



A Comparative Study on $\text{Na}_2\text{Fe}_{0.6}\text{Mn}_{0.4}\text{PO}_4\text{F}/\text{C}$ Cathode Materials Synthesized With Various Carbon Sources for Na-ion Batteries

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$\text{Na}_2\text{Fe}_{0.6}\text{Mn}_{0.4}\text{PO}_4\text{F}/\text{C}$ composite materials are synthesized with various carbon sources via a simple spray-drying method in this study, and the effect of carbon sources on structure, morphology, and electrochemical properties of $\text{Na}_2\text{Fe}_{0.6}\text{Mn}_{0.4}\text{PO}_4\text{F}/\text{C}$ materials are investigated in detail. XRD and SEM results indicate that the reduction ability of carbon sources has a key impact on the structure and morphology of $\text{Na}_2\text{Fe}_{0.6}\text{Mn}_{0.4}\text{PO}_4\text{F}/\text{C}$ composite materials. Among these $\text{Na}_2\text{Fe}_{0.6}\text{Mn}_{0.4}\text{PO}_4\text{F}/\text{C}$ materials, the sample prepared with ascorbic acid presents a uniform hollow spherical architecture. Electrochemical analysis demonstrates that the $\text{Na}_2\text{Fe}_{0.6}\text{Mn}_{0.4}\text{PO}_4\text{F}/\text{C}$ sample prepared with ascorbic acid has optimal electrochemical performance. The sample shows high discharge capacities of 95.1 and 48.1 mAh g^{-1} at 0.05C and 1C rates, respectively, and it exhibits an improved cycle stability (91.7% retention after 100 cycles at 0.5C), which are superior to $\text{Na}_2\text{Fe}_{0.6}\text{Mn}_{0.4}\text{PO}_4\text{F}/\text{C}$ materials prepared with other carbon sources. This study demonstrates that the reduction ability of carbon sources significantly influences the electrochemical properties of fluorophosphate/C composite materials. This work also provides a promising strategy to obtain high performance cathode materials for sodium-ion batteries.

Keywords: sodium-ion batteries, cathode materials, $\text{Na}_2\text{Fe}_{0.6}\text{Mn}_{0.4}\text{PO}_4\text{F}$, spray drying, electrochemical performance

INTRODUCTION

In recent years, the demand for lithium-ion batteries (LIBs) has increased sharply due to the rapid development of large-scale energy storage and electric vehicles (Wu et al., 2016; Li et al., 2020; Nie et al., 2020a; Shen et al., 2020; Sui et al., 2020a). However, the available lithium resources in the Earth's crust are very limited. By contrast, the reserves of sodium are much more abundant than lithium (Sui et al., 2020b; Zhou et al., 2020). Therefore, the sodium-ion battery is a promising alternative to LIBs, and has attracted extensive attention in recent years (Liu et al., 2021). Nevertheless, the operating voltage and energy density of sodium-ion batteries (SIBs) are generally lower than those of LIBs, as the standard electrode potential of Na/Na^+ (-2.71 V) is higher than that of Li/Li^+ (-3.04 V) (Zhu et al., 2013; Wu et al., 2019; Nie et al., 2020b). Obviously, it is very important to develop new cathode materials with high voltages to improve the energy density of SIBs (Wu et al., 2018a; Zheng et al., 2018).

The development of fluorophosphate cathode materials with high working potential and high theoretical capacity has become a research hotspot, and various fluorophosphate materials have been reported, including Na₂MPO₄F (M = Fe, Mn, Co and Ni) (Barpanda et al., 2018; Li et al., 2018; Wu et al., 2018b), NaVPO₄F, and Na₃V₂(PO₄)₂F₃ (Cai et al., 2018; Subramanyan et al., 2021). Among these fluorophosphate materials, Na₂MnPO₄F is attracting significant attention due to its optimal theoretical capacity and suitable working potential. Firstly, the theoretical specific capacity of Na₂MnPO₄F is as high as 250 mAh g⁻¹ when the two sodium-ions are completely removed (~125 mAh g⁻¹ for one sodium-ion) (Wu et al., 2018b; Sharma et al., 2020). Secondly, based on the strong induction effect and strong negative charge of F⁻, Na₂MnPO₄F owns high working potential (3.66 and 4.67 V vs. Na/Na⁺) and excellent thermal stability (Wu et al., 2018b), and its working potential is within the stable window of electrolytes. In addition, manganese is low cost and abundant in the Earth. These advantages mean Na₂MnPO₄F has a broad application potential. Although Na₂MnPO₄F shows such great potential advantages, there are some problems that impede the application of Na₂MnPO₄F. Na₂MnPO₄F is a broadband insulator, and the low electronic conductivity seriously affects its electrochemical performance. For example, the Na₂MnPO₄F sample synthesized by solid state method (Ellis et al., 2010) shows almost no electrochemical activity. At present, there are few reports on the modification of Na₂MnPO₄F cathode materials. Most recently, we have prepared a series of solid solution materials of Na₂Mn_{1-x}Fe_xPO₄F/C (0 < x < 1) by introducing Fe element and coating with carbon to improve the electrochemical properties of Na₂MnPO₄F (Tang et al., 2020). Our results show that the introduction of Fe and carbon coating can significantly improve the electrochemical activity of Na₂MnPO₄F. In a series of the Na₂Mn_{1-x}Fe_xPO₄F/C samples, Na₂Fe_{0.6}Mn_{0.4}PO₄F/C shows the best electrochemical performance. However, the above report did not investigate the effect of carbon sources on the structure and properties of the material, and did not optimize the type of carbon source. Thus, this paper aims to optimize the carbon source to increase the porosity of Na₂Fe_{0.6}Mn_{0.4}PO₄F/C, optimize the carbon coating effect to inhibit the primary particle overgrowth, and thus build a good conductive network to further improve the electrochemical performance of Na₂Fe_{0.6}Mn_{0.4}PO₄F.

EXPERIMENTAL

Chemicals

Sodium carbonate (Na₂CO₃, 99.8%) was purchased from Aladdin. Iron citrate (FeC₆H₅O₇, A.R.), manganese acetate tetrahydrate (Mn(CH₃COO)₂·4H₂O, A.R.), ammonium dihydrogen phosphate (NH₄H₂PO₄, A.R.), sodium fluoride (NaF, 99%), oxalate acid (H₂C₂O₄, 99.8%), ascorbic acid (C₆H₈O₆, 99.8%), citric acid (C₆H₈O₇, 99.5%), and glucose (C₆H₁₂O₆, 99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used directly without further purification.

Materials Synthesis

The Na₂Fe_{0.6}Mn_{0.4}PO₄F/C composite materials were synthesized by a simple spray-drying method. Firstly, 3.18 g Na₂CO₃, 3.45 g NH₄H₂PO₄, 1.26 g NaF, 4.41 g C₆H₅O₇·Fe·H₂O, 2.23 g Mn(CH₃COO)₂·4H₂O, and carbon source (1.98 g oxalate acid, 3.87 g ascorbic acid, 4.72 g citric acid, or 4.35 g glucose) were dissolved in 200 ml deionized water to form a mixed solution. Considering the burning loss, the theoretical mass of carbon sources was calculated as 10 wt% of the product (Na₂Fe_{0.6}Mn_{0.4}PO₄F/C). Secondly, the above solution was dried by a spray drier (Shanghai Attainpak DC1500) to prepare the spherical precursor powders. The spraying speed is 250 ml h⁻¹, and the inlet and outlet air temperatures are 200° and 80°C, respectively. Finally, the precursor powders were heated at 300°C for 3 h and then calcined at 625°C for 6 h in an argon atmosphere to obtain the final Na₂Fe_{0.6}Mn_{0.4}PO₄F/C products.

Characterization

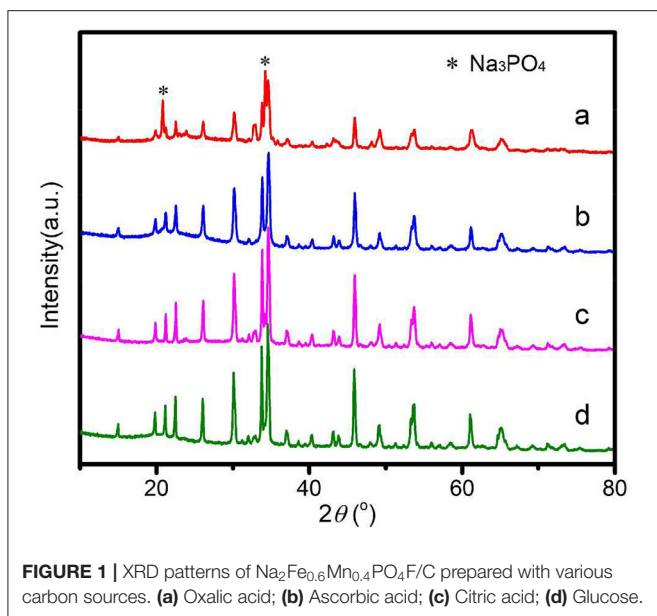
The crystalline structure of Na₂Fe_{0.6}Mn_{0.4}PO₄F/C was studied by X-ray diffraction (XRD, Rigaku Ultima IV). The morphology of samples was observed by scanning electron microscope (SEM, Hitachi SU5000). Carbon content of Na₂Fe_{0.6}Mn_{0.4}PO₄F/C was measured with a carbon sulfur analyzer (HCS-140).

Battery Fabrication and Electrochemical Tests

Firstly, Na₂Fe_{0.6}Mn_{0.4}PO₄F/C powders and acetylene black and poly(vinylidene fluoride) in the weight ratio of 8:1:1 were blended in N-methyl pyrrolidinone to form a homogeneous slurry, then the slurry was spread uniformly on an aluminum foil and dried at 120°C for 12 h in vacuum. The dried foil was pressed into discs (Φ = 12 mm) to act as the cathode plate. An Na-foil (Φ = 14 mm) and glass fiber film disc (Φ = 16 mm) were used as the anode and separator, respectively. A solution of 1 M NaClO₄ dissolved in 95% PC and 5% FEC was used as the electrolyte. The cells were tested with LAND battery test system at room temperature between the voltage range of 1.5–4.5 V (vs. Na/Na⁺). The electrochemical impedance spectroscopy (EIS, amplitude: 5 mV; frequency: 0.01–100 kHz) was measured by a CHI660D electrochemical workstation.

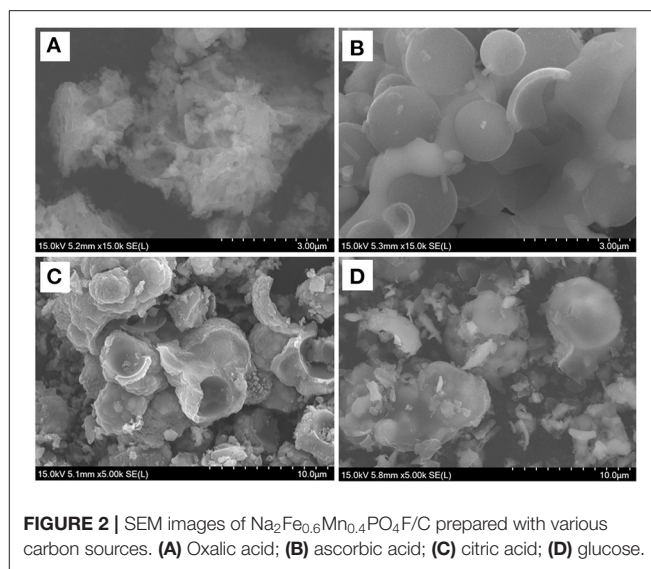
RESULTS AND DISCUSSION

The XRD patterns of Na₂Fe_{0.6}Mn_{0.4}PO₄F/C synthesized with different carbon sources are shown in **Figure 1**. As shown, all diffraction peaks of the samples can be fully indexed to typical Na₂Fe_{0.6}Mn_{0.4}PO₄F material (PDF#87-0467) with space group *P2₁/n*. The Na₂Fe_{0.6}Mn_{0.4}PO₄F/C samples synthesized with ascorbic acid, citric acid, and glucose were all pure and no impurities were detected. However, for the Na₂Fe_{0.6}Mn_{0.4}PO₄F/C sample prepared with oxalic acid, the diffraction peaks of Na₃PO₄ (PDF#71-1918) can be observed, indicating that impurities are produced in the preparation of the Na₂Fe_{0.6}Mn_{0.4}PO₄F/C sample. There are no obvious diffraction peaks related to C that can be observed in the XRD patterns, mainly because the carbon in Na₂Fe_{0.6}Mn_{0.4}PO₄F/C is amorphous. The carbon contents of Na₂Fe_{0.6}Mn_{0.4}PO₄F/C



samples prepared with oxalic acid, ascorbic acid, citric acid, and glucose are determined by carbon sulfur analyzing instrument, and the results are 7.1, 7.4, 7.9, and 8.1 wt%, respectively. It can also be seen that the synthesized Na₂Fe_{0.6}Mn_{0.4}PO₄F/C samples with different carbon sources show different peak intensities and widths: the sample prepared with glucose exhibits the highest peak intensity, citric acid takes the second place, and the sample prepared with oxalic acid presents the lowest peak intensity. Normally, high peak intensity and narrow half-peak width indicate large particle sizes of the sample, which will result in unfavorable diffusion and transmission of sodium ions in electrochemical reactions. Interestingly, the order of the reduction ability of the carbon sources in this work is glucose < citric acid < ascorbic acid < oxalic acid, and the difference of reduction ability of four different carbon sources might cause a discrepancy of peak intensity and width. In other words, the relatively high reduction ability of oxalic acid made it difficult to prepare pure Na₂Fe_{0.6}Mn_{0.4}PO₄F/C material.

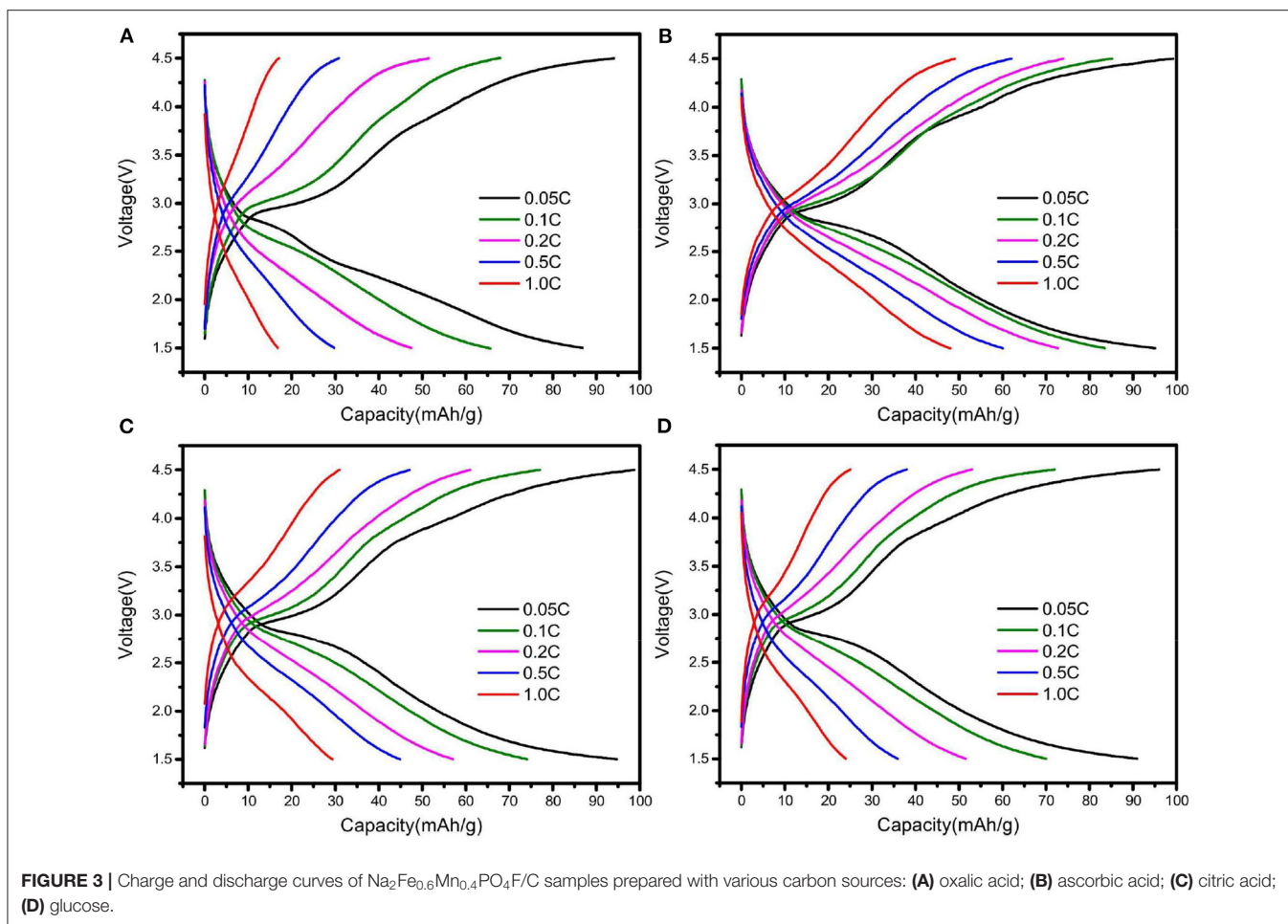
SEM was employed to analyze the structure and morphology of synthesized Na₂Fe_{0.6}Mn_{0.4}PO₄F/C samples with different carbon sources. It is obvious that carbon sources play a key role in structural construction of Na₂Fe_{0.6}Mn_{0.4}PO₄F/C material. As shown in **Figure 2A**, the synthesized Na₂Fe_{0.6}Mn_{0.4}PO₄F/C material with oxalic acid exhibits an irregular porous agglomerates morphology with an unclear crystal border, and no spherical structure was observed. It is noted that the formation of the porous structure might be relevant to the decomposition of oxalic acid. The Na₂Fe_{0.6}Mn_{0.4}PO₄F/C material prepared with ascorbic acid, as shown in **Figure 2B**, displays a hollow spherical shape with a compact surface, and the size distribution is in the range of 1–2 μm. For the Na₂Fe_{0.6}Mn_{0.4}PO₄F/C material prepared with citric acid (**Figure 2C**), the particles fail to keep the uniform hollow spherical shape, which gradually turned into irregular spheres/agglomerates. Using glucose as a carbon source,



the synthesized Na₂Fe_{0.6}Mn_{0.4}PO₄F/C material (**Figure 2D**) exhibits a damaged spherical shape with irregular particles, and the average size of the damaged spheres is about 3–5 μm. Interestingly, the particle size is decreased with the increase of reduction ability of carbon sources. This phenomenon may provide guidance for the synthesis and optimization of Na₂Fe_{1-x}Mn_xPO₄F series materials.

The rate performance of Na₂Fe_{0.6}Mn_{0.4}PO₄F/C materials synthesized with different carbon sources is shown in **Figure 3**. As shown in **Figure 3A**, the Na₂Fe_{0.6}Mn_{0.4}PO₄F/C material prepared with oxalic acid delivers a specific capacity of 86.9 mAh g⁻¹ at 0.05C, and the corresponding coulombic efficiency is 92.3%. The discharge capacities can achieve 65.7, 47.5, 29.8, and 16.8 mAh g⁻¹ at current densities of 0.1, 0.2, 0.5, and 1C, respectively (**Figure 3A**). For the Na₂Fe_{0.6}Mn_{0.4}PO₄F/C material prepared with ascorbic acid, the discharge capacities rise to 95.1, 83.5, 72.7, 60.0, and 48.1 mAh g⁻¹ at current densities of 0.05, 0.1, 0.2, 0.5, and 1C, respectively (**Figure 3B**). However, the rate performance of Na₂Fe_{0.6}Mn_{0.4}PO₄F/C material prepared with citric acid and glucose is unsatisfactory (e.g., the discharge capacities are only 30 and 24.0 mAh g⁻¹ at 1C, **Figures 3C,D**). Obviously, the discharge capacities and rate performance of Na₂Fe_{0.6}Mn_{0.4}PO₄F/C materials are closely related to the type of carbon sources, and the material prepared with ascorbic acid shows improved rate performance compared with the materials prepared with the other three carbon sources.

Figures 4A–D shows the rate-cycling performance of Na₂Fe_{0.6}Mn_{0.4}PO₄F/C synthesized with different carbon sources. All Na₂Fe_{0.6}Mn_{0.4}PO₄F/C samples exhibit stable cycle performance at high current densities. Normally, a low current density corresponds to deep charge/discharge behavior, which may cause volume expansion and the irreversible structural change of cathode material. Conversely, a high current density corresponds to shallow charge/discharge behavior, and the structural change of the cathode material is unapparent. The discharge capacity of Na₂Fe_{0.6}Mn_{0.4}PO₄F/C sample prepared



with ascorbic acid is as high as 95 mAh g⁻¹ after the test, reverting to 0.05C after cycling at various current rates, while the values are only 84, 93, and 88 mAh g⁻¹ for the materials prepared with oxalic acid, citric acid, and glucose. The long cycle performance of Na₂Fe_{0.6}Mn_{0.4}PO₄F/C samples synthesized with different carbon sources are shown in **Figure 4E**. The material prepared with ascorbic acid endures 91.7% of its initial capacity after 100 cycles at 0.5C, while only 44.6%, 88.6%, and 78.3% of the initial capacities are retained for the materials synthesized with oxalic acid, citric acid, and glucose. The result further demonstrates that the Na₂Fe_{0.6}Mn_{0.4}PO₄F/C material prepared with ascorbic acid exhibits outstanding electrochemical performance.

In order to further reveal the effect of various carbon sources on the electrochemical properties of Na₂Fe_{0.6}Mn_{0.4}PO₄F/C samples, electrode reaction kinetics were investigated by EIS. **Figure 5A** shows Nyquist plots of four synthesized Na₂Fe_{0.6}Mn_{0.4}PO₄F/C by using an equivalent circuit, and all curves consist of a diagonal line and a semicircle. In the equivalent circuit, R_s and R_{ct} represent the equivalent ohmic resistance of the cell and charge transfer, respectively. Considering the surface of the working electrode is not

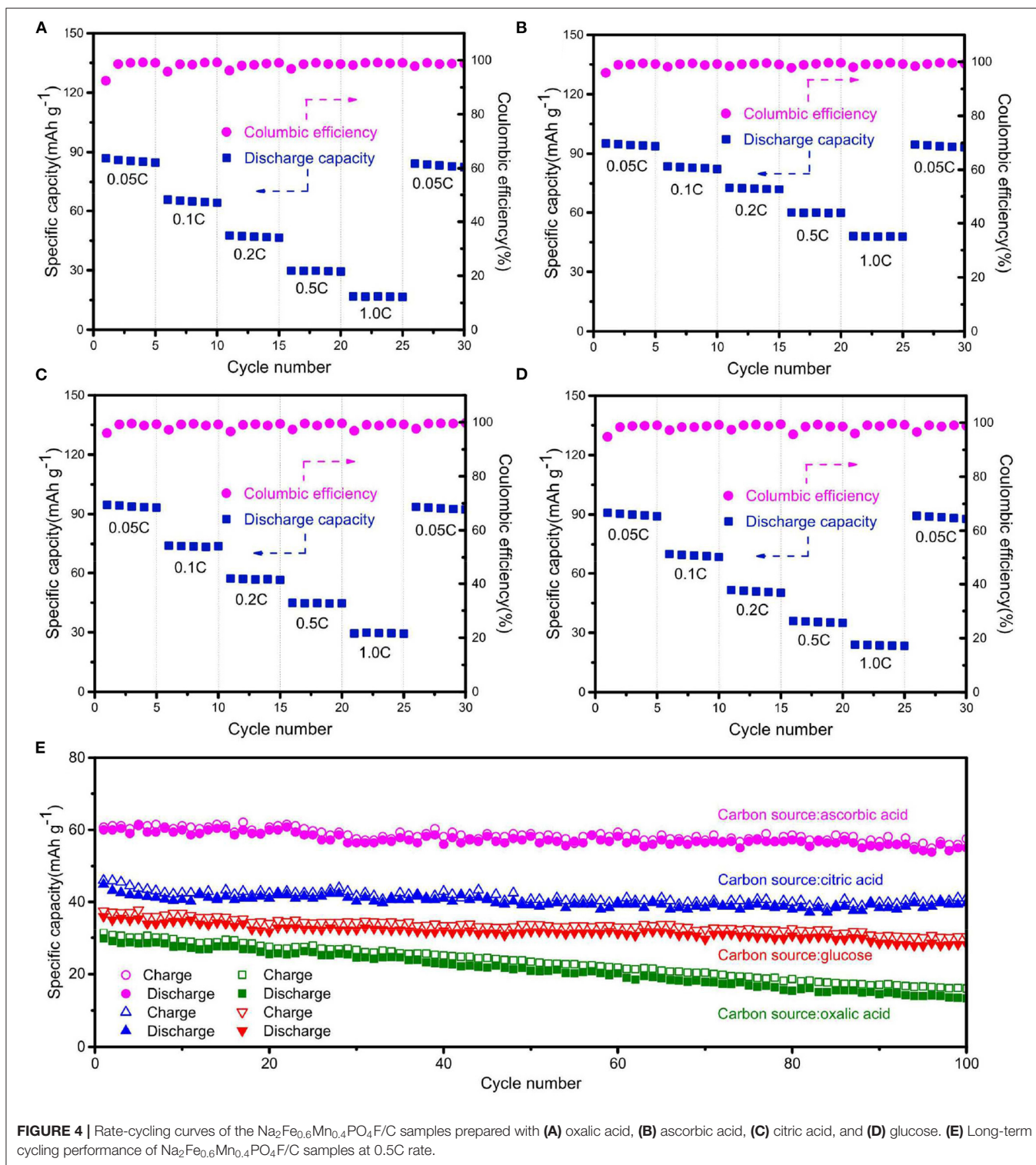
absolutely smooth, CPE is used to describe the double layer capacitance, and W refers to Warburg impedance (Cui et al., 2016). As can be seen from **Figure 5B**, the equivalent ohmic resistance (R_s) of these four Na₂Fe_{0.6}Mn_{0.4}PO₄F/C materials is similar, while the material prepared with ascorbic acid exhibits much lower charge-transfer resistance (R_{ct}) than the other three synthesized materials, which indicates that the material prepared with ascorbic acid presents the lowest electrochemical polarization.

The sodium ion diffusion coefficient (D) was also calculated by the following formula.

$$D = R^2 T^2 / 2A^2 n^4 F^4 C^2 \sigma_w^2 \quad (1)$$

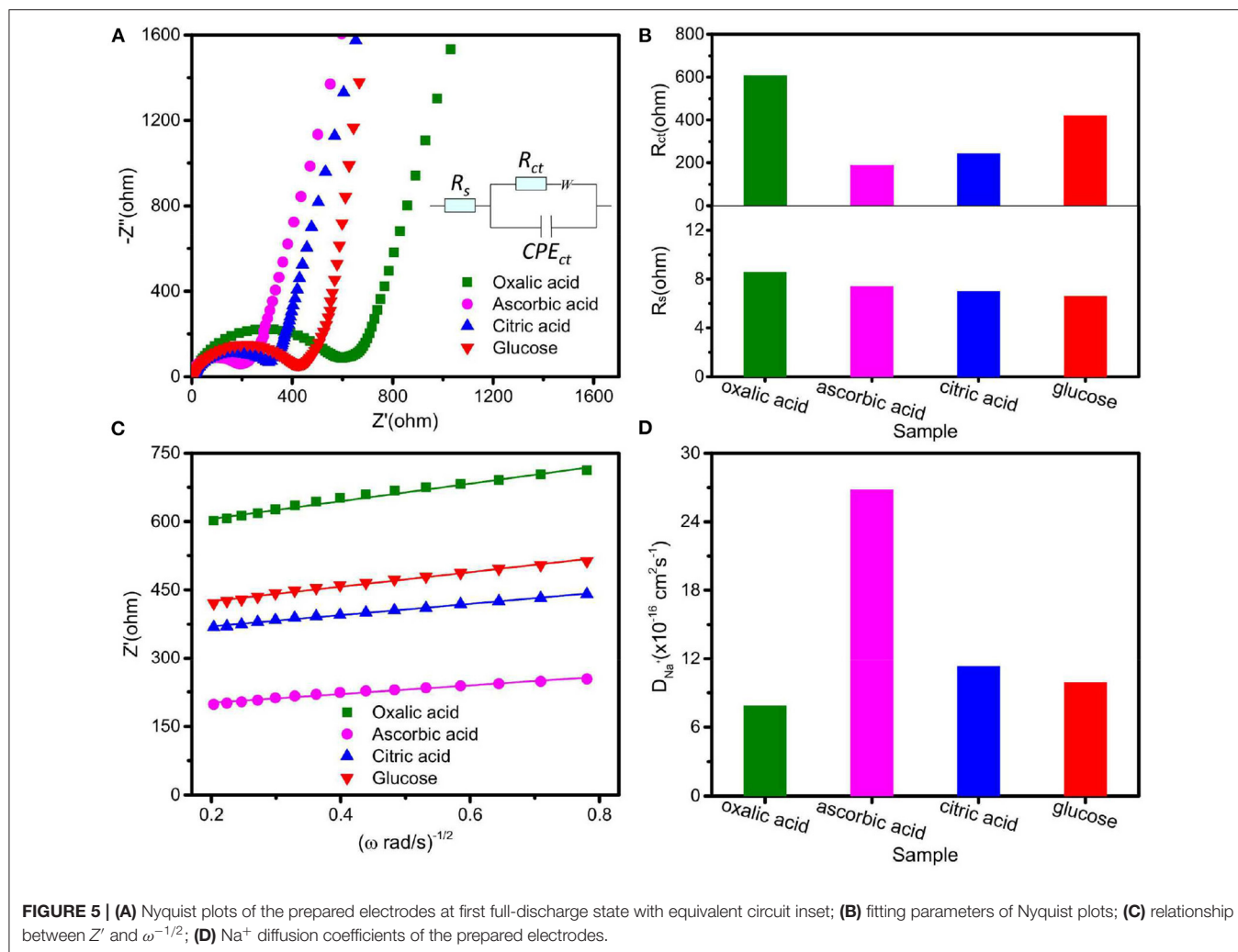
$$Z' = R_s + R_{ct} + \sigma_w \omega^{-1/2} \quad (2)$$

Where R , T , A , n , F , C , σ_w , and ω represent the gas constant, the absolute temperature, the electrode surface area, the charge transfer number of the electrochemical reaction, Faraday's constant, concentration of Na⁺ ions, Warburg impedance coefficient, and angular frequency, respectively. By calculation (as shown in **Figures 5C,D**), it is found that the material prepared with ascorbic acid presents the highest sodium ion



diffusion coefficient, $2.68 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$, which might be due to its high contact area between the electrode material and electrolyte as well as its low crystallite size. The impurities are unfavorable for the sodium ion diffusion; that is why the Na₂Fe_{0.6}Mn_{0.4}PO₄F/C sample prepared with oxalic acid shows

the lowest sodium ion diffusion coefficient. These results indicate that the Na₂Fe_{0.6}Mn_{0.4}PO₄F/C prepared with ascorbic acid exhibits high specific capacity, improved rate performance, and excellent cycle stability, and it is expected to be a promising cathode material with high energy density and power density.



CONCLUSIONS

In summary, the effect of various carbon sources on the structure and electrochemical properties of synthesized Na₂Fe_{0.6}Mn_{0.4}PO₄F/C cathode materials is investigated in this study. The results show that the reduction ability of carbon sources plays a key role in the morphology of Na₂Fe_{0.6}Mn_{0.4}PO₄F/C materials, and the material prepared with ascorbic acid presents the most perfect hollow spherical shape. The electrochemical tests demonstrate that the Na₂Fe_{0.6}Mn_{0.4}PO₄F/C material prepared with ascorbic acid exhibits outstanding electrochemical performances. Its high discharge capacities (95.1 mAh g⁻¹ at 0.05C), improved rate property (48.1 mAh g⁻¹ at 1C), and long cycle stability (endures 91.7% of its initial capacity after 100 cycles at 0.5C) specifically are superior to Na₂Fe_{0.6}Mn_{0.4}PO₄F/C materials prepared with other carbon sources. Electrode reaction kinetics show that the material prepared with ascorbic acid presents lower electrochemical polarization than other materials, which is in accordance with the results of electrochemical tests. This study points out the relationship between the reduction

ability of carbon sources and electrochemical properties of Na₂Fe_{0.6}Mn_{0.4}PO₄F/C materials, and it also provides a promising strategy to achieve cathode materials with high energy density and power density.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding author/s.

AUTHOR CONTRIBUTIONS

ST, YS, and LW did the main experiment and wrote the manuscript. YS and LW were involved in the discussion of the experiment and revised the manuscript and also provided the financial support. XZ and BW assisted with the material synthesis and properties analysis. All authors contributed to the article and approved the submitted version.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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