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Effect of Glutaraldehyde on Electrical Properties of Arrowroot Starch + NaI Electrolyte System

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ABSTRACT: A biopolymer based electrolyte system has been developed using NaI as dopant salt and Arrowroot starch as polymer matrix. Problem of fungal growth in such system has been removed by the addition of Glutaraldehyde (GA). The conductivity of the Arrowroot + NaI electrolyte system is of the order of 6.7×10^{-4} S cm^{-1}. Starch without crosslinker GA seems to be highly unstable and prone to fungal growth whereas the GA crosslinked electrolyte is quite stable. Color of the material as well as its conductivity data indicate that presence of GA affects the salt dissociation and multiplets formation. Ionic transference number of system is ≥ 0.95 indicating that prepared system is ionic conductor/electrolyte. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 1–7, 2011

Key words: starch; solid polymer electrolyte; glutaraldehyde; biopolymer; conductivity; crosslinking

INTRODUCTION

Since 1970 polymer electrolytes are widely studied because they show favorable properties of soft conducting network and solid shape/size. Scientists are continuously looking for a better polymer host which could assist salt dissociation and ion transport along with being cost effective and eco-friendly.[1–7] Biopolymers being cost effective, biodegradable and easily available in nature have an edge over the synthetic polymers and hence are receiving great attention these days. Chitosan, Agar-agar, Starch etc.[8–10] are few in series. Starch is an excellent alternative for electroactive polymers which is abundant in nature, cheap and biodegradable. The hanging OH in its structure is supposed to help salt dissociation and ion transport. Recently many reports are seen in the literature exploring starch as electroactive polymer. These studies vary from the pure starch systems to the modified starch and use. These modifications vary from plasticization to functional groups modification. Different techniques such as reactive extrusion[11,12] solution casting of gelatinized starch[2,9,10] etc. are being used to get films of starch-based electroactive polymers. Spectral studies of these systems have shown that water in starch makes strong hydrogen bonding. Both doped cation and H$^+$ are mobile in system. High water content in these materials is supposed to help dissociation of salt as well as movement of cation. Chemical modifications are reported to modify the T_g values. The low T_g values obtained by these methods are important to ensure good ionic conductivity. The physical modifications were made by the plasticization process of starch and cellulose derivatives with glycerol and ethylene glycol etc.

We have tried a simple solution cast technique, to prepare starch based electroactive material, which is commonly used for synthetic polymers. However starches being very sensitive to preparatory conditions (such as amount of solvent, cooking temperature, and cooking time)[13] required optimization of these preparatory conditions to get homogeneous/granule free morphology of complex system.

In our laboratory methanol (protic solvent), acetone (aprotic solvent) and water are being used as solvents for solution cast technique. From physical handling point of view, the water has been found best solvent among the three studied solvent. Water containing starch-salt complex are soft films hence can be cut into desired shape and size but fungus can be seen within two–three days for low salt concentration (wt % <35). Materials with high salt concentration are stable but multiplet formation is known to decrease conductivity at high

concentration in polymer electrolytes.[14] In this work we have tried to get fungal free electrolyte by cross-linking it with Glutaraldehyde (GA). Success has been achieved and fungal free/stable electrolyte even with small salt concentration has been prepared which has shown no degradation even after 24 months. The present article discusses the preparation and characterization of GA crosslinked arrowroot starch complexed with NaI. Adopted preparatory condition resulted in granular free morphology which is confirmed from Scanning electron microscopy. Salt choice is biased by the fact that "iodine and starch" have well-studied relationship.[15] Moreover Na^+ ion conductors are receiving great attention as cheap and safe alternative to Li^+ ion electrolyte.[16–25]

EXPERIMENTAL

Starch (Jyoti Chemical laboratories, India), NaI (Loba Chemie, India) and GA (Loba Chemie, India) has been used for the study. The material has been prepared by the solution cast techniques. In a glass beaker different wt % of salt has been taken with 0.5 g of the starch. Distilled water is used as solvent. Starch along with salt was cooked in water at 60°C for 30 minutes with continuous stirring on a magnetic stirrer. Solvent was evaporated till the material dried. For GA crosslinked complexes, GA has also been added in the solution at the initial stage. GA crosslinked materials were soft films with smooth surface. Hence they were cut into pieces of required shape/size for further studies. Silver foil has been used as electrode material.

Optical photographs of the samples were taken by Sony Cyber shot (DSC-S730). The FT/IR of the samples was recorded from a Jasco FT/IR 5300 in KBr from 400 to 4000 cm^{-1}. SEM micrographs have been taken using JEOL JXA 8100 Electron Probe Microanalyzer. A.C. Conductivity measurements have been carried out using Hioki HiTester LCR meter (3522-50) in the frequency range of 10 Hz–100 KHz. Bulk conductivity of material has been estimated by Cole- Cole plot using sample dimension by the formula

$$\sigma = 1/Z_{real} \ (L/A)$$

Where Z_{real} is real part of impedance and L and A are sample thickness and area respectively. Ionic transference number has been measured from the polarization experiment by using Graphtec XY recorder (WX 3000). A constant voltage is applied across Ag/Starch+GA+NaI/Ag cell and current is monitored as a function of time. During polarization, current decreases with time until it become constant. Using initial and final (constant) values of current t_{ion} is calculated using following equation

(a)

(b)

Figure 1 SEM micrograph of (a) starch doped with 30%NaI and 2 mL GA (b) starch doped with 40%NaI and 2 mL GA.

$$t_{ion} = (I_{initial} - I_{final})/I_{initial}$$

RESULTS AND DISCUSSION

For morphological investigations, SEM studies have been carried out. Figure 1(a,b) show SEM micrograph at 200 magnifications. The micrographs do not show any granules. Some features are seen in these micrographs which are observed to increase with increasing salt concentration from 30% [Fig. 1(a)] to 40% [Fig. 1(b)]. Thus the feature can be correlated with excess salt coming out of the system.[12]

Figure 2 shows optical photographs of electrolyte (starch + NaI system) pure and crosslinked with GA. Pure electrolyte (i.e., "without GA") is dark
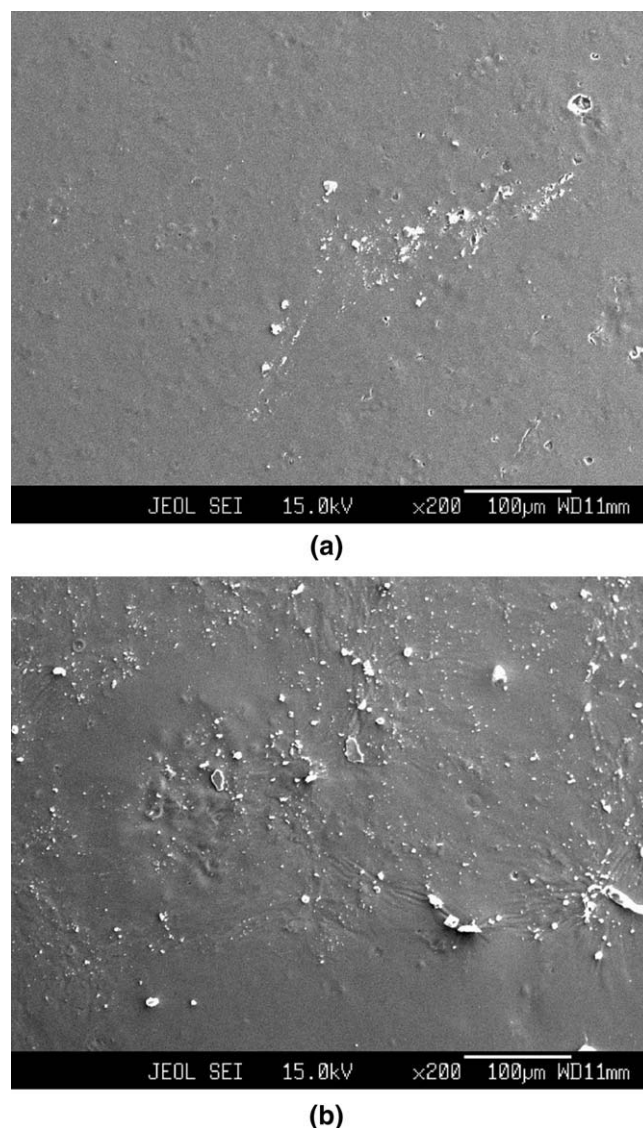
Figure 2 Photo of starch-salt complexes (a) without Glutaraldehyde (b) with Glutaraldehyde. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

blue/blackish colored material. Material crosslinked with GA has yellow hue. Beside the color difference fungal growth (a white branched structure) is also found in the "without GA" system. Amylose in starch is responsible for the formation of a deep blue/blackish color in the presence of iodine. The iodine multiplets slip inside of the Amylose coil. It is well established that Amylose form helical structure. When iodine goes inside this helical structure it gets enough space and environment to make multiplets.[26] If enough space and oxidizing agents are available in helices to accommodate higher multiplets then materials goes to blackish blue otherwise it can have any thing from blackish blue to yellow hue.[27] A possible correlation between the color and presence of GA in the system can be proposed according to available chemistry of Starch and GA and information relating starch iodine behavior. Figure 3 shows the chemical bonding of GA and starch.[28] Accepting this chemical structure we can say that presence of GA changes the hanging —OH and oxygen of OH get attached to the C through covalent bonding by releasing water. This will certainly reduce the oxidizing power of this O resulting in reduced chances of the iodine multiplet formation. Presence of GA, also, decreases the free space between the starch molecules which will again reduce the chances of multiplet formation (multiplets will require more space in comparison to single ions).

The most important factor for ion transport in polymer-salt complex is the acceptance of salt in polymer matrix. If the polymer matrix supports the
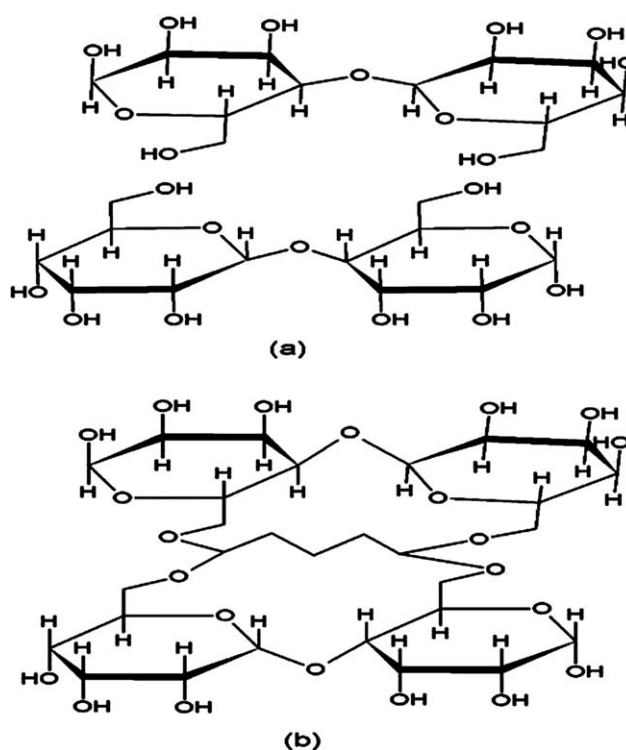

Figure 3 Chemical bonding of (a) starch (b) starch crosslinked with Glutaraldehyde.

TABLE I
IR Spectral Data of Different Constituents

Peak position for (cm^{-1})				
NaI	AS	AS+NaI	AS+NaI+GA	GA
462	523	475	524	968
601 [M]	575	678	578	1003
1154	707	794	1025	1109
1619 [M]	765	915	1153	1151
2025 [M]	857	1079	1377	1358
3382 [M]	929	1431	1648	1442
3566 [M]	1014	1576	1714	1646
	1081	1654	2937	2097
	1156	2855	3407	2957
	1378	2923		3403
	1460	3422		
	1516			
	1651			
	2928			
	3422			

M, peaks which are present in pure NaI are missing in complexed system.

salt dissolution then salt loses its characteristics. The simplest method to check this is IR spectral studies of pure matrix, pure salt, and the complex prepared. Table I shows the IR spectral data for NaI, Arrow-root starch (AS), AS+NaI and AS+NaI+GA and GA. NaI has lost all its original peaks in the AS+NaI or AS+NaI+GA system (except one at 1154 for which we cannot comment as a peak at the same position is present in the pure AS also). This confirms that salt (NaI) is fully dissociated in the starch matrix. Hence starch seems to be a good biopolymer host matrix, ready to accept the salt and remain stable for long time when crosslinked with GA. A new peak at 2855cm^{-1} is found in AS+NaI system. This can be associated with bonding of salt elements to the starch molecule. There are only two possibilities of starch and salt interaction, i.e., Na^{+} ion getting attached with the —O— available in the starch or I- and its multiplets are associating with the starch molecule. No spectroscopic peaks near 2855 cm^{-1} is found in literature for starch and iodine interaction.[29] Hence the probability of Na getting attach to the -O- of starch seems to be more feasible interaction. There are many probable sites where Na^{+} ion can get associated with starch as shown in Figure 4. The peak at 2855 cm^{-1} is drastically modified in the presence of GA system and it occurs at 1714 cm^{-1}. This indicates that GA is strongly influencing the starch and salt interaction and now Na^{+} attached motion of starch is resulting in restricted and slow vibration of molecule. Besides this many IR spectral peaks of native starch are modified in presence of the salt confirming the association of salt with starch.

Material without GA is prone to fungal growth and degradation hence electrical characterization has
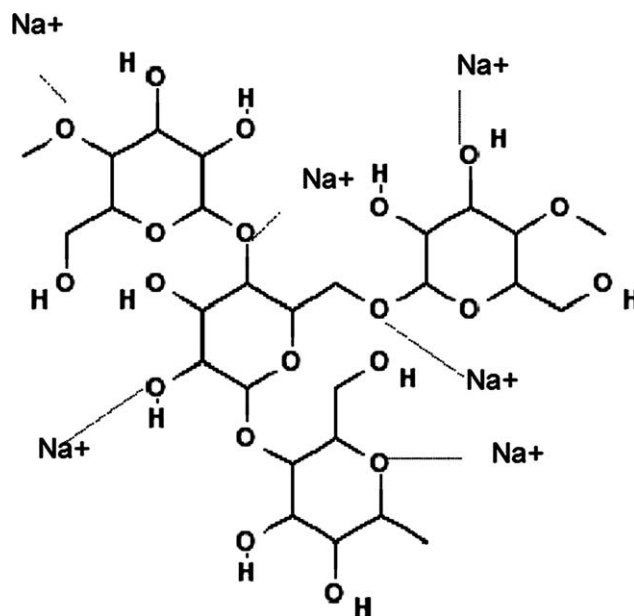
Figure 4 Probable attachment of Na^{+} ion with starch molecules.

been carried out only on GA containing materials. Conductivity of a system depends upon the availability of charge carriers and mechanism (or path) for its transport. Grotthus mechanism of ion transport is well-accepted mechanism in many polymer systems. In this mechanism movement of ions are associated with the flexibility/movement of the polymer chains[30] especially having moieties to which ions are connected. For present system we may propose this mechanism as shown in Figure 5 in which Na+ is getting associated with hanging hydroxyl oxygen whose vibrational motion will assist cation movement. The proposed mechanism, along with the chemical bonding of starch and GA shown in Figure 3 suggests that increasing amount of GA will suppress the transport phenomenon. To
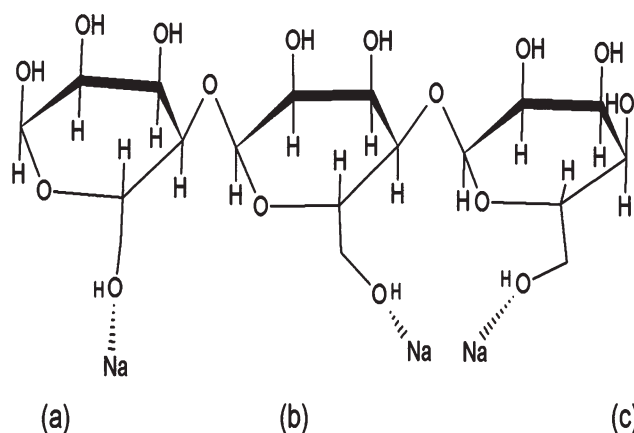

Figure 5 Possible mechanism of Na^{+} ion transport assisted by oxide ion of starch.
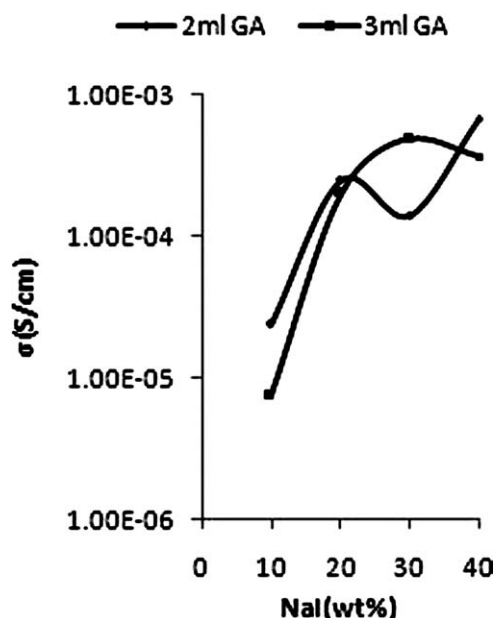
Figure 6 Bulk conductivity of the Starch-Salt complex Versus wt % of NaI.

confirm our hypothesis we have prepared two series of starch and NaI complex: (i) GA = 2 mL in 1 g starch and (ii) GA = 3 mL in 1 g starch.

Figure 6 shows the conductivity versus wt % of salt concentration graph for both the series. Values of conductivity for both the system are listed in Table II. Each series in itself follow the well understood trend in polymer-salt complex where conductivity shows two peaks when salt concentration is varied. At low salt concentration conductivity increase with increasing salt concentration is due to increased number of charge carrier. Formation of ion pairs at moderate concentration is proposed to explain the minima in the conductivity Versus wt % of salt graphs.[10] For explaining the subsequent increase in conductivity, scientists have different opinions. Fuoss theory of triplet ion formation[31,32] proposes the formation of triplet ion and their movement, whereas the other theory emphasis that charge carriers are still single ions which are available because of redissociation of triplets/ion-pairs.[33,34]

Comparison of the two series indicates that increased amount of GA is decreasing the conductivity. The minimum in the conductivity peak is shifted towards the higher salt concentration. Both these results can be explained on the basis of our hypothesis that Na$^+$ is moving with the support of oxygen in hanging hydroxyl group through "Grotthus mechanism." With increased amount of GA more —O of hanging hydroxyl group are being engaged by GA resulting in decreased chances of Na getting attached to them. The bonding of Starch and GA also results in restricted movement and decreased

mobility of side chains of starch. The salt dissociation depends upon its interaction with host matrix hence has to be affected by addition of GA. Decreased salt dissociation means less number of free charge carrier. Since the available number of free ions are decreased for the same salt concentration. Hence ion-pair formation will also be decreased resulting in minima shifting towards high salt concentration for 3 mL GA. In consequence the redissociation/multiplet ion formation will also shift towards higher salt concentration in 3 mL GA containing complex. Plot shown in Figure 6 is exactly of the same nature as predicted by our hypothesis. Thus the amount of GA has brought two important changes (i) in materials with 3 mL GA the position of conductivity maxima is shifted to a higher salt concentration and (ii) the σ is always greater for 2 mL GA with respect to 3 mL GA except for 30% NaI. Addition of GA seems to prohibit the formation of higher multiplets which is in accordance to our hypothesis. Increased value of GA decreased the available free space and hence the salt remains dissociated even at high salt content and multiplets formation is shifted for higher concentration.

Water absorption is a known phenomenon in starch. Hence we expected rise in conductivity with increase in Relative humidity. Materials showing smooth variation in its characteristics with humidity are very important for fabrication of humidity sensing devices. We have used a closed chamber having electrical outlets to study these characteristics. The saturated salt solution of different salts and silica gel has been used to achieve different humidity level. Hygrometer is used to measure the Relative humidity in the chamber. Figure 7(a) shows the set up.

Humidity dependence of impedance is shown in Figure 7(b). We have preferred to express the data in terms of impedance instead of resistivity or conductivity because area and thickness of material changes as it absorbs the water. Also from the device fabrication point of view impedance/conductance are more important parameter than resistivity/conductivity. In the starch + NaI electrolyte system Impedance is decreasing exponentially with

TABLE II
Conductivity vs. Concentration for Different GA Containing Samples

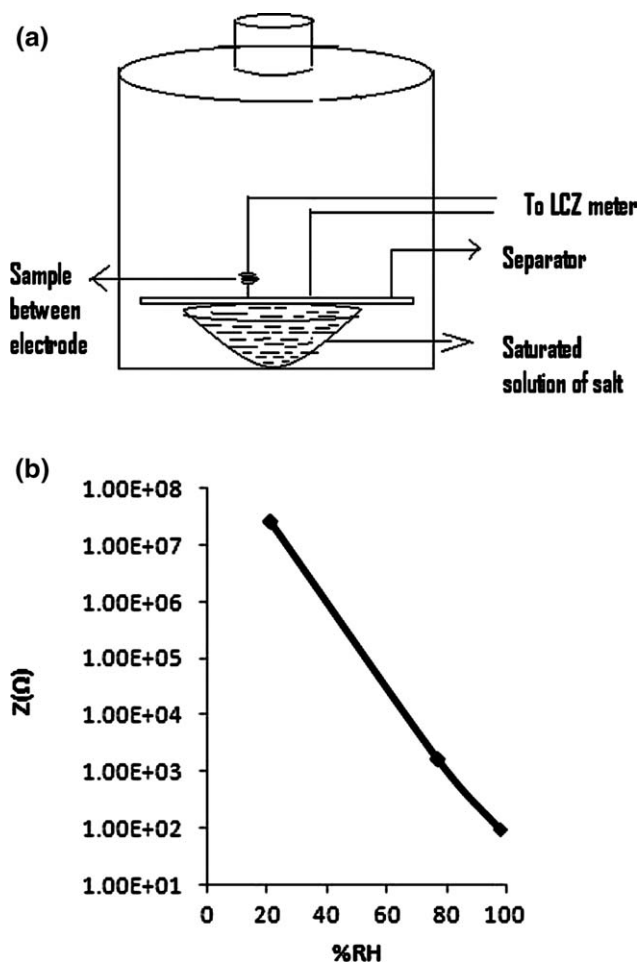| Wt % of salt	Conductivity for 2 mL GA containing system (S/cm)	Conductivity for 3 mL GA containing system (S/cm)
10	2.4e-5	7.5e-6
20	2.5e-4	2.0e-4
30	1.4e-4	4.9e-4
40	6.7e-4	3.7e-4

Figure 7 (a) Setup for Humidity Dependence (b) Humidity dependence of impedance (for electrolyte with 40% salt and 2 mL GA).

increasing RH which signifies the importance of prepared material from application point of view.

Ionic transference number (t_{ion}) shows the fraction of conductivity due to ion transport. For any electrolyte system it is very important parameter. There are many methods to measure this parameter.[35] In present paper we are using Wagner's Polarization method in which dc voltage is applied across the sample and initial and final current is noted. Circuit arrangement used for this is shown in Figure 8(a). Figure 8(b) shows the current Versus time plot drawn using Graphtec XY recorder (WX 3000). Value of Resistance used in the setup should be comparable with that of sample. Hence before carrying out the measurement impedance of material is measured so that suitable R can be selected. Ionic transference number estimated by Wagner's polarization is ∼ 0.95 for 2 mL GA where as for 3 mL GA it is ∼ 0.91. The decreased value of t_{ion} is in accordance with our hypothesis regarding effect of GA on the starch based electrolyte. Figures 3 and 5 clearly suggest that increased amount of GA will obstruct

Na$^+$ getting attached to oxygen of hanging hydroxyl group (which is supposed to assist ion transport). Hence movement of Na$^+$ will be hindered resulting in decreased ionic contribution to the conductivity of system. Increased value of GA will increase obstruction and decrease flexibility of polymer chain as well as the oxygen sites available to assists the Na$^+$ transport hence t_{ion} has a lower value in higher GA containing system.

CONCLUSIONS

Success has been achieved in developing the fungal free/stable starch based electrolytes with the help of GA as crosslinker. IR spectroscopy confirms dissociation and dissolution of NaI in Starch. The conductivity is found to be ∼ 6.7×10^{-4} S cm^{-1} which is good in view that prepared electrolyte can be easily cut in the desired shape and size. The ionic transference number
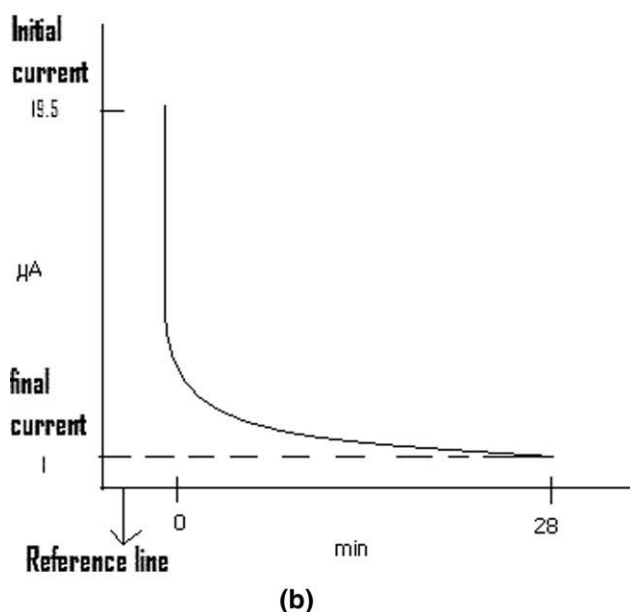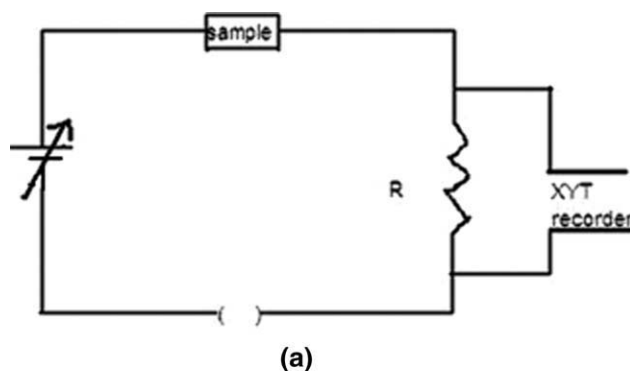

Figure 8 (a) Circuit arrangement for Wagner Polarization (b) Current Versus Time curve. (On the time scale '0' is the point when the voltage has been applied to the sample).

up to 0.94 is achieved in prepared system , confirming that starch is a very good candidate to develop electrochemical materials. Being biodegradable it will prove to be environment friendly also. Exponential dependence of impedance on humidity makes it interesting for fabrication of humidity sensing devices.

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