (C_4H_6O_4Ni·4H_2O, A.R, Sinopharm Chemical Reagent Co. Ltd.), manganese acetate tetrahydrate (C_4H_6O_4Mn·4H_2O, A.R, Sinopharm Chemical Reagent Co. Ltd.) and deionized water were mixed and ball-milled for 2 h, followed by spray pyrolysis under hot air in rather short time to produce spherical particle. Note that the homogeneous mixing of the materials can be achieved via spray pyrolysis. After pyrolysis, carbothermal reduction was carried out under inert atmosphere at 650 °C for several hours to obtain a final LiFe_{0.98}Ni_{0.01}Mn_{0.01}PO_4/C composite. LiFe_{0.98}Ni_{0.01}Mg_{0.01}PO_4/C and LiFe_{0.98}Mn_{0.01}Mg_{0.01}PO_4/C composites were accordingly obtained under equimolar dopant. LiFePO_4/C composite was also synthesized in a similar fashion for comparison purpose without the addition of dopant.
2.2. Characterization
In order to characterize crystal structure of the synthesized sample, X-ray diffraction (XRD, D/MAX-B, Rigaku Co., Japan) with Cu Kα radiation (λ=0.15418 nm) was operated at 40 kV, 40 mA with a step of 0.02 degree/min, a scanning rate of 6.30 degree/min. The carbon content of samples were determined by Elemental analyzer (Vario EL III, Elementar Analysensysteme GmbH, Germany). Raman spectroscopy measurements were performed under Laser Micro-Raman Spectroscopy System (Raman, Invia, Renishaw Co., England) with a 514 nm excitation line upon samples. The morphology of the sample was observed under field-emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan) and high-resolution transmission electron microscope (HR-TEM, JEM-2100, JEOL, Japan).

2.3. Assembly of cells
For electrochemical measurements, cells were assembled with lithium metal disks as counter/reference electrodes. The working electrode was fabricated by dispersing 80 wt% electrode material, 10 wt% carbon black (Shanghai Haohua Chemical Co. Ltd.), and 10 wt% polyvinylidene fluoride (Shanghai Dongfu Chemical Technology Co. Ltd.) binder in N-methyl-2-pyrrolidone (Shanghai Lingfeng Chemical Reagent Co. Ltd.) as solvent to form a homogeneous slurry. The slurry was then coated on Al foil (Hefei Kejing Materials Technology Co. Ltd.), the current collector, with a coating thickness of 100 μm. The coated electrodes were dried in vacuum at 120 °C overnight. Finally, the two-electrode configuration (2016 stainless steel coin cell, Hefei Kejing Materials Technology Co. Ltd.), with working and counter/reference electrode sandwiched by a polypropylene separator (Shanghai Chemical Reagent) and a few drops of electrolyte (Guangzhou Tianci Materials Technology Co. Ltd.), was assembled in an Argon-filled glove box (Shanghai Mikrouna China Co. Ltd.) with oxygen and moisture content less than 0.1 ppm.

2.4. Electrochemical measurement
All the electrochemical measurements were implemented at room temperature. To characterize electrochemical performance of the synthesized sample, galvanostatic charge/discharge tests were conducted in the voltage range of 2.5-4.2 V via a battery tester (LAND CT2001A, Wuhan Land.) at a series of current rates. The discharge capacities of experiment cells were calculated on the mass of electrode materials.

Cyclic voltammetry (CV) test was performed to investigate reaction kinetics of the electrode in the voltage range of 2.5-4.2 V on an electrochemical workstation (CHI660D, Shanghai Chenhua) at various scanning rates. The lithium ion diffusion coefficient (\(D_{Li^+}\)) was calculated from the relationship between peak currents and the square root of scanning rates from the cyclic voltammetry curve.

Electrochemical impedance spectroscopy (EIS) measurement was also carried out on the same electrochemical workstation with the amplitude of 5 mV over the frequency range of \(10^5\) to \(10^{-2}\) Hz and data fitting was conducted with a fitting software (Zsimpwin). Last ten dots selected from the Nyquist plots were leveraged to derive ionic diffusivity of lithium (\(D_{Li^+}\)).

3. Results and discussion
X-ray diffraction analysis is employed to characterize crystal structure before and after ion co-doping. Fig. 2 shows X-ray diffraction patterns of LiFe_{0.98Ni0.01Mg0.01}PO_4/C, LiFe_{0.98Mn0.01Mg0.01}PO_4/C, LiFe_{0.98Ni0.01Mn0.01}PO_4/C and LiFePO_4/C composites. The intense diffraction peaks of samples are indexed well to the olivine structured LiFePO_4 with the space group of Pnma (JCPDS Card No. 81-1173) and no obvious impurity peaks are detected, suggesting that minor co-doping is not able to alter crystal structure of LiFePO_4/C. Otherwise, the XRD pattern of biphasic blend would be presented as broad integrated signals from individual peaks of each crystal [18]. What’s more, residual carbon during carbothermal reduction which is rather essential to enhance its electronic conductivity (~ 3.8 wt%, determined via elemental analysis) is not well crystallized. Lattice parameters are displayed in
Table 1. It is evident that lattice volume has a slight decrease upon co-doping, in good agreement with the fact that radius of nickel ion (0.69 Å), manganese one (0.60 Å) and magnesium one (0.66 Å) which are shorter than that of iron one (0.74 Å), therefore indicating the successful incorporation of metal ions abovementioned.

Table 1. Calculated lattice parameters and graphitization degree of samples.

| Samples                     | a (Å)  | b (Å)  | c (Å)  | V (Å³) | Ig/Io |
|-----------------------------|--------|--------|--------|--------|-------|
| No. 81-1173                 | 10.332 | 6.010  | 4.692  | 291.35 | -     |
| LiFePO₄/C                   | 10.339 | 6.000  | 4.693  | 291.19 | 1.14  |
| LiFe₀.₉₈Ni₀.₀₁Mn₀.₀₁PO₄/C   | 10.331 | 6.007  | 4.687  | 290.87 | 1.19  |
| LiFe₀.₉₈Mn₀.₀₁Mg₀.₀₁PO₄/C   | 10.329 | 6.008  | 4.686  | 290.80 | 1.15  |
| LiFe₀.₉₈Ni₀.₀₁Mg₀.₀₁PO₄/C   | 10.334 | 6.006  | 4.688  | 290.97 | 1.18  |

It is widely acknowledged that Raman spectroscopy could be utilized to distinguish the crystal phase from carbon phase, and further determine the quality of carbon coatings. It’s found that bands from 200 cm⁻¹ to 1100 cm⁻¹ corresponded to the vibrational motions of the crystal phase while bands from 1100 cm⁻¹ to 2000 cm⁻¹ were attributed to vibrations of carbon phase. Notably, the peaks observed at ~1356 cm⁻¹ and ~1606 cm⁻¹ owing to disordered carbon (sp³) and graphite carbon (sp²),
therefore, were named as D band and G band. Generally, the graphitization degree of carbon phase can be demonstrated by intensity ratios between graphite carbon (sp²) and disordered carbon (sp³), that is, \( I_G/I_D \). As presented in Fig. 3, the Raman spectra of samples are in good accord with the literature [23]. The bands below 400 cm\(^{-1}\) are attributed to lattice vibrations of LiFePO\(_4\) [24]. D band and G band are also detected, suggesting the composition of crystal LiFePO\(_4\) phase and amorphous carbon one. Table 1 lists calculated graphitization degree. As being listed, \( I_G/I_D \) is slightly increased with substitution, manifesting that the electrical conductivity would be improved with a more conductive thin carbon phase[16]. Besides, a bit higher graphitization degree of co-doped LiFePO\(_4\)/C composite partly shows that dopant could also be regarded as catalyst for graphitization and crystal growth.

![Raman spectra](image.png)

Fig. 3. Raman spectra of LiFe\(_{0.98}\)Ni\(_{0.01}\)Mg\(_{0.01}\)PO\(_4\)/C, LiFe\(_{0.98}\)Mn\(_{0.01}\)Mg\(_{0.01}\)PO\(_4\)/C, LiFe\(_{0.98}\)Ni\(_{0.01}\)Mn\(_{0.01}\)PO\(_4\)/C and LiFePO\(_4\)/C samples.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are widely applied to observe the morphology and microstructure of electrode materials, further illustrating the consequent superior electrochemical performance. From Fig. 4A, the morphology like haw cluster is observed, in good agreement with grape-like morphology reported in the literature [20] to some degree. It might be because of lattice distortion induced from ion co-doping that individual particles tended to stack with each other rapidly, thus controlled in a relatively small size and regular shape. The typical scanning electron microscopy (SEM) image of LiFe\(_{0.98}\)Ni\(_{0.01}\)Mn\(_{0.01}\)PO\(_4\)/C displayed in Fig. 4B reveals its hierarchy configuration. Furthermore, LiFe\(_{0.98}\)Ni\(_{0.01}\)Mn\(_{0.01}\)PO\(_4\)/C exhibits a fascinating surface structure, a sphere with handsome opening pores. Subsequently, above outstanding microstructure of LiFe\(_{0.98}\)Ni\(_{0.01}\)Mn\(_{0.01}\)PO\(_4\)/C finally makes it favorable for lithium ions to transport and electrolyte to access [23].

As presented in Fig. 4C and 4D, the selected transmission electron microscopy (TEM) micrographs of LiFe\(_{0.98}\)Ni\(_{0.01}\)Mn\(_{0.01}\)PO\(_4\)/C composite are observed at different magnifications. A dark area and some grayish dents surrounding it being shown in Fig. 4C are found consistent with that in reference [16]. With the increase of magnification at the grayish dents, it could be discovered that a layer of thin and transparent film with the thickness about ~5 nm, attributed to amorphous carbon, coated on the outer surface of the particles. The lattice fringe of LiFePO\(_4\) with a distance of ~ 0.458 nm matches well with the space of its (101) crystal plane.
Fig. 4. Scanning electron microscopy (SEM) images (A, B) and transmission electron microscopy (TEM) micrographs (C, D) of LiFe$_{0.98}$Ni$_{0.01}$Mn$_{0.01}$PO$_4$/C.

To illustrate the effect of ion co-doping, galvanostatic tests are conducted on samples and the results are shown in Fig. 5. Fig. 5A displays typical initial discharge profiles of LiFe$_{0.98}$Ni$_{0.01}$Mg$_{0.01}$PO$_4$/C, LiFe$_{0.98}$Mn$_{0.01}$Mg$_{0.01}$PO$_4$/C, LiFe$_{0.98}$ Ni$_{0.01}$Mn$_{0.01}$PO$_4$/C and LiFePO$_4$/C at 0.2 C, where C corresponds to the current rate. The obvious discharge potential plateau at ~3.5 V is attributed to the redox couple of Fe$^{3+}$/Fe$^{2+}$. Remarkably, the initial discharge profile of LiFe$_{0.98}$M$^{II}_{0.02}$PO$_4$/C (M$^{II}$=Ni, Mn, Mg) composite via co-doping sustains a longer potential plateau and higher capacity than LiFePO$_4$/C indicating the more Li$^+$ diffusion paths owing to ion co-doping [25]. When it comes to the efficiency of ion substitution, it seems that co-doping with nickel and manganese is more efficient than that with other substitution portfolios. As previous literature reported, LiNiPO$_4$ and LiMnPO$_4$ has been assumed to have much higher redox potential of ~5.2 V and ~4.29 V [26], thus making LiFe$_{0.98}$Ni$_{0.01}$Mn$_{0.01}$PO$_4$/C electrode a bit higher working voltage upon substitution with nickel and manganese. Notably, the higher working potential, more powerful electrical vehicle will be, showing a bright prospect of nickel and manganese incorporation into LiFePO$_4$. Meanwhile, as presented in Fig. 5B, LiFe$_{0.98}$Ni$_{0.01}$Mn$_{0.01}$PO$_4$/C composite prepared by carbothermal reduction combined with spray pyrolysis delivers a discharge capacity of 142.3 mAh/g, 137.7 mAh/g, 131.8 mAh/g, 118.3 mAh/g and 85.3 mAh/g at 0.2 C, 0.5 C, 1 C, 2 C and 5 C respectively while LiFePO$_4$/C only yields 126.9 mAh/g, 114.4 mAh/g, 100.3 mAh/g, 77.0 mAh/g and 45.3 mAh/g. It might be ascribed to the synergistic effect of vicariant lithium phosphates, that is, LiFePO$_4$, LiNiPO$_4$ and LiMnPO$_4$.

Fig. 5C reveals cyclabilities of LiFe$_{0.98}$Ni$_{0.01}$Mn$_{0.01}$PO$_4$/C and LiFePO$_4$/C when discharged at various current rates including 0.2 C, 1 C, 2 C, 5 C, 1 C and 0.2 C each for 5 times are presented in Fig. 5C. Discharge specific capacities of them fade as current rates increase whereas they are enabled to retrieve its capacity when lower current rates are applied later. In addition, it should be noted that the discharge specific capacity of LiFe$_{0.98}$Ni$_{0.01}$Mn$_{0.01}$PO$_4$/C composite seems to get easier access to recovery after high rate cycling. Therefore, the fabulous ratability could be ascribed to carbon layer, which partly buffers the phase transition during discharging. Besides, LiFe$_{0.98}$Ni$_{0.01}$Mn$_{0.01}$PO$_4$/C sustains a remarkable ratability, presenting a capacity retention of 97%, 93%, 83% and 60% at 0.5 C, 1 C, 2 C and 5 C (vs. the specific capacity at 0.2 C), respectively. Fig. 5D reveals cyclabilities of LiFe$_{0.98}$Ni$_{0.01}$Mn$_{0.01}$PO$_4$/C and LiFePO$_4$/C at 1 C and 5 C, respectively for 100 cycles. Over 100 cycling, LiFe$_{0.98}$Ni$_{0.01}$Mn$_{0.01}$PO$_4$/C almost maintains the capacity loss of around 6.3% and 37.7% (vs. the specific capacity at 0.2 C), accordingly at 1 C and 5 C, much lower than those of LiFePO$_4$/C composite (22.9% and 63.3%). The excellent cyclability of co-doped LiFePO$_4$/C further indicates intact crystal structure of LiFePO$_4$/C after co-doping, corroborating with XRD results.
Fig. 5. Electrochemical performance: A) typical initial discharge profiles of LiFe_{0.98}Ni_{0.01}Mg_{0.01}PO_4/C, LiFe_{0.98}Mn_{0.01}Mg_{0.01}PO_4/C, LiFe_{0.98}Ni_{0.01}Mn_{0.01}PO_4/C and LiFePO_4/C at 0.2 C; B) typical discharge capacities of LiFe_{0.98}Ni_{0.01}Mn_{0.01}PO_4/C and LiFePO_4/C at various current rates; C) discharge specific capacity of LiFe_{0.98}Ni_{0.01}Mn_{0.01}PO_4/C and LiFePO_4/C at various current rates; D) cyclabilities of LiFe_{0.98}Ni_{0.01}Mn_{0.01}PO_4/C and LiFePO_4/C at 1 C and 5 C, respectively for 100 cycles.

After rate test, working electrodes of the LiFe_{0.98}Ni_{0.01}Mn_{0.01}PO_4/C and LiFePO_4/C composite were investigated via cyclic voltammetry test and electrochemical impedance spectroscopy measurement to evaluate their electronic and ionic conductivities, thus further proving their electrochemical performance.

As displayed in Fig. 6A, the anodic and cathodic peaks appear on both curves are ascribed to extraction and insertion of Li⁺ during charging and discharging. Generally the profile of LiFe_{0.98}Ni_{0.01}Mn_{0.01}PO_4/C is sharper and more symmetric than that of LiFePO_4/C, verifying that the kinetics of redox reactions is accelerated due to the incorporation of Ni and Mn. On the other hand, the potential separation between redox peaks of LiFe_{0.98}Ni_{0.01}Mn_{0.01}PO_4/C and LiFePO_4/C composite is 0.30 V, much lower than that for LiFePO_4/C (0.41 V), suggesting an enhanced reversibility with the abatement of polarization. According to the Randle-Sevick equation, the Li⁺ diffusion coefficient could be deduced as well [27]. The Randle-Sevick equation is presented as follows,

\[
I_p = 2.69 \times 10^4 \times n^{1/2} \times A \times C \times D^{1/2} \times v^{1/2}
\]

where \(I_p\) is the peak current (A) during charge and discharge process, \(n\) is the number of electrons transferred per molecule, \(A\) is the surface area of the electrode (cm²), \(C\) is the concentration of Li⁺ (mol/cm³), \(D\) is the expected Li⁺ diffusion coefficient (cm²/s), and \(v\) is the scanning rate (V/s). It is worth noting that this equation can be used to calculate Li⁺ diffusion coefficient in not only solid phase (\(C_s = 2.291 \times 10^{-2}\) mol/cm³) but also liquid phase (\(C_l = 1.0 \times 10^{-3}\) mol/cm³). [28] Take LiFe_{0.98}Ni_{0.01}Mn_{0.01}PO_4/C composite as an example, cyclic voltammetry profiles at a series of scanning rates of 0.1, 0.2, 0.3, and 0.4 mV/s (Fig. 6B) reveal that the height and potential separation of redox peaks increase alongside the increment of scanning rate. Fitting linear, as shown in the inset of Fig. 6B, is obtained to find that Li⁺ diffusion coefficient are 4.176×10⁻¹¹ cm²/s and 2.192×10⁻⁸ cm²/s, accordingly in lattice and electrolyte. Overall, faster Li⁺ diffusion in lattice seems play a much more important role in improving electrochemical performance.

As an essential kind of electrochemical impedance spectroscopy, Nyquist plot is extensively employed. Fig. 6C presents the Nyquist plots of the LiFe_{0.98}Ni_{0.01}Mn_{0.01}PO_4/C and LiFePO_4/C composite and utilized equivalent circuit diagram. With the reduction of frequency from 10⁴ Hz to 10⁻² Hz, the Nyquist plot exhibits a compressed semicircle and a sloping line on both samples. The intercept at \(Z'\) axis in high frequency region corresponds to the electrolyte resistance (\(R_e\)) while the charge transfer resistance (\(R_{ct}\)) is ascribed to the radius of semicircle in high-to-medium frequency range. The slope of line in the low frequency region represents the Warburg impedance (\(W\)). The following formulas [29] are usually used to study reaction kinetics,
\[ Z = R_e + R_{ct} + \sigma_\omega \omega^{1/2} \]  \hspace{1cm} (2)

\[ D_i = \frac{1}{2} \times \left( \frac{RT}{A \times n' \times F^2 \times C_s \times \sigma_\omega} \right)^2 \]  \hspace{1cm} (3)

Here, \( \sigma_\omega \) is the Warburg factor (\( \Omega \text{ cm}^2/\text{s}^{1/2} \)) associated with \( \text{Li}^+ \) diffusion coefficient, \( \omega \) is the angular frequency (\( \omega = 2\pi f \)), \( D_i \) is the \( \text{Li}^+ \) diffusion coefficient in solid phase (cm\(^2\)/s), \( R \) is the gas constant (J mol\(^{-1}\)K\(^{-1}\)), \( T \) is the absolute temperature (K), \( A \) is the surface area of the electrode (cm\(^2\)), \( n \) is the number of electrons transferred per molecule, \( F \) is the Faraday constant (C/mol), \( C_s \) is the concentration of \( \text{Li}^+ \) (mol/cm\(^3\)). As seen in Fig. 6D, linear fitting of samples from the last ten dots is conducted. Derived fitting parameters are shown in Table 2. Obviously, the charge transfer resistance of LiFe\(_{0.98}\)Ni\(_{0.01}\)Mn\(_{0.01}\)PO\(_4\)/C composite is even less than half of LiFePO\(_4\)/C, demonstrating the improved charge carrier mobility for co-doped sample. Herein, sound proof manifested above make it rather clear that LiFe\(_{0.98}\)Ni\(_{0.01}\)Mn\(_{0.01}\)PO\(_4\)/C exhibits the most outstanding electrochemical activities among all the co-doped LiFe\(_{0.98}\)M\(_{\text{II}}\)\(_{0.02}\)PO\(_4\)/C (M\(_{\text{II}}\)=Ni, Mn, Mg) composites.

### Table 2. Derived impedance parameters and corresponding factors.

| Samples            | \( R_e (\Omega) \) | \( C_{dl} (\mu\text{F}) \) | \( R_{ct} (\Omega) \) | \( W (\Omega \text{ cm}^2/\text{s}^{1/2}) \) | \( \sigma_\omega \Omega \text{ cm}^2/\text{s}^{1/2} \) | \( D_i (\text{cm}^2/\text{s}) \) |
|--------------------|---------------------|-----------------------------|------------------------|--------------------------------|--------------------------------|-----------------------------|
| LiFe\(_{0.98}\)Ni\(_{0.01}\)Mn\(_{0.01}\)PO\(_4\)/C | 11.85               | 1.96                        | 267.1                  | 87.52                          | 34.157                          | 3.822×\(10^{-14}\)          |
| LiFePO\(_4\)/C     | 19.59               | 2.74                        | 694.1                  | 64.62                          | 35.495                          | 3.540×\(10^{-14}\)          |

\( R_e \) is electrolyte resistance; \( C_{dl} \) is double layer capacitance; \( R_{ct} \) is charge transfer resistance; \( W \) is Warburg impedance; \( \sigma_\omega \) is Warburg factor; \( D_i \) is \( \text{Li}^+ \) diffusion coefficient in solid phase.

A clear and precise link to electrochemical performance remains difficult to come up with despite a relatively detailed study. However, some common perception appears from the perspective of physicochemical properties and electrochemical performance discussed above: 1) trace ions incorporated can stabilize its crystal structure and control the crystal growth; 2) conformal carbon layer coated on the surface of LiFePO\(_4\) acts as a fantastic electronic bridge for the transfer of ions and electrons; 3) numerous inter-connected pores make electrolyte easier to penetrate into each particle,
thus transporting lithium ions quickly; 4) hierarchy configuration fabricated via spray pyrolysis constructs a super three-dimensional network architecture without undesirable deposition and aggregation in nano-sized materials.

4. Conclusions
In summary, we presented a cost-effective and time-efficient plot to obtain hierarchical LiFe$_{0.98}$M$^{II}_{0.02}$PO$_4$/C (M$^{II}$=Ni, Mn, Mg) composites. Regular morphology and uniform doping could be achieved through facile and scalable spray pyrolysis. Trace ions incorporated into LiFePO$_4$ can also serve as catalyst for graphitization and crystal growth. Among all the co-doped LiFe$_{0.98}$M$^{II}_{0.02}$PO$_4$/C (M$^{II}$=Ni, Mn, Mg) composites prepared by the same approach, LiFe$_{0.98}$Ni$_{0.01}$Mn$_{0.01}$PO$_4$/C shows particularly better electrochemical performance. When discharged at 1 C, LiFe$_{0.98}$Ni$_{0.01}$Mn$_{0.01}$PO$_4$/C composite exhibits a high discharge capacity of ~135 mAh/g with a capacity retention approaching 95% after 100 cycles. The much more excellent ratability and superior cyclability of LiFe$_{0.98}$Ni$_{0.01}$Mn$_{0.01}$PO$_4$/C might be ascribed to the synergistic effect of vicariant lithium phosphates, that is, LiFePO$_4$, LiNiPO$_4$ and LiMnPO$_4$. Consequently, approach above could also be employed to other cathode and anode materials, promoting the development of next-generation electrochemical energy storage devices.

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