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Enhancing the performance of green solid-state electric double-layer capacitor incorporated with fumed silica nanoparticles

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ABSTRACT

Solid polymer electrolyte (SPE) based on fumed silica nanoparticles as nanofillers, hydroxylethyl cellulose (HEC) as host polymer, magnesium trifluoromethanesulfonate salt and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ionic liquid is prepared by solution casting technique. The ionic conductivity, interactions of adsorbed ions on the host polymer, structural crystallinity and thermal stability are evaluated by electrochemical impedance spectroscopy (EIS), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and thermogravimetric analysis (TGA), respectively. Ionic conductivity studies at room temperature reveals that the SPE with 2 wt. % of fumed silica nanoparticles gives the highest conductivity compared to its counterpart. The XRD and FTIR studies confirm the dissolution of salt, ionic liquid and successful incorporation of fumed silica nanoparticles with host polymer. In order to examine the performance of SPEs, electric double-layer capacitor (EDLC) are fabricated by using activated carbon electrodes. EDLC studies demonstrate that SPE incorporated with 2 wt. % fumed silica nanoparticles gives high specific capacitance (25.0 F/g) at a scan rate of 5 mV/s compared to SPE without fumed silica. Additionally, it is able to withstand 71.3% of capacitance from its initial capacitance value over 1600 cycles at a current density of 0.4 A/g.

1. Introduction

In this modern era, the usage of electronic and electrical equipment is increasing dramatically, which created the alarming issues of managing and disposing of electronic as well as electrical waste (e-waste). The e-waste generated from the use of cell phone became the second highest contributor to the total e-waste in accordance to the European Union Directive [1]. Moreover, hazardous materials such as heavy metals (i.e. copper, aluminium, chromium, lead, mercury, etc.), flame retardants, plastic casings and energy storage devices (i.e. batteries and supercapacitor) are produced from the e-waste of cell phone [2]. Consequently, the managing and disposal of huge volume of e-waste and the release of numerous hazardous materials (flame retardants and heavy metals) may pose a threat to the environment and human health [3,4]. Therefore, materials (heavy metals from the flame retardants plastic casings) recovery was adopted to reduce the discharge of harmful wastes to the environment [5]. However, in order to manage e-waste and to reduce its dumping space, biodegradable energy storage devices are critically needed as an alternative of conventional energy storage devices for latest technological equipment.

Batteries and supercapacitors are the most commonly used energy storage devices in the cell phone, laptops and other portable electronic devices. Supercapacitors (electrochemical capacitors or ultracapacitors) gained its popularity since 1800 owing to its higher power and energy densities than batteries and conventional capacitors, respectively [6]. Supercapacitors are categorized into pseudocapacitors and EDLCs according to their charge storage mechanism [7]. An EDLC has more influential advantages such as larger specific capacitance, higher specific power and longer life cycle than a pseudocapacitor [8]. On top of that, EDLC have an additional feature that is environmental friendly by using various natural and synthetic biodegradable polymers namely chitosan, starch, iota(ι)-carrageenan, xanthan gum, cellulose derivatives and poly(vinyl alcohol) (PVA) were utilized as the host polymers for EDLCs [9,10].

Herein, EDLC based on biodegradable SPE has been fabricated using HEC as host polymer. HEC has many electron-donating atoms per

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Table 1
Compositions and designations for HEC: $MgTf_2$: EMIMTf: fumed silica complexes.

Compositions (wt. %) HEC: $MgTf_2$: EMIMTf: Fumed silica	Designations
36.0: 24.0: 40.0: 0.0	HE40
47.2: 11.8: 40.0: 1.0	HS1
46.4: 11.6: 40.0: 2.0	HS2
45.6: 11.4: 40.0: 3.0	HS3
44.8: 11.2: 40.0: 4.0	HS4

monomer that provide spaces for the adsorption of charge carriers through ion-dipole interaction. Subsequently, it fulfills the most important criteria of a polymer electrolyte that is high ionic conductivity and charge storage capacity which makes it suitable candidate for energy storage applications. On top of that, HEC is a green material with excellent solubility in water, biocompatibility, easy availability, low cost and nonionic behavior [11,12].

However, supercapacitors fabricated by biodegradable SPE comprising of HEC as host polymer and magnesium trifluoromethanesulfonate ($MgTf_2$) salt suffers from low ionic conductivity at room temperature ($\sim10^{-9}$ to $\sim10^{-7}$ S/cm) even though it has outstanding features such as compact structure with no leakage problem, low flammability, good flexibility, safety, stable contact between the electrode and electrolyte [13]. Therefore, ionic liquids are employed to enhance the conductivity of SPEs. They offer wider potential window, high electric conductivity and excellent thermal stability. Herein, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMIMTf) ionic liquid (IL) is used to improvise the conductivity of the SPE.

Besides IL, metal oxide nanoparticles as nanofillers can play significant role in boosting the mechanical strength and ionic conductivity of SPE by interacting with mobile ions. Fumed silica (SiO_2) nanoparticles has been chosen as filler in this study owing to their large contact surface area and amorphocity [14]. According to Kim et al. (2003), these nanoparticles are able to create better adsorption with both host polymer and salt through hydrogen bonding due to its reactive silanol (Si–OH) groups [15]. Thus, it leads to the superior interfacial stability due to which it is widely used as reinforcing nanofiller for silicon rubber, high and low temperature resistant elastomer (in wires, cables and automotive components) and thermal insulation materials, thickening and anti-setting agents in liquid systems (coatings, adhesives, printing inks, cosmetics, foods and fire extinguisher powders) [16,17].

Based on the above facts, SPEs (with and without fumed silica nanoparticles) were prepared and these SPEs were characterized by using EIS, XRD, TGA and FTIR. The performance of the SPEs towards the EDLC is evaluated by using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and EIS. It was found that the introduction of fumed silica nanoparticles into the SPE not only enhanced the ionic conductivity and thermal stability, but also facilitated the better penetration and entrapment of ions into the bulk electrodes.

2. Experimental

2.1. Materials

Activated carbon (AC) BP20 and N-methyl-2-pyrrolidone (NMP) (Purity 99.5%) were obtained from Kuraray Chemical Co. Ltd., Japan and Merck, Germany, respectively. HEC, $MgTf_2$, EMIMTf, fumed silica nanoparticles, carbon black (Super P) and poly(vinylidene fluoride) (PVdF) were purchased from Sigma–Aldrich, USA. Deionized water (DI) was used for the preparation of aqueous solutions.

2.2. Preparation of biodegradable nanocomposites SPE

Fumed silica nanoparticle were activated by the method reported by Taghizadeh and Aghjekohal (2015) [18]. HEC, $MgTf_2$ and activated fumed silica nanoparticles were pre-heated for 1 h at 100 °C to remove moisture. After that, HEC, $MgTf_2$, EMIMTf and different wt. % of activated fumed silica nanoparticles (presented in Table 1) were mixed in DI using bath sonication for 30 min followed by constant stirring for 24 h at room temperature. Finally, the homogeneous slurry was cast on a Teflon coated aluminum foil and allowed to evaporate at 70 °C. After drying, a thin solid film of polymer electrolyte was obtained.

2.3. Characterizations of SPE

Ionic conductivity was measured using an AC impedance technique using HIOKI 3532-50 LCR HiTESTER, over a frequency range from 50 to 1000,000 Hz and temperature range of 30–120 °C. SPE films were mounted on the holder with stainless steel (SS) blocking electrodes under spring pressure with the configuration of SS/SPE/SS blocking electrodes. Bulk resistance was obtained from the complex impedance plots of the SPE. The ionic conductivity (σ), and the activation energy (E_a) of the SPE complexes was calculated by the following equations:

$$\sigma = \frac{d}{R_b A} \tag{1}$$

where "d" is thickness of film (cm), "R_b" is bulk resistance obtained from Cole-Cole plot (Ω), and "A" is the area of the film (cm^2).

$$\sigma_T = \sigma_o \exp\left(\frac{-E_a}{kT}\right) \tag{2}$$

where "σ_T" is the ionic conductivity at different temperature, "σ_o" is the conductivity pre-exponential factor, "k" is the Boltzmann constant, "E_a" is the activation energy and "T" is the absolute temperature.

Complex impedance data, Z*, can be represented by its real, Z′, and imaginary, Z", parts by the relation

$$Z^* = Z' - jZ'' \tag{3}$$

where $Z' = |Z|\ \omega \cos\theta$, $Z'' = |Z|\ \omega \sin\theta$ and j is constant.

The equations for the dielectric permittivity, ε′, the dielectric loss, ε′′, the real modulus, M′, and the imaginary modulus M" can be illustrated as

$$\varepsilon\prime = \frac{Z\prime\prime}{\omega C_o\left[(Z\prime)^2 + (Z\prime\prime)^2\right]} \tag{4}$$

$$\varepsilon\prime\prime = \frac{Z\prime}{\omega C_o\left[(Z\prime)^2 + (Z\prime\prime)^2\right]} \tag{5}$$

$$M\prime = \frac{\varepsilon\prime}{\left[(\varepsilon\prime)^2 + (\varepsilon\prime\prime)^2\right]} \tag{6}$$

$$M\prime\prime = \frac{\varepsilon\prime\prime}{\left[(\varepsilon\prime)^2 + (\varepsilon\prime\prime)^2\right]} \tag{7}$$

FTIR studies were conducted by using Themoscientific Nicolet iS10 FTIR spectrometer which was equipped with an internal reflection accessory. The resolution of the spectrum was 4 cm^{-1} in the wavenumber region between 4000 cm^{-1} and 400 cm^{-1} recorded in the transmittance mode. XRD patterns of SPEs were measured using Siemens D5000 diffractometer with Cu–Kα radiation (λ = 1.5406 Å) and thermal properties were studied using TGA Q500 V20.13 Build 39 (TA, Instruments, New Castle, DE, USA) with a temperature up to 800 °C.

2.4. Preparation of electrode

The ink for the fabrication of the electrode was prepared by mixing 80 wt. % of activated carbon, 10 wt. % of carbon black and 10 wt. % of PVdF binder in NMP solvent under ultrasonication. The mixture was constantly stirred overnight at ambient temperature until homogenous