IMPEDANCE SPECTROSCOPIC ANALYSIS OF POLY ANILINE FILMS FOR PHOTOVOLTAIC APPLICATIONS

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INTRODUCTION

All the energy consumed by humans in an entire year is less than the energy from the sunwhich strikes the earth in 1 hour (Lewis, 2007).Therefore, solar energy conversion is a highly attractive routefor clean and renewable power for the future. During the past decades,photovoltaiccells have attracted much attention. Organic Photovoltaics (OPV) as low cost alternatives to conventional inorganic photovoltaic devices, aregetting enormous attentiontoday because of theirflexibility, light weight and solution processability (O'Regan, Gratzel, 1991; Hagfeldt, Gratzel, 1995). Organic solar cell devices are fabricated using polymers such as Poly(3-hexylthiophene-2,5-diyl) (P3HT), poly(3,4-ethylenedioxythiophene) (PEDOT) and polyaniline (PANI), which play the role of p-type material as the hole conductor orelectron donor. Among them, PANI is an excellent host for trapping semiconducting nanomaterials and conducts the electric charges through the polymeric chain due to extended π-electron conjugation (SadiaAmeen *et al.*,2013).The conductivity of this polymer can be varied by doping them with different protonic acids and it is soluble in organic solvents, like toluene, xylene, chloroform and*m*-cresol (Cao *et al.,* 1992). Polyaniline has been the most widely studied material as a unique member of the conducting polymer family because itselectrical properties can be reversibly controlled by both oxidation and protonation and it has high environmental stability and conductivity (Milind et al. 2006).

Electrochemical Impedance spectroscopy (EIS) is a powerful technique for the characterization of electronic or ionic transport processesof materials used in OPVs.In this paper, we report our work on characterization ofpolyaniline thin film prepared for OPV applications with Impedance Spectroscopy to calculate dielectric losses at room temperature.

METHODOLOGY

Chemical oxidative polymerisation of aniline togive the conducting emeraldine salt was carried out using ammonium persulphate as initiator in the presence of 1.5 Mcamphor sulphonic acid (CSA) at ~ 4 ºC. The reaction was carried out for 4h.The green precipitate formed, which was the polyaniline doped camphor sulphonic acid (PANICAS)was filtered, washed with waterfollowed by acetone. Thesamples were then dried in an oven at 60 °C for 6h.

Polymer suspensionfor spin coating was made by dissolvingPANICASin *m*-cresol(20 mg ml^{-1}) and stirring the suspension for 2h. PANICAS film was coatedon conducting tin oxide (CTO) glass plates(12 Ω cm^{-2}) by the following method. CTO glasses were cleaned well and Scotch tapes were sticked on one edge of the conducting glass to keep unexposed tothe film to make electrical contacts in later stage.Polymer dispersion was spin coated on CTO glass plates at 2500 rpm for one minute to obtain the PANICAS films.These films weredried at 80^0C on a hot plate for 10 minutes.Different thicknesses were obtained by repeated coatings. The thickness of the films was determined gravimetrically. Pt sputtered onCTO glass waspressed on the PANI filmto make the electrical contact.

TiO_2 film of ~ 10 μm thick was deposited on conducting tin oxide glass by the following method. Titanium isopropoxide 5 ml was mixed with 5.5 ml of acetic acid. The mixture was diluted with 10 ml of propan-2-ol and 5 ml of water was added drop wise keeping the solution

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vigorously stirred. Hydrolyzed titanium isopropoxide was mixed with 0.6 g of Degussa P-25 TiO_2 powder. A cleaned CTO glass plates cut into the size of 1 x 1.5 cm^2 was placed on a hot plate at 120 ºC and the viscous TiO_2past was spread on the conducting surface and sintered at 450 ºC for 10 min. Coating and sintering process were repeated several times until a film of 10 µm is formed. TiO_2 film was dyed with Ru N3 dye. Dye coated TiO_2 filmsas well as the bare TiO_2 films were spin coated with PANICAS dissolved in *m*-cresol (20 mg ml^{-1}) and dried at 80 ºC on a hot plate. Pt coated CTO glass was pressed on the filmsas previous to make the electrical contact.

Electrochemical impedance spectra ofthese films were measured withGW InstekLCR meter using the software provided with the instrumentto couple with a computer, in the frequency range from 20 Hz to 1 MHz usingan ac signal of 20 mV. The measured impedances and the phase angles of the films at different frequencies were used to draw Nyquist plots. The impedance spectra were use to characterize the films for their dielectric losses.

RESULTS AND DISCUSSION

Figure 1 shows the molecular structures of polyaniline and the camphor sulphonic acid and their interacting mechanism. Camphor sulphonic acid is used to dope polyaniline to increase its electrical conductivity. Sulphonic group in the dopant ionically interact with the electron lone pairs of nitrogen in the polymer chain tomakeit positively charged. This makes the polymer ironically conductive.There exist two types of ionic conductions in this type of highly doped polyaniline films. One is along the polymeric chain and the other is across the adjacent polymer chains which are termed as interchain and intrachain conduction respectively.

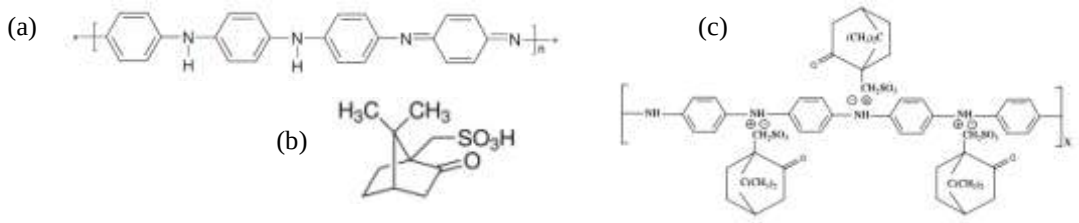

Figure 1: Molecular structures of (a) polyaniline and (b) Camphor sulphonic acid

Impedance spectroscopy (IS) measures the dielectric properties of a medium as a function of frequency.It is based on the interaction of the dielectric medium with an external electric field that gives informationon the impedance of a system over a range of frequencies. Therefore the frequency response of the system reveals the energy storage and dissipation propertieswhere the data obtained by IS is expressed graphically in a Bode plot or in a Nyquist plot. Figure 2 depicts the Nyquist plots of polyaniline films of different thicknesses deposited on CTO glass by spin coating technique.

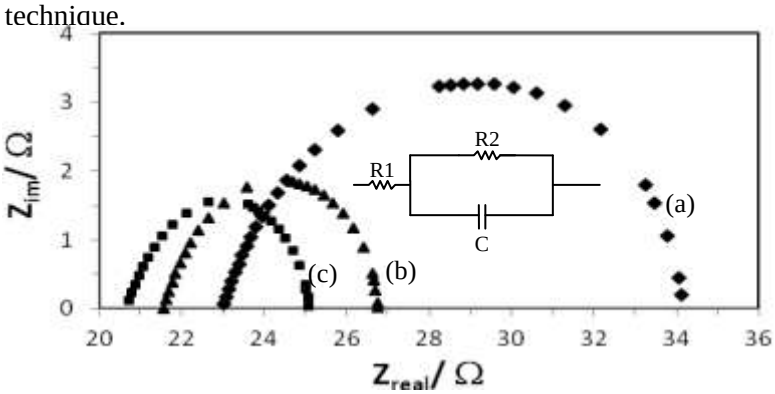

Figure 2: Nyquist plots of polyaniline films (a) 0.5µm (b) 1 µm (c) 1.5 µm thicknesses. Insertion is the equivalent circuit for the polyaniline films

PANI film deposited on CTO glass model a cell where the contact resistance (R1) in series with the parallel combination of capacitance (C) and resistance (R2) of the film. Subsequently, it is possible to find the equivalent circuit and the significnce of the different components.The given
Impedance Spectra were analyzed for resistance and capacitance values of the components of the
equivalent circuit modeled in the insert of figure 2. They are given in table 1 for Nyquist plots of different thicknesses of the films depicted in figure 2.

Table 1: resistive and capacitive values of equivalent circuits

Film Thickness (μm)	R_1 (kΩ)	R_2 (kΩ)	C (μF)
0.5	23.1	11.0	7.0
1.0	21.5	05.2	5.8
1.5	20.7	04.4	5.2

It is evident from Table 1, that all the circuit parameters such as parallel and series resistances and capacitance of the equivalent circuits decrease when the film thickness increases. This behavior of the film can be explained by modeling the polymer chain arrangement in thin films and thick filmsas shown in figure 3.The polymer chains are arranged in parallel with the substrate in thin films but for thick films they have the freedom to arrange randomly. Therefore in thin films, interchain conduction is parallely along the film and intrachain conduction is across the film which restrict the conduction mechanisms. But there is no such a limitationfor thick films that both the interchain and intrachain conduction can contribute for conduction parallel and across the film. Therefore change of degree offreedom of conduction in the film resultsto lower R1 and R2 values when the film thickness increases.Decrement of capacitance of the film when the film thickness increase is understood bythe inverse relationship of capacitance and the thickness of the film.

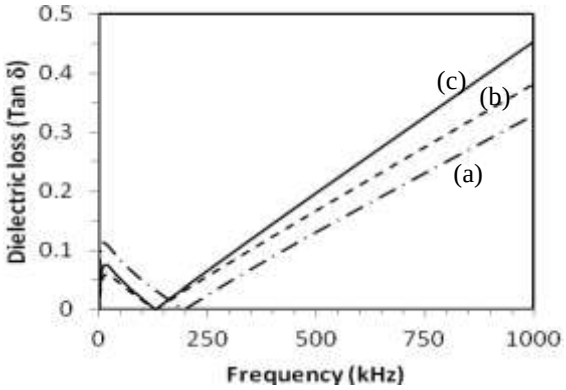

Figure 3: Model illustrating PANICAS polymer chain arrangement in a (a) thin film (b) thick film

Figure 4: Dielectric loss of polyaniline films (a) 0.5μm (b) 1 μm (c) 1.5 μm thick measured at different frequencies that deposited by spin coating on CTO glass.

Dielectric loss quantifies thematerial's inherent dissipation of electromagnetic energy into heat. It can be represented byloss tangent, tan δ which refers to the phasor in the complex plane of a Nyquist plot whose real and imaginary parts are the resistive and reactive counterpart.It is clear from figure 4 that the dielectric loss increase with the film thickness at high frequencies but decreases in the zero to 250 kHz frequency range. Dielectric loss occurs in PANICAS films due to ionic conduction at low frequencies and dipolar polarization at high frequencies. Both the ionic conduction and dipolar polarization in an a.c. field leads to dielectric relaxation. Dielectric relaxation is the lag in ionic conduction or dipole orientation behind an alternating electric field. When the film is thin ionic conduction across the film occurs mainly by intrachain conduction. But for thickfilms ionic conduction across the film also occurs due to interchain conduction. Since the intrachain conductivity contributes to an increase in dielectric loss than the interchain conductivity, dielectric loss is higher in thin

films. But at high frequencies bipolar polarization become prominent so that the dielectric loss increases with the film thickness.

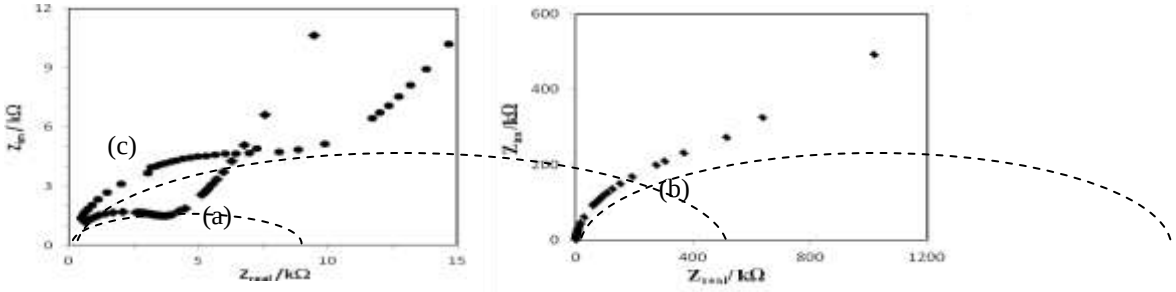

Figure 4Nyquist plots of (a) TiO2 film (b) Dye coated TiO_2 film (c) PANICAS film deposited on a dye coated TiO_2 film

A dye sensitized solid state solar cell (DSSC) of the hetero-structure TiO_2/Dye/PANICAS was constructed and impedance was measured by taking Nyquist plots for bare TiO_2 film, Dye coated TiO_2 film and PANICAS deposited TiO_2 film coated with the dye. It is clear from these plots that the resistance of TiO_2 film increases by more than two decades after coating the dye on the film and decrease again to the same order of magnitude by coating the PANICAS film on the dye coated TiO_2 film.

CONCLUSIONS/RECOMMENDATIONS

Poly aniline deposited on CTO glass can be represented by a simple configuration of single resistor in series with a RC transfer circuits in impedance spectroscopic measurements. The variation of impedance of films with different thicknesses and dielectric losses of the films can be explained by interchain and intrachain conduction of the films. Impedance of DSSC of the heterostructureTiO_2/Dye/PANICAS is of the same order of magnitude that as the impedance of bare TiO_2 film.

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