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Hydrothermal Zirconia Powders: A Bibliography

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Abstract

This paper provides references for zirconia powder processing, especially hydrothermal processing and for the properties of hydrothermal zirconia. © 1998 Elsevier Science Limited. All rights reserved

Keywords: ZrO_2, powders: chemical preparation, hydrothermal powders

1 Introduction

In recent decades there has been great emphasis on the benefits which are provided by attention to powder quality in there processing of ceramics.[1–9] Over the same period, there has been widespread recognition of the promise of zirconia for a wide range of applications.[10–16] For some of these, high purity source materials are required.[17–22]

2 Zirconia powders

Methods for the preparation of fine zirconia grains are shown in Table 1.[17–28]

3 Hydrothermal synthesis

Procedures for hydrothermal synthesis and indications of the benefit of the materials have been frequently reviewed.[1,17–52]The major differences between hydrothermal processing and other technologies are shown in Table 2.[1,30,52] The subdivision of such synthesis are shown in Table 3. [20]

4 Hydrothermal zirconia

Since 1960, publications have appeared in the application of hydrothermal synthesis to zirconia. [30,53–61]

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There are several methods to prepare zirconia powder under hydrothermal condition, including (1) hydrothermal oxidation; (2) hydrothermal crystallization; (3) hydrothermal decomposition; (4) hydrothermal homogeneous precipitation; and (5) the reactive electrode submerged are process.

4.1 Hydrothermal oxidation[23,24,62]

Starting materials are zirconium metal clip and/or powder and water or solution of Ca, Mg, or Y in nitrate or chrolide form. Schematic illustration is shown in Figs 1 and 2.

Below 200°C, there is no reaction between Zr metal and water; at 300°C there is formation of hydride, above 400°C, Zr hydride decomposes to form the oxide and hydrogen. Microstructure of zirconia powder by this method is shown in Fig. 3. Solution of Y, Ca, or Mg nitrate allows the preparation of the stabilized zirconia. Reaction of zirconium and water is as follows:

$$2Zr + 2H_2O \xrightarrow{300^\circ C} ZrH_2 + ZrO_2 + H_2 \rightarrow ZrH_2Zr + H_2,$$

$$ZrH_2 + 2H_2O \xrightarrow{>400^\circ C} ZrO_2 + 3H_2$$

4.2 Hydrothermal crystallization[62]

Starting material was hydrous zirconia prepared from $ZrCI_4$ solution with 3N NH_4OH, filtered, dispersed in distilled water and refiltered. The precipitate is dried at 120°C for 48 h. Distilled water and solution of salts are used as mineralizers. Figures 4–6, and Table 4 indicate the results from hydrothermal crystallization.

4.3 Hydrothermal decomposition

P. Reynen *et al.*[58] have described the conditions for this process as listed in Table 5. The associated chemical reaction is as follows:

Table 1. Methods for fine ZrO_2 grain (revision by Sōmiya)

1. Mechanical (Powder mixing)	a. Ball milling b. Attrition milling c. Vibration milling	Refs 17–22
2. Thermal decomposition	a. Heating (evaporation) b. Spray drying c. Flame spraying d. Plasma spraying e. Vapor phase (CVD) f. Freeze drying (cryochemical) g. Hot kerosene drying h. Hot petroleum drying	Refs 16–22
3. Precipitation or hydrolysis	a. Neutralization and precipitation b. Homogeneous precipitation c. Coprecipitation d. Salts solution c. Alkoxides f. Sol–gel	Refs 17–22
4. Hydrothermal	a. Precipitation (coprecipitation) b. Crystallization c. Decomposition d. Oxidation e. Synthesis f. Electrochemical g. Mechanochemical h. RESA (reactive electrode submerged arc)	Refs 23,24
	Hydrothermal + microwave	Refs 25–27
	Hydrothermal + ultrasonic	Ref 27
5. Melting and rapid quenching		Refs 17–22

Table 2.
Major differences between hydrothermal processing and the other technology

1.	Powders are formed directly from solution.
2.	Powders are anhydrous, crystalline or amorphous. It depends on producing of hydiothermal powder temperature.
3.	It is able to control particle size by hydrothermal temperature.
4.	It is able to control particle shape by starting materials.
5.	It is able to control chemical, composition, stichometry, etc.
6.	Powders are highly reactive in sintering.
7.	Many cases, powders do not need calcination.
8.	Many cases, powders do not need milling process.

Main sources: Refs 1,8,49,50

Table 3. Hydrothermal Synthesis [17–22]

Hydrothermal crystal growth
Hydrothermal treatment
Hydrothermal alternation
Hydrothermal dehydration
Hydrothermal extraction
Hydrothermal reaction sintering
Hydrothermal sintering corrosion reaction
Hydrothermal oxidation
Hydrothermal precipitation
Hydrothermal crystallization
Hydrothermal decomposition
Hydrothermal hydrolysis-hydrothermal precipitation
Hydrothermal electrochemical reaction
Hydrothermal mechanochemical reaction
Hydrothermal + ultrasonic[25–27]
Hydrothermal + microwave[25–27]

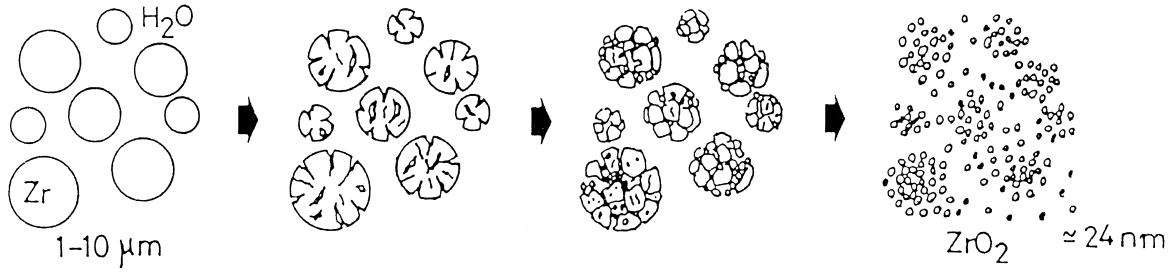

Fig. 1. Schematic illustration of hydrothen-nal oxidation of zirconia powder.[20]

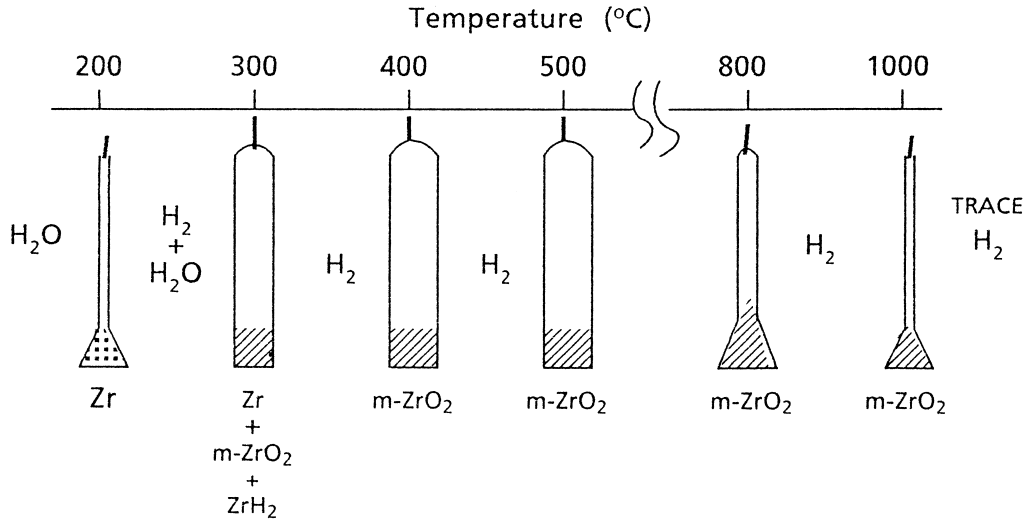

Fig. 2. Schematic illustration of the processes in the hydrothermal oxidation for monoclinic ZrO_2 powder under 1000 kg cm^{-2} in Pt capsule and hydrothermal reaction sintering for ZrO_2 (Ref. 20).

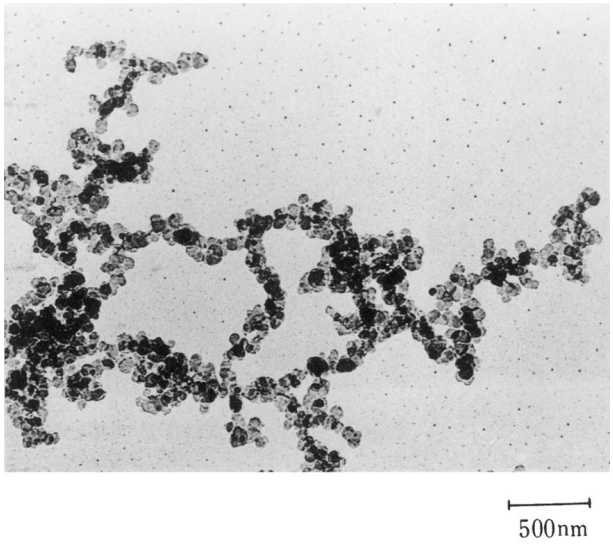

Fig. 3. Microstructure of zirconia by hydrothermal oxidation.[23,24]

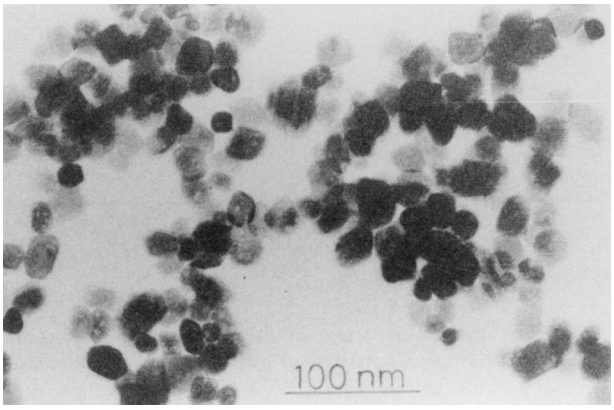

Fig. 4. Transmission electron micrograph of monoclinic ZrO_2 produced by hydrothermal crystallization at 400°C under 100 MPa for 24 h using 8 wt% KF solution.[62]

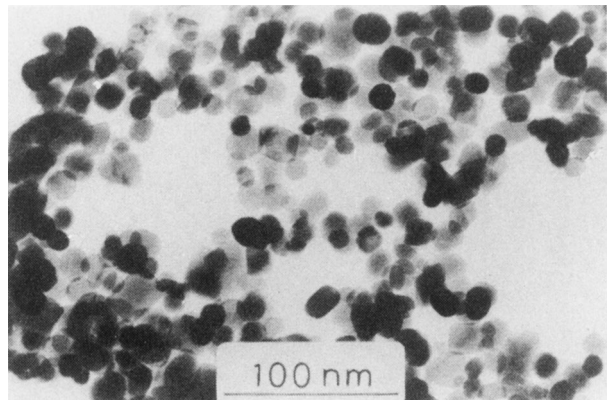

Fig. 5. Transmission electron micrograph of tetragonal (70%) and monoclinic (30%) ZrO_2 powders produced by hydrothermal crystallization at 300°C under 100 MPa for 24 h using 15 wt% LiCl solution.[62]

Table 4. Phases present and crystallise size products hydrothermally crystallized at 100 MPa for 24 h[62]

Mineralizer	Temperature (°C)	Average crystallite size (nm)	
		Tetragonal ZrO_2 (nm)	Monoclinic ZrO_2(nm)
KF (8 wt%)	200	Not detected	16
KF (8 wt%)	300	Not detected	20
NaOH (30 wt%)	300	Not detected	40
H_20	300	15	17
LiCI (15 wt%)	300	15	19
KBi. (10 wt%)	300	13	15

Table 5. Hydrothermal decomposition (after Ref. 58)

$ZrSiO_4$	18·43 wt%
$Ca(OH)_2$	14.9
NaOH	4.67
H_2O	62
Liquid/solid ratio	2
NaOH concentration in the solution	7 wt%
Mol ratio $Ca(OH)_2/ZrSiO_4$	2
Temperature	350°C
Vapor pressure	170×10^5 Pa
Reaction time	8 h

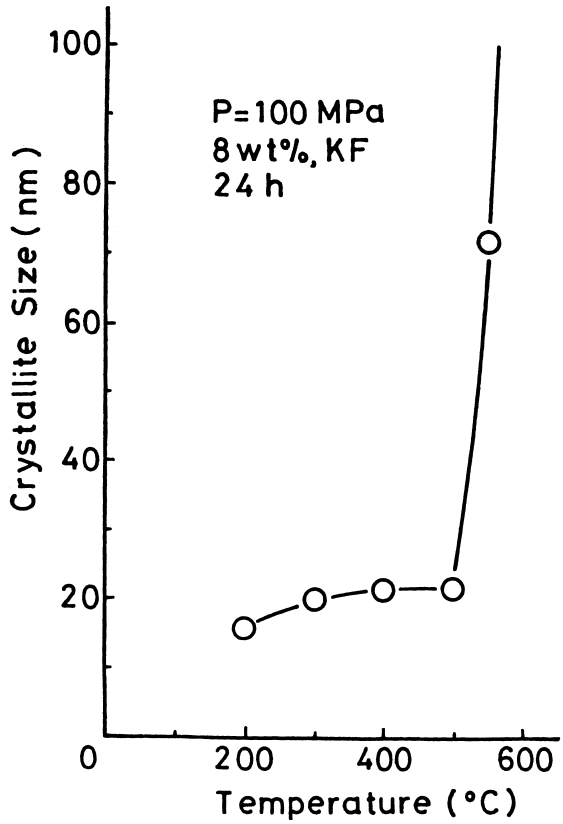

Fig. 6. Variation with temperature of crystallite size of monoclinic ZrO_2 produced by hydrothermal crystallization under 100 MPa for 24 h using 8 wt% KF solution.[62]

Table 6. Typical characteristics[65]

Powder		ZY30	ZY80	ZP20
Chemical composition	ZrO_2 (wt%)	94·7	86·0	> 99·9
	Y_2O_3	5·2	13·9	—
	$A1_2O_3$	0·010	0·010	0·005
	SiO_2	0·010	0·010	0·005
	Fe_2O_3	0·005	0·005	0·005
	Na_2O	0·001	0·001	0·001
	Cl^-	< 0·0 1	< 0·01	< 0·01
	Ignition loss	1·5	1·5	8·0
Crystallite size	(nm)	22	22	20
Average particle size[a]	(μm)	0·5	0·5	1·5
Specific surface area[b]	($m^2\,g^{-1}$)	20	25	95
Sintered Specimens		1400°C×2 h	1500°C×2 h	
Bulk density	($g\,cm^{-3}$)	6·05	5·85	
Bending strength[c]	(MPa)	1000	300	
Fracture toughness[d]	($MPam^{1/2}$)	6·0	2·5	
Vicker's hardness	(GPa)	12·5	11·0	
Thermal expansion	20~1000°C(×10^{-6}/°C)	11·0	10·6	

[a]Photo Sedimentation Method.
[b]B.E.T. Method(N2).
[c]3-point Bending Method.
[d]M.I.Method.

$$ZrSiO_4 + xCa(OH)_2 \rightarrow$$
$$ZrO_2 + xCaO.SiO_2 \cdot H_2O + (x-1)H_2O$$

4.4 Hydrothermal homogeneous precipitation [63–65]

Hydrothermal homogeneous precipitation yields fine zirconia powders by the process shown in

Table 7. Characteristics of zirconia powder by hydrothermal homogeneous precipitation[20]

1. Homogeneous
2. Grain size—fine grain
3. Coagulation not aguloration
4. Crystallinity
5. Flow ability—forming
6. Sinterability
7. No pore in grain

Fig. 7. Pictures of powders by TEM is shown in Fig. 8. Properties of these single crystals and/or soft agglomerated powders are shown in Table 6. Characteristics Of Y_20_3 containing ZrO_2 prepared by hydrothermal homogeneous precipitation are shown in Table 7. Microstructure and characteristics of sintered body are shown in Fig. 8 and in Table 7, respectively. Grain size of the fully dense sintered body produced from powders prepared by hydrothermal homogeneous precipitation is as small as 2–5 μm. This hydrothermal powder of zirconia is very close to an ideal powder with properties listed in Table 8.

4.5 RESA[23,24]

RESA: The reactive electrode submerged arc process for making fine oxide and non-oxide powders (10–1000 nm) have been developed by

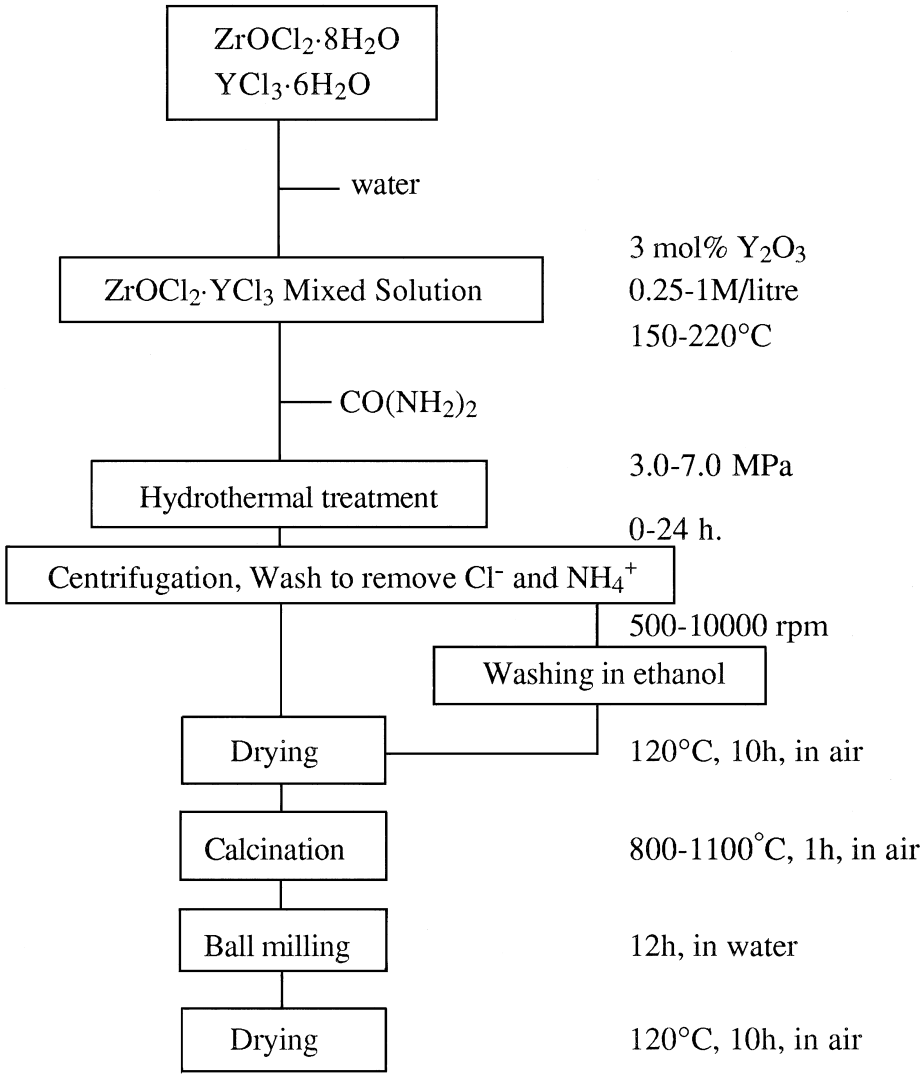

Fig. 7. Processing flow sheet of the hydrothermal homogeneous precipitation method.[65]

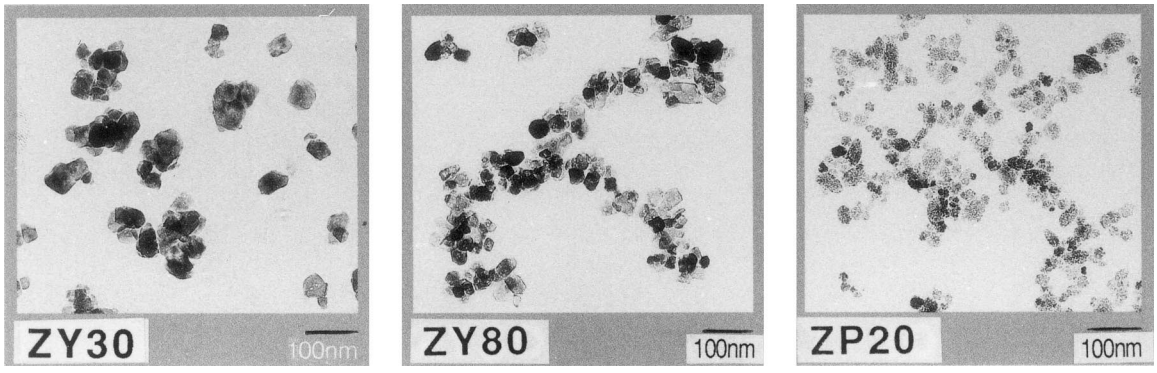

Fig. 8. Microstructure of hydrothermal homogeneous precipitation zirconia.[65]

Table 8. Ideal powder[20]

1. Fine powder less than lμm
2. Soft or no agglomeration
3. Narrow particle size distribution
4. Morphology, sphere
5. Chemical composition controllable
6. Microstructure controllable
7. Uniformity
8. Free flowing
9. Less defects, dense particle
10. Less stress
11. Reactivity, sinterability
12. Crystallinity
13. Reproducibility
14. Process controllable

Kumar and Roy.[23,24] The arc provides a region of high temperature and high pressure in a short time.

4.6 Microwave–hydrothermal method[25–27]

Komaneri *et al.* have reported the microwave–hydrothermal synthesis of ceramic powders. They used concentrations of $ZrOC1_2{\cdot}8H_2O$ such as 0·5 and/or 1 Mol and temperatures of 164 and 194°C.

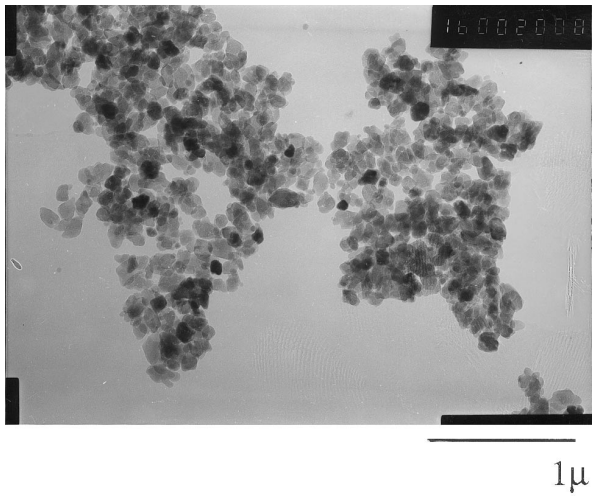

Fig. 9. Microstructure of zirconia powder by hydrothermal homogeneous precipitation at 200°C under 6·3 MPa for 24 h.[65]

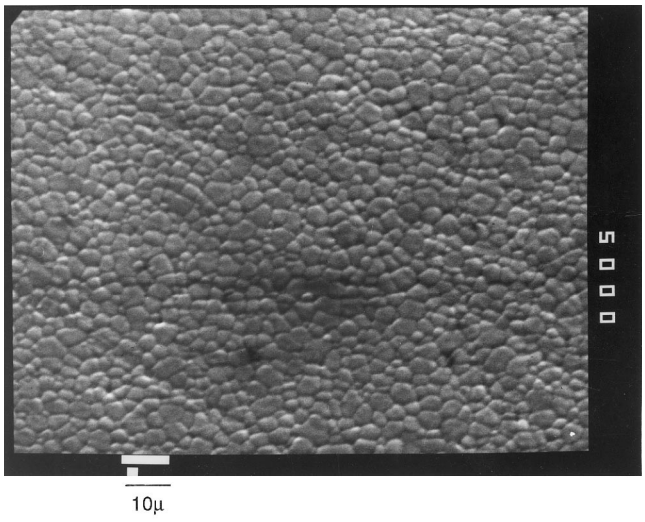

Fig. 10. Microstructure of the sintered zirconia, Y_2O_3 mol %, 1400°C, 2 h, (calcined at 1000°C for 1 h).[65]

Duration times were very short. The yielded crystalline powder was monoclinic ZrO_2.

4.7 Hydrothermal electrochemical method[28]

Zirconium metal plate is used as a working electrode (anode). Anodic oxidation is conducted in 200 ml of $Y(NO_3)_3$ solution using a platinum plate as counter electrode and reference electrode. A ZrO_2 film is formed on the Zr metal plate. As low as 250°C with a voltage of 4·5 V or less, and pH of less than 5, there was formation of ZrO_2 on the surface of Zr metal.

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