

ELECTRICAL AND CATALYTIC PROPERTIES OF SOME OXIDES WITH THE  
FLUORITE OR PYROCHLORE STRUCTURE

PART 1: SYNTHESIS, CHARACTERIZATION AND CONDUCTIVITY

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ABSTRACT

In view of their possible use as electrocatalysts, several oxides with the fluorite or pyrochlore structure were investigated. Part I of this paper deals with the synthesis, characterization and electrical conductivity of these materials. All lanthanide titanates investigated (partly doped with Bi) show the pyrochlore structure and are poor conductors, except for the compounds containing Tb. For Nd-zirconates, partly substituted with Ce, the degree of order depends on the amount of Ce and temperature treatment. Ionic and in some cases mixed conductivity was observed. Part II reports about the catalytic activity for CO oxidation.

INTRODUCTION

Aims

Recent literature data indicate that several solid electrolytes have catalytic properties, which are of interest for applications in electrocatalytic reactors, fuel cells, oxygen sensors and pumps (e.g. [1-6]). In these investigations mainly stabilized zirconia is used as the oxygen ion conducting electrolyte and some noble metal as the electrode material. The electrocatalytic oxidation or reduction reaction takes place at the electrolyte-electrode-gas interphase, the electrode and/or the electrolyte surface providing the catalytically active sites.

In the electrocatalytic reaction scheme the electrolyte serves as a reservoir for oxygen ions or oxygen vacancies, which can be pumped towards the interphase region by applying a proper voltage across the electrolyte. Meanwhile the electrochemical potential of the oxygen species or vacancies at the reaction sites is strongly influenced, even for rather low oxygen ion mobilities within the electrolyte. This may strongly affect the reaction kinetics, provided that electrons or electron-holes are available locally for charge transfer. Therefore mixed conductivity of the electrolyte surface-layer may be advantageous.

In this paper it is our aim to scan a number of materials that might be used as catalytically active substrates in particular for electrocatalytic applications. In part I the synthesis and characterization of these materials

are reported, with special attention paid to structural aspects and bulk electrical properties. Part II deals with some catalytic properties. A rather simple and well known reaction (oxidation of carbon monoxide) has been chosen as a test reaction. This provides information about the kinetics of the reaction and thus about the important steps in the reaction scheme (e.g. adsorption and charge transfer).

Results will be used in future electrocatalytic investigations on selected compositions.

#### Electrode and electrocatalytic process

It has been pointed out by several authors (e.g. [3,5-7]) that both electrode material and electrolyte substrate are of great importance to activity (and selectivity) of the (electrocatalytic) reaction employed. The process studied most frequently is the cathodic and anodic reaction of molecular oxygen, as encountered in oxygen sensors and pumps. Detailed knowledge of the critical steps in the reaction mechanism is still lacking, but, up to now, a noble metal seems to be essential as electrode material at lower temperatures, except in one case reported by Badwal [8]. At higher temperatures, as encountered in fuel cells, other electrode materials are possible like metals (e.g. Ni) and oxides (e.g.  $\text{In}_2\text{O}_3$  and several perovskites), depending on the working circumstances (oxidising, reducing) [9]. Impurities on or in contact with the electrode material greatly influence the performance of the electrode reaction, possibly due to decreased or increased adsorption possibilities for oxygen [10]. Besides this electronic and catalytic function of the electrode material, other steps of the reaction process are also relevant. Schouler concludes that at lower temperatures a combined effect of electrode material and electrolyte properties (e.g. oxygen vacancy concentration and activation enthalpy of bulk ionic conductivity) determines the electrode resistance. At higher temperatures the rate determining step is related to the migration of oxygen vacancies in the electrolyte. He also notes that some electronic conductivity of the electrolyte surface has a positive influence [7]. Verkerk et al., investigating stabilized bismuthsesquioxides, conclude that Bi enhances the adsorption and/or surface diffusion of oxygen, thus increasing the electrolytic contribution in the electrode process and resulting in a lower electrode resistance [11]. From these examples it can be seen that the main features of the electrode reaction are determined by:

- i) adsorption and/or surface diffusion of oxygen on the electrode and electrolyte surface;
- ii) availability of sites for charge transfer between the adsorbed species and electrode (triple line) or mixed conductive electrolyte;
- iii) diffusion of oxygen ions or vacancies within the electrolyte surface layer.

From studies of electrocatalytic reactions on oxygen conducting electrolytes the same three features of the electrode reaction become apparent: an enhanced reaction rate in water vapour reduction is reported for yttria stabilized zirconia doped with  $\text{CeO}_2$ , due to an increased number of charge transfer sites [6]; a high concentration of electrons and oxygen vacancies leads to a high reaction rate for NO-decomposition [3]. Also in oxidation processes a major role is ascribed to the electrolyte material, for instance to scandium stabilized zirconia [1]. Therefore electrolyte topayers with catalytic properties and possessing electronic conductivity in addition to ionic conductivity will promote the electrocatalytic reaction and will overcome or at least reduce the use of expensive noble metals. This is illustrated to some extent in [8].

Materials investigated

We have restricted our choice of materials being investigated to oxides with the fluorite or pyrochlore structure and stoichiometry  $A_2B_2O_7$ . The pyrochlore structure can be considered as a fluorite super structure with doubled unit cell in which cations, anions and vacancies are all ordered. Several oxides were found to be reasonably good oxygen ion conductors with a rather low activation enthalpy [11,13,14]. Various substitutions of cations are possible within this pyrochlore structure. Moreover catalytic properties of pyrochlore oxides have been reported for several systems [15]. The two types of lattice oxygen with different binding energy, present in the structure, may lead to an improved selectivity for particular redox reactions [16]. These characteristics of pyrochlores and the features of the electrode and electrocatalytic reaction process, mentioned in the previous section, have led to the following selection of materials for preliminary investigations:

- Bismuth doped rare earth titanates:  $(Bi_x Ln_{1-x})_2 Ti_2 O_7$  (Ln = Eu, Tb, Y, Er and  $x = 0.00, 0.20, 0.40$ )
- Neodymium cerium-doped zirconates:  $Nd_2 (Ce_x Zr_{1-x})_2 O_7$  ( $x = 0.00, 0.05, 0.10$  and  $0.20$ ).

Oxygen ion conductivity for titanates was reported for  $Y_2 Ti_2 O_7$  [17] and  $Er_2 Ti_2 O_7$  [13].  $Nd_2 Zr_2 O_7$  was found to have a small p-type electronic conductivity in addition to an ionic conductivity with an activation enthalpy of about 70-80 kJ/mol. [12,14,22]. In the titanate series it is tried to introduce electronic conductivity with terbium and to obtain an enhanced adsorption behaviour with bismuth; cerium is expected to introduce an electronic contribution to the conductivity of  $Nd_2 Zr_2 O_7$ . In these zirconates the degree of pyrochlore order can be varied. This will result in variation of the character of the vacant oxygen sites, and in ordering and alignment of cations.

EXPERIMENTAL

All materials were prepared by means of a wet chemical synthesis in order to obtain fine grained and homogeneous powders. A viscous solution of citrate complexes of the constituent metal-ions was thermolyzed and the product was calcined [18]. The calcination was performed at temperatures between 600 and 1000°C during 6-12 hours. The powders were then divided into separate batches and either sintered into dense ceramics for electrical transport measurements or subjected to different heat treatments in order to perform the structural and catalytic experiments (part II). Sintering temperatures were 1000°C (20 hrs) for the Bi containing titanates, 1300°C (40 hrs) for the Bi free titanates and 1550°C (40 hrs) for the zirconates. Densities of at least 95% for the titanates and 92% for the zirconates were always obtained. Heat treatments for powder batches were 1000°C (60 hrs) for the Bi containing titanates, 1200°C (60 hrs) for the other titanates and 1050, 1350 and 1550°C (5 hrs) for the zirconates. The composition of the synthesized specimens was checked by X-ray fluorescence analysis and was found to deviate less than 1% from the desired composition. The Bi containing titanates showed some Bi deficiency. X-ray powder diffractometry was carried out on a Philips PW1050 diffractometer using Cu-K $\alpha$  radiation and Si as internal standard.

For electrical measurements disc-shaped specimens were used with Pt-sputtered electrodes with thickness of about 0.2  $\mu$ m. Ionic transference numbers were determined by means of the e.m.f.-method using air and pure oxygen as reference gases. The experimental setup has been described elsewhere [12]. Conductivity measurements were carried out using frequency dispersion techniques by means of a Solartron 1174 FRA. Analysis of the data, generally in the range of  $1-10^6$  Hz, enables one to distinguish between bulk, grain boundary and electrode contributions to the total impedance. The measurements were carried out in the temperature range 300-700°C. Some

comparative conductivity measurements on  $\text{Nd}_2(\text{Ce}_x\text{Zr}_{1-x})_2\text{O}_7$  ( $x = 0.0$  and  $0.20$ ) were kindly performed at Imperial College, London (GB).

#### X-RAY-DIFFRACTION

The pyrochlore structure was observed for all titanates. The lattice parameters agree well with those reported in literature [29] and are tabulated in table I. For the compositions  $\text{Nd}_2(\text{Ce}_x\text{Zr}_{1-x})_2\text{O}_7$  ( $x = 0.00, 0.05, 0.10, 0.20$ ) the degree of pyrochlore order was found to depend both on the temperature of the heat treatment and on the Ce-content, as was clear from the intensity of the superstructure reflections characteristic for the pyrochlore structure. According to our aim to correlate electrical and catalytic properties to ordering effects, the structure parameters were refined within spacegroup  $\text{Fd}\bar{3}\text{m}$ , using a least squares refining computer program. For the materials subjected to  $1550^\circ\text{C}$  about 29 hkl-reflections, resulting (by overlapping) in about 20 observed intensities, were taken into account. For powders subjected to  $1350^\circ\text{C}$ , 7 hkl-reflections were used, three of which were superstructure reflections. A percentage of pyrochlore order (% pyr), defined as twice the difference between the occupation factor of the 16c site by Nd, and that factor for the completely disordered structure (0.5) was calculated from the refinement results. Although resembling the definition of a long range order parameter, a definite order model is not suggested at this moment. The % pyr parameter may refer to either complete phase separation, or formation of a hybrid phase consisting of microdomains, or development of partial long range order. Crystallographic data of the  $1350^\circ$  and  $1550^\circ\text{C}$  materials are given in table II. The unit cell dimension versus Ce-content has been given in fig. 1. A value for  $x = 0.40$  is included, which is twice the fluorite value observed for this compound. From these data several conclusions can be drawn:

- In contrast to reference [20], it is believed that complete Ce-solubility in the pyrochlore phase extends to  $x = 0.10$ . For  $x > 0.10$  an increase in lattice parameter is observed, due to an increased disorder, which is confirmed by the decreased value of % pyr for  $x = 0.20$  at  $1550^\circ\text{C}$ .
- No evidence for separation in phases having different chemical composition is observed (No splitting or broadening of X-ray lines). A lattice parameter for  $x = 0.20$  ( $1550^\circ\text{C}$ ), based only on the superstructure-reflections, is not different from the value obtained from all reflections. In order to distinguish between partial long range order and a hybrid phase model, application of electron microscopy seems to be necessary.
- Values of % pyr are considerably lower for  $1350^\circ\text{C}$  materials than for  $1550^\circ\text{C}$  materials. It is believed that at  $1350^\circ\text{C}$  complete pyrochlore formation is kinetically hindered, which is most prominent at  $x = 0.20$ . X-ray reflection linewidths are comparable for both kinds of materials.

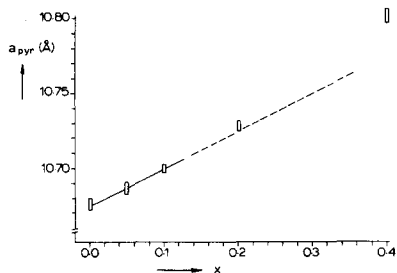


FIG 1

Unit cell parameter versus Ce content at  $1550^\circ\text{C}$  in  $\text{Nd}_2(\text{Ce}_x\text{Zr}_{1-x})_2\text{O}_7$

TABLE I  
Unit cell Parameter for Titanates

Compound	Unitcell (Å)
$\text{Y}_2\text{Ti}_2\text{O}_7$	10.102 (1)
$(\text{Bi}_{0.2}\text{Y}_{0.8})_2\text{Ti}_2\text{O}_7$	10.155 (1)
$(\text{Bi}_{0.4}\text{Y}_{0.6})_2\text{Ti}_2\text{O}_7$	10.203 (1)
$\text{Tb}_2\text{Ti}_2\text{O}_7$	10.158 (1)
$(\text{Bi}_{0.4}\text{Tb}_{0.6})_2\text{Ti}_2\text{O}_7$	10.229 (2)
$\text{Eu}_2\text{Ti}_2\text{O}_7$	10.210 (2)
$\text{Er}_2\text{Ti}_2\text{O}_7$	10.075 (3)

TABLE II  
Unit Cell Dimension and Refinement Results for  $\text{Nd}_2(\text{Ce}_x\text{Zr}_{1-x})_2\text{O}_7$

	x=0.00	x=0.05	x=0.10	x=0.20	x=0.40
$a_{\text{pyr}}$ (Å) 1)	10.676(4)	10.687(4)	10.700(3)	10.728(3)	10.801(5)
1350°C					
% Pyr 2)	68(10)	66(8)	64(8)	42(12)	-
$x_{\text{O}}$ (48f) 3)	0.415(3)	0.419(3)	0.421(3)	0.383(4)	-
$R_1, R_2$ 4)	1.43 1.33	1.09 1.12	1.00 1.05	0.81 0.50	-
1550°C					
% Pyr 2)	91(10)	89(10)	93(9)	81(9)	-
$x_{\text{O}}$ (48f) 3)	0.416(2)	0.414(1)	0.417(2)	0.415(3)	-
$R_1, R_2$ 4)	4.88 2.72	2.09 1.47	2.99 1.96	3.27 2.62	-

1) Unit cell dimension for the pyrochlore structure (1550°C).  
For  $x = 0.40$  twice the fluorite value was taken.

2) % pyr as defined in text

3)  $x_{\text{O}}$  (48f) is the position parameter for 48f anions in the pyrochlore structure. For fluorites this value is 0.375.

$$4) R_1 = 100 * \frac{\sum |I_{\text{obs}} - I_{\text{calc}}|}{\sum I_{\text{obs}}} \quad R_2 = 100 * \sqrt{\frac{\sum w(I_{\text{obs}} - I_{\text{calc}})^2}{\sum w I_{\text{obs}}^2}}$$

#### ELECTRICAL PROPERTIES

##### Transference numbers

As stated in the second part of the introduction, materials exhibiting mixed (ionic and electronic) conductivity might be interesting materials as electrode top-layers on solid electrolytes. Therefore the ionic transference number was determined with a concentration cell method in order to separate between the ionic and electronic contribution of the total conductivity. The e.m.f. of a concentration cell is given by:

$$\text{e.m.f.} = \frac{R T}{4 F} \int_{p\text{O}_2^I}^{p\text{O}_2^{II}} t_i d(\ln p\text{O}_2)$$

$R, T$  and  $F$  have their usual meanings in this equation and  $p\text{O}_2^I$  and  $p\text{O}_2^{II}$  are the oxygen partial pressures across the electrolyte specimens with Pt electrodes. In all experiments air and pure oxygen were used. When the electronic contribution to the total conductivity increases, erroneous  $t_i$ -values may be found, due to the transport of oxygen through the specimen [21]. Therefore good refreshment of the gases at the electrodes was employed. No stable e.m.f. could be detected for  $(\text{Bi}_x\text{Y}_{1-x})_2\text{Ti}_2\text{O}_7$  ( $x = 0.00, 0.20$  and  $0.40$ ), indicating that both ionic and electronic conductivity are small at the temperatures of investigation. For  $\text{Y}_2\text{Ti}_2\text{O}_7$  this is in contrast to reference [17], in which it is stated that  $\text{Y}_2\text{Ti}_2\text{O}_7$  is an ionic conductor as  $t_i \approx 1$  between 500 and 800°C.  $(\text{Bi}_x\text{Tb}_{1-x})_2\text{Ti}_2\text{O}_7$  ( $x = 0.00$  and  $0.40$ ) samples showed a stable e.m.f. close to zero, so these materials are predominantly electronic conductors. For the specimens  $\text{Nd}_2(\text{Ce}_x\text{Zr}_{1-x})_2\text{O}_7$  the situation is more complicated. The ionic transference number depends both on temperature and Ce-content. In fig. 2 values of  $t_i$  have been plotted. In general, variation of  $t_i$  with temperature can be explained assuming different activation enthalpies for ionic and electronic contributions, but change in stoichiometry with temperature may give rise to a varying  $t_i$  value too. For  $\text{Nd}_2\text{Zr}_2\text{O}_7$  the deviation of  $t_i = 1$  at temperatures above 700°C has been attributed previously to the onset of a p-type electronic contribution [22]. This behaviour is suppressed by introducing a few percent of cerium

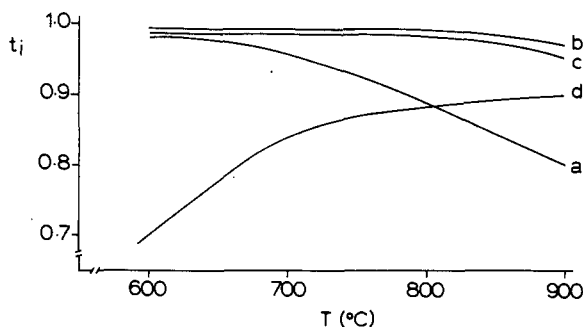
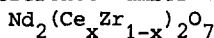


FIG. 2

Ionic Transference Number for Compounds

a)  $x = 0.00$ ; b)  $x = 0.05$ ; c)  $x = 0.10$ ; d)  $x = 0.20$ 

( $x = 0.05$  and  $0.10$ ), as  $t_i$  is close to 1.0 for these samples at all temperatures. It is believed that the electronic defects of  $\text{Nd}_2\text{Zr}_2\text{O}_7$  are compensated by electrons donated by  $\text{Ce}^{3+}$  present in the structure, as observed in other Ce-oxides. In the compound with  $x=0.20$  this n-type contribution probably becomes apparent, especially at lower temperatures, where  $t_i$  decreases. Consequently the small n-type electronic conductivity must have a lower activation enthalpy than the ionic conductivity.

### Conductivities

Impedance diagrams for specimens  $\text{Nd}_2(\text{Ce}_x\text{Zr}_{1-x})_2\text{O}_7$  in the frequency range 1-10<sup>6</sup> Hz showed bulk and grain boundary polarization effects at the lower temperatures.

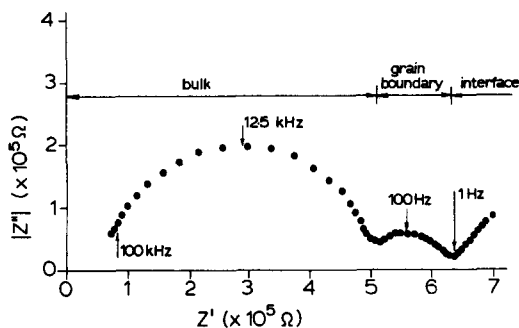
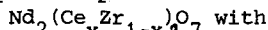


FIG. 3

Typical Impedance Plot for

with  $x = 0.010$ ;  $T = 360^\circ\text{C}$ ;  $p\text{O}_2 = 1.0$  atm.

A typical example is given in Fig.3. Above about 500°C electrode polarization becomes visible, obscuring the grain boundary effects. For ease of interpretation bulk and grain boundary conductivities were taken together and were considered as the total conductivity of the specimens. The conductivity values obeyed an Arrhenius behaviour and activation enthalpies and pre-exponential factors were calculated using the relation:

$$\sigma = \frac{\sigma_0}{T} \exp(-\Delta H/RT)$$

(see table III).

TABLE III

Activation Enthalpies and Pre-exponential Factors for Total Conductivities of Specimens  $\text{Nd}_2(\text{Ce}_x\text{Zr}_{1-x})_2\text{O}_7$

$\text{Nd}_2(\text{Ce}_x\text{Zr}_{1-x})_2\text{O}_7$	$x = 0.00$	0.05	0.10	0.20
$\Delta H$ (kJ/mol)	79 (+4)	72 (+4)	93 (+4)	99 (+4)
$\sigma_0$ ( $\Omega^{-1}\text{m}^{-1}\text{K}$ )	$5 \times 10^4$	$1 \times 10^5$	$1 \times 10^6$	$4 \times 10^6$

The value of  $\Delta H$  for  $x = 0.00$  agrees with values previously reported in literature [12,13,23]. Variations of  $\Delta H$ -values for nominally equal compositions can be attributed to differences in sample preparation and small differences in stoichiometry. In general disorder in the pyrochlore structure (due to deviation from stoichiometry, heat treatment or choice of cations) leads to higher activation enthalpies as has been explained in ref. [13]. The same phenomenon accounts for the investigated zirconates. For low Ce-content the activation enthalpy is between 70 and 80 kJ/mol, but for  $x = 0.10$  and especially for  $x = 0.20$  a considerable increase is found. For  $x = 0.20$  this is the more prominent when the conductivities are corrected for the electronic contribution. Then an activation enthalpy for ionic conductivity is found of 110 ( $\pm 6$ ) kJ/mol. The substitution of Zr by Ce increases the average radius of the B-cation and thus increases the amount of disorder [13].

Impedances of specimens  $(\text{Bi}_x\text{Y}_{1-x})_2\text{Ti}_2\text{O}_7$  turned out to be larger than  $10^7 \Omega\text{m}$  and are too high to be measured accurately with the electrical circuits used (at temperatures below 900 K). Activation enthalpies for these specimens are in the order of 180-200 kJ/mol. It was evident that the conductivity increased with the amount of Bi in the specimens. For specimens  $(\text{Bi}_x\text{Tb}_{1-x})_2\text{Ti}_2\text{O}_7$  frequency-independent impedances were found, consistent with the transference numbers obtained, indicating electronic conductivity. The activation enthalpies are in the order of 70-85 kJ/mol. Below 550°C a lower value was found than above this temperature. The conductivity decreases in reducing atmospheres. It is believed that the (p-type) electronic conductivity can be described by a hopping model, between  $\text{Tb}^{3+}$  and  $\text{Tb}^{4+}$  sites. Therefore the actual stoichiometry should be  $(\text{Bi}_x\text{Tb}_{1-x})_2\text{Ti}_2\text{O}_{7+y}$ , the ratio  $\text{Tb}^{3+}/\text{Tb}^{4+}$  depending both on temperature and  $p\text{O}_2$  applied.

TABLE IV  
Electrical Conductivities at 700K and 1000 K

Compound	$\sigma(700\text{K})$ $\Omega^{-1}\text{m}^{-1}$	$\sigma(1000\text{K})$ $\Omega^{-1}\text{m}^{-1}$	ref.
$\text{Nd}_2\text{Zr}_2\text{O}_7$	$9 \times 10^{-5}$	$4 \times 10^{-3}$	this work
$\text{Nd}_2(\text{Ce}_{0.05}\text{Zr}_{0.95})_2\text{O}_7$	$6 \times 10^{-4}$	$1.7 \times 10^{-2}$	" "
$\text{Nd}_2(\text{Ce}_{0.10}\text{Zr}_{0.90})_2\text{O}_7$	$1.8 \times 10^{-4}$	$1.5 \times 10^{-2}$	" "
$\text{Nd}_2(\text{Ce}_{0.20}\text{Zr}_{0.80})_2\text{O}_7$	$2.1 \times 10^{-4}$	$2.6 \times 10^{-2}$	" "
$\text{Gd}_2\text{Zr}_2\text{O}_7$	$1.3 \times 10^{-2}$	$6.8 \times 10^{-1}$	[12, 13]
$\text{Tb}_2\text{Zr}_2\text{O}_7$	$1.7 \times 10^{-1}$	$1.4 \times 10^0$	[13]
$\text{ZrO}_2(17\% \text{YO}_{1.5})$	$1.1 \times 10^{-2}$	$2 \times 10^0$	[24]
$\text{Y}_2\text{Ti}_2\text{O}_7$	$< 10^{-7}$	$5 \times 10^{-5}$	this work
$(\text{Bi}_{0.4}\text{Y}_{0.6})_2\text{Ti}_2\text{O}_7$	$< 10^{-7}$	$4 \times 10^{-4}$	" "
$\text{Tb}_2\text{Ti}_2\text{O}_7$	$6.8 \times 10^{-4}$	$3 \times 10^{-4}$	" "
$\text{Er}_2\text{Ti}_2\text{O}_7$	$1.5 \times 10^{-6}$	$5.3 \times 10^{-4}$	[13]

In table IV total conductivities are collected for all compounds investigated, together with some values for other materials previously investigated. From these values it can be seen that the ionic conductivities of the materials investigated in the current study are relatively poor. Interesting catalytic effects have been found, however, (part II) and therefore it is still interesting to see if

these materials can be applied in electrocatalytic applications when they are used in thin layers. Electronic conductivity can be realized using Tb or Ce. Especially Tb-zirconates seem to be promising [13].

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