Bananas go paraelectric

VIEWPOINT

Bananas go paraelectric

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Abstract
Using a banana as an example, we demonstrate how the ferroelectric-like hysteresis loops
measured in inhomogeneous, conducting materials can easily be identified as non-intrinsic.
With simple experiments, the response of a banana to electric fields is revealed as characteristic
for an inhomogeneous paraelectric ion conductor. Not even absolute beginners in dielectrics
should identify this biological matter as ferroelectric.

(Some figures in this article are in colour only in the electronic version)

In some recent publications it was pointed out that hysteresis loops of electrical polarization P versus field E can easily arise from experimental artifacts, e.g., surface polarization [1–3]. The occurrence of characteristic $P(E)$ hystereses is a hallmark feature of ferroelectricity. Thus there is the risk of misinterpreting non-intrinsic loops as evidence for ferroelectric behavior. In an original recent work appearing in this journal [2], measurements on a piece of the skin of a banana were used to point out this danger, especially for scientists working in the field of multiferroics, whose background is mainly ferromagnetism and who are inexperienced in interpretation of data of electrical hysteresis loops. In the present work, we demonstrate for the same type of sample how to properly distinguish intrinsic and non-intrinsic hysteresis loops. It is revealed that bananas can be easily identified as paraelectric ionic conductors, even at the lowest level of experimental expertise. This can be done by using different contacts, different sample geometries and by measuring hysteresis loops as a function of frequency.

In investigating and characterizing dielectric matter, it is good experimental practice to start with dielectric spectroscopy as a function of temperature, which usually already reveals most of the underlying physics. To characterize the skin of bananas, even room temperature measurements are sufficient. For our investigations, we used typical, commercially available bananas (*Musa acuminata Colla*) (inset of figure 1). In a variety of measurements, we found that the banana skin is a complex material and quite different dielectric properties can be obtained depending on the piece of the skin (outermost yellow skin, more 'fleshy' inner parts, fiber-like parts, etc), contact geometry (coplanar, parallel-plate) and ripeness of the banana (green, yellow, or brown outer appearance) used for sample preparation. In [2], no clear specification of the sample preparation is provided. For the results shown in the present work, we used coplanar silver-paint contacts applied to the outer yellow skin of the banana with typical areas of 10 mm^2 and a distance of 0.2–0.5 mm. This led to the best reproducibility of the dielectric results for different parts of the skin of a single banana and even for different fruits of varying origin and age. For details on the experimental setups used to determine the dielectric properties, the reader is referred to [4–6].

The results of our dielectric measurements at room temperature are shown in figure 1. For completeness and to identify characteristic processes, we show the real and imaginary parts of the dielectric constant (ε' and ε'') and the real part of the conductivity σ', which is proportional to the loss multiplied by frequency. Of course, banana skin is a typical biological material, which is strongly inhomogeneous and a good ionic conductor, due to its water content. Focusing on ε' (figure 1(a)), we see that at the highest frequencies the dielectric constant is close to 35. With decreasing frequency the dielectric constant strongly increases, reaching apparent colossal values as large as 700 millions. These huge values clearly point towards blocking electrodes where the ionic charges are accumulated close to the contacts. The appearance of colossal values of the dielectric constant is a well-known phenomenon for biological materials [7]. As revealed by
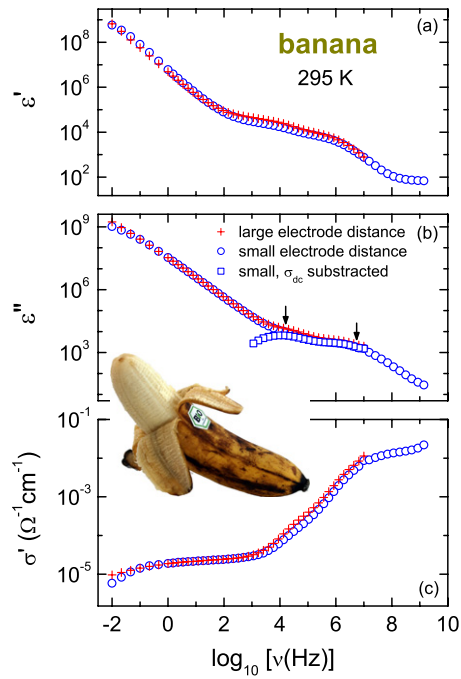
Figure 1. Broadband dielectric spectra of dielectric constant (a), dielectric loss (b) and conductivity (c) of banana skin at room temperature. The inset shows a typical exemplar of *Musa acuminata Colla* used to extract the sample. The circles and plus signs show the results for two samples with electrode distances differing by a factor of about 2. The squares in (b) were obtained after subtracting the dc conductivity (2.82×10^{-5} Ω^{-1} cm^{-1}). The arrows indicate the approximate positions of two relaxation modes. Note that due to the ill-defined geometry and sample inhomogeneity, the given absolute values can only be a rough estimate.

Figure 2. $P(E)$ hysteresis loops of banana skin at room temperature for two different frequencies. Note that due to the ill-defined geometry and sample inhomogeneity, the given absolute values can only be a rough estimate.

figure 1(a), at intermediate frequencies the banana exhibits a sequence of relaxations, which also is characteristic for biological systems [7]. By subtracting the dc conductivity from the dielectric loss shown in figure 1(b), two relaxation modes can indeed be identified in the kHz and the MHz regions (arrows in figure 1).

Figure 1(c) shows the conductivity, where the significant onset of blocking processes can easily be identified by the decrease towards low frequencies at $\nu < 1$ Hz. The use of larger electrode distance should shift this onset to longer times or lower frequencies, which is indeed observed in figure 1(c). In any case these simple measurements provide a clear frequency scale for proper measurements of hysteresis loops. Figures 1(a) and (c) document that the timescale where blocking effects will dominate is below the 1 Hz to 100 Hz region. In this regime, any measurement of the field dependence of the polarization will be strongly influenced by charging and discharging processes of the electrode boundaries [3].

In figure 2, we present results of hysteresis loop measurements as a function of frequency, which provide important insight into the underlying physics. Figure 2 documents two hysteresis loops as measured at 1 Hz (a) and 11.3 kHz (b). For these measurements we used a home-built high-precision setup based on a Sawyer–Tower circuit [5]. For both sets of measurements, the hysteresis has been
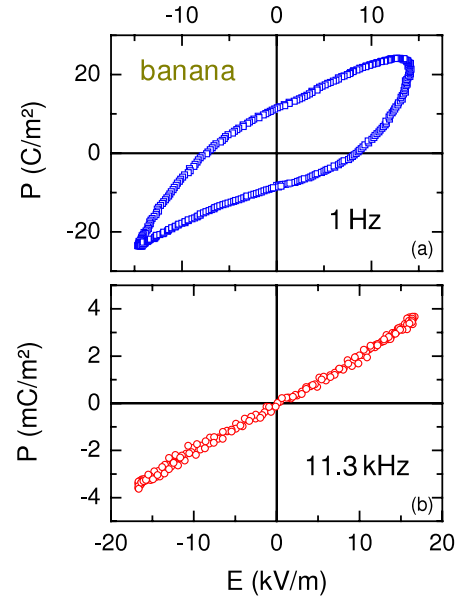
corrected for dc (Ohmic) conductivity processes by subtracting horizontal ellipses. An alternative method of correction would be a shifting of the phase of the response signal to correct for relaxational contributions. Details are outlined in [5]. In principle, at 11.3 kHz both charge transport and relaxational modes contribute (cf figure 1) and both types of correction should be applied, simultaneously. As they are difficult to separate, we decided to correct for the dominating conductivity contribution only, but a pure phase-shift correction reveals similar behavior. Clearly the results in figure 2(a) are highly nonlinear. At this low frequency of 1 Hz, the ionic conductor is still in the blocking regime and the average timescale of charging and discharging plays an important role, also introducing asymmetry to the hysteresis loops [3]. It immediately becomes obvious that these results are not a fingerprint of ferroelectricity: performing the experiments at higher frequencies, far outside the blocking regime, the banana shows a paraelectric response (figure 1(b)). The example of a banana thus nicely demonstrates that even with small experimental effort (variation of measuring frequency in the present case) the non-intrinsic nature of hysteresis loops can be revealed.

In conclusion, in the present work we have proposed some simple experimental checks by which even scientists who are not experts on ferroelectricity can easily avoid misinterpretations of polarization measurements. Following the work by Scott [2], we have demonstrated this on the very instructive (and tasty) example of a banana. It should be noted that contact effects are only one source for an erroneous detection of ferroelectric hystereses. Also charge transport or relaxational phenomena can generate $P(E)$ hysteresis loops. All these can be corrected as outlined in this contribution. Needless to say, this course of action was rigorously taken

in [6]. We also would like to point out that for biological matter all the expert articles 'emphasizing the risk in obtaining spurious artifacts' that are cited in [2] (e.g., [1] in the present work) are meaningless for the subject under study. A banana is dominated by ion transport and there is no one-to-one correspondence with electronic materials, and a blocking electrode in an ion conductor certainly is different to a Schottky-like electrode [3].

Acknowledgments

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