



Sodium carboxyl methyl cellulose and polyacrylic acid binder with enhanced electrochemical properties for $\text{ZnMoO}_4 \cdot 0.8\text{H}_2\text{O}$ anode in lithium ion batteries



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ABSTRACT

$\text{ZnMoO}_4 \cdot 0.8\text{H}_2\text{O}$ nanorods as anode materials for lithium ion batteries are obtained through facile aqueous solution method. The electrochemical properties of $\text{ZnMoO}_4 \cdot 0.8\text{H}_2\text{O}$ have been investigated for the first time with the mixture of sodium carboxyl methyl cellulose and polyacrylic acid (CMC/PAA) as binder. The experiments show that the CMC/PAA binder significantly improves the cycling performance and rate capability of $\text{ZnMoO}_4 \cdot 0.8\text{H}_2\text{O}$ compared with the conventional polyvinylidene-fluoride (PVDF) and CMC. The electrode of $\text{ZnMoO}_4 \cdot 0.8\text{H}_2\text{O}$ with CMC/PAA displays a stable reversible discharge capacity of 479 mA h g^{-1} at 100 mA g^{-1} , a capacity fading rate of 0.7% per cycle to the second cycle and a higher initial coulombic efficiency of 89%. A capacity of 435 mA h g^{-1} at 100 mA g^{-1} can recover after 50 cycles even following the discharge/charge process with the high current density of 500 mA g^{-1} . In addition, the CMC/PAA binder lowers Ohmic resistance and increase the lithium diffusion coefficient. All these advantages highlight the application of CMC/PAA binder used in $\text{ZnMoO}_4 \cdot 0.8\text{H}_2\text{O}$.

1. Introduction

Rechargeable lithium ion batteries (LIBs) have been intensively adopted in portable computers, mobiles and electric vehicles (EVs), as well as hybrid electric vehicles (HEVs) [1,2,3]. To meet ever increasing demands of energy density, metal molybdates, such as NiMoO_4 [4,5], MnMoO_4 [4,6,7,8], FeMoO_4 [9], Na_2MoO_4 [10], Li_2MoO_4 [11] and CoMoO_4 [4,5,12,13] have attracted particular attention. Since Mo exists in several oxidation states ranging from +6 to 0 during the conversion reaction process, they deliver large capacity at the beginning of the electrochemical process. However, the capacity fade rapidly for their large volume expansion and poor electronic conductivity. To mitigate these problems, many extensive and profound studies have been investigated, such as nanosizing [10], carbon coating [11] and doping [14]. Recently considerable attention has been paid to the other components of electrode, such as electrolytes [15], separators [16] and binders [17]. Binder is a vital component of electrode which must ensure the integrity of the morphology and structure of the electrode, provide good adhesion to the current collectors and should not swell with the organic solvents [18].

Currently, the most commonly used binder in XMoO_4 is polyvinylidene-fluoride (PVDF), which has been widely used for cathodes

and anodes based on its good electrochemical stability and high adhesion to the current collectors and electrode materials. However, PVDF is easily dissolved by nonaqueous liquid electrolytes to form viscous gel polymer electrolyte, which leads to capacity decreasing and cycle performance deterioration [19]. Moreover, PVDF has poor flexibility which against the continued Li^+ insertion/extraction of the active material during the cycling [20]. Furthermore, PVDF is relatively costly and always dissolved in volatile *N*-methyl-2-pyrrolidone (NMP), which causes serious environmental problems [21]. When used as binder in XMoO_4 , the electrochemical performances are not as ideal as expected. X.D. Liu et al. [11] studied $\alpha\text{-Na}_2\text{MoO}_4$ powder delivers a reversible specific capacity of 195 mA h g^{-1} at 30 mA g^{-1} after 30 cycles, an initial coulombic efficiencies of 46% and a capacity of 200 mA h g^{-1} at 30 mA g^{-1} which can recover $\sim 330 \text{ mA h g}^{-1}$ after 50 cycles with the current density of 480 mA g^{-1} . Therefore, it is desirable to seek an alternative binder to enhance the electrochemical properties.

Another kind of binder for commercial LIBs is the nature derived polymers sodium carboxyl methyl cellulose (CMC). The greatest advantage of CMC is the use of water as solvent rather than toxic organic solvent. Moreover, CMC is cheap and easy to dispose at the end of the battery life, thus definitely leading to cheaper and greener electrode

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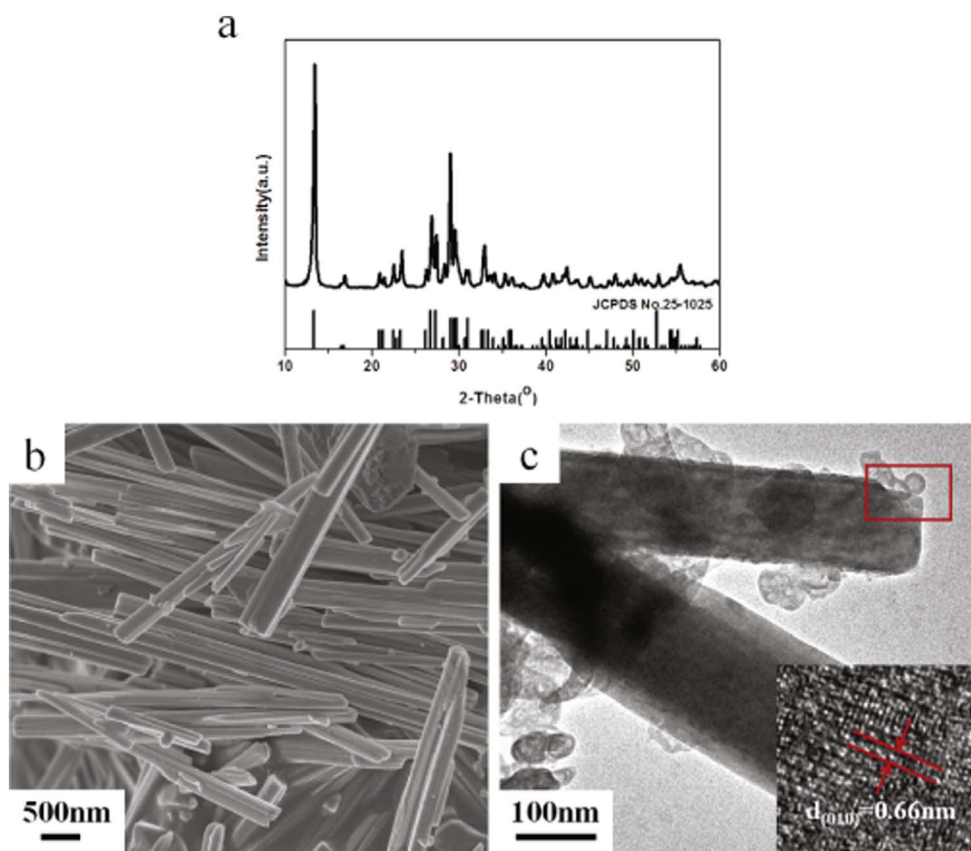


Fig. 1. (a) XRD pattern, (b) SEM image and (c) TEM image of the synthesized sample.

processing [22]. However, the electrode of CMC is easy to crack in discharge/charge process, which greatly influences the electrochemical properties. Recently, polyacrylic acid (PAA) is a viable binder for materials that undergo large volume expansion/reduction during Li^+ insertion or alloying [23,24], when used with CMC may leading to better electrochemical performance [25,26], the improved performance can be attributed to the carboxylic functional groups. Also the mixture binder of CMC and PAA can enhance the stability of the precursor suspension and improve adhesion strength between the copper substrate and active material, which is beneficial for decreasing volumetric change and preventing excessive electrolyte uptake.

Up to now, there have been fewer reports about $\text{ZnMoO}_4 \cdot 0.8\text{H}_2\text{O}$ and its electrochemical properties. In this work, we synthesized $\text{ZnMoO}_4 \cdot 0.8\text{H}_2\text{O}$ nanorods by a facile aqueous solution method at room temperature with the assistance of sodium dodecyl sulfate (SDS), and investigated the electrochemical performances of $\text{ZnMoO}_4 \cdot 0.8\text{H}_2\text{O}$ fabricated with PVDF, CMC and CMC/PAA as binders. The $\text{ZnMoO}_4 \cdot 0.8\text{H}_2\text{O}$ electrode with CMC/PAA showed much better electrochemical properties compared to the traditional PVDF and CMC binder.

2. Experimental

2.1. Synthesis of $\text{ZnMoO}_4 \cdot 0.8\text{H}_2\text{O}$

$\text{ZnMoO}_4 \cdot 0.8\text{H}_2\text{O}$ was synthesized by a facile aqueous solution route. All the reagents were analytical reagent grade without further purification. In a typical procedure, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added into deionized water respectively. The SDS was introduced in each of them. Then $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ solution was added to $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution drop by drop to form homogeneous solution under magnetic stirring at room temperature. After several hours magnetic stirring, the solution was placed at room temperature without

any stirring or shaking. The white precipitation was collected, filtered, washed and then dried.

2.2. Characterization

The crystalline structure of the as-prepared powder was characterized by X-ray diffraction (XRD, Rigaku D/max-2000) with Cu K α radiation ($\lambda = 0.15406$ nm). The morphology of the sample was observed by scanning electron microscopy (SEM, Hitachi, S-4800) and transmission electron microscope (TEM, FEI Tecnai G2 F20 S-TWIN). The X-ray photoelectron spectroscopy (XPS, PHI-5400) spectrum was performed with a Surface Science Instruments Spectrometer focused monochromatic Al K α radiation 1486.6 eV.

2.3. Electrochemical measurements

Electrochemical experiments were carried out using standard CR2032 type coin cells. The working electrodes were prepared by mixing 80 wt% $\text{ZnMoO}_4 \cdot 0.8\text{H}_2\text{O}$ with 10 wt% acetylene black and 10 wt% binder (PVDF, CMC, CMC/PAA (1:1, wt%)) dissolved in solvent (NMP, H_2O) to form slurry, which was then coated onto a copper foil. Herein, three different cases have been made: $\text{ZnMoO}_4 \cdot 0.8\text{H}_2\text{O}$ electrodes with PVDF binder and NMP solvent (Z-PVDF), CMC binder and H_2O solvent (Z-CMC) and CMC/PAA binders and H_2O solvent (Z-CMC/PAA). Pure lithium foil was used as the counter electrode. 1 M LiPF_6 in ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) (1:1:1 in volume) as the electrolyte and Celgard 2400 polypropylene as separator. The cells were assembled in glove box filled with highly pure argon gas (O_2 and H_2O levels < 0.5 ppm).

Galvanostatic discharge/charge cycling were then tested on Neware battery testing system (Neware Technology Ltd.). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analysis were tested on electrochemical station (CHI660E, Chenhua, China).

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