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A novel high-performance cylindrical hybrid supercapacitor with $Li_{4-x}Na_xTi_5O_{12}$/activated carbon electrodes

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ABSTRACT

A cylindrical hybrid supercapacitor was fabricated using $Li_{4-x}Na_xTi_5O_{12}$ as an anode and activated carbon as a cathode. $Li_{4-x}Na_xTi_5O_{12}$ ($0 \le x \le 0.6$) powder was successfully crystallized, and the grain size of $Li_{4-x}Na_xTi_5O_{12}$ decreased with increasing Na content. This indicated that Na can enhance the electrochemical performance due to smaller grain size and ionic conductivity. However, excessive Na content causes a distortion of the original $Li_4Ti_5O_{12}$ structure during cycling. The hybrid supercapacitor with the $Li_{3.7}Na_{0.3}Ti_5O_{12}$ anode shows similar electrochemical performance to $Li_{3.4}Na_{0.6}Ti_5O_{12}$, and approximately 92% of the maximum cycle performance is retained, even after 5000 cycles at 2.5 Ag^{-1}.

Introduction

Recently, much research has focused on energy storage devices, especially lithium ion batteries and supercapacitors. The goal of these devices is to increase energy density and cycle life and lowering fabrication costs. Lithium ion batteries store energy by redox reactions in the bulk electrode. The charge/discharge efficiency of the lithium ion batteries is high, ranging from 75 to 90%, and a discharge rate is slow. On the other hand, supercapacitors store charge in a double layer formed on a surface area of micro-porous material. The charge/discharge efficiency of supercapacitors is in the range of from 85 to 98%, and a discharge rate is fast [1,2]. To maximize the advantages of these two devices, a hybrid supercapacitor was designed. The hybrid supercapacitors are a mixed forms of lithium ion batteries and supercapacitors, and the hybrid supercapacitors have high energy density as the batteries and high power density as the supercapacitors [3]. The hybrid supercapacitor proposed here consists of active carbon derived from supercapacitors as a cathode material and Na-doped $Li_4Ti_5O_{12}$ derived from lithium ion batteries. The concept of the proposed hybrid supercapacitor is shown in Fig. 1. There are many cathode candidate materials, such as $Li_4Ti_5O_{12}$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, $LiCoO_2$, and $LiMn_2O_4$, which have been studied for application to hybrid supercapacitors. Among them, lithium titanate spinels, $Li_4Ti_5O_{12}$ (LTO), are regarded as promising anode materials due to the advantages of being cheap, safe, and easy to prepare [4,5]. $Li_4Ti_5O_{12}$ also shows zero strain in the unit cell volume during

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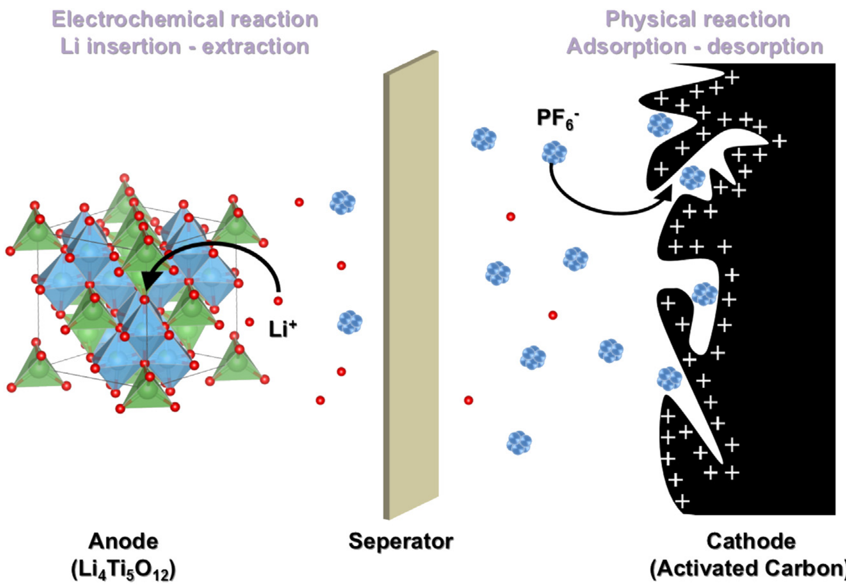

Fig. 1 – Schematic diagram of hybrid supercapacitor.

charge–discharge behavior. When Li ions are inserted into spinel $Li_4Ti_5O_{12}$, phase changes into rock salt $Li_7Ti_5O_{12}$ occur. The charge–discharge processes can be expressed by Equation (1) [5,6]:

$$Li_4Ti_5O_{12} + 3Li^+ + 3e^- \leftrightarrow Li_7Ti_5O_{12},\ E = 1.55\ V \quad (1)$$

There is a voltage plateau at about 1.55 V (vs Li/Li^+) and a theoretical capacity of 175 mA hg^{-1}. However, $Li_4Ti_5O_{12}$ have inferior Li + diffusion coefficient ($<10^{-6}$ cm^2 s^{-1}) and inferior electronic conductivity ($<10^{-13}$ S cm^{-1}) to cause the large capacity loss during the discharge process [7,8].

There are many methods that have been studied to enhance conductivity, including i) manufacturing methods such as solid-state reaction, sol–gel method, hydrothermal method, spray pyrolysis method, molten salt method, and microwave irradiation [9], as well as ii) doping methods ($3M^{3+} = 2Ti^{4+} + Li^+$) such as those used to obtain $Li_{4/3-y/3}M_yTi_{5/3-2y/3}O_4$ (Fe^{3+} [10], Ni^{3+} [11] and Cr^{3+} [11,12]), $Li_4M_yTi_{5-y}O_{12}$ (Mn^{4+} [10] and V^{4+} [10], Al^{3+} [13]), and $Li_4Al_xTi_{5-x}O_{12-y}F_y$ [14]. Chen et al. reported that the doping of Mg^{2+} for Li^+ in the $Li_4Ti_5O_{12}$ structure to obtain $Li_{4-x}Mg_xTi_5O_{12}$ with mixed Ti^{3+}/Ti^{4+} valence [8] enhances the conductivity of $Li_4Ti_5O_{12}$.

We fabricated an asymmetric hybrid supercapacitor using Na-doped spinel $Li_{4-x}Na_xTi_5O_{12}$ as an anode material and investigated the effect of Na doping on the electrochemical properties. Characteristics of the LTO such as long life cycle and excellent cycle performance by zero-strain were examined [5,6]. The theoretical capacity of LTO is 175 mA hg^{-1}, and the actual discharge capacity is 160 mA hg^{-1}.

In recent years, many studies have improved the conductivity of LTO, which showed primary capacity loss and poor rate capability due to low conductivity [6]. To improve the conductivity of LTO, various methods are used, such as synthesizing nanosized particles, coating carbon onto the surface of the particles, mixing carbon into particles, and doping various transition metal ions in Li, Ti, or O sites (such as Ba^{2+}, Sr^{2+}, Al^{3+}, Zn^{2+}, Mg^{2+}) [4,15,16]. Previous studies reported that Na doped Li based materials improved the electronic conductivity [16–19]. The larger channel for transport of Li^+ is provided and Li + diffusion is promoted because of the ionic radius of Na^+ (1.02 Å) larger than that of Li^+ (0.76 Å) made largely lattice of $Li_4Ti_5O_{12}$ [16,19].

Na-doped LTO has not been studied previously, so we studied the effect of Na concentration on the electrochemical characteristics of LTO. To obtain enhanced LTO conductivity, we investigated the effect of the contents of Na on the structural and electrochemical characteristics of LTO.

Experiments

Synthesis and characterization of $Li_{4-x}Na_xTi_5O_{12}$

Na-doped spinel-$Li_4Ti_5O_{12}$ was fabricated by solid-state methods using Li_2CO_3 (Junsei, 98%), TiO_2 (Junsei, 99.0%), and Na_2CO_3 (Aldrich, 99.95%) as starting materials [20]. Na at a small concentration of 0–0.6 mol% was added to pristine spinel-$Li_4Ti_5O_{12}$. The powders were mixed and ground in ethyl alcohol for 24 h using a ball mill.

The mixture was dried in an oven at 100 °C for over 24 h. And then mixture were calcined at 800 °C for 2 h under air atmosphere because of the $Li_4Ti_5O_{12}$ powders obtained [6].

We observed the crystal structures and morphologies of the fabricated powders by X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM).

Preparation of electrode and cell assembly

The positive electrode of the hybrid supercapacitor was made with activation carbon (AC). The negative electrodes of the hybrid supercapacitor were fabricated by Na-doped $Li_4Ti_5O_{12}$,