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A novel electrochemical supercapacitor based on $Li_4Ti_5O_{12}$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$

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$Li_4Ti_5O_{12}$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrode materials were prepared by solid state reaction. The structures and morphologies of these electrode materials were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The electrochemical properties of the samples were investigated by cyclic voltammograms and charge–discharge tests. Among the composition explored, the electrochemical supercapacitor, which contained active carbon (AC) mixed with 10% $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ and $Li_4Ti_5O_{12,}$ achieved the best specific capacitance of 178.6 F g^{-1} at 80 mA g^{-1} and maintained 92.5% specific capacitance value after 50 cycles.

1. Introduction

Electrochemical supercapacitors are a promising energy storage technology for applications where high power density and long-cycle life are required [1]. Active carbon (AC) with large surface areas and suitable pore structures can be used as electrochemical supercapacitor active materials. However, the energy density of carbon as an electrode is much lower than that of secondary lithium ion batteries, which limits the application field [2,3]. It is well known that capacitor performances are improved by optimizing the pore structure of the carbon materials [4,5]. One of the most useful approaches is to develop a hybrid system that typically consists of an electrochemical double-layer capacitor (EDLC) electrode and a lithium ion battery electrode, such as AC/$Ni(OH)_2$, AC/MnO_2, AC/$Li_4Ti_5O_{12}$ and AC/$LiMn_2O_4$ systems [6–8]. Compared with AC/AC system, the hybrid system shows significant improvement on the working voltage and the energy density [9].

Most recently, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ has been investigated as lithium ion batteries material, due to its high thermal stability, low cost and low toxicity [10,11]. Another potential lithium ion batteries material, spinel-type $Li_4Ti_5O_{12}$, has also achieved more focus owing largely to its zero-strain characteristics during Li-ion insertion/extraction process [12–14]. Knowing the unique properties of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ and $Li_4Ti_5O_{12}$ materials, we investigate the possibility that these two types of materials could be used as electrochemical supercapacitor electrode materials. In the present work, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ is synthesized by solid state reaction and then mixed with AC at various ratios as the positive electrode material, aiming to improve power density and energy density, at the same time, $Li_4Ti_5O_{12}$ is synthesized as the negative electrode material. This hybrid system is then made up with $Li_4Ti_5O_{12}$ as negative electrode and AC mixed with $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ as positive electrode.

2. Experimental

$Li_4Ti_5O_{12}$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ were produced by solid state reaction. Syntheses of $Li_4Ti_5O_{12}$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ were carried out with analytic materials such as Li_2CO_3, TiO_2, NiO, MnO_2 and Co_2O_3. Of these five raw materials, Li_2CO_3 was highly volatile, especially at high temperature. So, excess Li_2CO_3 was used to compensate for the loss of Li during calcinations. The molar ratio of Li and M (transition metal ions) was usually taken as 1.08:1. The raw materials were mixed by ball-milling for 8 h in ethanol and dried 80 °C for 12 h. The dry powder was then pre-sintered in a tube furnace at 500–750 °C for 8 h and sintered at 800–850 °C for 16 h in air.

Powder X-ray diffraction (Philips X Pert Pro Super X ray diffractometer) employing CuKα radiation was used to identify the phase composition of the synthesized materials. The electrochemical performance tests were conducted using Land battery test system and CHI 660 B electrochemical workstation.

To test the specific capacitance, the synthesized $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ power was mixed with active carbon as active material. This active material was then mixed with acetylene black and PVDF glue at the weight ratio of 80:10:10 and pressed into films, dried in vacuum at

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120 °C for 12 h as positive electrode. The electrochemical supercapacitors were assembled in a Ar-filled glove box with Celgard 2400 micro-porous polyethylene membrane as the separator and 1 M $LiPF_6$ in the mixture of ethyl carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume ratio) as the electrolyte. The negative electrode for the electrochemical supercapacitor was made of $Li_4Ti_5O_{12}$. For the specific capacitance test, the supercapacitors were charged and discharged at 80 mAg^{-1} between 1 V and 2.5 V.

3. Results and discussion

The structure of the synthesized $Li_4Ti_5O_{12}$ was characterized by X-ray diffraction measurement (Philips XRD, CuK_α radiation with $\lambda = 1.5418$ Å). Fig. 1a showed the XRD patterns of $Li_4Ti_5O_{12}$ powder. The diffraction peaks of the sample could be indexed as spinel lithium titanate (cubic phase, space group Fd3 m) and in accordance with spinel-type $Li_4Ti_5O_{12}$ (JCPDS Card no. 49-0207). This result concluded that $Li_4Ti_5O_{12}$ had been successfully synthesized. The structure of the synthesized $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ was also revealed by XRD measurements (Fig. 1b). All diffraction peaks in each pattern were sharp and well defined, and could be indexed a hexagonal α-$NaFeO_2$ structure with R3 m space group (JCPDS Card no. 09-0063). No impurity phases were observed in this material according to XRD analysis. Furthermore, the narrowness of diffraction peaks indicated good crystallinity of the material.

The SEM images of $Li_4Ti_5O_{12}$ were shown in Fig. 2a. It revealed that the synthesized power had irregular particle shape, but a relatively small and uniformed particle size. The particle size was in the range of 0.5–1.2 μm. Fig. 2b showed the microstructures of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powder. The powders had a relatively large particle size and a broad side distribution, in comparison to $Li_4Ti_5O_{12}$ power. Some of the power particles were aggregated.

Fig. 3a shows cyclic voltammograms of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ positive electrode materials at a scan rate of 10 mV s^{-1}. It is clear that all electrodes present a nearly perfect quasi-rectangular voltammogram curve. This suggests that these electrode materials have good electrochemical properties. Besides, 10 wt% electrode possesses the bigger inner integrated area than the others, indicating that the specific capacitance of 10 wt% is much larger than the others.

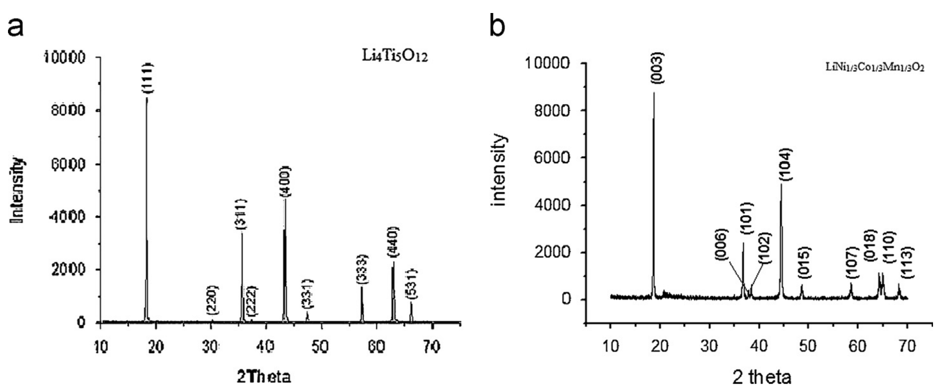

Fig. 1. XRD patterns of $Li_4Ti_5O_{12}$ (a) and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (b).

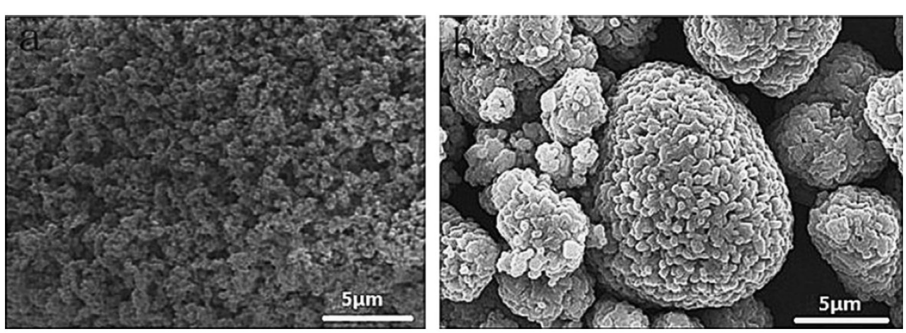

Fig. 2. SEM images of $Li_4Ti_5O_{12}$ (a) and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$(b).

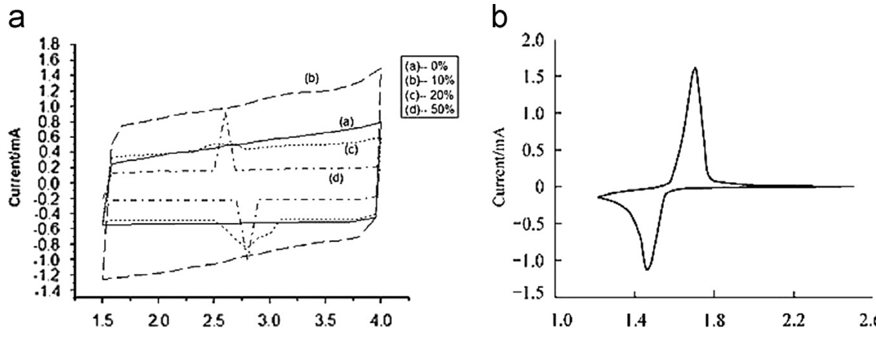

Fig. 3. Cyclic voltammograms of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (a) and $Li_4Ti_5O_{12}$ (b).