Fabrication of hybrid tin oxide-cellulose nanocomposite as the flexible and thin supercapacitor

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Abstract

Microfibrillated cellulose (MFC) with reinforcing effects is a useful building block in the fabrication of flexible and thin supercapacitors. Herein, a hybrid tin oxide-cellulose nanocomposite was hydrothermally produced and coated on MFC thin films to form a supercapacitor. The hybrid tin oxide-cellulose thin films were structurally analyzed using scanning electrode microscopy, Fourier transform infrared spectroscopy and X-ray diffraction. The cellulose thin film with the highest loading of hybrid tin oxide-cellulose nanocomposite exhibited a specific capacitance of 225.88 F/g at 100 mV/s and 486.38 F/g at 20 mV/s in the three-electrode electrochemical system. In addition, it revealed good cyclic stability up to 40 cycles run continuously with 95% cyclic retention. The high specific capacitance and superior cyclic stability could be related to the enhanced charge mobility and ion diffusion between the solid and electrolyte interface. The cellulose thin film coated with flower-like hybrid nanocomposite showed great potential in energy storage.

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Abstract
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and coated on MFC thin films to form a supercapacitor. The hybrid tin oxide-cellulose thin films were structurally analyzed using scanning electrode microscopy, Fourier transform infrared spectroscopy and X-ray diffraction. The cellulose thin film with the highest loading of hybrid tin oxide-cellulose nanocomposite exhibited a specific capacitance of 225.88 F/g at 100 mV/s and 486.38 F/g at 20 mV/s in the three-electrode electrochemical system. In addition, it revealed good cyclic stability up to 40 cycles run continuously with 95% cyclic retention. The high specific capacitance and superior cyclic stability could be related to the enhanced charge mobility and ion diffusion between the solid and electrolyte interface. The cellulose thin film coated with flower-like hybrid nanocomposite showed great potential in energy storage.

KEYWORDS

capacitance, microfibrillated cellulose, tin oxide, thin film

— INTRODUCTION

Supercapacitors with high-power output, long-term cyclability, and rapid charging-discharging cycles in electrochemical energy storage systems have been extensively developed in the past decade\(^1\). Conventional batteries with such attractive features cannot be produced because charging-discharging mechanisms involve electrochemical reactions\(^2\). However, supercapacitors also have pitfalls since the poor energy density and limited energy capacitance can affect the overall performance of electrochemical energy storage systems. As the key element in a supercapacitor, electrode materials play a crucial role in the overall electrochemical performance\(^3\). The electrode must also possess a highly interconnected porous structure to allow the diffusion of ions in the material during charging and discharging, as well as a high surface area with active sites for charge storage to overcome mentioned drawbacks\(^4\). Besides the highly efficient, cheap and sustainable supercapacitors are in great demand\(^5\).

Cellulose-based electrodes have been developed to meet the increasing demand for supercapacitors. Cellulose contains a large number of hydroxyl groups\(^6\) on its reactive sites and provides various hybridization opportunities with different active nanomaterials to form conductive nanocomposites\(^7\). Cellulose nanofiber (CNF) and microfibrillated cellulose (MFC) are particularly appealing for flexible energy storage systems because of their high aspect ratio, outstanding mechanical properties and excellent physical qualities\(^8\). They can form hydrogel with a three-dimensional structure and abundant hydrated groups, as well as aerogel with a highly porous network. More importantly, CNF and MFC can also be easily transformed into flexible thin films due to fiber entanglement. Conductive thin films with supercapacitance were successfully developed by incorporating carbonaceous nanomaterials into cellulose. Deng et al.\(^9\) reported on the electrospun cellulose acetate thin film with an electrochemical capacitance of 105 F/g after incorporating multiwalled carbon nanotubes and carbonization in one of the earliest works. Without MWCNTs, the carbonized cellulose nanofiber-activated carbon thin film only attained a capacitance up to 88 F/g\(^10\). Conductive polymers such as polyaniline (PANI)\(^11\), polyvinyl alcohol-borax (PVAB)\(^12\), and polypyrrole (PPy)\(^12,13\) were further incorporated to improve film conductivity. In addition to MWCNTs and carbon nanofibers (CNFs), reduced graphene oxide (rGO) was extensively used to produce CNF-based supercapacitors in recent works\(^16,17\). Other conductive fillers such as tin oxide (SnO\(_2\))\(^18\), molybdenum disulfide (MoS\(_2\))\(^12\), cobalt oxide (Co\(_3\)O\(_4\))\(^19\), lithium chloride (LiCl)\(^20\), and ZnO nanoparticles were reported in the development of CNF-based supercapacitors as well. Compared to CNF, MFC possesses a wider size distribution that includes nano and microfibers. MFC can be produced at a lower cost than CNF since MFC production can be sustainably accomplished by mechanical treatment without enzymatic or chemical pre-treatment. MFC based supercapacitors were also developed, although they were not widely reported in the literature. Liu et al.\(^21\) impregnated carbonized chitosan into the porous MFC framework before drying it into a flexible thin film with a specific capacitor of 139.6 F/g. Without the formation of a porous framework through freeze-drying, a specific capacitance of 53 F/g was only obtained even rGO-SnO\(_2\) nanocomposite was blended into MFC to form a supercapacitor\(^22\). Differently, carbon aerogel with a capacitance as high as 330 F/g was successfully produced from MCF, carbon quantum dots and graphene oxide (GO) through blending, bidirectional freeze-casting, freeze drying and carbonation\(^23\).
Herein, the flexible and thin supercapacitor was fabricated from MFC and SnO2-cellulose nanocomposite. SnO2-cellulose nanocomposite was first hydrothermally produced before being coated on the MFC thin film. Hu et al. reported that the hydrothermal treatment of rice husk nanocellulose in the presence of SnO2 not only resulted in homogeneous dispersion of SnO2 nanoparticles, but also improved crystallinity of SnO2 nanoparticles. In addition, MFC was stabilized in the organic solvent using LiCl before hydrothermal synthesis of nanocomposite and fabrication of MFC thin films. LiCl could stabilize MFC in the organic solvent and improve conductivity. The flexible SnO2-cellulose thin films were characterized to understand the chemical and physical properties before the evaluation of specific capacitance.

— RESULTS AND DISCUSSION

2.1 — Morphology and chemical properties of MFC based supercapacitors

The hybrid SnO2-cellulose nanocomposite was successfully produced via hydrothermal treatment at 120 °C for 4 h. Brown and viscous composites formed after the hydrothermal treatment. The nanocomposites with an increasing amount of SnO2 (4, 8, 12 wt%) were coated on MFC thin films (1 wt%) to form flexible and thin supercapacitors. Delamination was not observed since coatings also contained MFC. More importantly, the self-standing MFC thin films retained their flexibility after coating, as shown in Fig. 1 (a) and (b). SEM images of MFC thin films before and after coating were presented in Fig. 1 (c) and (d). The surface of MFC thin film was considerably rough due to MFC entanglement. Fig. 1 (d) shows the hybrid SnO2-cellulose nanocomposites attached to the MFC thin film, revealing a flower-like structure with more active sites for charge storage to form an outstanding energy storage system. EDX results (Fig. 1 (e) and (f)) were displayed along with SEM images. The presence of SnO2-cellulose nanocomposite was confirmed by the appearance of Sn element.

Fig. 2 displays FTIR spectra of MFC, MFC-4SnO2, MFC-8SnO2 and MFC-12SnO2 thin films between 500 to 3500 cm\(^{-1}\). A broad peak at 3327.14 cm\(^{-1}\) was initiated by the stretching of -OH groups since MFC was rich in hydroxyl groups. These hydroxyl groups could improve the film capacitance upon interacting with activating agent or electrolyte. The peak obtained at 2899.01 cm\(^{-1}\) could be credited to CH-stretching. Meanwhile, the band observed at 1641.42 cm\(^{-1}\) could be associated with the water content of the amorphous region in the MFC. C-O-C stretching in MFC also induced a peak to appear at 1029.99 cm\(^{-1}\). Two common peaks at 3329.14 cm\(^{-1}\) and 1641.42 cm\(^{-1}\) were observed from the FTIR spectra of MFC-4SnO2, MFC-8SnO2 and MFC-12SnO2 thin films because of the stretching and bending of additional O-H groups after incorporation of SnO2. Peaks obtained within low wavenumbers (500-1000 cm\(^{-1}\)) could be attributed to SnO2. Multiple peaks were generated at 534 cm\(^{-1}\), 541 cm\(^{-1}\), and 565.14 cm\(^{-1}\) due to the presence of SnO2 in the MFC-4SnO2 thin film, as shown in the inset of Fig. 2(b). The MFC-8SnO2 thin film also exhibited peaks at 572.86 cm\(^{-1}\) and 852.54 cm\(^{-1}\) which could be assigned to the Sn-O and O-Sn-O bending as well as Sn-O stretching. The peaks appeared at 547.78 cm\(^{-1}\), 559.36 cm\(^{-1}\), 852.54 cm\(^{-1}\), and 931.62 cm\(^{-1}\) for the MFC-12SnO2 thin film (inset of Fig. 2(d)) due to SnO2 hybridization on the cellulose thin film.

The crystallinity changes of MFC thin films after incorporating SnO2 are shown in Fig. 3. The blue diffractogram represents MFC crystallization, and it exhibits a precise core peak at 2θ = 22.4° and two broad peaks at 2θ = 14.3° and 2θ = 16.1°. The amorphous peak of MFC was maintained in all samples at 2θ = 22.4° which justifies that the incorporation integration of SnO2 did not affect the crystallization of MFC. The broad amorphous peak of SnO2 at 2θ = 29.8° of (1 0 1) plane was clearly shown in the diffractogram of MFC-8SnO2 and MFC-12SnO2 samples. The peak at 2θ = 43.3° of (2 0 0) plane in the diffractogram of the MFC-8SnO2 sample could be associated with the Sn bond, which nearly disappeared in the other two samples.

The peak of the SnO bond could be further detected in the diffractogram of the MFC-8SnO2 sample at 2θ = 47.68° of (1 1 2) plane, but it was less visible in the diffractogram of the MFC-12SnO2 sample. The observation could be caused by the agglomeration of SnO2 particles at a high concentration. The crystallization during hydrothermal processing was successfully attained for the MFC-8SnO2 sample, as compared to MFC-4SnO2 and MFC-12SnO2 samples.

— Electrochemical properties and capacitance of MFC based supercapacitors
The CV analysis of MFC-4SnO2, MFC-8SnO2, and MFC-16SnO2 samples was conducted at different scan rates, ranging from 20-100 mV/s (Fig. 4). The CV curve obtained for all samples strongly suggested that SnO2-cellulose nanocomposite could be utilized for pseudocapacitive purposes. Redox peaks appeared, and oxidation curves moved towards positive potential while reduction curves moved towards negative potential. The MFC-12SnO sample exhibited a higher current response compared to other samples, indicating the best capacitive behaviour due to the highest loading of active material. The shape of the redox curve at different scan rates for all the samples was sustained even at a high scan rate. This observation confirmed the ion diffusion through porous structures and the high-rate capability of electrodes. In this work, the specific capacitance was calculated using CV data instead of galvanostatic charge-discharge (GCD) analysis. As reported by others\textsuperscript{35}, the capacitance values determined using the data of CV or GCD showed insignificant deviation. Fig. 4(d) shows the specific capacitance obtained for each sample with different scan rates. At the maximum scan rate, the specific capacitances of MFC-4SnO, MFC-8SnO, MFC-16SnO samples were 101.10, 99.06 and 225.88 F/g, respectively. At the minimum scan rate, their specific capacitances increased to the range of 113.83- 486.38 F/g. This capacitance trend proved the pseudocapacitive nature of SnO\textsubscript{2}-cellulose nanocomposite. At low scan rates or current densities, the electrolyte ions had sufficient time to move across the active sites, resulting in high capacitance values. A high scan rate fastened ion movement and reduced the interaction between ions and the surface of electroactive material. The reduced interaction subsequently caused a reduction in capacitance value.

At the same time, the capacitance value was affected by the loading of electroactive materials on MFC thin films. The thickness of MFC thin films coated with SnO\textsubscript{2}-MFC nanocomposite was measured and then compared against the specific capacitance of each samples at 50 mV/s while maintaining the volumetric capacitance. Charge accumulation through ion acceleration was highly benefited from the high loading of electroactive material. Electrochemical impedance spectroscopy (EIS) was used to evaluate the electrochemical kinetics of the MFC thin films coated with SnO\textsubscript{2}-MFC nanocomposite. Nyquist plot in Fig. 5(b) displays a suppressed semicircle at high-frequency region for all the samples. The suppressed semicircle could be considered a signature of the least charge transfer resistance, indicating facile charge movement at the electrolyte/electrode interface due to excellent electrochemical capacitance\textsuperscript{36}. At the low-frequency region, the oblique line was attributed to the fast ions diffusion path and charge transfer from electrolyte to the electrode interface\textsuperscript{37}. As compared with pristine MFC, MFC-4SnO2, MFC-8SnO2 and MFC-16SnO2 samples shifted to the left due to the low bulk resistance. The slope of this graph (Fig. 5(b)) is directly proportional to the ion transfer rate\textsuperscript{38}. Hence, the MFC-16SnO2 thin film was expected to attain a higher ion transfer rate than MFC-4SnO2 and MFC-8SnO2 thin films. A high loading of electroactive material results in a low ions diffusion resistance, as reported by others\textsuperscript{39}. Thus, the MFC-16SnO2 thin film with low charge transfer resistance could be recommended as the electrode material of electrochemical energy storage systems\textsuperscript{40}. In addition, cyclic stability analysis is utmost important to determine the electrode capability for real time applications in energy storage system. The cyclic stability was observed when the MFC-16SnO2 thin film was tested for 40 cycles at the maximum scan rate of 100 mV/s in 1 M KOH. The CV curve is shown in Fig. 5(c). The specific capacitance of fabricated thin film was retained at 95% even after performing 40 cycles (Fig. 5(d)), indicating the superior durability of the MFC-16SnO2 thin film. This slight reduction in stability was mainly due to the high scan rate of 100 mV/s that prevented the return of ions to their initial position during the reverse voltage scan.

— CONCLUSIONS

In nutshell, the hybrid tin oxide-cellulose thin film was fabricated using hydrothermal and dip-coating method in this work. The obtained composite thin film with superior conductivity could be directly utilized as foldable electrodes for supercapacitors. Electrochemical testing apparently shows that integration of hybrid nanocomposites enhances the capacitive performance. Nonetheless, the XRD patterns explains the high concentration of SnO\textsubscript{2} content in the composite thin film may tend to agglomerate and hard to disperse well to achieve miscibility which is essential factor for better supercapacitor. Thus, SnO\textsubscript{2} content in composite thin film must be controllable. The fabricated flexible thin film achieved favorable specific capacitance of 225.88 F/g at 100 mV/s and 486.38 F/g at 20 mV/s and cyclic stability with 95% capacitance retention.
after 40 cycles. The flexible standalone composite thin film utilizes SnO2 as conductive filler whereby MFC was used as a main substrate and mechanical support also known as biopolymer based binder which able to offer broad future in the next generation for energy storage system application.

— MATERIALS AND METHODS

4.1 — Materials

MCF was supplied as an aqueous colloidal suspension (2 wt%, Exilva) was acquired from Borregaard (Norway). LiCl, SnO2 (average particle size of 1 μm), dimethylformamide (DMF, >99.9%), potassium hydroxide (KOH, >99.5%), tin oxide (99%), and dimethylacetamide (DMAc, >99.9%) were obtained from Sigma Aldrich. All the chemicals were used as received without any further purification. Distilled water was utilized throughout the experiment.

— Fabrication of MFC thin films

LiCl solution with a concentration of 10 wt% was first prepared by stirring LiCl in DMAc at 80 °C. After cooling to room temperature, 1 wt% of MCF was then dispersed in DMAc for 30 min under stirring. Later, MFC suspension was mixed with 10 wt% of LiCl/DMAc for 30 minutes. This mixture was then vacuum filtered using Whatman filter paper and MFC thin films was dried overnight in oven at 60°C.

— Preparation of hybrid tin oxide-cellulose nanocomposites

2 wt% of MFC was diluted into 0.2 wt% of MFC suspension using DMF under stirring for 4 h at ambient temperature. Different SnO2 loadings (4, 8, 12 wt%) were dispersed in DMF separately and sonicated for 3 h before mixing with MFC suspension (0.2 wt%) and stirred for another 1 h at 60 degC. Then, SnO2-MFC mixtures were hydrothermally treated at 120 degC. Dark brown slurries were produced after 4 h.

— Preparation and characterization of tin oxide-cellulose thin films

MFC thin films were dip-coated with SnO2-MFC nanocomposite slurries for 1 h. The coated thin films were dried in an oven at 80 degC overnight to form flexible supercapacitors. After drying, they were rinsed with distilled water and dried at 200 degC for 2 h. These thin films were denoted as MFC-4SnO2, MFC-8SnO2, MFC-12SnO2, respectively. The surface morphology of these thin films was study using scanning electron microscopy (SEM, TM3000 Hitachi, Japan), while their chemical properties was studied using X-ray diffraction (XRD, Bruker Advanced X-ray Solution D8, Cu Kα radiation, λ = 0.154 nm) and Fourier transform infrared spectroscopy (FTIR, Nicolet iS10, Thermo Scientific, USA). The electrochemical properties such as cyclic voltammetry (CV) and cyclic stability were studied using μStat 300 BiPotentiostat electrochemical workstation with the three-electrode system using 1 M of KOH solution as the electrolyte solution. The electrochemical impedance spectroscopy (EIS) data was collected using Metrohm Autolab potentiostat electrochemical workstation.

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