



Electrical conductance through adsorbed water molecules on freshly fractured glass surfaces



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ABSTRACT

Plate glass sheets of low emissivity glass were cut into small rectangles and scratched with a diamond tipped scribe from one edge to another. The scratch was deep enough to locally remove the conducting tin oxide surface and to fracture the glass beneath, leaving behind conducting electrodes on either side. They were connected by gold wires to a standard meter to measure the complex admittance at different relative humidities (14–79%) and frequencies (20 Hz to 1 MHz). The raw data was converted to the complex susceptibility after subtracting the signal due to the bulk glass substrate and analyzed using the universal dielectric response model developed by Jonscher. The change in the conductance and capacitance, as measured in a parallel mode, gave a measure of the humidity sensing ability of the scratch and roughly followed an exponential dependence. A control plain glass sample showed a very small effect. The Jonscher index “ n ” for the susceptibility (χ') in the high frequency range was seen to be about +0.5, which is characteristic of ionic or hopping conductance and which we expect to be the Grotthuss process. The somewhat lower values of the index seen for the dielectric loss (χ'') data are typical of a lossy material. A combined plot of χ' versus χ'' of all the data for all humidities and frequencies showed that the Jonscher model was well obeyed in the present work, with a log–log slope close to one as required by the model. Although one scratch sample is highlighted in this work, measurements are presented that show reproducibility between a number of samples as well as a minor amount of aging in repeat measurements on the same sample.

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1. Introduction

This article is a continuation of my previous work that also studied the electrical conduction through water layers adsorbed from a humid atmosphere. For bismuth iron molybdate pellets, oxygen vacancies were produced by chemical reduction in a methanol atmosphere at elevated temperatures [1–3]. On the oxidized surface (vacancy free) the Grotthuss chain reaction was the dominant mechanism, but on the reduced surface (with vacancies) Fermi level shifts were seen. The slope of a plot of the change in surface conductance versus humidity (log–log) is a measure of the number of molecular water layers [1]. A value of from one to four showed the Grotthuss chain reaction whereas less than one implied Fermi level shifts. The DC polarization humidity dependence [2] which demonstrated ionic polarization of the adsorbed water layers confirmed the Grotthuss mechanism. This early DC conductance work also showed that the oxidized bismuth iron molybdate surface is hydrophobic and that at high humidity, water vapor adsorbs in clusters that display bulk properties. This was most clearly shown by

a series of isothermal measurements of the change in the surface conductance versus humidity (log–log) that were converted into a series of isoconductance curves [3]. The latter were fitted to the Clausius–Clapeyron equation in order to determine the isosteric heats of adsorption for various thickness of adsorbed water. This demonstrated hydrophobic behavior.

More recently, AC admittance measurements have expanded my study of the phobic or philic nature of water adsorption. Mesoporous compacted powders of various silicates were studied [4], where it was seen that there is an optimal balance between the hydrophobic versus the hydrophilic nature of the surface. The use of a number of different organosilanes allowed the production of a range of hydrophilic versus hydrophobic interaction with humid air. In this, as in all my AC work, the “universal” dielectric response method developed by Jonscher [5,6] is used to analyze the complex admittance. In studying the effect of humidity on the electrical conductivity of mesoporous polythiophene [7] it was concluded that humid air had no significant effect on electrical conduction through the adsorbed water layer itself, but that the presence of surface water molecules affected the polythiophene conduction that occurs through the overlap of adjacent π -bonds.

The following review of the most common mechanisms used to explain electrical conduction through adsorbed water layers

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follows that of previous work [7–9]. Water molecules will irreversibly chemisorb onto available cation sites as hydroxyl groups when the surface is dry, and thus remain stable to any further changes of humidity at low to moderate temperature. This forms the base for the reversible physisorption of water molecules, which is a strong function of humidity. Electrical conduction can only occur through the water layers by the electrical migration of either protons or hydronium ions. A single monolayer of chemisorbed hydroxyl groups can conduct by proton hopping, due to hydroxyl dissociation under the influence of an applied electrical field, but if physisorbed water is present then hydronium ions can diffuse or migrate as a unit. At a high concentration of physisorbed water only some of the water molecules will be ionized as H_3O^+ and the extra proton will hop from molecule to molecule, by a process called the Grotthuss chain reaction [10]. Finally, at extremely high humidity, water will condense to fill a spherical mesopore if its radius is not too large, due to a surface tension effect attributed to Kelvin [8,11]. In the bulk liquid water thus produced both the Grotthuss process and hydronium ion diffusion may occur. This succession of mechanisms naturally gives a rapid increase of conductance with increased humidity [8,10,12].

In the present work we will look at the AC electrical conductance and capacitance across deep scratches on tin oxide coated glass plates under increasingly humid atmosphere. When glass is scratched, percussion fractures are formed which expose fresh, mostly silica, surfaces that initially are comprised of a large number of broken and dangling bonds. Before these bonds can interact with the atmosphere, surface reconstruction occurs to produce strained bonds [13]. Water vapor in the air then chemically reacts with these strained bonds to produce surface silanols (SiOH groups). The silanol concentration produced does not have a strong dependence on atmospheric humidity and will occur even in a good vacuum [13–15]. At higher humidity water vapor will then continue to physisorb onto the silanol chemisorbed layer. It has also been shown that water will physisorb preferentially onto H-bonded hydroxyl groups as opposed to freely vibrating ones [16,17]. It is important to note here that this process only readily occurs on a freshly fractured glass surface and not on a smooth glass plate that has been thermally annealed by the manufacturing process.

In focussing on the electrical properties of the adsorbed water layer alone, we hope to expand our knowledge of the dominant mechanism of transport. The usefulness of this technique as a possible humidity sensor is incidental to the present work, which was discovered serendipitously.

2. Experimental details

In these experiments a plate glass sheet of low emissivity glass was cut with a diamond saw into a number of roughly 2 by 3 cm rectangles. The glass was obtained from PPG Canada Inc. of Thunder Bay, Ontario, some years ago and is normally used to reduce radiant heat losses through windows. We are using it for the transparent conducting properties ($100\ \Omega$ square) of the doped tin oxide film that coats the glass on one side. The plate itself is ordinary soda glass that typically has a composition of roughly 72% SiO_2 , 13% Na_2O , 9% CaO , and 6% MgO .

The conducting film was scratched with a diamond tipped scribe from one side of the glass rectangle to the other so as to separate two regions of conducting film that act as electrodes. The scratch was deep enough to remove the tin oxide and to fracture the glass beneath as shown in Fig. 1. This is an optical microscope image of a section of the scratch at a magnification of forty. The width of the scratch is about 0.2 mm over a length of about 20 mm in total, but only 2 mm of this length is shown in Fig. 1. Percussion flaking is seen on either side as well as finer damage in the middle. The

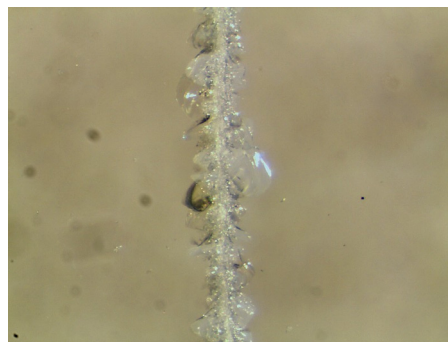


Fig. 1. Digital capture from an optical microscope of scratch sample S2. The length of the scratch segment shown is 2 mm.

flaking produces a new surface that has never been exposed to the air. The scratches were cleaned with methanol to remove any loose ground glass. Gold wire leads (0.1 mm diameter) were attached to the conducting film on either side of the scratch using a colloidal suspension of silver in methyl isobutyl ketone (electrotag 415), manufactured by Acheson Colloids Canada. The contacts were then set to dry for a few hours.

A control sample was also created using the tin oxide free back surface of a glass rectangle. Here two parallel lines of silver dag were painted onto the surface in order to mimic the electrode arrangement of the scratch in the other samples. The smooth or plain glass gap thus formed was about 1.5 mm wide over a length of 10 mm. Gold wires were connected to the dag as before. The fact that this control is considerably wider than the scratch was not important as will soon be seen.

A humidity controlled chamber used for powdered samples, as described in a previous work [4], was adapted for use of the glass samples. By inverting the stand holding co-axial electrodes the non-conducting bottom of the glass rectangles could be attached to a flat Teflon surface with scotch tape folded to be double sided. The gold wire leads were then connected with silver dag to metal posts that ran to the outside. The 182 cm³ Plexiglas chamber also held a concentrated salt solution vial used to control the humidity of the sealed chamber. This was done in accordance with criteria set forth in the 1998 Annual Book of ASTM Standards [18].

Seven salt solutions were used in the present work. These are LiCl (11.3%), $\text{KC}_2\text{H}_3\text{O}_2$ (22.5%), MgCl_2 (32.8%), K_2CO_3 (43.2%), $\text{Mg}(\text{NO}_3)_2$ (52.9%), NaCl (75.3%), and KCl (84.3%) where the relative humidities are the nominal values measured at 25 °C [18]. The humidity values that are used here were obtained by a direct calibration of the sample chamber using a commercial probe made by Vaisala (HMI-32, probe type HMO-36) which was previously calibrated in a standard chamber supplied by the manufacturer. After a 20 h equilibrium the relative humidity values that we will use are as follows: LiCl (14%), $\text{KC}_2\text{H}_3\text{O}_2$ (25%), MgCl_2 (37%), K_2CO_3 (42%), $\text{Mg}(\text{NO}_3)_2$ (53%), NaCl (71%), and KCl (79%) measured at a laboratory temperature of about 22 °C.

The steel rods at the top of the Plexiglas chamber were connected with simple clamps to the 16047A test fixture of a Hewlett Packard 4284A precision LCR meter. The chamber was surrounded with a grounded Faraday cage and the meter was configured to measure capacitance (C_p) and conductance ($G = 1/R_p$) in a parallel configuration. All measurements were computer controlled through an IEEE interface by programs written by the author. The admittance spectra were measured using 95 frequency values from 20 Hz to 1 MHz, set to give roughly equal spacing on a logarithmic scale. The scans were completed over a period of 10 min. The program used also allowed the automatic repetition of scans over an extended period with a set delay between scans, both day and night. For example, every 12 h for two days. In this way the approach

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