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Preparation and characterization of an all solid supercapacitor based on polyaniline-Al_2O_3 layer on aluminium alloy-Al-2024

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The characteristics of an all solid state supercapacitor based on polyaniline (Pani)-Al_2O_3 coating on aluminium alloy 2024 (Al-2024) surface prepared by the constant current method have been investigated. Three stages are observed in the potential- electrolysis time relation for the simultaneous preparation of the dielectric layer and the conducting polymer on the aluminium foil. The deposition of polyaniline film has been confirmed by cyclic voltammetry. The solid state capacitor has been studied by AC impedance spectroscopy and the capacitive behaviour of the cell is discussed in terms of Nyquist plots, complex capacitance and complex power. The study revealed that the capacitor has comparatively good capacitance, ranging from 450 to 600nF/cm^2, a low time constant and also very low resistance. The normalized reactive power, |Q|/|S| and active power |P|/|S| versus frequency plot for the solid state capacitor allow an overview of the whole frequency behaviour of the supercapcitors, ranging from a pure resistance at high frequency to a pure capacitance at low frequency. When a capacitor is used as a source stiffening capacitor and is buffering the supply by delivering initial current, a lower RC time constant allows delivering significantly more current. So this type of solid-state capacitor can be used for the DC-DC converter modules.

Keywords: Supercapacitors, Electrochemical deposition, Polyaniline, Aluminium Alloy Al-2024, Solid electrolyte

IPC Code (s): H01G9/025

Supercapacitors are promising devices for delivering high power density. Digital communications, Micro-systems such as micro sensors and other devices that require electrical energy at high power levels in relatively short pulses have prompted considerable research on super capacitors[1-2]. Various electrolytes such as aqueous, and non aqueous liquid electrolytes and solid electrolytes are used for capacitor assembly. Solid electrolytes are advantageous over liquid electrolytes in respect of easy handling and reliability without electrolyte leakage. The general requirement for use in a solid electrolytic capacitor are considered[3] to be high conductivity, processability to impregnate elements of capacitors, solid adhesion to dielectric films, heat resistance, long life and no reaction with metals used as dielectric films etc.

Solid state capacitors based on conducting polymers have been studied widely in recent years due to their good adhesion to dielectric films, good performance at high frequency and temperature and excellent stability[4-9]. As a part of our ongoing research program on conducting polymer devices[10,11], the simultaneous preparation of an Al_2O_3 dielectric film and a poly aniline solid polymer electrolyte on an aluminium alloy, Al-2024 foil and the capacitive characteristics of the resulting solid state capacitor using AC impedance spectroscopy are reported herein.

Experimental Procedure

Materials

All chemicals used in the study were of Analar grade. Aluminium alloy 2024 panels were purchased from Q panel(Cleveland, OH). Aniline was used after distillation over zinc dust and was always stored in dark. All aqueous solutions were prepared using Milli Q water.

Preparation and characterization of Pani/Al_2O_3/Al

Aluninium alloy 2024 panel of 1 cm^2 surface area was immersed in 2 N NaOH for 3 min, which dissolves the native oxide film on the surface. The pretreated aluminium alloy foil was then immediately immersed in the electrolyte containing 0.1 M aniline and 0.2 M oxalic acid that had been purged with nitrogen to remove dissolved oxygen. The galvanostatic deposition of Pani on the aluminium alloy foil was done at 8 mA cm^{-2} current density for about 35 min. A counter electrode of platinum foil (1 cm^2) and saturated calomel electrode as reference electrode were used. All the electrochemical studies were done using AUTOLAB from Eco-Chemie. The surface micrographs of deposited Pani on Al alloy film were taken by an optical microscope at a magnification of 20X. The electrochemically deposited Pani was further confirmed by cyclic voltammetry (Autolab). The capacitive characteristics of the cell were analyzed by AC impedance spectroscopy in the frequency range of 100 Hz to 10^6 Hz. The assembly of the solid state capacitor based on Pani/Al_2O_3/Al-2024 is shown in Fig. 1.

Results and Discussion

The relationship between potential and electrolysis time for preparation of Pani/Al_2O_3/Al in a galvanostatic deposition of Pani on Al alloy foil is shown in Fig. 2. The figure shows roughly three stages of deposition. During the first stage, in the voltage range of zero to four, the formation of aluminium oxide film is accompanied by the formation of nuclei of Pani in the pores of Al_2O_3. The increase in the potential from 0 to 4V with increase in electrolysis time from 0 to 500 s is mainly due to the formation of aluminium oxide and negligible amounts of copper oxides in the first stage. Oxalic acid acts as supporting electrolyte and a dopant in the Pani film to assist in penetration of Pani film into the pores of Al_2O_3 film and formation of nuclei on the aluminium substrate. After this, in the second stage, the main reaction is propagation of conducting pani film based on the nuclei formed in the first stage. The lower rate of increase in the potential with electrolysis time is due to the conductivity of Pani film. With further increase in electrolysis time, the voltage increases rapidly from 5.0 to 10 V, which is identified as the third stage. This is mainly due to the over oxidation of Pani within the pores of Al_2O_3 as well as a significant decrease in the conductivity of the Pani/Al_2O_3 film located between the aluminium substrate and aqueous electrolyte. Same kind of behaviour has been reported in case of poly pyrrole-Al_2O_3 supercapacitor also[8]. The surface of the bare Al alloy film turns greenish after the electrochemical deposition of Pani. The cyclic voltammetric response of the deposited film in 0.1 M sulphuric acid at different scan rates is shown in Fig. 3, which confirms the smooth and successful formation of the Pani over the substrate.

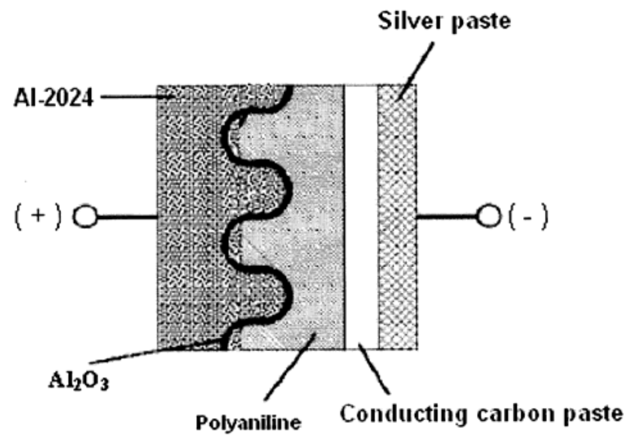

Fig. 1—Assembly of the Pani/Al_2O_3/Al-2024 solid-state capacitor.

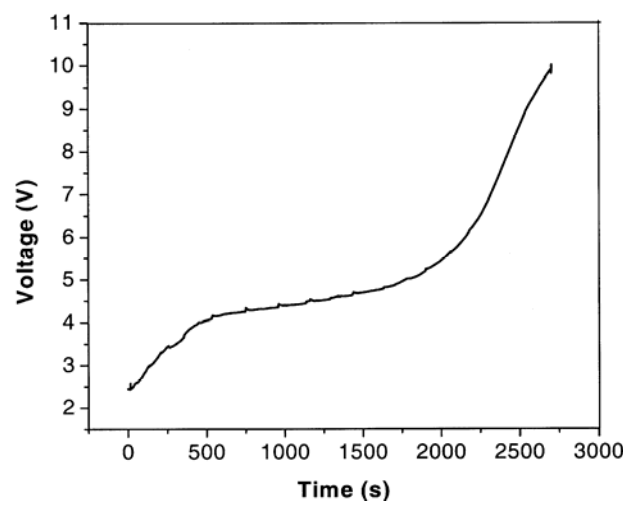

Fig. 2—Potential-electrolysis time relationship for the deposition of Pani on Al-2024 at a current density of 8 mA cm^{-2}.

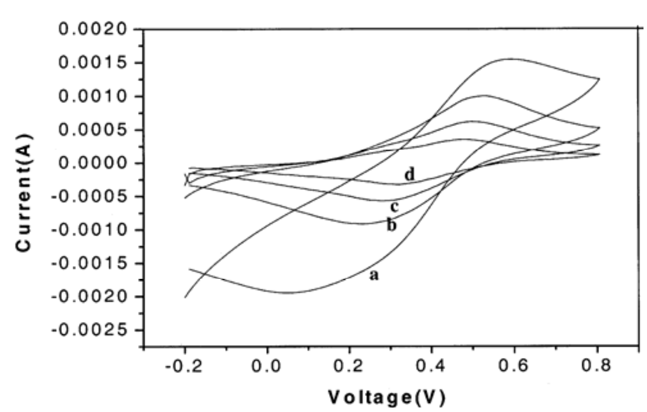

Fig. 3—Cyclic voltammograms of the Pani on Al-2024 in 0.1 M sulphuric acid at scan rates of (a) 50, (b) 20, (c) 10 and (d) 5 mV/s.

The cyclic voltammetric response of the Pani/Al_2O_3/Al capacitor at different voltage scan rates is presented in Fig. 4. The capacitance calculated from the voltammogram was 45 to 60 μFg^{-1}. The capacity of the solid state capacitor for a standard 1 cm^2 with 10 mg cm^{-2} polyaniline was found to vary between 450 to 600 nano Farad cm^{-2}, indicating a better performance compared to Tantalum[12] and polypyrrole- Al_2O_3 super capacitors[8].

The capacitance, internal resistance and time constant are of importance for considering the capacitor performance. Supercapacitors generally oscillate between two states; resistance at high frequencies and capacitance at low frequencies. Between these two states it behaves like a resistance capacitance transmission line circuit[12-15]. The impedance spectrum in the form of Nyquist plot (complex plane impedance plot) is presented in Fig. 5.

As can be seen from Fig. 5, the imaginary part of the impedance is a straight line making an angle of almost 90° with real axis, characteristic of pure capacitive behaviour[1,12]. The evolution of real part and imaginary capacitance versus frequency for the solid state capacitor have been shown in Figs 6 and 7. The observed dependence of capacitance of the cell on frequency at very low frequency levels is shown in the insert. The figures show the constant capacitance of the capacitor for a wide range of high frequency. At very low frequencies capacitance increases but highly frequency dependent. The equivalent series resistance calculated from the plot was found to be around 0.1Ω, similar to Tantalum dielectric capacitor[12].

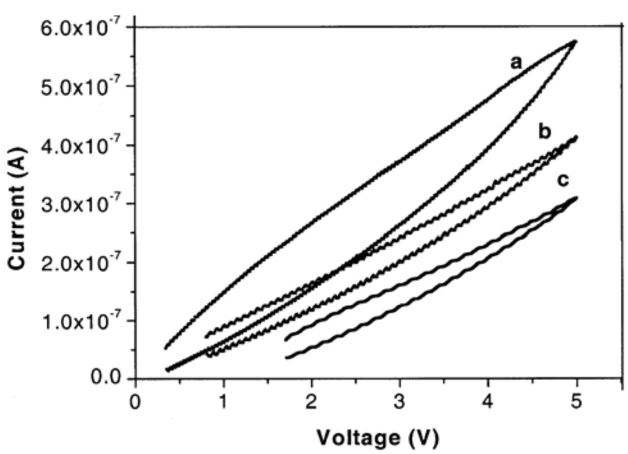

Fig. 4—Cyclic voltammograms of Pani/Al_2O_3/Al-2024 solid-state capacitor at scan rates of (a) 100, (b) 75 and (c) 50 mV/s.

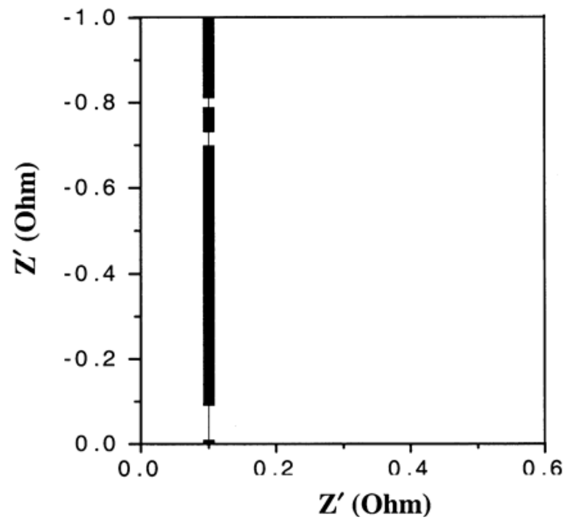

Fig. 5—Nyquist plots for the 1 cm^2 Pani/Al_2O_3/Al-2024 solid-state capacitor.

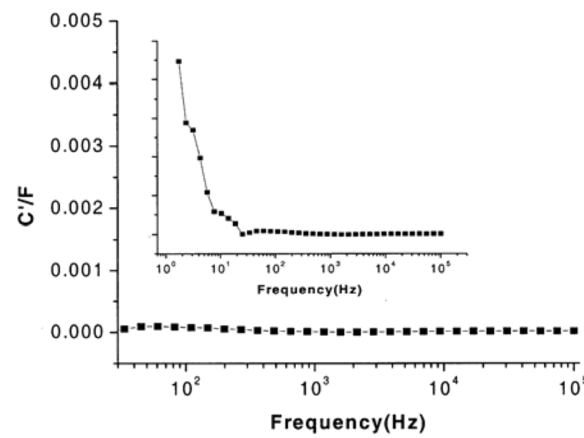

Fig. 6—Evolution of the real part of the capacitance versus frequency for the 1 cm^2 Pani/Al_2O_3/Al-2024 solid-state capacitor.

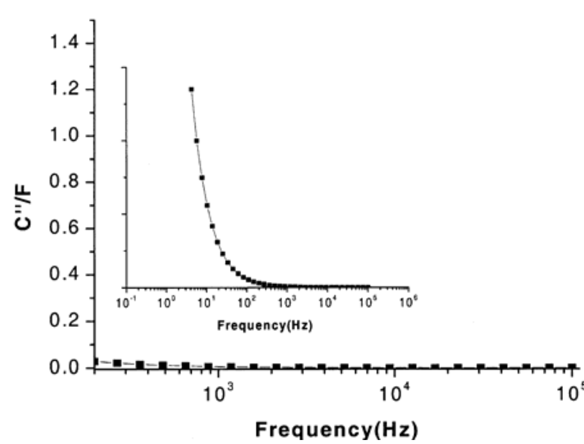

Fig. 7—Evolution of the imaginary part of the capacitance versus frequency for the 1 cm^2 Pani/Al_2O_3/Al-2024 solid-state capacitor.

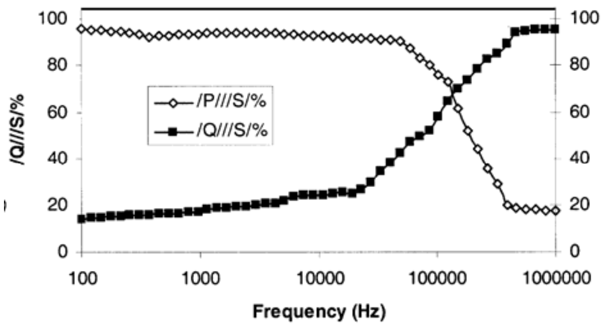

Fig. 8—Normalized reactive power|Q|/|S|% and active power |P|/|S|% versus Frequency (Hz) for the 1 cm^2 cell Pani/Al_2O_3/Al-2024 solid-state capacitor.

Figure 8 presents the normalized reactive power, |Q|/|S| and active power |P|/|S| versus frequency plot for the solid state capacitor. The theoretical details of this plotting technique can be found elsewhere[16]. This plot provides information regarding the change from resistive to capacitive behaviour of the system. The change occurs roughly from 1 MHz (resistive) down to 10 kHz (capacitive) i.e., over one order of magnitude. For carbon capacitors, this is generally over three orders of magnitude. Hence this capacitor has high efficiency even at high frequencies. The plot also enables the calculation of time constant, also known as dielectric relaxation time, τ_o. The time constant for the solid state capacitor under study was calculated to be 8 μs, which is comparable to that reported earlier[13]. When a capacitor is used as a source stiffening capacitor and is buffering the supply by delivering initial current, a lower RC time constant allows delivering significantly more current. So this type of solid-state capacitor can be used for the DC-DC converter modules. The time constant τ_o, represents[12] a transition for the super capacitor between a resistive behaviour for frequency higher than $1/\tau_o$ and a capacitive behaviour for frequencies lower than $1/\tau_o$, indicating that the present system can efficiently be used up to 1 MHz.

Conclusions

Polyaniline and Al_2O_3 barrier layer are prepared simultaneously on Al alloy 2024 by the constant current method. The plot of potential versus electrolysis time indicates three stages, namely the formation of Al_2O_3 and the nucleation of Pani within the pores of Al_2O_3, the propagation of Pani on the Al_2O_3 barrier layer and the over oxidation of the Pani located in the pores of Al_2O_3. The capacitive characteristics of the cell, Pani/Al_2O_3/Al-2024 are investigated by AC impedance spectroscopy. The study reveals that the capacitor has comparatively good capacitance, ranging from 450 to 600 nF/cm^2, a low time constant and also very low resistance. The normalized reactive power, |Q|/|S| and active power |P|/|S| versus frequency plot for the solid state capacitor allow an overview of the whole frequency behaviour of the supercapcitors, ranging from a pure resistance at high frequency to a pure capacitance at low frequency. When a capacitor is used as a source stiffening capacitor and is buffering the supply by delivering initial current, a lower RC time constant allows delivering significantly more current. So this type of solid-state capacitor can be used for the DC-DC converter modules.

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