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Fabrications of Poly(vinylidenefluoride-co-hexafluoropropylene) Nanofibers Containing Inorganic Filler by Electrospinning Technique and Its Application to Dye-Sensitized Solar Cells

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We prepared Poly(vinylidenefluoride-co-hexafluoropropylene) (PVDF-HFP) nanofibers containing nano-sized inorganic $BaTiO_3$ filler by electrospinning technique, and applied to the dye sensitized solar cells (DSSCs). This technique compensates the draw back of leakage of the electrolyte in DSSCs. Moreover, electrospun PVDF-HFP nanofibers containing inorganic filler have better ionic conductivity than those of without filler, and the DSSC device using inorganic filler showed better efficiency than without inorganic filler. The best result of V_{oc}, J_{sc}, FF, and η of the DSSC devices using the electrospun PVDF-HFP nanofibers containing 20 wt% inorganic $BaTiO_3$ filler were the values of 0.70 V, 12.9 mA/cm^2, 0.58 and 5.15% under AM 1.5, respectively. We also measured up-take, ionic conductivity and porosity to investigate the effect of electrolyte in the electrospun nanofibers.

Keywords Dye-Sensitized solar cells; electrospinning; PVDF-HFP nanofibers containing nano-sized inorganic filler

1. Introduction

Gratzel and O'Regan made their efforts to Dye-Sensitized Solar Cells (DSSCs) since 1991 [1], the maximum efficiency of 11% has been reported using Ruthenium complex dye, liquid electrolyte, Pt counter electrode under AM 1.5 [2,3]. DSSCs are one of the remarkable renewable energy sources because of their variety of advantages like low cost, easy fabrication, and economical than the convection p-n junction

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solar cell. However, the long term stability is less due to evaporation of their liquid electrolyte when thermal and light stress exposed to them. There is a tendency to use quasi-solid state electrolytes to replace liquid electrolytes [4,5]. In the past decades, many studies have been carried out to alternate with liquid electrolyte, and great progresses have been achieved. To make electrolyte solidification, gelled matrices, and polymerization reactions were used [6,7]. However, in all these cases of quasi-solid state electrolytes, the DSSCs showed considerably lesser solar to electricity conversion efficiencies compared to those of liquid electrolyte ones. The lesser performance of the DSSCs with quasi-solid state electrolyte was attributed to the slow movement of the ions in the electrolytes, owing to their viscous nature [8]. Also, viscous electrolytes do not penetrate easily into the pores of TiO_2 films [8]. However, the ionic conductivity and photovoltaic performance can be maintained at a satisfactory level using electrolytes containing electrospun nanofibers membrane [9]. The electrospun Poly (vinylidenefluoride-co-hexafluoropropylene) (PVDF-HFP) nanofibers maintain the electrolytes which reduce evaporation of the electrolyte from device [9]. Electrospinning technique is one of the promising techniques to produce polymer solutions or melts into continuous fibers with diameter range from a few nanometers to a few micrometers [10]. During electrospinning process, when applied voltage at capillary tip to overcome surface tension of the polymer solution finally the fluid polymer solutions change into solidify nanofibers [11]. Electrospinning technique has been studied since the 1930s and a number of polymers can be electrospun such as nylon 6, 6 [12], polycarbonate [13], polyacrylonitrile [14], PVDF-HFP [15], cellulose acetate and so on [16]. Polymer nanofibers prepared by electrospinning technique have unique properties like large surface area, highly porous, easy fast processing and so on. And the electrospun nanofibers have many applications like filtration, biomedical application, wound dressing, and cosmetics [10,11]. Among these polymers, electrospun PVDF-HFP nanofibers were reported good polymer membrane in Li-ion batteries and DSSC devices due to its high porosity and high surface area [9,17]. Electrospun PVDF-HFP nanofibers also have attractive electrochemical properties, such as high ionic conductivity, high electrochemical stability, and adequate resistance with electrolyte [17–19]. In previous our work, we successfully prepared electrospun PVDF-HFP nanofibers, and have also applied to polymer membrane electrolyte in DSSC devices [9]. Nano-sized inorganic $BaTiO_3$ filler in electrospun PVDF-HFP nanofibers have better ionic conductivity and stable resistance between electrolyte and electrode than nanofibers without the filler [18]. There have been reports additional of a number of inorganic fillers such as TiO_2, Al_2O_3, SiO_2, and Li_3N in solid polymer electrolytes [20]. The effect of these additives to solid polymer electrolyte; 1) enhancement of the volume fraction of the amorphous phase in the polymer complex that supporting the ion transport process; 2) increase in the glass transition temperature (Tg) that suppresses the polymer chain motion responsible for ion transport [20]. In this study, we prepared electrospun PVDF-HFP nanofibers containing nano-sized inorganic $BaTiO_3$ filler and also applied them to electrolyte as polymer membrane in DSSC devices. Before applying the electrospun PVDF-HFP nanofibers containing nano-sized inorganic $BaTiO_3$ filler in electrolyte, we measured SEM image, ionic conductivity, porosity, and electrolyte uptake of the electrospun nanofibers. Finally, we fabricated DSSC devices using electrospun PVDF-HFP nanofibers containing nano-sized inorganic $BaTiO_3$ filler, and studied photovoltaic performances. To evaluate the electrochemical characteristics of the DSSC devices, we also measured electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. *Materials*

TiO_2 paste Ti-Nanoxide HT/SP (9 nm), cis-diisothiocyanato-bis(2,2′-bipyridyk-4,4′-dicarboxylate) ruthenium(II) bis(tetrabutylammonium) (N719 dye), 1-propyl-3-methylimidazolium iodide (PMImI) as an ionic liquid, Suryne (60 μm) as a sealing material, FTO glass (15 Ω/square) and Pt solution (H_2PtCl_6) were purchased from Solaronix SA. Iodine (I_2), lithium iodide (LiI), 4-tertbutylpyridine (TBP), acetonitrile (AN), varelonitrile (VN), PVDF-HFP (Mw: 400,000), $BaTiO_3$ (30∼50 nm) were purchased from Aldrich Co., and used without the purification.

2.2. *Preparation of PVDF-HFP Nanofibers Containing Nano-Sized Inorganic $BaTiO_3$ Filler*

To prepare the electrospun PVDF-HFP nanofibers containing nano-sized inorganic $BaTiO_3$ filler, 15 wt% PVDF-HFP and $BaTiO_3$ (10, 20, 30, and 40 wt% to PVDF-HFP) were dissolved separately in acetone/N,N-dimethylacetamide (DMAc) (7:3, w/w) for 4 hours at room temperature to dissolve wholly the material in the solvent, and then two solutions were mixed together. The mixed solutions were stirred again for 24 hours at room temperature to mix up PVDF-HFP and nano-sized inorganic $BaTiO_3$ filler. Then, we prepared the electrospun PVDF-HFP nanofibers containing nano-sized $BaTiO_3$ filler by the electrospinning technique. To prepare the electrospun PVDF-HFP nanofibers containing nano-sized inorganic $BaTiO_3$ filler with the suitable morphology, we used the following electrospinning technique parameters. The applied voltage (voltage supplier: NNC-ESP100, Nano NC Co., Ltd.) was 12 kV, tip-to-collector distance (TCD) was 18 cm, and the concentration of PVDF-HFP was 15 wt%. We used a syringe pump (781100, Kd Scientific) to control flow rate of the solution, the solution flow rate was 1.5 ml/h. On all occasions, we used the same electrospinning parameters. The electropsun PVDF-HFP nanofibers containing nano-sized inorganic $BaTiO_3$ filler were dried in a dry oven at 45°C for 24 hours to evaporate the solvent wholly. In all cases, the thicknesses were 15 μm by using digimatic micrometer.

2.3. *Fabrications of DSSC Devices*

We fabricated sandwiched type of DSSC devices composed of nanocrystalline oxide film, ruthenium complex dye, electrolyte, and Pt counter electrode. As a substrate, the FTO glass substrates were cleaned with detergent, water, acetone, and ethanol in the sonicator. After that, the working electrode was prepared as follows. The TiO_2 paste (Ti-Nanoxide HT/SP) was deposited on the above cleaned glass by doctor blade method using scotch tapes to delimit the thickness of the TiO_2 film, and sintered at 120°C for 30 min, 275°C for 5 min, 375 for 5 min, 475°C for 5 min and at 550°C for about 30 min. The sintering process was completed and the TiO_2 deposited electrode was cooled down from 550°C to *ca.* 60°C at the controlled cooling rate (5°C/min) to avoid any cracking of the glass. The thickness of sintered TiO_2 film was calculated from cross section of SEM image.

The nanostructured TiO_2 electrode was dipped in an anhydrous ethanolic solution of 0.5 mM N719 dye at 55°C for 24 hours. To prepare the counter electrode, two small holes were drilled (1 mm diameter) on the FTO glass, and several drop of hydrogen hexachloroplatinate (IV) hydrate (H_2PtCl_6) solution was dropped on the cleaned FTO glass substrate, followed by drying and sintered at 450°C for 30 min. We put prepared electrospun PVDF-HFP nanofibers containing nano-sized inorganic $BaTiO_3$ filler (five kinds of DSSC devices were made) between the dye adsorbed TiO_2 electrode and Pt counter electrode. Dye adsorbed TiO_2 electrode and Pt counter electrode were clipped together, and the edges of the devices were sealed with 1 mm side strip of Suryne by hot-melt method. The electrolytes were inserted into the holes on the Pt counter electrode. Two small holes were sealed with cover glasses after the electrospun PVDF-HFP nanofibers containing nano-sized inorganic $BaTiO_3$ filler were fully saturated the electrolyte. The structure of the fabricated DSSC device is shown in Figure 1.

2.4. *Measurements*

The nanostructure and surface morphology of the nanostructured TiO_2 films and electrospun PVDF-HFP nanofibers containing nano-sized inorganic $BaTiO_3$ filler were characterized by Scanning Electron Microscope (FE-SEM, Hitachi S-4200, Hitachi). The resistance for the ionic conductivity was measured by alternating current (AC) impedance test using an electrochemical impedance analyzer (Reference 600, GAMRY instruments). A blocking cell of stainless steel/electrospun nanofibers/stainless steel was used in 1–10^6 Hz of frequency range at room temperature. The applied bias voltage and ac amplitude were set the open circuit voltage of cells and 50 mV, respectively. The EIS data were also measured with impedance analyzer at same condition using FTO/TiO_2/electrolyte/Pt/FTO cells under AM 1.5 of the illumination, and fitted by Z-MAN software (WONATECH) and Echem analyst (GAMRY). A light source (150 W PECCELL) was used as the irradiation source for the I-V measurement. The photovoltaic characteristics of DSSC devices were measured using a Solar Simulator (150 W simulator, PEC-L11, PECCELL) under a simulated solar light with an ARC Lamp power supply (AM 1.5, 100 mW/cm^2). The solar simulator was calibrated to Si reference cell verified. The active area of DSSC device was 0.25 cm^2.

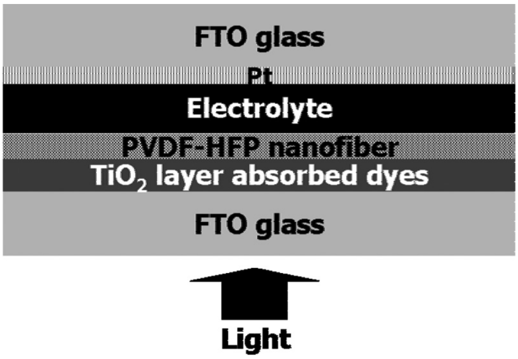

Figure 1. Structure of fabricated DSSC device using electrospun PVDF-HFP nanofibers containing nano-sized inorganic $BaTiO_3$ fillers.

3. Results and Discussion

The cross section SEM image of sintered TiO_2 film is shown in Figure 2. The thickness was calculated about 12 µm.

We prepared the different concentrations of the nano-sized inorganic $BaTiO_3$ filler to PVDF-HFP to characterize the effects of nano-sized inorganic $BaTiO_3$ filler. As the nano-sized inorganic $BaTiO_3$ filler amount to electrospun PVDF-HFP increased, the viscosity of mixture solutions (PVDF-HFP and $BaTiO_3$ filler in acetone & DMAc solution) increased. Several electrospinning parameters like applied voltage, the tip-to-collector distance (TCD), and flow rate were changed to form well organized morphology. By parameters during the electrospinning process, the diameter and the morphology of the nanofibers also changed. Among many kinds of parameters, we used electrospinning parameters on 12KV of applied voltage, 18 cm of TCD (distance tip to the collector), and 1.5 ml/h of flow rate. The more nano-sized inorganic $BaTiO_3$ filler amount increased in electrospun PVDF-HFP nanofibers containing nano-sized inorganic $BaTiO_3$ filler, the more irregular the molpology of the electrospun nanofibers became. The images of the electrospun PVDF-HFP nanofibers without $BaTiO_3$ filler and containing nano-sized inorganic $BaTiO_3$ filler by FE-SEM are shown in Figure 3.

To measure the electrochemical properties of the electropsun PVDF-HFP nanofibers containing nano-sized inorganic $BaTiO_3$ filler, the prepared electrospun PVDF-HFP nanofibers were soaked in an electrolyte solution in an oven at 45°C for 2 hours. When the saturated electrospun PVDF-HFP nanofibers containing nano-sized inorganic $BaTiO_3$ filler was taken from the electrolyte solution, the excess electrolyte on the nanofibers surface was removed. The electrolyte solution was consisting of 0.05 M of I_2, 0.1 M of LiI, 0.60 M of PMImI and 0.5 M TBP in AN/VN (1:1, v/v) solvent. The ionic conductivity of the electrospun PVDF-HFP nanofibers containing $BaTiO_3$ filler in blocking cell of stainless steel/electrospun nanofibers/stainless steel was obtained by AC impedance test (frequency range : $1 \sim 10^6$ Hz).

The ionic conductivity (σ) was calculated by the given formula

$$\sigma = d/(SR) \tag{1}$$

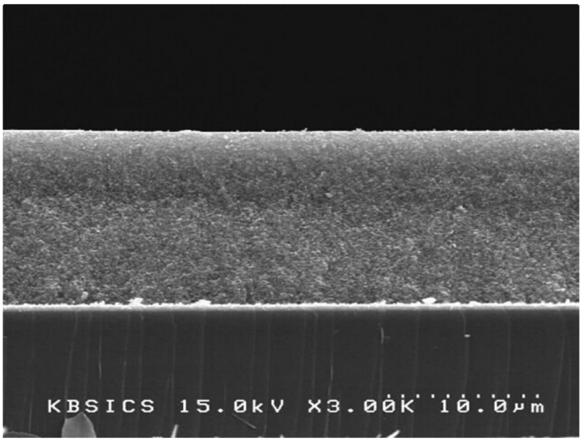

Figure 2. Corss section SEM image of sintered TiO_2 film.

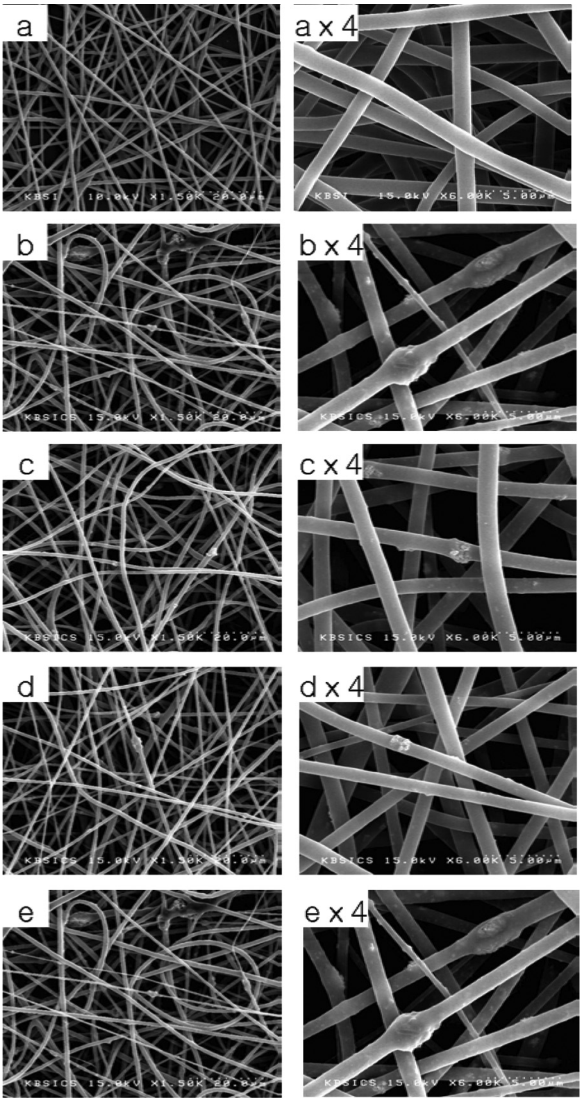

Figure 3. The images of the electrospun PVDF-HFP nanofiber containing $BaTiO_3$ fillers by FE-SEM. (Right images are maginified left images 4 times); a : Electrospun PVDF-HFP nanofiber without $BaTIO_3$ fillers; b : Electrospun PVDF-HFP nanofiber containing 10 wt% $BaTiO_3$ fillers; c : Electrospun PVDF-HFP nanofiber containing 20 wt% $BaTiO_3$ fillers; d : Electrospun PVDF-HFP nanofiber containing 30 wt% $BaTiO_3$ fillers; e : Electrospun PVDF-HFP nanofiber containing 40 wt% $BaTiO_3$ fillers.

where d and S are the thickness and area of the electrospun PVDF-HFP nanofibers containing nano-sized inorganic $BaTiO_3$ filler, respectively; R is the bulk resistance from alternating current (AC) impedance test. The ionic conductivity of the electrospun PVDF-HFP nanofibers was 1.87×10^{-3} S/cm, and electrospun PVDF-HFP nanofibers containing nano-sized inorganic $BaTiO_3$ filler were $2.36 \pm 0.9 \times 10^{-3}$ S/cm which were calculated from the thickness and the area of the electrospun PVDF-HFP nanofibers were 30 µm and 1.767 cm^2, respectively. The ionic conductivity of electrospun PVDF-HFP nanofibers containing nano-sized inorganic $BaTiO_3$ filler showed higher value than that of without filler. However, the ionic conductivities showed similar values when $BaTiO_3$ filler amount increase in electrospun PVDF-HFP nanofibers. To investigate the retention ability of an electrolyte solution in electrospun PVDF-HFP nanofibers with or without $BaTiO_3$ fillers, the electrolyte uptake and leakage were measured. The uptake of the electrolyte solution was determined by soaking the electrospun PVDF-HFP nanofibers with a size of 2.0 cm × 2.0 cm in a 0.05 M of I_2, 0.1 M of LiI, 0.60 M of PMImI and 0.5 M TBP in AN/VN (1:1, v/v) solvent. The weights of the wetted electrospun PVDF-HFP nanofibers were measured against their soaking time after the removal of the excess electrolyte solution that remained on the surface of the electrospun nanofibers.

The electrolyte uptake (U) was calculated according to the following formula:

$$U = [(m - m_0)/m_0] \times 100\% \tag{2}$$

where m and m_0 are the masses of wet and dry of the electrospun nanofibers, respectively. The porosity (P) of the electrospun PVDF-HFP nanofibers was calculated from the density of the electrospun PVDF-HFP nanofibers (ρ_m, g/cm^3) and the density of pure PVDF-HFP ($\rho_p = 1.767$ g/cm^3). The porosity of the electrospun nanofibers was calculated by following fomula:

$$P(\text{vol. }\%) = (1 - \rho_m/\rho_p) \times 100 \tag{3}$$

The density of the electrospun PVDF-HFP nanofibers were determined by measuring the volume and the weight of the electrospun PVDF-HFP nanofibers. The uptake of the electrospun PVDF-HFP nanofibers with and without nano-sized inorganic $BaTiO_3$ filler showed 732.4 ± 50% and 627%, respectively. The porosity of theirs showed 90.2 ± 0.7% and 90.5%, respectively. The uptakes showed higher value with nano-sized inorganic $BaTiO_3$ filler in electrospun PVDF-HFP nanofibers than without $BaTiO_3$ filler. The porosities were showed similar values whether the $BaTiO_3$ filler was included in electrospun PVDF-HFP nanofibers or not. This indicates that

Table 1. Ionic conductivity[a], electrolyte uptake[b], and porosity of electrospun PVDF-HFP nanofibers[c] containing nano-sized inorganic $BaTiO_3$ filler

$BaTiO_3$ (wt %)	Ionic conductivity ($\times 10^{-3}$ S/cm)	Uptake (%)	Porosity (%)
0	1.87	627.0	90.5
10	2.00	734.7	90.9
20	2.18	748.5	90.1
30	2.93	692.3	90.2
40	2.33	754.0	89.7

[a] All the conductivities were measured at 50 mV (amplitude), 1~10^6 Hz (frequency), and open circuit voltage.

[b] Electrolyte was consisting of 0.05 M of I_2, 0.1 M of LiI, 0.60 M PMImI, and 0.5 M of TBP in solvent of AN:VN (1:1, v/v).

[c] On all conditions, the thickness of nanofibers are 30 µm.

Table 2. Photovoltaic characteristics[a] of DSSC devices using electrospun PVDF-HFP nanofibers[b] containing nano-sized inorganic $BaTiO_3$ filler in electrolytes[c]

$BaTiO_3$ (wt %)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	Efficiency (%)
0	11.0	0.71	0.56	4.57
10	11.4	0.71	0.62	5.06
20	12.9	0.70	0.58	5.15
30	11.7	0.70	0.60	4.92
40	11.7	0.71	0.61	4.97

[a] All the devices were measured by a solar simulator under illumination at AM 1.5 condition.

[b] The thickness of the electrospun PVDF-HFP nanofibers were 15 μm.

[c] The electrolyte was consisting of 0.05 M of I_2, 0.1 M of LiI, 0.6 M of PMII and 0.5 M of TBP in the solvent of AN/VN (1:1, v/v).

during electrospining process, nano-sized inorganic $BaTiO_3$ fillers do not influence electrospun PVDF-HFP nanofibers morphology forming pores. The all values of ionic conductivity, uptake, and porosity changes are summarized in Table 1.

Then, we fabricated DSSC devices using electrospun PVDF-HFP nanofibers containing nano-sized inorganic $BaTiO_3$ filler, and the photovoltaic effects and EIS were investigated. The best result of V_{oc}, J_{sc}, FF, and η of the DSSC devices using the electrospun PVDF-HFP nanofibers containing nano-sized inorganic $BaTiO_3$ filler were the values of 0.70 V, 12.9 mA/cm^2, 0.58 and 5.15% under AM 1.5, respectively, and all the data are summarized in Table 2 and their I-V curves are shown in Figure 4.

The value of J_{SC} was higher in nanofibers with nano-sized inorganic $BaTiO_3$ filler than that of without them. In general, the high crystallinity of polymer membrane is one of the major factors of the low ionic conductivity of electrolytes [22]. When nano-sized inorganic $BaTiO_3$ filler were mixed, the polymer nanofibers were changed to amorphous phase from crystalline phase. Therefore, nano-sized inorganic $BaTiO_3$ filler helps the ion transporting in the polymer nanofibers electrolyte on DSSC. We measured EIS to evaluate the efficiency of DSSC devices with nano-sized inorganic $BaTiO_3$ filler containing in electrospun PVDF-HFP nanofibers. We investigated interfacial charge transfer resistances from EIS data. The Nyquist plots of the FTO/TiO_2/electrolyte/Pt/FTO cells and charge transfer resistances are shown in Figure 5 and their data are summarized in Table 3, respectively.

The R_S, $R1_{CT}$, and $R2_{CT}$ are series resistance, the charge transfer resistance of Pt/electrolyte interface, and the charge transfer resistance of TiO_2/electrolyte interface, respectively. The device with the nano-sized inorganic $BaTiO_3$ filler, the charge transfer resistance at the TiO_2/electrolyte interface ($R2_{CT}$) was lower than those of electrospun PVDF-HFP nanofiber without $BaTiO_3$ filler. This mainly indicates that nano-sized inorganic $BaTiO_3$ filler helps the ion transporting between electrodes. The Bode plots of the FTO/TiO_2/electrolyte/Pt/FTO cells are shown in Figure 6.

The equivalent circuit of DSSC device is shown in Figure 7.

Bode plot shows the frequency which is determined by the effective electron life time [21]. They were shown similar electron lifetime among five devices containing nano-sized inorganic $BaTiO_3$ filler or not. The higher efficiency of the DSSC device is largely caused by high ionic conductivity due to nano-sized inorganic $BaTiO_3$ filler.

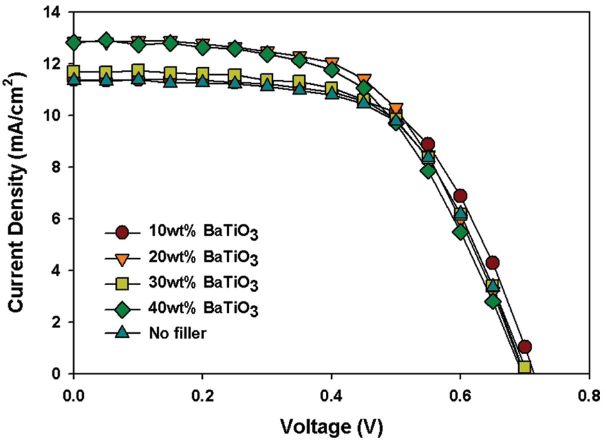

Figure 4. I-V curves of DSSC devices using prepared PVDF-HFP nanofibers containing nano-sized BaTiO$_3$ fillers.

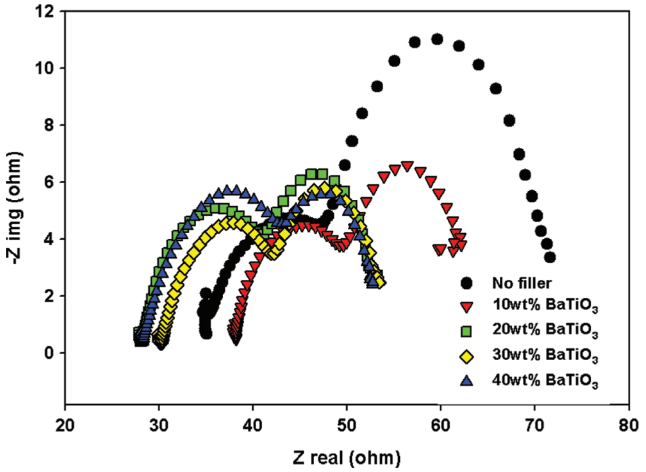

Figure 5. Nyquist plots the FTO/TiO$_2$/electrolyte/Pt/FTO device using electrospun PVDF-HFP nanofiber containing nano-sized BaTiO$_3$ fillers electrolyte.

Table 3. The series resistances (R_S), the charge transfer resistance of the Pt/electrolyte ($R1_{CT}$), and charge transfer resistance of the TiO$_2$/electrolyte ($R2_{CT}$) in the DSSC devices under AM 1.5 condition by the EIS measurement[a]

BaTiO$_3$ (wt %)	R_S	$R1_{CT}$ (Ω)	$R2_{CT}$ (Ω)
0	34.45	15.56	21.88
10	37.84	11.85	13.57
20	31.20	14.38	11.73
30	30.02	13.00	11.25
40	28.05	16.58	9.34

[a] All the conductivities were measured at 50 mV (amplitude), 1~10^6 Hz (frequency), and open circuit voltage.

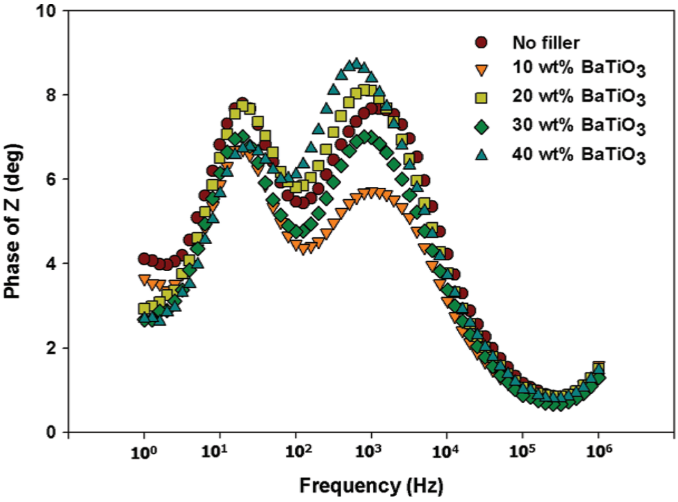

Figure 6. Bode plots the FTO/TiO_2/electrolyte/Pt/FTO device using electrospun PVDF-HFP nanofiber containing nano-sized $BaTiO_3$ fillers electrolyte.

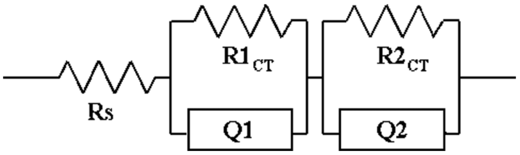

Figure 7. The equivalent circuit of the DSSC device. (R_{S}: Series resistance, $R1_{CT}$: charge transfer resistance of Pt/electrolyte, $R2_{CT}$: charge transfer resistance of TiO_2/electrolyte, Q1 and Q2: constant phase element).

4. Conclusion

We have successfully fabricated DSSC devices using electrospun PVDF-HFP nanofibers containing nano–sized inorganic $BaTiO_3$ filler. Ionic conductivity of electrospun PVDF-HFP nanofibers containing nano-sized inorganic $BaTiO_3$ filler showed higher values than that without $BaTiO_3$ filler. The efficiency of DSSC devices using electrospun PVDF-HFP nanofibers containing nano-sized inorganic filler showed higher value than that without nano-sized inorganic $BaTiO_3$ filler. The charge transfer between TiO_2/electrolyte interfaces ($R2_{CT}$) showed lower value using electrospun PVDF-HFP containing nano-sized inorganic $BaTiO_3$ filler. The nano-sized inorganic $BaTiO_3$ filler itself helped the ion transporting in the electrolyte on DSSC device, moreover, the filler made nanofibers amorphous which suppress polymer chain motion responsible for ion movement.

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