

Water-induced degradation in lead zirconate titanate piezoelectric ceramics

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Water-induced degradation in lead zirconate titanate (PZT) piezoelectric ceramics was studied by a comparison experiment. In one treatment, PZT rings were immersed in a 0.01 M NaOH solution for long periods of time; in the other treatment, PZT rings were placed in a 0.01 M NaOH solution and hydrogen was evolved onto their silver electrodes by the electrolysis of water. No degradation occurred to samples immersed in the NaOH solution; but for the samples that were also treated by electrolysis of water, serious degradation occurred as their mechanical quality factor decreased dramatically and their dielectric loss increased considerably. $I-V$ measurement showed that the resistance decreased greatly in the degraded samples, which could be explained by the formation of charge carriers due to the reduction reaction of atomic hydrogen from the electrolysis of water. It was proposed that the reduction reaction of atomic hydrogen at ambient temperature is an important origin for the degradation of piezoelectric ceramic devices. © 2002 American Institute of Physics. [DOI: 10.1063/1.1479205]

Piezoelectric ceramics, namely poled polycrystalline ferroelectrics, have been successfully developed for applications in numerous electromechanical devices, such as ultrasonic transducers, resonators, sensors, ultrasonic motors, actuators, and transformers.¹ It is expected that many other devices will also be fabricated using piezoelectric ceramics. One of the major challenges in the continuing development of piezoelectric ceramics has been to improve the stability and reliability of piezoelectric ceramic devices. The properties of piezoelectric devices, especially those working under high stress and high field, usually exhibit obvious degradation over the course of their lifetime. Sometimes sudden failure even occurs to devices in service. Degradation in piezoelectric ceramic devices is a rather complicated process. Large mechanical vibration induced by high electric field may cause the formation of microcracks in piezoelectric devices. The formation and propagation of the microcracks cause damage to the devices. Another important source of degradation is depolarization, especially for those devices which undergo a substantial rise in temperature by the heat generated during operation.² Degradation is also influenced by environmental factors, including temperature, pressure, and humidity. It was reported that the lifetime of piezoelectric devices decreases dramatically with increased temperature and humidity.³

Though many investigations have been carried out to study the degradation mechanisms of piezoelectric ceramic devices and much valuable knowledge has been obtained, some aspects of the degradation process remain unclear. It is generally believed that the role of water in the degradation process lies in the fact that water facilitates the electromigration of silver electrodes along the grain boundaries of piezoelectric ceramics.^{3,4} In other words, water mainly reacts with

the metallic component of the devices. Some recent studies, however, show that, in the presence of electricity, water has a more profound influence on the ceramic bodies of lead-based relaxor ferroelectric multilayer ceramic capacitors and (Ba,Pb)TiO₃-based thermistors and leads to serious degradation.^{5,6} This indicates that the role of water in the degradation of electroceramic devices should not be simply limited to the electromigration of the silver electrodes. Reaction between water and electroceramics should receive much more attention and should be studied in-depth. The present study aims to investigate the reaction between water and piezoelectric ceramics and study its effect on the properties of the piezoelectric ceramic-based devices.

Lead zirconate titanate (PZT) ceramic rings, Morgan PZT-8 [with an approximate composition of Pb(Zr_{0.4}Ti_{0.6})O₃, together with a number of dopants], from Morgan Electro Ceramics (USA) were used in the experiment. The rings were 2.30 mm thick, with an inner and outer radius of 2.50 and 6.35 mm, respectively. Silver electrode was coated on the two major surfaces of the rings. The rings were poled in the thickness direction and were suitable for application as Langevin sandwich transducers in a wire bonding machine.⁷ Two different treatments were performed on the rings for comparison. In the first treatment, some samples were immersed in a 0.01 M NaOH solution for some long periods of time and then taken out, washed by deionized water, and dried. In the second treatment, some rings were placed in a 0.01 M NaOH solution and dc voltages were applied between the silver electrode of the rings and an anode in the solution. Electrolysis of water occurred due to the applied dc voltages and hydrogen was evolved on the silver electrode of the rings while oxygen was evolved on the anode. So this treatment is referred to as "hydrogen charging" hereafter. The solution was kept agitated by a magnetic agitator and the temperature was kept constant at 25 °C. The

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dc voltages were removed after some designated periods of time and the samples were taken out, washed and dried. Impedance/phase versus frequency spectra of the PZT rings were measured by an Agilent 4294 A impedance analyzer. I - V characteristics of the rings were recorded by a Keithley 237 dc source/measure unit. A ZJ-3D piezo d_{33} meter (manufactured by Beijing Institute of Acoustics, China) was used to measure the piezoelectric charge coefficient d_{33} of the rings. Microstructural analyses were carried out by a scanning electron microscope STEROSCAN 440.

Microstructural analyses showed that the PZT rings were of a very dense microstructure. It was difficult for water to permeate into the rings. Accordingly, no noticeable change could be observed in the properties of the rings after the first treatment. It should be pointed out that some rings have been immersed in the NaOH solution for 20 days. These facts suggest that, in the absence of an electric field, the dilute NaOH solution does not influence the PZT rings by permeation.

In contrast, serious degradation occurred in those samples treated by hydrogen charging. The PZT rings vibrate in the thickness mode when they are used in a wire bonding machine. The impedance/phase spectra of the thickness vibration mode for an as-received PZT ring is shown in Fig. 1(a). The peak of minimum impedance corresponds to the resonance of the thickness vibration mode. The impedance and the frequency of the peak are the resonance impedance Z_r and the resonance frequency f_r , respectively. The peak of maximum impedance corresponds to the anti-resonance of the thickness vibration mode. The impedance and the frequency of the peak are the anti-resonance impedance Z_a and the antiresonance frequency f_a , respectively. The ring was then placed in 0.01 M NaOH solution and subjected to a dc voltage of 3 V between its silver electrode and the anode in the solution. Under this voltage the cathodic current density was around 0.2 mA/cm². The treatment was interrupted several times and the ring was taken out for measurement after being dried. The impedance/phase spectra of the thickness vibration mode obtained in these measurements are shown in Figs. 1(b), 1(c), and 1(d). For these measurements, the hydrogen charging treatment was conducted for 40, 80, and 120 h, respectively. It is clear that with increased hydrogen charging time, the resonance impedance Z_r increases while the antiresonance impedance Z_a decreases. Both the resonance frequency f_r and the antiresonance frequency f_a are shifted slightly to higher frequency after the hydrogen charging. The degradation of this PZT ring can also be seen in the changes in the mechanical quality factor Q_m , which is the reciprocal of the mechanical loss, and the dielectric loss at 1 kHz, as shown in Fig. 2. The mechanical quality factor Q_m was calculated by the equivalent circuit method with the Agilent 4294 A impedance analyzer.⁸ The mechanical quality factor Q_m decreases dramatically while the dielectric loss increases considerably by the treatment, which implies that the treatment will cause more mechanical loss and more dielectric loss when the ring is used in a wire bonding machine.

As no degradation occurred in those samples immersed in NaOH solution without the application of dc voltages, it can thus be concluded that the electrochemical reactions induced by the dc voltages are the cause of the degradation.

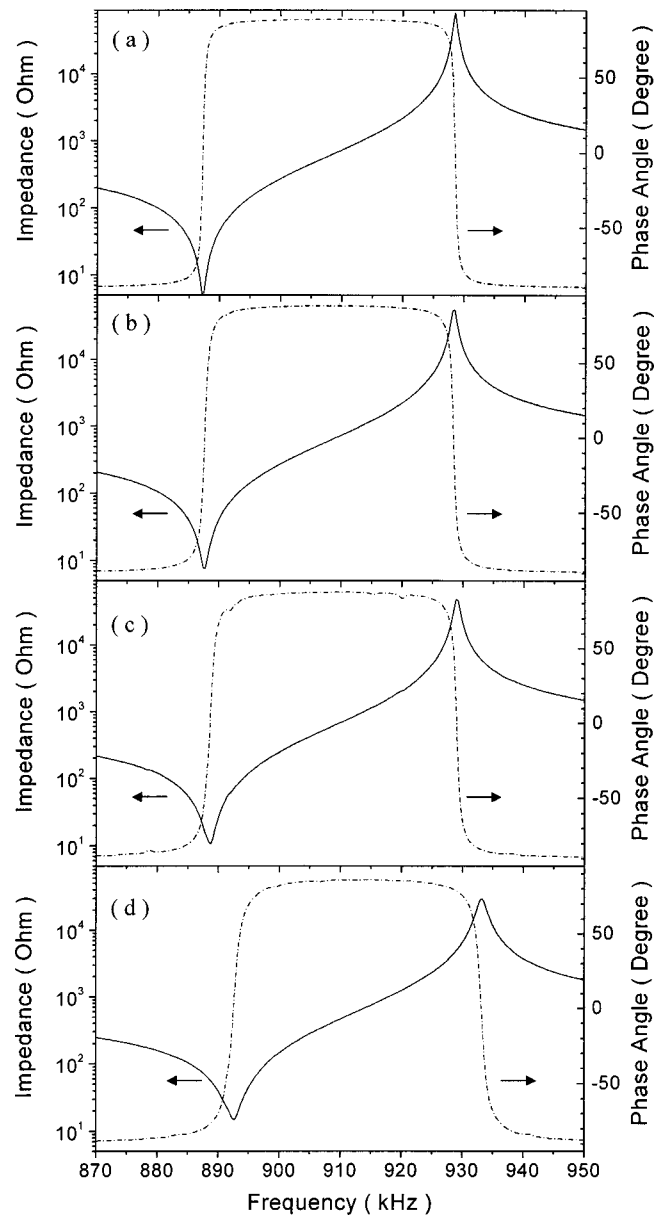


FIG. 1. Impedance/phase vs frequency spectra of the thickness vibration mode of a PZT ring: (a) as-received, (b) after 40 h hydrogen charging, (c) after 80 h hydrogen charging, (d) after 120 h hydrogen charging.

Hydrogen was evolved on the silver electrode of the PZT rings when dc voltages were applied, which can be written as



where H_{ads} represents an adsorbed hydrogen atom. Hydrogen atoms are very reactive and exist only as intermediate products.⁹ Some of them may react with other matter encountered in their path, although most of them combine with one another to form hydrogen molecules. Some researchers have shown that atomic hydrogen generated by electrolysis of water can diffuse into ceramics and induce reduction reactions at ambient temperature, which greatly changes the properties of the ceramics.^{5,6} The degradation of the PZT rings in this study can also be explained by the reduction reaction of hydrogen atoms.

According to some previous studies, the reduction reaction of atomic hydrogen results in the formation of charge

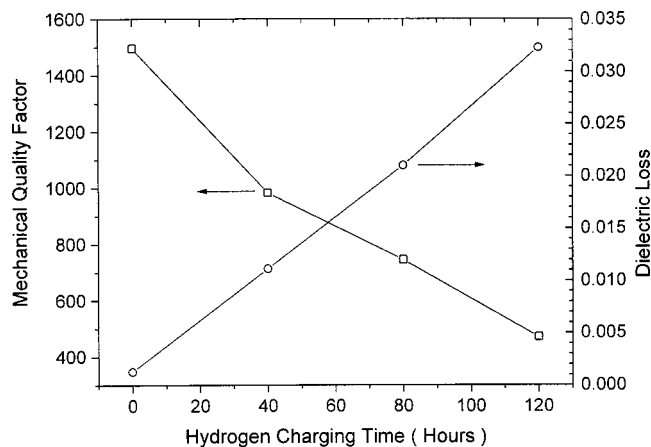


FIG. 2. Dependence of the mechanical quality factor Q_m and the dielectric loss (1 kHz) on the hydrogen charging time.

carriers in lead-based relaxor ferroelectric ceramics and greatly decreases the resistivity.^{5,10} In this study, it was found that the resistivity of the degraded samples was also greatly decreased. Figure 3 shows the I - V measurement results obtained for the sample whose impedance spectra have been shown in Fig. 1. The two curves correspond to the two measurements taken for the as-received state and after 120 h of hydrogen charging. It is evident that the hydrogen charging treatment increases the conductivity by about three orders of magnitude. It is well known that a high resistivity is of great importance for various piezoelectric applications, and the degradation observed in this study is obviously related to the increase in the conductivity of the rings.

Hydrogen gas reacts with PZT ceramics only at elevated temperatures. In this study, however, the reduction reaction occurred at ambient temperature. The cause of the reduction must have been atomic hydrogen rather than molecular hydrogen. The formation of atomic hydrogen at ambient temperature resulted from the application of dc voltages in this study. So electricity plays a vital role in the degradation. Some researchers proposed that hydrogen is incorporated into $(\text{Ba,Sr})\text{TiO}_3$ and PZT thin films when hydrogen reacts with them at relatively low temperatures (below 550 °C).^{11,12} Similarly, it is reasonable to assume that hydrogen is incorporated into PZT in this study and the reduction reaction can be expressed as



where H_i represents an interstitial proton. It is assumed that hydrogen is in interstitial sites and is ionized. Free electrons are formed so the resistivity is greatly decreased in the degraded samples. Further study of the reaction details is in progress and the results will be reported elsewhere.

The piezoelectric coefficient d_{33} of the as-received PZT rings was around 215×10^{-12} C/N. It is found that the hydrogen charging treatment has no noticeable influence on this coefficient. This indicates that no depolarization occurred in the degraded samples in this study. However, as the hydrogen charging decreases the mechanical quality factor and increases the dielectric loss of the PZT rings, a greater temperature rise will occur when the rings vibrate under electrical driving, which in turn will enhance depolarization.

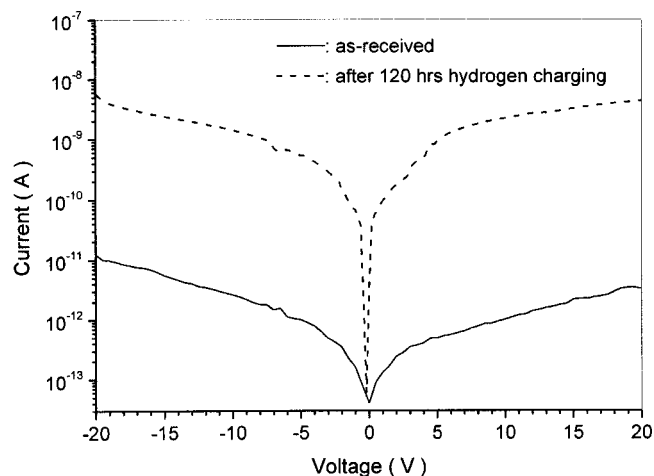


FIG. 3. Influence of hydrogen charging on the I - V characteristics of a PZT ring.

In summary, this study clearly shows that water causes serious degradation of lead zirconate titanate piezoelectric ceramics through the reduction reaction of atomic hydrogen. Some researchers have demonstrated that a thin water film can form on the surface of ceramic components by condensation of aqueous vapor in air.¹³ When piezoelectric ceramic devices are operated under some voltage and a thin water film is present, atomic hydrogen can be formed by electrolysis of water, which in turn leads to degradation of the devices by the reduction reaction. So the reaction between atomic hydrogen and piezoelectric ceramics should be studied in detail and efforts should be made to prevent water-induced degradation of piezoelectric ceramic devices.

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