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Preparation of ThO_2/Y_2O_3 Powders by the Sol–Gel Method for Solid Electrolytes

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Abstract

Stable Th/Y oxide sols were prepared by peptization of the washed hydroxides and converted by different solidification methods to sinterable ThO_2/Y_2O_3 powders which were compared with coprecipitated ThO_2/Y_2O_3 powder. The best powder properties were obtained if the Th/Y oxide sol was solidified by internal gelation. Slip casting and subsequent cold isostatic pressing of the sol–gel-derived powder resulted in densities of sintered crucibles or plates of 98·8%, direct cold isostatic pressing in 99·5% of the theoretical density. EMF measurements using sol–gel-derived ThO_2/Y_2O_3 plates gave results which agreed with data from measurements using ZrO_2/Y_2O_3 solid electrolytes and with literature data.

Stabile Th/Y-Oxidsole wurden durch Peptisierung der gewaschenen Hydroxide hergestellt und mit unterschiedlichen Gelierungsmethoden in sinterfähige Pulver überführt, die dann mit gemeinsam gefällten ThO_2/Y_2O_3-Pulvern verglichen wurden. Die besten Pulvereigenschaften ergaben sich, wenn das Sol durch innere Gelierung verfestigt wurde. Schlickerguß und nachfolgende kaltisostatische Verdichtung der kolloidchemisch hergestellten Pulver führte zu Dichten gesinterter Tiegel oder Platten von 98·8%, direktes kaltisostatisches Verpressen zu 99·5% der theoretischen Dichte. EMK-Messungen mit kolloidchemisch hergestellten ThO_2/Y_2O_3-Platten ergaben Werte, die mit Meßergebnissen an ZrO_2/Y_2O_3-Festelektrolyten und mit Literaturdaten übereinstimmen.

Des sols d'oxydes de Th/Y stables ont été préparés par peptisation des hydroxydes lavés et convertis par diverses méthodes de solidification en poudres de ThO_2/Y_2O_3 frittables, lesquelles ont été comparées à une poudre de ThO_2/Y_2O_3 coprécipitée. Les meilleures propriétés des poudres ont été obtenues lorsque le sol d'oxydes Th/Y était solidifié par une gélification interne. Un coulage en barbotine et un pressage isostatique à froid subséquent de la poudre obtenue par sol–gel a conduit à des densités de 98·8% des creusets ou des plaques frittées tandis qu'un pressage isostatique à froid effectué directement a donné 99·5% de la densité théorique. Les mesures de forces électromotrices (EMF) pratiquées sur des plaques ThO_2/Y_2O_3 obtenues par sol–gel ont donné des résultats en accord avec ceux obtenus sur des électrolytes solides ZrO_2/Y_2O_3 et avec les données de la littérature.

1 Introduction

Solid electrolytes are essential ceramic components in galvanic cells used for measuring electromotive forces (EMF) at high temperatures.[1] The most common solid electrolytes consist of solid solutions of ZrO_2–CaO or ZrO_2–Y_2O_3. These solid solutions are characterized by a CaF_2-type lattice with partial replacement of Zr^{4+} ions by Ca^{2+} or Y^{3+} ions respectively, resulting in the formation of O^{2-} vacancies in the anion sublattice. The observed oxygen ion conductivity at high temperatures is due to these O^{2-} vacancies. A second effect of the CaO or Y_2O_3 addition is the stabilization of the cubic high-temperature phase of ZrO_2 at lower temperatures, i.e. the suppression of the cubic to tetragonal and the tetragonal to the monoclinic phase transitions. The latter in particular would cause degradation of the sintered body on cooling from high temperatures because of the volume change during this transformation. A typical application of such zirconia-based solid electrolytes is the direct measurement of very low oxygen partial pressures in hot gas mixtures or in metallic melts.

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Disadvantages of zirconia-based solid electrolytes are

- the destabilization of the cubic phase in long duration heat treatments or following numerous thermal cycles causing crack formation or failure of the ceramic component,
- the limitation of the lowest measurable oxygen partial pressure to about 10^{-18} bar at 1000°C,
- the chemical attack of zirconia solid electrolytes by molten fluorides.

Alternatively to zirconia-based solid electrolytes, ceramics consisting of ThO_2/Y_2O_3 solid solutions can be used.[2] Thorium dioxide exists from room temperature up to its melting point of about 3400°C as a single phase with a CaF_2 lattice. Another advantage is the nearly pure ion conductivity of ThO_2/Y_2O_3 solid solutions at much lower oxygen partial pressures at temperatures ranging from 600 to 1500°C.[3] For example, at 1000°C these limits are ThO_2/Y_2O_3, 10^{-6}–10^{-25} bar; ZrO_2/CaO, 10^{5}–10^{-18} bar.

Measurements of the specific electrical conductivity of ThO_2/Y_2O_3 solid solutions as a function of the Y_2O_3 content resulted in a maximum at about 15 mol.% $YO_{1\cdot5}$.[4] Therefore all solid electrolytes prepared by the sol–gel process as described in this paper consisted of 85 mol.% ThO_2 and 15 mol.% $YO_{1\cdot5}$.

2 Powder Preparation

The Th/Y oxide sol was prepared by the following steps:

- Solution of 1 kg $Th(NO_3)_4 . 5H_2O$ and 93·7 g $YCl_3 . 6H_2O$ in 3 litres distilled water,
- addition of this solution with stirring to 3 litres ammonia solution (25% NH_3),
- filtration and washing the precipitate about ten times with 2 litres distilled water,
- peptizising the ion-free washed precipitate by boiling in 3 litres water after adding nitric acid (100 ml 65% HNO_3).

After about 2 h boiling the initially white suspension becomes a translucent colloidal solution (Th/Y oxide sol). This sol can be stored for months without any settling of solid material.

Starting from the stable sol the sinterable powders were prepared by using the following three different methods:

(1) Drying at room temperature in a flat open glass container. First a translucent sticky gel is formed which becomes hard after about 1–2 days.

(2) Freeze drying by dropping the sol in liquid nitrogen followed by drying at −30 to −15°C in vacuum for about 100 h. The resulting powder consists of spherical agglomerates which can be easily crushed forming a very fine powder.

(3) Internal gelation of the sol by adding a saturated solution of hexamethylenetetramine (HMTA = $(CH_2)_6N_4$). The gelation starts during the addition of the HMTA solution, and is completed by heating to 90–100°C. The resulting gel is washed by distilled water with some ammonia, dried at room temperature for 24–48 h, and finally dried for some hours at 100°C.

Additionally one powder was prepared by means of the commonly used coprecipitation route:

- Dissolving of 1 kg $Th(NO_3)_4 . 5H_2O$ and 93·7 g $YCl_3 . 6H_2O$ in 3 litres distilled water,
- precipitation by adding NH_3 solution until the precipitation is complete,
- filtration and washing with distilled water and, finally, with acetone,
- drying at room temperature in a flat open glass container as already described.

The further treatment of the four powders was identical:

- Crushing of any crude agglomerates existing in the dried powder,
- calcining at 800°C for 6 h,
- milling in a zirconia beaker with zirconia balls for 30 min.

3 Characterization of the Powders

The following methods were used to characterize the four thoria–yttria powders:

—Emanation thermoanalysis (ETA),
—thermogravimetry (TG),
—differential thermoanalysis (DTA),
—X-ray diffractometry (XRD),
—scanning electron microscopy (SEM),
—particle size analysis (PSA),
—measurement of the specific surface area (BET),
—sintering behaviour.

Emanation thermoanalysis (ETA) uses the fact that thorium is always in radioactive equilibrium with the short-lived radon isotope Rn 220 (half life: 55 s), also called 'thorium emanation' or 'thoron'. The desorption rate of this noble gas isotope depends on the free inner surface of Th-containing compounds and, consequently, on its change with temperature. Therefore the released Rn 220 activity into a slowly

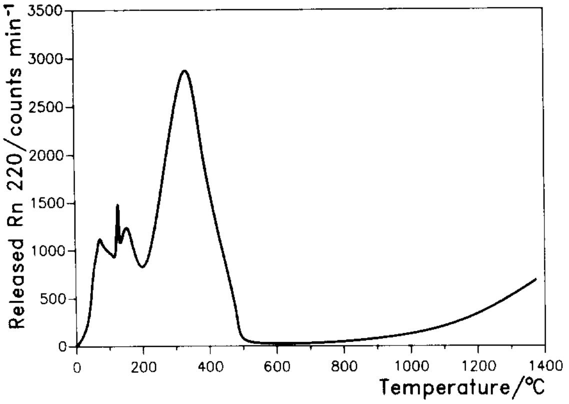

Fig. 1. Radon 220 emission of a freeze-dried thoria/yttria powder as a function of temperature.

streaming gas (e.g. Ar/H_2) is a measure of changes in the free surfaces with temperature, and, additionally, of degassing processes during heating.[5] A typical radon emission curve of a freeze-dried thoria gel powder as a function of temperature is shown in Fig. 1. After desorption of adherent water and other volatile components in the temperature range of 25–200°C the chemically bonded water was volatilized between 250 and 500°C. At temperatures above 500°C the ThO_2 powder is free of volatile compounds. Similar results were obtained for all different thoria gel powders, also by using thermogravimetric measurements (TG) and by differential thermoanalysis (DTA).

The X-ray diffraction patterns of calcined thoria–yttria powders contain exclusively the peaks of the $(Th,Y)O_{2-x}$ solid solution; peaks of Y_2O_3 could not be detected.

The lattice constant of the cubic elementary cell was found to be $a = 0{\cdot}5578$ nm. The lattice parameter of pure ThO_2 is $a = 0{\cdot}5597$ nm.[6] With 15 mol.% $YO_{1\cdot5}$ the elementary cell contains an average of 3·4 ions Th^{4+}, 0·6 ions Y^{3+} and 7·7 ions O^{2-}, corresponding to the composition $Th_{0\cdot85}Y_{0\cdot15}O_{1\cdot925}$. The theoretical density was calculated from these data: $\rho_{TD} = 9{\cdot}235\ \mathrm{g\,cm^{-3}}$.

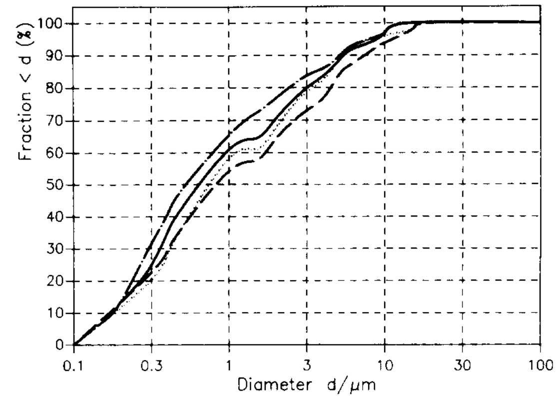

Fig. 2. Particle size distribution of four thoria/yttria powders. - · - · -, Internal gelation, $d_{50} = 0{\cdot}51\ \mu m$; ———, coprecipitation, $d_{50} = 0{\cdot}62\ \mu m$; ······, normal drying, $d_{50} = 0{\cdot}74\ \mu m$; — — —, freeze drying, $d_{50} = 0{\cdot}77\ \mu m$.

Scanning electron microscopy (SEM) has shown that the shape of the powder particles was nearly spherical, with sizes ranging from about 0·1 μm up to about 10 μm; the larger ones are agglomerates of small particles with sizes smaller than 1 μm. The particle size distribution was measured by means of the Shimadzu particle size analyser (SA-CP3) using the sedimentation rate of the powder particles in water. From the results of these measurements it can be seen that the four powder varieties have very similar particle size distributions with median sizes below 1 μm and a tendency to form agglomerates (Fig. 2). The finest powder is made by internal gelation of thoria–yttria sol. This powder has a higher specific surface compared with the other powders (see the results of the BET measurements, Table 1). Particle sizes calculated from the specific surface assuming uniform spherical particles were found to be smaller than the measured d_{50} size, indicating a degree of agglomeration.

In order to test the sinterability of the four thoria–yttria powder varieties, small pellets were made by uniaxial precompacting at 80 MPa followed by cold isostatic pressing at 200 MPa. These pellets were

Table 1. Particle size distribution and specific surface of thoria–yttria powders

	Powder			
	ND	*FD*	*CP*	*IG*
Particle sizes				
d_{10} (μm)	0·25	0·25	0·18	0·18
d_{50} (μm)	0·74	0·77	0·62	0·51
d_{90} (μm)	5·6	7·3	5·6	5·2
Specific surface, BET ($m^2\,g^{-1}$)	7·5	10·3	26·3	34·2
Particle size, calculated, d_{BET} (μm)	0·087	0·063	0·025	0·019
Degree of agglomeration	8·5	12·2	25·1	26·8

ND = Normal drying; FD = freeze drying; CP = coprecipitation; IG = internal gelation.
d_{10} = 10% of the powder has diameters below d_{10}; d_{50} = 50% of the powder has diameters below d_{50}; d_{90} = 90% of the powder has diameters below d_{90}.

Table 2. Geometrical density of pellets from different thoria–yttria powders ($\rho_{TD} = 9{\cdot}235\,g\,cm^{-3}$)

	Powder			
	ND	*FD*	*CP*	*IG*
Green density, ρ_G ($g\,cm^{-3}$)	5·84	5·76	5·65	5·42
Sintered density, ρ_S ($g\,cm^{-3}$)	6·86	7·15	8·51	8·74
Percentage of theoretical density ($100 \times \rho_S/\rho_{TD}$)	74·3	77·4	92·1	94·6

heated with heating rates of 120°K h^{-1} to 1700°C and sintered at this temperature for 12 h. The resulting geometrical densities are quite different (Table 2). The highest density was obtained from the powder prepared by internal gelation (IG) of thoria–yttria sol followed by the coprecipitated (CP) powder. The densities of pellets from the normally dried (ND) and the freeze-dried (FD) sol–gel powders were much lower.

According to these results it was decided to use for all further investigations the powder prepared by internal gelation (powder IG).

4 Preparation of Solid Electrolytes by Slip Casting

Thin-walled crucibles or thin plates from thoria–yttria powder can be formed using the slip casting technique. To meet the special requirements of this technique it was necessary to optimize some powder characteristics.

The most important parameters are:

- The grain size distribution of the powder,
- the calcining temperature of the powder,
- the zeta potential which controls the slip viscosity,
- the influence of surfactants on the zeta potential and the rheology of the slip,
- the influence of the pH value,
- the powder concentration in the suspension.

The grain size distribution of the powder was found to be strongly dependent on the milling conditions. Table 3 includes data for the grain size distribution of sol–gel thoria–yttria powders obtained after different milling procedures.

The very fine powders are *not* suitable for preparing ceramics using the slip casting technique because of the slow rate of green body formation and the high degree of shrinkage during water removal, probably causing cracks. Better properties can be expected for powders obtained by 15 min dry milling *before* calcination: the median grain size (d_{50}) is 3·5 μm and the broad grain size distribution ($d_{10} = 0{\cdot}4\,\mu m$ to $d_{90} = 12\,\mu m$) guarantees high green density: the fine particles fill the cavities between the coarse particles. Therefore this powder was preferentially used for the slip casting experiments.

An important parameter is the zeta potential which is the potential difference between the liquid electrolyte and the electrical double layer from ion adsorption on the electrically charged particle surface. In ceramic oxide slips a high zeta potential is connected with a low viscosity.[7] The zeta potential is influenced by surfactants and by the pH value of the suspension.

Surfactants, e.g. Dispex A 40 (Allied Colloids Company), consist of ammonia salt of polymeric organic acids. Their influence on the rheology of a 63·5% theoria–yttria slip at pH = 4 can be seen from Fig. 3.

With 0·054 wt% Dispex (related to the amount of powder) this slip behaves like a Newton liquid: the shear rate is proportional to the shear stress. Without Dispex addition, however, the slip shows pseudoplastic flow behaviour with higher viscosity at the lower shear rates. The optimization of the Dispex concentration is shown in Fig. 4 where the

Table 3. Grain size distribution of thoria–yttria powders as a function of the milling conditions before or after calcination at 800°C

Powder treatment	*Grain size distribution*		
	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)
15 min dry milling and 30 min wet milling after calcination	0·1	0·3	3·1
30 min dry milling after calcination	0·2	0·5	5·2
15 min dry milling after calcination	0·2	1·1	6·5
5 min wet milling after calcination	0·3	2·6	7·8
15 min dry milling before calcination	0·4	3·5	12·0

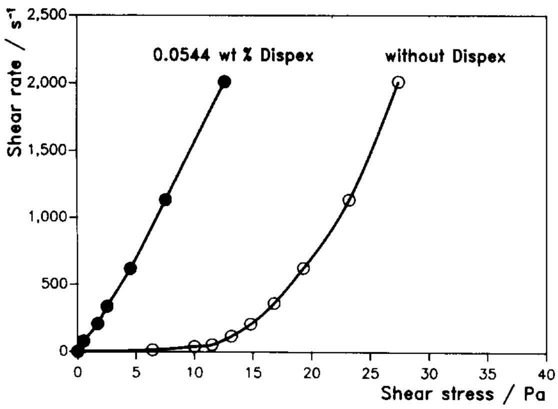

Fig. 3. Influence of Dispex A 40 on the rheology of a thoria/yttria slip at pH = 4.

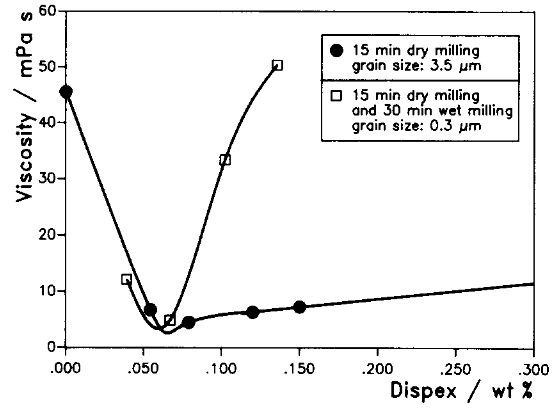

Fig. 4. Viscosity of thoria/yttria slips as a function of the Dispex concentration at pH = 4.

slip viscosity has a minimum at 0·05–0·10 wt% Dispex. The very sharp increase in viscosity at higher Dispex concentrations for very fine powders shows again that such fine powders are not very suitable for slip casting.

The viscosity of thoria–yttria slips can be decreased by addition of hydrochloric acid.[7] Dependent on the grain size distribution of the powder the minimum of viscosity was found at pH ≃ 4 and, in some cases, additionally at pH ≃ 2. With increasing powder concentration the viscosity is increased. The oxide concentration has to be a compromise between flowability of the slip and the shrinkage of the green body during water extraction. Best results were obtained at ThO_2/Y_2O_3 contents between 63 and 74 wt%.

Table 4. Influence of the calcining temperature on specific surface and crystallite size of ThO_2/Y_2O_3 powders

Calcining temperature (°C)	*Specific surface ($m^2 g^{-1}$)*	*Crystallite size (nm)*
600	57·2	1·6
800	36·3	2·0
1 000	15·4	3·5

The first casting experiments resulted in a significant influence of the calcining temperature which controls the specific surface and the crystallite size (obtained from line-broadening measurements of X-ray diffraction patterns) of the powder (Table 4). Slips prepared from powders calcined at 600°C were quite unsuitable: in all cases cracks were found in the green bodies. The reason for this may be the difference of drying rate between the surface and the centre of the slip-cast bodies, resulting in surface tensile stresses. Increased specific surface of the powder leads to increased shrinkage rates and therefore to higher tensile stresses.

Slip casting experiments with powders calcined at 800 or 1000°C resulted in crack-free ThO_2/Y_2O_3 ceramics even after sintering. The sintering conditions were heating rate, 120 K h^{-1}; sintering temperature, 1700°C; sintering time, 12 h; atmosphere, air.

Some suitable combinations of slip properties and the resulting sintered densities are given in Table 5. Slips prepared from powders with a calcination temperature of 800°C were thixotropic, i.e. their viscosity increases with decreasing shear rates. They were suitable for casting thin thoria–yttria plates only. Better results were obtained using powders calcined at 1000°C. These slips were not thixotropic and therefore suitable for casting small thoria–yttria crucibles. With a Dispex concentration of 0·08% and sufficiently high oxide content of the slip, sintered densities up to about 97% of the theoretical density could be reached.

Even higher densities could be obtained by additional cold isostatic pressing (CIP) of slip-cast crucibles at a pressure of 320 MPa. By this method

Table 5. Data for crack-free sintered thoria–yttria ceramics made by slip casting from sol–gel-derived powders

Calcining temperature (°C)	*Dispex (%)*	*Oxide (%)*	*pH*	*Sintered density*		*Shape*
				($g cm^{-3}$)	*(%TD)*	
800	0·80	63·5	2·2	8·83	95·6	Plate
800	0·80	66	1·8	8·89	96·3	Plate
1 000	0·80	64	4·1	7·94	86·0	Crucible
1 000	0·08	74	4·5	8·93	96·7	Crucible
1 000	0·08	74	4·5	9·12	98·8	Crucible (slip-cast and cold isostatically pressed)

Table 6. Data for sintered thoria–yttria ceramics made by cold isostatic pressing from sol–gel-derived powders

Calcining temperature (°C)	*Powder density ($g\,cm^{-3}$)*	*Green density*		*Sintered density*		*Plate dimensions*	
		($g\,cm^{-3}$)	*(%TD)*	*($g\,cm^{-3}$)*	*(%TD)*	*ϕ (mm)*	*h (mm)*
600	7·2	4·48	48·5	9·19	99·5	13	3·5
800	8·4	4·95	53·6	9·06	98·1	13	3·5
1 000	8·0	4·73	51·2	9·17	99·3	13	3·5

nearly 99% of the theoretical density (9·235 $g\,cm^{-3}$) was measured after sintering.

5 Preparation of Solid Electrolytes by Cold Isostatic Pressing

The sol–gel-derived thoria–yttria powders were found to be very suitable for direct use of the CIP technique. Contrary to the slip-casting technique, powders with high specific surface areas could be pressed and sintered without crack formation. The powders were prepressed uniaxially with a 140 MPa load followed by cold isostatic pressing at 320 MPa. The sintering conditions were the same as used for the slip-cast specimens. Results of three experiments with different calcining temperatures of the powders are summarized in Table 6.

6 Test of Thoria–Yttria Solid Electrolytes by EMF Measurements

For testing the sol–gel-derived ThO_2/Y_2O_3 solid electrolytes a galvanic cell was constructed consisting of a Mn_3O_4/MnO cathode, an Fe/FeO anode, and one of the sintered solid electrolyte plates, with 85% ThO_2 and 15% Y_2O_3. The electromotive force (EMF) of the galvanic chain

$$Pt/Fe,FeO/Th_{0\cdot85}Y_{0\cdot15}O_{1\cdot925}/MnO,Mn_3O_4/Pt$$

is caused by the following chemical reactions at the electrodes:

$$2Mn^{3+} + 2e^- \rightarrow 2Mn^{2+}$$
$$Fe \rightarrow Fe^{2+} + 2e^-$$

The equipment for the EMF measurements[8] comprised a zirconia crucible containing a stack of three pellets consisting of the measuring sample (Mn_3O_4/MnO cathode), the electrolyte pellet ($Th_{0\cdot85}Y_{0\cdot15}O_{1\cdot925}$), and the reference sample (Fe/FeO anode). The electrical connections consisted of platinum. For better contact the three pellets were pressed together and sealed by a glass melt in order to avoid any chemical reactions with the gaseous environment (Fig. 5).

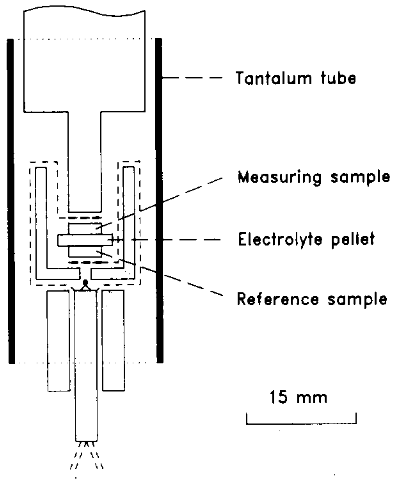

Fig. 5. Equipment for the EMF measurements.

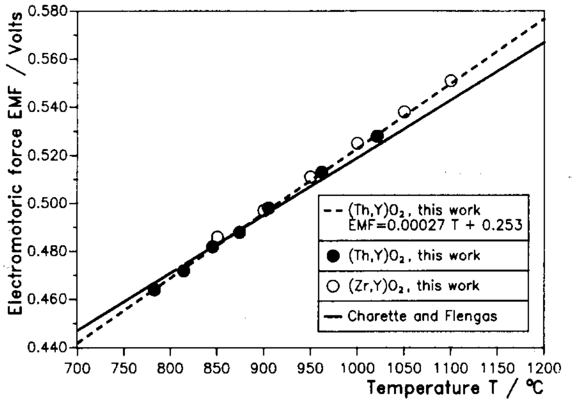

Fig. 6. Results of the EMF measurements.

The results of the EMF measurements are plotted in Fig. 6. This diagram compares EMF data using $(Th, Y)O_{2-x}$ solid electrolytes as described in this paper with EMF data using $(Zr, Y)O_{2-x}$ solid electrolytes, measured in this laboratory,[8] and literature data published by Charette & Flengas.[9] The very good agreement of all these data demonstrates that sol–gel-derived thoria–yttria solid electrolytes can be used successfully for EMF measurements.

7 Summary

Stable Th/Y oxide sols can be prepared by peptization of the washed hydroxides. Sinterable ThO_2/Y_2O_3 powders were prepared from the sol by

—drying at room temperature,
—freeze drying at −15 to −30°C in vacuum,

—internal gelation after adding hexamethylenetetramine at 90 to 100°C.

Samples were characterized by X-ray diffraction analysis, particle size distribution measurements, determination of the specific surface (BET) and investigation of the sintering behaviour.

The best characteristics of sinterable ThO_2/Y_2O_3 powders and crack-free dense sintered ceramics were obtained by internal gelation of the sol.

The conditions of forming plates and small crucibles from the sol–gel-derived powder by slip casting and by cold isostatic pressing were investigated. Slip casting and subsequent cold isostatic pressing resulted in 98·8%, and direct cold isostatic pressing in 99·5% of the theoretical density after 12 h sintering at 1700°C.

EMF measurements with the sol–gel-derived ThO_2/Y_2O_3 solid electrolytes in a solid oxide galvanic chain demonstrated the suitability of these solid electrolytes.

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