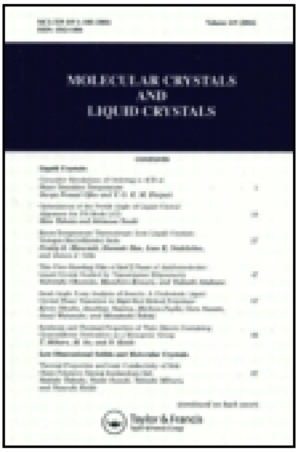

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Frequency Dependent Conductivity of Emeraldine: Absence of Protonic Conductivity

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An experimental study of the frequency dependence of the conductivity of emeraldine polymer as a function of moisture content and protonation level is presented. A decrease in the conductivity and dielectric constant are observed to occur with pumping. The detailed frequency and composition behavior of these data are inconsistent with the proposed proton exchange assisted conduction of electrons (PEACE). The experimental results are shown to be consistent with the role of charging energy limited tunneling among small granular polymeric metal particles formed upon protonation of emeraldine.

I. INTRODUCTION

Polyaniline is a family of polymers that has been under intensive study recently because the electronic properties can be modified through variations of either the number of protons, the number of electrons, or both.[1–12] These materials provided an opportunity to study unusual electronic defect states including the presence of solitons,[13–15] polarons,[16,17] bipolarons,[16,17] excitons,[5,18] twistons,[19] and conformons.[20] Studies by Ginder, et al.[21] of the magnetic susceptibility variation with protonation of the emeraldine base form of the polymer revealed a metallic Pauli susceptibility approximately linearly proportional to the percent protonation. A model of phase segregation to fully protonated "metallic" regions and unprotonated "insulating" regions was proposed. The transition to a metallic state was suggested to coincide with the change in electronic structure to form a polaronic metal. Optical absorption data and band structure calculations of Stafstrom, et al.[22] support the formation of a polaronic metal upon protonation of emeraldine. The *dc* and electric field dependent conductivity, as well as thermopower studies, of protonated emeraldine polymer have been interpreted by Zuo, et al.[23] in terms of charging energy limited tunneling between these metallic islands.

It is well known that the resistance of films of both the emeraldine base and 50% protonated emeraldine hydrochloride polymer decrease by a factor of ~3–4 when exposed to water vapor. The resistance increases only very slowly on removing the water vapor under dynamic vacuum. The rapid increase in measured conductivity with exposure to water vapor and slow decrease of measured conductivity under dynamic vacuum was pointed out by Angelopoulos, et al.[24] as being consistent with the postulated[21,23] structure of emeraldine hydrochloride "islands" in a matrix of undoped or slightly doped material. However, recently Travers and Nechtschein have proposed[25,26] that a conduction mechanism based on electron hopping between localized states, that is proton exchange-assisted conduction of electrons (PEACE), is the dominant mechanism for charge conduction. We summarize here the results of our recent studies of the frequency dependence of the conductivity of emeraldine polymer as a function of protonation level for frequencies in the range of *dc* and 10^1 Hz through 10^{10} Hz. The data are presented as a function of exposure to room atmosphere and dynamic pumping. The results indicate no change in the conductivity as the frequency is varied through the frequency for proton exchange. These data confirm that the proton exchange does not mediate the electronic conduction mechanism. Our results are shown to be consistent with charging energy limited tunneling among the metallic emeraldine hydrochloride islands.

II. EXPERIMENTAL TECHNIQUES

The free standing emeraldine base films were prepared from chemically synthesized emeraldine base and subsequently treated with HCl over appropriate pH values to achieve the protonation level desired.[21] The low field four probe temperature dependent conductivity experiments were carried out using a previously described technique.[27] The audio frequency (10^1 through 10^5 Hz) measurements were performed using gold coated compressed polyaniline pellets with typically 1 cm diameter circular gold coating as electrodes. Heating effects during the gold deposition were eliminated by using 500-ns pulses with a low repetition rate. A gold coated guard ring was used to eliminate possible fringe effects by employing a General Radio Capacitance Conductance Bridge in its three terminal configuration.[28] The real and imaginary components of the microwave frequency (6.5×10^9 Hz) dielectric constant were measured using the cavity perturbation technique of Buravov and Shchegolev.[29,30] The data were acquired using a Hewlett-Packard model 8350B Sweep Generator and a 6.5 GHz (TM_{010}) cavity, using a Janis Supervaritemp dewer for temperature control. Measurement of change of cavity frequency and Q together with an experimentally acquired depolarization factor enables the calculation of ε and σ.

III. EXPERIMENTAL RESULTS

We have measured the four-probe dc conductivity of films of emeraldine salt before and after pumping. As previously reported by Zuo, et al.,[23] the temperature dependence of the conductivity for samples after being pumped on varies as:

$$\sigma \propto \exp\left(-(T_0/T)^{1/2}\right) \qquad (1)$$

The constant T_0 in the exponent was found to be nearly independent of concentration for [Cl]/[N] between 0.3 and 0.5. For [Cl]/[N] < 0.3, T_0 began to increase rapidly. This result was interpreted in terms of percolation of the granular polymeric metal islands at a concentration of [Cl]/[N] ~ 0.3 and the continued presence of barriers between these granular metal islands as the protonation level was increased up through and including [Cl]/[N] = 0.5. The limiting T_0 for heavily protonated samples was found to be $T_0 = 7800$K.

In Figure 1 we present the temperature dependence of the four-probe conductivity of a sample of emeraldine salt ([Cl]/[N] ~ 0.5) before and after pumping for a period of >20 hours. The after pumping data is in agreement with our earlier reported data with σ (300K) ~ 0.2 S/cm and $T_0 = 7800$K. The data for the same sample without evacuation before cooling shows a higher conductivity at room tem-

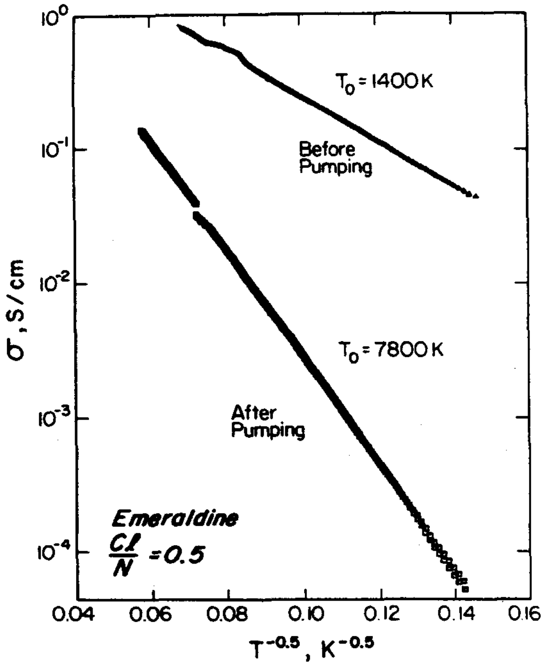

FIGURE 1 Four-probe dc conductivity for emeraldine salt polymer film, [Cl]/[N] = 0.5 vs. $T^{-0.5}$ for film cooled to 200K before evaluation and film evacuated at room temperature for ~20 hours.

perature (σ(300K)~ 1 S/cm) and a similar temperature dependence with a much weaker slope, T_0 = 1400K. The small glitch in the temperature dependent conductivity reflects pumping on the sample at reduced temperature in order to better control the temperature. This pumping below temperatures of 200K is unlikely to lead to significant desorption of H_2O due to the reduced vapor pressure at these lower temperatures.

We have monitored the variation of the conductivity and dielectric constants with elapsed time for dynamic pumping at room temperature. Figure 2 shows the conductivity of a [Cl]/[N] ~ 0.5 sample at microwave frequencies (6.5 × 10^9Hz) as a function of pumping time. The microwave dielectric constant for the same sample as a function of pumping time is also shown. It is clear that the four-fold decrease in the microwave conductivity as a function of pumping is similar in magnitude as the decrease of the dc conductivity after evacuation of the sample. The time dependence of the dielectric constant is very similar to that of the dc and microwave conductivity although the

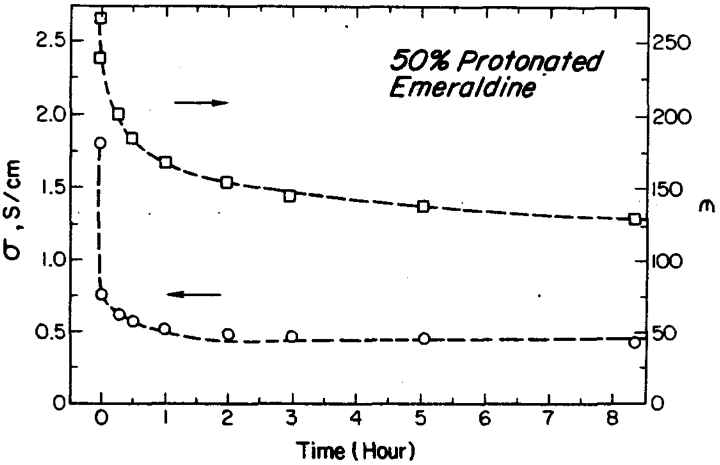

FIGURE 2 Microwave (6 × 10^{10} Hz) conductivity and dielectric constant for emeraldine salt polymer at room temperature as a function of pumping time.

dielectric constant asymptotes to a value not quite a factor of two smaller than the unpumped value.

The frequency and composition dependence of the conductivity of emeraldine before and after pumping is summarized in Figure 3. The two- to four-fold decrease in conductivity with pumping for a sample of composition [Cl]/[N] = 0.5 is visible together with a reduced change for a sample of composition [Cl]/[N] = 0.3. The frequency dependence of the conductivity for each of these samples together with that for pumped samples at [Cl]/[N] = 0.08 and unprotonated emeraldine are also shown. To within experimental error, the conductivity is observed to be independent of frequency, from dc through audio frequency (10^1 through 10^5) to a microwave frequency (10^{10} Hz) for compositions of [Cl]/[N] $\geqq$ 0.3, *independent of pumping on the sample*. For a sample of [Cl]/[N] = 0.08, the conductivity is independent of frequency up through nearly 10^6 Hz with a frequency dependence observed in the microwave regime. For the unprotonated sample, [Cl]/[N] = 0, the conductivity is nearly frequency independent through 10^3 Hz becoming more frequency dependent as the frequency is increased.

IV. DISCUSSION

A review of the data show a presence of two clear trends: (1) there is significant variation of conductivity and dielectric constant with

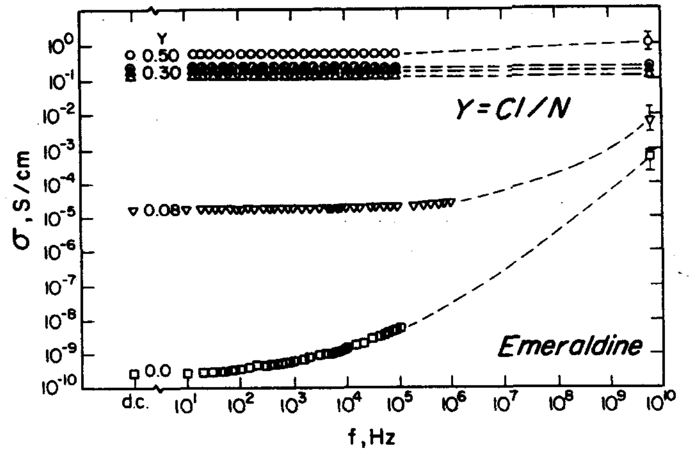

FIGURE 3 Log of room temperature conductivity vs. log of frequency for emeraldine polymer of differing [Cl]/[N] ratios. Where two sets of data are shown, [Cl]/[N] = 0.50 and 0.30, the upper set are for unpumped samples, the lower curves are for samples pumped on for at least 6 hours. The data for the [Cl]/[N] = 0.08 and 0.0 samples is taken after pumping for at least 6 hours.

pumping on the sample especially at high protonation levels; (2) the time behavior of the conductivity is in agreement with earlier reported results of Angelopoulos, et al.[24] and other workers.[25,26] Detailed studies of the proton NMR in polyaniline as a function of exposure to water vapor has clearly demonstrated the presence of two types of water molecules: one indicated as a liquid phase and the second as a solid phase.[25,26] Analysis of the NMR data indicated that the typical exchange time for protons to move between the solid to liquid phase was $\tau_{ex} \sim 10^{-3}$ seconds at 290K. On the basis of the presence of the water and the rapid exchange of protons, the Grenoble group proposed[25,26] that there was a new conduction mechanism that was called proton exchange-assisted conduction of electrons or (PEACE).

Our study of the frequency dependence of the conductivity provides a direct probe of the relevance of proton exchange to the actual electronic conductivity mechanism. We monitor the conductivity as a function of frequency for frequencies between 10^1 to 10^{10} Hz, spanning from times long to times short compared to the proton exchange time. We observe in Figure 3 that the conductivity does *not* vary as the frequency is varied. This demonstrates directly that the electronic conduction mechanism is independent of the proton exchange between the solid and liquid phases.

The origins of the H_2O dependence of the conductivity remain important. Since the temperature dependence of the conductivity still varies as exp-$(T_0/T)^{1/2}$ before pumping, it is proposed that the conductivity is still dominated by charging energy limited tunneling[31] between the granular metal regions in the protonated polymer. It is proposed that the presence of the H_2O primarily affects the height and breadth of the barrier between the metallic regions. That is, with increasing H_2O content, the apparent separation of the metallic islands and/or the height of the barrier between the metallic islands decreses making tunneling much more favorable. A decrease in the dielectric constant with pumping is in accord with an increase of the width of the barrier and resulting change in the effective capacitance among the metallic grains. Note that the decrease of dielectric constant with decreasing temperature[32] suggests the increasing role of disorder and localization within the metallic grains as the temperature is reduced. For very lightly protonated samples, the dominant conduction mechanism will involve charge motion within the "unprotonated" regions, with the variation of the audio frequency conductivity with light protonation supporting the presence of a small number of protonation induced charges within the "insulating" polymer regions.[33]

The origin of the barriers among the granular polymeric metal particles is of fundamental importance. The presence of chain ends, crosslinks, protonated amine groups (NH^{2+}), or nonstoichiometric emeraldine (nonequal numbers of oxidized or reduced groups) may be the cause of these barriers. The preparation of materials without the barriers would enable the measurement of the transport properties of intrinsic protonated emeraldine. These properties may be substantially different than those of the forms of polyaniline studied on to date.

SUMMARY

Both the dc and frequency dependent conductivity of fully protonated emeraldine polymer are observed to vary with the moisture level in the sample. A corresponding variation in the microwave frequency dielectric constant has also been observed. The frequency dependence of the conductivity is shown to be inconsistent with the proposed PEACE mechanism for conduction in this material. The observed behavior is consistent with the role of moisture sensitive barriers in charging energy limited tunneling among the granular metal particles formed upon protonation of emeraldine.

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