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LETTER

Effects of electrochemical hydrogen charging on electrical properties of WO_3 ceramics

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Tungsten trioxide (WO_3) films are used extensively in eletrochromic devices [1], surface acoustic wave gas sensors [2] and photo-catalytic degradation [3]. In recent years, there has also been a growing interest in WO_3-based ceramics. Due to their high dielectric constant, WO_3 ceramics have been proposed for applications in ceramic capacitors [4]. WO_3-based semiconducting ceramics have been successfully used for detection and control of toxic gases. In 1994, Makarov et al. reported nonlinear current–voltage characteristics of Na_2CO_3 and MnO_2-doped WO_3 ceramics [5]. Now much progress has been achieved in preparing WO_3-based ceramic varistors with low breakdown voltage [6]. Their high dielectric constant enables them to act as a varistor in parallel with a capacitor, which is attractive for applications in elimination of electrical noise of micro-motors, protecting contact of delays and absorbing discharges of some circuits.

For practical applications, it is important for materials to exhibit stable physical properties in the course of time. Unfortunately, the electrical properties of sintered WO_3 ceramics have been found quite instable. When a constant DC voltage is applied on a WO_3 ceramic sample, the current responded very slowly and its magnitude would decay even by a factor of 10 with increasing time [7]. It is a great challenge to improve the stability of the physical properties of WO_3 ceramics and there have been extensive researches on it. In ZnO-based ceramic varistors and $Pb(Zr,Ti)O_3$ (PZT) thin film capacitors, the reduction of hydrogen from the electrolysis of water has been recognized as an important origin for degradation of their electrical properties [8, 9]. Presently, we have studied the influence of hydrogen on WO_3 ceramics. Our results show that hydrogen greatly changes the properties of WO_3 ceramics and much attention should be paid to it in WO_3-based components and devices.

Analytical grade (≥99%) WO_3 powder was ball-milled with de-ionized water for 24 h. After drying, 1 wt% PVA was added as binder and the powder was pressed into pellets of 16 mm in diameter and 2 mm thick. The pressed pellets were sintered at 1150 °C for 2 h. Silver electrodes of 4 mm in diameter were fired onto the centers of the two major surfaces of the pellets. Some pellets were placed in a 0.01 M NaOH solution and DC voltages were applied between their silver electrodes and a counter Pt electrode in the solution. The applied DC voltages induced electrolysis of water and the silver electrodes of the pellets acted as the cathode with hydrogen deposited on them. This treatment is referred to as ‘‘electrochemical hydrogen charging’’ hereafter. The DC voltages were removed after some designated periods of time and the pellets

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were taken out, washed and dried. For reference, some other WO_3 pellets had been simply immersed in 0.01 M NaOH solution with no voltages applied. The frequency spectra of capacitance and dielectric loss between the silver electrodes of the pellets were measured on an Agilent 4294 A impedance analyzer. Resistance between the silver electrodes of the pellets was obtained through a Keithley 2000 multimeter using its resistance measurement (2 wire) function. An X-ray diffractometer (Philips PW 3719) with Cu K_α radiation was used for phase detection.

For those WO_3 ceramic pellets that had been simply immersed in the NaOH solution for reference, dielectric and resistance measurements showed that the immersion resulted in no noticeable changes in their electrical properties after cleaning and drying. It indicates that the WO_3 ceramics were chemically stable in water when no electricity was present. For those samples treated by electrochemical hydrogen charging, however, a quite different result was observed. As an example, the measuring results obtained for a representative sample were reported below. A 3 V DC voltage had been applied between its silver electrodes and the Pt electrode in the NaOH solution and the electrochemical hydrogen charging had been interrupted many times for measurement. Figure 1 shows the change in resistance measured between its two silver electrodes in the course of electrochemical hydrogen charging. It can be seen that the electrochemical hydrogen charging exhibited a great influence on the resistance, which was decreased by more than two orders of magnitude through 0.5 h of electrochemical hydrogen charging. The frequency spectra of capacitance and dielectric loss measured for the sample as-sintered and after 0.5 h of electrochemical hydrogen charging were shown in Fig. 2, respectively. Both the capacitance and the dielectric loss were increased by about 10 times over the measuring frequency range (from 10^2 to 10^6 Hz). Obviously, the increase in dielectric loss was in agreement with the decrease in resistance. So the physical properties of WO_3 ceramics are extremely unstable when electrochemical hydrogen charging occurs, which must be due to the reaction between hydrogen and WO_3.

The deposition of hydrogen on cathode during the electrolysis of water can be expressed as:

$$H_2O + e^- \rightarrow OH^- + H_{ads}, \tag{1}$$

$$H_{ads} + H_{ads} \rightarrow H_2, \tag{2}$$

where H_{ads} represents an adsorbed hydrogen atom. Adsorbed hydrogen atoms are very reactive. Though most of them combine with one another to form hydrogen molecules as shown in Eq. 2, some of them may react with other matters in their path. Our previous works showed that adsorbed hydrogen could cause lattice decomposition for some oxides and some new phases will be formed [10]; while for some other oxides, hydrogen enters into the oxide lattice and only exists in interstitial sites [11]. In this study, X-ray diffraction patterns taken on the sample as-sintered and after 32 h of electrochemical hydrogen charging are shown in Fig. 3, respectively. A new peak appeared at $2\theta = 24.1°$ for the hydrogen-charged sample, as marked by an asterisk in the figure. And the intensity of the peak at $2\theta = 23.2°$ had been greatly increased. So some

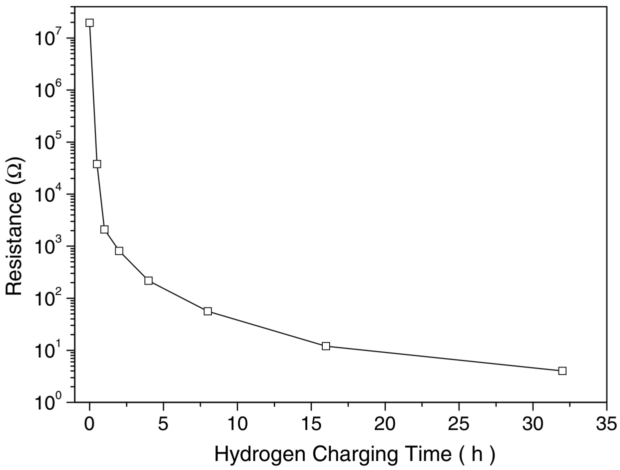

Fig. 1 Relationship between resistance and electrochemical hydrogen charging time for a WO3 ceramic pellet

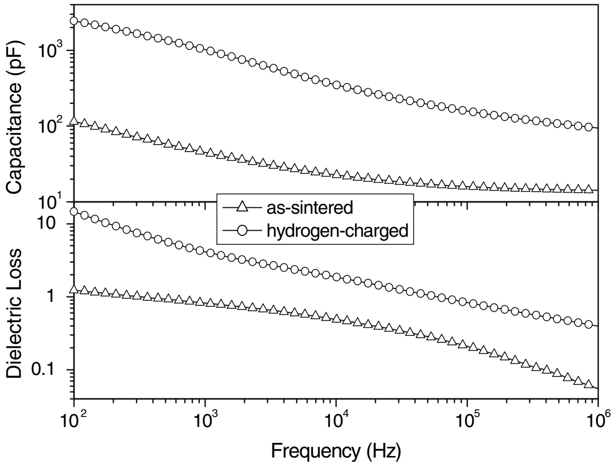

Fig. 2 Frequency spectra of capacitance and dielectric loss of a WO_3 ceramic pellet measured as sintered and after 0.5 h of electrochemical hydrogen charging, respectively

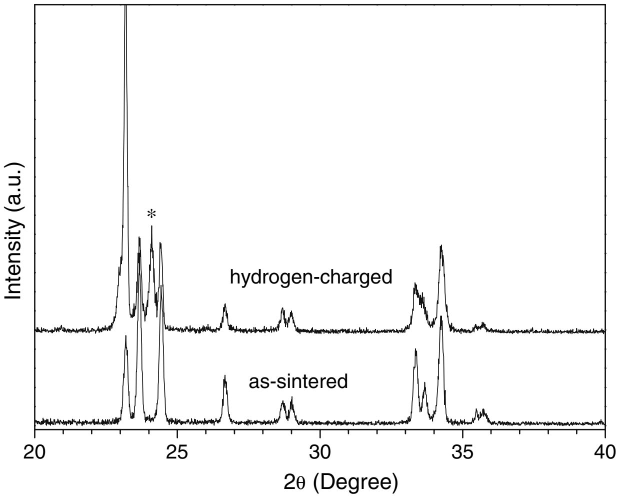

Fig. 3 X-ray diffraction patterns taken on the surface of a WO_3 ceramic pellet as-sintered and after 32 h of electrochemical hydrogen charging, respectively

new phases had been formed through the electrochemical hydrogen charging in the present study.

It is well known that of the electrochromism of WO_3 is due to the formation of tungsten bronze by the injection of some small cations from electrolytes into the interstitial sites of the tungsten oxide matrix, which can be written as [1]:

$$WO_3 + x M^+ + x e^- = M_xWO_3, \quad (3)$$

where M represents H, Li, Na etc. and the electron is from cathode. It should be pointed out that an obvious darkening could be observed in the surface of WO_3 ceramics in the course of electrochemical hydrogen charging. According to JCPDS files #23–1448 for $H_{0.1}WO_3$, #23–1449 for $H_{0.33}WO_3$ and #75–0058 for $H_{0.5}WO_3$ [12], the strongest peak for $H_{0.1}WO_3$ is (110) with $2\theta = 24.17°$; for $H_{0.33}WO_3$, it is (100) with $2\theta = 23.58°$; while for $H_{0.5}WO_3$, it is (100) with $2\theta = 23.68°$. Obviously the new peak in Fig. 3 could be identified as (110) of $H_{0.1}WO_3$. And the greatly enhanced peak should indicate the formation of $H_{0.33}WO_3$ and/or $H_{0.5}WO_3$. So we believe that tungsten bronze had also been formed in our study in the following way:

$$WO_3 + x H_{ads} = H_xWO_3. \quad (4)$$

Namely, some adsorbed hydrogen atoms from the electrolysis of water entered into WO_3 lattice and tungsten bronze phase was formed with the incorporated hydrogen. Ion intercalation into WO_3 may give rise to shallow donor energy levels and charge carriers are thus increased [13]. This explained why the resistance was greatly decreased and the dielectric loss was greatly increased in the hydrogen-charged samples. Figure 4 shows the R-T characteristic measured for the sample after 32 h of electrochemical hydrogen charging through standard four-probe method. The resistivity had a strong negative-temperature-coefficient (NTC) so the hydrogen-charged sample exhibited a typical NTC-type semiconducting behavior.

It should be emphasized that this study clearly shows that the properties of WO_3 ceramics can be greatly changed by hydrogen in a very short time. Although the influence of hydrogen from the electrolysis of water has been recognized as an important cause for properties degradation in many electroceramic components and devices, its influence on WO_3 ceramics must be among the most serious ones. As working voltages can induce electrolysis of water condensed from environmental moisture, WO_3 ceramic components and devices would exhibit very unstable electrical properties when they are applied in some humid environments. So much attention should be paid to this hydrogen-induced degradation when WO_3 ceramic components and devices are designed for practical applications. Protection measures, such as polymer coating, should be adopted when the applications allow.

In summary, the electrical properties of WO_3 ceramics were seriously degraded when hydrogen was deposited on the silver electrodes fired on them through the electrolysis of water: The resistance was decreased by orders of magnitude in a very short time, the capacitance and the dielectric loss were considerably

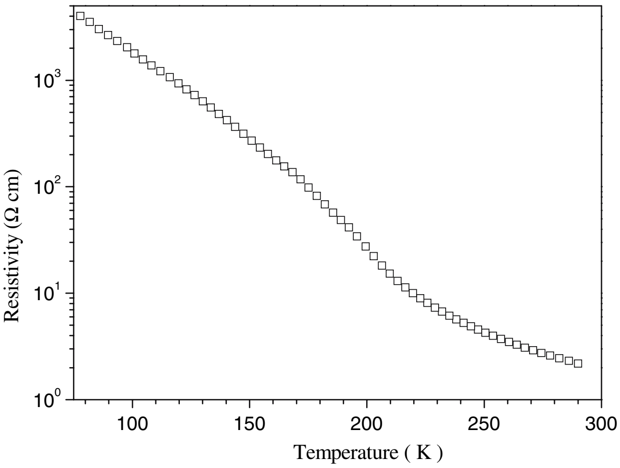

Fig. 4 Temperature dependence of resistivity measured for a WO_3 ceramic pellet after 32 h of electrochemical hydrogen charging

increased in the measuring frequency range. X-ray diffraction analysis showed that tungsten bronze phases, $H_{0.1}WO_3$ and $H_{0.33}WO_3$ and/or $H_{0.5}WO_3$, were formed in the hydrogen-charged samples. It was proposed that atomic hydrogen generated from the electrolysis of water enters into WO_3 and the lattice was reformed to those of tungsten bronze phases. Tungsten bronze phases showed a typical NTC-type semiconducting behavior and the degradation in hydrogen-charged WO_3 can be well explained by the formation of tungsten bronze phases. Hydrogen-induced degradation occurs very quickly in WO_3 ceramics and great attention should be paid to prevent it for WO_3 ceramic components and devices.

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