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Transparent, flexible and solid-state supercapacitors based on room temperature ionic liquid gel

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ABSTRACT

This paper describes a novel strategy to make fully transparent, solid-state and flexible supercapacitors based on room temperature ionic liquid (RTIL) gel and ITO electrodes coated on transparent polymer substrate without a separator, which enables the roll-to-roll technique for fabrication of such supercapacitors as printable devices. This is the first type of transparent electrochemical double layer capacitor (EDLC) based on ionic liquid gel.

1. Introduction

The ever-increasing demand for the storage of electrical energy in portable and multi-functional device such as transparent displays, touch screens with transparent energy storage systems and multi-energy harvesting devices, using hybrid photovoltaic–supercapacitor–battery systems drives technological improvements in supercapacitors and research on flexible and transparent electronics. Supercapacitors are very attractive for portable electronics as well as automotive applications due to their high specific power and durability.

Next generations of portable devices will require solid-state supercapacitors with high power density, flexibility and transparency to meet the various design and power needs. Current transparent electrodes made of stamped/printed carbon nanotubes (CNTs) [1–4] face the challenge of mass production and it is always critical to optimize the CNT density to achieve the best trade-off of transparency vs. overall efficiency of the device. In addition, the possible toxicity of CNTs [5] restricts their applications for end users in our daily lives. This paper introduces an environmentally friendly, safe, flexible and transparent supercapacitor based on room temperature ionic liquid (RTIL) gel composing 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]) and cellulose.

RTILs are molten salts with a melting point close to or below room temperature. They are composed of ions of opposite charges that only loosely fit together (usually bulky organic cations and smaller anions). The properties of high conductivity, non-volatility, low toxicity, large electrochemical window (i.e. the electrochemical potential range over which the electrolyte is neither reduced nor oxidized on electrodes) and good electrochemical stability, make RTILs suitable for applications in electrochemical devices such as sensors [6] and supercapacitors [7]. Solutions containing up to 25 wt.% cellulose can be formed as viscous pastes in chloride-containing RTILs. The greatest solubility was obtained using [BMIM][Cl] as the solvent [8]. When suitable concentration of cellulose (around 10 wt.%) was dissolved in [BMIM][Cl], the viscous solutions obtained were optically anisotropic between crossed polarizing filters and displayed birefringence [9]. The formation of liquid crystalline solutions of cellulose may have useful applications for the generation of new materials. In addition, compositions between 5 and 10 wt.% cellulose are more readily prepared. Such gel-like materials that conserve anisotropy in the solid phase are especially desirable, yielding enhanced mechanical properties. The supercapacitor reported in this paper using [BMIM][Cl] and cellulose gel composite is a completely transparent and flexible electrochemical device that one can bend and twist.

2. Experimental

[BMIM][Cl] was purchased from solvent innovation (Merck) GmbH. Cellulose nano-particles were from Sigma–Aldrich. The supercapacitor electrodes are made by coating a flexible polymeric substrate, polyethylene naphathalate (PEN), with ITO (Fig. 1a). The RTIL gel electrolyte, [BMIM][Cl] composing of 6 wt.% cellulose was used, which forms a totally transparent electrolyte when dried

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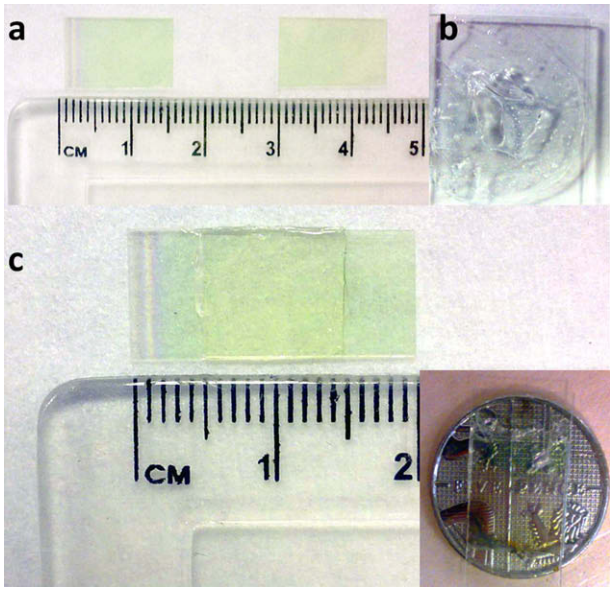

Fig. 1. (a) ITO coated on transparent polymer PEN, (b) sticky and transparent gel electrolyte composed of [BMIM][Cl] RTIL and cellulose, (c) the transparent supercapacitor assembled.

(Fig. 1b). Since cellulose was evenly distributed in the gel, it can function as a separator of the supercapacitors simultaneously. The RTIL gel is coated on the flexible ITO electrodes and packaged as totally transparent supercapacitors as shown in Fig. 1c.

2.1 Coating of ITO on PEN

The ITO coating process uses remote, high density plasma (10^{13} ions cm^{-3}) that is generated in a side arm adjacent to the deposition chamber (Fig. 2). This side arm is referred to as the plasma launch system (PLS). It consists of a quartz tube surrounded by a copper antennae coil. The antennae couples RF power into the argon gas at reduced pressure. Electromagnets at the exit of the PLS enhance and steer the plasma onto the target. Under these conditions the argon ions have insufficient energy (between 30 and 50 eV) to sputter. The application of a sufficiently high, negative DC bias to the target results in a uniform current density of approximately 20 mA cm^{-2} over the full surface area of the target. This yields high rate, uniform erosion of the target surface and hence the name given to this technique is high target utilisation sputtering, or HiTUS. An In:Sn target with a purity of 99.995% and an indium to tin ratio of 90:10 wt.% has been used. Prior to deposition, the target is sputter cleaned in an Ar plasma for 5 min to remove any oxide that may have formed after venting. Oxygen is then fed in as the reactive gas and conditions are allowed to stabilise for a further 5 min before the shutter is opened and deposition commences.

By using a remotely generated plasma, which is not driven from the target, independent control of the target voltage and plasma intensity can be realized. This gives more flexibility over deposition variables and also results in the virtual elimination of target poisoning since the full surface area of the target is uniformly eroded. Using the HiTUS system, ITO deposition rates of up to 90 nm/min are achievable from a 4" diameter target, approximately an order of magnitude faster than with conventional RF magnetron sputtering. Due to the target–substrate separation of 18 cm, this high energy technique does not result in damage to film growth from high energy ion bombardment. The substrates are secured to a rotating platform that is located away from the plasma. This makes it possible to deposit ITO with excellent properties and at high rate onto temperature sensitive, polymeric materials.

The electrochemical properties of the assembled transparent supercapacitors were studied by cyclic voltammetry and galvanostatic measurement using Autolab (PGSTAT 302N).

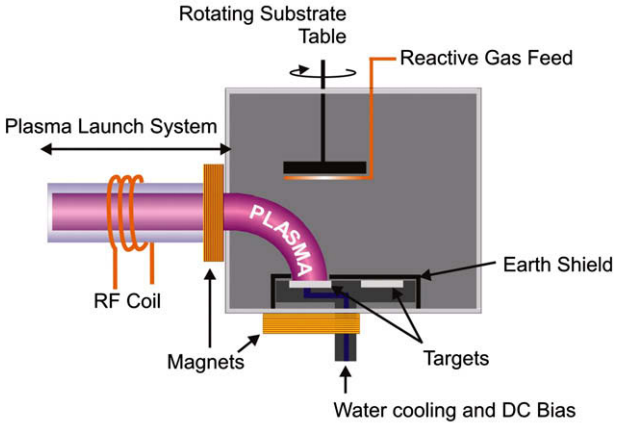

Fig. 2. Schematic showing the HiTUS system. Launch and steering electromagnets focus the plasma onto the water cooled target. Application of a negative DC bias to the target results in high rate, uniform erosion of the target surface.

3. Results and discussion

Flexible polymeric electrode made by coating PEN with ITO gives a film with high transparency as indicated in Fig. 1a. PEN is flexible, lighter and more rugged than conventional glass substrates and meets the demand for roll-up screens in the flexible displays market. Many properties of PEN such as its transparency, melting temperature, coefficient of thermal expansion (CTE) and tensile strength (275 MPa, which is higher than any rival polymers) render it more suitable for electronics than other polymeric materials. In addition, its glass transition temperature is approximately 120 °C and its melting temperature is approximately 270 °C. These are higher than the other widely used transparent plastics such as polyethylene terephthalate (PET) and enable its use for a wider array of applications. In this work, ITO, with an average transmission

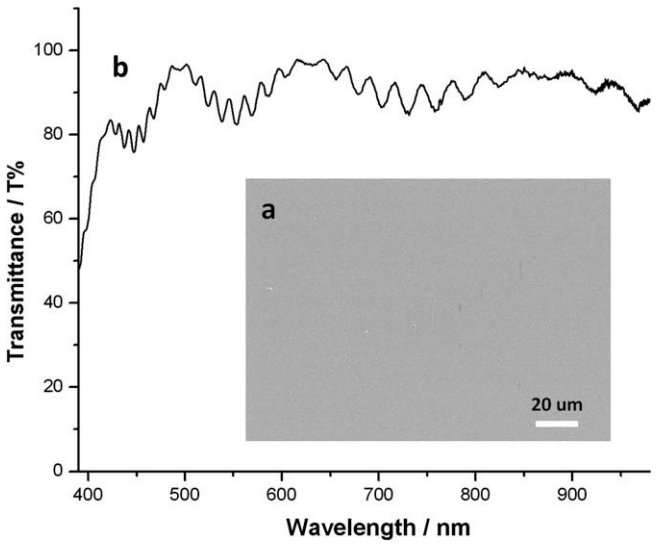

Fig. 3. (a) SEM image of the surface of the ITO prior to construction of the complete device. (b) Transmission profile of the ITO deposited onto the PEN substrate. The average transmission of the coating is 91.8% from wavelength of 450 nm–800 nm.

of 91.8% between the wavelength of 450 nm and 800 nm and a sheet resistance of 7.7 Ω/□ has been deposited onto planarised PEN substrate materials with no substrate heating. The ITO is coated by means of high target utilisation sputtering (HiTUS) technology. Fig. 3a shows SEM image of the surface of the ITO. The film surface is smooth and free from irregularities making it suitable for use as a bottom contact electrode. Thickness measurements were made using a Taylor Hobson Talystep surface profilometer and the sheet resistance values were taken from a 4 point probe. The average thickness of the ITO coated on PEN is about 470 nm. The optical transmission of the films was measured using an Avaspec 2048 fiber optic spectrometer with wavelength in the range of 350 nm–1000 nm. All profiles were measured with respect to the uncoated substrate and therefore represent the transmission of the coating alone. Fig. 3b shows the transmission profile of 470 nm thick ITO deposited onto planarised PEN. It should be noted that the high frequency fringes are due to a 5 μm thick adhesion layer applied to the reverse side of the substrate by the manufacturer. The low frequency interference fringes are due to the ITO coating. An abrupt drop in transmission is clearly seen at approximately 400 nm. This represents the electronic absorption edge of the ITO.

The electrochemical properties of the supercapacitors were studied by cyclic voltammetry and galvanostatic measurement using Autolab. Fig. 4a shows the typical result of a cyclic voltammetry measurement. The device is cycled from −0.5 V to 0.5 V with a scan rate of 5 mV/s. The capacitive behaviour of the device is clearly observed in this figure with a near rectangular-shaped cyclic voltammogram curve indicating good capacitive characteristics for the device. Specific capacitance, C_{spec} (F/g), can be calculated from the following equation [10]:

$$C_{spec} = \frac{i}{v}\left(\frac{1}{m}\right)$$

where, i is the constant discharging current, m is the mass of the active materials within the electrodes, and v is the speed of voltage change dV/dt.

Galvanostatic charge–discharge measurements were used to evaluate the specific capacitance and the internal resistance of the devices in a two-electrode configuration. The electrochemical galvanostatic measurement was carried out using 1 mA current for charging and discharging and the result is shown in Fig. 4b. Internal resistance (iR) drop can be observed in each pulsing measurement in Fig. 4b. This is due to the equivalent series resistance of ITO electrodes, RTIL electrolytes and the contact resistance between the electrodes. The RTIL gel electrolyte can reduce the contact resistance more than conventional solid electrolytes by providing adhesive contacts with charge collecting electrodes. The slope of the discharge curve (dV/dt) can be used to calculate the specific capacitance. The specific capacitance of our device is about 18 F/g, which is similar to the supercapacitors (22 F/g) composed of densely-aligned carbon nanotube electrodes [7]. In addition, by engineering the deposition of ITO, the charge collecting ability of the transparent electrodes as well as the specific capacitance can be improved further.

In summary, a supercapacitor with the features of optical transparency and mechanical flexibility has been fabricated using transparent RTIL gel electrolyte and the ITO electrodes coated on PEN. This is the first type of transparent EDLC based on ionic liquid gel. Conventional energy storage devices have neither mechanical flexibility nor optical transparency, which confirms our device's potential for applications in flexible and transparent electronics. This approach may be able to work as the platform for future transparent and flexible devices. In addition, the flexible ITO electrodes made by HiTUS technology and the gel-like electrolytes without separators can enable printing and/or roll-to-roll mass production of such supercapacitors. Enhancement of specific capacitance and related power/energy density is under development to improve the device performance for practical applications.

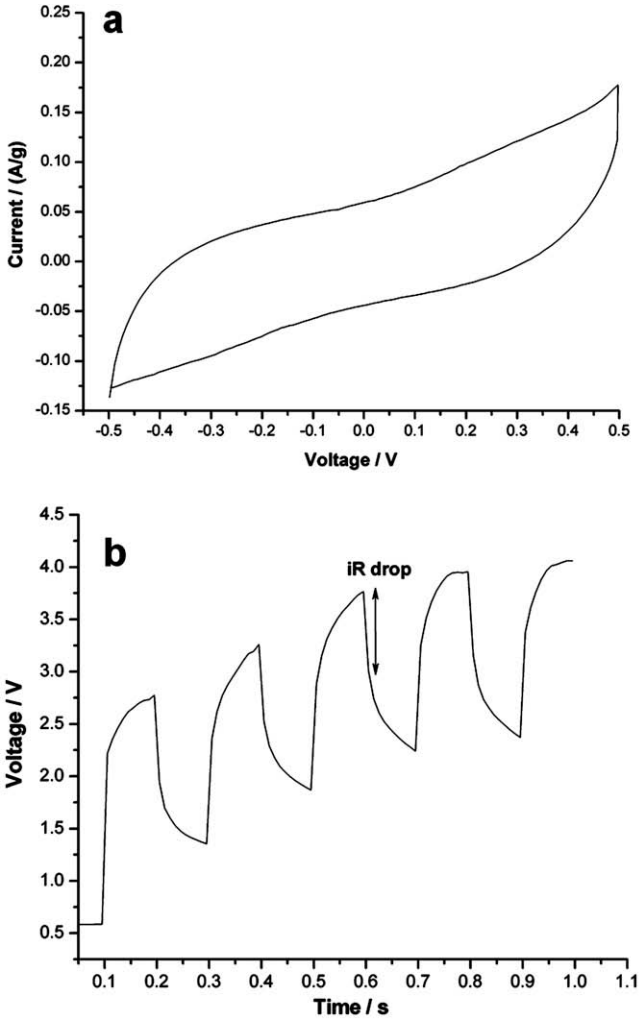

Fig. 4. (a) Cyclic voltammogram of the transparent supercapacitor made of RTIL gel and ITO polymer substrate. This measurement is carried out with a scan rate of 5 mV/s at room temperature. (b) Galvanostatic charge–discharge measurement of the transparent supercapacitor with charge–discharge current of 1 mA.

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