

# PREPARATION AND PROPERTIES OF COMPOSITE SOLID POLYMER ELECTROLYTE FOR STRUCTURAL CAPACITOR

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## ABSTRACT

The modified silica was synthesized by sol-gel method using methacryloxypropyl trimethoxysilane (MAPTMS). Composite solid polymer electrolytes, differing by the MAPTMS feed rate, were prepared. We prepared composite solid polymer electrolytes (SCPEs) composed of poly (ethylene glycol) monomethyl ether acrylate (PEGA), 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIm][OTF]) and inorganic filler. The two type of fumed silica were used. One has unmodified surface, the other has organically modified surface. The CSPEs formed by appropriately adding ionic liquids in the PEGA prior to thermal cure. The ratio between PEGA and ionic liquid was 7:3, and 5:5, respectively. The effect of silica surface properties on the characteristics of CSPEs was investigated. Fourier transform infrared (FT-IR) spectroscopy, electrochemical impedance spectroscopy and cyclic voltammetry were used.

## 1. INTRODUCTION

Supercapacitors are electrical energy storage device, which provided low cost, high power density, high cycle-life, large capacitance, high power delivery, fast charge-discharge rate, and mechanical robustness [1]. Supercapacitors are used in a wide range of applications such as the hybrid electric vehicle (HEV), pulse power, memory protection, and medical equipment [2-3]. The supercapacitors store electrical charge in an electric double layer at the interface between a high-surface-area carbon electrode and electrolyte [4]. The supercapacitors consist of two electrodes separated by a porous membrane and an electrolyte ionically connecting both electrodes. The electrode is made of an aluminum current collector foil, supporting the activated carbon powder. Chung and Wang [5] first suggest the use of carbon fiber reinforced polymer in structural electronics. The several researchers were studied structural electronics such as structural batteries, structural capacitors, and structural fuels [6-7]. The supercapacitors store electrical charge in an electric double layer at the interface between a high-surface-area carbon electrode and electrolyte. Composite solid polymer electrolytes (CSPEs) containing mesoporous inorganic filler delivers better mechanical strength, higher ionic conductivity, and good anode/electrolyte interfacial property. High ionic conduction of CSPE containing mesoporous inorganic filler has been generally explained by Lewis acid-base interaction. We produced structural capacitor made from carbon fiber/epoxy prepreg and composite solid polymer electrolyte. The carbon fiber/epoxy prepreg fabric was used as packaging material.

## 2. EXPERIMENTAL

### 2.1 Materials

The poly (ethylene glycol) monomethyl ether acrylate [PEGA, Mn 480; Aldrich] was used as received. 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate [[EMIm][OTF]; C-tri Co] as ionic liquid and cumene hydroperoxide [CHP; Aldrich; 80%], were used without further purification. Fumed silica (SiO<sub>2</sub>) and methacryloxypropyl trimethoxysilane [MAPTMS] were supplied by Aldrich,

Commercially available activated carbon electrodes (130  $\mu\text{m}$ ), with carbon layer (100  $\mu\text{m}$ , 1800 $\text{m}^2/\text{g}$ ) attached to an aluminum (Al) current collector (30  $\mu\text{m}$ ), was purchased from Vinatech.Co, Korea.

## 2.2 Preparation of 1A9OMe based composite solid polymer electrolytes

The composition of PEGA/[EMIM][OTF] based CSPEs listed in Table 1. The ionic liquid and inorganic filler were added to the appropriate 1A9OMe, and stirred for 30min. The viscous solution was cast onto Teflon casted a glass plate. The casted sample was heated at 80  $^{\circ}\text{C}$  for 16 h, then raised to 110  $^{\circ}\text{C}$  for 1 h, after which the oven was allowed to cool to room temperature. CHP was added in quantity 1.5 w/w % resins. The composite solid polymer electrolyte samples were coded as poly (PEGA/[OTF]\_I\_AB\_) electrolytes defined as above. The I represented type of inorganic filler, the A symbolized contents of PEGA and the B symbolized contents of ionic liquids.

Sample	PEGA (g)	[EMIm][OTF] (g)	Inorganic particle (g)
PEGA /[OTF]_73	7	3	0
PEGA /[OTF]_55	5	5	0
PEGA [OTF]_SiO2_73	7	3	0.1
PEGA /[OTF]_SiO2_55	5	5	0.1
PEGA /[OTF]_mSiO2_73	7	3	0.1
PEGA /[OTF]_mSiO2_55	5	5	0.1

Table 1. The composition of PEGA/[EMIM][OTF] based composite solid polymer electrolytes

## 2.3 Manufacture of structural capacitor

The structural supercapacitors were assembled by sandwiching SPEs between active carbon electrodes, and vacuum sealed with carbon fiber/epoxy prepreg. Manufacture process of structural capacitor set up in earlier work [8]. The structural capacitors were sandwiched between peel-plies. The mold was sealed with butyl tape and vacuum bag. The mold was placed in oven and heat up to 80 $^{\circ}\text{C}$  for 16 hours under vacuum condition to achieve void-free. A manufacture of the structural capacitor laminates is shown in Figure 1.

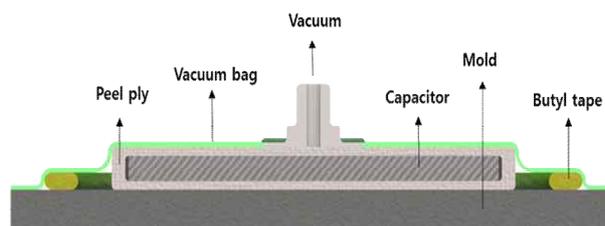


Figure 1. Manufacture of the structural capacitor laminates.

## 3. RESULTS AND DISCUSSIONS

### 3.1 Structural properties

Silica nanoparticle with methacrylate group on the surface was investigated using Fourier transform infrared spectroscopy in the attenuated total reflectance mode (FTIR-ATR). The FTIR-ATR spectra obtained for fumed silica ( $\text{SiO}_2$ ) and modified silica ( $\text{mSiO}_2$ ) were shown in Figure 2. In FTIR-ATR spectra, the broad peak in 3300~3400 $\text{cm}^{-1}$  due to Si-OH stretching bond was decreased intensity value and the sharp peak in 1720 corresponding to C=O and peak in 1640 and 935  $\text{cm}^{-1}$  corresponding C=C bond of methacrylate group appeared. Also, the peaks in the range of 1000~1300  $\text{cm}^{-1}$  and around 815  $\text{cm}^{-1}$  in Fig.2 correspond to Si-O-Si antisymmetric stretching vibration mode in the fumed silica.

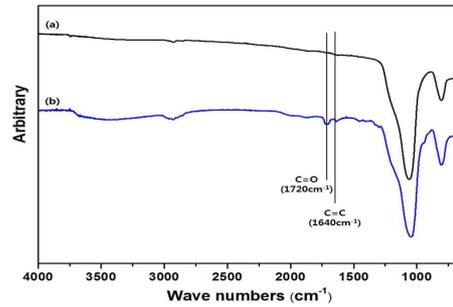


Figure 2. FTIR-ATR spectra of (a) SiO<sub>2</sub> and (b) mSiO<sub>2</sub>.

### 3.2 Electrochemical analysis

Figure 3 shows ionic conductivity obtained from impedance spectroscopy at room temperature. The ionic conductivity of PEGA/[OTF] based SPEs with a different concentration of [EMIm][OTF] was  $4.9 \times 10^{-4}$  and  $2.3 \times 10^{-4}$  S/cm, respectively. The ionic conductivity of PEGA/[OTF]<sub>SiO<sub>2</sub></sub> based CSPEs with a different concentration of [EMIm][OTF] was  $4.5 \times 10^{-4}$ , and  $2.8 \times 10^{-4}$  S/cm, respectively. The ionic conductivity of PEGA/[OTF]<sub>mSiO<sub>2</sub></sub> based CSPEs with a different concentration of [EMIm][OTF] was  $3.0 \times 10^{-4}$  and  $8.1 \times 10^{-5}$  S/cm, respectively. The conductivity value of SPEs depends on the relative contents of two completing effects. As ILs concentration was increased, ionic conductivity was decreased due to formation of ion pair and interaction of ion-dipolar moment. Thus, the highest ionic conductivity of SPEs was found to be  $4.90 \times 10^{-4}$  S/cm in a PEGA/[OTF]<sub>73</sub>. Addition of inorganic filler, ionic conductivity of CSPEs was decreased. The ionic conductivity of CSPEs with SiO<sub>2</sub> was higher than that of CSPEs with mSiO<sub>2</sub>, due to OH group contents of silica surface.

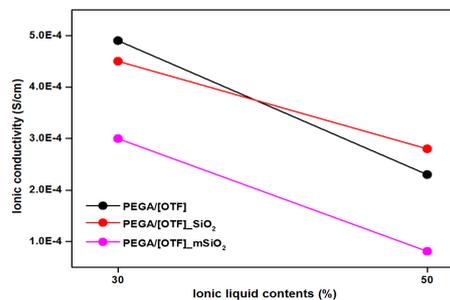


Figure 3. Ionic conductivity of CSPEs for PEGA with different concentration of [EMIm][OTF].

The cyclic voltammetry was carried out at 25 °C at the scan rate of 10mV/s over the range from 0 to 3V. The specific capacitance of supercapacitor using CV curve was shown in figure 4. The ratio between PEGA and ionic liquids was 7:3, and 5:5, respectively. The specific capacitance of PEGA/[OTF] based SPEs with a different concentration of [EMIm][OTF] was same value as 13.0 F/g. The specific capacitance of PEGA/[OTF]<sub>SiO<sub>2</sub></sub> based CSPEs with a different concentration of [EMIm][OTF] was 7.9 and 7.4 F/g, respectively. The specific capacitance of PEGA/[OTF]<sub>mSiO<sub>2</sub></sub> based CSPEs with a different concentration of [EMIm][OTF] was 6.7 and 5.8 F/g, respectively. As ILs concentration was increased, specific capacitance was slightly decreased. Addition of inorganic filler, the specific capacitance of CSPEs was decreased. The specific capacitance of CSPEs with SiO<sub>2</sub> was higher than that of CSPEs with mSiO<sub>2</sub>.

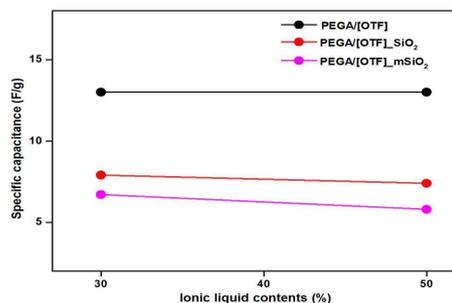


Figure 4. The specific capacitance of CSPEs for PEGA with different concentration of [EMIm][OTF].

#### 4. CONCLUSIONS

We prepared CSPEs composed of PEGA as oligomer, [EMIm][OTF] as the ionic liquid and inorganic filler. The ratio between PEGA and ionic liquids was 7:3, and 5:5, respectively. In the FT-IR spectrum of modified SiO<sub>2</sub>, the observed peaks are assigned as follows: a characteristic carbonyl peak (C=O stretching) is at 1720 cm<sup>-1</sup>, the C=C peak at 1640 and 935 cm<sup>-1</sup>. The electrochemical properties of CSPEs for supercapacitor are investigated using electrochemical impedance spectroscopy, and cyclic voltammetry. The ionic conductivity of PEGA/[EMIm][OTF] based SPEs with a different concentration of [EMIm][OTF] was 4.9\*10<sup>-4</sup>, and 2.3\*10<sup>-4</sup> S/cm, respectively. The ionic conductivity of PEGA/[OTF]\_SiO<sub>2</sub> based CSPEs with a different concentration of [EMIm][OTF] was 4.5\*10<sup>-4</sup>, and 2.8\*10<sup>-4</sup> S/cm, respectively. As addition of inorganic filler, ionic conductivity was lower than the neat SPEs. The specific capacitance of PEGA/[OTF] with a different concentration of [EMIm][OTF] was 13, and 13 F/g, respectively. The specific capacitance of PEGA/[EMIm][OTF]\_SiO<sub>2</sub> based CSPEs with a different concentration of [EMIm][OTF] was 7.9, and 7.4 F/g. As addition of inorganic filler, the specific capacitance was lower than the neat SPEs. Also, the ionic conductivity and specific capacitance of CSPEs with SiO<sub>2</sub> was higher than that of CSPEs with mSiO<sub>2</sub>.

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