# PROBLEMS CONNECTED WITH THE CONSTRUCTION AND THE FUNCTIONING OF THE PROTOTYPE OXIDISING CATALYTIC CONVERTER WITH THE WASHCOAT REPLACED BY THE SPATIAL STRUCTURE OF CARBON NANOTUBES

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***Abstract***

*Nanomaterials and nanotubes represent a relatively new area of science and industrial practice. The authors of the article suggest replacing the standard washcoat of the catalytic converter and using the nanotubes, which is expected to substantially increase the contact surface of the catalytic layer with the exhaust gases. The article presents the problems in constructing the prototype catalytic converter as well as solving them and the construction of the converter. The constructed prototype oxidising catalytic converter was constructed by covering the standard ceramic core with cell density equal to 400 cpsi. The layer of nanotubes with an extended surface contact with exhaust gases was covered with platinum in a much lower amount than in a standard converter. The prototype converter was assembled in the exhaust systems of modern, turbo-charged diesel engines. The converter was subject to preliminary research on the engine test bed and in the road test NEDC. The research outcomes of conversion of the prototype converter confirm the possibility of applying nanotubes in the atmosphere of exhaust gases. They also indicate that if the existing problems were solved, the converters built according to the prototype converters could be used on an industrial scale. The most significant problems to be solved can be observed in covering the core with the nanotubes layer of an organised spatial structure. Moreover, it is essential to obtain such features of the platinum cluster which enable to lower the light-off temperature. An analysis of benefits resulting from applying the described prototype converter and possible technical solutions aiming to reduce the observed technical problems are included in the summary of the article.*

***Keywords:*** *oxidising catalytic converter, carbon nanotubes*

## 1. The future of nanomaterials in the automotive industry

Nanotechnology is commonly regarded as one of the key technologies of the 21$^{st}$ century and its importance results from some of the unique properties of nanomaterials – mechanical, electrical, thermodynamic and optical properties, much different from the properties of conventional construction materials [1, 2, 4]. Carbon nanomaterials create crystalline structures of extremely limited concentration of defects. The crystalline structure ensures a high hardness and mechanical durability, at least an order higher than in the case of steel and, at the same time, a very high plasticity [9, 10]. The crystalline structure, created by the carbon atoms placed in the plane of a graphen, is presented in Fig. 1. The rolled graphen constitutes a carbon nanotube [6-8].

A number of inspiring examples of using nanotubes, e.g. in constructing catalytic converters, can be found in literature [3]. The authors of the paper assume that it is vital to test the possibility of using the carbon nanotubes in the catalytic converter in the exhaust system of the internal combustion engine.

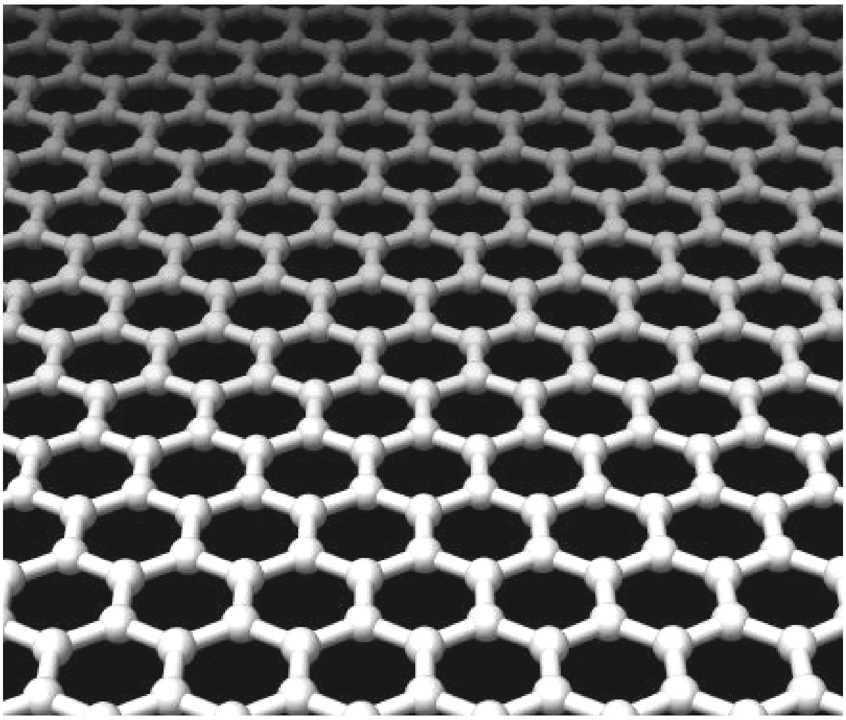

*Fig. 1. The structure of graphen*

The ratio of the body surface to its volume increases as the volume decreases. The nanotube, which can be seen as a slim cylinder of a diameter measured in nanometres and a height greater by a few orders, is characterised by a favourable ratio of its surface to volume and, consequently, it can be an advantageous ground for the catalytic layer of the converter.

## 2. Preliminary research of the pre-prototype of the nanotubes converter on the engine test bed

The standard construction of a catalytic converter includes a ceramic core, covered with a washcoat, increasing its roughness and the surface of contact with the exhaust gases. In the case of the oxidising converter applied in diesel engines, platinum covers the washcoat. The authors constructed a pre-prototype converter in which the washcoat had been replaced with a nanotube layer and covered with platinum nanoparticles of 4nm diameter. Only a certain part of the exhaust gases stream is directed to the pre-prototype converter. The diameter of the converter amounts to 84mm while the length of its core amounts to 20mm and the cell density is equal to 400 cpsi. The pre-prototype converter was built in the Department of Thermodynamics of the Poznan University of Technology, within the confines of international cooperation with the Boston College, US, and Hahn-Meitner-Institut in Berlin. A typical picture of the obtained converter surface observed by a transmission electron microscope can be seen in Fig. 2. More detailed information concerning the process of growing nanotubes can be found in K. Kempa's publication [5].

Conversion research with regard to selected toxic components of exhaust gases was conducted in the laboratory of internal combustion engines at the Poznan University of Technology.

The Volkswagen TDI engine, AXE, was used in the experiment. The engine complies with the emission limits EURO 4. The research of the exhaust gasses was implemented by means of an exhaust gas testing unit, TESTO 360. Fig. 3 presents the view of the engine test stand with the Volkswagen TDI engine, a testing analyser, TESTO 360, and the pre-prototype converter.

The pre-prototype converter cannot be treated as a fully functional device, ready for industrial use in the present form of the product. The exhaust gases conversion rate and the flow resistance could not be accepted. The parameters would be unacceptable due to, e.g., the size of the core.

However, the authors aimed to check the basic functioning of the pre-prototype converter. They also intended to draw preliminary conclusions. Tab. 1 presents the preliminary research outcomes.

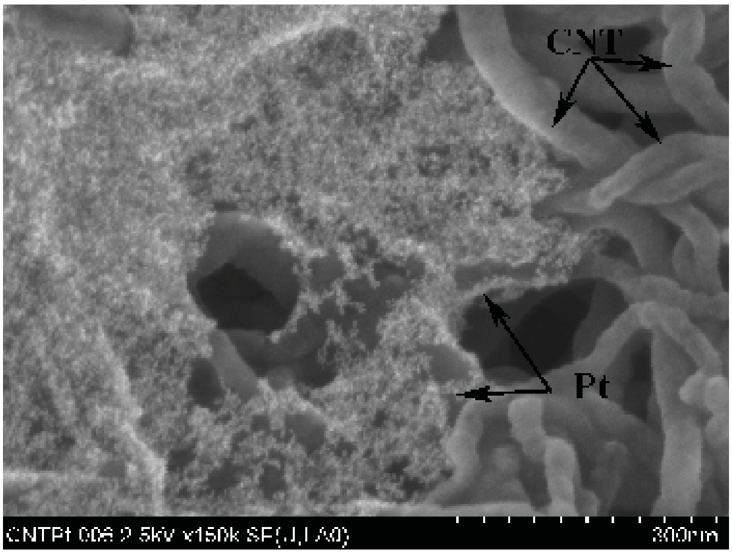


*Fig. 2. Carbon nanotubes covered with nanoparticles of platinum. Real picture of the pre-prototype contact surface with exhaust gases obtained by means of a transmission electron microscope*

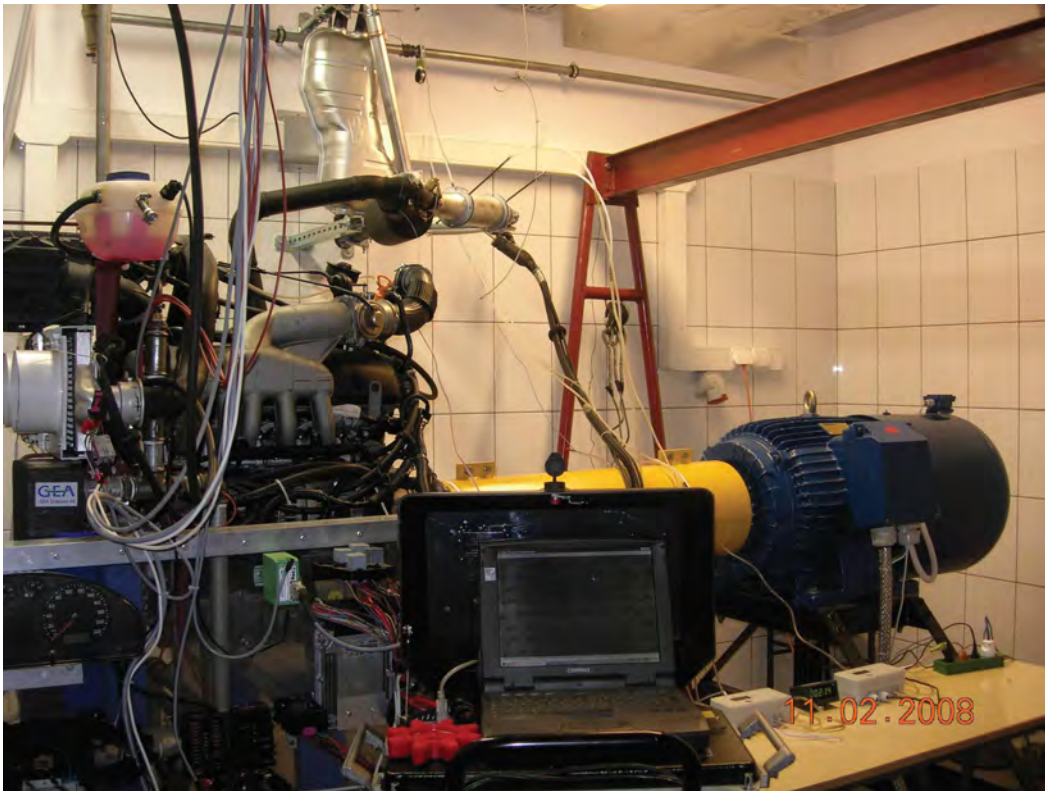


*Fig. 3. Engine test stand*

The research was conducted for selected settings of the engine, corresponding with the conditions of real exploitation. The research concept assumed that the exhaust gases stream, after leaving the engine, would become parted. The first part would then flow through the pre-prototype converter while the other part would flow through the standard catalytic converter used by the engine manufacturer. The concentrations of CO and CH were measured before the converters and, additionally, behind the pre-prototype converter and the standard converter.

*Tab. 1. Outcomes of preliminary engine test results*

| Engine setting point | Engine speed | Fuel injection | exhaust gas temperature after turbine | CO before converter | CO after pre-prototype converter / standard converter | CH before converte r | CH after pre-prototype converter / standard converter |
|---|---|---|---|---|---|---|---|
| - | [rpm] | [mg/inj.] | [°C] | [ppm] | [ppm] | [%] | [%] |
| 1 | 1800 | 25 | 467 | 135 | 56/7 | 0.053 | 0.040/0,041 |
| 2 | 2500 | 15 | 387 | 160 | 51/7 | 0.072 | 0.057/0,038 |
| 3 | 2500 | 10 | 282 | 333 | 183/6 | 0.102 | 0.081/0,039 |

Preliminary tests of the conversion of the initial pre-prototype units, whose sample outcomes are presented above and also the microscopic study of the surface of the converters inspired the authors to introduce construction improvements in the following prototypes. The most significant change consisted in increasing the concentration of platinum and, simultaneously, keeping the overall amount of platinum at a level lower by a few orders than the standard solution. Tab. 2 shows the outcomes of using the following version of the pre-prototype converter, consisting of three segments, marked in the research by the codes E, D and C of diameters of 84 mm and overall length of 69 mm.

*Tab. 2. The conversion of the improved pre-prototype converters*

| Engine setting point | Engine speed | Fuel injection | exhaust gas temperature after turbine | Absolute air pressure after compressor | Mass of the cylinder charge | CO before converter | CO after pre-prototype converter / standard converter |
|---|---|---|---|---|---|---|---|
| - | [rpm] | [mg/inj.] | [°C] | [mbar] | [mg/cycle] | [ppm] | [ppm] |
| 1 | 2000 | 25 | 451 | 1560 | 610 | 85 | 14/15 |
| 2 | 2000 | 15 | 388 | 1245 | 370 | 178 | 4/5 |
| 3 | 800 | 6 | 118 | 1050 | 450 | 128 | 115/5 |

The outcomes of measuring the conversion of oxidising pre-prototype converters constructed with the use of nanotubes confirm the possibility of extending the application area of nanotubes by the engine exhaust after-treatment systems. No measurable loss of conversion was observed in the pre-prototype converter during the research which took a number of hours. Therefore, it can be assumed that nanotubes remain stable in the specific environment created by the exhaust gases. A direct comparison between the pre-prototype converters and the standard converter is only possible to a limited degree, as long as the pre-prototype converter has a significantly smaller core and only a part of the exhaust gases flow through it. At the same time, sample outcomes of the conversion of CO presented in Tab. 2, obtained for the improved pre-prototype converter refers to moderate engine load, are better than for the standard converter. The mechanism which makes the pre-prototype converter stop working in idle conditions needs to be explained.

## 3. Research of the light-off temperature of the nanotube converter

The earlier presented research has implied the possibility of obtaining a great conversion degree for some nanotube converters which, especially in moderate engine load conditions, were even higher than those for standard converters. At the same time, a significant lack of operation of nanotube converters was observed under idle conditions and for very low load. Thus, an additional test was conducted in order to determine the light-off temperature of a selected pre-prototype converter.

The test consisted in starting the engine cold, obtaining thermal stabilisation for the engine speed amounting to 900 rpm and a gradual increase in the load from idle conditions to the full load.

The changes in the load were obtained by gradually increasing the fuel injection by 2 mg per injection while by every following step, thermal stabilisation was awaited. The gathered information is presented in Fig. 4.

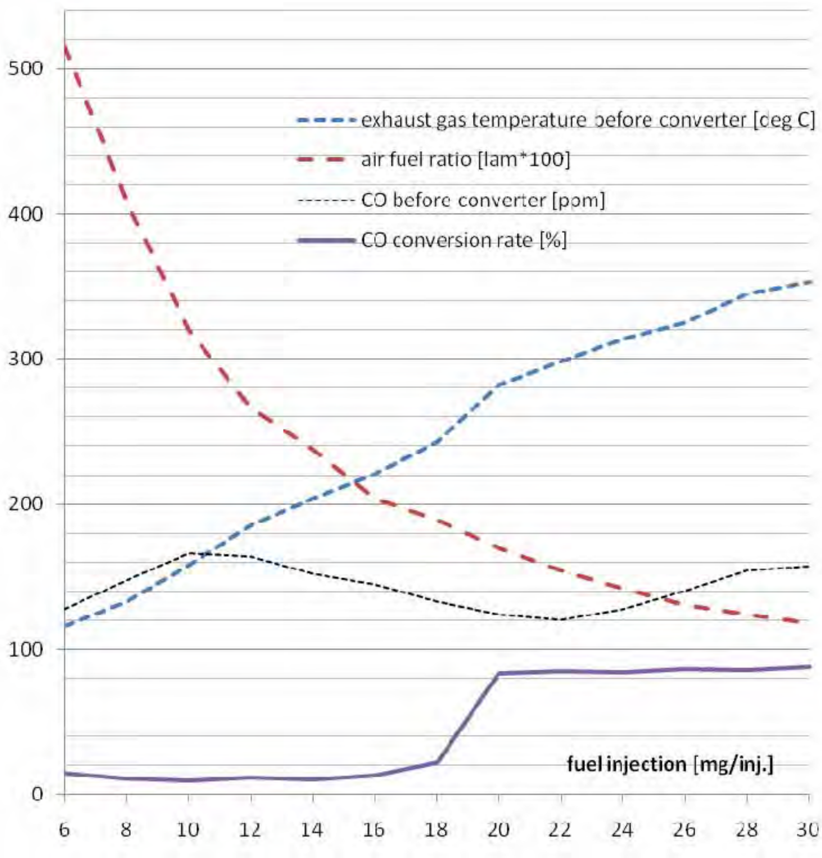


*Fig. 4. The influence of exhaust gases temperature on the conversion of the nanotube converter*

The outcome research allows drawing the following conclusions:

- the nanotube converter shows extremely unfavourable low-temperature properties,
- the light-off temperature was reached only for the fuel injection of 18 mg per injection, which was accompanied by an increase in the exhaust gas temperature by 250 Centigrade. The injection of 18 mg corresponds with a half of the maximum injection,
- in full load conditions, the air fuel ratio reached a value below 1.2, which caused the standard catalytic converter started showing measurable reduction activity.
- The concentration of NOx in the exhaust gases, measured after the standard converter amounted to 1.446 ppm while it reached 2.152 before the converter. Clearly, the nanotube converter did not show such properties.

## 4. NEDC test for the nanotube full flow converter

The research was conducted on the FIAT Panda MultiJet 1.3 SDE. A close-coupled converter is an integral part of the engine. Studies of emissions were conducted according to EKG UNO 83.05/B and the EU directive 70/220/EWG with subsequent changes up to the change of Directive 203/76/EU, according to the road test NEDC. The research programme included performing separate tests for a car without a catalytic converter, a car with a standard converter and a car with a number of nanotube converter versions, replacing the standard converter.

Figure 5 shows a modal analysis of exhaust gas emission during the extra-urban part of the NEDC cycle, starting at second 800 after the engine cold start. The figure shows, e.g., the emissions of CO for different catalytic converters and the emissions before the converter.

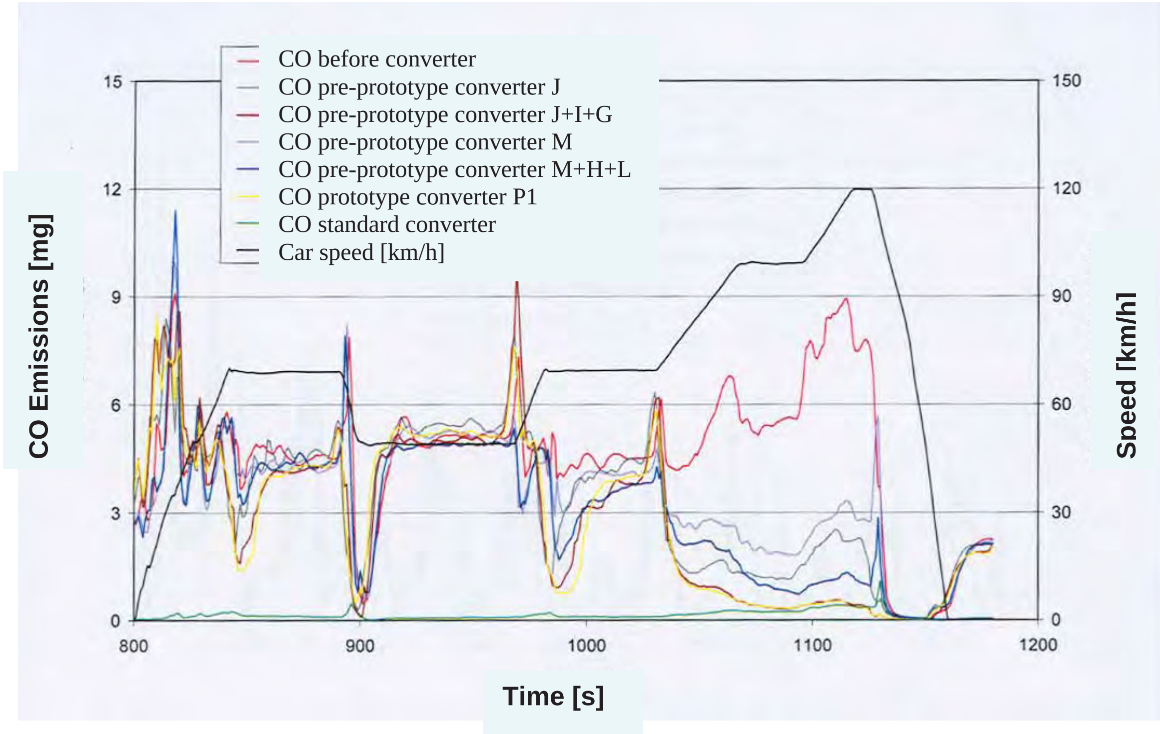


*Fig. 5. CO emissions in the EUDC phase of the NEDC test for FIAT Panda 1.3 Multijet with different versions of catalytic converters*

The outcomes of the car test confirm the earlier noticed relationship. All nanotube converters start working in the final part of the test, around second 1030 from engine start, after exceeding the car speed of 70 kph. The standard converter works from the very beginning of the NEDC test and makes it possible to reach an average total conversion at least four times higher than the nanotube converters. Therefore, the prototype converters in their present shape cannot replace the standard converter as they do not meet the limits of exhaust gas emissions. It needs to be stressed that the surface of the nanotube converters is much smaller than that of a standard converter. The prototype converters were not invented to replace the standard converter, but in order to examine the working of the nanotube converter in real conditions.

## 5. Summary and conclusions

The unique properties of nanomaterials make it possible to revolutionise the hitherto technical solutions in, among others, the automotive industry. It can be assumed that we are now witnessing the initial phase of applying nanomaterials on industrial scale. Particularly inspiring properties in the aspect of automotive constructions are shown by the nanotubes and the catalytic converter is one of their possible applications. The property of nanotubes consisting in a particularly high ratio of surface to volume allows increasing the contact surface of catalytic layer with the exhaust gases. Thus, a substantial reduction in the use of platinum was made available by sustaining a high conversion at the same time, which also increases the efficiency in platinum use. Each of the studied cores of the nanotube converters was covered by platinum whose weight did not exceed 20mg while standard oxidising converters include about 3g of platinum. Numerous research series conducted on different engines in different laboratories confirm that the suggested nanotube converter can, under certain conditions, ensure a conversion comparable to that of a standard converter or even higher. At the same time, the nanotube converter at its present stage shows extremely unfavourable low-temperature features. The time between the cold engine start and the beginning of the converter operation is too large to meet the emission limits.

The unfavourable low-temperature of the constructed converters may result from a number of highly unpredictable factors. One of these may lie in the unordered structure of the grown nanotubes, shown in Fig. 2. The problem can be solved by using metal cores and growing nanotubes in a magnetic field, which is a commonly applied method for the spatial ordering of nanotubes.

The major success of the described project is that the nanotubes can well be incorporated into the structure of the catalytic converter and they are not damaged under normal operating conditions. The authors claim that the obtained results confirm the theoretically-anticipated benefits resulting from the described application of nanomaterials and they constitute the first step in the process of optimisation. The industrial application of the nanomaterial converter is subject to analysing its benefits and costs in comparison to the standard converter. Owing to the observed substantial decrease in the cost of producing nanomaterials, the research of applying nanomaterials is worth continuing.

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