High temperature and pressure chemical sensors based on Zr/ZrO$_2$ electrode prepared by nanostructured ZrO$_2$ film at Zr wire

Ronghua Zhang*, Xuetong Zhang, Shumin Hu
Laboratory of Geochemical Kinetics, Institute of Mineral Resources, Chinese Academy of Geological Sciences, Baiwanzhuang Road 26, Beijing 100037, PR China

**Abstract**

A Zr/ZrO$_2$ oxidation electrode was fabricated for in situ measurement of pH values of high temperature aqueous solutions. Combined with a Ag/AgCl reference electrode, the Zr/ZrO$_2$ sensor responded rapidly and precisely to the pH of the solutions over a wide range of temperatures. The Zr/ZrO$_2$ electrode was made by oxidizing Zr metal wire with a Na$_2$CO$_3$ melt to produce a thin film of ZrO$_2$ on the Zr wire surface. The nanostructure of the ZrO$_2$ thin film was characterized using high-resolution transmission electron microscopy (HRTEM) observations. The nature of the nanostructured ZrO$_2$ thin film on the Zr of the Zr/ZrO$_2$ electrode plays a vital role in the construction of Zr/ZrO$_2$ chemical sensors, particularly when the electrode is utilized for in situ measurement of the electrochemical parameters of aqueous solutions at high temperatures and pressures.

Chemical analyses of the ZrO$_2$ thin films revealed that the Zr/ZrO$_2$ interface is divided into five zones from the outermost zone to the center: (1) prismatic and oxygen-rich ZrO$_2$ zone; (2) ZrO$_2$; (3) oxygen-rich Zr; (4) oxygen-bearing Zr; and (5) Zr metal. Especially, the outermost oxygen-rich ZrO$_2$ zone of the films is composed of nanometer-sized monoclinic crystals.

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1. Introduction

1.1. High temperature and pressures chemical sensor

Scientists have been working on developing novel solid sensors for the in situ measurement of the chemical parameters of liquids, e.g., pH, H$_2$, H$_2$S, and CO$_2$ under extreme conditions. There is growing interest in miniature, multi-electrode deployable devices, which are highly sensitive, selective, and stable at high pressures and high temperatures [1–4]. And also, the ultimate use of the solid-state sensors will be for long-term monitoring deployment in nature, laboratories, and in industrial processes.

Solid-state sensors have been investigated for the in situ measurement of pH of hydrothermal vent fluids at mid-ocean ridges and for direct determination of certain chemical parameters or species (e.g., salinity, H$_2$, H$_2$S) of aqueous solutions under extreme conditions [5–9]. Recent advances in materials science and sensor technology have resulted in the development of yttria-stabilized zirconia (YSZ) ceramic-based pH, H$_2$, and H$_2$S sensors, e.g., the YSZ/HgO/Hg sensor. The YSZ/HgO/Hg sensor can be used in high temperature–pressure solutions up to 400 °C and 40 MPa [5–7]. In the last 20 years, a considerable amount of research has been reported on both measuring pH at elevated temperatures and pressures and interpreting electrochemical reactions on electrodes [1,2,5,6,8–15].

1.2. Zr/ZrO$_2$, transition metal oxide

Transition metal oxides, as an important multifunctional material, have received a great deal of attention during the last few years due to their unique applications in microelectronic and opto-electronic devices, and for their application in the self-assembled growth of three-dimensional nanoscale systems, such as fuel cell batteries [16], conductive ceramics [5,6], solar cells [17], heterogeneous catalysts [18–21], photo-catalysts [22,23], and also, electrochemical cells.

A metal/metal oxide couple that has desirable chemical stability and sensitivity in the pH ranges of interest under extreme conditions should be selected [5–9]. Many metal/metal oxide electrodes (e.g., YSZ/HgO/Hg or Cu/CuO$_2$, Ir/IrO$_2$, Zr/ZrO$_2$, W/WO$_3$) have been examined at high temperatures up to 300 °C in the past few years, most notably by Macdonald and his group, who successfully demonstrated the desirable properties of W/WO$_3$ [5,9,11,12,14,15]. Nevertheless, previous attempts to employ these pH sensors in hydrothermal systems were partially successful at high temperatures above 200 °C, e.g., YSZ/HgO/Hg. But the YSZ/HgO/Hg electrode is not sensitive at temperatures below 200 °C [7,8]. A Ti/TiO$_2$ electrode has been used to replace the YSZ/HgO/Hg sensing electrode to...
measure the pH of hydrothermal solutions [7]. Accordingly, in this study, a pH sensor with a metal/metal oxide electrode having a stable valent of metal oxidation state over a wide temperature range is required, in which the valence is not changeable particularly at high temperatures. We found that the nature of the Zr/ZrO₂ electrode is much better than the Ti/TiO₂ electrode (e.g., Zr⁴⁺ is not changeable in a wide temperature range). Moreover, the Zr/ZrO₂ electrode has a well-known corrosion resistance and favorable mechanical stability [8,14]. The Zr/ZrO₂ electrode can be used for highly accurate pH measurements over a large variety of temperatures from 2 to 400 °C and is thus a good alternative to the YSZ/HgO/Hg electrode.

1.3. Functional nanostructured transition metal oxide thin films

Metallic oxide films have been extensively investigated due to their relevance in the fields of electrochemistry, wear and corrosion. The determination of the electrochemical and mechanical properties of these films is important in predicting the suitability of the film for surviving realistic environments, e.g., conditions of high temperature and pressure.

The synthesis and characterization of various wide band gap metal oxide nanostructures such as nanowires, nanofilms, nanorods, nanobelts, nanobridges and nanowalls has attracted great interest due to their size, morphology-related properties, and their emerging applications in novel functional nanodevices [24]. For instance, the advantages of nanotechnology are applicable to sensor development. In addition, studies on well-ordered oxide films or bulk-oxide surfaces are becoming more popular and important [25–29].

In this study, we provide a method for coating a ZrO₂ film on Zr metal by oxidation of a carbonate melt to make a Zr/ZrO₂ electrode. It was found that through experimental studies, the ele-
trochemical properties of the Zr/ZrO₂ electrode are dependent on the structure and chemical composition of the ZrO₂ films on the Zr metal. And the ZrO₂ film for the electrode is composed of monoclinic nanocrystals, having an O/Zr atomic ratio of more than 2 (i.e., an oxygen-rich ZrO₂ film).

Also, to assess the viability of the Zr/ZrO₂ electrode (combined with a Ag/AgCl reference electrode) as a pH sensor in fluids with high salinity (3.5 wt% NaCl) and low to moderate pH, we performed experiments at temperatures up to 200 °C and pressures of 20–40 MPa. Experiments have shown that the Zr/ZrO₂-pH sensor is sensitive over a wide temperature range from 2 to 200 °C and possesses corrosion resistance, chemical stability, and favorable mechanical stability under demanding reaction conditions.

2. Experimental

2.1. Design of high temperature and pressure chemical sensors

A pH sensor was fabricated consisting of a Zr/ZrO₂ electrode and Ag/AgCl reference electrode. The overall potential of the cell was found to be a function of the activity of H⁺. Thus, the electrochemical cell is described as follows:

\[
\text{Ag|AgCl|Cl}^{-, \text{H}^{+}, \text{H}_2\text{O}|\text{ZrO}_2|\text{Zr}}
\]  

(1)

2.2. Preparation of nano-ZrO₂ film on a Zr wire for electrode

2.2.1. Melt oxidation

Zr metal wire (Φ ~ 1 mm) with a purity of >98% was cleaned ultrasonically using acetone to remove fine particles from the surface of the wire at room temperature. The Zr metal was then rinsed with distilled water, and dried at 70–80 °C. Zr metal thread was put in Na₂CO₃ melt in an Al₂O₃ crucible with a Au liner. It is known that melting Na₂CO₃ will favor oxidation of Zr, which is maintained at 890 °C for 1–1.5 h. Oxidation of Zr by melting Na₂CO₃ can be illustrated by the following reactions:

\[
\text{Na}_2\text{CO}_3 = \text{CO}_2 + \text{Na}_2\text{O} \quad (2)
\]

and

\[
2\text{CO}_2 + \text{Zr} = \text{ZrO}_2 + 2\text{CO} \quad (3)
\]

The thin ZrO₂ films were observed and analyzed using field-emission scanning electron microscopy (FESEM; HITACHI S-4200), electron probe micro-analysis (EPMA; JXA8800R electron probe micro-analyzer) and high-resolution transmission electron microscopy (HRTEM; JEM-2010 electron microscope).

As shown in Fig. 1, the SEM observations of the ZrO₂ thin film structure indicate that the Zr/ZrO₂ interface structure consists of a ZrO₂ zone (20 μm in thickness) and an oxygen-rich Zr metal zone (15 μm).

2.2.1.1. The performances of the different electrodes. The Zr metal of the Zr/ZrO₂ sensors was oxidized over different time lengths and oxygen fugacity, resulting in different electrochemical properties.

Two different melting methods were tested to make the ZrO₂ thin films. The first method involved placing Na₂CO₃ powder and Zr metal threads into an Al₂O₃ crucible (with a Au liner), and heating the loaded crucible in a furnace from room temperature to 890 °C. The heating process was performed over a period of 1.5–2 h with a rate of about 450 °C/h. When the temperature reached 890 °C, the furnace was maintained at this temperature for 1–1.5 h. Oxidation of Zr by melting Na₂CO₃ can be illustrated by the following reactions:

\[
\text{Na}_2\text{CO}_3 = \text{CO}_2 + \text{Na}_2\text{O} \quad (2)
\]

and

\[
2\text{CO}_2 + \text{Zr} = \text{ZrO}_2 + 2\text{CO} \quad (3)
\]

The melting point of Na₂CO₃ is about 858 °C. For the first method, the Zr wire was oxidized by O₂ air for 1–1.5 h at high temperature below 858 °C until the Na₂CO₃ melted, in which case, oxygen fugacity was determined by O₂ air. During oxidation of the Zr wire by O₂ air, the diffusion of oxygen into the Zr wire was rapid. The Zr wire was continuously oxidized by the Na₂CO₃ melt over 1–1.5 h.
For the second method, Zr was oxidized by the Na₂CO₃ melt over a large proportion of the oxidation process. In this process, the Zr and ZrO₂ oxidation–reduction equilibrium was determined by the oxygen fugacity buffer, CO₂/CO, as shown in Eq. (3). Oxygen diffusion into the Zr wire was found to be slow due to contact with the Na₂CO₃ melt.

Only in the second method, namely the short time melt oxidation of the Zr metal, did the reaction result in a good Zr/ZrO₂ electrode that can be employed for measuring the pH of high temperature–pressure aqueous solutions. In this case, the 20 µm thick ZrO₂ film coated on the Zr wire is solid and continuous (see Fig. 1a–d) [30].

2.3. Sensor fabrication

The major part of the Zr metal wire, except the sensor end (ZrO₂ film on Zr) and the opposite end (connected to the voltmeter), was covered with a heat-shrinkable PTFE tube, which was then sealed in the structure of the Zr/ZrO₂ sensor (Fig. 2).

The Ag/AgCl electrode functioned as the reference electrode for the potential (pH) measurements. Briefly, Ag wire was placed in a YSZ tube containing AgCl powder, which was then melted to form a thick AgCl film on the Ag wire surface. And also, a ceramic porous plug was put in one end of the tube. This is the sensor part (Ag/AgCl) used for the electrolytic contact with the test solution. A heat-shrinkable, PTFE tube was then used to cover the other end of the Ag wire, and the Ag wire was then sealed within the YSZ tube, leaving only a small part of the Ag wire exposed for connection to the voltmeter.

2.4. Experimental set-up for the pH sensor

A high temperature and pressure experimental equipment was set up as a testing facility to measure the Zr/ZrO₂ sensor potentials. The testing facility is schematically depicted in Fig. 3. We performed experiments in a computer-controlled Ti flow reactor, which is especially resistant to corrosion by acidic NaCl-bearing fluids. The Ti flow reactor is a flow-through reactor with a sealed titanium pressure vessel. The sensor was placed inside the vessel. A back-pressure regulator was used to control the pressure of the flowing fluid in the apparatus. An additional pressure gauge placed in the flowing system provided pressure readings. Also, a pressure sensor

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**Fig. 3.** The high temperature, high-pressure pH measurement system: (a) measurement system consists of pressure vessel with multi-electrode holes; furnace and temperature controller; pump, solution reservoir; back pressure regulator; (b) high-pressure vessel: (1) Ag/AgCl electrode; (2) Zr/ZrO₂ electrode; (3) fluid inlet and fluid outlet; (4) hole for thermocouple; (5) upper part of vessel; (6) lower part of vessel.
was connected to the flow system to provide an accurate pressure reading of ±0.01 MPa (0.1 bars). A high-pressure liquid pump offers a liquid flow velocity range from 0.1 to 9.9 mL/min. In the measurement system of flowing fluids, the fluids were maintained at a constant high-pressure, e.g., at 27 MPa. The pressure of the flowing fluids varied within ±0.05 MPa (0.5 bars). A heating device comprising a thermocouple, a heating furnace, and a proportional temperature controller was used to control the cell temperature. The temperature reading was accurate to within ±0.1 °C, and the stability was accurate to within ±0.1 °C.

Seven holes were made on the top of the pressure vessel, into which the fluid inlet, fluid outlet, thermocouple, four different electrodes can be introduced (Fig. 3b). The thermocouple, tubing, the Zr/ZrO2 electrode, and the Ag/AgCl reference electrode were sealed into the pressure vessel. The measurement system was connected to a computer to record the data obtained from the cell potentials, temperature and pressure readings, and monitor all of the parameters simultaneously. The measurement system can obtain six channels of data in 1 s. Particularly, the equipment can also be used to determine the sensitivity of the Zr/ZrO2 electrode to the pH of the fluids at high temperatures and pressures.

An advantage of this facility is that the Zr/ZrO2 electrode and associated reference electrode have a direct access to the fluid phase under the experimental conditions, which ensure in situ measurements. Experiments commenced with continuously flowing fluids (2–4 mL/min of 3.5 wt% NaCl solution) having pH values (25 °C) of between 1.5 and 8. The pH of the source solution was changed by adding HCl or NaOH to afford a range of test solutions with desired pH values. As the fluid flowed through the reactor, the cell potential was measured with an electrometer having an input impedance of 1013 Ω.

2.4.1. Test solution

Standard buffer solutions were obtained from Hanna Instruments: HI7004 – pH 4.01 buffer solution (25 °C, ±0.01 pH), HI7007 – 7.01 buffer solution (25 °C, ±0.01 pH); HI7010 – 10.01 buffer solution (25 °C ±0.01 pH), NaCl–HCl–H2O (or NaCl–NaOH–H2O) solutions were also prepared from the source solution made of 3.5 wt% NaCl aqueous solution.

As shown in Fig. 4, the slope of the cell potential versus pH values at room temperature and high temperature were measured using the HANNA pH meter connected to our electrometer. Similarly, the pH values for the effluence solutions were measured using the HANNA pH meter under room conditions, while the pH values at high temperature were calculated using an equilibrium solution model.

The theoretical pH values of the test solutions were calculated using HCh code, which equilibrium calculation and database are demonstrated to be identified [31–33]. The deviation of the cell potentials measured using the HANNA pH meter and the Zr/ZrO2–pH sensor connected to our electrometer at room temperature was only 0.1 mV. The deviation in our measurements of the cell potentials was generally within ±0.5 mV at high temperature. See Ref. [13].

3. Results and discussion

3.1. Testing of Zr/ZrO2 sensor

The testing sensor was prepared by installing a Zr/ZrO2 electrode into a high-pressure flow reactor with a suitable reference electrode, such as Ag/AgCl. The electrochemical cell for pH measurement can be derived from Eq. (1). The overall cell potential for Eq. (1) at a specific temperature and pressure is a function of pH, can be described as follows:

\[
\Delta E(V)_{TP} = \Delta E_{cell} + \frac{2.3026 RT}{F} \log \frac{a(H^+)}{a(H_2O)}
\]

As predicted from theoretical considerations, pH at 20 °C was calculated systematically with pH25 °C. We calculated pH at 20 °C corresponding to the measured cell potential at 20 °C, which is equal to 0.487 V.

Verification can also be extended further by comparing the electrode response characteristics with the calculated potential and pH data at high temperatures. To carry out this assessment of sensor potential (ΔE(V)_{TP}), we first predict the distribution of aqueous species in the NaCl–HCl–H2O system at high temperature and pressure, and then calculate the theoretical potential of Zr/ZrO2 at 20 °C.
well with that predicted from available thermodynamic data. Results reveal a good agreement between the two independently obtained predicted values for NaCl–NaOH–H2O for basic). Experimental measurements confirm the theoretically measured potential. The slope of the potential versus pH plot should be \(2.303 \times \frac{R}{F}\) at 20 °C, \(58.1 \text{ mV}\) at 20 °C and \(-94.3 \text{ mV}\) at 200 °C, respectively. Also, the electrochemical experiments demonstrate that the Zr/ZrO2 electrode fluctuates with rising temperature from low temperature to 200 °C. It was found that the potential increased during the first 20 min as the temperature increased to 200 °C, and then decreased over the next 40 min, and finally it became progressively stable. This phenomenon proves that the ionic solid conductivity of a metal–oxide ZrO2 is often affected by the variation of temperature. If the electrode is used in field observations, it will be necessary to perform calibration tests (for instance, prepare pH buffer solutions). Moreover, it would also be necessary to monitor the response of the cell potential with elapsed time to establish when the cell becomes stable, as shown in Fig. 7.

This study reports a new method for preparing a Zr/ZrO2 electrode using melting Na2CO3, and suggests that the Zr/ZrO2 electrode with a sealed structure has application in in situ measurements of pH for high temperature and high-pressure aqueous solutions (Fig. 2). Also, the electrochemical experiments demonstrate that the cell potential of the Zr/ZrO2 electrode responds to changes in the pH of the fluids at temperatures from 20 to 200 °C. However, compliance with the Nernstian equation has been demonstrated in principle. The Zr/ZrO2 electrode can be exactly calibrated using the theoretical prediction of the NaCl–HCl–H2O solution.

The experiments indicate that some data points deviated from the theoretical slope, and this deviation could be derived from a non-equilibrium electrochemical reaction at the electrodes. For instance, when an electrochemical reaction occurred at the elec-

![Fig. 5.](image-url)

![Fig. 6.](image-url)

observed. The results indicate that the in situ sensor responds rapidly and reversibly to the pH change of the test solution.

As can be seen in Fig. 7, the cell temperature, pressure and corresponding sensor potentials were monitored over a period of 10 h. Despite fluctuations in the pressure, the potential was observed to remain stable, and hence the Zr/ZrO2 sensor is estimated to be viable for measuring pH in the NaCl–HCl–H2O system under the selected operating conditions.

The flow-through experiments at 200 °C reveal that the Zr/ZrO2 sensor demonstrates a rapid and reversible response to changes in pH of the input aqueous solutions, as shown in Fig. 7. Moreover, changes in the pH of the input solutions from pH 3.5 to 1.9 were virtually instantaneously recorded and matched by corresponding changes in cell potential.

Fig. 7 also shows that the potential of the Zr/ZrO2 electrode fluctuates from low temperature to 200 °C. It was found that the potential increased during the first 20 min as the temperature increased to 200 °C, and then decreased over the next 40 min, and finally it became progressively stable. This phenomenon proves that the ionic solid conductivity of metal–oxide ZrO2 is often affected by the variation of temperature. If the electrode is used in field observations, it will be necessary to perform calibration tests (for instance, prepare pH buffer solutions). Moreover, it would also be necessary to monitor the response of the cell potential with elapsed time to establish when the cell becomes stable, as shown in Fig. 7.

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The theoretical prediction with actual electrochemical measurements under the same chemical and physical conditions, which reveals a good agreement between the measured \(\Delta E(V)_{T,P}\) and the theoretically calculated sensor potential \(\langle \Delta E(V)_{T,P,calc}\rangle\) (Fig. 5b).

As shown in Fig. 6, the measured cell potential values of the Zr/ZrO2 sensor at 200 °C, \(\Delta E_{T,P}\), are plotted against the calculated pH values at higher temperatures and pressures, \(pH_{T,P}\), reveals excellent linearity between \(\Delta E_{T,P}\) and \(pH_{T,P}\) at 200 °C.

One way to view the viability of the Zr/ZrO2-pH response is to examine and evaluate the slope of the plot of measured \(\Delta E(V)_{T,P}\) versus corresponding changes in pH (in situ) of the test solution. As the slope is consistent with the theoretical Nernst slope, the Zr/ZrO2-pH response is true and accurate.

For a pH sensor at equilibrium, the Nernst equation predicts that the slope of the potential versus pH plot should be \(2.303 \times \frac{R}{F}\) at 20 °C, \(58.1 \text{ mV}\) at 20 °C and \(-94.3 \text{ mV}\) at 200 °C. This study reports a new method for preparing a Zr/ZrO2 electrode using melting Na2CO3, and suggests that the Zr/ZrO2 electrode with a sealed structure has application in situ measurements of pH for high temperature and high-pressure aqueous solutions (Fig. 2). Also, the electrochemical experiments demonstrate that the cell potential of the Zr/ZrO2 electrode responds to changes in the pH of the fluids at temperatures from 20 to 200 °C. However, compliance with the Nernstian equation has been demonstrated in principle. The Zr/ZrO2 electrode can be exactly calibrated using the theoretical prediction of the NaCl–HCl–H2O solution.
trodes, low flow rates will prevent equilibrium with the test solution from being reached over a short time (Fig. 8). Since the Zr/ZrO₂ sensor in solution is not strictly a complete equilibrium system, but rather displays a mixed potential resulting from a balance between a partial anodic process \( \text{Zr} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 4\text{H}^+ + 4\text{e}^- \) and a partial cathodic reaction \( \text{e}^- + \text{H}^+ \rightarrow \frac{1}{2}\text{H}_2 \) occurring at the sensor surface [9,15]. The occurrence of an electrochemical reaction in the Zr/ZrO₂ couple or ZrO₂ tube (or YSZ tube) has previously been reported [1,34].

3.2. Characterization of ZrO₂ thin films

As mentioned above, we found two kinds of ZrO₂ thin films on the Zr wires. Some of these ZrO₂ films are used for making good electrodes (type 1), while the usefulness of the others has still to be identified (type 2). The short time period for the melting method is considered better to fabricate good electrodes (type 1).

We analyzed the Zr/ZrO₂ interface structures of those electrodes, and simultaneously tested the sensor sensitivity to the pH of the fluids, then found the electrochemical nature of the electrodes are dependent on the characteristics of the ZrO₂ thin films on the Zr wire. This work helps us to optimize the methods and techniques to produce a good ZrO₂ film for making a high temperature sensor.

The structural characteristics of the Zr/ZrO₂ interface for type 1 are different from those of type 2 (Fig. 9). An EPMA study indicates that the type 1 Zr/ZrO₂ interface is composed of a ZrO₂ zone and an oxygen-rich Zr metal zone on the Zr surface. The component image shows that the ZrO₂ zone in the Zr/ZrO₂ interface is about 20 μm thick, as shown in Fig. 9a. The topographical image shows a film of 40 μm thickness (ZrO₂ zone and oxygen-rich Zr metal zone) was formed on the Zr metal surface, as shown in Fig. 9d.

Additional observations of the cathode luminance of the ZrO₂ zone indicate that it consists of two different parts, an outer part and an inner part. The outer part of the ZrO₂ zone exhibits a very strong luminance. Moreover, the cathode luminance image of the ZrO₂ zone shows that the outer part is the brightest part and corresponds to the oxygen-rich ZrO₂, which characterizes a dense and continuous film.

The inner ZrO₂ zone has a relatively weak cathode luminance, characteristic of low oxygen density, see Fig. 9c. Second electron images show that the Zr–ZrO₂ interface (thin ZrO₂ films on the Zr surface) is divided into five zones. See Fig. 9b and Table 1.

Fig. 9 shows that the type 2 Zr/ZrO₂ interface is different from that of the type 1 Zr/ZrO₂ interface. The component image of the cross-section of the type 2 Zr/ZrO₂ interface shows that the thin film is about 50 μm thick. A TOPO image of the type 2 Zr/ZrO₂ interface is also wider than that of the type 1 Zr/ZrO₂ interface by about 50 μm. A second electron image of the cross-section of the thin films having the type 2 Zr/ZrO₂ interface can be divided into five zones, but their thicknesses are different from those of type 1 (See Fig. 10 and Table 1).
A topography change from the outer part to the inner part in the Zr–ZrO₂ interface was observed using SEM. The SEM micrographs reveal that the outer part of the ZrO₂ zone comprises good prismatic crystals of ZrO₂, which are fibrous and vertically disposed throughout the interface. However, in the inner part, the prismatic crystals of ZrO₂ are not as well developed (Fig. 1).

The results of EPMA and SEM indicate that the content of oxygen decreases in the profile from the outermost zone to the center of the fresh Zr metal wire, and the content of zirconium increases simultaneously. Fig. 10a and b shows that the element concentrations of Zr and O change with depth up to 100 nm. And the interface of the Zr/ZrO₂ electrode is divided into five zones: (1) prismatic and oxygen-rich ZrO₂; (2) ZrO₂ zone; (3) oxygen-rich Zr metal; (4) oxygen-bearing Zr metal; and (5) Zr metal. These analyses indicate that the zoning structure of the Zr/ZrO₂ interface is originated from the variation of oxidation state of the metal and oxygen density. See Table 1.

For the Zr/ZrO₂ interface structure for type 1: the first zone, oxygen-rich ZrO₂ zone comprises good prismatic crystals and contains oxygen 38–32% (wt), and Zr (59.38–65.9%), where the O/Zr atomic ratio ranges from 3.45 to 2.6, and the thickness of the Zr/ZrO₂ interface structure is of the order of 8–10 μm (See Table 1). The second ZrO₂ zone contains oxygen 30.6–27.5%, and Zr is 67.06–70.2%, and comprises crystals, of which the prismatic crystalline form is not well developed. The O/Zr atomic ratio of the second ZrO₂ zone ranges from 2.56 to 2.2, and the thickness of the structure is of the order of 8–10 μm.

The third zone, oxygen-rich Zr metal, contains oxygen 7.5–2% and Zr 89–94%, and an O/Zr atomic ratio which ranges from about 0.4 to 0.1, with thickness of 15 μm. The three zones all demonstrate a reasonable hardness. The fourth zone of oxygen-rich Zr metal has an oxygen content of <2%, and an O/Zr atomic ratio which ranges from 0.09 to 0.01, with thickness of 8 μm. The fifth zone of Zr metal was found to have no oxygen content.

### Table 1

<table>
<thead>
<tr>
<th>Zr/ZrO₂ Distance from the surface (μm)</th>
<th>Thickness (μm)</th>
<th>Zr (wt%)</th>
<th>Hf (wt%)</th>
<th>Oxygen (wt%)</th>
<th>O/Zr ratio</th>
<th>Crystalline</th>
<th>Cathode luminescence</th>
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<tbody>
<tr>
<td>Zr/ZrO₂ interface structure of good electrode (type 1)</td>
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<tr>
<td>1. ZrO₂</td>
<td>0–10</td>
<td>~10</td>
<td>59.3–65.9</td>
<td>1.8–2.0</td>
<td>38–32</td>
<td>3.45–2.6 average 2.89</td>
<td>Prismatic crystal</td>
</tr>
<tr>
<td>2. ZrO₂</td>
<td>10–20</td>
<td>10</td>
<td>67.1–70.2 (at 75 boundary)</td>
<td>2.0–2.1</td>
<td>30.6–27.4</td>
<td>2.56–2.2</td>
<td>Weak</td>
</tr>
<tr>
<td>3. ZrO₂</td>
<td>20–35</td>
<td>15</td>
<td>89.7–94.0</td>
<td>2.3–2.9</td>
<td>22.6–2</td>
<td>1.68–0.4 0.4–0.1</td>
<td></td>
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<tr>
<td>4. O-rich Zr</td>
<td>25–45</td>
<td>~15</td>
<td>89.2(91)–93.9</td>
<td>&gt;94.9</td>
<td>0.27–0</td>
<td>0.09–0.1, to 0</td>
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<td>5. Zr</td>
<td>&gt;53</td>
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<td>Zr/ZrO₂ interface structure of bad electrode (type 2)</td>
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<tr>
<td>1. ZrO₂</td>
<td>0–10</td>
<td>10</td>
<td>73.2–70.9</td>
<td>2.3–2</td>
<td>24–27</td>
<td>1.86–2.18</td>
<td>Not well-developed prismatic crystal</td>
</tr>
<tr>
<td>2. ZrO₂</td>
<td>10–25</td>
<td>15</td>
<td>70.4–91.1</td>
<td>1.9–2.7</td>
<td>26.8–6</td>
<td>2.19–0.6</td>
<td>Weak</td>
</tr>
<tr>
<td>3. O-rich Zr</td>
<td>25–45</td>
<td>20</td>
<td>89.2(91)–93.9</td>
<td>2.5(2.7) 2.9</td>
<td>8.1 to –2.9</td>
<td>0.6–0.1</td>
<td></td>
</tr>
<tr>
<td>4. O-bearing Zr</td>
<td>45–53</td>
<td>9</td>
<td>0.27–0</td>
<td>0.27–0</td>
<td>0.19–0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Zr</td>
<td>&gt;53</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes:

* The electric probe has RSD1% for metal elements.
* The high value of O/Zr is only present at surface, at <20 nm depth. We have standard sample of ZrO₂ for probe analysis, and those metal analyses are accurate. And also, we repeat probe analyses three times for contents of those elements. In addition, XPS spectrum analyses indicate that the first zone is rich in oxygen. Hf is HfO₂ form.
Fig. 10. EPMA second electron image of the cross-section of type 1 and type 2 of ZrO₂ thin films: from the outmost zone to the center, Zr–ZrO₂ interface are divided into five zones: (1) oxygen-rich ZrO₂; (2) ZrO₂ zone; (3) oxygen-rich Zr metal; (4) oxygen-bearing Zr metal; (5) Zr metal. (a) Zr–ZrO₂ interface type 1; (b) Zr–ZrO₂ interface type 2. It is found that Zr content in type 1 oxygen-rich ZrO₂ film is lower than them in the type 2 (relative analytical deviation for ZrO₂, RSD is about 1–5% as oxide content range 50–20%). It indicates RSD is about 1%, if the oxide content is more than 50%.

For the type 2 structure, the first zone in the Zr/ZrO₂ interface does not comprise prismatic crystals and contains lower oxygen (24–27%), and Zr 73.23 (73.01)–70.91% contents, where the O/Zr atomic ratio ranges from 1.86 to 2.18. See Fig. 1e and f. The second ZrO₂ zone contains about 27% oxygen, and 70.5% Zr, and an O/Zr atomic ratio of 2.1. The thicknesses of these zones are larger than those of type 1. The thicknesses of the O-rich Zr zone and O-bearing Zr zone for type 2 are wider than those of type 1 (see Table 1). It is found that the ZrO₂ film of type 2 is more rich in Zr than that of type 1.

HRTEM images of the crystal lattices of the ZrO₂ films (type 1) show that the oxygen-rich ZrO₂ thin films are constructed of nanometer-sized crystals (about 50–100 nm), as shown as Fig. 11. Such thin films are characterized by their very stable chemical and mechanic properties brought about by the tightly packed crystal particles, thereby protecting against erosion. The distance between the crystal planes is 3.7 Å, which is good agreement with the (0 1 1) plane of monoclinic class, based on which the crystal system of ZrO₂ is considered to belong to. The distance of another important crystal plane (1 1 1) was calculated to be 3.16 Å [35].

In addition, the TEY (total electron-yield) EXAFS (extended X-ray absorption fine structure) method for measuring current is a new and sensitive technique that employs synchrotron radiation. The TEY-EXAFS method is good for testing the ZrO₂ film on the Zr wire thread. Experimental observation using the TEY-EXAFS method proves that the ZrO₂ thin film belongs to the monoclinic class. See Appendix A.

3.3. Nature of ZrO₂ thin film

Properties of the Zr/ZrO₂ electrode originate from the nanometer-sized structure of the ZrO₂ thin film (type 1). It has previously been reported that cathode luminescence is related to the presence of defects in the solid (metal and silicate) structure. Theoretically, cathode luminescence is also considered to occur as a result of defects in the solid structure. These defects may be dislocations or other structural defects, vacancies or non-stoichiometry [36,37].

The brightest part of the cathode luminescence image for the ZrO₂ zone is the oxygen-rich ZrO₂ zone (Fig. 9). The bright part on the rim is about 5–10 µm in width, which corresponds to the width of the oxygen–rich ZrO₂ (the width of a good column crystal ZrO₂, type 1). In addition, this part is characterized as having a high O/Zr atomic ratio and a high oxygen content (Table 1). The bright part of the cathode luminescence for type 2 is not continuous, and is usually 5 µm in width.

3.3.1. Oxygen-rich ZrO₂ film and point defects

The O/Zr atomic ratio in the oxygen-rich ZrO₂ film is more than 2, which indicates non-stoichiometry. An XPS (Thermo VG Scientific Co. Sigma Probe) study of the oxygen-rich ZrO₂ film indicates that the oxygen bonding of ZrO₂ belongs to negatively charged bivalence oxygen. Previous reports suggest that oxygen in the
after etch by Ar ion scattering; (c) O1s binding energies of type 1 ZrO2 film, before and after scattering with Ar ion, and O1s in type 2 ZrO2 film. These binding energies are approximately similar. After scattering the surface with Ar ion, spectra for type 1 and type 2 ZrO2 film exhibit both one Zr3d peak.

Fig. 12. Binding energy of Zr and O of ZrO2 film based on XPS spectrum analyses. (a) Zr3d of the type 1 ZrO2 film, comparing with them of type 2; (b) Zr3d of ZrO2 film after etch by Ar ion scattering; (c) O1s binding energies of type 1 ZrO2 film, before and after scattering with Ar ion, and O1s in type 2 ZrO2 film. These binding energies are approximately similar. After scattering the surface with Ar ion, spectra for type 1 and type 2 ZrO2 film exhibit both one Zr3d peak.

An analysis of the XPS spectrum for an area of the 100 \( \mu \text{m} \times 100 \mu \text{m} \) shows that the Zr3d binding energy for the type 1 ZrO2 film is about 182.47 eV, and the observed values are similar to that value, as depicted in Fig. 12b.

Fig. 12a shows that the Zr3d binding energy value and its electric signal intensity in the type 1 ZrO2 film was found to be different from that of the type 2 ZrO2 film. The Zr3d binding energy for the type 1 ZrO2 film is characterized by a high electric signal. On the other hand, the Zr3d binding energy for the type 2 ZrO2 film is relatively high conductivity, and thus its signal is weak and the peak for the Zr3d binding energy is split as Zr3d5/2 and Zr3d3/2. It is considered that the difference in conductivity indicates that the type 1 ZrO2 film is tight and has an excess of zirconium ion site vacancies, therefore leading to a low conductivity. In contrast, the type 2 ZrO2 film is not tight or asymmetric (Fig. 9), and has a higher Zr content than the type 1 ZrO2 film (Table 1), particularly where the O/Zr atomic ratio is <2.

The O/Zr atomic ratios were obtained from analyses of the corresponding XPS spectra, which are calculated based on the peak area of the O1s/(Zr3d + Zr3p1 + Zr3p3) signal. The XPS spectrum indicates that the O/Zr atomic ratios of the type 1 ZrO2 film are larger than the O/Zr atomic ratios of the type 2 ZrO2 film. An analysis of the XPS spectrum for an area of the 100 \( \mu \text{m} \times 100 \mu \text{m} \) shows that the O/Zr atomic ratio is about 2.5. After scattering the surface of the ZrO2 film with Ar ions for 6–10 min, the ZrO2 film surface was etched to 20 nm depth, and the XPS analyses indicate that the O/Zr atomic ratio is about 2.05. It is considered that the high O/Zr atomic ratio is present at the surface layer of the ZrO2 film within 20 nm, where the Zr content is about 60 wt% (see Table 1).

Analyses of the XPS spectrum for the type 2 ZrO2 film indicate that the O/Zr atomic ratios at the surface are not uniform. The O/Zr atomic ratios in some parts are lower than 2, while at other parts of the surface are more than 2. After Ar ion scattering, the O/Zr atomic ratios of the etched surface are close to 2.

Probe analyses also indicate that the Zr metal zone of the Zr/ZrO2 interface is rich in oxygen. As shown in Fig. 9d, the TOPO image of the Zr/ZrO2 interface reveals that the ZrO2 zone and oxygen-rich Zr zone are both 35 \( \mu \text{m} \) in width, and both demonstrate nearly the same high rigidity, which is different from fresh Zr metal. Results prove that the oxygen-rich Zr metal is not like pure Zr metal, as shown in Fig. 9d. If oxygen adopts a molecular form in the oxygen-rich Zr metal, it would not behave with the same high rigidity.

When the O/Zr atomic ratio is more than 2, a number of Zr\(^{4+}\) ion vacancies are present in the ZrO2 film, introducing point defects. This might be the case where Zr\(^{4+}\) ions are missing, and the extra negative charges are introduced into the structure. To maintain a charge balance, a vacancy might be created where Zr\(^{4+}\) would be located. Again, four O\(^{2-}\) anions would be converted to four O\(^{-}\) anions. It is assumed that the charge balance must be maintained so that the crystalline material as a whole is electrical neutral [1]. The charge would have to be balanced with an O\(^{-}\) on the O\(^{2-}\) site in the ZrO2 film. It is considered that this situation would have happened in the ZrO2 film which is an ionic solid.

As this assumption is understood to be correct, it is suitable to infer that the cathode luminescence image for the type 1 ZrO2 film is stronger than that for the type 2 ZrO2 film. Because, electrons from the cathode ray contact the point defects in the surface of the oxygen-rich ZrO2 zone, i.e., from vacancies and non-stoichiometry, then this would produce a strong bright light.

\[
\text{O}^- + e^- \rightarrow O^{2-} + (\text{Zr}_{(1-x)} \text{O}_2) \quad (5)
\]

A continuous, dense and thick ZrO2 film (type 1) in the metal-to-metal oxide interface is important to make a high temperature and pressure chemical sensor, for instance a pH sensor. As usual, in the first step, H\(^+\) is adsorbed on the surface of the Zr/ZrO2 electrode, and these H\(^+\) then pass through the ZrO2 film if the oxygen-rich ZrO2 film is not in its molecular form in the adsorption state [35].
ZrO₂ film is continuous, resulting in the following electrochemical reaction which would occur continuously:

\[ 4H^+ + 4e^- + ZrO_2 \rightarrow Zr + 2H_2O \quad (6-1) \]

This oxidation-reduction reaction is a normal electrode reaction.

Because the O/Zr atomic ratio is higher than 2, more negative bivalence oxygen anions are present in the metal, and more Zr⁴⁺ ion vacancies occur in the metal. This reaction would easily occur in this way:

\[ 4H^+ + (4 - 4x)e^- + [Zr(1-x)O_2]_{(O-rich ZrO_2)} \rightarrow Zr(1-x) + 2H_2O \quad (6-2) \]

where Zr(1-x)O₂(0-rich ZrO₂) refers to the oxygen-rich ZrO₂ film.

As mentioned above, Eq. (6-2) is the anodic reaction process (Zr + 2H₂O → ZrO₂ + 4H⁺ + 4e⁻). And reaction Eq. (7) also occurred at the ZrO₂ film [2,38].

\[ H_2O = 2H^+ (aq) + \left[ O_2^-_{(Zr(1-x)O_2)} \right] \quad (7) \]

In addition, the potential determined on the Zr(1-x)O₂(0-rich ZrO₂) film was attributed to the equilibria of Eqs. (5), (6-1), (6-2) and (7).

Briefly, the Zr₁₋ₓO₂/Zr cell potential is stable and corresponds linearly with pH variations. Oppositely, in other cases (type 2), as oxygen in air takes an important role in the oxidation of the Zr surface, the oxygen diffuses deeper into the Zr metal. And the oxygen in the ZrO₂ film (type 2) is not continuous and not dense. When H⁺ passed through the ZrO₂ film, if the oxygen distribution in the ZrO₂ film is not continuous, the above electrochemical reaction would not occur in such media of the ZrO₂ film. Particularly, if the O/Zr atomic ratio in the ZrO₂ zone is <2, such as that in the type 2 ZrO₂ film where there is no Zr⁴⁺ ion vacancy. Alternatively, where there are extra positive charges in the metal and the oxygen density is low, then reactions (6-1) and (6-2) would not occur easily. Therefore, the cell potential would not be stable and would not respond linearly with pH variations. And this kind of Zr/ZrO₂ is not good for electrodes.

These differences in the electrochemical property and structure between type 1 and type 2 ZrO₂ films are derived from the differences in film formation. When the Zr wire was oxidized by Na₂CO₃ melt, high-density oxygen was adsorbed at the Zr surface, thereby oxidizing the Zr surface. Thus, a solid continuous oxygen-rich ZrO₂ film formed at the Zr metal. Oppositely, when Zr wire was heated in O₂ air, low-density oxygen was adsorbed onto the Zr surface, and the Zr was oxidized slowly resulting in the type 2 ZrO₂ film.

4. Conclusion

The use of a Na₂CO₃ melt for oxidation of Zr to form a thin ZrO₂ film on the metal surface was found to be a good method for making Zr/ZrO₂ electrodes. Controlling the oxidation condition, we obtain dense, continuous nanostructured ZrO₂ films on the metal surface having adequate thickness. The resultant nanostructured ZrO₂ film is an oxygen-rich ZrO₂ film.

The experimental measurements of the Zr/ZrO₂ sensor potential against an Ag/AgCl reference electrode indicate that the sensor potential responds linearly with the pH of NaCl-HCl-H₂O (and NaCl-NaOH-H₂O) over a wide range at temperatures from 20 to 200 °C. The slope of the potential versus pH plot at 200 °C is close to the theoretical value of the Nernst slope for the test solution at electrochemical equilibrium.

The fabricated Zr/ZrO₂ sensors can be accurately calibrated and applied under high temperature and pressure conditions. The Zr/ZrO₂ sensor is expected to find use for in situ measurement of pH in aqueous fluids in nature, in laboratories and in industrial processes over a wide temperature range, especially for hydrothermal vent fluids at mid-ocean ridges without the limitations associated with the YSZ-pH sensors currently available.

Acknowledgements

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Appendix A. Appendix

TEY (total electron-yield current measurement) method is one of the new developments for near surface EXAFS (extended X-ray absorption fine structure) experiment by using synchrotron radiation facilities. TEY method is good for testing the ZrO₂ film on thread of Zr. The XAFS were measured on beam-line 4W1B 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. Synchronzation radiation from the storage ring was monochromatized by Si (1 1 1) double crystal. The coating of ZrO₂ 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 ZrO₂ thin film are at 18,028 ev. Theoretical calculation absorption spectra of ZrO₂ indicate that the crystal systems of ZrO₂ thin film are monoclinic class [35]. 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).

References
