

Efficiency of supercapacitor with CaTiO₃-filled polysulfone separators

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Abstract. Supercapacitors are one of the energy storages designed to serve the increasing demand for electricity nowadays. They are durable and can charge electricity faster and keep electric charge longer. In this study, electrodes for supercapacitors were made from aluminum foils coated with carbon nanotube film and separated by electrolyte solution and a separator. A separator could prevent short circuit but allow ions to pass through, and consequently increased storage layers of electric charge. The separators used in this study were made from polysulfone containing CaTiO₃ 0.5, 1.0 and 2.0 wt% with perovskite properties, high dielectric constant, electrical resistivity and energy density. After that, they were built in coin-cell form. It was found from the study that the addition of 2.0 wt% CaTiO₃, the largest proportion of all samples, provided a maximum specific energy at 4.03 mWh/g and a maximum specific capacitance at 4.64 F/g. accounting for 2.17-time higher than that of polysulfone without CaTiO₃. The functional group analysis of PSF and CaTiO₃ separators showed that the increasing of CaTiO₃ in the PSF separators, the 2958 cm⁻¹ in C-H stretch peaks reduced, and consequently specific energy and specific capacitance were higher. Thus, supercapacitors with CaTiO₃-filled polysulfone separators are suitable for improving efficiency of supercapacitors in energy storage from electrical supply.

1. Introduction

The constantly increasing demand for electric energy in the present world results in the need for energy storage such as batteries, capacitors and supercapacitors. The problems are that batteries require long charging time while providing short cycle time and capacitors, though can be fast charged, have low storage capacity and discharge quickly. Thus, supercapacitors with durability, faster electric charge and longer electric storage are developed. Since electrodes for supercapacitors were made from aluminum foils coated with carbon film [1,2], and separated by an electrolyte solution and a separator to prevent short circuit but allow ions to pass through, storage layers of electric charge increase when dielectric material is added to separator sheets. The added material possesses perovskite properties including catalyst, sensor and high dielectric constant. Calcium titanate (CaTiO₃) is a high-dielectric-constant substance with high electrical resistivity and high energy density [3]. Because of its wide space between the particles, CaTiO₃ allows greater amount of energy to be stored, which is called internal-barrier-layer-capacitor model. It is suitable for inventing ceramic capacitors and polymer capacitors [4] by using polysulfone-based polymers as a polymer sheet [5,6] which has low dielectric constant and porosity [7].

In this study, the researcher was interested in developing supercapacitors using CaTiO₃-filled polysulfone separators by analyzing functional groups in the separators using FT-IT techniques and

oxidation numbers of Ca, Ti and O ion using XPS technique in order to increase the efficiency of supercapacitors in energy storage from electricity sources such as wind turbines and solar cells.

2. Materials and methods

In this section, the preparation of electrodes, electrolyte solution, CaTiO_3 and separators is elaborated. To prepare nano-carbon electrodes, LA 133 (Linyi Gelon LIB Co., Ltd.) was dissolved in Di water and mixed well. Then, nano-carbon was added to the LA 133 adhesive solution and stirred at 60°C for 3 hours. After that, it was poured into a 5 x 10 cm aluminum foil sheets, scrapped longitudinally and at 120°C for 30 minutes to obtain films on an aluminum sheets used as electrodes. Electrolyte solution was made of the mixture of Tetraethylammonium tetrafluoroborate with solution density at 1 M and Acetonitrile. CaTiO_3 was prepared by ball milling 1 mol calcium oxide powder with 1 mol titanate dioxide power for 6 hours and sintering at $1,000^\circ\text{C}$ for 8 hours. CaTiO_3 crystal structure, then, was investigated using X-ray diffraction (XRD) (Bruker, model D2 PHASER) in the range of $10 - 80^\circ$. For separators, 15 wt% Polysulfone (PSF) was dissolved in Dimethylacetamide (DMAc) and stirred well at 60°C for 4 hours. Then, the solution was poured onto glass, scrapped using doctor blade and immersed in DI water to allow the PSF separators to have phase transformation before they took out from the glass. The separators with 15 wt% PSF solution were filled with CaTiO_3 at 0.5, 1.0 and 2.0 wt%, respectively. Through the steps above, 4 separators were obtained. The surfaces of the separators were examined through scanned images of electrodes using Field Emission Scanning Electron Microscope (FE-SEM) (Carl Zeiss, model AURIGA), and functional group analysis was used to analyze the CaTiO_3 - filled separators using FT-IR spectrometer (PerkinElmer, model Spectrum Two). After that the oxidation state of Ca, Ti and O ion of CaTiO_3 -filled separators was investigated using X-rays Photoelectron spectroscopy (XPS) technique from BL3.2a beamline at the Synchrotron Light Research Institute (SLRI), Thailand. To assemble supercapacitor, nano-carbon electrodes on aluminum foil and the separators were cut into circles with 1.6 cm and 1.8 cm diameters, respectively (see figure 1), then coin-cell were made with a hydraulic press. Their efficiency was measured with the Battery Testers System (NEWARE, model BTS 3000) by charging and discharging 10 mA current under electric potential difference (V) of 2.5 V in order to analyze specific energy (W) and calculate specific capacitance (C) as shown in equation (1).

$$W = 1/2 CV^2 \quad (1)$$

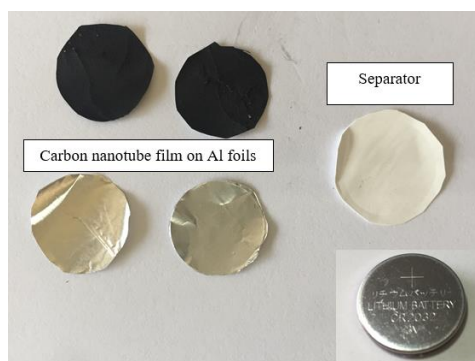


Figure 1. Nano-carbon electrodes and coin-cell separators of supercapacitors.

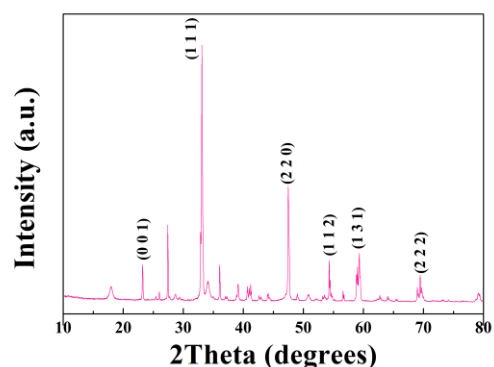


Figure 2. Crystal structure of CaTiO_3 from XRD technique.

3. Results and discussion

Calcium oxide and titanium dioxide in a 1:1 mole ratio was mixed and sintered at $1,000^\circ\text{C}$ for 8 hours to generate CaTiO_3 , then its crystal structure was examined using XRD technique as shown in figure 2. After measuring the diffraction angle 2-theta range of $10-80^\circ$, it was found that the crystal structure corresponds to CaTiO_3 (ICSD code: 031864) with planes 001, 110, 220, 112, 131 and 222. The examination of polysulfone (PSF) surface in DMAc solution as shown in figure 3(a) and polysulfone

containing CaTiO₃ 0.5, 1.0 and 2.0 wt% as shown in figure 3(b)–(d) revealed that the increasing amount of CaTiO₃ in PSF separators results in the replacement of CaTiO₃ particles in the porosity.

The functional group analysis of PSF and CaTiO₃ separators using FT-IR spectrometer as shown in figure 4 was conducted. The results revealed no interesting peak in the PSF separators. However, for CaTiO₃-filled PSF separators, the peak at 2958 cm⁻¹ in C-H stretch, at 1589 and 1487 cm⁻¹ in C-C stretch, at 1240, 1150, 1105 and 1015 cm⁻¹ in C-N stretch and at 835 cm⁻¹ in C-H stretch were observed. Additionally, the greater amount of CaTiO₃ made all of the aforementioned peaks weaker. The analysis of XPS spectra of 2wt% CaTiO₃-filled separators as in figure 5 showed that the oxidation numbers of Ca ions were Ca2s, Ca3s Ca2p and Ca3p; those of Ti ions were Ti2p and Ti3p and those of O ions were O1s and O2s.

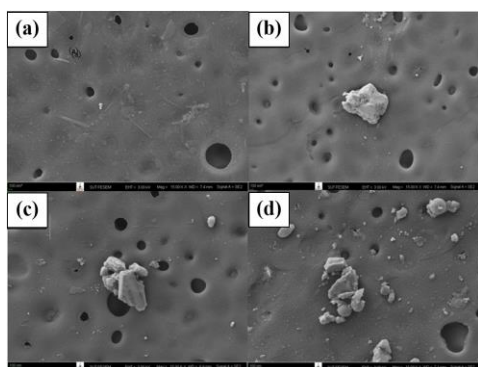


Figure 3. FE-SEM image of separators of (a) PSF (b) PSF with 0.5% CaTiO₃, (c) PSF with 1.0% CaTiO₃ and (d) PSF with 2.0% CaTiO₃.

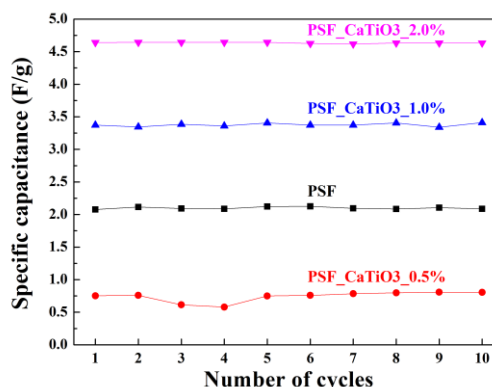


Figure 4. FT-IR spectra of CaTiO₃-filled PSF separators.

The efficiency of supercapacitor using CaTiO₃- filled PSF separators in the weight percentage of 0.5, 1.0 and 2.0 wt% to analyze specific energy (as shown in figure 5) and specific capacitance (as shown in figure 6) using Battery Testers system, brand NEWARE model BTS 3000 (as shown in table 1) was examined. The results showed that supercapacitors with PSF separators held specific energy at 1.85 mWh/g and specific capacitance at 2.13 F/g. Supercapacitors with CaTiO₃-filled separators in the weight percentage of 2.0% (PSF_CaTiO3_2.0%) generated specific energy and specific capacitance at 4.03 mWh/g and 4.64 F/g, respectively. Supercapacitors with CaTiO₃-filled separators in the weight percentage of 1.0% (PSF_CaTiO3_1.0%) generated 2.96 mWh/g of specific energy and 3.41 F/g of specific capacitance, respectively. The specific energy and specific capacitance produced by CaTiO₃-filled separators in the weight percentage of 0.5% (PSF_CaTiO3_0.5%) were the least as they were marked at 0.70 mWh/g and 0.81 F/g, respectively.

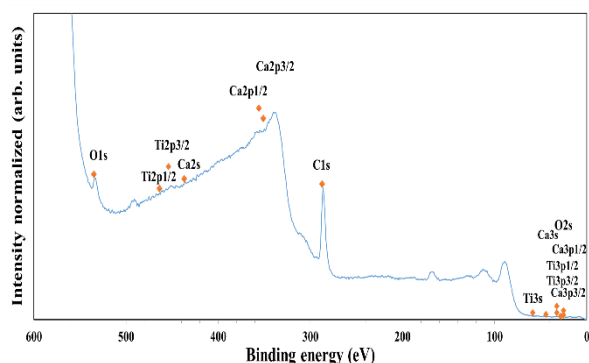


Figure 5. XPS spectra of supercapacitors with 2 wt% CaTiO₃-filled polysulfone separators.

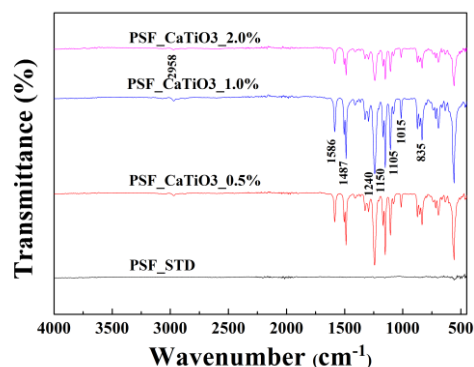


Figure 6. Specific capacitance of supercapacitors with CaTiO₃-filled polysulfone separators.

Table 1. Maximum specific energy and specific capacitance of supercapacitors with CaTiO₃-filled polysulfone separators.

Sample	Specific energy	Specific capacitance
	(mWh/g)	(F/g)
PSF	1.85	2.13
PSF_CaTiO3_0.5%	0.70	0.81
PSF_CaTiO3_1.0%	2.96	3.41
PSF_CaTiO3_2.0%	4.03	4.64

It was found from the study that the mixture of CaO and TiO₂ in a 1:1 mole ratio with sintering at 1,000°C for 8 hours to generate CaTiO₃ caused phase transformation of crystal structure. This corresponds to the crystal structure of CaTiO₃. The analysis of FE-SEM images of PSF separators from XRD technique revealed that the greater amount of CaTiO₃ replaced porosity in separators which lowered porosity and consequently increased storage layers of electric charge.

The functional group analysis of PSF and CaTiO₃ separators showed that the increasing of CaTiO₃ in the PSF separators, the 2958 cm⁻¹ in C-H stretch peaks reduced, and consequently specific energy and specific capacitance were higher. The analysis of XPS spectra of CaTiO₃-filled separators revealed the presence of Ca, Ti and O ion. It can be seen when the amount of CaTiO₃ in PSF separators increases, the amount of Ca, Ti and O increases accordingly, and this is in line with the decrease of C-H stretch peaks (2958 cm⁻¹) making energy storage more effective. Thus, supercapacitors with 2.0 wt% CaTiO₃ provided a maximum specific energy at 4.03 mWh/g and a maximum specific capacitance at 4.64 F/g accounting for 2.17-time higher than that of PSF separators without CaTiO₃, and followed by the addition of 1.0% CaTiO₃ while the addition of 0.5% CaTiO₃ could produce the least.

4. Conclusion

The addition of CaTiO₃ in PSF separators can increase storage layers of electric charge. Supercapacitors filled with 2.0% CaTiO₃ provided 2.17-time higher than the polysulfone without CaTiO₃. Thus, supercapacitors with CaTiO₃-filled polysulfone separators are suitable for improving efficiency of supercapacitors in energy storage from electrical supply and electronic devices.

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