J. Pure Appl. & Ind. Phys. Vol.2 (1), 17-27 (2012)

Transient Current Studies in Hydrochloric Acid (HCL) Doped Polyaniline (PANI) Film Electrets

DEVENDRA K. SAHU[1], AMIT K. GUPTA[1], SHANKER LAL[1], SANTOSH K. SAHU[2] and VIKRAM S. YADAV[3]

[1]Department of Physics, R.S. Government Degree College, Lalitpur-284403 U.P. India.
[2]Neelam Engineering College, Agra,-243221 U.P. India.
[3]Department of Applied Science & Humanities, Bundelkhand Institute of Engineering & Technology, Jhansi-284128 U.P. India.

ABSTRACT

In the present paper charging and discharging transient currents in hydrochloric acid (HCL) doped Polyaniline (PANI) film (25μm) electrets were measured as a function of temperature (40-90^{o}C), poling field 05MV/m and electrode combinations i.e. Al-Al, Al-Cu. The current-time characteristics have different slop values lying between 0.43 to 0.62 and 0.78 to 0.98. The polarization is considered to be due to dipolar reorientation associated with structural motion and space charge relaxations due to trapping of injected charge carriers in energetically distributed traps.

Keywords: Transient current, hydrochloric acid, polyaniline (PANI), polarization.

1. INTRODUCTION

Transient current charging and discharging currents were investigated to understand time dependent polarization effect in doped conducting polymer. The discharge current may be the mirror image of the charging current except that a steady state current is not reached. Hence, discharging currents can yield information about charging processes even when the corresponding charging current is masked by conduction current at charging. Quantitative as well as qualitative analysis can be made on comparing the experimental values experimental conditions[1]. The results of this technique can also be compared with those of some other electrical studies, like thermally stimulated discharge current [TSDC] and isothermal surface charge decay, etc. to get clear and justified conclusions. Transient Current measurements are tedious-on being carried out over a long time is not a regular study but nevertheless it is a very useful one, giving far more consistent results than the others. This being so on account of electrical and other perturbing influences affecting the charging process far less than in other experiments involving decays processes.

The mechanism of the time-dependent polarization effect may be studied from an analysis of transient currents in charging and discharging modes with

respect to polarizing fields, temperature and electrode materials. In continuation of our previous work[2-4]. The present work reports the results of such studies with doped PANI.

2. EXPERIMENTAL DETAILS

In the present investigation samples were thermally poled with field 05 MV/m at various temperatures ranging from 40-90^{0}C for 120 min. during which the transient currents in the charge mode was observed 2 min after the application of the field. The current was also observed in the discharge mode for the same period of time, 2 min after the removal of the field. The polarization was carried out by connecting a dc power supply (EC-HV 4800D) in series with an electrometer which was carefully shielded and grounded to said ground loops and extraneous electrical noise.

After making proper electrical connections, the sandwiched sample mounted on electrode assembly was placed inside the thermostat and allowed to attain required temperature. It took about 1.5 hrs. When the sample attained the desired temperature, a dc voltage was applied. A sudden must of current observed in the beginning decreases with time. Its initial as well as steady value was recorded. At lower voltages and temperatures, it took longer period to reach the steady state while at higher voltages and temperatures; steady state was obtained in considerable low period. The effect of voltage variation in current was noted in increasing the voltage at fixed temperatures while temperature variation was measured keeping voltage constant and increasing the temperature. A fresh sample is used for such set of observation. The electrometer was specially designed to measure very small direct current (ranging from 10^{-6} to 10^{-13} amp), low d.c. potentials from high impedance source, small charges and high resistance.

3. RESULTS AND DISCUSSION

The time dependence of the charging and discharging transient currents in hydrochloric acid (HCL) doped Polyaniline (PANI) films having thickness 25µm has been investigated over a period of time 01-120 minutes. Figures no. 1 & 2 shows typical charging currents vs time characteristics for charging mode of doped Polyaniline for an applied field of 5 MV/m at temperatures 40, 60, 80 and 90°C for Al-Al & Al-Cu electrode system respectively. The discharging current versus time curves for an applied field of 5MV/m at temperatures 40, 60, 80 and 90°C for Al-Al and Al-Cu electrode system are shown in Figure no. 3 &4 observed for the doped PANI . These curves shows that the current decays at a faster rate for the first few minutes and then the decay rate slow down to reach the steady value.

Figures no. 5 & 6 are shown the thickness variation (i.e. 10, 25, 50 µm) in charging & discharging mode respectively for the same. Thinnest (10µm) film exhibit more current than thick (50µm) films for PANI.

Figure no. 7 & 8 shows the electrode effect on charging and discharging currents on doped polyaniline (PANI) at temperature Tp= 40°C for an applied field of Ep=5MV/m .The curves for both electrodes i.e. Al-Al & Al-Cu in charging & discharging mode was not similar for PANI but all the curves having similar decaying nature at higher values of time.

The transient current flowing through a dielectric after the application or removal of a step voltage decays logarithmically following the Curie–von Schweidler law

$$I(t) = A(T)\, t^{-n}, \qquad (1)$$

Where *I* is the current, A *(T*) the temperature-dependent factor, *t* the time after application or removal of the external voltage and *n* a constant which is generally close to unity.

The current, in the time domain, for the short time region is characterized by the relation

$$I(t) \alpha\, t^{-n}; \qquad 0 < n < 1; \qquad (2)$$

We are doing transient current measurements and as such quantitative variation of A (*T*) is not seen.

The Curie–von Schweidler law was found to be obeyed with the increase in temperature in doped PANI. The transient charging and discharging currents are the mirror images of each other in most of the cases in doped PANI which is the essential condition for tunnelling, dipole or electrode polarization process. No change in behaviour of charging and discharging currents is noticed when the transient current polarity is found to be positive in both the cases of charging and discharging modes and observed current approaches stable value in relatively short period under high fields. Curves illustrating the time dependence of charging as well as discharging transients are characterised by two regions, which are designated as short time long time regions, respectively. By comparing the values of activation energy for different configuration, it is evident that the value of activation energy is, in general, much higher in the case of dissimilar electrode combination than for similar configuration for doped PANI. The increment in the current in approximately the name for whole range of temperatures. The nature of the thermodynamics is non linear but similar for all temperatures. The curves show two distinct regions with different slopes, have a knee at a point.

From the above characteristics, it is evident that at least two distinct mechanisms shall be responsible for the current decay. One mechanism is operative in the range of short time giving rise to a straight line on log I vs t plot with a particular value of decay constant, n_1, and the other mechanism is operative in the range of long time giving rise to another straight line in log I vs t plot with a decay constant, n_2, of higher value. We now try to analyse the observed results in the light of the existing models, i.e., dipolar relaxation[5,6], tunneling to empty traps[7,8], charge injection leading to space charge effects[9,10] and electrode polarization[11,12]. The variation of such currents with time, temperature, field and electrode materials. In the case of tunnelling to empty traps, it is well established that the tunnelling current should be independent of temperature and proportional to the field at moderate field. However, in the present case, charging and discharging transients at fixed times show .thermal dependence and exhibit a complex dependence on the electric field. Thus, it seems that tunnelling to empty traps can be ruled out as a possible mechanism for the observed transients. In the case of electrode polarization, the transient currents are reported to be proportional to t^{-n} with the value of decay constant n = 0 at short times,

and n > 1 at longer times. However, in the present case, at short times the value of n is found to vary from 0.43 to 0.62 for similar electrode system and from 0.78 to 0.98 for dissimilar electrode combinations. These observations show that the process of electrode polarization is unlikely to be dominant in the present case.

Analysing the experimental results further, we know that dipolar relaxation can also account for t^{-n} type of time dependence. However, it was to be borne in mind that, as a general rule, dipolar processes involved in polymer are characterised by a distribution in relaxation times and that overlapping of several processes are likely to be present. This also implies that the Curie law can only be considered more or less a rough approximation of the real time dependence and can only depict the transient phenomena over short periods of time. Keeping this in mind, the following points may be considered in favour of this model.

The existence of two main relaxations in doped polyaniline (PANI) which are labelled as α and β in ascending order of temperature. The relaxation involving local motions of the side carbonyl group occurs around 90^0C. α relaxation is associated with the conformational motions of the main chain segments and takes place near the glass transition temperature, 170^0C. The second relaxation labelled β is reported to result from the ionic space charge polarization and occurs at 200^0C, well above the glass transition temperature.

The charging and discharging currents are mirror images of each other over most of the temperature range. Thus, it seems likely that the dipolar relaxation process in doped polyaniline (PANI) could be responsible for the transient component of charging and discharging current. It may be noted here that linear dependence on field as expected of a dipolar process has been observed in polymers only when current are measured at temperatures sufficiently lower than the glass transition temperatures. It seems that at shorter times only dipoles with short relaxation times are oriented/reoriented resulting in a smaller vale of decay constant, n_1. However, at longer time dipoles with longer values of relaxation time also start orienting/reorienting resulting in a current that decays/changes at a faster rate resulting in a higher value of n_2.

It has been observed that current shows complex field dependence. Further, the activation energy has been found to increase with the time of observation for both polymers. Thus, it can be concluded that the observed current may have contribution from charge carriers hopping amongst localized states. The presence of amorphous regions in doped polyaniline (PANI) entails existence of localized states in the band gap.

In fact, systems dominated by hopping of ionic and electronic charge carriers, generally, show a transient decay divided into two successive domains. With the aid of two site models[13-14] has derived an expression for transient behaviour which allows only value of n, i.e. there is no restriction on the value of n. The model assumes that the localized states which are distributed in energy and charge carriers undergo limited transitions to adjacent sites. The observed increase in the value of activation energy at longer times may be explained by the hopping mechanism which requires the existence of such localized

states distributed in energy. Thus, it seems that hopping of charge carriers may also be a possible mechanism for the observed transient.

The increase in the value of activation energy at longer times may adequately be explained in the light of transients controlled by space charge formation in the bulk of the sample. The following observed characteristics are in support of the space charge mechanism: The complex dependence of the isochronal transients on the field strength supports the contention that the field at the electrode (cathode or anode) is modified by the space charge. Charges can be injected directly from the electrodes leading to space charge formation inside the dielectric. These charges may get trapped at various trap levels. The faster decay of current corresponding to a higher value of constant n_2 in the long time region for different samples indicates the existence of energetically distributed localized trap levels. It seems that at shorter times, only shallow trap levels get filled/emptied contributing to a charging/discharging current that changes at a slower rate. However, at longer times deeper traps capture/release the charges due to which current decays at the observed faster rate an observed activation energy value is greater[15-17]. It has been observed in the present investigation that the magnitude of the transient current is generally higher in case of similar electrode system. This can be understood in the light of interfacial polarisation. It seems that due to the higher conductivity of doped polyaniline (PANI), more interfacial charge is localised on doped polyaniline (PANI) during charging using similar electrode configuration, giving a higher value of charging transients. Similarly, during discharging a higher conduction current will flow in polyaniline (PANI) resulting in a higher value of the discharging current. The complex nature of field dependence may be explained in the manner that the internal field created by the interfacial polarisation decreases the external applied field. The effect of the internal field would be to decrease the apparent charge carrier mobility. The interfacial charge is thus expected to exhibit a maximum at a certain field value. However, the internal field due to interfacial polarisation becomes nearly constant at higher polarising fields. The effect of the internal field may then decrease relative to the applied external field so that the apparent mobility of charge carriers again increases. The interfacial space charge shall, therefore, again increase for higher polarising fields. Solid polymers are not in thermodynamic equilibrium at temperatures below their glass transition. For such materials, free-volume enthalpy and entropy values are greater than they would be in equilibrium state. The gradual approach to equilibrium affects many properties, e.g., the free-volume of the polymer may decrease. The decrease in free volume lowers the mobility of chain segments and also charge carriers. The decrease in mobility may be expected to reduce conductivity. At higher electric fields, a change in mobility may take place faster than at lower fields and also recombination of charge carriers may be more. This may be responsible to make the observed current in the present case to approach a stable value in relatively shorter periods under high fields. The field

dominant behaviour, more so that lower polarising temperatures hints at the initial current being controlled by the bulk phenomena such as polarisation effects and/or ionic currents. The dipolar relaxation seems to be the major contributor to the transient current, particularly at lower polarising temperatures.

The decaying trends of currents with time, the superliner nature of the isochronal currents against fields, the electrode & thickness dependence nature of the transient current seems to be sufficient and reliable ground to assume that the possible controlling mechanism for the transient phenomenon is the dipolar relaxation, charge injection and formation of trapped charges. Charge injection from the electrodes, with subsequent trapping of injected charges in or near surface region gives rise to homo space charge and the thermal release of charge carriers from the traps. Before a trapped space charge injected at higher fields is thermally released, a space charge barrier is present at the electrodes, which suppresses the entrance of charge carriers into the sample. Thus, the observed current remains smaller.

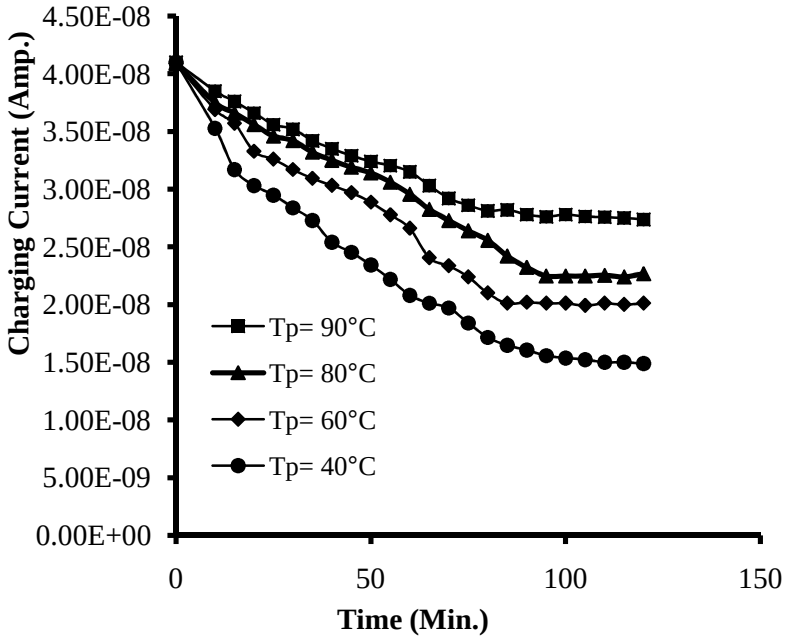

Fig.1 Transient Current vs time in charging mode for doped polyaniline(PANI) 25 µm poled E_p 5MV/m with different T_p i.e 40,60,80 and 90°C for Al-Al electrode system

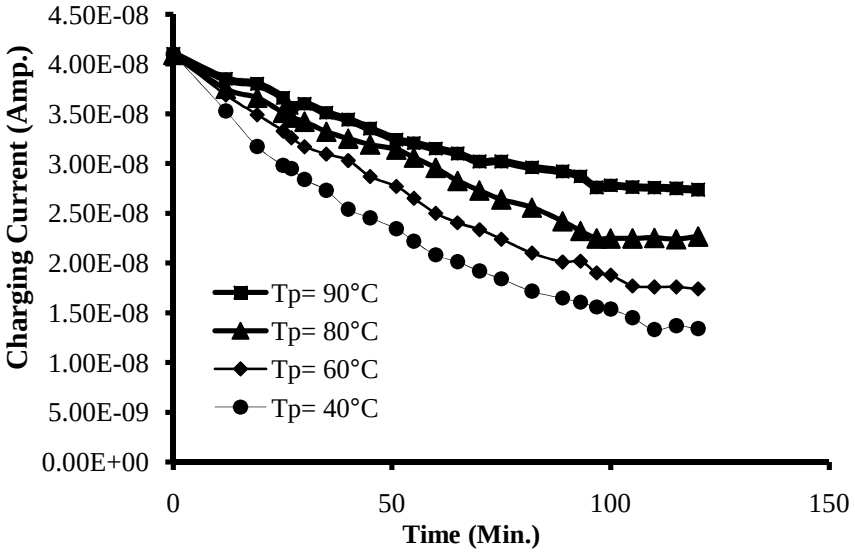

Fig. 2 : Transient Current vs time in charging mode for doped polyaniline(PANI) 25 µm poled E_p 5MV/m with different T_p i.e 40,60,80 and 90°C for Al-Cu electrode system

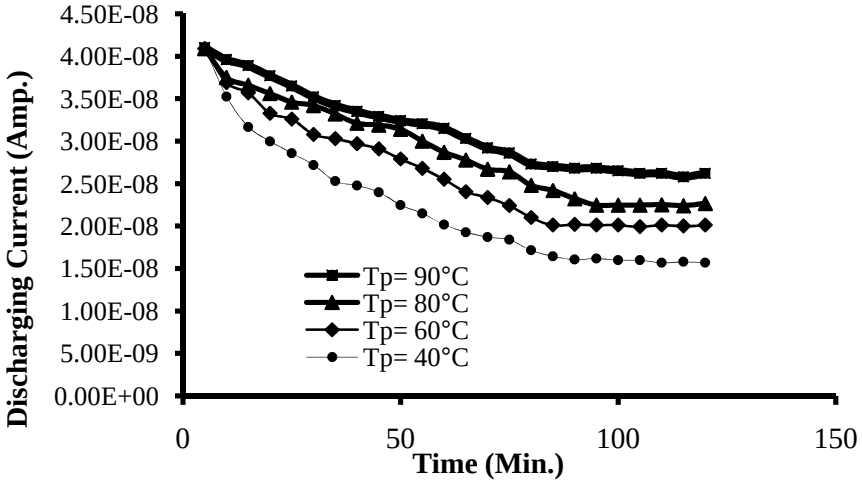

Fig.3 Transient Current vs time in discharging mode for doped polyaniline (PANI) 25 µm poled E_p 5MV/m with different T_p i.e 40,60,80 and 90°C for Al-Al electrode system

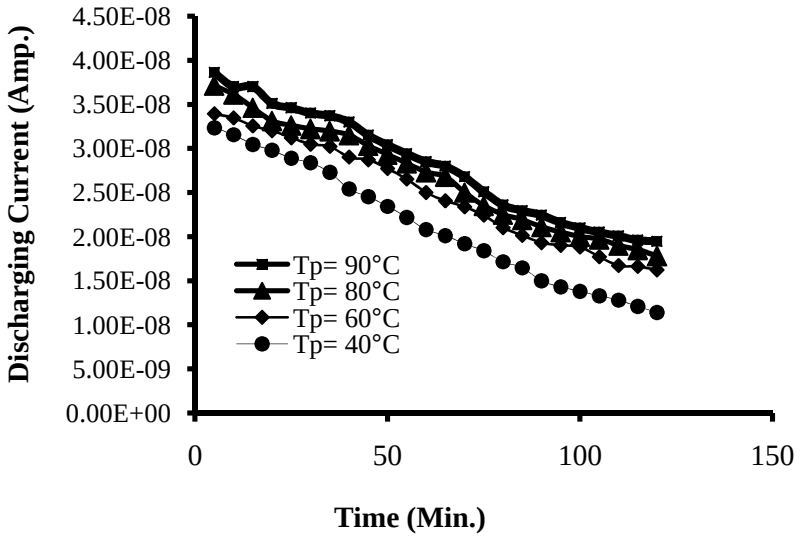

Fig.4 Transient Current vs time in discharging mode for doped polyaniline (PANI) 25 µm poled E_p 5MV/m with different T_p i.e 40,60,80 and 90°C for Al-Cu electrode system

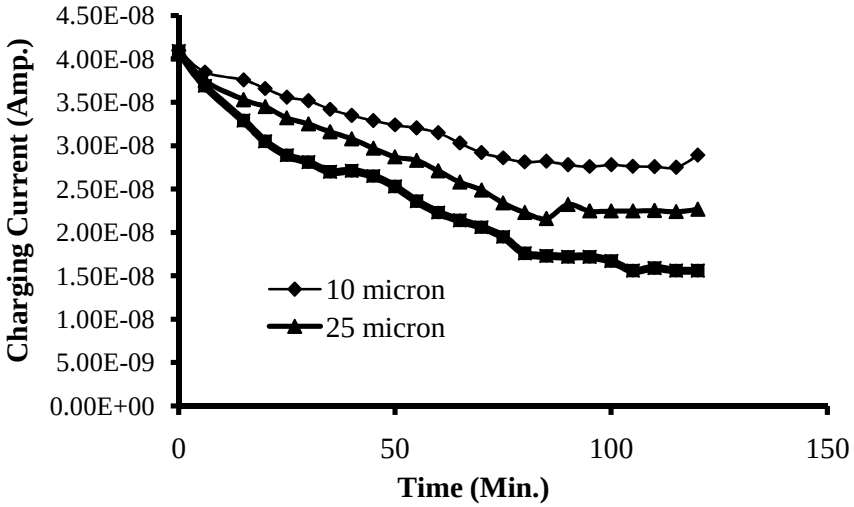

Fig. 5 Transient Current vs time in Charging Mode for doped Polyaniline(PANI) at Tp=80°C for different thickness 10,20 and 50 micron for Al-Al electrode system

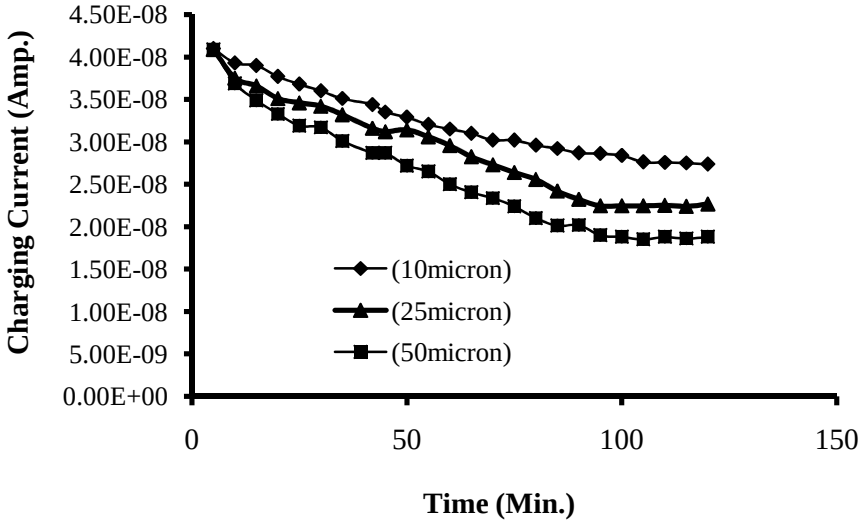

Fig.6 Transient Current curve in charging mode for doped polyaniline(PANI)at Tp=80ºC for different thickness i.e 10,25,50 micron for Al-Cu electrode system

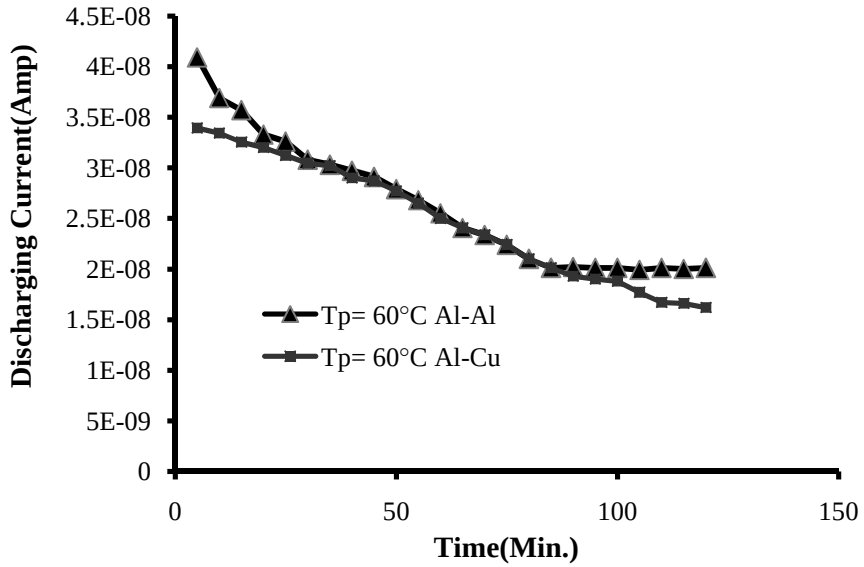

Fig.7 Electrode effect on discharging currents on doped PANI at given temperatures (40ºC) with constant polarization field Ep=5MV/m

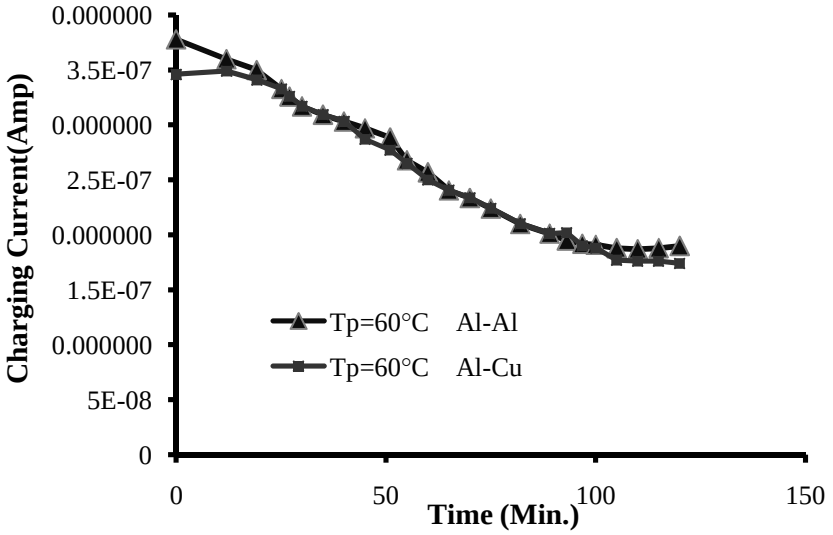

Fig.8 Electrode effect on charging currents on doped PANI at given temperatures (40ºC) with constant electric field Ep=5MV/m

4. CONCLUSIONS

The decaying trends of currents with time, the superliner nature of the isothermal currents against fields, the electrode dependence nature of the transient current seems to sufficient and reliable ground to assume that the possible controlling mechanism for the transient phenomenon is the charge injection and formation of trapped charges.

5. ACKNOWLEDGEMENT

The authors are thankful to the Principal GDC, Lalitpur, for providing laboratory facilities. One of them (Devendra K. Sahu) is indebted to the University Grants Commission, New Delhi, for providing minor research Project to him. (F. No. 8-2 (159)/2011(MRP/NRCB).

REFERENCES

1. S. E. Cumminsand, L.E. Cross, *Appl. Phy. Lett*. 10, pp. 14 (1997).
2. A. K. Gupta, R. V. Sharma & D. K. Sahu, *International J. of Health Science*, 3, 167-171 (2009).
3. P. K. Khare, D. K. Sahu, A .Verma, R. K. Srivastava, *J. Pure Appl Phys*, 42, 693-696 (2004).
4. Devendra K. Sahu, P. K Khare & R K Srivastava, *Indian J. Phys.* 78(11), 1206 (2004).
5. D. K. Das Gupta and K. Joyer, *J. Phys. D. Appl. Phys.*9,pp.829 (1976).
6. S.E. Cumminsand, L.E. Cross, *J. Appl. Phys.* 30,pp. 2268 (1968).
7. L. E. Crossand, R. C. Pohanka, *J. Appl. Phys.* 39, pp. 3992 (1968).
8. C. F. Pulvari, *Proc. Intern. Mtg. Ferroelectricity* 1,pp. 347 (1966).

9. N. N. Kranjinik, *et al., Fix. Tverd. Tela* 10,pp. 260 (1968).
10. Y. Kawamura, S. Nagai, J. Hirose, and Y. J. Wada, *Polym. Sci. Pt. A−2 Polym. Phys.* 7, pp.1559 (1969).
11. E. I. Knizhnik, C. D. Mamchich and Soed. *Vyrokomolek* 11, pp. 1665 (1969).
12. H. Sasabe, S. Saito, M. Asahina and H. Kakutani, *J. Polym. Sci. Pt. A−2, Polym. Phys.* 7,pp.1405 (1969).
13. H. Kakutani and M. Asahina, *J. Polym. Sci. Pt. A−2 Polym. Phys.* 7, pp. 1473 (1969).
14. I. G. L. Link, *Dielectric Properties of Polymers*, Volume 2, North Holland Publ. Co., Amsterdam (1972).
15. C. R. Aschcraft and R. H. Boyd. *J. Polym. Sci. Polym. Phys.* Ed., 14, pp. 2153 (1976).
16. J. M. Pochan and D. F. Hinman, *J. Polym. Sci. Polym. Phys*. Ed. 14, pp. 2285 (1976).
17. W. A. Philips, *Proc. Res. Soc.* 319, pp.565 (1980).