



Characteristics and electrochemical performance of $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ used as cathode for aqueous rechargeable lithium battery

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ABSTRACT

$\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ cathode materials are synthesized by a sol–gel method and the precursor calcinations. The phase structures and morphologies are characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). Galvanostatic charging/discharging cycles of as-prepared $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ are performed in the saturated LiNO_3 aqueous solution. The initial discharge capacities of $(\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C})/\text{LiV}_3\text{O}_8$ aqueous rechargeable lithium battery are $123.09 \text{ mAh g}^{-1}$ and $107.00 \text{ mAh g}^{-1}$ at 0.05 C and 0.1 C, respectively. And it delivers a capacity of 66.77 mAh g^{-1} at 50 C which is greater than that of 20 C and 30 C, exhibiting good cycling performance at 50 C. This is the first report of a successful utilization of $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ as cathode material for ARLB and the lithium-ion diffusion coefficients of the $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ are calculated from the cyclic voltammetry data.

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1. Introduction

Lithium-ion batteries have been widely used in the electronic consumable devices, electric vehicles and large-scale energy storage. While they are generally assembled with organic electrolyte, they still cannot meet high power instruments due to safety issue arising from the volatile and flammable organic electrolytes. Therefore, it is of importance to explore new energy storage to improve their safety.

Aqueous rechargeable lithium battery (ARLB) was first put forward by Dahn et al. [1] which consists of LiMn_2O_4 cathode and VO_2 anode in 5 M LiNO_3 aqueous electrolyte. In comparison to the traditional lithium-ion battery with organic electrolytes, ARLB has several potential advantages such as greater safety and lower cost. Moreover, the ionic conductivity of aqueous electrolyte is much greater than that of the organic electrolyte, which could enable the ARLB to be applied at higher cycling rate with lower electrolyte resistance. Consequently, some cathode materials were used for the ARLB, including LiMn_2O_4 [2–5], LiCoO_2 [6–8], LiNiO_2 [9,10], MnO_2 [11–14], and $\text{LiTi}_2(\text{PO}_4)_3$ [15,16]. In recent years, much attention has focused on lithium orthophosphates used as the cathode of ARLB due to their high energy density and chemical stability. For LiFePO_4 , Mi et al. [17] investigated the deintercalation/intercalation

behaviors and calculated the corresponding lithium-ion diffusion coefficient of LiFePO_4 . Xia's group [18] reported $(-)\text{LiTi}_2(\text{PO}_4)_3|\text{Li}_2\text{SO}_4|\text{LiFePO}_4(+)$ ARLB exhibited better capacity retention by eliminating oxygen in the aqueous electrolyte and investigated the mechanism of lithium-ion intercalation in the aqueous electrolyte [19]. The latest literature [20] about modified LiMnPO_4 prepared with TiS_2 additive showed that the first discharge capacity in LiOH electrolyte is 90 mAh g^{-1} and its cycling performance was poor at 0.5 mA cm^{-2} . Thus, it is crucial to improve the electrochemical performance of LiMnPO_4 in the aqueous electrolyte.

As well known, LiMnPO_4 is an insulator with ca. 2 eV energy band gap [21] and the Jahn–Teller effect will cause the interface mismatch of lithiated phase and delithiated phase, which lead to its low electronic conductivity ($<10^{-10} \text{ S cm}^{-1}$) [22]. In order to improve its poor electrochemical performance originating from the low electronic conductivity, different approaches have been made by synthesizing nano-sized particles [23–25] and coating carbon [26,27] or doping metal cation to form multi-transition metal olivine compounds [28–32]. Of course, there have been many literatures on the performance of multi-transition metal compounds [28,33–36] in the organic electrolyte, but the electrochemical performances of these compounds used for the ARLB have attracted only little attention. Xia's group [37] reported $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ combined with activate carbon showed good cycle ability and high rate capability. Zheng [7] pointed out that $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ had a better rate capability and only 9.1% capacity loss after 1000 cycles at 80 C in 2 M LiNO_3 solution.

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Minakshi [38] studied the crystal structure and phase transition of $\text{Li}(\text{Co}_{0.5}\text{Ni}_{0.5})\text{PO}_4$ in an aqueous solution.

In this paper, $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ compounds were prepared by a sol–gel method and sintering process. The ARLB was assembled with $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ and LiV_3O_8 in saturated LiNO_3 solution. The galvanostatic charging/discharging experiments were used to evaluate the electrochemical behaviors of $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ and the lithium-ion diffusion coefficients of $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ were studied with CV data.

2. Experimental

$\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ was synthesized by a sol–gel and calcinations process. $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, P_2O_5 and citric acid with a molar ratio of 1:0.5:0.5:1:1 were dissolved in 40 mL ethanol solution. The mixture solution was rigorous stirred for 12 h in nitrogen gas, and then heated at 353 K to get xerogel. Finally, the xerogel was fired at 773 K for 5 h in the purified argon gas flowing

to prevent the oxidation of Fe^{2+} to obtain $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$. LiV_3O_8 was synthesized as describe as previous publication [5].

The three–electrode cell was constructed with the $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ cathode (15 mm in length, 5 mm in width, 0.2 mm in thickness, and active material weighing 12 mg) as the working electrode, LiV_3O_8 anode (with identical dimensions to the cathode) as counter electrode, and saturate calomel electrode (0.242 vs. SHE/V) as reference electrode. The working electrode was prepared as following: mixing active materials ($\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$), acetylene black and polyvinylidene fluoride (PVDF) in a weight ratio of 80:10:10 using N-methyl-2-pyrrolidone as solvent, the black slurry was uniform mixed with ultrasonic process for 2 min, then coated on nickel mesh followed by drying at 373 K for 10 h under vacuum. The counter electrode was prepared by the same method as the working electrode described above. The relative ratio of cathode and anode amounts is 1:1.2. The neutral electrolyte was prepared by dissolving appropriate amount of $\text{LiOH} \cdot \text{H}_2\text{O}$ in the saturated LiNO_3 solution, and the experimental deoxygenated electrolyte was

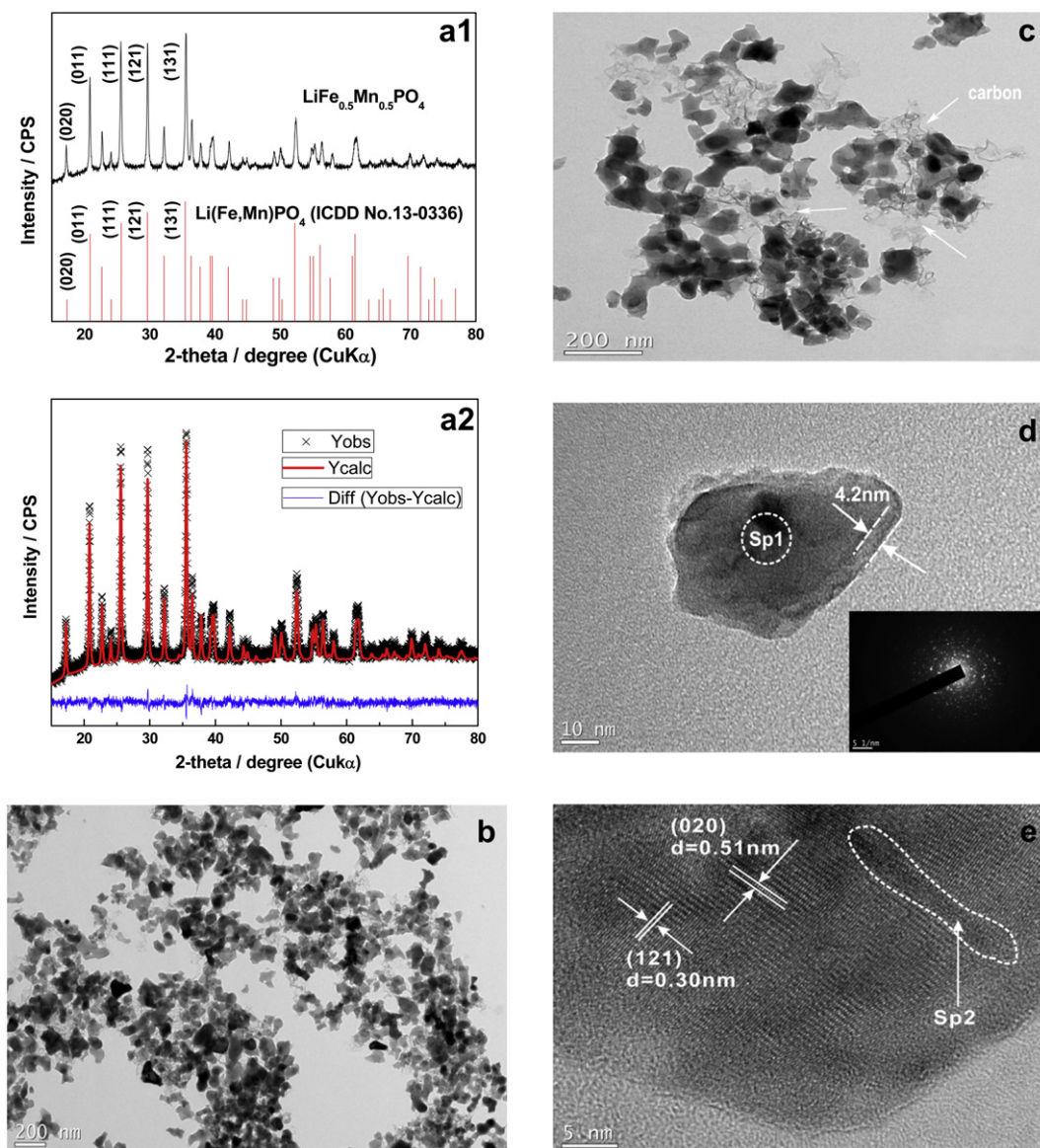


Fig. 1. (a1) XRD pattern comparison between the $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$ and ICDD No. 13-0336. (a2) The Rietveld refinement result of $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$. (b–d) TEM images and (e) HRTEM images of $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$.

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