Perovskite coatings in microwave - assisted soot filter regeneration

Zhang, Y.

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Chapter 6

Microwave-assisted in-situ regeneration of a perovskite coated Diesel soot filter

ABSTRACT

Dielectric heating may be used as an *in-situ* technique for the periodic regeneration of soot filters, as those used in Diesel engines. As generally the Diesel exhaust temperatures are below the soot light-off temperature, passive regeneration is not possible. Presently we have investigated the dielectric heating of a monolithic soot filter, coated with a La$_{0.8}$Ce$_{0.2}$MnO$_3$ perovskite. This type of perovskite has suitable dielectric properties, i.e. a high dielectric loss factor, and simultaneously acts as an oxidation catalyst. It is shown that a perovskite coated cordierite filter, covered with synthetic carbon, can be fully regenerated with selectivity towards CO$_2$ close to 100 %. In contrast, the same filter without such a coating can only be partially regenerated. Moreover, considerable amounts of CO are formed. The La$_{0.8}$Ce$_{0.2}$MnO$_3$ coating is shown to have excellent temperature shock resistance and thermo-chemical stability. It is shown that the microwave cavity design is crucial to obtain a uniform filter heating. Following the development of such a design, microwave assisted soot filter regeneration becomes feasible.

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6.1 INTRODUCTION

Diesel engines are widely used in many on- and off-road applications as they combine a high fuel economy, a high durability and low maintenance costs. The disadvantage of Diesel engines is that they generate pollutants, hazardous to human health. Particularly the emission of particulates such as soot is dangerous due to their potential mutagenic and carcinogenic activity [1,2]. For this reason, a drastic emission abatement policy for Diesel emissions is currently being implemented by the United States, Japan and Europe in the coming 5 years [1,3,4].

Diesel particulate matter consists mainly of highly agglomerated solid carbonaceous material and ash, in addition to volatile organic and sulphur components [5,6]. Soot formation and morphology have been extensively investigated [6-9]. Based on these studies, different exhaust control strategies have been proposed over the past decades to reduce particulate emissions, i.e. passively regenerated filters using homogenous fuel additives or catalytically active filters [10,11]. A major problem is the fact that Diesel exhaust temperatures are generally low as compared to soot light-off temperatures. Hence, additional filter or exhaust gas preheating is normally required. Alternatively, dielectric heating may be applied [12]. The advantage is that dielectric heating is a bulk heating technique and therefore it is fast and selective. Microwave heating has been applied in many organic chemical reactions, and surprisingly high reaction rates have been reported [12-14]. Also, dielectric heating has been applied to reduce HC, CO and NOx emissions during cold-start [15]. These authors showed that Pd-Ce based catalysts can be heated rapidly and uniformly by using microwave-absorbing ceramic foams containing Fe3O4, TiO2, NiO and SiC. Gao et al. [16] demonstrated that for microwave-assisted Diesel ceramic soot filters a regeneration efficiency close to 80 % can be reached. Nixdorf and co-workers [17] reported similar efficiencies for filter cartridges made of silicon carbide fibres. However, a general remaining problem to be resolved is the CO formation during regeneration. Gao et al. and Nixdorf et al. [16,17] for example observed a dramatic increase in the CO emission during regeneration.

The objective of the present work is to assess the feasibility of microwave assisted soot filter regeneration for filters coated with a material that is both catalytically active, and has suitable dielectric properties. Perovskites are examples of such materials [18-22]. Synthetic carbon was used as model soot, since soot contains approximately 70 % of
carbon. The soot filter regeneration is studied using synthetic carbon deposited on both an uncoated filter, and a filter coated with a La_{0.8}Ce_{0.2}MnO_3 perovskite. Aspects covered included the regeneration efficiency, CO formation, the temperature uniformity and the thermal shock resistance and thermo-chemical stability. Estimates were obtained for the convective heat loss to be expected in case of realistic gas-hourly space velocities in the filter. In this way the basic parameters for assessing the feasibility of microwave regeneration of a perovskite coated soot filter were obtained.

### 6.2 EXPERIMENTAL

#### 6.2.1 Sample preparation

A perovskite-type oxide, La_{0.8}Ce_{0.2}MnO_3 (99.9%), as manufactured by Praxair Specialty Ceramics, prepared by combustion spray pyrolysis, was used as a coating material. The monolithic filter used consists of a cordierite flow-through substrate (Corning Inc.) (length = 40 mm, diameter = 15 mm, cell density = 400 cpsi). A filter coated with 14 wt% perovskite (MP1) has been prepared by dip coating with an aqueous suspension of 50 wt% perovskite, followed by calcination at 1123 K and a heating rate of 2 K min^{-1}. For this filter, the heating and cooling rates and heat loss characteristics have been studied with respect to exposure to a dielectric field, along with the temperature distribution throughout the monolith.

The resistance towards thermal shock was tested for two monolithic filters. MP2 was first moistened with doubly distilled water, followed by dip coating with a perovskite suspension (60 wt%), dried, and calcined by heating with 2 K min^{-1} to 1123 K. MP3 was prepared by the same procedure except being moistened before dip coating by water.

Finally, soot filter regeneration is mimicked using synthetic carbon. In order to obtain a homogeneous temperature distribution, rectangular monoliths (length 40 mm, width 14 mm and thickness 5 mm) were used as substrates (Corning Inc.). These were placed in a specially designed rectangular quartz reactor. Two filters were prepared according to the procedure described above: one coated both with perovskite and synthetic carbon (Merck, 98 % carbon) (MPC) and another one with synthetic carbon (Merck, 98 % carbon) only (MC). For all monoliths, the obtained compositions are given in table 6.1.
Table 6.1: Designation of cordierite monolithic filters. Loadings are given as a function of the total weight.

<table>
<thead>
<tr>
<th>Monolith</th>
<th>Perovskite Loading (wt%)</th>
<th>Carbon Loading (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP1</td>
<td>14.0</td>
<td>-</td>
</tr>
<tr>
<td>MP2</td>
<td>5.40</td>
<td>-</td>
</tr>
<tr>
<td>MP3</td>
<td>34.6</td>
<td>-</td>
</tr>
<tr>
<td>MPC</td>
<td>36.4</td>
<td>2.1</td>
</tr>
<tr>
<td>MC</td>
<td>-</td>
<td>6.2</td>
</tr>
</tbody>
</table>

6.2.2 Microwave heating system

The experiments were performed with a set-up consisting of an inlet manifold connected to a reactor specially designed for exposure to microwave radiation, see figure 6.1.

Figure 6.1: Scheme of a 2.45 GHz microwave set-up: (a) water trap, (b) oxygen trap, (c) mass flow controller, (d) microwave source (Muegge), (e) generator (Muegge), (f) circulator (Philips), (g) stub tuners (Muegge), (h) power sensor (Rhode & Schwarz), (i) optical fibre (Luxtron, accufiber), (j) quartz tubular reactor, (k) water load, (l) Quadrupole mass spectrometer (Balzers, Prisma QMS 2000).
The inlet manifold consists of two mass flow controllers, allowing reactant compositions to be changed. The reactant and product concentrations in the effluent are measured by a mass spectrometer. The microwave system comprises a travelling wave once-through set-up with a microwave source with a continuously variable power supply (1 kW) operating at 2.45 GHz. This system consists of a circulator, a three-stub tuner section, an applicator $TE_{10}$, and a water dummy load. The stub tuners serve to minimise the reflected microwave radiation. The microwave source is protected from the reflected radiation by means of a circulator. A quartz sample tube (i.d. = 18 mm), is placed perpendicular to the direction of propagation. The bed temperature is assessed by means of an optical fibre with a lower detection limit of 373 K. The optical fibre was calibrated in a conventional furnace against a thermocouple over the range 293 – 923 K.

6.2.3 Thermal stability and temperature distribution

The thermal stability of the coating towards dielectric heating is studied for MP1 (see table 1) by rapid and repeated heating at an incident microwave power supply of 200 W in a helium flow. In addition the thermal stability of perovskite coating was assessed in a specially developed thermal shock test system (figure 6.2). Two filter elements MP2 and MP3 were tested by exposing them to 600 subsequent temperature cycles between 393 K and 853 K. The surface morphology of the tested filters was studied using Scanning Electron Microscopy (Jeol, JSM-6330F).

The temperature distribution in MP1 has been investigated by measuring the temperature at difference positions in the filter as pointed out in figure 6.3. The average surface temperature of the monolithic filter was measured at those positions at an incident power of 100 W, 200 W and 300 W respectively.
Figure 6.2: Principal of the set-up for assessing thermal shock resistance. Temperature cycle: 353 K – 853 K, time period of 2.20 min.

Figure 6.3: Location of temperature registration to determine the temperature distribution for MP1: points 1, 2, and 3 indicate the locations of temperature measuring points.
6.2.4 Filter regeneration procedure
Temperature-programmed oxidation of the synthetic carbon deposited on the monolithic filters with and without La$_{0.8}$Ce$_{0.2}$MnO$_3$ perovskite coatings (MPC and MC, respectively) was carried out in a single-mode cavity as described above, using a O$_2$ (Praxair, 99.5%)/He (Praxair, 99.999%) gas mixture (v/v 5/95, GHSV = 10700 hr$^{-1}$). In each test, the temperature was raised from 293 K to 1023 K at maximum heating rate (295 K·min$^{-1}$) and maintained at the target temperature for one hour.

6.3 RESULTS AND DISCUSSION

6.3.1 Dielectric heating properties
A La$_{0.8}$Ce$_{0.2}$MnO$_3$ perovskite coated monolithic filter (MP1) was repeatedly heated at an incident power of 200 W and cooled down in a helium flow. In figure 6.4, it is shown that heating proceeds in a repeatable way to a constant temperature (834 K). Even after a large number of heating and cooling cycles, the heating behaviour remains unchanged, indicating an excellent thermal and chemical stability of the coating during repeated dielectric heating cycles.

![Graph](image)

Figure 6.4: Three subsequent dielectric heating cycles in He (GHSV = 1000 hr$^{-1}$) at 200 W for a La$_{0.8}$Ce$_{0.2}$MnO$_3$ perovskite coated monolithic filter (MP1); (○): temperature; (□): incident power supply.
Since the ceramic cordierite monolithic substrate can be considered transparent to the dielectric field due to its low dielectric constant and loss factor (see table 6.2), it can be assumed that microwave energy is selectively absorbed by the perovskite coating only. In figure 6.5, it can be observed that the absorbed microwave power increases more or less linearly with the observed temperature, which indicates an increase of the dielectric loss at high temperatures.

Table 6.2: The dielectric constant (\(\varepsilon'\)) and loss factor (\(\varepsilon''\)) of cordierite and La\(_{0.8}\)Ce\(_{0.2}\)MnO\(_3\) perovskite.

<table>
<thead>
<tr>
<th></th>
<th>Dielectric constant ((\varepsilon'))</th>
<th>Dielectric loss factor ((\varepsilon''))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cordierite</td>
<td>2.9</td>
<td>0.14</td>
<td>[23]</td>
</tr>
<tr>
<td>La(<em>{0.8})Ce(</em>{0.2})MnO(_3)</td>
<td>21.0</td>
<td>3.6</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 6.5: The ratio adsorbed-to-incident power versus the observed temperature at an incident power of 200 W for La\(_{0.8}\)Ce\(_{0.2}\)MnO\(_3\) perovskite coated monolithic filter (MP1), GHSV = 1000 hr\(^{-1}\), in helium.

Whereas a homogeneous temperature distribution throughout the filter is desired, large differences across the filter exist in reality for a travelling wave microwave system. The
microwave field is directed towards the catalytic bed through a waveguide, where the electric field is no longer a uniform plane wave. The wave propagating through the waveguide in the x direction is the sum of two plane waves and has a sinusoidal form across the width, or y direction, of the waveguide (figure 6.6) [24].

Figure 6.6: A waveguide operating in the TE$_{10}$ mode with an electric field propagating in the x direction.

In order to obtain an estimation of temperature variations over the filter, the temperature during dielectric heating was measured at three positions in filter MP1 (figure 6.3). It could be observed that the temperature is highest in the centre of the filter, while the lowest temperature was found at the centre of the outer layer of the filter, where the lowest amplitude of the electric field exists (figure 6.7). The temperature difference is about 100 K at these supplied incidence powers, pointing out that the temperature is strongly non-uniform when a single mode cavity is used.

In order to reduce the temperature gradient across the filter, and thus ensure that the average surface temperature of the filter is high enough for carbon burn-off under the existing test conditions, rectangularly shaped filters (MPC and MC) have been used for filter regeneration at an operating temperature of 1023 K.
6.3.2 Thermal shock resistance

For practical applications, the thermal stability of the coating is of great importance. As the coating is periodically exposed to rapid heating and cooling, no erosion or blocking of the monolith channels should occur, even after thousands of cycles. Hence, the thermal stability of the coating was tested by repeated thermal shock experiments carried out by means of a specially developed set-up (figure 6.2). The surface morphology of the coating material was studied using SEM for monolithic filters MP2 and MP3. No significant loss in weight after the test could be observed. Also the surface structure after the test remained identical, as shown in figure 6.8. The big clusters in figure 8a belong to the cordierite substrate. Due to its low perovskite loading (5.4 wt%), the coating does not completely cover the surface of the substrate for MP2. Some cracks were observed on the surface of filter MP3 (figure 6.8b). These were also present immediately after calcination, indicating that they originate from the drying and calcination procedure. As this coating is rather thick at the position of the crack, i.e. at the corner of the filter channel, it can well be attributed to shrinkage of the coating during drying. Surprisingly, the coating with a high loading shows a finer surface structure. Possibly, the thin coating dries homogeneously, while for a thicker coating net migration of small particles to the surface may occur, leading to further levelling of the layer thickness. For neither of the filters, additional abrasion occurs during
the thermal shock experiment, indicating that the thermal stability of the coating is adequate for the present purpose.

Figure 6.8: SEM images of monolithic filter MP2 before (a) and after (b) the thermal shock test. Ditto before (c) and after (d) for MP3.

### 6.3.3 Filter regeneration

Temperature-programmed oxidation of synthetic carbon was carried out for filters MPC and MC, respectively. When the ceramic filter coated with carbon only (MC) is subjected to temperature-programmed dielectric heating, the onset of the formation of CO and CO$_2$ can be observed at 700 K. This is accompanied by a drop in the O$_2$ concentration (figure 6.9).
Figure 6.9: Temperature-programmed filter regeneration during microwave heating over an uncoated filter (MC); feed gas: O\textsubscript{2}/He (v/v 5/95, GHSV = 10700 hr\textsuperscript{-1}); \(dT/dt = 295\) K/min; \(dX_{\text{CO}}/dt\) and \(dX_{\text{CO}_2}/dt\) are formation rates of CO and CO\textsubscript{2}, respectively. Temperatures below 373 K are out of the low detection limit of the optical fibre.

After reaching a maximum temperature, the temperature continuously drops. Three stages can be distinguished: (1) initially dielectric heating results in a continuous temperature rise as result of microwave absorption by carbon, (2) a rapid temperature increase due to the exothermicity of carbon oxidation and (3) a final stage where temperatures drop, even for the maximum power input, due to the loss of the microwave absorbing medium and the reduced heat released by oxidation. Such stages were also observed by Ma et al. [23] for microwave-heated combustion of carbonaceous materials. The heating efficiency, and
thus the maximum attainable temperature, depends directly on the amount of carbon that is present on the filter. When the microwave power used is insufficient to reach carbon light-off temperatures, the carbon conversion remains incomplete [25]. For the MC filter, carbon is partially converted into CO, rather than CO$_2$ and the overall carbon conversion is limited to about 65 wt%.

For the filter coated with both perovskite and carbon (MPC) turning on the dielectric field leads to a rapid temperature rise, even for an incident power below 250 W.

![Graph](image)

Figure 6.10: Temperature-programmed filter regeneration during microwave heating over a monolithic filter coated with perovskite (MPC); feed gas: O$_2$/He (v/v 5/95, GHSV = 10700 hr$^{-1}$); $dT/dt = 295$ K/min; $dX_{CO}/dt$ and $dX_{CO2}/dt$ are formation rates of CO and CO$_2$, respectively. Temperatures below 373 K are out of the low detection limit of the optical fibre.
Under these conditions, the carbon light-off temperature is reached within 2 minutes. CO\(_2\) formation starts at about 700 K (figure 6.10), reaches a maximum and subsequently drops as a result of the continuously decreasing carbon loading. Only a negligible amount of CO can be detected in the outlet, providing evidence that the perovskite coating is effective in converting any primary CO to CO\(_2\). In contrast to what was observed for the uncoated filter, thanks to the presence of the perovskite coating the temperature of the filter can be maintained on a constant, high level, allowing regeneration efficiency close to 100%.

6.3.4 Heating characteristics at high space velocities

It is important to establish whether the soot light-off temperature can be reached under conditions where space velocities are used in the order of 50,000 hr\(^{-1}\). Such a value is well beyond the capabilities of the experimental set-up used by us. Experiments with a varying space velocity in the range of 1000 – 8000 hr\(^{-1}\) were carried out using helium. Within this space velocity range the final temperature reached at an incident power of 300 W is linearly correlated with the gas-hourly space velocity (figure 6.11).

![Graph showing linear regression line for temperature vs. gas space velocity](image)

**Figure 6.11:** The observed temperature of monolithic filter MP1 versus gas hours space velocity during 600 s of dielectric heating at an incident power of 300 W, GHSV = 1000 hr\(^{-1}\) to 8000 hr\(^{-1}\). – Linear regression line.
Extrapolation to a space velocity of 50,000 hr\(^{-1}\), results in an estimated the surface temperature of \(~700\) K with an error less than 10 %. Since the thermal conductivity of air is much lower than that of helium, it can be expected that the surface temperature of the filter will be higher for air. Carbon burn-off temperatures range from 673 K – 723 K [17]. Therefore, up to space velocities of 50,000 hr\(^{-1}\), self-sustained carbon burn-off can be maintained.

### 6.4 CONCLUSION

Soot filters may in principle be regenerated in a dielectric field, by making use of the microwave absorbing properties of soot. However, carbon light-off temperatures can only maintained for a short period, as in this case the carbon itself is the only high-loss dielectric material present. Also substantial amounts of undesired CO are formed. As is presently shown, this way of regeneration can be improved substantially by using a filter coating that pairs suitable dielectric with catalytic properties. An example of such a coating material is a La\(_{0.8}\)Ce\(_{0.2}\)MnO\(_3\) perovskite. Using this filter coating the oxidative regeneration of a filter loaded with synthetic carbon proceeds to completion, is fast and demonstrates a high selectivity towards CO\(_2\). The La\(_{0.8}\)Ce\(_{0.2}\)MnO\(_3\) coating exhibits excellent thermal stability as demonstrated by thermal shock tests. An analysis of the convective heat losses according to our estimates showed that, for cold inlet gases, the soot light-off temperature of 700 K can be reached for space velocities up to 50,000 hr\(^{-1}\).

The non-homogeneous electric field distribution in the monomode cavity, this cavity gives rise to substantial temperature gradients in the filter. Cavity modifications – to obtain a more uniform temperature distribution – are currently underway.

### REFERENCES