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Heterogeneous carbon/N-doped reduced graphene oxide wrapping LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ composite for higher performance of lithium ion batteries

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Abstract:

In this work, heterogeneous carbon/N-doped reduced graphene oxide wrapping LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ (LMFP/C/N-rGO) composites were synthesized successfully via a simple solvothermal method coupled with further calcination. The composites were characterized by XRD, SEM, TEM and XPS, and their electrochemical properties were evaluated by CV, EIS and charge-discharge test. The LiMn$_{0.8}$Fe$_{0.2}$PO$_4$/C particles were uniformly grown on the surface of three-dimensional N-doped reduced graphene oxide (N-rGO). The interconnected N-rGO among LMFP particles and amorphous carbon coating on LMFP surface build a continuous conductive network which helps the fast transmission of electron. Lithium ion batteries with LMFP/C/N-rGO exhibit superior discharge capacity, rate capability and cycling stability, bringing a broad prospect for the future applications.
Keywords: LiMn\textsubscript{0.8}Fe\textsubscript{0.2}PO\textsubscript{4}; N-doped reduced graphene oxide; Lithium ion battery; Cathode material

1. Introduction

Along with the increasing pressure brought by energy crisis and environmental pollution, the demand for green energy storage devices is growing stronger. As one of the promising storage technology, lithium ion batteries (LIBs) have been widely used in mobile phones, laptops, electrical vehicles (EVs) and hybrid electrical vehicles (HEVs) [1-3]. The LIBs mostly consist of electrolyte, isolation material, anode and cathode material. The cathode material directly affects the performance of LIBs, and its cost directly determines the commercialization process of LIBs. Increasing the research on cathode materials is the most effective way to improve the performance of LIBs.

Among many cathode materials, olivine structure phosphate-based compounds, LiMPO\textsubscript{4} (M=Fe, Mn, etc.) have been widely studied in the past decades for their large discharge capacity, high stability, reasonable price, safety and environmental friendliness [4-6]. Compared to the commercial LiFePO\textsubscript{4} (LFP), LiMnPO\textsubscript{4} (LMP) has a larger potential plateau of 4.1 V (3.4 V for LFP), which can bring higher energy density. However, the inherent poor electronic conductivity ($<10^{-10}$ S·cm$^{-1}$) and low lithium-ion diffusion coefficient ($<10^{-16}$ cm$^2$·s$^{-1}$) are even worse than that of LFP [7-9]. Last several years, LiMn$_{1-x}$Fe$_x$PO$_4$ (LMFP) solid solution material formed by substitution of Mn$^{2+}$ with Fe$^{2+}$ is favored by researchers, which can not only promote the electrical conductivity, suppress Jahn-Teller effect but also provide larger discharge voltage and
energy density [10-12]. Furthermore, some other modification methods such as nanosizing, carbon coating are still employed to improve its electrochemical performance.

To date, various carbon conductive layers such as amorphous carbon, reduced graphene oxide (rGO) and carbon nanotubes are frequently used to surmount the poor electronic conductivity [13-16]. Among them, rGO receives extensive attention and widespread application for its excellent electronic conductivity, large specific surface area and good structural flexibility [17, 18]. Moreover, it is recently reported that doping with heteroatom, especially nitrogen, can effectively enhance the electronic conductivity of rGO [19-21]. Nitrogen located in the VA group, adjacent to carbon, and they have very similar atomic structure, doping with nitrogen does not destroy the crystalline structure of carbon materials. The lone pair of electrons carried by nitrogen atoms can increase the charge density of the material and provide more electron carriers in the conduction band thus enhance the electronic conductivity. And, the nitrogen-containing function groups can enhance the wettability of rGO [21-23].

At present, there are limited papers about N-doped graphene or N-doped reduced graphene oxide (N-rGO) used in cathode materials. Early work by Kim et al. [23] fabricated the LiFePO₄/N-doped reduced graphene oxide nanocomposite using urea as nitrogen source and demonstrated a capacity of 166 mAh·g⁻¹ at 0.5 C. Recently, Wang et al. [24] prepared N-doped graphene decorated LiFePO₄@C composite. Cui et al. [25] modified Li₃V₂(PO₄)₃/C with N-doped graphene nanosheets which was synthesized by
sintering graphene at 850 °C for 1 h in NH₃ atmosphere. All the N-doped graphene mentioned above were nanosheets with a two-dimensional structure.

In our previous work, Wang et al. [26] prepared graphene-LiMn₀.₈Fe₀.₂PO₄/C composites with graphene added after dispersed in ethylene glycol-water during solvothermal method. Liu et al. [27] developed an iron-assisted carbon coating strategy to guide the formation of uniform and highly graphitized carbon layers on surfaces of the LiMn₀.₈Fe₀.₂PO₄ to yield cathode materials with improved electrochemical performance. Here, we attempt to construct the three-dimensional N-rGO in a simple and eco-friendly method and use it to improve the electronic conductivity of LMFP. GO can be easily N-doped by urea, reduced to rGO and self-assembled into three-dimensional structures through the π-π conjugation effect among GO sheets. The synergetic effect of N-rGO conductive network among LMFP particles and amorphous carbon on LMFP surface was particularly analyzed. The resulting composite materials and batteries were investigated and analyzed in detail by various analytical methods.

2. Experimental

2.1. Synthesis of materials

GO was purchased from Suzhou Tan Feng graphene Tech Co.,Ltd. All the remaining reagents were obtained from Tianjin Feng Chuan Chemical Reagent Technologies Co.,Ltd and were directly used without treatment.

The N-rGO was synthesized by a simple and pollution-free hydrothermal reaction. First, 180 mg GO was well dispersed in 360 ml deionized water with ultrasonic
treatment for 2 h; then, 3.6 g urea was added to the GO solution followed by stirring for another 1 h. The final solution was transferred to a 200 ml Teflon-lined stainless steel autoclave and heated at 160 °C for 3 h. GO was easily N-doped by urea, reduced to rGO and self-assembled into three-dimensional structures. After the reaction finished, the autoclave was naturally cooled to room temperature, and the final product was washed by water until the solution become neutral. The N-rGO powders were obtained by freeze-drying overnight.

The LMFP/C/N-rGO composites were synthesized by a simple hydrothermal method with further heating treatment as schematically illustrated in Fig. 1. The N-rGO powder (2 wt% of the theoretical weight of LMFP) was pre-sonicated in water to prepare uniform dispersions. Typically, the N-rGO dispersion and a stoichiometric number of MnSO₄·H₂O, FeSO₄·7H₂O, H₃PO₄ (85 wt%) and ascorbic acid were dissolved in ethylene glycol-water mixed solution. Then the solution of LiOH·H₂O was added dropwise into the above solution and kept a molar ratio of Li:Mn/Fe:P fixed at 3:1:1. The suspension was vigorously stirred for 20 min under the nitrogen atmosphere, and then transferred into a 200 ml Teflon-lined stainless steel autoclave and heated at 240 °C for 4 h. After cooling to room temperature, the gray precipitate was filtered, thoroughly washed respectively with ethanol and deionized water and dried at 45 °C for 12 h. For the carbon coating on the surface of LMFP, the obtained products were then mixed with glucose and heated at 350 °C for 3 h, then carbonized at 650 °C in a tube furnace under nitrogen atmosphere. As a contrast, the samples without N-rGO were also fabricated
and named LMFP/C. Samples with rGO but without N-doping were named as LMFP/C/rGO composites. The carbon content of LMFP/C was 7 wt% while the carbon content of LMFP/C/rGO and LMFP/C/N-rGO was 9 wt% (7% amorphous carbon + 2 wt% rGO or N-rGO).

Fig. 1. Depiction of the synthesis process of heterogeneous carbon/N-doped reduced graphene oxide wrapping LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ composite

2.2. Characterizations

The crystal structure of the as-prepared samples was characterized by X-ray diffraction (XRD, Bruker D8 Advance, Germany) with Cu Kα radiation in the 2θ range of 10~80° at the scan rate of 6°/min. The Raman spectrum was performed by DXR Microscope spectroscopy with 532 nm blue laser beam. The morphology and structure were carried out by scanning electron microscope (SEM, FEI NanoSEM450, America) and transmission electron microscopy (TEM, JEOL JEM-2800, Japan). The composition of LMFP/C/N-rGO was studied by X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB250Xi, America).
2.3. Electrochemical measurements

The working electrodes were prepared by blending the active material, Super-P and polyvinylidene fluoride at a weight ratio of 8:1:1. The slurries were spread on Al foil and dried at 120 °C in a vacuum oven for 12 h. The Al foil was then cut into small circles with 14 mm in diameter. The metallic lithium was used as anode. The electrolyte was 1 mol·L⁻¹ LiPF₆ dissolved in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) at volume ratio of 1:1:1. And the PP/PE/PP film (Celgard 2400) was used as the isolation material. All coin-type half cells were assembled in an argon-filled dry glove box and further tested at 25 °C. The charge-discharge tests were carried out using a program-controlled Battery Test System (CT-2001A, Land, Wuhan, China). And the cells were charged at a constant current-constant voltage (CC-CV) protocol and discharged at a galvanostatic protocol in the voltage range of 2.0-4.6 V. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed by the electrochemistry workstation (CHI650B, Chenhua, Shanghai, China).

3. Results and discussion

3.1. Characterization of the structure and morphology

Fig. 2 shows the XRD patterns of the LMFP/C, LMFP/C/rGO and LMFP/C/N-rGO samples. All the diffraction peaks match well with the standard pattern of the olivine phase of LiMnPO₄ with Pnmb space group (JCPDS # 74-0375), and no other impurity peaks are observed. The sharp diffraction peaks suggest the good crystalline of the
LMFP/C/rGO and LMFP/C/N-rGO particles, indicating that rGO or N-rGO does not affect the LiMnPO₄ crystal structure [28]. The carbon phase is barely observed in the samples, suggesting the residual carbon from glucose pyrolysis exists in amorphous form. The diffraction peaks of reduced graphene oxide were not found for the relatively low content of rGO and N-rGO.

![XRD patterns of the LMFP/C, LMFP/C/rGO and LMFP/C/N-rGO.](image)

Raman spectroscopy was further used to analyze the structure of carbon undetected by XRD and the results are shown in Fig. 3. All of the three samples contain two strong peaks at around 1348 and 1600 cm⁻¹ attributing to D-band and G-band, respectively, where D-band stands for the disorders or defects in carbon and G-band represents the graphitic carbon. The intensity ratio between D and G band symbolises the degree of the defects on the surface of carbon. The I_D/I_G ratios of the LMFP/C, LMFP/C/rGO and LMFP/C/N-rGO are 0.853, 0.899 and 0.910, respectively. The LMFP/C/N-rGO shows higher I_D/I_G values standing for more defects after N-doping. This is consistent with previous N-doped graphitic materials [29, 30].
Fig. 3. Raman spectra of the LMFP/C, LMFP/C/rGO and LMFP/C/N-rGO

The surface morphology of N-rGO is characterized by scanning electron microscopy (SEM) as shown in Fig. 4a. The N-rGO contains many flakes with about 10 microns in size. And the flakes stack together to form a three-dimensional structure. There is no difference between GO and N-rGO whether in shape or in size, except for nitrogen doping. The open channels among the interconnected N-rGO can ensure the penetration of electrolyte thus facilitate the diffusion of Li\(^+\) which should beneficial for the rate performance. Fig. 4b–d shows the microscopy of LMFP/C, LMFP/C/rGO and LMFP/C/N-rGO. LMFP/C particles present uniform rod-like shape with around 300 nm in length. The distribution of particles is relatively uniform and there is no agglomeration occurred. From Fig. 4c and Fig. 4d, LMFP particles with smaller size are grown on the surface of both rGO and N-rGO. The addition of rGO and N-rGO doesn’t change the rod-like structure but partly limits the growth of LMFP crystals. Profited from the increased wettability by nitrogen-containing function groups, the contact between N-rGO and LMFP is closer and more uniform than that between rGO
and LMFP.

TEM and HRTEM were further utilized to investigate the microstructure of LMFP/C/N-rGO as shown in Fig. 4e and Fig. 4f. LMFP particles present rod-like structure with 200~300 nm in size, consistent with SEM results. The LMFP/C particles are uniformly grown on the surface of N-rGO. Fig. 4f shows the HRTEM of LMFP/C/N-rGO, the LMFP is tightly coated by the thin amorphous carbon layer with a thickness of about 2 nm, through which the Li$^+$ can easily pass [16, 31]. The interconnected N-rGO combining with amorphous carbon formed a continuous conductive network for the fast transmission of electrons.
Fig. 4. SEM images of (a) N-rGO, (b) LMFP/C, (c) LMFP/C/rGO, (d) LMFP/C/N-rGO; (e) TEM images of LMFP/C/N-rGO and (f) HRTEM images of LMFP/C/N-rGO

The X-ray photoelectron spectroscopy (XPS) was utilized to further examine the composition and the chemical state of the atoms in LMFP/C/N-rGO. The full XPS spectrum of LMFP/C/N-rGO exhibits the binding energy at 60.62 eV for Li 1s, 139.51 eV for P 2p, 298.62 eV for C 1s, 410.62 eV for N 1s, 539.22 eV for O 1s, 660.62 eV for Mn 2p, and 740.62 eV for Fe 2p, respectively. The O 1s spectrum can be divided into four peaks at 530.9, 531.6, 532.1 and 533.4 eV corresponding to O-P, O-C, O=C and O-C=O, respectively [32, 33]. The N1s spectrum in Fig. 5c contains three components: the pyridine N at 398.5 eV, the pyrrolic N at 400.4 eV and the graphitic N at 401.4 eV. The graphitic N formed when carbon atoms in the hexagon grid within the graphene layers are substituted by nitrogen atoms. Addition to three single bonds, graphitic N has two electrons and an empty orbital that can form $\pi$ bonds. The graphitic N has one more electron than C, which can enhance the electrical conductivity N-rGO [27, 34, 35]. The C 1s spectrum in Fig. 5d consists of five peaks at 284.8, 285.8, 286.7, 287.9 and 289.8
eV, respectively ascribed to C-C, C-N, C-O, C=O and O-C=O. The existence of C-N bond in LMFP/C/N-rGO further confirms the formation of N-rGO.

Fig. 5. (a) Full XPS spectra of LMFP/C/N-rGO; High resolution XPS spectra of LMFP/C/N-rGO: (b) O 1s, (c) N 1s, (d) C 1s.

3.2 Electrochemical performance

Fig. 6a shows the initial charge-discharge curves of LMFP/C, LMFP/C/rGO and LMFP/C/N-rGO at 0.2 C within a voltage from 2.0 V to 4.6 V. There are two voltage plateaus at around 3.6 V and 4.1 V which could respectively be attributed to the redox reaction of Fe$^{2+}$ $\leftrightarrow$ Fe$^{3+}$ and Mn$^{2+}$ $\leftrightarrow$ Mn$^{3+}$ in all three samples. However, the charge-discharge curves of LMFP/C/N-rGO shows an unexpected plateau at around 3.3
V, which may be influenced by external factors, such as the instability of electrolyte and the instability of battery system. At 0.2 C, the discharge capacity of LMFP/C/N-rGO, LMFP/C/rGO and LMFP/C are 156.7, 152 and 147.1 mAh·g⁻¹ showing that the N-rGO can significantly enhance the discharge capacity of the sample. The conductive network formed by N-rGO and amorphous carbon can connect the LMFP particles with each other so that more particles can participate in the charge-discharge process causing the higher discharge capacity [36, 37]. Furthermore, the inset of Fig. 6a is the partially enlarged drawing of the initial charge-discharge profiles, the voltage interval between the charge and discharge plateaus of LMFP/C/N-rGO is 0.165V which is much lower than that of LMFP/C/rGO (0.238V) and LMFP/C (0.236V). The smaller voltage interval means the smaller polarization, which might ascribe to the improved electronic conductivity by the introduction of N-rGO. The electronic conductivity of N-rGO, rGO and amorphous carbon were measured by four-probe meter (SDY-4, China). As shown in Table 1, the electronic conductivity of N-rGO was higher than rGO and amorphous carbon, which further demonstrated that the N-doping indeed enhance the conductivity of rGO.

Table 1 Comparisons of the conductivity of N-rGO, rGO and amorphous carbon

<table>
<thead>
<tr>
<th>Samples</th>
<th>Conductivity(S·cm⁻¹)</th>
</tr>
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<tbody>
<tr>
<td>N-rGO</td>
<td>254.06</td>
</tr>
<tr>
<td>rGO</td>
<td>165.87</td>
</tr>
<tr>
<td>amorphous carbon</td>
<td>0.44</td>
</tr>
</tbody>
</table>
Shown in the Fig. 6b is the discharge curves of LMFP/C/N-rGO from 0.2 C to 10 C. The specific discharge capacities of LMFP/C/N-rGO are 156.7, 148.2, 135.4, 118.3, 99.4 and 70.3 mAh·g\(^{-1}\) at 0.2, 0.5, 1, 2, 5 and 10 C, respectively. The comparison of rate performance for LMFP/C, LMFP/C/rGO and LMFP/C/N-rGO at different rates are performed in Fig. 6c. With the increase of the rate, the discharge capacity drops due to the one-dimensional Li\(^+\) diffusion channel which is the inherent nature of the material. It is clearly seen that LMFP/C/N-rGO shows a higher discharge capacity than LMFP/C/rGO and LMFP/C at different rate. For example, at 0.2 C LMFP/C/N-rGO exhibits a discharge capacity of 155 mAh·g\(^{-1}\) which is higher than that of LMFP/C/rGO (152.5 mAh·g\(^{-1}\)) or LMFP/C (147.4 mAh·g\(^{-1}\)). This can be observed much easier when the rate increased to 10 C. LMFP/C/N-rGO can still exhibits 51.9% of the initial discharge capacity while LMFP/C can only possess 27.8%. After 30 cycles, the cell is further charged and discharged at 0.2 C again. The discharge capacity of LMFP/C/N-rGO recovers to 154.1 mAh·g\(^{-1}\) which is almost the same as the incipient capacity. All the results indicate that with the addition of N-rGO, LMFP/C/N-rGO shows the better rate performance. Compared with rGO, N-rGO showed higher electronic conductivity. More importantly, the introduced nitrogen-containing functional groups increased the wettability between graphene and organic electrolyte, leading to the improved lithium-ion transport and lower polarization. Those two factors contribute
to why the electrochemical performance of LMFP/C/N-rGO improved. The results align with the previously reported papers [21].

Fig. 6d is the long-term cycling performance of LMFP/C, LMFP/C/rGO and LMFP/C/N-rGO at 0.2 C. It is shown that the cyclic curve of LMFP/C/N-rGO is much flatter than the other two samples. After 100 cycles, the discharge capacity of LMFP/C/N-rGO can still maintain 145.5 mAh·g⁻¹ with the capacity retention of 92.8%, while the other two samples can only maintain 90.3% and 86.7%. The N-rGO can improve the cyclic ability of materials due to the following reasons: (i) The N-doping greatly enhanced the electronic conductivity of rGO, and the introduced nitrogen-containing functional groups increased the wettability between graphene and organic electrolyte, leading to the smaller polarization which is beneficial to the cycle ability of LMFP/C/N-rGO. (ii) The existence of N-rGO accommodated the volume change of the electrode during Li⁺ insertion/extraction.
Fig. 6. (a) The initial charge/discharge curves of LMFP/C, LMFP/C/rGO, LMFP/C/N-rGO at 0.2 C, (b) The discharge curves of LMFP/C/N-rGO at different rates, (c) The rate performance at various discharge rates of LMFP/C, LMFP/C/rGO and LMFP/C/N-rGO (d) The cycling performances of LMFP/C, LMFP/C/rGO and LMFP/C/N-rGO at 0.2 C.

The synergy effect of N-rGO and amorphous carbon plays an important role in improving the electrochemical performance of LMFP. N-rGO is micron scale, and it is difficult to completely encapsulate every nano-scaled LMFP particles. At this time, the amorphous carbon is introduced to completely cover the surface of LMFP to overcome its initial disadvantages of insufficient electronic conductivity. LMFP particles are close to insulator, the surface amorphous carbon increases its conductivity, enabling the transmission of electrons. However, the conductivity of amorphous carbon is far less than that of N-rGO, so is the electronic transmission ability. In the whole composite materials, electrons travel through the system just like buses. Although amorphous carbon acted as the channel for electron transmission, but it is too narrow. Here, the LMFP/C particles are adhered on the surface of N-rGO. Benefit by the ultra-high conductivity, the N-rGO acted as a highway for the fast transmission of electronics,
while amorphous carbon is the narrow branches of the highway. When there is no N-rGO, electrons are forced to travel on the narrow branches. But, when electrons encounter with N-rGO, it is preferentially transmitted on the N-rGO highway. N-rGO and amorphous carbon together form a continuous conductive network for the fast transmission of electrons, as showed in Fig.7. Furthermore, the open channels among the interconnected N-rGO can ensure the penetration of electrolyte thus facilitate the diffusion of Li$^+$. N-rGO can also partly limit the growth of LMFP crystals, shorten the diffusion path of Li$^+$ which are beneficial for the rate performance. All these factors contribute to the improvement of the electrochemical performance of LMFP.

Fig. 7 The diagram of mechanism for electronic transmission in the conductive network formed by N-rGO and amorphous carbon

Fig. 8a shows the cyclic voltammograms for LMFP/C, LMFP/C/GO and LMFP/C/N-rGO performed in a potential range of 2.0-4.5 V at a scan rate of 0.1 mV/s. All the three samples present two pairs of redox peaks at around 3.5 V and 4.1 V, corresponding to the transformation of Fe$^{2+}$/Fe$^{3+}$ and Mn$^{2+}$/Mn$^{3+}$. For LMFP/C, the
voltage gaps between $Fe^{2+}/Fe^{3+}$ and $Mn^{2+}/Mn^{3+}$ are 0.406 V and 0.195 V. For LMFP/C/rGO, the gap decreases to 0.388 V and 0.184 V. With the addition of N-rGO, the voltage gaps decrease more quickly to 0.372 V and 0.145 V, indicating higher reversibility and electrochemical activity of LMFP/C/N-rGO. Also, higher peak current of LMFP/C/N-rGO is observed compared with LMFP/C and LMFP/C/rGO, which reflected to higher specific capacity in keeping with the previous charge/discharge tests. Fig. 8b shows the CV curves of the LMFP/C/N-rGO at the scan rate of 0.1~0.4 mV/s, along with the illustration of the peak currents and the square root of scan rate. The linear relationship means that the intercalation and deintercalation behavior of $Li^+$ in the material are diffusion-controlled.

Electrochemical impedance spectroscopy (EIS) measurements were also performed to study the $Li^+$ transport kinetics and internal resistance of LMFP/C, LMFP/C/rGO and LMFP/C/N-rGO, as displayed in Fig. 8c. All the curves consist of two parts: the semicircle at high frequencies and the straight line at low frequencies. The high frequency intercept impedance is attributed to the uncompensated resistance ($R_s$) including the contact resistance among particles, the resistance of electrolyte, and the resistance between the electrode and current collector. The semicircle corresponds to the charge transfer resistance ($R_{ct}$) at the interface between electrode and electrolyte. The slope symbolizes the Warburg impedance ($W_s$), which reflects $Li^+$ diffusion on the crystal lattice of electrode materials [38, 39]. The plots are fitted by Z-view based on the equivalent circuit inserted in Fig. 8c and the fitting results are summarized in Table 1.
The charge transfer resistances of LMFP/C, LMFP/C/rGO and LMFP/C/N-rGO are 369.1, 216.1 and 110.4 Ω, respectively. It is obvious that the charge transfers resistance of LMFP/C/N-rGO is significantly reduced, probably due to the improved electronic conductivity by the continuous conductive network.

The apparent Li\textsuperscript{+} diffusion coefficients (D) could be calculated using the following equation [7, 40]:

$$D = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2}$$  \hspace{1cm} (1)

where R is the gas constant, T is the absolute temperature (K), A is the surface area of the cathode (cm\textsuperscript{2}), n is the number of electrons involved in the redox process, F is the Faraday constant, C is the Li\textsuperscript{+} concentration, and σ is the Warburg factor associated with Z’ which can be calculated using the following equation [24]:

$$Z’ = R_c + R_{ct} + \sigma \omega^{-1/2}$$  \hspace{1cm} (2)

The fitting curves of Z’ and the inverse square root of angular frequency (ω\textsuperscript{-1/2}) are shown in Fig. 8d. The lithium ion diffusion coefficients of LMFP/C, LMFP/C/rGO and LMFP/C/N-rGO are calculated to be 1.89×10\textsuperscript{-14}, 4.77×10\textsuperscript{-14} and 1.33×10\textsuperscript{-13} cm\textsuperscript{2}·s\textsuperscript{-1} respectively. The LMFP/C/N-rGO shows a higher lithium ion diffusion coefficient than LMFP/C/rGO. Considering that the same electrolyte was used and samples had nearly same particle sizes, the improvement of lithium ion diffusion coefficients was due to the introduction of N. N-doping in graphene not only enhanced its electronic conductivity, but also improved the wettability between graphene and organic electrolyte. Therefore, the N-rGO built more efficient pathways for both Li\textsuperscript{+} and electron compared with
pristine rGO, leading to improved Li$^+$ transport [30,41]. What’s more, N induced defects to lower the activation energy for Li$^+$ diffusion, thus increasing the Li$^+$ diffusion rate [42]. These two factors lead to the increase of lithium ion diffusion coefficient.

Fig. 8. (a) CV curves of LMFP/C, LMFP/C/rGO and LMFP/C/N-rGO at a scan rate of 0.1 mV/s, (b) CV curves of LMFP/C/N-rGO at different scan rates, (c) EIS profiles of LMFP/C, LMFP/C/rGO and LMFP/C/N-rGO, (d) The fitting curves of $Z'$ and reciprocal square root of the angular frequency at low frequency region of LMFP/C, LMFP/C/rGO and LMFP/C/N-rGO.
Table 2 The fitting resistance values of LMFP/C, LMFP/C/rGO and LMFP/C/N-rGO

<table>
<thead>
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<th>Samples</th>
<th>Rs/(Ω)</th>
<th>Rct/(Ω)</th>
<th>σ/(Ω s(^{1/2}))</th>
<th>D/(cm(^2)s(^{-1}))</th>
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<tr>
<td>LMFP/C</td>
<td>5.4</td>
<td>369.1</td>
<td>115.4</td>
<td>1.89×10(^{-14})</td>
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<tr>
<td>LMFP/C/rGO</td>
<td>3.78</td>
<td>216.1</td>
<td>72.74</td>
<td>4.77×10(^{-14})</td>
</tr>
<tr>
<td>LMFP/C/N-rGO</td>
<td>6.8</td>
<td>110.4</td>
<td>43.57</td>
<td>1.33×10(^{-13})</td>
</tr>
</tbody>
</table>

4. Conclusion

In summary, heterogeneous carbon/N-doped reduced graphene oxide wrapping LiMn\(_{0.8}\)Fe\(_{0.2}\)PO\(_4\) (LMFP/C/N-rGO) composites have been synthesized via a simple solvothermal method successfully. Compared with LMFP/C and LMFP/C/rGO, the LMFP/C/N-rGO exhibits higher discharge capacity, better rate capability and better cycling stability. The interconnected N-rGO among LMFP particles and amorphous carbon coating on the surface of LMFP bridge a continuous conductive network which helps the fast transmission of electron, leading to the excellent electrochemical performance of lithium ion batteries with LMFP/C/N-rGO. In general, N-rGO plays an active role in improving electrochemical properties of LMFP, which can also be applied to other electrode materials to enhance their electronic conductivity.

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Graphical abstract
HIGHLIGHTS

- Heterogeneous carbon/N-doped reduced graphene oxide wrapping LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ composites were synthesized by solvothermal method coupled with further calcination.

- The unique heterogeneous carbon/N-doped reduced graphene oxide structure enhances the electronic conductivity of LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ particles, leading to better electrochemical performance.

- The interconnected N-rGO among LMFP particles and amorphous carbon coating on the surface of LMFP bridge a continuous conductive network which helps the fast transmission of electron.