Ion exchanging electrodes from porous glass

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Low frequency electrical properties of numerous organic and biological materials depend on the transport of ions. Commonly used electrodes, such as metal films or Nesa glass, are blocking ones. When studying thin layer samples one must seriously account for, generally unknown, influence of an electrode. It has been shown previously that ion-exchanging membranes may serve as ion-injecting electrodes. However, problems with supporting of thin samples were reported. Porous glass has been used for preparation of ion-exchanging electrodes, for the studies of liquid crystals and polymers.

1. Introduction

The transport of ions through interfaces is a feature of biological systems. For the studies of electrical properties of materials the use of injecting electrode is common in semiconductors where electronic transport takes place. The same can be indicated in the field of electronic conduction of aromatic organic solids where electron injecting electrodes are used. However, the experiments on electrodes which are capable of injecting the ions material are rarely reported. The aim of the present contribution is to discuss the concept of injecting electrodes made from porous glasses suitable for time-domain dielectric techniques. The novelty is related to the possibility of using the above mentioned technique to the study of thin films. The use of thin films is of importance because of relatively high fields needed for the observation of ion injection from an electrode [1].

2. Property of the electrode

The electrode having the property of exchanging of ions with organic material ready for time-domain dielectric experiments must fulfill certain requirements:

1. It is useful if ion injection is electric field enhanced. This would enable zero-time for charge injection process, which is the essential condition for time-of-flight studies.

2. The electrode should represent a reservoir of carriers and the electrode resistance should be negligible in respect to that of the material investigated.

3. The electrode should have necessary mechanical properties (rigidity, flatness) enabling the study of materials in thin layers.

3. Experimental

We have found that the porous glass plates are really suitable for preparation of ion-

injecting electrode. The electrode has been prepared similarly to that of former works [1], [2]. The samples have been measured by means of modern TD set-up [3]. The preparation of the samples was as follows: liquid crystal was placed between electrodes. The ion source was made of porous glass saturated with water solution of agar-agar and NaCl. Diameter of the pores was 20—40 nm. The resistance of the electrode has been checked and found less than kΩ in full range of times explored. To check the injecting properties of electrode the following materials have been used: cholesteryl oleate and hexyl-cyano-biphenyl (6BC). The sample has been constructed in the way shown in Fig. 1. The thickness of the layer was controlled by pieces of
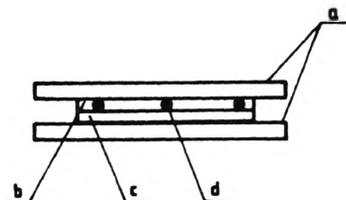
Fig. 1. Construction of the sample. a — electrodes SnO_2, b — liquid crystal 6CB, c — injecting electrode (porous glass in water solution of agar-agar and NaCl), d — optical fibres

a calibrated glass fiber of 0.2 mm in diameter. The time-domain set up (automated, computer controlled) has recorded the current *vs.* time curve. The voltage was applied in steps (from 0 to 10 V, regulated, 4 mV step). Both charge (applied voltage step) or discharge (applied 0 voltage step after charging transient) transients were recorded.

4. Experimental proof of ion exchange through the interface

The proof of ion exchange through electrode—LC interface comes from the following experimental findings:

1. Big (at least one order of magnitude) difference in charging and discharging current (Fig. 3). In comparison, the difference in charging and discharging currents for SnO_2 electrode, as observed, is negligible, excpet for very long times (Fig. 2) The SnO_2 electrodes are considered as blocking electrodes to liquid crystals. As one can see from Fig. 2, the electrode process can be seen for the times longer than 10^3 s.

2. As can be seen from Figure 3, there exists the difference in the value of charge and discharge currents. This difference may be due to additional charges injected from an electrode.

5. Interpretation

In the case of dipolar polarization as well as ionic polarization with no significant reactions at the electrodes, the reversibility of charge-discharge process is observed [4]. Therefore, the current *vs.* time curves should look similar to those from Fig. 2. However, in the case of ion injection which may be treated as the reaction of creating
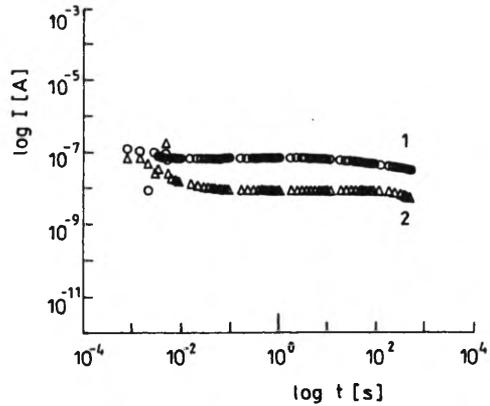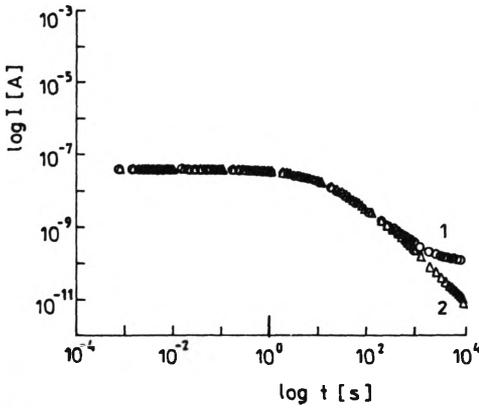
Fig. 2. Log of the current *vs.* log of the time for hexyl-cyano-biphenyl (6CB) sample supplied with SnO_2 electrode. Voltage applied $U = 7$ V, temperature $T = 293$ K, sample thickness 0.2 mm (1 — charging, 2 — discharging)

Fig. 3. Log of current *vs.* log of time for hexyl-cyano-biphenyl (6CB) sample supplied with ion-exchanging electrode. Voltage $U = 9$ V, temperature $T = 293$ K, sample thickness 0.2 mm (1 — charging, 2 — discharging)
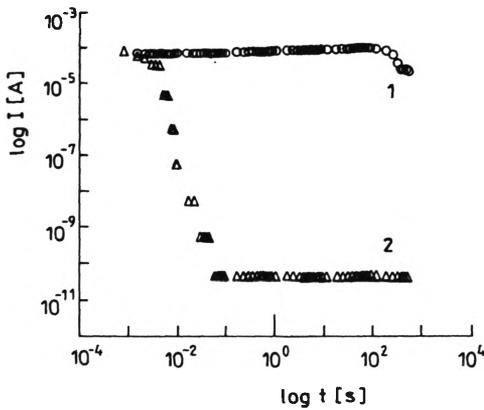
Fig. 4. Log of current *vs.* time for polymer-chitosan/poly/2-amino-2-deoxy-,D-glucose/ sample supplied with ion-exchanging electrode. Voltage $U = 1$ V, temperature $T = 293$ K, sample thickness 0.1 mm (1 — charging, 2 — discharging)

the ion of one sign at the electrode/material interface, the current symmetry is broken as one may see from Fig. 4. This is not only because of different carrier densities, but also due to space charge. This assumption leads to the second evidence that is from space charge limited current (SCLC) theory [5]. The nonstationary, one carrier SCLC current would exhibit a maximum in time domain. The authors do not know any other explanation of the observed transient current maxima.

6. Conclusions

The porous glass filled with ion-exchanging materials provides an ion-exchanging electrode suitable for organic materials. The electrode can be used for the preparation of samples which are suitable for investigation of liquid-like materials.

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