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Aspects of Surface Ionic Conduction

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Bulk ionic and mixed electrical conduction have investigated in many ionic, polymeric and complex systems. The surface ionic conduction has paid a little attention so far. The surface ionic is important for development of various ionic devices and sensors. The present work makes an attempt towards an experimental investigation of the characteristics of surface ionic conduction. The various aspects of measured surface ionic conduction, like frequency dispersion, dielectric behavior and nature response, are analyzed from theoretical view-point. The marked distinctions of surface ionic conduction over bulk ionic conduction are also analyzed. The said analysis is carried out over pure ionic, polymeric and electro-active-bio-polymeric surfaces. The overall results obtained contain many new and interesting aspect of the conducting behavior

Key Words: Surface conduction, ionic conductor, natural membrane

INTRODUCTION

During past few decades thin films, multiplayer structure and other 2-D system gained tremendous importance over bulk solids. In theses type 2-D systems most of the physical properties changes, in a characteristics way due to quantum confinement or size effect¹. The electronic structure of the surface with z-confinement is different from the electronic structure of the same solid in bulk state. The mentioned 2-D systems are investigated in an elaborate way due to their tremendous technological application¹ potential towards the development of modern technologies. Two dimensional system in metallic, semiconductor and polymeric system are studied to a great extent however ion conducting systems paid a little attention in this regard. Surface and surface properties are always amazing and interesting.

Recently it has been found that the surface properties of ion conducting system are very interesting and important towards the development of various sensors. Surface morphology of 2 D supra-molecular structure has been studied². Ultra-thin Layer of Lipids in Polymer film and its electric properties a new sorption method to prepare a model Bio-membrane system has been studied³. Recently Humidity sensing characteristics of hydro-tungstite thin films has also been studied⁴.

In this present work total surface electrical conduction was investigated over surface of a bulk protonic / superionic conductor. In the investigation total S010 Ghosh et al.

electrical conductivity $\sigma(\omega)$ and its various aspects were measured using impedance analyzer. The nature of d.c surface conduction was also investigated over the surface of a natural bio-membrane. The over all results are very interesting and discussed in the following sections.

EXPERIMENTAL

A slab of solid Gum Arabica⁵ was prepared, with pure powder of the same from E-Merk (India), following sol-gel process⁶ and adequate drying. Experimental specimen was prepared by firm contact of two polished narrow Custrips over the polish surface of the developed specimen. The surface of the bulk specimen was used for a.c. electrical measurement.

The natural membrane of outer Onion surface was properly cleaned and fixed over a thick glass surface. Thin narrow pair of Cu electrodes was fixed over that by pressure in a mechanical arrangement. Two identical such specimens, (i) electrodes parallel to the fibre direction of the membrane (ii) electrodes perpendicular to that direction, were employed for d.c electrical measurement.

General procedure

Unlike semi-conductor or metallic surface conductivity measurement⁷, which use four probe method , the two probe electrode is used here. The current flowing between the electrodes under application of external p.d may use (i) a direct surface conduction using surface state (ii) through few layers below the surface, within the bulk states. There may have surface space charge effect adjacent to the electrodes. Analysis of surface study may be done by realizing a surface as slab of solid with few parallel planes in x-y plane perpendicular to z-axis. This is known as slab method, originally introduces in the theoretical study of surface phonon⁸.

Detection Method

The Impedance spectroscopy of the developed Gum Arabica specimen was investigated, between frequency range 1 Hz to 100 KHz HIOKI 3522 LCR/Z Analyzer (Japan). Experimental specimen, of the Onion membrane with two high polished copper strip electrodes, was subjected to the measurement of d.c voltampere (V-I) characteristics of the specimen to investigate its d.c characteristics. The measurement was carried out by a Kithley (USA) 2400 series electrometer. The measurements were carried out at room temperature 25 C.

RESULTS AND DISCUSSION

Using the measured data, of the complex impedances at various frequencies of the impressed a.c. field under three different external conditions, impedance plot was done and shown in Fig.1. The results show that the surface conduction is very sensitive on external factors (i) illumination (ii) humidity. Some marked Vol. 21, No. 10 (2009)

discontinuities on the impedance plot are the clear indicators of the surface relaxation in the low frequency region i.e below 11KHHz.

Fig.2 shows the variation of total conductivity, estimated from a.c measurement, with the frequencies of the impressed a.c. It shows that the variation of total electrical conduction at low frequency is more sensitive to external factors compared to that in high frequency region. The high frequency conductivity dispersion shows that it obeys the Jonscher power law⁵, $\sigma(\omega) = A \omega^n$, like that in the bulk conduction. The estimated value of the exponent n=0.91, which is lower than corresponding bulk value⁵ n=0.96.



Fig. 1: Impedance plot (Gum Arabica surface): Real Z Vs -ImZ. The Legends correspond to the mentioned measurement condition. p.d 1Volt a.c Electrode separation D=0.45 cm and electrode length L=2.5 cm. Room temperature 25C. Normal humidity 65% max. humidity = 87%



Fig. 2: Conductivity dispersion plot of (Gum Arabica surface) $\log \sigma(\omega)$ vs $\log f$ f =frequency/Hz. Experimental parameters same as those in Fig.1



Fig. 3 : Volt Ampere Characteristics of Onion membrane surface: V (volt) Vs I (Current): Legend corresponds to the mentioned measurement condition Electrode separation D=0.30 cm and electrode length L=2.5 cm. Room temperature 25 C. Normal humidity 65%.

S012 Ghosh et al.

Fig.3 shows d.c volt-ampere characteristics of the Onion membrane surface. It shows a very strong asymmetry between longitudinal (along the fibre direction) and transverse conduction.

The nature of surface ionic conduction as may be analyzed from Fig.1 and Fig.2 involve some conduction mechanism and dielectric relaxation some of which are different from that in bulk process. Recently⁹ it has been analyzed that formation of two- dimensional Polarons that are absent in Three-Dimensional crystals. The estimated values of $\sigma(\omega)$ involves direct surface contribution and a part of bulk contribution from few adjacent layers below the surface. The observed nature of the d.c. electrical conduction over Onion membrane surface is the electronic contribution to the total surface conduction.

Conclusions

Surface of bulk materials, membranes and two dimensional ionic/ protonic sytems exhibits ionic conductivity. The conduction mechanism in the said systems are very sensitive to external condition like, illumination, humidity etc.

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