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Development of oxygen-permeable ceramic membranes for NO_x-sensors

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Abstract

Several mixed ionic–electronic conductors such as $Gd_{1-x}Ca_xCoO_{3-d}$ (GCC) and $La_{1-x}Sr_xCo_{1-y}Cu_yO_{3-d}$ as well as composite materials like $Gd_{1-x}Ca_xCoO_{3-d}$ / $Ce_{1-x}Gd_xO_{2-d}$ (GCCCGO) have been investigated with respect to their use as highly selective membranes within a new amperometric sensor system. Materials characterisation was carried out concerning surface reactions of the membranes, thermal expansion, and electronic as well as oxygen permeation properties. Taking advantage of the effective medium theory, the optimum component-ratio for the composit ceramic GCCCGO with respect to permeation behaviour has been predicted. Based on experimental and modelling data, the overall performance of a system using a GCCCGO membrane has been determined. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Composites; Ionic conductivity; Membranes; Perovskites; Sensors

1. Introduction

Continuous improvements to reduce the NO-concentration in the exhaust gas of lean-burn engines meeting future legislation standards have led to new catalyst-systems. These require NO-sensors for optimum performance with respect to on-board-diagnose systems (OBD). Yet, detecting low amounts of NO_x in the exhaust gas of cars can only be carried out using sophisticated sensor systems. In the past, especially amperometric sensor systems based on electrolytes like yttria stabilised zirconia have successfully been developed for this purpose.[1,2] However, this method is based on the highly selective removal of molecular oxygen present in the measuring gas prior to the detection of the NO-concentration. Today, electrodes usually consist of modified noble metals like Pt. The aim of this work was to evaluate the use of ceramic membranes alternatively to these noble metal systems.[3,4]

2. Experimental

Powders used for analysis of the surface catalytic activity were prepared by means of a spray-freeze/freeze drying method. In the case of samples requiring larger amounts of material, e.g. pastes and disc-type specimens, EDTA and citrate methods have been applied.[3,5–8] The resulting finely distributed amorphous oxide/carbonate mixtures were calcined at 950°C to form a powder of the desired phases. The final powdered products were analysed by means of XRD. For conductivity measurements, pellets were prepared by uniaxial pressing (560×10^9 Pa) and subsequent sintering at 1150–1250°C for 16 h. The density obtained was more than 94% (± 2%). Extensive polishing using diamond paste (particle size 1 μm) was applied, ensuring a minimised surface roughness for the polarisation measurements. The oxygen ion conductivity was determined from steady state current-voltage curves at electron blocking microcontacts.[9] Yttria stabilised zirconia (YSZ) was used, representing an oxygen ion conductor with negligible electron conductivity under the applied conditions (microcontact tip radius ranging between 40

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and 60 μm).[10] Characterisation of the electronic conductivity was carried out taking advantage of the van der Pauw 4-point-method with cylindrical specimen of 6 mm diameter and 3 mm of height, contacted by sputtered electrodes (50 Å of CrNi).[11] The catalytic activity of the compounds has been determined using a flow reactor, consisting of heated stainless steel and quartz tubing. The gas composition was analysed before and after passage through the sample. C_xH_y-components were detected using a FID analyser (Testa FID 123). NO_x was measured by means of the chemoluminescence method (Rosemount 951A). To cope with the effect of NO_2-formation generated by the oxidation of NO with O_2 in the cooler parts of the reactor the total amount of NO_x was determined. Carbon oxides were measured by a non-dispersive infrared analyzer (NDIA) (Uras 10E Hartmann & Braun). Finally, an electrochemical cell served for the determination of the oxygen content. To exclude any influence of the plug and tubing materials on the results, reference measurements were carried out, showing no conversion of NO to oxygen and nitrogen or N_2O within the chosen temperature range.

3. Results and discussion

The principle of the new NO-sensor is based on two amperometric pump units for oxygen ions according to Fig. 1. To achieve a linear signal output, the sensor needs to be operated in a diffusion limited mode by means of a barrier and channel system.[12] Based on YSZ as the electrolyte material, the NO concentration is determined reducing this gas species at the second electrode. For this purpose, however, no oxygen must be present at the electrode at any time. Thus, in a first stage, the O_2-molecules are removed by means of a mixed ionic electronic conducting (MIEC) membrane. The oxygen permeation through the membrane is driven by a strong gradient in PO_2, applied by the first pumping cell situated below the mixed conductor. Therefore, the unit can also be used for measuring the O_2 content in the exhaust gas. To reduce reactions and interface formations between the MIEC and the electrolyte, the membrane is mounted on top of a carrier structure.[13] Oxygen extracted from the diffusion channel is consequently pumped into a reference channel on the rear side of the ceramic multilayer.

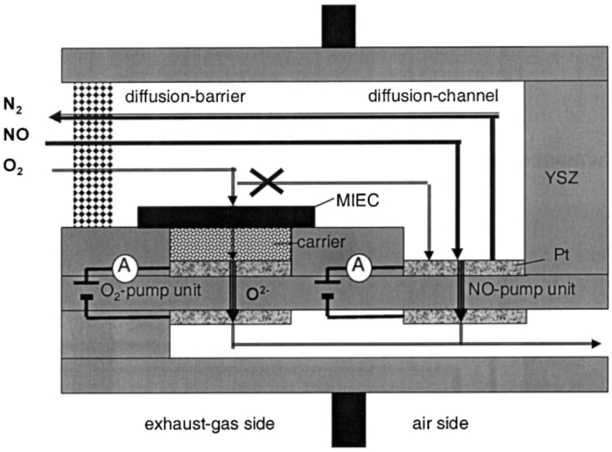

Fig. 1. Operating principle of NO_x-sensor with oxygen-permeable membrane.

To match sensing requirements, the determination of surface reactions of the membranes at elevated temperatures has been carried out. According to the results in Table 1 the well known membrane material $La_{0.6}Sr_{0.4}Co_{0.8}Cu_{0.2}O_3$[14] is not suitable for this purpose, due to the catalytic activity of the surface reducing the NO content within the diffusion channel prior to the second pumping unit. On the other hand, $Gd_{1-x}Ca_x CoO_{3-d}$ hardly promotes the oxidation as well as the reduction of NO_x even in the presence of hydrocarbons like C_3H_6. Hence, concerning catalytic requirements, this material can be used for operation temperatures below 800°C.

Nevertheless, the ionic conductivity of this material is not sufficient for the required permeation rate of the membrane as can be drawn from Table 2. Detection signals of 10 nA/ppm NO achieved by permeation through an effective membrane surface of 30 mm² with NO concentrations ranging between 50 and 1200 ppm require an ionic conductivity level of at least 2.5×10^{-5} Ω^{-1} cm^{-1} for a membrane of 20 μm thickness.[3] Moreover, the electronic conductivity level needs to exceed the ionic, ensuring that no transport limitation arising from electric fields due to the ambipolar diffusion can occur.

Table 1
Starting temperature for NO_x reduction. Gas composition: mixture 1: 900–1050 ppm NO in N_2; mixture 2: 850 ppm C_3H_6, 950 ppm NO with 2% O_2 in N_2

Material	T_{start} (°C); mixture 1	T_{start} (°C); mixture 2
$La_{0.6}Sr_{0.4}Co_{0.8}Cu_{0.2}O_{3-d}$	550	–
$Gd_{0.7}Ca_{0.3}CoO_{3-d}$	> 800	> 800
$Ce_{0.8}Gd_{0.2}O_{2-d}$	> 800	> 800
$Gd_{0.7}Ca_{0.3}CoO_{3-d}$ / $Ce_{0.8}Gd_{0.2}O_{2-d}$ 1:1	> 800	420

Table 2
Comparison of ionic and electronic conductivity at 700°C in air

Material	$\sigma_{ion,air}$ 700°C (Ω^{-1} cm^{-1})	$\sigma_{el,air}$ 700°C (Ω^{-1} cm^{-1})
$La_{0.6}Sr_{0.4}Co_{0.8}Cu_{0.2}O_{3-d}$	6×10^{-2} [13]	2×10^{2}
$Gd_{0.7}Ca_{0.3}CoO_{3-d}$	2×10^{-5}	2×10^{-2}
$Ce_{0.8}Gd_{0.2}O_{2-d}$	1×10^{-2}	2×10^{-5} [14]
$Gd_{0.7}Ca_{0.3}CoO_{3-d}$ / $Ce_{0.8}Gd_{0.2}O_{2-d}$ 1:1	2×10^{-4}	6×10^{-3}
$Gd_{0.7}Ca_{0.3}CoO_{3-d}$ / $Ce_{0.8}Gd_{0.2}O_{2-d}$ 1:2	8×10^{-4}	2×10^{-3}
$Gd_{0.7}Ca_{0.3}CoO_{3-d}$ / $Ce_{0.8}Gd_{0.2}O_{2-d}$ 1:4	2×10^{-3}	2×10^{-4}

To cope with this demand, the ionic conductor $Ce_{0.8}Gd_{0.2}O_{2-d}$ was chosen as one part of a ceramic composite formed with GCC.[15] This led to some multiple benefits concerning its application. Most important, this ceramic composite, like GCC, does also exhibit negligible catalytic activity towards NO (Fig. 2). The level of ionic conductivity is increased drastically in comparison to GCC as can be drawn from Table 2. Optimising the ratio between GCC and CGO within the composite, this increase can be achieved, simultaneously maintaining a sufficient level of electronic conductivity. Taking advantage of the effective medium theory by Wu et al.,[16] the optimum ratio for the ceramic composite GCCCGO with respect to permeation behaviour has been predicted (Fig. 3). Whereas the percolation model of Kirkpatrick[17] excellently describes the values for the σ_{el}, large deviations for σ_{ion} have been observed. Though the reason for this behaviour is still under investigation, we assume a change in Gd dopant level within the ion conducting phase being responsible for this effect. Slight changes, easily taking place during the sintering process, seem to affect the ionic conducting phase much more than the electronic conductor GCC. Although conductive properties usually dominate the behaviour of MIEC membranes concerning oxygen transport properties, limitation due to surface exchange kinetics have to be considered keeping in mind the thickness of the membrane.[18] Hence, by means of ^{18}O-isotopic exchange and depth profiling described elsewhere,[19] the limiting step for permeation has been determined. The results are reported in Table 3.

Concerning the possibilities to cofire membrane materials with yttria-stabilized zirconia, a ceramic well known for its use as lambda-sensors,[20] addition of CGO is also improving the GCC system (Table 4). Since differences in the coefficient of thermal expansion (TCE) of more than 1–2 ppm/K usually lead to crack formation within multilayer structures during sintering and operation in high temperature gradients, the use of pure GCC is impossible.

To determine the overall performance of the sensor system, samples based on GCCCGO have been manufactured using thick film technology. For this reason, several carrier structures have been tested to optimise oxygen transport between the membrane and the pumping unit (Fig. 4). According to the results in Fig. 5, optimisation of oxygen permeation is possible. Nevertheless, the experimental oxygen fluxes are significantly lower than the theoretically expected values. Investigations of the membrane/carrier-interfaces have led to the conclusion that the high sintering temperatures lead to the formation of phases with reduced transport properties. Furthermore, the permeation behaviour drastically decreases within sulphur containing gases.[3]

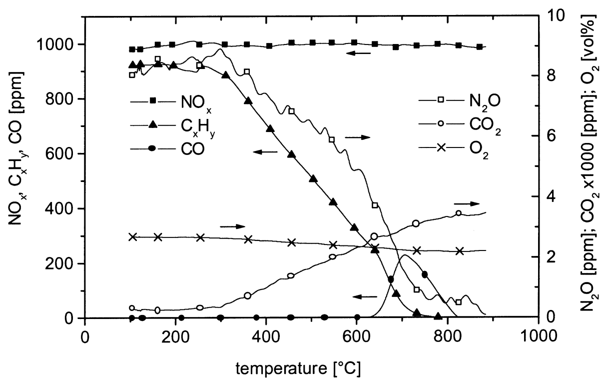

Fig. 2. Temperature dependency of resulting gas mixture of NO_x, C_xH_y, CO, N_2O, CO_2 and O_2 in the measuring-gas after flow through powder mixture of $Gd_{0.7}Ca_{0.3}CoO_{3-d}/Ce_{0.8}Gd_{0.2}O_{2-d}$ 1:1. Feedgas composition: 1000 ppm NO + 950 ppm C_3H_6 + 3%O_2 in N_2.

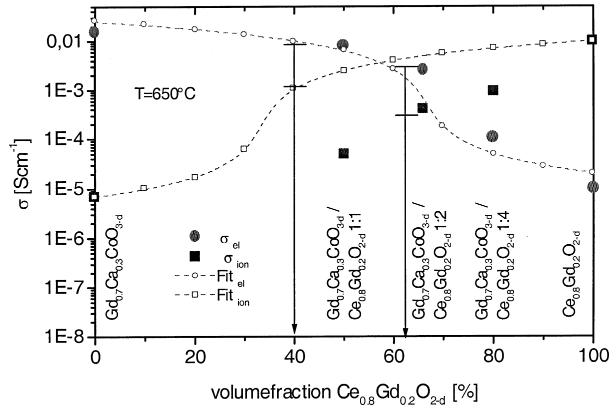

Fig. 3. Ratio dependency of the ionic and electronic conductivity of GCCCGO.

Table 3

Experimental data concerning oxygen permeation rate, activation energy for oxygen ion transport, measuring temperature of permeation rate, thickness of specimen, critical thickness of material and calculated value of permeation for membrane of 20 μm thickness, $\Delta P_{O_2} = 10^{-1}$ bar and P_{O_2} ref being air at 800°C

Material	$J_{O_{2,exp.}}$ (mol s^{-1} cm^{-2})	E_{act} (eV)	At T (°C)	At d (mm)	L_c (mm)	$J_{O_{2,theor.}}$ (mol s^{-1} cm^{-2})
$La_{0.6}Sr_{0.4}Co_{0.8}Cu_{0.2}O_{3-d}$	1.2×10^{-6}	1.1	850	1.5	0.5	1.6×10^{-6}
$Gd_{0.7}Ca_{0.3}CoO_{3-d}$	3.9×10^{-7}	3.0	903	0.89	0.01	1.3×10^{-10}
$Gd_{0.7}Ca_{0.3}CoO_{3-d}/Ce_{0.8}Gd_{0.2}O_{2-d}$ 1:1	7.9×10^{-9}	1.2	863	1.5	0.1[a]	6.1×10^{-8}
$Gd_{0.7}Ca_{0.3}CoO_{3-d}/Ce_{0.8}Gd_{0.2}O_{2-d}$ 1:2	6.3×10^{-9}	1.4	863	1.5	0.1[a]	4.4×10^{-8}
$Gd_{0.7}Ca_{0.3}CoO_{3-d}/Ce_{0.8}Gd_{0.2}O_{2-d}$ 1:4	1.8×10^{-8}	1.3	863	1.52	0.1[a]	1.3×10^{-7}

[a] "Worst-case" calculation based on data for CeO_2 by Kilner.[21]

Table 4
Average linear coefficient of thermal expansion (TCE) between 200 and 800°C in air and Ar 4.8 with Oxisorb™ filter

Material	TCE (ppm K^{-1}) in air	TCE (ppm K^{-1}) in Ar
$La_{0.6}Sr_{0.4}Co_{0.8}Cu_{0.2}O_{3-d}$	14.9	–
$Gd_{0.7}Ca_{0.3}CoO_{3-d}$	20.2	21.2
$Ce_{0.8}Gd_{0.2}O_{2-d}$	10.2	11.1
$Gd_{0.7}Ca_{0.3}CoO_{3-d}$ / $Ce_{0.8}Gd_{0.2}O_{2-d}$ 1:1	10.6	10.8
$Gd_{0.7}Ca_{0.3}CoO_{3-d}$ / $Ce_{0.8}Gd_{0.2}O_{2-d}$ 1:2	10.5	9.8
$Gd_{0.7}Ca_{0.3}CoO_{3-d}$ / $Ce_{0.8}Gd_{0.2}O_{2-d}$ 1:4	10.1	9.7
8Mol%YSZ	9.7	9.0

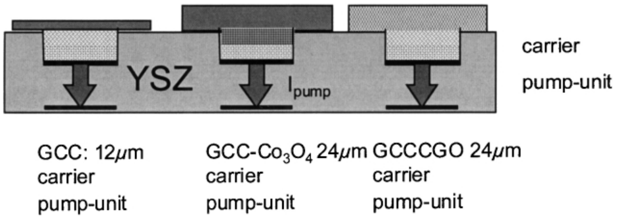

Fig. 4. Variation of carrier structure for optimisation of oxygen-permeation through GCC and GCCCGO membranes.

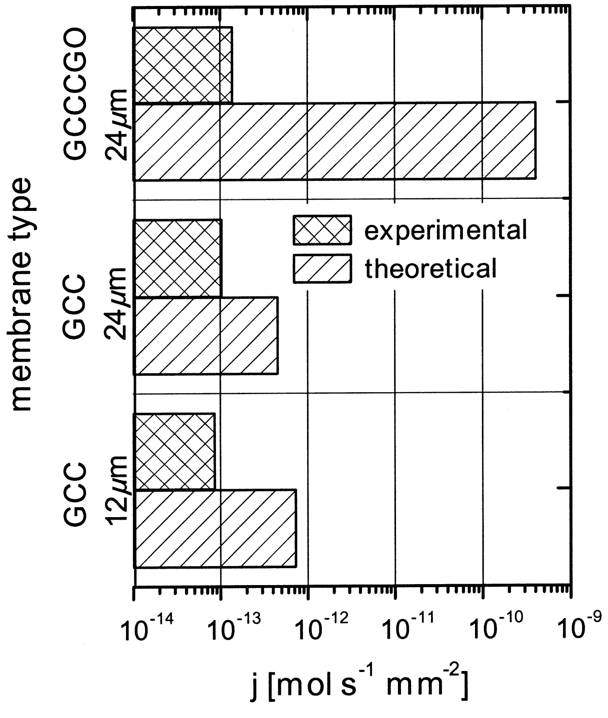

Fig. 5. Influence of carrier structures on the oxygen-permeation rates at 770°C.

4. Conclusions

The use of mixed conducting ceramics as highly selective membranes in amperometric NO_x-sensors for exhaust gas applications has been investigated. We have been able to proof the theoretical capabilities of the new system. However, insufficient permeation properties as well as the lack of stability in sulphur containing environment is still preventing testing in real exhaust gas today. Yet this drawback might be overcome by fuels with lower sulphur content in the near future.

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