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Solid-state supercapacitors with ionic liquid gel polymer electrolyte and polypyrrole electrodes for electrical energy storage

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ABSTRACT

In this work, solid-state supercapacitors with ionic liquid gel polymer electrolyte and polypyrrole symmetrical electrodes were fabricated and characterized. The ionic liquid 1-butyl-3methylimidazolium tetrafluoroborate ($BMIBF_4$) was mixed with poly (vinylidene fluoridehexafluoropropylene) P(VdF-HFP) to form gel electrolyte. The polypyrrole electrode was prepared by ultra-short pulsed current electropolymerization over flexible graphite sheets, and was synthesized using $LiClO_4$ and H_2SO_4 electrolytes. Both electrodes were conditioned by using cyclic voltammetry (CV) for approximately 20 cycles before electrochemical testing. The single electrodes produced maximum area capacitance densities of 403.23 mF cm^{-2} and 336.08 mF cm^{-2}, synthesized in H_2SO_4 and $LiClO_4$ electrolytes, respectively at a scan rate of 10 mV s^{-1}. The electrochemical performance of the PPy solid-state supercapacitor was evaluated using CV, CD, and EIS with a maximum area capacitance density of 31.84 mF cm^{-2} (equivalent to a specific capacitance of 19.9 F g^{-1})obtained from EIS for the supercapacitor synthesized in H_2SO_4. The specific energy and specific power were evaluated from CD and were found to be 0.143 Wh kg^{-1} and 6.39 kW kg^{-1}, respectively at 3 mA cm^{-2}.

1. Introduction

Development of renewable energy systems is of crucial importance due to the rapid increase of global concerns towards clean and efficient energy resources, such as batteries, fuel cells, and supercapacitors. Supercapacitors (or electrochemical capacitors) are very useful in applications that require high power levels over short periods of time such as digital communication systems and hybrid electric vehicles [1]. Supercapacitors are being actively researched due to their remarkable features including high power density, long cycle life, low-maintenance cost, and environmental friendliness [1–5,10].

A typical supercapacitor consists of two electrodes and an electrolyte ionically conducting both electrodes. Supercapacitors are generally classified into three main categories based on the charge storage mechanism: (1) electrical double layer capacitors (EDLCs), (2) pseudocapacitors, and (3) hybrid supercapacitors. EDLCs store electrical energy by the electrostatic charge accumulation at the electrode-electrolyte interface, and they are typically fabricated using carbon-based electrodes such as graphene and activated carbon. Pseudocapacitors store electrical energy by Faradic redox reactions near the surface of the electrode and within the bulk of the electrode materials. That's why pseudocapacitors generally possess higher specific capacitances than EDLCs. Pseudocapacitors are typically fabricated using conducting polymers and metal oxides and their composites. The third category of hybrid supercapacitors combines the first two and consists of two different types of electrodes.

Conducting polymers such as Poly (3,4 -ethylenedioxythiophene) (PEDOT), Polypyrrole (PPy), and Polyaniline (PANI) are being actively and extensively studied as supercapacitor electrode materials due to their high specific capacitance owing to the Faradic redox processes that generate pseudocapacitance [6–8]. They are also compatible with both aqueous and organic electrolytes [7]; and therefore, considered promising candidates for energy storage applications. Conducting polymer PPy, which stores electrical energy by undergoing redox processes of doping and dedoping of electrolyte ions [8], is considered among the most studied conducting polymers due to its high conductivity, high storage ability, good thermal and environmental stability, high doping/dedoping rates, and low cost [6,11].

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It is important to mention here that the electrolyte plays an important role in the energy storage capabilities of a supercapacitor. Most of the work that has been done so far in this area utilized conventional aqueous and organic electrolytes. Ionic liquid gel polymer electrolytes could be a unique replacement to conventional electrolytes due to their excellent chemical and thermal stability, non-volatility, and wider electrochemical potential window [12–16]. In this work, the solid-state design of supercapacitors is created with ionic liquid gel polymer electrolyte and polypyrrole electrodes. The solid-state design of supercapacitors reduces the thickness of the device and makes it highly compact and reliable to be integrated with other renewable energy devices such as solar cells [9,12–16]. This paper goes over polypyrrole electrode synthesis, solid-state design of supercapacitors, and their electrochemical performance in storage of electrical energy.

2. Experiment

2.1. Preparation of PPy film

The pulsed electropolymerized growth of the PPy film was carried out in a three-electrode electrochemical cell over a flexible graphite substrate which was used as a working electrode. The precursor electrolyte was prepared by dissolution of 0.1 M monomer pyrrole and 0.5 M H_2SO_4 in deionized water. For comparison, another PPy electrode was prepared by dissolution of 0.1 M monomer pyrrole and 0.2 M $LiClO_4$ in deionized water. A platinum sheet was used as a counter electrode and the electrochemical potentials were measured against a saturated Ag/AgCl reference electrode. The electropolymerization was carried out by applying sequential unipolar anodic current pulses of current density $\sim$4 mA cm^{-2} for 10 ms on and 100 ms off. Followed by the growth, the electrodes were rinsed in deionized water and naturally dried prior to supercapacitor cell assembly.

2.2. Preparation of gel polymer electrolyte

The electrolyte was 1butyl-3-methylimidazolium tetrafluoroborate ($BMIBF_4$) room temperature ionic liquid formulated as polymer gel by mixing the vacuum dried $BMIBF_4$ to a solution of P (VdF-HFP) polymer in acetone in the 80:20 wt ratio. The mixture was magnetically stirred for at least 10 h. The viscous solution of gel polymer electrolyte was used to fabricate solid-state supercapacitor cells.

2.3. Fabrication of supercapacitor cells

The ionic liquid gel polymer electrolyte was spread gently on top of each electrode covering an active surface area of 1.0 cm^2. Both electrodes were then placed on top of each other and pressed lightly to form the complete cell. This supercapacitor cell in solid-state design was then left overnight to dry naturally prior to any further evaluation. The main advantages of such a cell design are to simplify the fabrication process, reduce the thickness of the device that in turn creates reliable and environmentally friendly supercapacitor structure.

2.4. Electrochemical characterization of solid-state supercapacitor

The electrochemical performance of the solid-state supercapacitor was evaluated based on cyclic voltammetry (CV), galvanostatic charge-discharge (CD), and electrochemical impedance spectroscopy (EIS), using Solatron 1287 Electrochemical Interface and Solatron Impedance Analyzer (Model: 1260).

The area capacitance density of supercapacitor cells was evaluated using the equation,

$$C = \frac{ia + |ic|}{2s}, \tag{1}$$

where *ia* and *ic* are the anodic current and cathodic current respectively, and *s* is the scan rate.

The specific capacitance was calculated from the CD curves using the equation,

$$C_d = \frac{i.\Delta t}{m.\Delta V} \tag{2}$$

where *i* is the constant discharge current density, Δt is the discharge time, m is the total mass of both electrodes and ΔV is the voltage drop upon discharging (excluding the IR drop). The energy and power densities were evaluated from CD using the equations $E = {}^1/_2\, C_d\, V^2$ and $P = V^2/4m.ESR$, respectively, where *m* is the mass of the electrode and ESR is the equivalent series resistance.

The impedance measurements were carried out using the Solatron Impedance Analyzer (Model: 1260) in the frequency range from 10 mHz to100 kHz using ac signal of 10 mV amplitude. The area capacitance density values of the solid-state supercapacitor cell were evaluated from impedance analysis using the equation

$$C = \frac{1}{2\pi f Z''}, \tag{3}$$

where *Z*" is the imaginary part of the impedance.

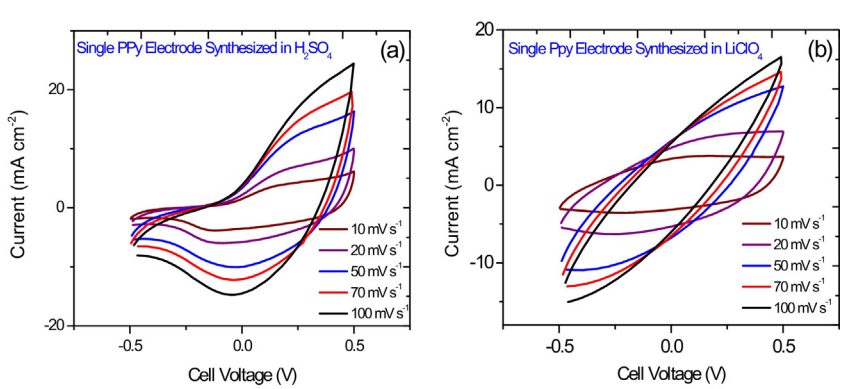

Fig. 1. CV curves of single ppy electrode synthesized in (a) H_2SO_4 and (b) $LiClO_4$.