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APPLICATION OF MICROWAVE CAVITY PERTURBATION TECHNIQUES IN CONDUCTING POLYMERS

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Abstract

Microwave cavity perturbation (MCP) techniques have been applied to measure complex microwave conductivities of conducting polymers. We find MCP is suitable for polymers with a large range of conductivities. In our experiment it is possible to determine the parameter α/N [(filling factor/depolarization factor)] within 5% for fairly conducting samples ($\sigma > 10^0$ S/cm) through the extrapolation of normalized frequency shift $\Delta f/f_0$ to the high conducting limits (i.e., high temperature limit) and/or the comparison with DC conductivity. For all cases the experimentally determined values for α/N are very close to the calculated ones based on the measurement of sample geometry. Some potential microwave applications of the conducting polymers are discussed.

Introduction

Microwave cavity perturbation (MCP) techniques[1] have been widely used to measure the conductivity (σ) and dielectric constant (ϵ) of many semiconductors[2] and low-dimensional conductors[3]. MCP has several advantages: (1) It is a contactless measurement. Hence it is free of contact resistance and possible contamination or damage of the samples. (2) The sample size needed for MCP is small. This is extremely useful when large samples are not available (a common case for many single crystal samples). (3) It is free of possible complicated current paths encountered in dc four-probe measurement, especially for highly anisotropic materials. The MCP has been applied to conducting polymers by many authors[4, 5]. For these applications it is important to correct for the morphology in which polymers often consist of loosely packed chains or fibers and that their effective volume might be considerably smaller than the measured one. Thus in the data analyses we have to consider the compactness of the samples[5, 6]. Also, since ϵ could be very large[6] and sensitive to temperatures (T)[5, 6], the approximations to simplify the data analyses by ignoring ϵ or assuming it as a constant[2] may not be suitable for many polymers.

In the following sections, we will briefly summarize the principles of MCP technique and give a few suggestions for data analyses. Then we will examine the applications of MCP to the conducting polyaniline hydrochloride and poly(o-toluidine) hydrochloride materials.

Microwave Cavity Perturbation

MCP techniques are based on the two assumptions: (1) the sample size is much smaller than the cavity size so that the electric field distribution outside the sample is essentially undisturbed; (2) the sample size is small compared to microwave skin depth so that the electric field is uniformly penetrated through the sample (depolarization regime). If the condition (2) is not satisfied, electric field can only penetrate in the skin depth (skin-depth regime) and a modified equation has to be used to evaluate σ (ϵ can not be obtained in this case)[7].

Under these two assumptions, one can relate the real and imaginary part of the dielectric constant ϵ' and ϵ'' to the normalized resonance frequency shift $\delta = (f - f_0)/f_0$ (f, f_0 are the resonance frequencies with and without a sample in the cavity) and normalized loss $\Delta = (F - F_0)/f_0$ (F, F_0 are full width at half-power of the cavity resonance with and without a sample in the cavity) in the following equation

$$\begin{aligned} \Delta/2 &= \frac{\alpha\epsilon''}{[1 + N(\epsilon' - 1)]^2 + (N\epsilon'')^2} \\ \delta &= \alpha\frac{(\epsilon' - 1)[1 + N(\epsilon' - 1)] + N(\epsilon'')^2}{[1 + N(\epsilon' - 1)]^2 + (N\epsilon'')^2} \end{aligned} \tag{1}$$

where N is the depolarization factor. For a long needle-like sample, it is

$$N = \frac{ab}{c^2}[\ln\frac{4c}{a+b} - 1] \tag{2}$$

where $a, b \ll c$ are three orthogonal semiaxes of an ellipse which approximates the sample dimensions. Here α is filling factor defined as

$$\alpha = V_s E_{0max}^2 / 2\int_{V_c} |E_0|^2 dv \tag{3}$$

E_{0max} is the unperturbed electric field magnitude (E_0) at the sample position; V$_s$, V$_c$ are the volumes of the sample and cavity. For the cylindrical cavity TM$_{010}$ mode, α=1.855V$_s$/V$_c$.

Solving Eq.(1) for ϵ' and ϵ'',

$$\begin{aligned} \epsilon' - 1 &= 1/N\frac{\delta(\alpha/N - \delta) - (\Delta/2)^2}{(\Delta/2)^2 + (\alpha/N - \delta)^2} \\ \epsilon'' &= \alpha/N^2\frac{\Delta/2}{(\Delta/2)^2 + (\alpha/N - \delta)^2} \end{aligned} \tag{4}$$

and $\sigma = \omega\epsilon_0\epsilon''$ (ω is angular frequency and ϵ_0 is vacuum dielectric constant). The uncertainties and irregularities of sample shape will cause large errors in estimates of α and N, and therefore lead to large errors in ϵ' and ϵ''. The following suggestions are useful for reducing these errors. If ϵ'' or $\epsilon' \gg 1/N$, one obtains

$$\delta \rightarrow \alpha/N \tag{5}$$

Thus one can measure α/N if the samples are very conducting but its skin depth is still larger than sample thickness. Generally speaking, this is the case for the polymer samples with $\sigma > 1$ S/cm. Experimentally σ often increases dramatically as T increases[5, 6] and hence at the high T (300K) we expect to see δ approaching a constant value. Note that the cross section of samples should be as large as possible since the larger cross-section means larger N and more likely that the condition $\epsilon \gg 1/N$ is satisfied. Also, since the error in N is usually larger than the error in α, the experimentally measured values of α and α/N should be used to determine N.

It is noted that Δ show a maximum as the conductivity varies over a large range. Thus when the temperature is reduced the conductivity decreases, Δ is expected to increase to a value Δ_{max} followed by a decrease upon further cooling. The Δ_{max} occurs at $1 + N(\epsilon' - 1) = N\epsilon''$ and corresponds to $\delta_{max} \approx (1/2)\alpha/N$ if $\epsilon' \sim$constant $\ll 1/N$. This relation is very useful for situations where the highly conducting limit is not reached but the maximum in $\Delta(T)$ is observed in the experiment[2].

If Δ_{max} is not recorded in the experiment, α/N can not be measured from the experiment and large errors in α/N may be result. Fortunately, in this case the values of σ and ϵ obtained from Eq.(4) are not sensitive to the α/N[2] so that the uncertainties in α/N will not cause serious errors in ϵ and σ.

Experimental Setup

In our usual configuration, we utilize a cylindrical TM_{010} cavity at resonance frequency 6.5 GHz. The cavity is made of oxygen-free high conductivity copper; upper and lower plates were placed on the cylindrical body of the cavity with indium O-rings as spacers and then pressed together. Application of the O-rings guarantee uniform electric contacts between pieces and minimizes cavity loss due to surface current dissipation and radiation at the joints. The Q value of the empty cavity is approximately 6000 at room temperature. The sample to be measured is held in a quartz or teflon tube. This sample holder is adjusted so that it will not cause a frequency shift when inserted in the cavity. The cavity system is enclosed in a Janis varitemp dewar filled with He gas. The microwave source is a Hewlett-Packard model 8350B sweep generator. Signals are recorded using a in Nicolet NIC-370 Signal Averager and added up 256 times to suppress noise. A LeadingEdge PC computer is connected to NIC-370 to analyze data. Temperature is controlled by a LakeShare DTC-500 Cryogenic Temperature Controller.

Application to Conducting Polymers

We have studied protonic acid HCl doped polyaniline (PAN-ES)[5] and its derivative poly(o-toluidine) (POT-ES)[6] using the MCP setup. The highest σ measured by our MCP setup is 10^2 S/cm for HCl doped stretch aligned PAN-ES. A very thin film (thickness $d < 10\mu m$) has to be used for $\sigma > 10^2$ S/cm or else the skin-depth-regime technique has to be employed. The lowest value measured measured for σ is 10^{-5} S/cm, below which the absorption is too small to perform an accurate measurement. The δ and Δ are plotted against T in Fig. 1 for two typical samples. It is obvious that δ of PAN-ES approaches the high σ limit. At $T = 300$K, $\delta = 0.0018$ and approaches $\delta_\infty \approx 0.0019$. The calculated value from Eq.(2) for α/N is 0.0020. Fig. 2 and Fig. 3 show how the values of ϵ and σ determined from the experimental δ and Δ depend on the value of α/N. This provides a means of testing the reasonableness of the analysis. The Fig. 3 indicates that $\alpha/N > 2.0 \times 10^{-3}$ is not likely since the temperature dependence of the 6.5 GHz conductivity would deviate substantially from that of the dc σ measured by 4-probe techniques. Fig. 2 and δ_∞ however demonstrate that $\alpha/N \leq 1.9 \times 10^{-3}$ is not acceptable either since at T=300 K $\delta = 1.8 \times 10^{-3}$ is still increasing. Therefore the optimum value for α/N is between ~0.0019 and 0.0020. The resultant errors at room temperature are 10% for σ and a factor of 3 for ϵ. The errors in σ and ϵ at low T are negligibly small, for σ and ϵ are not very sensitive to α/N when the experiment is performed at low σ side of the loss peak. We list in the Table I the values of calculated α/N, $2\delta_{max}$ and δ_∞ for 5 different samples that have been oriented to different degrees and have different thicknesses.

Table I Comparison of calculated α/N, δ_∞ and $2\delta_{max}$ for oriented polyaniline hydrochloride samples with different $N\sigma$

Sample	$N\sigma$	$(\alpha/N)_{cal}$	δ_∞	$2\delta_{max}$
1:3, $\perp$	moderate	0.00254	N/A	0.0033
1:3, $\parallel$	slightly high	0.0020	0.0023	0.0026
1:4, $\parallel$	high	0.0024	0.0032	0.0034
1:4, $\parallel$	extra high	0.0027	0.0026	0.0031
1:4, $\parallel$	high	0.0020	0.0019	0.0021

We can see from the Table I that the values of α/N obtained from calculation $(\alpha/N)_{cal}$ and measurement (δ_∞ or $2\delta_{max}$) differ no more than 30%. For samples with very low σ so that loss peak can not be observed in the experiment, we can safely use the calculated α/N to evaluate their ϵ and σ. The errors are small since the ϵ and σ are very insensitive to α/N in this case. POT-ES system is an example of this case. The calculated α/N is 1.82×10^{-3}. If we increase (decrease) α/N a factor of two (an exaggerate error bar!) the calculated σ and ϵ only change slightly. The results at room temperature are presented in the Table II

Table II Comparison of σ and ϵ of POT-ES determined for three different values of α/N

α/N	σ(S/cm)	ϵ
0.0036	0.011	9.8
0.0018	0.014	10.8
0.0009	0.025	13.3

For such poorly conducting samples, a 30% error in α/N causes an error in σ of 20% and in ϵ of 5%. The value for σ is very close to dc $\sigma \approx 0.011$ S/cm measured by four-probe techniques. Note that in this case ϵ is less sensitive than σ to α/N in contrast to high conducting case where ϵ is much more sensitive than σ.

Microwave Applications of Polyaniline

Before we conclude, we note that polyaniline and its derivatives have dramatic change in their microwave absorption properties upon protonic acid doping. The fully doped polyaniline salt form has loss tangent $\tan\delta$ as high as 10 while its undoped base form has $\tan\delta = 0.02$ at room temperature. This large range of $\tan\delta$ can be controlled by electrochemical potentials. This makes polyaniline unique in many practical applications, for example, electrochemically controlled micro-wave switch, attenuator, waveguide load, heating and melting; polyaniline can be easily coated on the metal surface to absorb microwave signal from radars, etc. An unusual application is use of the microwave absorption to generate heat for welding (joining) two plastic components. By controlling the derivatization, we can obtain the materials with desired microwave absorption properties.

Conclusion

We reported the application of microwave cavity perturbation (MCP) technique in the "depolarization regime" to the measurement of the complex microwave conductivity of conducting polymers. A TM_{010} cavity with resonant frequency 6.5 GHz was designed for these measurements. We find MCP can be used for the measurement of a large range of conductivities ($10^{-5} - 10^{2}$ S/cm). The major experimental error is the uncertainty of parameter α/N. For fairly conducting samples (10^{0} S/cm and up), by varying the temperatures and hence the conductivities of the samples, it is possible in our experiment to determine the parameter α/N within 5% through the extrapolation of normalized frequency shift δ to the high conducting limits (i.e., high temperature limit), the comparison with dc conductivity or estimate from the normalized frequency shift corresponding to the loss peak. For all cases the experimentally determined values for α/N and calculated ones based on Eq.(2) differ no more than 30%. For extremely low conducting samples, we can safely use the calculated α/N to determine the sample conductivity and dielectric constant and errors are small. For various samples the dielectric constant can be determined within a factor of 3-4 and conductivity within 10%-20%.

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Figure captions

Figure 1 *The normalized frequency shift* δ *and loss* Δ *as a function of temperature for HCl doped polyaniline salt and poly(o-toluidine) salt.*

Figure 2 *The calculated conductivities* σ *for different* α/N *values based on Eq.(4) and the comparison with dc* σ *measured by a four-probe technique. The dc* σ *behaviors as* $\sigma \propto \exp[-(T_0/T)^{1/2}]$*[6].*

Figure 3 *The calculated temperature dependence of dielectric constant* ϵ *for different* α/N *values based on Eq.(4).*

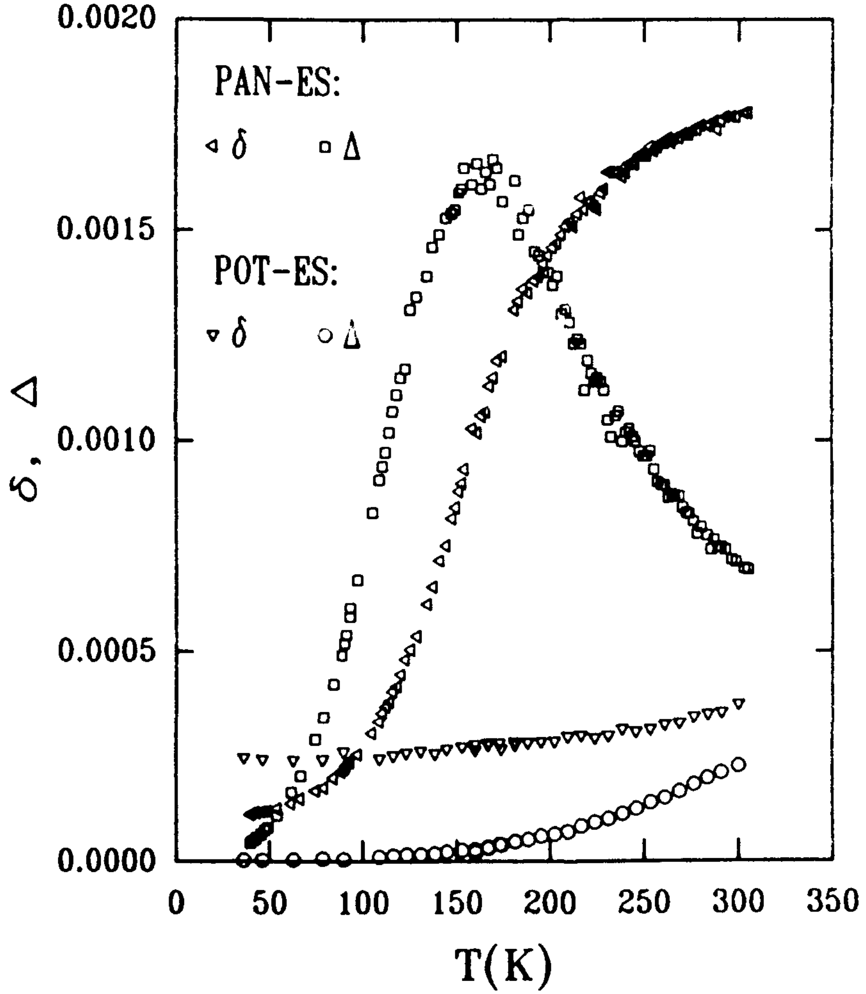

Figure 1, Wang, et al.

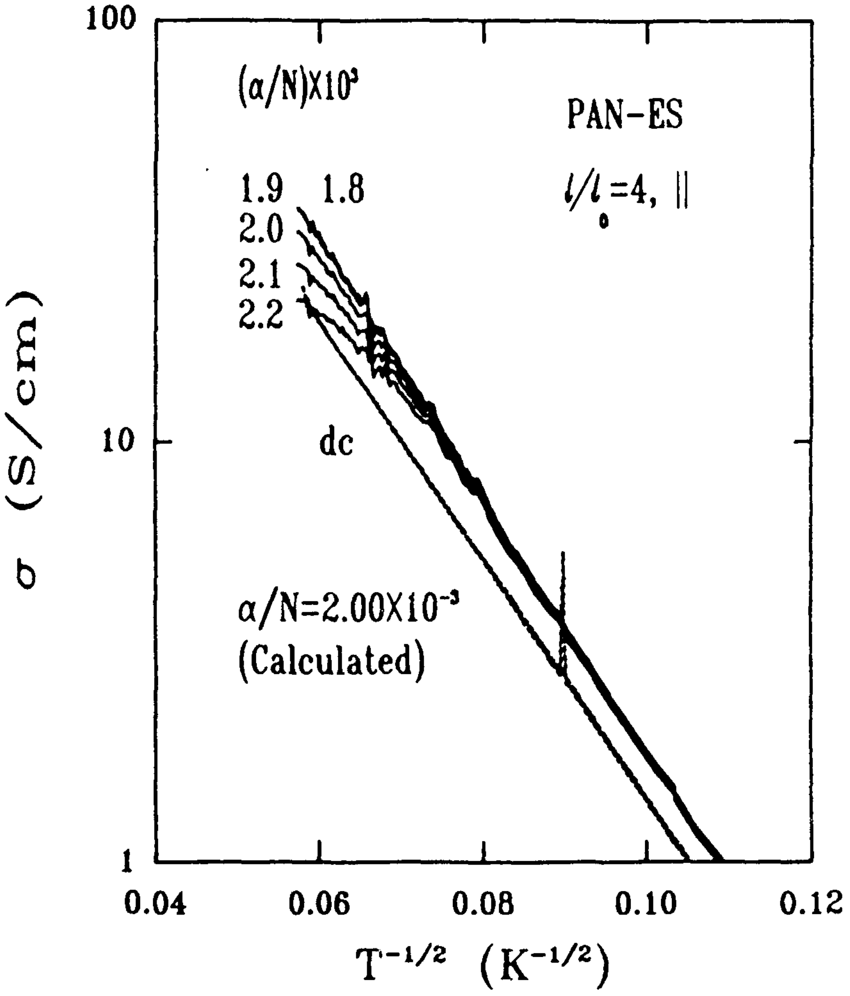

Figure 2, Wang, et al.

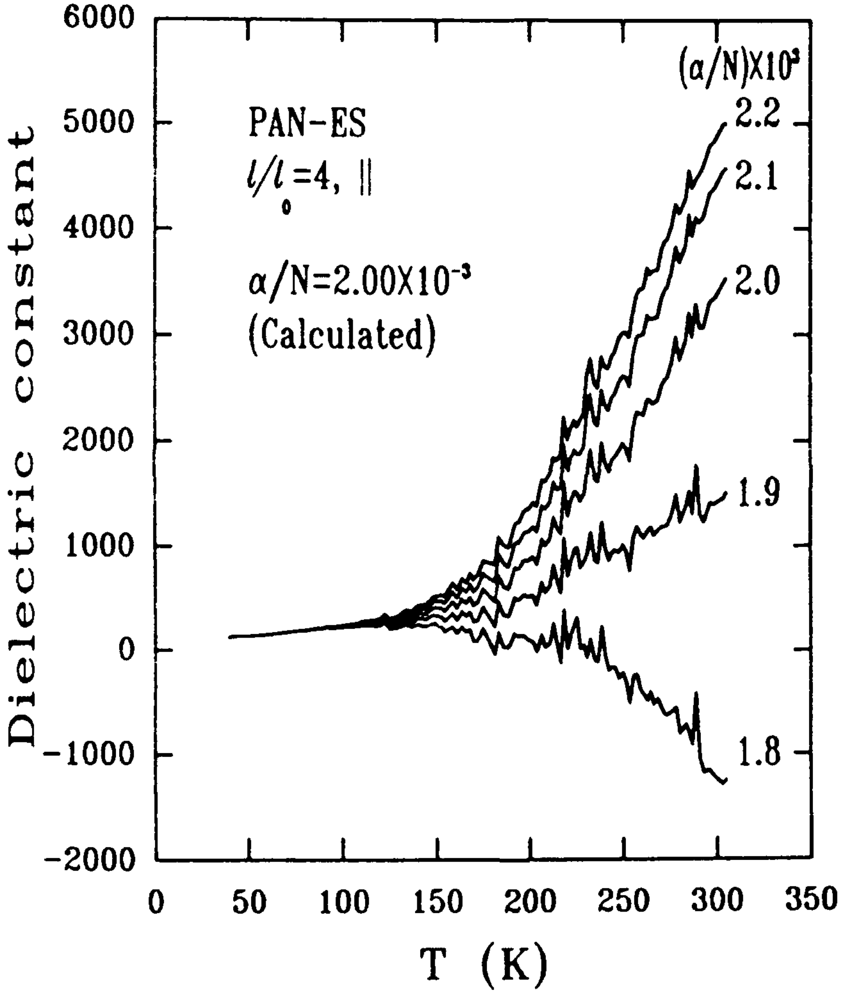

Figure 3, Wang, et al.