Final report

1.1 Project details

Project title	TEG for Energy Efficiency in Heavy Vehicles
Project identification (program abbrev. and file)	EUDP 64013-0169
Name of the programme which has funded the project	EUDP
Project managing company/institution (name and address)	TEGnology ApS, Lundagervej 102, 8722 Hedensted. Denmark
Project partners	Aarhus University, DTU Energy, PANCO GmbH, MAHLE GmbH, VOLVO AB
CVR (central business register)	33370873
Date for submission	06. March 2013

1.2 Short description of project objective and results

Transportation of goods is consuming an increasing part of our transport fuel, and heavy automotive applications are expected to rely on internal combustion engines for many years to come.

The overall objective of the project is to develop and demonstrate an efficient and inexpensive thermoelectric generator for heavy vehicles based on newly developed thermoelectric materials.

The project has succeeded to provide world class results from modules developed with new materials. Towards the end of the project, the first test results of the new module indicate excellent performance at 400 C. This has the consequence that the final goal of a working demonstrator on a truck could not be reached in time. It is still the intention to produce suitable modules and test them with help from both MAHLE and VOLVO.

1.3 Executive summary

The main objective of the project was to produce a working thermoelectric generator suitable for mounting on a heavy goods vehicle. At the start of the project it was understood that TEGnology had further developed thermoelectric materials invented by Århus University and was close to a commercial module. It was envisaged that adjustments to the material and assembly techniques would be needed to provide a suitable device for the application. There was anticipated a small risk that the material may not perform as expected. It turned out that after the preliminary testing by MAHLE, there were serious issues with long term material stability at 400 ºC. The material issues were resolved by end of 2016 resulting in the request to extend the project by one year. Issues identified with the substrates and assembly were addressed in parallel, resulting in an improved design, also by the end of 2016. Further high temperature testing revealed an unexpected issue with the electrical contacts to one of the materials (magnesium silicide). The symptom being a slow increase in contact resistance when tested at 400ºC. The same does not occur for the other material (zinc antimonide) Extensive work has so far allowed operation at 400 C for a maximum of 100 hours, which is sufficient for prototyping but requires improvement for a commercial solution. This is the conclusion of WP1 attained at the end of 2016. The consequence of this is that there is no resource left within the project to initiate WP2.

The results have shown that the goal of a commercial thermoelectric generator is still within reach, presentations at international conferences have promoted the work. DTU have produced a first class theoretical understanding of the workings of a TE module, this is invaluable in developing new designs.

Resumé

Hovedformålet med projektet var at producere en funktionsdygtig termoelektrisk generator egnet til montering på en lastvogn. Ved starten af projektet blev det underforstået, at TEGnology havde videreudviklede termoelektriske materialer opfundet af Århus Universitet og var tæt på en kommerciel modul. Det blev forudset, at der vil være behov tilpasningerne af materiale og samlingsteknikker at tilvejebringe en egnet løsning. Der var forventet en lille risiko for, at materialet ikke kan udføre som forventet. Det viste sig, at der efter den indledende test af MAHLE, der var alvorlige problemer med langvarige materiale stabilitet på 400 ^{0}C. De materielle problemer blev løst ved udgang 2016, hvilket resulteret i anmodningen om at forlænge projektet med et år. Svagheder identificeret med substraterne og samling blev behandlet parallelt, hvilket resulteret i en forbedret udformning, også ved udgangen af 2016. Yderligere høj temperatur test afslørede et uventet problem med de elektriske kontakter til et af materialerne (magnesium silicid). Symptomet er en langsom stigning i kontakt modstand, ved 400^{0}C. Det samme forekommer ikke for det andet materiale (zink antimonide) Omfattende arbejde har hidtil tilladt drift ved 400 C i op til 100 timer, hvilket er tilstrækkeligt til prototyper men kræver forbedring for en kommerciel løsning. Det er konklusionen af WP1 nået ved udgangen af 2016. Konsekvensen af dette er, at der ikke er ressourcer tilbage i projektet at indlede WP2.

Resultaterne har vist, at målet med en kommerciel termoelektrisk generator er stadig inden for rækkevidde, og præsentationer på internationale konferencer har fremmet arbejdet. DTU har produceret en førsteklasses teoretisk modellering en TE modul, som er et suverænt redskab til udvikling af nye designs.

1.4 Project objectives

WP 0 Project management, stakeholder involvement and dissemination

Work Package leader: TEGnology
Participants: All
Start-stop: Month 1 – month 25
Tasks: Project management, stakeholder workshops, dissemination.

The content of this WP is general management, project meetings and general assembly, reporting and contracting, stakeholder involvement and dissemination to the identified interested parties, end of project seminar and general dissemination.

Project management proceeded as planned; all partners took turns in hosting the project meetings. During the meetings, even during technical differences of opinion, the tone remained polite and orderly keeping focus on the technological issues. As a point of order, Behr changed their name to MAHLE Behr. References to Behr, MAHLE, or MAHLE-Behr should, for the purposes of this report, be considered equivalent. Cooperation between all partners remained at the highest professional level. During the first project meeting it was agreed to stop the project at the end of WP2, as WP3 was simply an upscaling of the results from WP2 and not strictly a part of a demonstration program. This was approved by EUDP. Later, the project timeline was extended by 12 months, with agreement from all partners and EUDP. The extra time required was necessary because of unforeseen issues with the thermoelectric materials. (Described in WP1)

Task 0.2 Stakeholder workshops
Task leader: TEGnology
Participants: TEGnology, Behr, Volvo
Start-stop: Month 2, month 22

An essential part of the project is the involvement of stakeholder companies who work daily with heavy vehicles and motor operation. To ensure a good dialogue with fleet owners with the aim to achieve quality in the design process for the future product, two workshops will be carried out.

At the first project meeting (see Appendix 1 EUDP Project Partner Meeting….) it was recommended by all partners to wait with the workshops until we had a working generator containing the TEGnology modules. We therefore agreed to postpone the workshop(s) and combine them with a relevant exhibition. The original proposal was Dresden 2015, but in fact the milestone was completed by TEGnology participating in ICT Nashville (July 6-11 2014) and Hi Messe Denmark (22-24 September 2015).

Task 0.3 Dissemination
Task leader: TEGnology
Participants: All
Start-stop: Month 2 - month 25

The dissemination will aim at increasing the awareness of the stakeholders to the upcoming technology, so that road transport companies, fleet owners, district heating companies and other businesses with excess heat available will begin to look forward to the day they can purchase a TEG, either integrated in new products or for retrofitting in the existing engine applications.

In addition to the exhibition appearances above, contact has been maintained to customers and partners including::

Company	Sector	Needs
VOLVO Truck division	Heavy automotive manufacturer	Reduce fuel consumption of large vehicles
CEA (Grenoble)	Energy research	High temperature TE modules for development
Elring Klinger, Mahle, Gentherm	Automotive sub supplier	Medium and high TE modules for building into automotive engine components
Exodraft	Ventilation	Generate power from wood burning stove to provide power for chimney ventilation
Evident	Thermoelectrics development / manufacture	Research and development
KU Leuven University	Sensor application	Research and development
DELTA	WSN (Wireless Sensor Networks)	Low power TE modules for powering wireless sensors
TATA Technologies Ltd	Automotive manufacturing	Medium and high TE modules for building into automotive engine components
SCAN DK	Wood burning stoves	Self-powered “intelligent” wood burning stoves 12 volt charging and grid connect.
DFDS, MAN Diesel, ALFA LAVAL, Scanel	Maritime	Improve engine efficiency and reduce fuel consumption / emissions
Aalborg Portland Cement	Large Industry	Power generation from excessive waste heat

WP0 Milestone

KM1 - Stakeholder workshop in 2015 attended by at least 8 external companies.

Completed. TEGnology presentation and exhibition participation at ICT, Nashville HI-MESSE (exhibition)

WP 1 TE material and module development, laboratory testing, modeling and verification

Work Package leader: TEGnology

Participants: TEGnology, AU, Panco, DTU Energy, Behr

Start-stop: month 1-24

The objectives of this Work Package are to optimize the properties and stabilities of Zn_4Sb_3 and Mg_2SiSn materials for the TEG module and to test the electrical and mechanical properties of the modules.

Previous tests show that Mg_2SiSn is stable below 350 ^oC. But the module is expected to work at design parameters up to 400 ^oC. For product safety reasons the modules need to resist 450 ^oC for short periods of time. The primary aim is to understand the degradation mechanism of the material and develop methods to stabilize the material.

Furthermore, the thermal stability and mechanical properties of the electrodes, bonding agents and substrates also need to be improved accordingly so that they do not jeopardize the stability of the material.

This work package had three objectives:

- Optimise materials
- Optimise substrates
- Optimise assembly.

At the start, it was believed that all three objectives were close to being realized. In reality, each objective produced new challenges.

Material and module optimization encompassed both a theoretical model, developed by DTU Energy, and practical testing / analysis performed by AU. It must also be stated that there was a large degree of cooperation between the aforementioned partners in that DTU Energy provided some analysis of the materials behaviuor in the module and AU contributed with theoretical analysis. DTU Energy delivered the theoretical model which allows performance modelling of a module, thus saving valuable design time. AU were instrumental in stabilizing the materials at the molecular level.

PANCO proved invaluable in both providing test effort and supporting both DTU Energy and AU.

Panco has further developed and improved its technologies for the measurement equipment during the project and got many new ideas in sample holders for special samples which will be useful commercially. Please see the report from Panco, attached as appendix 2.

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Initial testing highlighted weaknesses in the p-type material especially under a temperature gradient. The necessary work to re-engineer the material became the reason to extend the project by 12 months. The work involved required manpower, but no heavy investment in equipment, so the overall budget remains unchanged. Further issues appeared with the assembly resulting in the switch from metal foil contact electrodes to PVD terminals on the material legs. Both the ceramic and the copper substrates proved unsuitable for extended operation at 400 °C. A replacement using suitable steel had to be designed. Finally, instability, observed also in the n-type material had to be rectified.

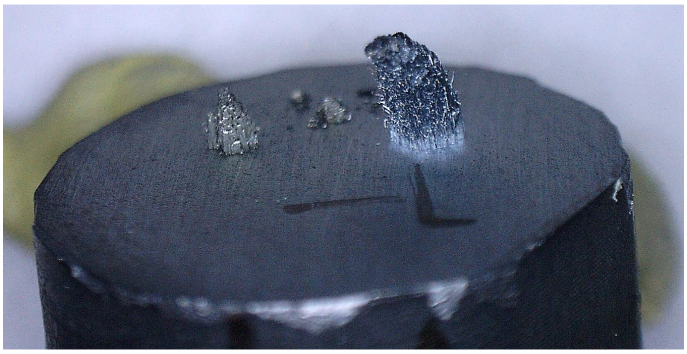

Figure 1 Instability in Zinc antimonide

Techniques to seal the module, or stabilize the material proved ineffective. Degradation mechanisms observed were present regardless of whether the test was performed in air, inert gas (argon), or vacuum. This indicate that the degradation is intrinsic to the material itself.

The one technique which could not be improved upon was the silver sinter method used for bonding the module together.

All interim milestones within WP1 have been met. After solving the materials and the contacts issues we have succeeded to fabricate a module which is capable of producing 4 watts at 400 °C. These results are among the highest results reported so far and are sufficient performance to claim M1, TEM design ready for WP2.

M1 - One recipe for TEM is approved for manufacture and testing in WP 2.
Completed end of month 36. The module is shown below, the datasheet is attached as appendix 3

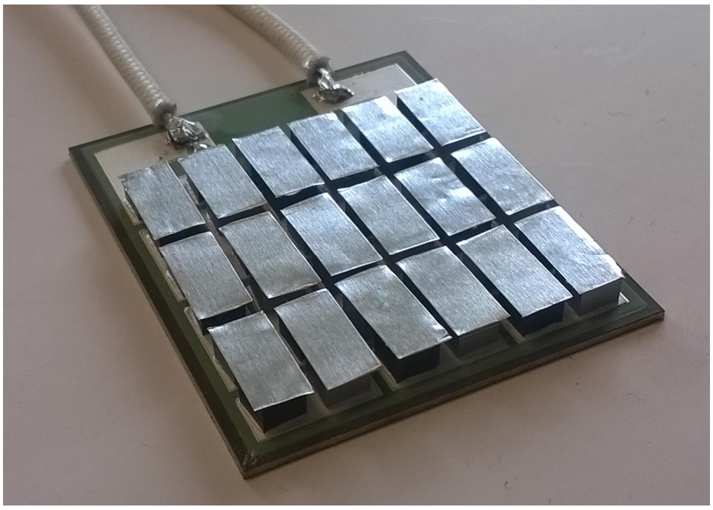

Figure 2 The TEGnology module, HP36-4-4-3 PT

WP 2 Core technology proof of concept - Integration of TE Module in 100 W_e bench scale
Work Package leader: Behr
Participants: Behr, VOLVO, TEGnology, DTU Energikonvertering
Start-stop: month 6-24

Contents:
During this period we have conducted the following tasks: Identification of design parameters, manufacture of TE modules for 100 W_e TEG PoC-prototype, geometry simulation, dynamic simulation, mechanical load simulation, power density, flow distribution, environment

tests, 20 W_e pre-test, 100 W_e power range Proof Of Concept test, reports on recommendations based on test results and identified design parameters.

Due to the late completion of M1 above, WP2 was never officially initiated. However, activities to determine user requirements and specifications are completed. Information from these activities has been used to guide the progress of WP1.

1.5 Project results and dissemination of results

WP 1 Tasks

1.1. Component stability and protection

1.1.1. Protective additives

Results:

Undoped, anion-doped (Sb, Bi), and cation-doped (Ca, Zn) solid solutions of $Mg_2Si_{0.4}Sn_{0.6}$ have been prepared by a commercially feasible large-scale solid state synthesis method. The compositional and structural stability of the prepared samples are investigated by high resolution synchrotron powder X-ray diffraction (PXRD) in the potential application temperature range of 300–750 K. Quantitative compositional and structural information are extracted from the multi-temperature PXRD data by the Rietveld method. Detailed analysis of the PXRD data reveals an irreversible thermally induced partial conversion of $Mg_2Si_{0.4}Sn_{0.6}$ into a discrete Sn-rich $Mg_2Si_{1-x}Sn_x$-phase in the undoped and anion-doped samples. On the other hand, the cation-doped samples only undergo very minor compositional and structural changes with increasing temperature, indicating a stabilizing effect of Ca and Zn on the $Mg_2Si_{0.4}Sn_{0.6}$ solid solution. The structural instability of the undoped and anion-doped samples is corroborated by the measured electrical resistivity as function of temperature in the same temperature range, in which a clear difference is observed between values during initial heating and subsequent cooling. In contrast, the resistivity data of the cation-doped samples exhibit good repeatability for two thermal cycles, confirming that cation doping greatly improves the thermal stability. This work highlights the importance of conducting multiple temperature cycles in the measurement of physical properties combined with a thorough structural characterization in studies of thermoelectric materials.
Cation (Ca, Zn) doping is found to have a stabilizing effect on the solid solutions. The thermally induced structural and compositional changes are reflected in the electric resistivity measured over the same temperature range, where large discrepancies between values obtained during the initial heating and the subsequent cycles are observed for the undoped and anion-doped samples. Consequently, the characterization of the thermoelectric transport properties is based on values measured during cooling after initially heating the samples to 725 K. The present work serves to illustrate the importance of conducting a meticulous structural characterization in studies of thermoelectric materials.

These results provided guidance of optimizing the performance and stability of our TE materials. We are now testing Mg_2SiSn with Zn and Ca doping, which will help us improving the stability above 400 ^oC.

Dissemination:

The results were published on the journal Inorganic Chemistry Frontiers,
DOI: 10.1039/c6qi00520a

1.1.2. Protective coating of TE components

Results:

Inorganic polymers and sol/gel materials react at 500 ^oC to high cross linked glasslike solids. Because of diffusion of coating material into the substrate during thermal treatment an interlayer was formed. This interlayer effect an excellent adhesion strength and thermal shock resistance.
Different polymer solutions and suspensions of coatings were applied to the TE materials. Pre-treatment and dip-coating conditions were optimized. Coated samples were then subjected to continues heating in air.
It is possible to protect TE materials against oxidation at higher temperatures by coating with inorganic polymers. But the oxidation protection, especially for Mg2SiSn is not very suffi-

cient. However, the method offers a broad field for optimization, which could be resumed in future development.

Dissemination:

The results were summarized in a technical report. (Ref Appendix 4 "Protective coating technical report")

1.2. Component/module interface

1.2.1. Alternative to electro plating of component terminals

Results:

Chemical plating was tried to apply metal on TE materials. But most of the chemical plating solvent turned out to be harmful to our materials. It was therefore not considered to be a feasible process. Thermal spraying of different metals was also attempted. The process was too violent for our material. It damaged the surface of the component materials.
Physical vaper deposition (PVD) was tested. It provides homogeneous barrier and conducting layers on the surface of the TE materials. The process is also highly tunable and controllable.

1.2.2. Alternative fastening methods

The severe working conditions makes the replacement of Ag sintering past very difficult. Ag paste sintering was proved to be the best available method to bond the components and substrates together.

1.2.3. Durability alternatives for substrate

Previous ceramic substrate was not able to meet the requirement of the module. A novel design of substrate using stainless steel was proved to be a reliable solution. It has much higher tolerance to the working conditions of our device. It is therefore being used in our products.

1.2.4. Sealing of module

Inorganic polymers and Aero-gel were envisaged to be able to seal the module, so the oxidation and sublimation of TE materials could be suppressed. However, the thermal mismatch between coating material and TE materials makes it hard to ensure an air-tight coverage at the conjunctions. As to the aero-gel, as a newly developed material, the commercial availability and knowledge accessibility are limited. Furthermore, during the project, we've developed materials that are stable within the working temperature range. This makes sealing less necessary.

1.3. TEM computer simulation

1.3.1. Modeling of the module

1.3.2. Module simulations

Activities and results:

Computer simulations were carried out in DTU Energy. The performance is estimated numerically as function of the load resistance, cold and hot side temperatures and the two geometrical parameters: The area ratio of the n- and p-type legs (A_n=A_p) and the length of the legs (l_n and l_p). The optimal load resistance, area ratio and lengths are determined for all realistic temperature spans, and the TEG is optimized both in terms of the efficiency and power pr. area. In addition, we characterize the TEG by presenting the accumulated efficiency, the accumulated power produced pr. area, the temperature profiles, heat fluxes, the produced voltages and currents.
At the largest temperature span considered (450 – 20 °C), the maximum efficiency is 10% obtained with an area ratio of A_n=A_p = 3.6, which is 50% more efficient than with equal areas. The maximum power pr. area is 2.7 W/cm^2 at A_n=A_p = 2, l_p = 2.8 mm and l_n = 2.64 mm. Choosing area ratios of around 3.8 and 2.1 ensure a TEG module optimized for efficiency and power pr. area, respectively.

The simulation not only predicts the upper limit of the TE module, also indicates the consequence of importance of each single parameter. It helps in orienting the optimization of a TE module.

Dissemination:

The activities and results were summarized in a final report. (Ref Appendix 5"Simulation report")

1.4. TE material and TEM testing

1.4.1. Performance testing of TE materials

1.4.2. Performance testing of TEM

1.4.3. Failure mode & lifetime testing

Activities and results:

Tests on the TE materials and modules were carried out mainly in TEGnology and Panco. Panco has upgraded their test facilities and is able to perform more sophisticated tests on both components and modules. TEGnology has designed and built 10 test ovens for module performance and lifetime tests. All ovens are equipped with temperature controller and water cooling system. The outputs of are automatically recorded by computer. Together with Panco, TEGnology has tested more than 200 modules till now. By comparing the output and lifetime, we were able to select our materials and improve the processes. For example, we've shown that simply by using a different barrier layer between TE materials and substrates, we were able to prolong the lifetime of a TE module from hours to weeks. We are working on increasing the lifetime to months, which we believe will enable us to dominate the market.

1.5. Analysis and reporting

All activities and results were documented and distributed among partners. Discussions and meetings were regularly held to address the issues and to make plans accordingly.

1.6 Utilization of project results

TEGnology has gained valuable technical and commercial knowledge of the market for high temperature thermoelectric modules. The technical results have allowed us to produce a module which satisfies the milestone M1 and is close to being a product. Contact with the market through appearances at conferences and exhibitions has grown our customer base to a point where as soon as the device matures we have customers waiting, This will trigger the expansion of TEGnology and the employment of more people. It is envisaged to employ up to two engineers, a salesperson and four operators. From our work on market research, we identified a new market for a low power device operating at low temperatures (typically around 60 °C.) This device is suitable for battery replacement in remote sensing applications. This has been launched as a product, followed up by a series of global press releases. Interest is growing and it has every sign of being a successful "spin-off" from this project

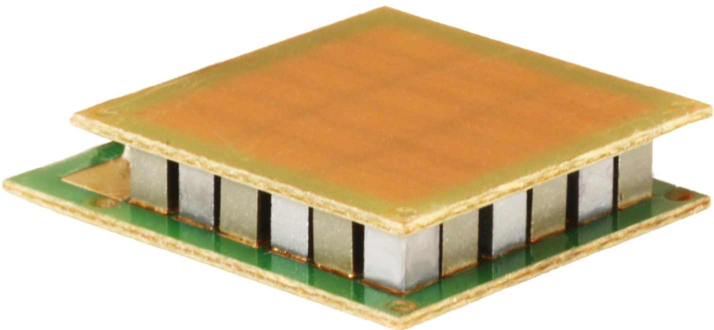

Figure 3 the FLIPETM-36 low temperature device (See Appendix 6)

1.7 Project conclusion and perspective

The final goal of the project was to produce a thermoelectric generator suitable for mounting on a heavy goods vehicle. The project did not reach this conclusion. It would be wrong however, to consider this a failure, more an admission that the task was, regrettably, underestimated. The major technical successes have been the demonstration of a module operating at 400 ºC and the launch of a "spin-off" product for battery replacement, the FLIPTEM-36. From the collaboration perspective, the project has brought together two major industrial players (VOLVO and MAHLE), two universities (Århus and DTU) and two SME's, (PANCO and TEGnology). It has been a most productive synergy and has every sign of continuing beyond the scope of this project. For this I would like to express my personal gratitude to all involved. Looking ahead, the project has opened the door to a new era of industrial TE devices using materials that are both readily available and operate up to 400 ºC. Note that there are no competitors operating reliably above 200 ºC today. From the global perspective, there is still a prime opportunity to reduce fossil fuel consumption with the consequential reduction in pollution. We may not have reached the final goal, but the journey has been very productive. Results have been produced, organisations from different countries and different disciplines have collaborated to a common goal. We look forward to the next stage with growing anticipation.

Paul Egginton. Project leader and CEO TEGnology.

Annex

Homepages:

TEGnology	www.tegnology.dk
PANCO	www.panco.de
Århus University	http://www.au.dk/en/
DTU Energy	http://www.energy.dtu.dk/
VOLVO Trucks	http://www.volvotrucks.com/splash.html
MAHLE	http://www.mahle.com/mahle/en/

Supporting documents

Appendix 1. EUDP Project Partner Meeting 19022014_MoM_FINAL
Appendix 2. EUDP Panco final report
Appendix 3. Data sheet HP36-4-4-3 PT
Appendix 4. Protective coating technical report
Appendix 5. Simulation Report
Appendix 6. Data sheet FLIPTEM-36