Cl$^-$ Doping Strategy to Boost the Lithium Storage Performance of Lithium Titanium Phosphate

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Because of energy storage limitations and the high demand for energy, aqueous rechargeable lithium batteries (ARLBs) are receiving widespread attention due to their excellent performance and high safety. Lithium titanium phosphate (LiTi$_2$(PO$_4$)$_3$) exhibits the potential to serve as anodes for ARLBs because it has a three-dimensional channel and a stable structure. We employed an anion (Cl$^-$) doping strategy to boost the lithium storage performance of LiTi$_2$(PO$_4$)$_3$. A series of LiTi$_2$(PO$_4$)$_3$/C composites doped with Cl$^-$ on PO$_4^{3-}$ were successfully synthesized with a sol-gel technique as anodes for ARLBs. The effects of chlorine doping with different content on the properties of LiTi$_2$(PO$_4$)$_3-x$Cl$_x$/C ($x = 0.05$, 0.10, and 0.15) were investigated systematically. The doping of chlorine in appropriate amounts did not significantly impact the main structure and morphology of LiTi$_2$(PO$_4$)$_3$/C. However, chlorine doping greatly increased the performance of LiTi$_2$(PO$_4$)$_3$/C. LiTi$_2$(PO$_4$)$_{2.9}$Cl$_{0.3}$/C (LCl-10) showed the best electrochemical properties. It delivered a discharge capacity of 108.5 and 85.5 mAh g$^{-1}$ at 0.5 and 15$^\circ$C, respectively, with an increase of 13.2 and 43.3 mAh g$^{-1}$ compared to blank LiTi$_2$(PO$_4$)$_3$ (LCl). In addition, the discharge capacity of LCl-10 was maintained at 61.3% after 1,000 cycles at 5$^\circ$C, implying an apparent improvement compared to LCl (35.3%). Our study showed that a chlorine-doped LiTi$_2$(PO$_4$)$_3$/C composite is a potential anode for high-performance ARLBs.

Keywords: aqueous rechargeable lithium batteries, anode, anion doping, lithium titanium phosphate, electrochemical performance
INTRODUCTION

With the advancement of modern society, environmental pollution, and energy shortages have become more serious (He et al., 2019; Jiang et al., 2019; Zhou et al., 2019; Huan et al., 2020; Li et al., 2020a,b). Electrical energy can be derived from various other forms of energy, however, as an effective means to solve these problems. The secondary battery system is a necessary device for energy conversion and storage (Wu et al., 2017; Fang et al., 2019; Yang et al., 2019; Lu et al., 2020). The needs of high-performance electronic devices and electric vehicles have motivated the rapid development of lithium-ion batteries (LIBs) in recent years. The demand for LIBs offering high energy density, low pollution, and long life has rapidly increased (Wang et al., 2012; Zhao et al., 2016; Hua et al., 2018; Zhang et al., 2020). Conventional LIBs typically use organic electrolytes, which have demonstrated poor rate performance and potential safety hazards. ARLBs can efficiently solve these problems because they are environmentally friendly, highly secure, and inexpensive (Zhu et al., 2016; Lakhnot et al., 2019). Indeed, many cathodes of ARLBs exhibit remarkable electrochemical performance, such as LiMn$_2$O$_4$ (Manjunatha et al., 2011), LiFePO$_4$ (He et al., 2011), and LiCoO$_2$ (Ruffo et al., 2011).

Compared to cathodes, the restricted performance of anodes cannot meet the need for high-performance from ARLBs. Excellent anode materials are a limiting factor for the development of ARLB. Currently, vanadium oxide [VO$_2$ (Li et al., 1994)] and vanadate [LiV$_2$O$_8$ (Zhao et al., 2011), NaV$_3$O$_8$ (Zhou et al., 2013)] have been used as anode materials. Nonetheless, these ARLB anodes have problems such as low capacity, poor cycle stability, and low rate performance. In recent times, the NASCION LiTi$_2$(PO$_4$)$_3$ anode for ARLBs has shown great potential because it has a three-dimensional channel and a stable structure (Huang et al., 2015). A NASCION-type structure is marked by an open framework, which accelerates the diffusion of Li$^+$ ions in crystal. TiO$_6$ octahedra and PO$_4$ tetrahedra comprise the LiTi$_2$(PO$_4$)$_3$ framework unit. The TiO$_6$ octahedron is connected to the PO$_4$ tetrahedron, and the structure contains a large gap channel (Vidal-Abarca et al., 2012). Wessells et al. (2011) fabricated LiTi$_2$(PO$_4$)$_3$ and demonstrated its potential as an ARLB anode. Luo and Xia (2009) reported a supercapacitor with LiTi$_2$(PO$_4$)$_3$ coated with carbon as the negative electrode, delivering a discharge capacity of 30 mAh g$^{-1}$.

However, the electrochemical performance of a LiTi$_2$(PO$_4$)$_3$-based electrode must be increased to meet the requirements of practical applications. Carbon coating, size reduction, and the introduction of a conductive agent are efficient strategies for boosting performance (Sun et al., 2015). Moreover, lattice doping is available as a means of raising anode performance (Mao et al., 2019). Wang et al. (2017) partly replaced F$^-$ on a PO$_4^{3-}$ site for LiTi$_2$(PO$_4$)$_3$ as an ARLB anode, with an energy density of 43.7 Wh Kg$^{-1}$. Liang et al. (2019) prepared Ga-doped LiTi$_2$(PO$_4$)$_3$ film via a hydrothermal method and found favorable capacity and cycling performance. Doping with anions such as F$^-$ and Cl$^-$ can promote the electrokinetics of electrodes by influencing electron configuration, further increasing the electrical and ionic

![FIGURE 1](image1.png) | Schematic illustration of the preparation process of the composites.

![FIGURE 2](image2.png) | XRD patterns of NaTi$_2$(PO$_4$)$_3$Cl$_{3x}$/C (x = 0.0, 0.05, 0.10, and 0.15) composites.
conductivity (Yue et al., 2013; Qi et al., 2015). In this paper, a Cl$^{-1}$ doping strategy was employed to boost the lithium storage performance of LiTi$_2$(PO$_4$)$_3$/C. LiTi$_2$(PO$_4$)$_3$–xCl$_{3x}$/C composites were successfully prepared with a facile sol-gel method. The lithium ion storage performance of anion-doped composites was systematically studied.

EXPERIMENTAL

Synthesis
All analytically pure chemical reagents were directly used without further treatment. The synthesis process of the materials is illustrated in Figure 1. Pristine LiTi$_2$(PO$_4$)$_3$/C was synthesized via a sol-gel technique as follows. Briefly, 1.7921 g of Ti(OC$_4$H$_9$)$_4$ was added to 20 mL of C$_2$H$_5$OH, and the Ti(OC$_4$H$_9$)$_4$/C$_2$H$_5$OH solution was kept at room temperature with magnetic stirring. Then, 0.2659 g of CH$_3$COOLi·2H$_2$O and 0.1700 g of phenolic resin were dissolved in the mixture, sequentially. Following this, 0.8924 g of concentrated H$_3$PO$_4$ was added into 15 mL of C$_2$H$_5$OH and added dropwise to the above mixed solution. The mixed solution was reacted in a sealed beaker at 60°C for 2 h with magnetic stirring. When the reaction was complete, the solution was evaporated at 80°C to obtain a precursor. Finally, the precursor was calcined at 750°C for 5 h in an Ar atmosphere; the prepared LiTi$_2$(PO$_4$)$_3$/C was named LCl. Moreover, LiTi$_2$(PO$_4$)$_3$–xCl$_{3x}$/C ($x = 0.05, 0.10$, and 0.15) composites were synthesized by partially replacing PO$_4^{3−}$ with Cl$^{−}$ in stoichiometry with LiCl. The corresponding LiTi$_2$(PO$_4$)$_{3−x}$Cl$_{x}$/C composites were denoted as LCI-05, LCI-10, and LCI-15.

Characterizations
X-ray powder diffraction (XRD, D/Max2500PC, Rigaku) was carried out to analyze the crystalline phase of the composites. A scanning electron microscope (S-4800, Japan) was used to investigate the morphology of the samples and cycled electrodes. Cycled electrodes were obtained after disassembling the cells, washing them with deionized water, and drying them in an oven. A thermal analyzer (TG50, Shimadzu) was used for thermogravimetric analysis (TGA) of the samples.

Electrochemical Measurements
The electrodes were prepared as follows. The electrodes consisted of an intermixture of acetylene black, active substance, and PTFE (mass ratio: 1:1:8). The intermixture was pressed on a steel mesh with a radius of 7 mm. In cells, LiMn$_2$O$_4$, the synthesized samples, a saturated Li$_2$SO$_4$ solution, and glass fiber were used as the cathode, anode, electrolyte, and separator, respectively. A galvanostatic charge-discharge test for the cells was executed on a CT2001A testing system. Rate performance was evaluated at 0.2, 0.5, 1, 2, 5, 8, 10, 15, and 1°C, respectively. The cycling performance was recorded under 5°C for 1,000 cycles. Cyclic voltammetry and electrochemical impedance spectroscopy were performed to explore the lithium ion storage performance of Li$^+$ ions using a CHI660E electrochemical workstation (Chenhua,
Cyclic voltammetry tests were executed with a voltage range of 0–1.85 V. Electrochemical impedance spectroscopy tests for electrochemically activated cells were conducted with a frequency of $10^5$–$10^{-2}$ Hz and an amplitude of 5 mV.

**RESULTS AND DISCUSSION**

The XRD patterns of the composites are presented in Figure 2. As shown, the main characteristic peaks of all composites were similar and exactly matched those of the NASICON LiTi$_2$(PO$_4$)$_3$ with an R-3c space group (JCPDS#35-0754). This demonstrated that doping with small amount of Cl had no effect on the main structure of LiTi$_2$(PO$_4$)$_3$. In addition, LCl-15 showed an impurity peak at 28.4 degrees, which demonstrated that a high Cl content slightly influenced the crystal structure of Cl-doped composites.

Representative SEM images of LCl and LCl-10 at various magnifications are displayed in Figure 3. As displayed, both materials were constituted by tiny primary particles at a nanometer scale. In addition, there was some agglomeration resulting from the high temperatures reached during the synthesis process. As for the morphology of the LCl-10 composite, it exhibited no obvious differences compared to pristine LCl, further implying that Cl doping had no obvious impact on the composite morphology.

The rate performance of the composites is shown in Figure 4A. Serious electrochemical polarization in a large current resulted in a decrease in the discharge capacity of all composites as the rate increased. The discharge capacity of Cl-doped LiTi$_2$(PO$_4$)$_3$ composites, particularly LCl-10, was increased compared to the original LiTi$_2$(PO$_3$)$_4$/C, indicating an improvement with Cl-doped anode materials. The difference in discharge capacity between Cl-doped LiTi$_2$(PO$_4$)$_3$ composites and the original LiTi$_2$(PO$_3$)$_4$/C became more obvious as the rate was increased. LCl-10 delivered a discharge capacity of 108.5 and 85.5 mAh g$^{-1}$ at 0.5 and 15$^\circ$C, respectively, an increase of 13.1 and 44.3 mAh g$^{-1}$ compared to pristine LCl. Charge-discharge curves for the LCl and LCl-10 composites at disparate rates are displayed in Figures 4B,C, respectively. There were two voltage plateaus for LCl and LCl-10, at about 1.0 and 1.5 V. The voltage plateaus of LCl-10 were wider and more stable compared to those of LCl, revealing the outstanding electrochemical performance of LCl-10.

The cycling properties of LCl and LCl-10 composites were studied at 5$^\circ$C for 1,000 cycles, and the results are shown in Figure 5A. The discharge capacity of both composites gradually increased during the first several cycles due to electrode activation. The maximal discharge capacity of LCl-10 (95.27 mAh g$^{-1}$) was higher than that of LCl (84.89 mAh g$^{-1}$). The discharge capacity of LCl-10 was maintained at 61.3% after 1,000 cycles, which was 25.1% higher than that of LCl (36.2%). Figure 5B shows that the coulombic efficiencies of LCl and LCl-10 were in the vicinity of 100%, revealing that the cells had almost no self-discharge. The charge-discharge curves for LCl and LCl-10 after various cycles are shown in Figures 5C,D, respectively. The relatively wider and more stable voltage plateau for
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FIGURE 5 | Cycling performances (A) and coulombic efficiency (B) for LCI and LCI-10 at 5°C for 1,000 cycles, charge-discharge curves for LCI (C) and LCI-10 (D) after different cycles.

LCI-10 demonstrated good electrochemical performance and stability, unveiling the remarkable cycling properties of LCI-10.

In order to study the structural stability of the electrode after multiple cycles, the electrode morphology was analyzed by SEM. The results for LCI-10 electrodes after 100, 500, and 1,000 cycles are shown in Figure 6. As can be seen, the LCI-10 electrode surface was smooth after 100 cycles, and the morphology remained stable even after 1,000 cycles, without apparent dissolution. This demonstrated that LCI-10 had excellent structural stability after a long period of charging and discharging.

Cyclic voltammetry tests of the cells for LCI and LCI-10 were carried out to study the electrochemical kinetics, and the results are shown in Figure 7. As can be observed, both LCI and LCI-10 had two obvious current peaks. Further, the current density of LCI-10 was higher than the corresponding current density of LCI. The higher current density and narrower peak potential difference of LCI-10 illustrated the excellent electrochemical property of LCI-10. The anodic and cathodic peak current density of LCI-10 at 1.6 V reached 0.38 and 0.38 A g⁻¹, respectively, with an obvious improvement compared to LCI (0.30 and 0.30 A g⁻¹). The peak potential difference of LCI-10 with a value of 0.12 V was smaller than that of LCI (0.15 V), indicating better electrochemical reversibility of the modified electrode.

An electrochemical impedance spectroscopy test was implemented to investigate the effect of Cl doping on the electrochemical kinetics. Nyquist plots and fitting results for LCI and LCI-10 are shown in Figure 8. The Nyquist plots were characterized by an intercept, a semicircle, and an inclined line at high, middle, and low frequencies, parallel to ohmic resistance ($R_s$) including the electrolyte and electrode, charge transfer resistance ($R_{ct}$) linked with the electrochemical reaction, and Warburg impedance ($Z_w$) related to the migration of Li ions, respectively. As can be seen, the electronic conductivity of LCI-10 did not change significantly compared to that of LCI. This indicated that Cl doping caused no obvious change in the electronic conductivity of the material. This was due to the improvement in electronic conductivity from the introduction of carbon. LCI-10 delivered an $R_{ct}$ value of 30.0 Ω, which was less than that of LCI (43.9 Ω), illustrating that the Cl doping had a positive effect on the electrochemical kinetics.

CONCLUSIONS

LiTi$_2$(PO$_4$)$_3$/C composites doped with chlorine on phosphate spots were successfully synthesized with a sol-gel technique. Chlorine doping did not significantly impact the main
structure and morphology of LiTi$_2$(PO$_4$)$_2$/C. Of all the samples, LCL-10 composites showed the optimum rate performance, and their advantages were more obvious at a higher rate. LCI-10 had a discharge capacity of 108.5 and 85.5 mAh g$^{-1}$ at 0.5 and 15°C, respectively, which was 13.1 and 44.3 mAh g$^{-1}$ higher than those of LCI. Moreover, the discharge capacity of LCI-10 was maintained at 61.3% after 1,000 cycles at 5°C, which was 25.1% higher than that of LCI (36.2%). In a word, LiTi$_2$(PO$_4$)$_2$/C doped with an appropriate amount of chlorine is a potential anode for high-performance ARLBs.

DATA AVAILABILITY STATEMENT

All datasets generated for this study are included in the article/supplementary material.

AUTHOR CONTRIBUTIONS

HL: carried out experiments and wrote the manuscript. YT: carried out experiments. ZX: performed analyzed experimental results. PW: designed experiments. ZL: revised the manuscript.

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