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A novel diesel particulate converter

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Abstract

A novel design of an electrochemical reactor for filtering and continuous combustion of soot particles was developed. Such a reactor consists of a porous, oxygen-ion conducting material covered by catalytically active, electron-conductive electrodes, electrical connections and an external power supply. The manufacturing process was developed for high-porosity, ion- and electron-conducting ceramic monoliths from nanosize powders by extrusion followed by coating techniques. The performed catalytic tests proved that the efficiency of the reactor for soot removal is above 90% at low flow conditions (GHSV $= 13\,000^{-1}$) and 75% for high flow (GHSV $= 39\,000^{-1}$) in the temperature range 250–500 °C. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Electrochemical reactor; Diesel engine; Ceramic monoliths

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1. Introduction

It is expected that the market for diesel engines in Europe will grow significantly in the near future (6–7 mill vehicles per year) due to their superior thermal efficiency, durability and reliability and, as a consequence of this, their economy in comparison to the traditional gasoline-powered engines. However, the stringent legislation in the EU (EURO 4 in 2004/5) poses some major challenges for the diesel passenger car which will be difficult to meet without secondary systems (Table 1).

Several techniques were developed for reducing emissions from diesel engines, such as modified or alternative fuels, engine modifications and finally after-treatment technologies [1–5]. Emissions of CO and HC from diesel engines are low and already fulfil standards, and therefore recently the major attention has been focused on the reduction of particulate (soot + SOF) and NO_x emissions [6]. The soot can be easily removed by filtering and oxidation. Particulate filters or traps with tiny pores that capture particles are commonly used for this purpose. As trapped material accumulates, resistance to flow increases and smaller particles are removed until resistance grows so much that regeneration is needed. However, regeneration adds significant cost and complexity, and it is a major obstacle to the widespread use of soot filters. Actually the regeneration is done by heating the filter electrically or by a burner to the ignition temperature of the soot. Such systems are in general too expensive and complicated in operation to gain general acceptance.

There are, however, other systems under investigation to fulfil the requirements of future standards [4–10]. Three systems have a chance to be commercialised in the near future. (i) The first system was developed by PSA in France [7]. The system is based on a periodic increase of the temperature of the porous SiC trap, even up to 1200 °C, by injection of an additional quantity of the fuel with an organometallic compound (Ce-based) which helps in a rapid

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Table 1
European emission limits for light-duty diesel vehicles [1]

	NO_x (g/km)	HC (g/km)	CO (g/km)	PM (g/km)	Valid from
EURO 3	0.40	0.05	1.00	0.05	2000
EURO 4	0.14	0.05	1.00	0.025	2004/5

oxidation of the collected soot (1–2 min). (ii) The second system has been developed by Toyota (the so-called DPNR system) in which absorbed nitric oxides are used for catalytic oxidation of the collected soot [8,9]. The new catalytic system employs three-element catalytic technology that has been developed for gasoline-fuelled vehicles. The new catalyst dramatically reduces both NO_x and diesel particulate soot materials in the diesel exhaust gases by as much as 80% compared to the current catalytic removal level. (iii) A completely new approach is presented by the concept of the electrochemical reactor (ECR) for filtering and continuous combustion of soot particles developed at Dinex Filter Technology A/S, Denmark [10]. The ECR consists of a highly porous, oxygen-ion conducting electrolyte (ceria–gadoline mixture) covered by catalytically active, electron-conductive perovskite (e.g. lanthanum–strontium–manganese (LSM) perovskite) based electrodes (Fig. 1). The porous reactor structure acts as a mechanical filter, trapping the soot particles from the exhaust gas. By polarising the reactor with an external power supply, the combustion process of the collected soot particles can be forced to take place at a low temperature. The lower temperature limit is defined by the ionic conductivity of the electrolyte material. Ceria–gadoline mixture was selected for this purpose which allowed the temperature of operation to go down to 250 °C. By construction of a multilayered system, the voltage over the reactor and the filtering properties can be adjusted to the desired levels. The voltage required for this purpose should be between 24 and 60 V. The HC and CO compounds could also be partly oxidised in the ECR. The following processes take place in the reactor:

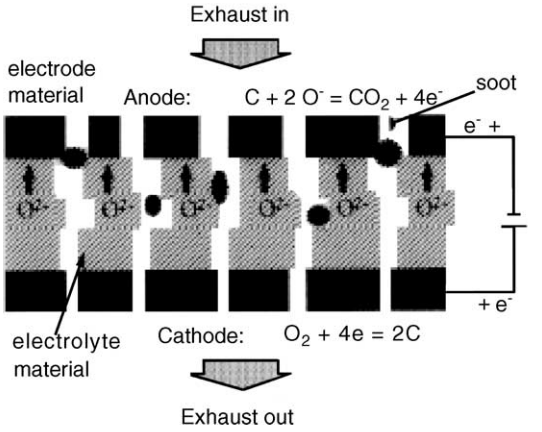

Fig. 1. Principle of the ECR [10].

1. Ionisation of oxygen from off-gases to oxygen-ions
$$O_2 + 4e^- \rightarrow 2O^{2-} \quad (1)$$
2. Migration of oxygen-ions inside the monolithic structure to a soot particle.
3. Oxidation of the soot particle to carbon dioxide
$$C + 2O^{2-} \rightarrow CO_2 + 4e^- \quad (2)$$
4. Removal of CO_2 with off-gases.

2. Experimental procedure

2.1. Materials

A cerium–gadolinium oxides (CGO) mixture and LSM oxides mixture of the perovskite-type in the form of nanopowders were used as basic materials for preparation of the ceramic part of the diesel soot converter. A mixture of commercial waxes was used as a pore former and methyl cellulose polymer as a temporary binder. Cobalt acetate was used as a sintering aid.

CGO mixture. Cerium dioxide has been increasingly used as a promoter in three-way catalysts (TWC) for automotive emission control in recent years. Under various redox conditions, the oxidation state of cerium may vary between +3 and +4. Owing to its nonstoichiometric behaviour, CeO_2 is shown to be a good promoter for oxygen storage [11]. Doped ceria, which has poor sinterability and electronic conductivity in a reducing atmosphere, was considered to have a potential as the solid electrolyte material [12]. On the basis of experimental works it was proved that the binding energy has revealed a minimum when Gd_2O_3 is used as a dopant [13,14]. Therefore the mixture of CGO with a molar ratio of 90/10 from

Rhodia Rare Earth's, F was selected for experiments. The selected parameters of CGO powder are as follows: CeO_2/Gd_2O_3 ratio, 89/11; density, 7.22 g/cm^3; crystallite size, 50–100 nm; specific surface area, 25.9 m^2/g [15]. The powder sinters very well at quite low temperatures, 600–1100 °C, due to the presence of nanosize particles.

Electrode material. In place of expensive platinum, some perovskite-type electronic conductors could be used as electrode materials [16]. Perovskite-type oxides (ABO_3 structure) are characterised by a mixed ionic-electronic conduction in solid electrolytes and they may be used in the preparation of electrode materials for the diesel soot converter, i.e. strontium-doped $LaMnO_3$ ($La_{0.9}Sr_{0.1}MnO_3$). Another specific feature of these perovskite-type oxides is that they can catalyse the simultaneous removal of NO and diesel soot particulates in the presence of oxygen. The LSM compound was purchased from Praxair, USA.

Pore former. Waxes coded TP P 450 and TP P 750 from Th.C. Tromm GmbH, D were used as pore former. These waxes are characterised by particle size distribution in the range 350–600 and 600–900 μm, respectively. Other characteristic properties of these waxes are: density, 0.93 g/cm^3; drop point at 105–115 °C; viscosity at 140 °C, 100–350 cPs.

Temporary binder. The water-soluble methyl cellulose (MC) type polymer grade A4M from Caldic Nederland BV, Nl was selected for fabrication of ceramic monoliths by the extrusion technique. Cellulose is widely used as a binder for ceramic extrusion because it is non-ionic, water-soluble and non-toxic [17]. Methyl cellulose burns out completely to carbon dioxide and water vapour at temperatures above 600 °C.

Other additives. A transition metal salt, cobalt acetate from Merck, D was used to study the effect of doping on the microstructure and electrical properties of ceramic materials in the system CeO_2–Gd_2O_3.

2.2. Methods of manufacture

The porosity of porous materials manufactured in a natural way is on the level of approximately 40 vol.%. To reach the porosity level above 70 vol.%, required in the case of catalytic diesel filters, it is necessary to use well-known methods for increasing the porosity of ceramic products, i.e. incorporation of volatile or combustible burn-outs that are lost during firing [18]. The extrusion of ceramic plastic pastes incorporating a volatile/combustible additive was selected as a major shaping technique for diesel soot traps. A number of paste compositions were prepared with a varied concentration and type of pore former. The aqueous solution of methyl cellulose grade A4M was added as a temporary binder/lubricant to the paste to improve its rheological and lubrication properties and to maintain a good strength of the material in the green stage. The extrusion of tubes with external/internal diameter of 14.4/10.0 mm and later multichannel monoliths was performed (external diameter of 84.0 mm, wall thickness of 8 mm and with square holes of sizes 8 × 8 mm^2). The samples were extruded from the paste prepared from the as-delivered, green CGO powder and also from compositions prepared from the green powder and pre-calcinated at 500, 700 and 900 °C powders. The sintering process was done in the temperature range from 800 to 1250 °C with dwelling time ranging from 1 to 4 h. In an attempt to increase the mechanical strength and, at the same time, decrease the back pressure of the porous material, cobalt acetate was added to some samples. Additionally some monoliths sintered at 950 °C for 2 h were impregnated with 10 wt.% aqueous solutions of this acetate. The impregnated samples were sintered at a 950 °C for 1 h. The selected samples in the tubular and multichannel forms were then coated with 25 wt.% water-based suspension of the LSM powder.

2.3. Characterisation and testing methods

The shrinkage of drying and sintering, open porosity, mechanical strength, back pressure, electrical resistance and microstructure were characterised for the dried/sintered samples. The open porosity of the sintered samples was measured using the water-immersion technique, and also, for comparison purposes, this parameter was also evaluated by mercury porosimetry and by optical microscopy. The microstructure was observed using optical microscopy and scanning electron microscopy (SEM) on polished and fractured samples. The thickness of the LSM coating was taken from the SEM pictures. The crushing strength was measured on the monolithic samples of diameter and height of approximately 25 mm in the INSTROM machine with a cross head speed of

0.5 mm/min (in the axis parallel to the axis of the channels). The results are reported as an arithmetical average of five measurements or statistically evaluated from 10 samples. The back pressure was measured on the tubular monoliths. One end of the tube was connected to a supply of air at room temperature, while the other end was closed. The gas volume was measured by a flowmeter, and the back pressure by an U-tube filled with water, and connected to the entrance side of the tube. Electrical resistance measurements were carried out employing a d.c. four-probe method. Details of the measurements were given in [15].

The ECR was assembled from a bundle of tubes or just consisted of the multichannel monolith. Every second channel was closed alternately from each monolith side. A silver paint was used on the end plates for establishing electrical connections to the electrode layer and connected to the external electric power supply to complete the circuit. This system was tested in a set-up built from the naturally aspired Mitsubishi diesel engine (1.8 l) and a control panel where the pressure drop, flow of gases, and concentrations of PM, NO_x, CO, CO_2 and SO_x were simultaneously measured. The measurements are made at steady conditions: 1550 rpm and power of 16.5 kW. The filter measurements were performed on a part of off-gases stream from the engine (approximately 20% of the full exhaust stream). The exhaust gas temperature at the filter position was between 300 and 320 °C. The PM was measured gravimetrically by filtering a part of the gas stream through Teflon-coated glass filters (Pallflex). The soot production under these conditions was 0.36 g/kW h. The NO_x, CO, CO_2 and SO_x concentrations were measured with a FTIR (Perkin-Elmer Spectrum 2000) equipped with a 20 m gas cell. The gas concentrations were measured relatively. The development of the back pressure over the filter element was monitored. The increase in the back pressure value was also taken as an indication of the soot accumulation. The decrease in the back pressure indicated the net soot combustion, and the constant back pressure was considered as a steady state condition where the soot is combusted with the same rate as it is accumulated in the filter. After each test the filters were inspected for soot accumulation. The influence of the ash from lubricating oil has not been investigated within this work.

3. Results and discussion

The composition of the plastic paste for extrusion consisted of the CGO powder in the range 50–25 vol.%, pore former in the range 50–75 vol.%, MC A4M in the quantity 4 wt.% (calculated relative to the combined weight of CGO and pore former), and water in the quantity of 20–25 wt.% (calculated relative to the combined weight of CGO and pore former).

The first experiments showed that it is necessary to introduce a maximum quantity of pore former (75 vol.%) to the paste to obtain the total porosity of the porous material above 70 vol.%. The second very important conclusion was that the pore former of a rectangular shape is only suitable for manufacturing of the crack-free ceramic monolith. Therefore in the further research only the rectangular shape pore former TP P 450 was used. The third conclusion from this preliminary research was that the use of as-delivered fresh powder has a negative influence on the extrusion properties of the paste and is a source of cracks during the drying process. To solve this problem the CGO powder was pre-calcinated at the temperatures of 500, 700 and 900 °C for 2 h and the pre-calcinated powder replaced the fresh powder in the composition of the plastic paste partly or totally. The performed tests with all pre-sintered powders indicated that the temperature of pre-calcination 900 °C was too high. The CGO material lost a lot of its reactivity and manufactured products were very weak, too weak even for the manual handling. Therefore 700 °C was selected as a standard pre-sintering temperature and a combination of the fresh powder with the pre-sintered powder was used in further experiments to avoid the drying cracks and to ensure a good sinterability of the mixture. The temperature of 950 °C was selected as an optimum temperature for the sintering process with a residence time of 2–4 h. The more detailed results of this investigation are reported in [15]. In such sintering conditions the growth of nanocrystals is very limited, the porosity is very high and the resulting strength is relatively good. However the developed porous CGO material with such strength cannot survive for a long time (minimum 100 000 km) in the real working conditions in diesel vehicles. Therefore it was necessary to improve the strength of the material either by increasing the temperature of sintering or by addition of sintering additives. The second option was more economically attractive and therefore the transition metal oxide (CoO) was introduced to the composition of the CGO material as a dopant. The sintered CGO samples were either impregnated with a 10 wt.% aqueous solution of the corresponding metal acetate or the metal acetate was introduced in the quantity of 1 wt.% to the composition of the standard paste before the extrusion process.

The second important parameter of the porous material, the back pressure, was too high, 83.2 kPa, in comparison to the required value which was less than 15.0 kPa. The performed analysis of the macro- and mesopores size distribution by linear intercept of the polished CGO samples revealed that the majority of macropores were between 20 and 300 μm. The average pore size differed from sample to sample, depending strongly on the pore former used and the sintering temperature. The average macropore size for the standard composition sintered at 950 °C for 2 h was 149.0 μm. A majority of pores, however, were closed. Thin walls were built from nanocrystalline CGO particles, close packed, and with mesopores of sizes between 20 and 100 nm (mercury porosimetry measurement). To lower the back pressure it was thus necessary to make the thin walls between the big pores more open. A differential sintering shrinkage of the thick/thin parts of the ceramic body was implemented to solve this problem. This improvement, however, was combined with a strong decrease in the open porosity value, from 77 to 69%. The cobalt oxide, however, must be introduced into the porous CGO structure by the impregnation process but not by a simple addition of the CoO to the plastic paste before the extrusion process (see Table 2, data for compositions M1 and M2). Addition of CoO to the CGO composition resulted in a much higher shrinkage of the ceramic body and a lower porosity, but on the other hand the permeability of the system was growing. The SEM investigation showed that the walls of large pores of samples made only from the CGO powder were formed from a thin, continuous film of CGO nanoparticles. Introducing very strong sintering aids such as CoO to the system, a higher shrinkage of the system was observed which resulted in the formation of cracks and holes in the thin walls thus making the structure more open for the flow of gases or liquids. The addition of CoO to the composition of CGO material has also an influence on the electrical resistance of the system, lowering its value by a factor 4.

Deposition of the electrode layer on the surface of the CGO monolith was made by a dip-coating technique using a 25 wt.% water-based suspension of the LSM powder. The CGO porous samples were coated once, which resulted in a coating with the thickness of approximately 100–200 nm. Coated samples were dried at ambient temperature and sintered at 900 °C for 1 h. The main concern was whether the LSM coating adheres well to the CGO material due to a significant difference in their coefficients of thermal expansion, 22.5×10^{-6}–$9.0 \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$, respectively, in the temperature range 20–900 °C. The

Table 2
Standard composition of the paste for extrusion, its further modifications, and the properties of the manufactured monoliths sintered at 950 °C for 2 h

Composition	Standard M0	Modified M1 (infiltrated with 10 wt.% co-acetate solution)	Modified M2 (1 wt.% CoO added to the paste)
CGO fresh (vol.%)	10.0	10.0	10.0
CGO pre-calcination at 700 °C (vol.%)	15.0	15.0	15.0
Pore former TP P 450 (vol.%)	75.0	75.0	75.0
Properties of the CGO samples sintered at 950 °C for 2 h			
Drying shrinkage (%)	8.3–14.5	–	–
Total (drying + sintering) shrinkage (%)	21.0–23.5	25.1 ± 0.4	27.9 ± 1.4
Total porosity (%)	76.5–77.0	68.4–69.7	60.0–61.0
Average pore size (μm)	149.0	–	–
Crushing strength (MPa)	2.24	6.8 ± 3.9	16.9 ± 0.6
Electrical resistance (kΩ/mm)	111	23	11
Back pressure (kPa)	83.2	10.4	559.6

Table 3
The catalytic efficiency test performed on the electrochemical clean-up system in the diesel engines

	Percentage of removed compounds (%)			
	PM	CO	HC	NO_x
Low flow conditions ($GHSV = 13\,000^{-1}$)	>90	75	65	<10
High flow conditions ($GHSV = 39\,000^{-1}$)	75	60	50	<10

formed coating adhered very well to the surface of the porous CGO material creating a good packing layer on it. The heating/air-cooling test between 20 and 600 °C (typical temperature shock for an exhaust system of a diesel engine) repeated 100 times did not show any influence on the quality of the coating.

In the first stage of the project the ECR was constructed from single stacking tubes and tested for soot removal. Then a porous multichannel monolith was produced by the extrusion process and employed for this task. In both the performed measurements an efficiency of above 90 % for soot removal at low flow ($GHSV = 13\,000^{-1}$) and 75% at high flow ($GHSV = 39\,000^{-1}$) was measured in the temperature range 230–320 °C (Table 3). The HC and CO compounds were also partly oxidised in the ECR with an efficiency up to 65 and 75%, respectively. The NO_x compounds were only partly removed from the off-gases and therefore an additional deNO_x system is necessary to remove the NO_x from the off-gases and fulfil the requirements of the EURO 4 standards. It was experimentally proved that the reactor operates efficiently in the temperature range 250–500 °C. A power supply and control system was powered from the vehicles battery. The fuel penalty from placing the reactor in the exhaust system was estimated to be less than 0.5%.

4. Concluding remarks

- An electrochemical system acting as a trap for the continuous removal of soot particles from diesel exhaust gas, with an efficiency of above 90%, has been developed.
- Perovskite-type nanocrystalline powders, CeO_2–Gd_2O_3 mixture and LSM, were applied successfully for manufacturing of the ceramic particulate trap by an extrusion/coating process. The mechanical strength and permeability parameters were adjusted by the addition of CoO sintering aid to the ceramic system. The porosity of the sintered monolith was approximately $70 \pm 2\%$, which with a suitable pore size distribution resulted in a low back pressure for the system, below 15.0 kPa.
- There still seems to be room for improvement of the system efficiency by optimization of the over-all physical shape and of the pore structure.
- The developed ECR for soot removal seems to be very promising and competitive with other clean-up systems developed for diesel engines exhaust. The system is very simple to introduce in existing exhaust systems. It is expected that the ECR filter will operate on all types of diesel engine, from the largest heavy-duty truck down to the smallest passenger car.
- On-road testing on passenger cars and heavy duty vehicles has been started, and depending on the results of these tests, commercialisation of the system is expected to begin in the near future.
- The system shows great promise and can be utilised both as a retrofit system on existing vehicles and as an original equipment manufacturing (OEM) system on new vehicles.

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