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ARTICLE

Hydrolysis Precipitation Synthesis of $SnO_2{\cdot}XH_2O$ as Electrode Materials for Supercapacitors

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Abstract: Electrode materials of $SnO_2{\cdot}XH_2O$ were synthesized by hydrolysis precipitation process. After calcination at various temperatures, the materials were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). XRD patterns confirm that the structure of $SnO_2{\cdot}XH_2O$ is tetragonal (rutile). TEM images reveal the morphology of the $SnO_2{\cdot}XH_2O$. TGA shows the water content in $SnO_2{\cdot}XH_2O$ decreases as the calcination temperature increases. Electrochemical tests, such as cyclic voltammetry (CV), chronopotentiometry and cycling were also performed to study the supercapacitor behavior of $SnO_2{\cdot}XH_2O$. CV results indicate that $SnO_2{\cdot}XH_2O$ calcined at 200 °C has a specific capacitance of 36.1 F/g at the scan rate of 5 mV/s in 0.5 mol/L H_2SO_4 electrolyte. Cycling test of the same sample also shows excellent long-term cyclic stability, which has lost less than 2% of the total specific capacitance after 2000 cycles. These results indicate that the prepared $SnO_2{\cdot}XH_2O$ materials are excellent candidates as electrode materials for supercapacitors.

Key words: $SnO_2{\cdot}XH_2O$; hydrolysis precipitation process; supercapacitors; electrochemical performance

Supercapacitors have received great attention in the filed of electrochemical energy storage and conversion due to their ability of delivering high levels of electrical power and long cycle life[1]. They can be categorized as electric double-layer capacitors (EDLCs) and faradaic pseudo- capacitors. EDLCs use the physical separation of electronic charge in the electrode and ions of the electrolyte adsorbed on the surface of electrode. And an optimal faradaic pseudocapacitors are charged by chemical sorption of a working cation of the electrolyte at a reduced complex at the surface of the electrode[2]. Many oxides, such as RuO_2 [3], MnO_2 [4], NiO [5] and Co_3O_4 [6] have been widely reported in the applications of faradaic pseudo-capacitors due to high specific capacitance.

Tin oxide (SnO_2) is now widely used in catalysis, gas sensors and lithium batteries [7-9]. Recent research towards the application of SnO_2 as supercapacitor materials has also brought much attention to the society. Selvan et al. synthesized SnO_2 and SnO_2@C by reactions under autogenic pressure at elevated temperatures, and SnO_2@C has a specific capacitance of 37.8 F/g[10]. In the meantime, Wu reported that Fe_3O_4-SnO_2 composites delivered specific capacitance of 33 F/g in Na_2SO_4 electrolyte [11]. Besides, thin films of $SnO_2{\cdot}XH_2O$ have been synthesized via a simple successive ionic layer adsorption and reaction method, delivering specific capacitance of 25 F/g in Na_2SO_4 electrolyte [12]. Similarly SnO_2 thin films were deposited by chemical route, showing specific capacitance of 66 F/g in Na_2SO_4 electrolyte [13]. While tin oxide thin films were prepared via a spray pyrolysis method, showing specific capacitance of 168 F/g in KOH electrolyte [14]. When amorphous tin oxide was potentiodynamically deposited onto stainless steel electrode, a specific capacitance of 285 F/g could be obtained [15]. We deduce that SnO_2 prepared at lower temperature delivers higher specific capacitance. And by comparing other oxides, such as RuO_2, the SnO_2 usually has higher specific capacitance in the form of hydrate.

In the report of Lee et al., strong acid H_2SO_4 electrolyte was

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found to be better than mild KCl [2], and SnO_2 was confirmed to be stable in H_2SO_4 electrolyte [16]. In order to improve the electrical conductivity, tin oxide hydrate need to be annealed, but the specific capacitance tends to be low if the temperature is much higher [17]. In the present work, $SnO_2{\cdot}XH_2O$ electrode materials have been synthesized by hydrolysis precipitation process and the effect of calcination temperature on the structure and the electrochemical performance of $SnO_2{\cdot}XH_2O$ has been investigated.

1 Experiment

$SnO_2{\cdot}XH_2O$ materials were synthesized by adding 144 mL of 2.5 mol/L ammonia solution to 60 mL of 1 mol/L $SnCl_4$ solution in an ice bath from 0 °C to 4 °C and stirred at around 3000 r/min thoroughly for 4 h. Then the resulting precipitate was collected by centrifugation, and washed several times with ethanol, then dried at 80 °C for 2 h. The precipitate was separated and calcined at 100, 150, 200, 250 and 300 °C for 2 h. The samples obtained were designated as SH-100, SH-150, SH-200, SH -250 and SH-300 accordingly.

XRD analysis was conducted using Deutschland RUKERD2 PHASER X-Ray diffractometer. TEM analysis was carried out with JEOL 2010 microscope. TGA analysis was carried out in N_2 using STAPT-1000 Deutschland LINSEIS thermogravimetric analyzer. The electrode was formed by mixing 75 wt% $SnO_2{\cdot}XH_2O$, 20 wt% super P, and 5 wt% PTFE as binder. Each of the slurry was then rolled into a thin sheet of titanium mesh. The electrochemical performances of the electrodes were studied in a three-electrode system in 0.5 mol/L H_2SO_4 electrolyte with CHI660C electrochemical workstation, where the $SnO_2{\cdot}XH_2O$ electrodes, platinum plate and saturated calomel electrode were applied as the working electrode, counter electrode and reference electrode, respectively. The electrochemical performances of $SnO_2{\cdot}XH_2O$ were tested using a CV method, chronopotentiometry and cycling test. The specific capacitance of the electrode can be calculated from the CV curves according to the following equation:

$$C=\frac{Q}{\Delta E\cdot m} \quad (1)$$

where C (F/g) is the specific capacitance, Q (C) is the average charge, m (g) is the mass of the $SnO_2{\cdot}XH_2O$ in the electrode, and $\triangle E$ (V) represents voltage range.

The capacitance from the constant current charge-discharge curve can be calculated using the following equation:

$$C=\frac{It}{\Delta E\cdot m} \quad (2)$$

where I (A) represents the total current, t (s) is the discharge time, the $\triangle E$ (V) represents potential during constant current discharge.

2 Results and Discussion

2.1 Structural study, thermal analysis and surface morphology

Fig.1a shows XRD patterns of $SnO_2{\cdot}XH_2O$ at around 26.6°, 33.9°, 51.8°, 64.7°, indexed as (110), (101), (211) and (112) planes, respectively with tetragonal rutile structure SnO_2, which is corresponding to JCPDS files No.41-1445. It is observed that the peaks are relatively broadened, which further indicates that the materials have low crystallinity. It is noted that the diffraction intensity increases and the full-width at half-maximum (FWHM) of diffraction peaks reduces with the increase of the annealing temperature, revealing the enhancement of the crystallization of the materials.

TGA curves was used to determine the water content of $SnO_2{\cdot}XH_2O$. It is found in Fig.1b that the $SnO_2{\cdot}XH_2O$ can stabilize to a temperature as high as 500 °C. There are two mass loss steps in the temperature range [18]: The first step ends at 175 °C of SH-100, SH-150, SH -200, SH-250 and SH-300 with loss of mass 11%, 10%, 8%, 8%, and 6%, respectively. This effect is reasonably attributed to the absence of physically adsorbed water[19]. Then the water content of the $SnO_2{\cdot}XH_2O$ materials is 12wt%, 7wt%, 7wt%, 5wt%, 6wt%, respectively. Theoretical mass loss of $SnO_2{\cdot}XH_2O$ approaches to anhydrous SnO_2. The above results indicate that percentage content of water in the $SnO_2{\cdot}XH_2O$ decreases as the calcination temperature increases.

The effect of annealing temperature on the morphology of $SnO_2{\cdot}XH_2O$ can be directly observed from the TEM images in Fig.2. $SnO_2{\cdot}XH_2O$ mainly consists of randomly dispersed, spherical particles. The TEM images reveal that the particles are mainly dispersed with submicron size and their outer surfaces are constructed of many small nanoclusters that are rapidly grown from the center of the spheres. The crystallinity of the $SnO_2{\cdot}XH_2O$ also increases with the increase of the temperature.

2.2 Electrochemical performance

Fig.3 shows the CV responses of $SnO_2{\cdot}XH_2O$ at the scan rate of 5 mV/s. All curves show rectangular shapes within the measured potential window, indicating a better ideal electrical and good capacitive behavior.

Fig.4 displays cyclic voltammograms of SH-200 in 0.5 mol/L H_2SO_4 electrolyte at different scan rates. It also can be observed that the response current of the electrode almost reverses instantaneously when the scan direction changes whether from anodic to cathodic scan or from cathodic to

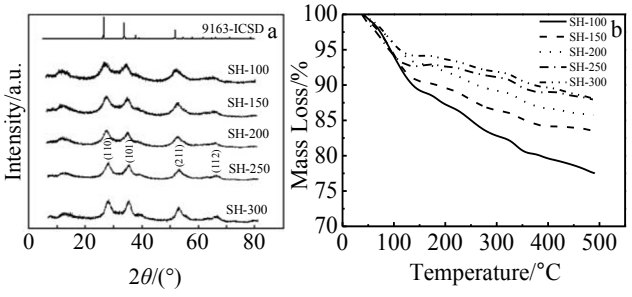

Fig.1 X-ray diffraction patterns (a) and TGA curves (b) of $SnO_2{\cdot}XH_2O$