Influence of Poling Conditions on the Gas Emission of PVDF

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1 Introduction

Poling PVDF in electric fields $\geq 50\mathrm{MV/m}$ results in a polarization by orientation of the cristallite dipoles. Under short circuit conditions about 50% of the polarization under field remains remanent. At room temperature this remanent polarization is unchanged for many years. The enormous stability of the remanent polarization is caused by Coulomb interaction between the oriented cristallite dipoles and charge carriers which are trapped at the boundaries of the crystallites [1]. The decrease of the electrical conductance with increasing pressure [2] indicates ionic charge transport in PVDF. Because strong charge injection is observed during the poling process of PVDF [3], a simple model for the formation of the ions can be considered [4]: Electrons are injected from the cathode into PVDF. This leads to splitting off F^- ions from the PVDF chains. By following radical reactions H atoms are formed. At the anode holes are injected and H^+ and again H atoms are splitted off from the PVDF chains. The ions migrate into the PVDF film and are partly trapped at the cristallite boundaries. Partly the ions recombine and escape from the film as H, F and HF gas during the poling process.

In former experiments we found a strong emission of HF during the poling process using a quadrupole mass spectrometer [4]. But in these experiments the possible contribution of surface discharges phenomena could not be excluded. More recent experiments with an improved electrode preparation and higher detection sensitivity verified the emission of HF gas and also weaker contributions of other chain fragments and absorbed gases like H_2O and CO_2 [5]. In addition we observed a very interesting time and field dependence of the gas emission (fig. 1):

An increasing field results in an increasing gas emission. During the period of constant field the gas emission decreases to a steady state value. Surprisingly after discharging the PVDF samples the gas emission increases momentarily to a value higher than under field. This zero voltage emission decreases with a time constant of ca. 100s. The majority of the observed masses between 1 and 50amu show the same time behaviour, but with different intensities. Poling PET under the same conditions we observed a gas emission which also

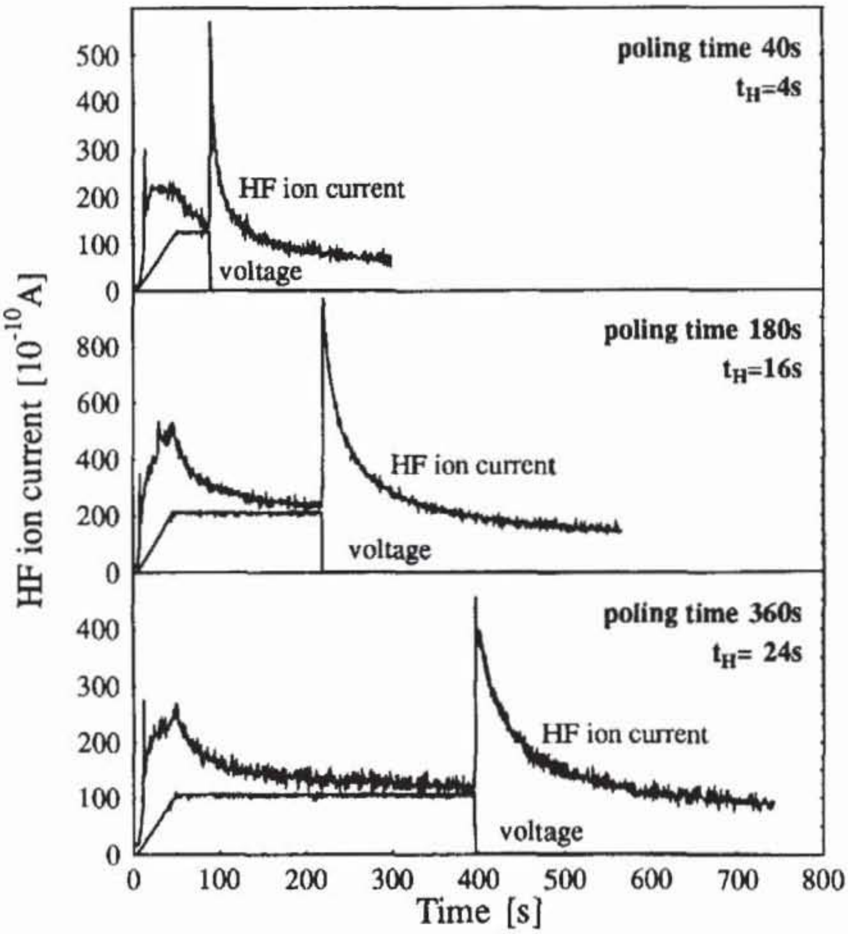

Figure 1: *Influence of the poling time on the HF gas emission of PVDF with positive porous electrode in front of the mass specrometer.*

increases with increasing field. But no zero voltage emission was observed [5]. In the following we investigate the influence of the poling time and the polarity of the applied voltage on the time dependence of the gas emission of PVDF. In addition we measure the polarization distribution in the PVDF samples after the poling experiments.

2 Experimental

Samples used were 25μm thick, biaxially stretched PVDF films with ca. 70% β-content. The samples were on one side covered with a 20nm thick, vacuum deposited, porous gold film. The other side was evaporated with an 150nm thick Al film. The diameter of the samples was 60mm. The PVDF films were

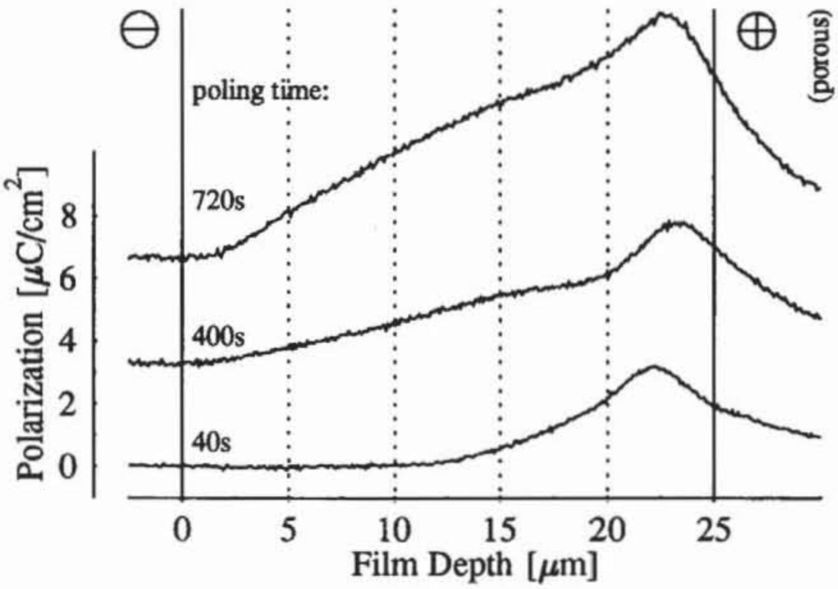

Figure 2: *Polarization distributions after different poling times 10mm away from the outer boundary.*

mounted into an UHV system and poled at about 10^{-8}mbar. The quadrupole mass spectrometer was mounted in front of the porous gold electrode. The high voltage (HV) was applied in steps of 50V to the samples until the electric field reached 100MV/m. After each voltage step a complete mass spectrum between 1 and 50 amu was recorded which took 0.8s. Then the voltage was increased by the next voltage step. Measured was the ion current transmitted through the quadrupole system. When the electric field reached 100MV/m the HV was kept constant. Afterwards the samples were kept under short circuit conditions and further mass spectra were recorded for 200s after the HV was switched off. After the samples were removed from the UHV system the polarization distribution in thickness direction was measured with the PPS method [6] with a spatial resolution of about 2μm.

3 Results

3.1 Influence of poling time

Fig. 1 shows the time dependend gas emission of HF during the poling process with different poling times. Additionally the time dependence of the poling voltage is indicated. As described in section 1 the gas emission increases with increasing field strength, decreases to a steady state value under constant field and rapidly increases under short circuit conditions to a value higher than under field. Remarkable is the increasing time constant of the decrease of the zero voltage emission with increasing poling time. The half width t_H of the zero voltage emission which is the time between removing the voltage and the decrease of the zero voltage emission to the half value increases from 4s at 40s poling time to 24s at 360s poling time.

Fig. 2 shows the spatial polarization distribution in thickness direction of samples which were poled with different poling times. The polarization was recorded 10mm away from the outer boundary of the samples. The polarization distributions in fig. 2 represent the polarization within the first 20mm from the middle area of the samples. At the boundaries we measured other distributions [7]. With increasing poling time the polarization increases, too. Simultaneously the polarization zone is getting broader.

3.2 Influence of the polarity

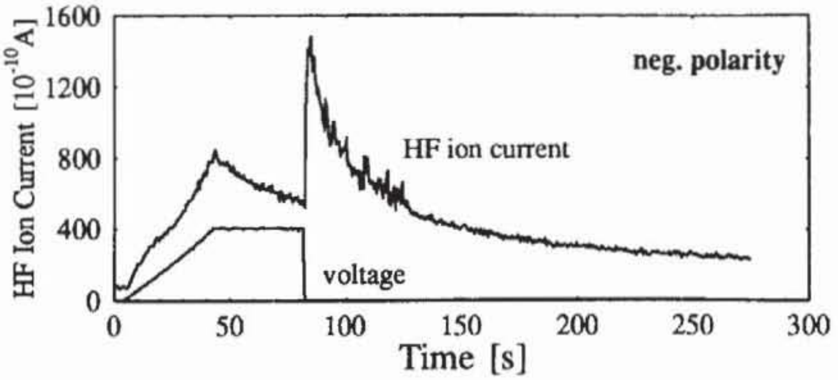

Figure 3: *HF gas emission with negative porous electrode.*

Fig. 3 shows the HF gas emission of a sample which was poled 40s with $E = -100\text{MV/m}$ (negative polarity). There is no significant difference between the gas emission at positive and negative polarity. But the zero voltage emission rises not so fast compared to fig. 1 (top). Experiments with a time resolution of the HF gas emission of 0.05s were made to investigate this carefully. In fig. 4 the rise of the HF zero voltage gas emission after poling with positive (top) and negative polarity (bottom) is shown with this better time resolution. The maximum of the zero voltage emission at negative polarity is broader than at positi ve polarity. The zero voltage emission at positive polarity takes its maximum at this moment if the voltage is zero, but at negative polarity 0.3s later.

Fig. 5 shows the spatial polarization distribution 7.5 and 15mm away from the outer boundary of the sample which was poled 40s with $E = -100\text{MV/m}$. In contrast to fig. 2 a polarization zone is seen near the non porous, positive Al

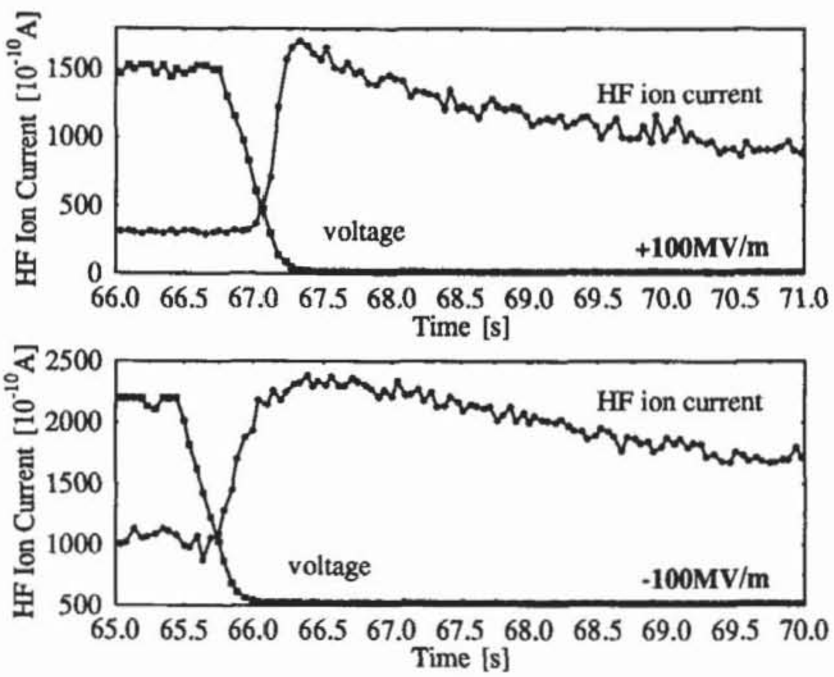

Figure 4: *Increasing of the zero voltage gas emission at positive (top) and negative (bottom) polarity.*

electrode. This polarization distribution is measured in the main area of the sample, whereas in a small area in the middle we measured again a polarization near the porous negative electrode cf. fig. 2 and [7].

4 Conclusions

If PVDF films are poled in electric fields of about 100MV/m charges are injected and ions are formed by electro chemical reactions. By partly recombination and by other reactions of this ions HF gas is built diffusing out of the sample through the porous electrode. This gas emission increases with increasing field strength. At constant field it decreases to a steady state value comparable to the space charge limited poling current of PVDF. Free ions are trapped in the polarization zone. Under short circuit conditions shallow trapped ions are freed and the gas emission increases strongly. The longer the poling time the broader the polarization distribution. Simultaneously the half width of the short circuit emisssion increases because of the decreasing conductivity of PVDF with increasing polarization. If the polarization zone is located near the non porous electrode (fig. 5) the recombined gas molecules

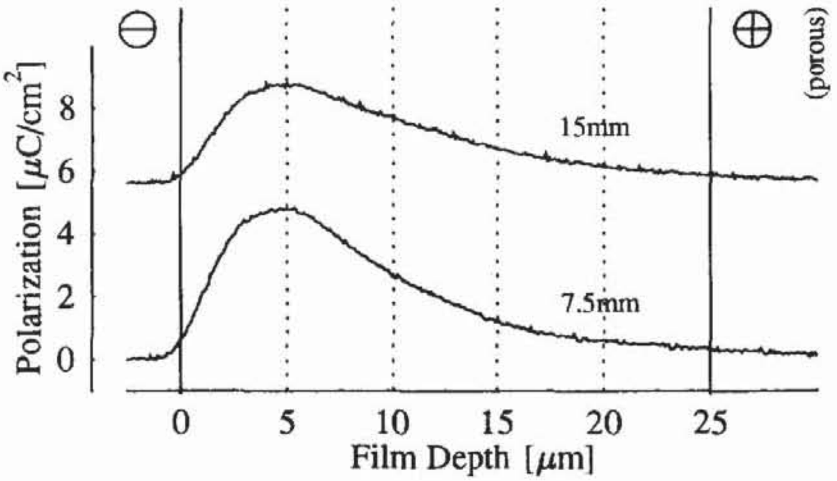

Figure 5: *Polarization distributions of the sample poled 40s with* $E = -100 MV/m$ *7.5 and 15mm away from the outer boundary.*

need longer time to reach the porous electrode. Therefore the gas emission under short circuit conditions is delayed by poling with negative polarity compared to positive polarity.

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