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On structural and high temperature electrochemical properties of ZrO_2 thin film coating on Zr metal produced by carbonate melt

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Abstract Melt of $NaCO_3$ can favor oxidation of Zr to form ZrO_2 thin film on Zr surface, which is used to make Zr/ZrO_2 oxidation/reduction electrode of pH sensor for testing elevated temperature aqueous solutions. Using SEM, EPMA, XPS, EXAFS and HRTEM, we found that ZrO_2 film is tightness and solid with 20 μm thickness composed by nanometer-sized monoclinic crystals. Zr/ZrO_2 interface is characterized of zoning structure according to topography and chemical composition in five zones: oxygen-rich ZrO_2, ZrO_2, oxygen-rich Zr metal, oxygen-bearing Zr and Zr from outmost to center. Melt oxidation process of Zr involved oxidation time, air and temperature. The air is important effect on structural and electrochemical properties of ZrO_2 thin film for making elevate temperature electrochemical sensor. If oxygen air largely presented in carbonate melting process, ZrO_2 thin film is not tightness and not for oxidation/reduction electrode.

Introduction

ZrO_2 is one of the most widely studied metal oxide materials due to its great technological application. ZrO_2 is ionic conductor, which can be used to make oxygen gas sensors in automotives and in measurements of dissolved oxygen in molten steels. ZrO_2 is also used as an additive in many electronic ceramics as well as refractory materials [1].

Recent advances in material science and sensor technology have resulted in the development of YSZ (yttria stabilized zirconia) ceramic-based on pH, H_2 and H_2S sensors. YSZ/HgO/Hg electrode companied with AgCl/Ag electrode has been used to test pH of hydrothermal systems. This chemical sensor can be used in testing high temperature–pressure solutions up to 400 °C and 40 MPa. But YSZ/HgO/Hg electrode is not sensitive at temperatures below 200 °C [2–5]. A metal/metal oxide couple that has the chemical stability and sensitive in the pH ranges of interest under the expected measurement conditions should be selected [5, 6].

Many functional electronic ceramic thin films are prepared and integrated onto silicon wafers, glasses and other substances. Oxide of titanium group, TiO_2 can be prepared and used in widely developing fields, for instance using as sensor materials.

In this study we select Zr in the titanium group to produce ZrO_2 thin film to make Zr (Zr/ZrO_2) hydrothermal chemical sensor. Usually, ZrO_2 film is utilized to make a coating on other metals in order to resist corrosion, or withstand high temperatures. Coating of ZrO_2 film on metals are usually performed by the different methods. Several techniques are available to produce thin films. Some of these include sputtering, chemical vapor deposition (CVD), plasma enhanced CVD and sol–gel [7–9]. We have tried to use sputtering and chemical vapor deposition (CVD) methods to produce high quality thin film of ZrO_2, but these ZrO_2 film coatings are not good for oxidation/reduction electrode. Finally, we utilized carbonate melt

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method to produce ZrO_2 thin film, which is suitable for high temperature chemical sensor. Many works have been made on ZrO_2 thin film, but these films are used for different objects [10–13].

As making the Zr/ZrO_2 electrode, we found some of those ZrO_2 films are used for high temperature sensor, and others are not useful. Then we analyzed the relations between the Zr/ZrO_2 interface structure and their electrochemical nature for the different electrodes. This work has helped us to optimize the methods and technique to produce a good ZrO_2 film for making high temperature sensor.

Experimental

Pure Zr metal thread was chosen (diameter is about 0.5–1 mm), which was cleaned ultrasonically at room temperature using acetone to remove fine particles, rinsed with distilled water, and dried at 70–80 °C.

Melt method

Melt of $NaCO_3$ can favor oxidation of Zr to form ZrO_2 thin film on Zr metal surface. Zr metal thread was put in Na_2CO_3 melt in Al_2O_3 crucible with Au liner. Melting temperature is maintained to be at 890 °C for 1–1.5 h. ZrO_2 thin film was formed on Zr metal, and this method is used to make Zr/ZrO_2 oxidation/reduction electrode.

Two melting methods can be used to make coating of ZrO_2 on Zr metal. Na_2CO_3 powders were crushed through 20 meshes, and its 6 g powders were put in Al_2O_3 crucible (with Au liner). Then we inserted one piece of Zr metal thread of 40 mm length in Na_2CO_3 powders, and covered 30 mm length metal thread with Na_2CO_3 powders. First method of Zr oxidation is to put the Al_2O_3 crucible with Zr metal threads in furnace and start heating at room temperature. The temperature increases to 890 °C in 3 h. The heating rate is 173 °C/h. And it remains 890 °C for 1–1.5 h. Then, ZrO_2 coating on Zr metal is formed.

The second method is heating furnace until 800 °C, then to put the Al_2O_3 crucible with Zr metal threads in the furnace. And continue heating to 890 °C in 40 min. The heating rate is 135 °C/h in order to allow carbonate melting rapidly. And it remains 890 °C for 1–1.5 h. Both methods can make a coating of ZrO_2. We have tested the above two methods for couple of years and produced a hundred electrodes, see authors' letters patent [14].

The ZrO_2 film on the Zr metal was observed by using microscope when it was made a polish section. Measured thickness of the ZrO_2 film is about 20 μm. In some cases, thin film is composed of a little thick ZrO_2 zone, and about 25 μm thickness on Zr metal. In the next step, we will identify the film structure and relative electrochemical properties.

Electrochemical properties

Combined with other electrodes, such as Ag/AgCl electrode, pH sensor of Zr/ZrO_2 was made. The overall electrochemical cell used in building chemical sensor can be described as follows:

$$\mathrm{Ag|AgCl|\ Cl^-,\ H^+,\ H_2O|ZrO_2|Zr}$$

The electrochemical experiments were performed in a computer-controlled Ti flow reactor, which is especially resistant to corrosion by acid NaCl-bearing fluids. That is a flow through reactor system with an apparatus, in which the chemical sensor can be put. Experiments commenced with the continuous flow rate (1–6 mL/min) of 3.5 wt% NaCl solution having pH (25 °C) between 1.5 and 8. As fluids flowed onto the reactor, cell potential was measured with an electrometer with input impedance of 10^{13} ohms. Uncertainties in the measurements were generally within ±0.5 mv. Cell potential $\Delta E(v)_{T,P}$ as function of pH can be described as:

$$\Delta E(V)_{T,P} = \Delta E^\circ + \frac{2.3026RT}{F}[\log a(Cl^{-1}) - 1/2 \log a(H_2O)] - \frac{2.3026RT}{F} pH_{T,P} \quad (1)$$

where $\Delta E_{T,P}$ is the sensor potential, here it is solely a function of pH at a given dissolved Cl and at T–P condition. And in the equation, F refers to Faraday constant, T represents K, and R is gas constant. ΔE° is the cell potential at standard state, which can be calculated from the standard state potential of $\Delta E^\circ_{(Ag/AgCl)}$ and $\Delta E^\circ_{(Zr/ZrO2)}$. $pH_{T,P}$ is pH at high temperatures and pressures. Figure 1 shows that the measured cell potential varies linearly with pH of the fluid at 200 °C.

Based on the above experiments, two kinds of Zr/ZrO_2 electrodes can be distinguished. It was found that 20 μm thickness of ZrO_2 film is suitable to be made of good electrode, which is called type 1 of ZrO_2 film. For type 1, cell potential of the Zr/ZrO_2 electrode is sensitive with solution chemistry, and responses linearly to pH. It possesses excellent electro-chemical properties for an electrode.

Analysis of synthesis process

Usually the second method is easy to produce good Zr/ZrO_2 electrode i.e., type 1. The essence of this method is that Zr metal was mainly oxidated by CO_2, produced from Na_2CO_3 melting process.

But the first method is not easy to make a suitable ZrO_2 coating on Zr metal. For the first melting method, Zr was slowly oxidated by oxygen in air in the temperature range of

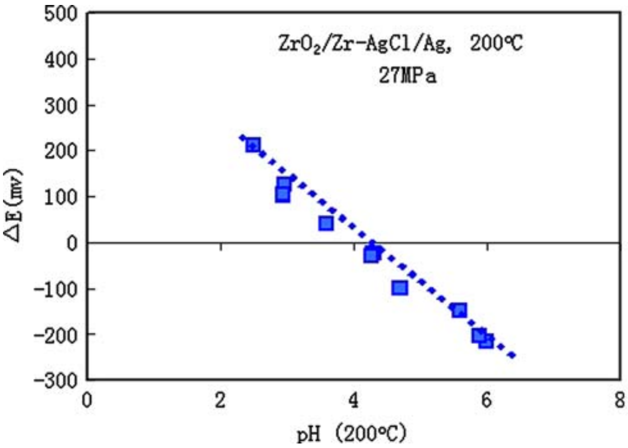

Fig. 1 Plot of Zr/ZrO_2 sensor potential against calculated pH for NaCl–HCl–H_2O solutions at 200 °C (Redrawn from [15].)

20–870 °C in 3 h until Na_2CO_3 was completely melted, and then continuously oxidated by Na_2CO_3 melt for 1–1.5 h.

Oxygen in air presented in the oxidation process of Zr in the first method. In this case, thin film is composed of a little thick ZrO_2 zone, and about 25 μm thickness on Zr metal, which is called type 2 of ZrO_2 film (Table 1b). For type 2, its cell potential does not response linearly to pH, which is not good for electrode. Comparison of the experiments of melts oxidation for Zr metal and the electrochemical experiments of testing electrodes indicate that the process of melt oxidations of Zr affects the electrochemical properties of the chemical sensor.

Analysis results of Zr/ZrO_2 interface

By using Electron Probe Microanalyzer (EPMA: JXA 8800R), Scanning Electron Microscopy (SEM: HITACHI S-4200), X-ray photo-spectroscopy (SAXPS: Thermo VG Scientific Sigma Probe), Extended X-ray Absorption Fine Structure (EXAFS) and High-Resolution Transmission Electron Microscopy (HRTEM: JEM-2010), we investigated topography, structure of ZrO_2 zone, chemical components of Zr/ZrO_2 interface and oxidation state of Zr for Zr/ZrO_2 electrode.

EPMA and SEM study

SEM study of the surface of ZrO_2 interface found that type 1 of ZrO_2 film is characterized of well crystallization with prismatic form, which are in radiated fibrous and developed in the surface 10 μm of total 20 μm thickness ZrO_2 film (Fig. 2a, b). But for the type 2 of ZrO_2 film, ZrO_2 is not well developed prismatic crystalline (Fig. 2c, d).

EPMA study also expressed that for the type 1 of ZrO_2 film, whose ZrO_2 zone on the Zr/ZrO_2 interface is about 20 μm thickness, expressed in the composition image (Fig. 3a). ZrO_2 zone of type 2 of ZrO_2 film is wider than that of type 1.

Through the second electron image of the two kinds of ZrO_2 film (good and bad electrode samples, i.e., type 1 and type 2, respectively), we found Zr/ZrO_2 interface having different zones on the crossing profile from the surface of ZrO_2 zone to the inner (Fig. 3b), which indicated the oxidation state of metal in the Zr/ZrO_2 interface behaves zoning structure. Figure 3b shows the bright light on the rim of the ZrO_2 zone, which is not real matter, produced by rim effect of EPMA.

More observation with the images of cathodoluminescence (CL) of the ZrO_2 zone clearly shows that ZrO_2 film consists of two different parts, the outer and the inner. The outer part of the ZrO_2 zone of the good electrode (Type 1) behaves very strong luminance, characterizing of high

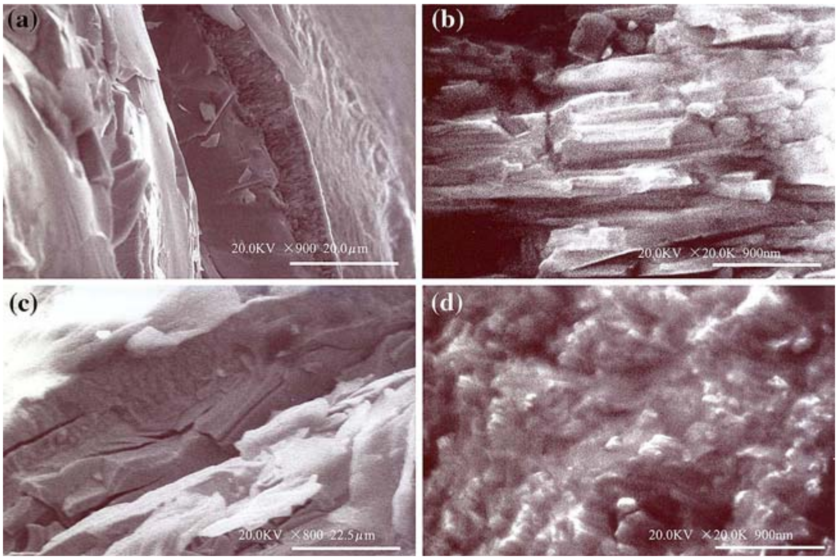

Fig. 2 SEM micrographs of ZrO_2 thin films of good and bad electrodes (type 1 and type 2) (**a**) SEM micrographs of fractography of ZrO_2 thin film of type 1 with 20 μm thickness; (**b**) The outmost zone of ZrO_2 thin film of type 1, prismatic crystals; (**c**) SEM micrographs of the fractography of ZrO_2 thin film of type 2 with 25 μm thickness; (**d**) The outmost zone of the ZrO_2 thin film of type 2 is not well developed crystalline of prismatic form

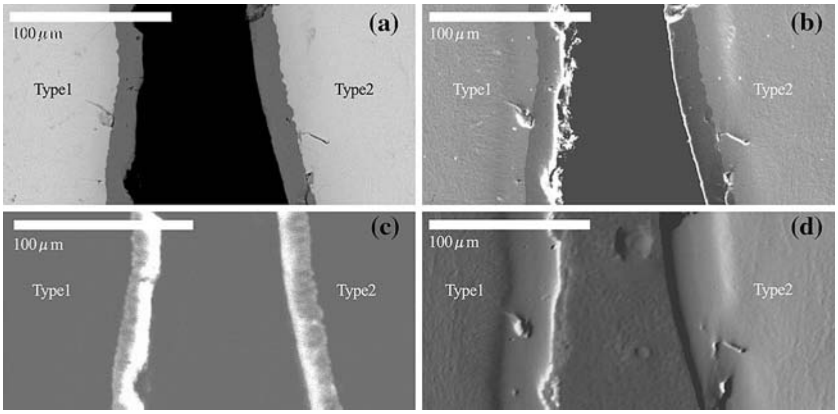

Fig. 3 EPMA images of cross section of type 1 and type 2 of ZrO_2 thin films. (**a**) EPMA component images of cross section of type 1 and type 2 of ZrO_2 thin films. For type 1, the outer zone is ZrO_2 thin film, with 20 μm thickness. For type 2, the outer zone is ZrO_2 thin film, with 25 μm thickness. (**b**) EPMA Second electron image of the cross section of type 1 and type 2 of ZrO_2 thin films: from the outmost zone to the center, Zr–ZrO_2 interface are divided into five zones: (1) oxygen-rich ZrO_2; (2) ZrO_2 zone; (3) oxygen-rich Zr metal; (4) oxygen-bearing Zr metal; (5) Zr metal. (**c**) EPMA images of cathodoluminescence of cross sections of ZrO_2 thin films of type 1 and type 2. Type 1 is good for electrode, which has a strong and continuous cathodoluminance in the outmost zone; type 2 is not good for electrode, which has not a continuous cathode luminescence in the outmost zone. (d) TOPO image of cross section of Zr/ZrO_2 electrode

oxygen density, continuous, and dense ZrO_2 film. Correspondingly, the ZrO_2 zone of bad electrode (Type 2) also has two parts in the cathodoluminescence image. Comparing with the outer ZrO_2 zone of good electrode, the outer ZrO_2 zone of the bad electrode has relatively weak cathode luminescence, and is not continuous (Fig. 3c).

It was reported that CL is related to presence of defects in solid (metal and silicate). Theoretically, CL occurs because of the presence of defects in solid structure. There are many types of defects, such as dislocations and other structure defects; vacancies and non-stoichiometry [16, 17].

For Zr/ZrO_2 interface, the brightness part of CL image of the ZrO_2 zone appeared in the oxygen-rich ZrO_2 zone. The bright part on the rim is about 5–10 μm, which is corresponding with the width of oxygen-rich ZrO_2 or the width of good column crystal ZrO_2 for type 1. The bright part of CL for type 2 is not continuous, and usually 5 μm width.

Cathodoluminescence occurred on the rim of the ZrO_2 zone, which is not related to foreign impurities on the surface of the ZrO_2 zone, such as carbon. Succedent XPS study provided evidence that there is no carbon on the rim (see next section).

As comparing Fig. 3a, b and c, EPMA component images, second electron image, cathodoluminescence image of cross section of type 1 and type 2 of ZrO_2 thin films from the outer part to inner part, we found that the first ZrO_2 zone in component image and second electron image have the same width, which is about 20 μm and behave cathodoluminescence phenomenon. Note it does not involve the bright rim in the second electron image (Fig. 3b). Luminescence zone is in ZrO_2 zone.

Figure 3d shows the TOPO image of the Zr/ZrO_2 interface. It is easily found that the outer part of the TOPO image of the Zr/ZrO_2 interface has 35 μm width for type 1 and 45 μm width for type 2. This outer part covers both the ZrO_2 zone and oxygen-rich Zr metal zone. Obviously, oxygen-rich Zr metal possesses a rather high hardness.

In the meantime, we made quantitative analysis following a section direction from outmost zone to the inner fresh metal. Table 1 shows the contents of Zr, O and Hf.

Above experimental results indicate that from the outmost zone to the center, the content of oxygen decrease and the content of zirconium increase (Fig. 4 and Table 1). And the interface of Zr/ZrO_2 (for good electrode: type 1) are divided into five zones: (1) prismatic and oxygen-rich ZrO_2, where O/Zr atomic number ratio ranges from 3.45 to 2.6, and ~10 μm thickness; (2) ZrO_2 zone, where O/Zr ratio ranges from 2.6 to 2.5, thickness ~10 μm; (3) oxygen-rich Zr metal, which contents oxygen 7–2% and O/Zr ratio ranges from 0.4 to 0.1, with thickness of 15 μm; (4) oxygen-bearing Zr metal; (5) Zr metal.

For the bad electrode (type 2), it has the same five zones also. But its outer ZrO_2 zone is not strong and continuous, and oxygen content and O/Zr ratio in the ZrO_2 zone are less than those of the good electrode. Oxygen-rich Zr zone is extensive thickness, with 20 μm. The three zones have a pretty hardness, with total thickness of 45 μm.

Zoning structure of Zr/ZrO_2 interface for two kinds of electrodes type 1 and type2 has been analyzed and its statistic results are listed in Table 1. The average thickness for each zone is also listed in Table 1.

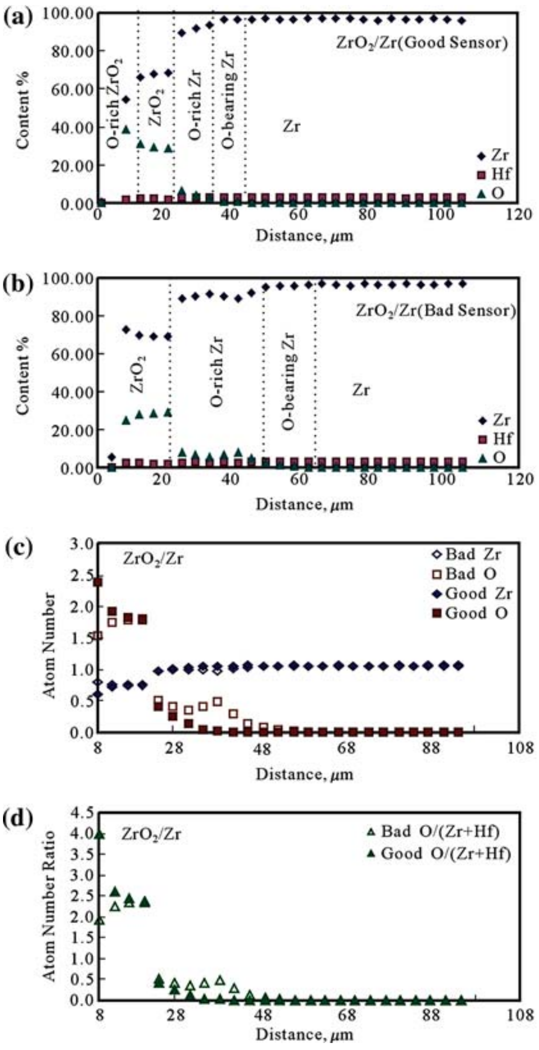

Fig. 4 Zr/ZrO$_2$ interface composition form ZrO$_2$ film surface to inner of Zr metal: (**a**) Type 1 of ZrO$_2$ film (for electrode), there is five zones; (**b**) Type 2 of ZrO$_2$ film (not for electrode), there is five zones. Compositions of the five zones are different with type 1; (**c**) Comparison of Zr and O contents in the five zones between type 1 and type 2; (**d**) Comparison of O/Zr ratio in the five zones between type 1 and type 2

XPS

X-ray photo-spectroscopy (XPS) has been applied to study surface of materials [18, 19]. Considered thin ZrO$_2$ film on Zr thread (tiny size of Zr/ZrO$_2$ electrode), we used Small Area X-ray photo-spectroscopy (SAXPS) to identify element valence of thin film. From purely electrochemical thermodynamics perspective, the most suitable electrode must possess good characterized components in terms of thermodynamics properties. So the valence of Zr is the key factor to judge the stability of Zr/ZrO$_2$ electrode. And XPS can help us to judge if there are some impurities existing in ZrO$_2$ thin films.

SAXPS spectra of ZrO$_2$ thin films are displayed in Fig. 5. Figure 5a and b show XPS spectra of ZrO$_2$ thin film of type 1 and type 2 etched 20 nm by Ar ion sputtering, respectively. These spectra include the main peaks of O(1s), Zr(3s), Zr(3p) and Zr(3d). The experimental results provide evidence that ZrO$_2$ thin film is composed of Zr^{4+} and O^{2-} and do not contain other impurities including carbon. So the cathodoluminescence of ZrO$_2$ thin film in EPMA is not due to impurities.

EXAFS experiment

EXAFS spectroscopy (Extended X-ray Absorption Fine Structure) has proved to be powerful method to obtain information on structure of solid surface. TEY (Total-electron-yield current measurement) method is one of new developments for near surface EXAFS experiment by using synchrotron radiation facilities [20]. TEY method is good for testing the ZrO$_2$ film on thread of Zr. The XAFS were measured on beam-line 4WlB at the radiation source of Beijing Synchrotron Radiation laboratory. The electron energy in the storage ring was operated at about 2.2 Gev, with a typical current of 50 mA. Synchromatized radiation from the storage ring was monochromatized by Si (111) double crystal.

The coating of ZrO$_2$ on thread of Zr can be directly put in the metal chamber with Kapton window for TEY measurements. We measured the Zr K-edge absorption for all the coating samples at room temperature, and found the main peaks of two kinds of ZrO$_2$ thin film are at 180,282 ev (Fig. 6a).

Theoretical calculation absorption spectra of ZrO$_2$ shown as Fig. 6b indicate that three crystal systems of ZrO$_2$ crystals: monoclinic class, tetragonal class and cubic class have different main peak positions, respectively. Comparison of two figures (Fig. 6a, b) provides evidence that ZrO$_2$ thin film belongs to monoclinic crystal system.

X-rays Absorption Near Edge Structure (XANES) calculations of zirconium oxide clusters were carried out using FEFF8 programs (version 8.10, from university of Washington) [21, 22], a real-space full multiple-scattering approach using self-consistent potential. The first three shells around a central Zr atom were constructed for the self-consistent field (SCF) potential calculation. The XANES spectra were calculated using the Hedin-Lundqvist self-energy with an energy dispersion of 0.5 eV to account for the core hole lifetime and the instrumental broadening effects. The full multiple scattering (FMS) calculations were performed on the clusters of all phases (monoclinic, tetragonal and cubic) with a size of 87 atoms. The crystallographic data of zirconium oxide of all phases were taken from the literatures [1, 23, 24]. The muffin-tin radii

Table 1 Zr/ZrO_2 interface structure of (a) good electrode (type 1) (b) bad electrode (type 2)

Zr/ZrO_2	Distance from the surface (μm)	Thickness (μm)	Oxygen (wt%)	O/Zr ratio	Crystalline	Cathodoluminescence
(a) Good electrode (type 1)						
1. ZrO_2	0–10	~10	38–32	3.45–2.6	Prismatic crystal	Strong, homogeneous
2. ZrO_2	10–20	10	30.6–29.8	2.6–2.5		Weak
3. O-rich Zr	20–35	15	29–7.5	1.68–0.4		
			7–2	0.4–0.1		
4. O-bearing Zr	35–42	~8	<2–0	0.09–0.01, 0		
5. Zr	>42					
(b) Bad electrode (type 2)						
1. ZrO_2	0–10	10	24–27	1.86–2.18	Not well developed prismatic crystal	Inhomogenous
2. ZrO_2	10–25	15	26.8–27.1	2.19–2.16		Weak
			27–6	2.1–0.6		
3. O-rich Zr	25–45	20	8–1.27	0.6–0.19		
			7–2	0.4–0.1		
4. O-bearing Zr	45–53	9	0.27–0	0.19–0		
5. Zr	>53					

Note that the thickness for each zone is the average measurements, which are obtained by EPMA and SEM methods

were automatically overlapped up to 1.15 to reduce the effects of discontinuities between adjacent regions of muffin-tin potentials. The Debye–Waller factors were set to zero because of their negligible influence on XANES spectra [21, 22].

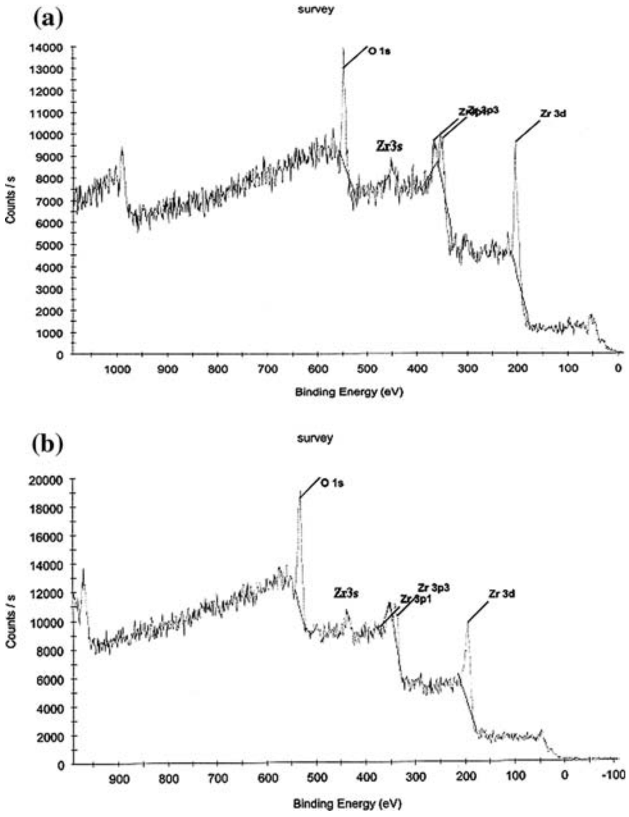

Fig. 5 XPS spectra of ZrO_2 thin film of Zr/ZrO_2 electrode etched 20 nm by Ar ion sputtering. (**a**) Type 1; (**b**) Type2

HRTEM

HRTEM images also show us microstructure images: ZrO_2 films of type 1 are constructed of nanometer-sized crystals (about 70–100 nm) (Fig. 7a). In the meantime, the chemical make-up of thin film was confirmed by EDS spectrum (Fig. 7b). This feature makes it suitable to be electrode in a chemical sensor.

Discussion and conclusions

Oxidation mechanism

According to the above results, we think melt oxidation method of forming ZrO_2 film on Zr metal is a good method, which can produce continuous ZrO_2 film on Zr metal. Based on our observations, oxidation time, air and temperature of oxidation process of Zr metal by carbonate melt play important roles in forming ZrO_2 film on the surface of Zr metal. If melting process of Na_2CO_3 is slow, Zr metal will be oxidized by oxygen in air and Zr/ZrO_2 interface structure like type 2 is not appropriate to be electrochemical sensor.

According to the first method, Zr metal was oxidated by oxygen air,

$$O_2 + Zr = ZrO_2 \quad (2)$$

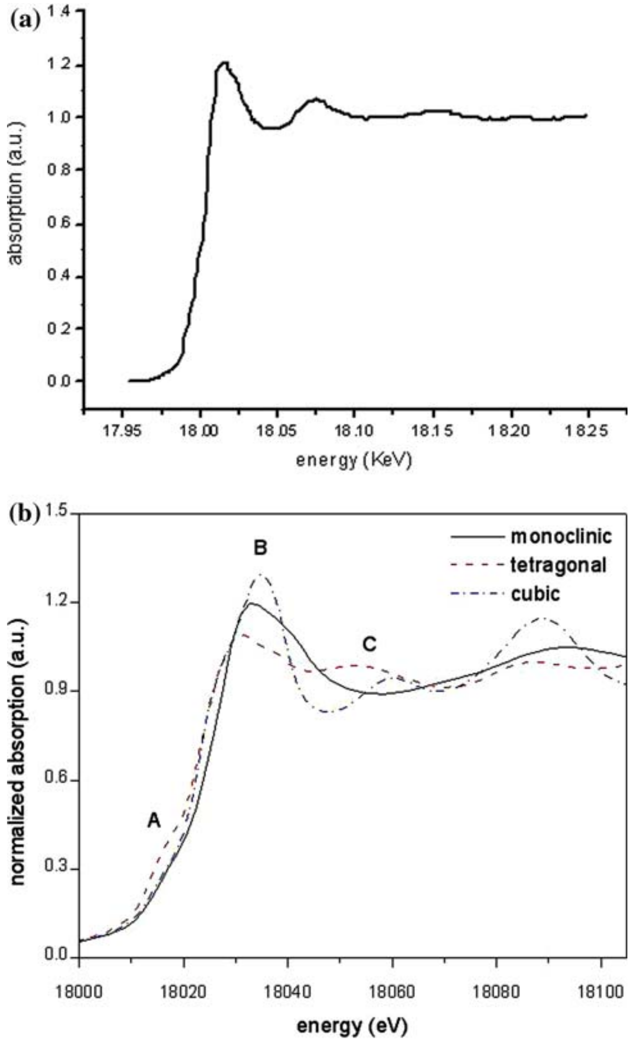

Fig. 6 EXAFS spectra of ZrO_2 thin films (**a**) Normalized XAFS spectrum of ZrO_2 obtained by TEY measurement; (**b**) One electron multiple scattering calculation of zirconium oxides. Calculated XAFS spectra of ZrO_2 of the three crystal systems: monoclinic, tetragonal, and cubic class. Some trends can be noted: ''A'' for tetragonal is biggest; ''B'' for cubic is most significant, and lowest for tetragonal; No ''C'' is shown for monoclinic. Local structure: Cubic-ZrO_2: Zr–O, N1 = 8, R1 = 2.208A (octahedral coordination); Tetragonal: Zr–O, N1 = 4, R1 = 2.065A, N2 = 4, R2 = 2.463A (almost tetrahedral); Monoclinic: Zr–O, N1 = 8, R1 = 2.043~2.265A

ZrO_2 film formed on Zr metal is not solid and O/Zr ratio on surface zone is less than 2.

During the synthesis process of second method, Na_2CO_3 melt oxidation process was derived from the following reactions at high temperature up to the melting point of Na_2CO_3.

$$Na_2CO_3 = CO_2 + Na_2O \tag{3}$$

$$2CO_2 + Zr = ZrO_2 + 2CO \tag{4}$$

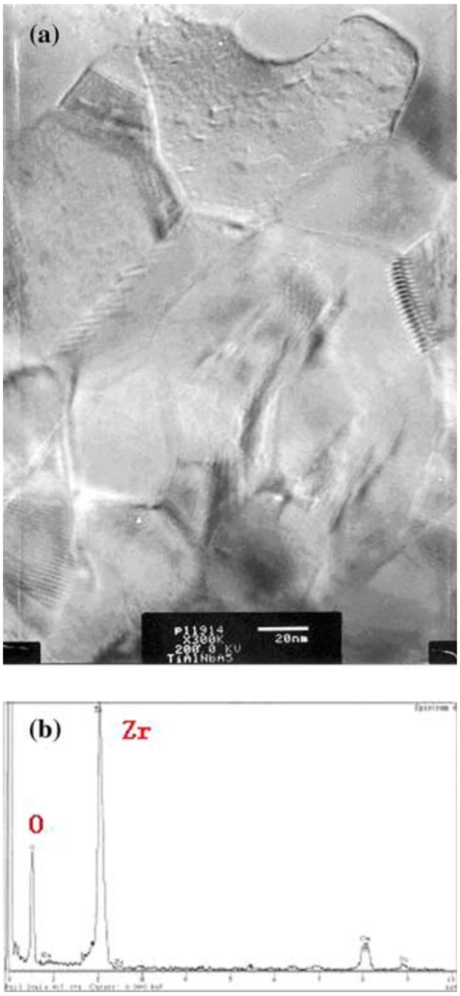

Fig. 7 HRTEM image of ZrO_2 thin film of good electrode (type 1) (**a**) HRTEM image of nanocrystalline ZrO_2 (about 70–100 nm), Magnification 300 k×, scale bar 20 nm. (**b**) EDS spectrum of nanocrystalline ZrO_2

Type 2 is formed in the coupling of the oxidation by oxygen air and the oxidation of carbonate melting. But type 1 is formed mainly by the oxidation of carbonate melting.

By studying electrochemical properties and using SEM, EPMA, XPS, EXAFS and HRTEM, analyses of topography, chemical composition and structure of ZrO_2 thin films revealed that there are two kinds of films: one is good for electrode, and the other is not. It was found that Zr/ZrO_2 interface structure affected the electrochemical feature.

Oxygen rich in ZrO_2 film and point defect

Oxygen rich in ZrO_2 film is interesting. When O/Zr atomic ratio is more than 2, oxygen rich in ZrO_2 film is non-stoichiometric. XPS study indicates that the oxygen bonding belongs to negative bivalence of ZrO_2. Oxygen is not molecule form in adsorption state.

We also predict that oxygen rich in Zr zone is also in structure. The TOPO image (Fig. 3d) shows that ZrO_2 zone and oxygen-rich ZrO_2 zone have 35 μm for type 1, and behave nearly similar high rigidity. That means the rigidity property of oxygen-rich Zr zone is similar with that of ZrO_2 zone. In the meantime, oxygen-rich Zr zone is different from Zr metal, shown in Fig. 3d. We think that structure oxygen presents in oxygen-rich Zr zone and in oxygen-rich ZrO_2 zone.

When O/Zr atomic ratio is more than 2, it will have vacancy of Zr^{4+} ion in ZrO_2 film, introducing point defect. This might be the case when there is a Zr^{4+} ion missed, and an extra negative charge is introduced into the structure. To maintain a charge balance, a vacancy might be created where Zr^{4+} would be located. Again, 4 O^{2-} anions would be turned to O^-. Authors assumed that a charge balance must be maintained so that the crystalline material as a whole is electrical neutral [1]. This situation would happen to ZrO_2 that is ionic solid.

As this assumption is correct, it is suitable to interpret that cathodoluminescence image of type 1 is stronger than that of type 2. Because, electrons from cathode ray reach to the point defect of the surface of oxygen-rich ZrO_2 zone, i.e., from vacancies and non-stoichiometry, then it would conduct a strong bright light.

Electrode reaction

A continuous, dense and thick ZrO_2 film (type 1) in the metal to oxide interface is important to make the high temperature and pressure chemical sensor, for instance pH sensor. As usual, in the first step, proton was adsorbed on the surface of ZrO_2/Zr electrode. Then H^+ passed through the ZrO_2 film, if the oxygen-rich ZrO_2 film is continuous, then following electro-chemical reaction would occur continuously:

$$4H^+ + 4e + ZrO_2 \rightarrow Zr + 2H_2O \qquad (5-1)$$

Above oxidation–reduction reaction is normal electrode reaction.

If O/Zr ratio is higher than two in the ZrO_2 film, more negative bivalence oxygen anion and more vacancies of Zr^{4+} ions present in it. The reaction (5-2) would easily occur in following way:

$$4H^+ + 4e + Zr_{(1-x)}O_{2(\mathrm{O-richZrO_2})} \rightarrow 2H_2O + (1-x)Zr \qquad (5-2)$$

where $Zr_{(1-x)}O_{2(\mathrm{O-richZrO_2})}$ refers to the oxygen-rich ZrO_2 film.

Thus, cell potential is stable and does response linearly with pH variations.

Oppositely, in other cases, as oxygen in air took important role in oxidation of Zr surface, then oxygen diffused into Zr metal deeper. And the oxygen in ZrO_2 film (type 2) is not continuous and not dense.

When H^+ passed through the ZrO_2 film**,** if the oxygen distribution in ZrO_2 film is not continuous, above electrochemical reaction would not occur in such media of ZrO_2 film. Particularly, if O/Zr ratio is less than 2, such as that in type 2, where there are more Zr^{4+} ion vacancies. Or there is more extra positive charge in metal, which is not easily able to conduct the reaction (5-1).

Therefore, cell potential is not stable and does not response linearly with pH variations. Therefore, this kind of Zr/ZrO_2 is not good for electrode. And also, ZrO_2 film conducts electricity through the motion of oxygen ions.

And also we found that a good electrode of Zr/ZrO_2 is composed of an oxygen-rich ZrO_2 film and a continuous film with an enough thickness.

In summary, melt of $NaCO_3$ used for oxidation of Zr to form a thin ZrO_2 film on metal surface is good method to make Zr/ZrO_2 electrode. As control the oxidation condition, we can obtain an adequate thickness and dense, continuous and nanometer-sized ZrO_2 films on metal surface, then make a good electrode of pH sensors for testing hydrothermal solutions.

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