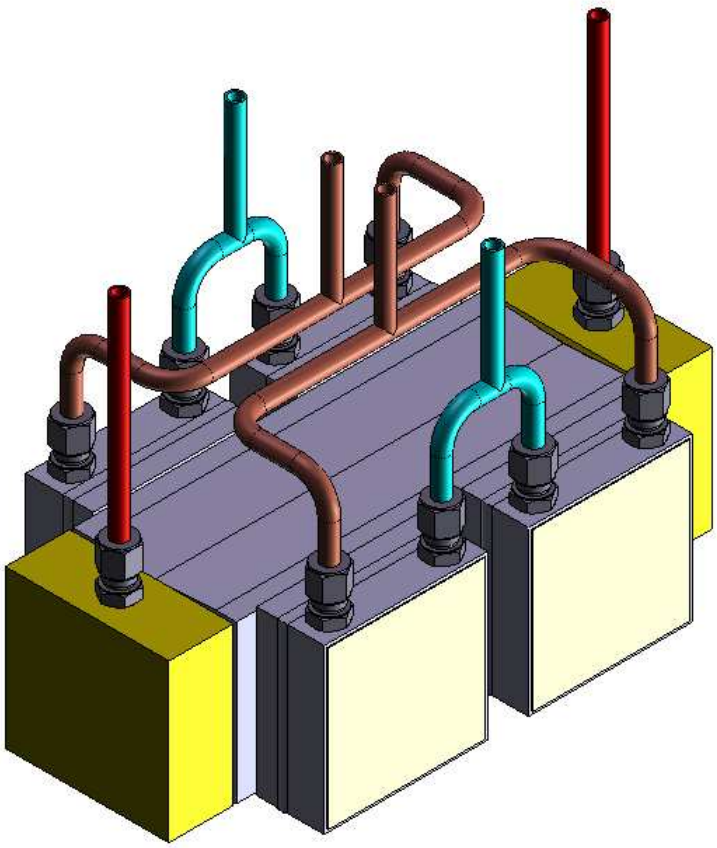
Final report

Project ID: SOFTEG 2007-1-7474



SOFC/TEG hybrid system

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Final report

Project title

SOFC/TEG hybrid system (Integration of a TEG module in a SOFC dummy hotbox)

Project description

The purpose of the project named SOFTEG has been to demonstrate the possibility of increasing the electrical efficiency of a solid oxide fuel cell (SOFC) micro combined heat and power (CHP) system by 5 to 8%, using a waste heat based thermoelectric generator. The combination of the SOFC, TEG (thermoelectric generator) and the utilization of system waste heat has been the basis for system design and development in this project.

The project had two main objectives/milestones agreed to be completed with useful practical results.

Objectives

First objective:

R&D of an integrated TEG and "dummy" SOFC hotbox to simulate an operational SOFC/TEG hybrid mCHP system. The dummy test hotbox is based on commercially available TE-elements/modules.

Second objective:

Development of a novel material for the next generation TE elements. The TE elements are developed and produced to meet the specifications of the commercial SOFC mCHP system with fixed parameters such as e.g. pressure loss and temperatures. The TE elements are used to design and build a TEG module for integration in a Dantherm Power SOFC system. The integration is planned to be completed in a phase 2 project and has not been a part of this project.

Milestones

WP1: Define product requirements and identify suitable TE elements.

WP2: Design of TEG (In 1. phase the TEG is purchased from Hi-Z)

WP3: Building TEG and merging TEG and SOFC hot box dummy

WP4: Test of integrated prototype

WP5: Optimization of TEG for SOFC chamber

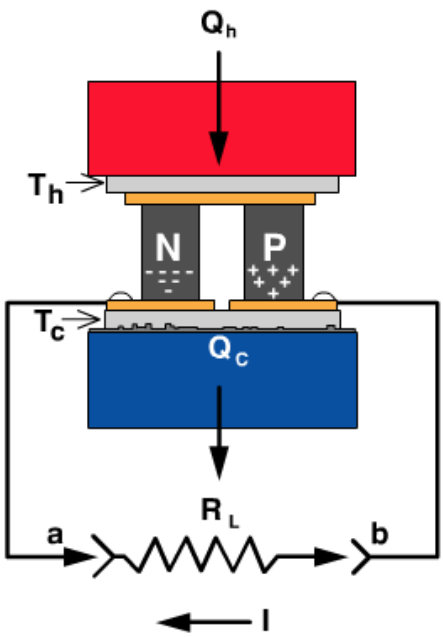
WP6: Development of suitable TE elements

WP7: Test

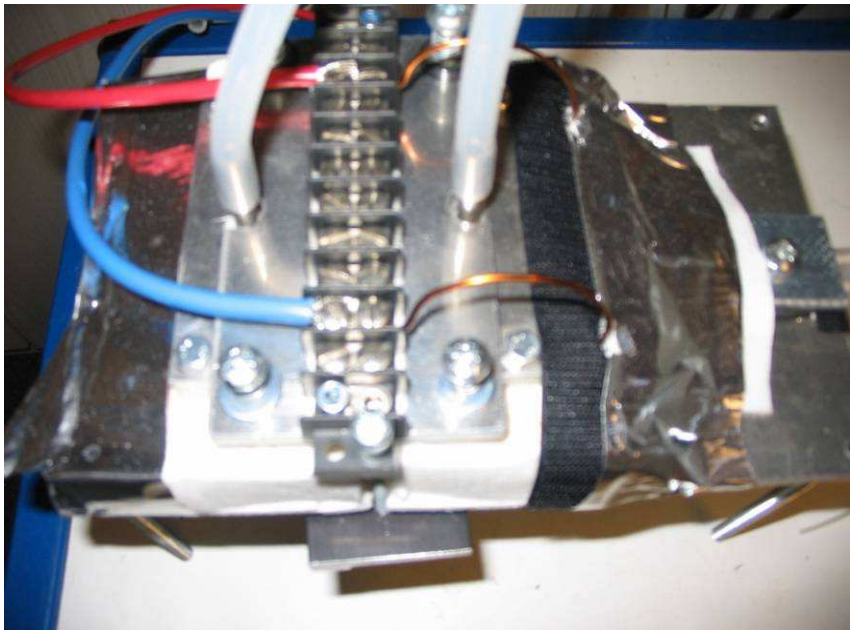
Technology

TEG

A TEG is a generator which, based on a temperature difference, produces electricity with no moving parts. Semiconductor materials, the so called Thermoelectric elements (or Peltier elements), are assembled in series, one side of each element connected to a hot surface and the other side being cooled. The temperature difference induces a transport of electrons in the elements, and by connecting the elements in series, these will act like a generator.



The TEG on a SOFC hotbox the TE elements are placed on the outside of the hot box and cooled on the outside by the chosen cooling media for the system. The SOFC hotbox is running at a temperature of around 500°C which makes it possible to use high temperature TE materials which have a relatively high electrical efficiency.



Picture shows a TEG module used in the "dummy" hotbox

SOFC

The solid oxide fuel cell (SOFC) technology has been under development in Denmark (by Risø/DTU and Topsoe Fuel Cells) as well as internationally for more than 20 years. The development has now reached a point where scale production of complete stacks is expected in the near future (by Topsoe Fuel Cells and others) As a result of this, the integration and demonstration of SOFC's in various applications is increasing. In Denmark, the first demonstration of SOFC in micro combined heat and power systems was recently initiated in the project "Dansk Mikrokraftvarme". To establish an internationally competitive Danish industry in the area of SOFC based systems these projects must be supported by the further development of fundamental competences related to advanced design and control of these systems. By increasing the total system electrical efficiency the SOFC based mCHP will reach an important milestone in the commercial roadmap.

Picture shows a Dantherm Power SOFC based mCHP system

Project Summery

The integration of a TEG module in a SOFC dummy hotbox has been proved to give potential increased electrical hotbox efficiency. The expected efficiency at min. 8% was not achieved due to the poor performance of the commercial TEG modules. It shows the need to further develop the specific novel TE material with properties that complies with the SOFC hotbox requirements in regards to temperatures, stability and cost.

The high performance material Zn_4Sb_3 is the target for implementation in SOFTEG since 1) it has been patented by AU and therefore is straightfor-

ward to use and 2) it is optimized precisely for the temperature interval of SOFTEG. The main problem is thermal stability and the present project has focused on understanding this aspect in detail through extensive multi-temperature synchrotron powder diffraction measurements. In has been shown that 1) zone melted material is superior to quench synthesis, 2) Cd doping significantly improves thermal stability of quench material and 3) both materials have improved stability in Argon atmosphere. These are important details, if a working module is to be developed. There are indications that grain size influences stability significantly, but this aspect needs further study.

The results from this project will be used to develop a TEG module based on the new TE materiel (zinc-Antimony) (Zn_4Sb_3) in a phase II project. A 2. generation SOFC/TEG hybrid module will be developed and tested in a Dantherm Power SOFC mCHP system using both commercially available TEG modules/materials and TEG modules based on the Zn_4Sb_3 material. The objective with a SOFTEG phase II project is to obtain a significant increase of the SOFC mCHP system electrical efficiency.

Using TEG for increasing the efficiency of fuel cell systems is a novel yet very promising application for TEG technology. In SOFC fuel cell systems and High Temperature PEM fuel cell systems heat is available at a high temperature and here TEG technology is expected to bring Dantherm and the Danish Fuel Cell Initiative one step ahead of the competitors on fuel cell systems for residential combined heat and power. This market is very big seen from a Danish perspective. In Denmark Alone around 30.000 boilers are exchanged every year which constitutes a market potential of 200 mill. EUR/year when the TEG/SOFC/PEM technology becomes competitive. In the rest of Europe where Dantherm today sells equipment under OEM brands, the market potential is much bigger. Using TEG for increasing efficiency on SOFC and HT-PEM systems will also open opportunities in a number of other potential business segments which are not yet quantified.

Final budget

	Virksomhed/Institution	Tilskud	Projektdeltager	Anden finansiering	Totale udgifter
1	Dantherm Power				0
2	AAU				0
3	AU				0
	I alt	0	0	0	0

Skive, 31. August 2009

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Appendix A – SOFTEG "dummy" Hotbox

Test "dummy" hotbox

System layout

The dummy SOFC hotbox, is divided into zones.

Zone 1) Dummy SOFC hotbox

Zone 2) TEG module

Zone 3) Heat exchanger module

Zone 4) Hot water tank

Picture shows first mock-up of the dummy sys-

Zone 1) Dummy SOFC hotbox:

The design of the dummy hotbox is based on the requirements and specifications for a fully operational SOFC hotbox developed by Dantherm Power. The SOFC hotbox is the reference system and will be the system used for integration the next phase TEG module. The overall system spec.:

- Heat output 1800 Watt.
- Air outlet temperature 334°C.
- Air outlet pressure (maintain 150L/min)
- Air flow 150L/min.
- Air inlet temperature (variable)

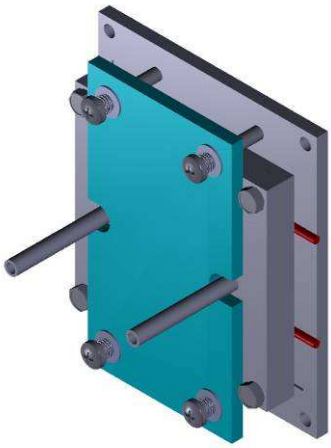
The system in zone 1 consists of the following components:

Air heater unit	Controls
Ambient air filter	Dummy SOFC chamber
Air pump/blower	Connection, warm air
Air flow meter	Connection, pre-heated ambient air

Zone 2) TEG module:

The module is built in two versions:

The first version is the objective of the first milestone using "commercial" TEG-elements, see sketch1, whereas the second version will be developed for phase 2 version using the novel material from AU in cooperation with the company PANCO (producer of the TEG modules). Both versions will be designed with air/water heat exchange using air on the hot side and water as cooling fluid.



Sketch shows TEG element

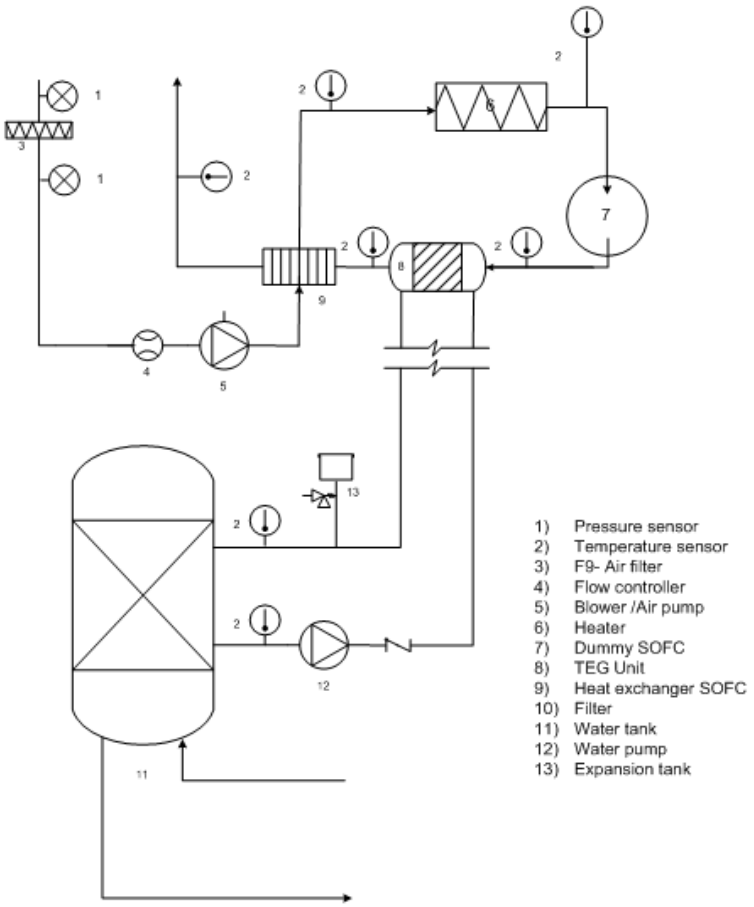
NOTE! : 1. version of the TEG module is designed to produce a power output of max. 100We whereas the 2. version in a phase 2 project will be designed for a 50We power output.

Zone 3) Heat exchange module

This module is an air to air heat exchanger and will be used to pre-heat the ambient inlet air to the SOFC stack. The pre-heating is done by using the waste heat in the outlet air from the TEG module.

Zone 4) Hot water tank

A hot-water tank is used to minimize the energy loss in the complete system config .The cooling water has a temperature at approx. 50°C for the 1. TEG version and 60 to 70°C for 2. version.

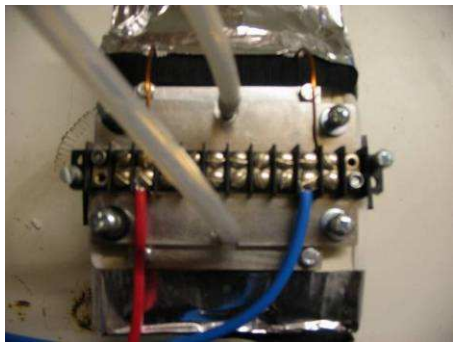


P&ID of the complete dummy test setup

Start-up and tests

After start-up and during test of the system all data has been logged for system optimization.

Test



The project was described as a combination of thermo electric system together with a SOFC mCHP system. As we know, the milestone is to increase the electrical efficiency of the mCHP system by using a novel thermo electric material from Aarhus University. However the material is produced in small amount and the Panco is working already ongoing the task of preparation of a small

module. It was agreed to build an early version of the thermo electric module for connection with SOFC hotbox by using some commercial TEG material.

For this case it was decided to choose a known Thermo Electric company

with experience in using the devices in vary direction of utilization of waste heat. The selected company is Hi-Z technology Inc. and the type of modules ordered of HZ-20.

The complete TEG module would be build with 5 sub modules of HI-Z 20 and the expected power would be about 90Watt, which was reduced to 75 watt after step up regulation in the DC-DC converter.

The power from each module was about 15 Watt.

A test unit was build using one single module of HZ-20.

The module has been tested continuously and periodically in order to observe the material performance.

Start up procedures and Test specification

In order to use the same procedure as the system connected to the SOFC Hotbox, the Single Thermo Electric module has exposed to immediate heat from the heat source. During one to two minutes, the temperature raise to the 225-250°C.

The cooling system was water with inlet temperature 30°C and the outlet temperature about 50°C. The real temperature for cooling water to the next version with the system build with material from Aarhus University is expected to be 45°C for inlet and 75°C for outlet.

Power output is measured by a very sensible electronic load with constant parameter as Current, Volt and Watt.

- Single module test: TEG module HZ-20
- Temperature on the hot side: 225°C
- Inlet temperature in cooling water: 30°C
- Outlet temperature in cooling water: 50°C
- Registered loss in converter: 20-25%
- Registered loos from the wires and connections: 2%
- Max Volt output: 1,8V
- Max current: 6,6A
- Maximum power performance after the converter: 12Watt
- Maximum Thermo Electric Power performance: 15,4 Watt

Level of test validation

The level of validation is in accordance to the specification and experimentally without using the real material for cooling units and the heat manifold.

Used test equipment

Equipment	Type	Calibrated
Electronic Load	PEL 300-120-60	Jun-2008
Thermometer	Fluke 52 II	Sep. 2008
Multimeter	Meterman 37XR	Sep. 2008
Ampmeter	ISO-TECH CM36II	Aug. 2008
Heater	Mica Thermofil	
Ac Load	Transformer	
Sensors	Thermocouples K	Nov.2008
DC converter	30Watt HZ-12-24	

Test cabinet

Test Cabin dim.	cm	100 x 150 x 220
Heat source	W	Max 500
Water inlet	°C	30
Water outlet	Bar	50
Ait Temperature	°C	22

Test unit

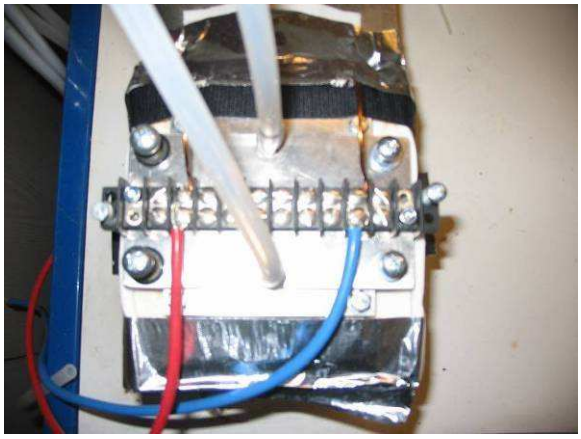
Cooling system	Aluminum cooling unit
Heat source	Mica Thermofil plate

Test procedures/startup preparation

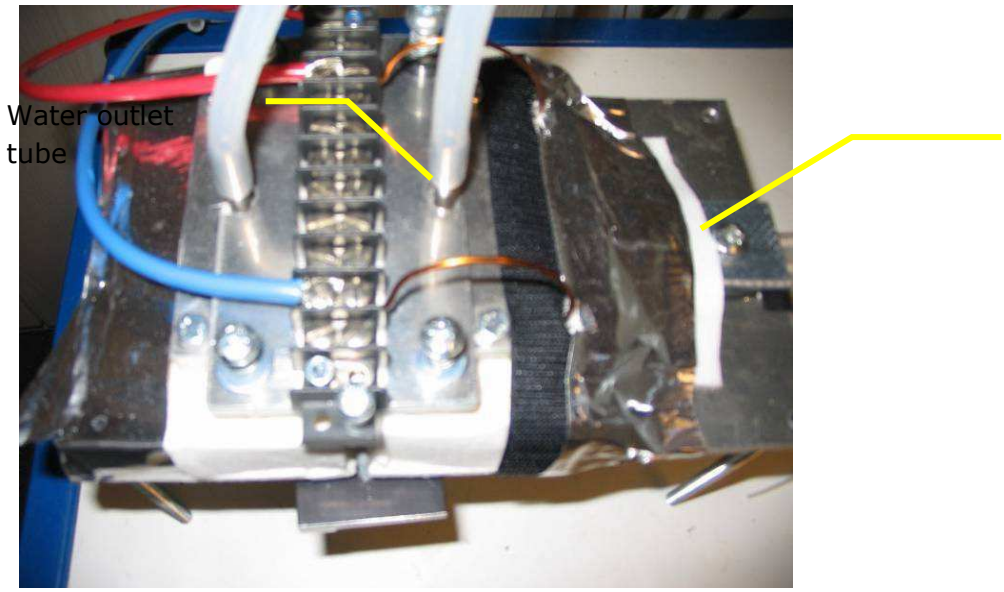
- Connection of 230V AC input.
- 2 minutes non automatic operation with AC power.
- Reset the system.
- Continue with auto thermal function
- Adjust the inlet temperature to 30 °C
- Adjust the outlet temperature to 50 °C
- Measurement with constant power after 5 minutes and during 5 minutes
- Measuring with constant Amps during 5 minutes
- Measurement with constant Volt during 5 minutes
- Procedure rapid after 15 Minutes
- Disconnect the main (230VAC).

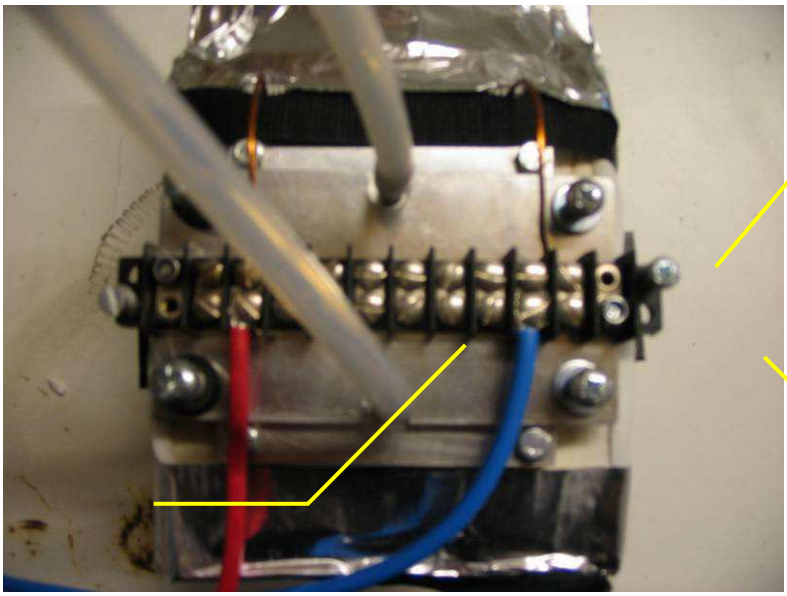
- Keep the outlet water temperature to 50oC under the cooling done procedure.

The test module and cooling system



Test Modul for single HZ-20

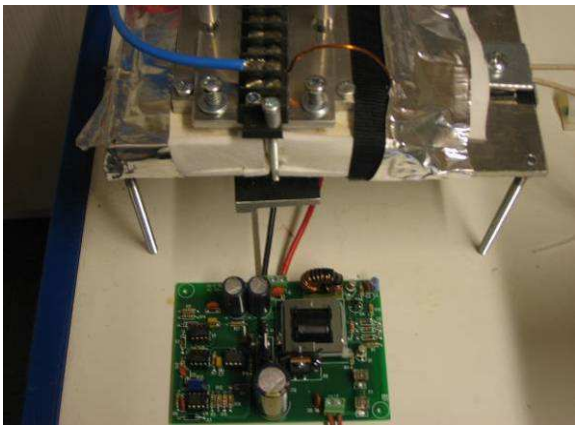




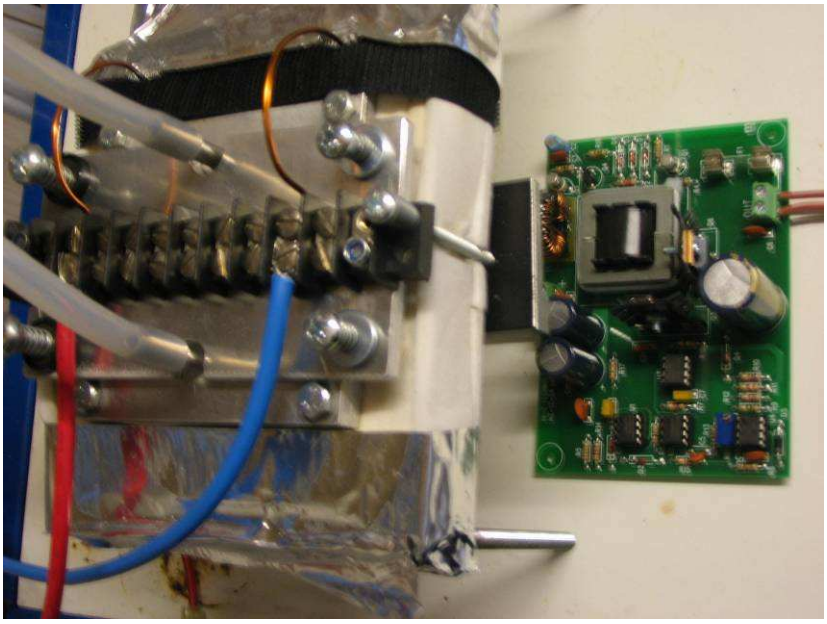
Wiring terminal

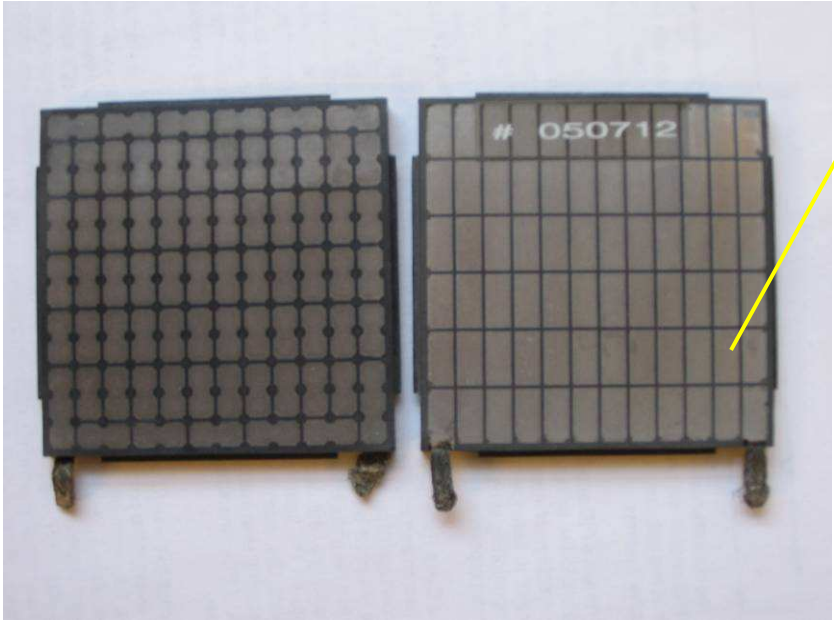
(-) pole

(+) Pole



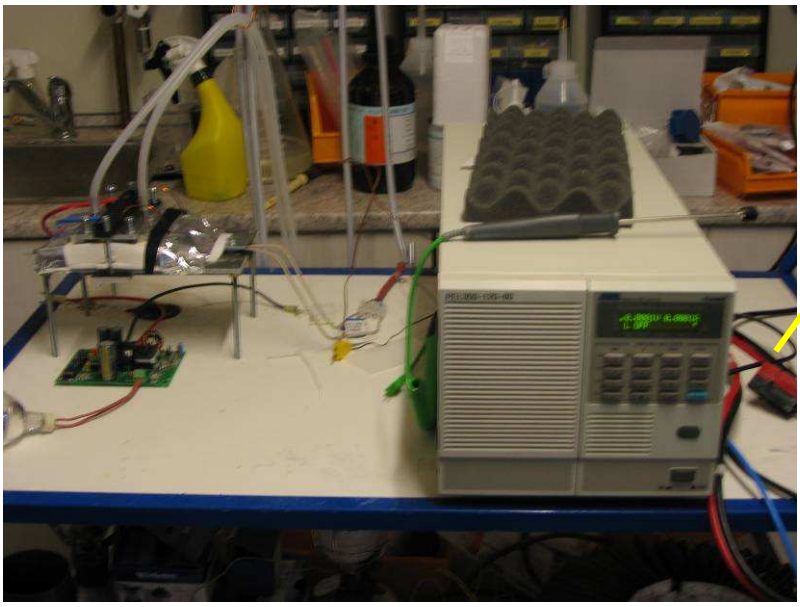
DC-DC converter outlet tube





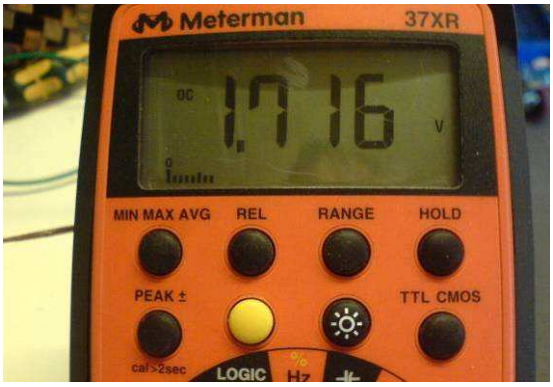
HZ-20
Module

Manuel Test with single HZ-20 Module

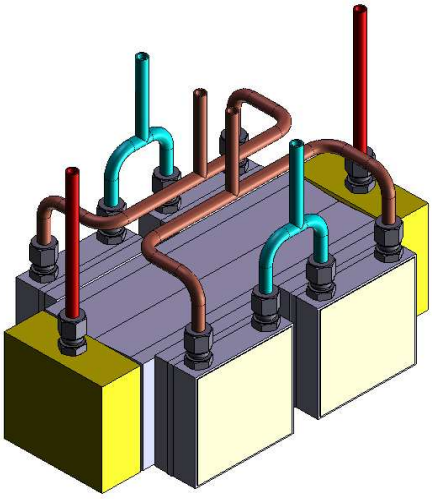


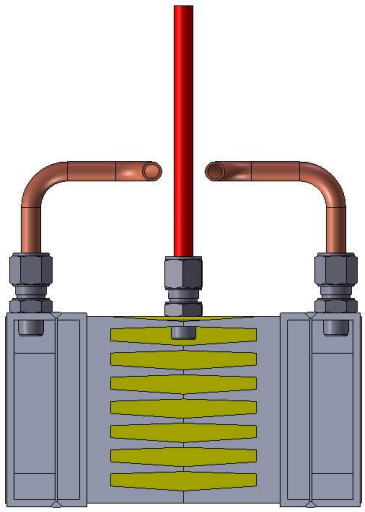
Electronic
Load

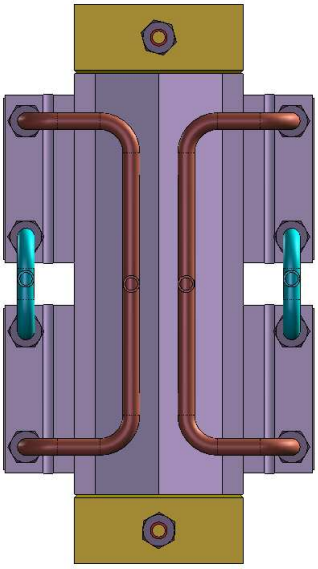
Load With 20 Watt light Bulb

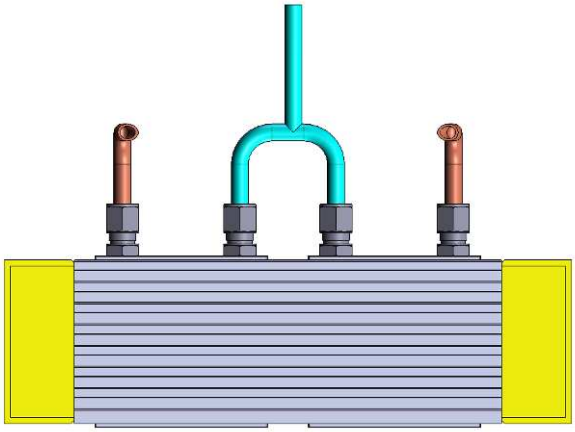


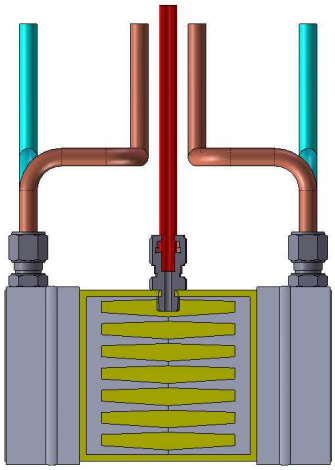
Drawings of 90Watt Module with HZ-20











After the investigation on the problems in the last step of the previous test with a single module, Dantherm completed and measured the energy loss, which was defined in two different zones. The energy loss was a main prob-

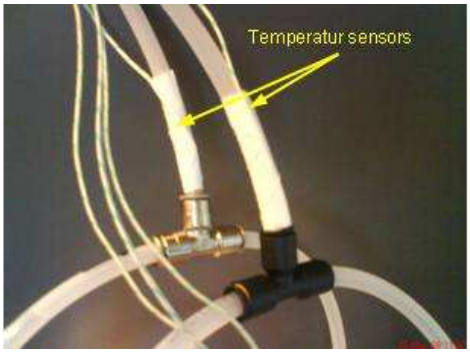
lem in the previous step and seems to be solved in this step of the integration.

The system evaluated with integration of four commercial thermoelectric modules. To comprise the heat transmission through the modules mounted closer to the heat inlet with modules mounted closer to the heat outlet, connected two set thermoelectric modules each set contain of two modules. This means that two modules connected in the series mounted closer to the heat inlet have 2 wires for electrical output connection and the other two modules have also two cables for electrical output connection.

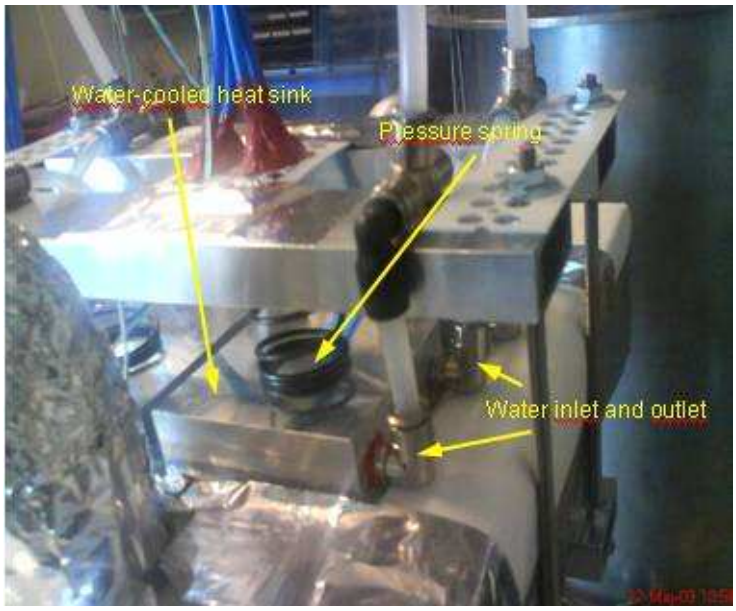
Then two set electrical output which gives the flexibility of separately measurement or measurement of all four modules in the series. Each module has a max current of 9A and the voltage is between 1,5-2 V.

Test of new setup

The new setup was build by a heat element absorbing the heat blown inside the heat box. The thermoelectric elements where mounted over the surface of the heat element/heat absorbent. The thermoelectric modules where mounted on the water-cooled heat sink. All the heat sinks modules connected to the one single tube (water-inlet tube) for feeding with water. Outlet water from all the heat sinks connected to a single tube (water-outlet tube). Each tube has a thermocouple sensor placed before the manifold for water inlet and after the manifold for water outlet. The thermocouples measure the temperature of the water inlet and outlet. Following photos shows the manifold and sensors for water connections.



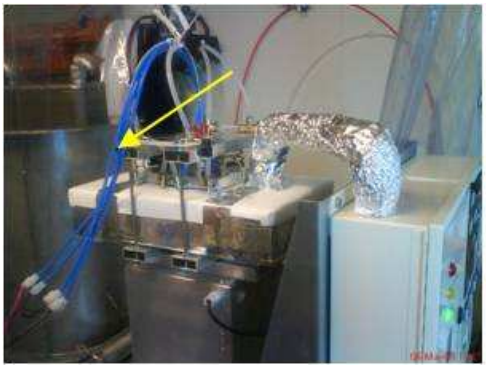
All the temperature sensors are connected to the data acquisition system, which register the variation of the temperatures in the TE device. The voltage output from thermoelectric modules is connected to the data acquisition system and DC-DC converter input terminals.

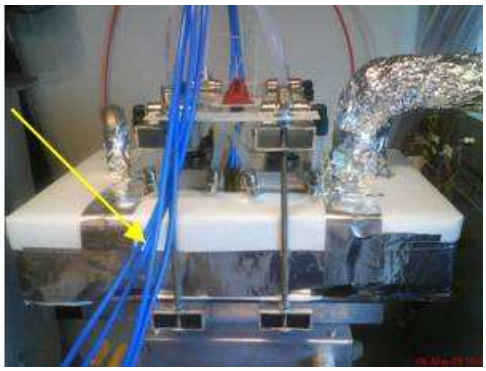


The output voltage from the DC-DC converter was connected to the electronic load and in the same time going to be measured and registered in the data acquisition system.

All the measurements happening from the start time. The photo on the right side shows the water-cooled blocks mounted on the cold side of the thermoelectric modules. There was one water-cooled heat sink for each thermoelectric module.

To minimize the energy loss appearing by the high electrical current, the wiring between the thermoelectric modules and the DC-DC converter has now changed with the appropriate cables. The following photos show the wiring between thermoelectric modules and the converter.

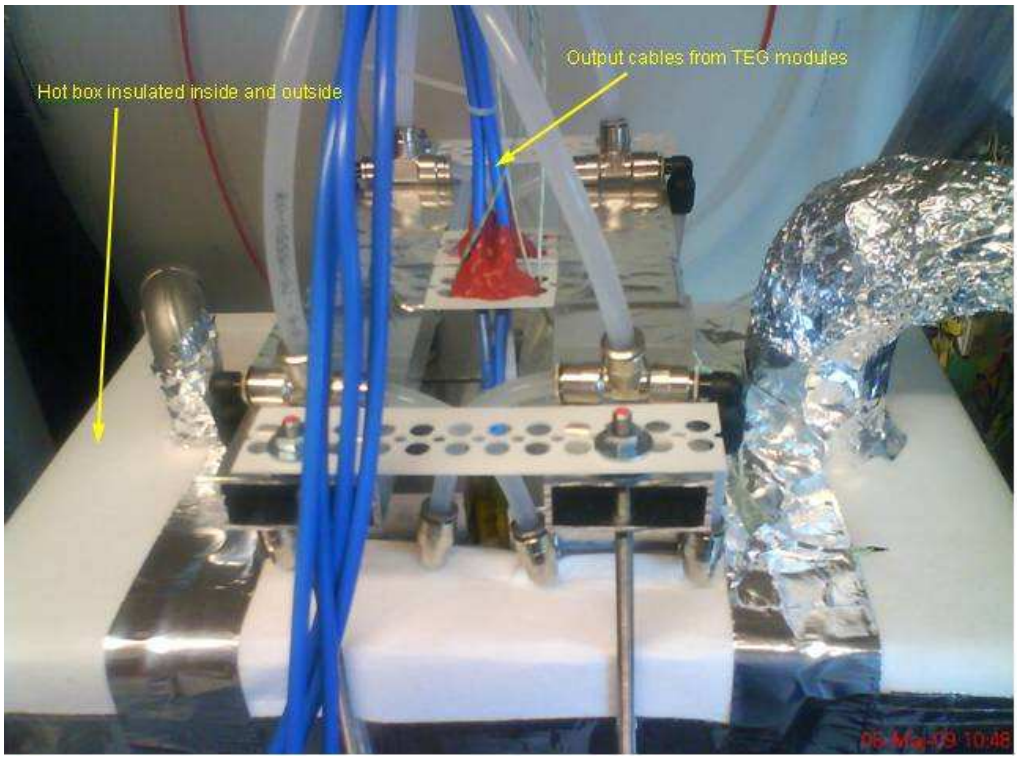




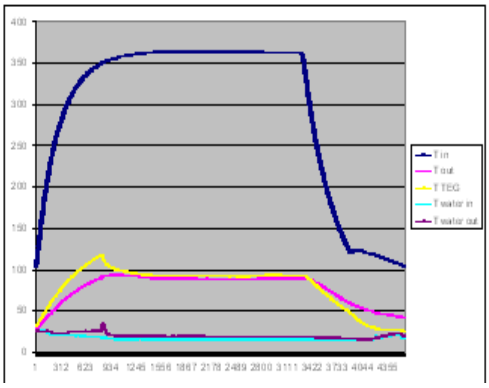
Following the experience from previous tests, the DC-DC converter was manually prepared for greater current tolerance in the printed circuit board for switch frequency.

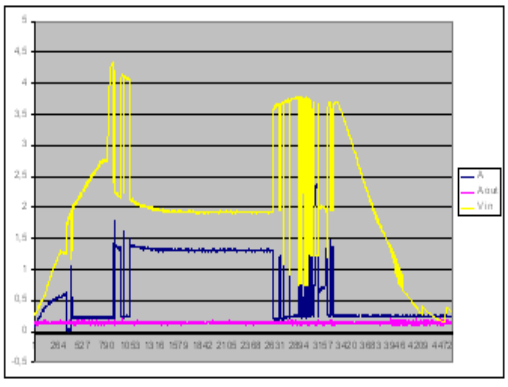
This can currently solve the problems of the energy loss in the converter circuit board. The value of switch frequency and the mosfet should also be under consideration, due to the energy loss factor.

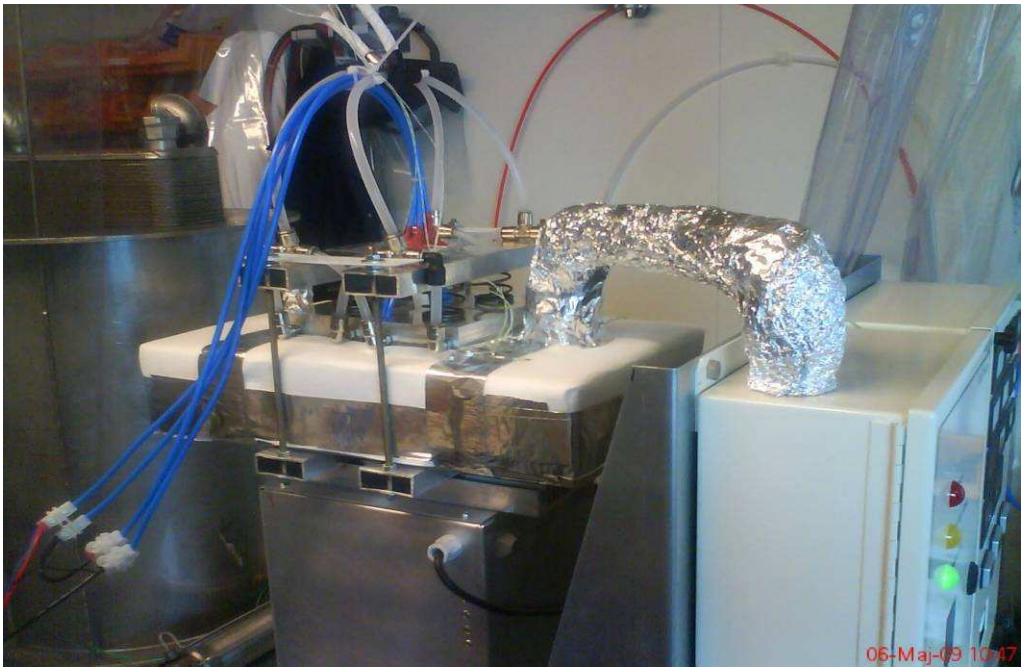
The photo done here shows the new test setup for max. 70 Watt electrical output when the necessary heat flow is applied:



The test result showed a very poor performance of the existing thermoelectric modules with a reduced figure of merit. However the system will work perfectly with the right material, which is going to be produced and prepared by Aarhus University and thermopile produced by the German company Panco GmbH.







Test setup

Appendix B – Novel TE material

Intro

The project of implementing a TEG in a SOFC hotbox will deal with maximum temperatures of ca. 500°C, and the system integration has shown that the warm side is optimally ca. 350°C. In the application it was suggested that the development of materials would be based on inorganic clathrates. However, at these temperatures inorganic clathrates, e.g. Ba8Ga16Ge30, are not optimal as they only reach ZT values close to 1 at 700-800oC. The temperatures are, on the contrary, optimal for Zn4SB3 which furthermore has the advantage of having been patented by the University of Aarhus. Literature shows other compounds such as TAGS ("AgPbSBTe" phases) and LAST (AgSbTeGe" phases) which both reach ZT values of ca. 1.5 at these temperatures, which is higher than that of Zn4Sb3. These compounds are, however, based on poisonous and comparatively rare elements, and thus a possible mass production may turn out to be problematic. In contrast, Zn4Sb3 consists of non-toxic and low-price elements. It was therefore decided to focus the production of materials on a continuous development of Zn4Sb3, e.g. through doping with cations.

Improve the stability of Zn4Sb3 by doping

The main problem of commercial application of Zn4Sb3 is that the high temperature stability is poor, meaning that at a thermal cycling above 250°C the material decomposes partially. The stability problem is reduced for the materials included in the patent of the University of Aarhus where Zn4Sb3 is synthesized by zone melting. It may be possible to improve the stability by doping. The main focus has therefore been on the preparation and characterization of zone melted Zn4Sb3 doped at first with Cd and Mg. Furthermore, large quantities of Zn4Sb3 (ca. 200 g) have been synthesized applying the fast thermal quench method. This material may be used for preliminary experiments for processing pellets for a thermoelectrical module (pressing, contacts, etc.).

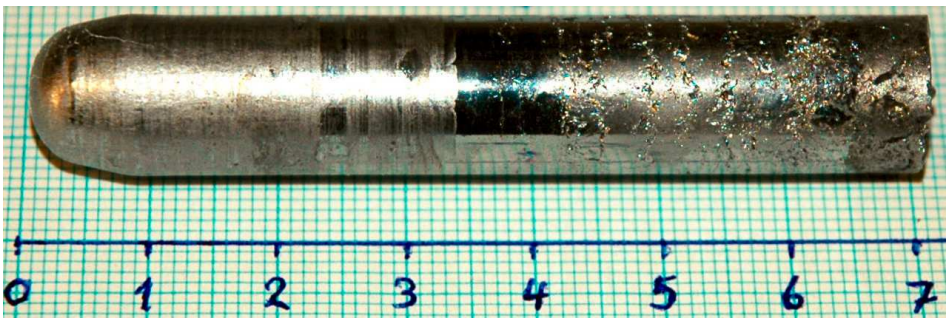


Figure 1. 2% Cd doped Zn4Sb3 produced by zone melting.

The samples have been characterized by powder diffraction to determine structure and purity. Moreover, is shown in Figure 1.

For all materials comprehensive characterization studies have been carried out with the purpose of determining phase purity, structure and thermoelectric properties. All synthesis products, including intermediates, have been analyzed by powder diffraction to determine structure and purity as well as to qualify possible impurity phases. Moreover, thermal stability has been examined by means of TGA/DSC measurements. Comprehensive thermoelectrical properties have been measured between 2 and 400 K at the Quantum Design instrument of the University of Aarhus, and the homogeneity of selected materials have been examined using a Seebeck microprobe which measures spatially resolved thermopower.

For zone melting synthesis an intermediate zone of pure Zn4Sb3 and doped feeding rod are produced. These are put together in a quartz ampoule which is closed in vacuum and mounted in a high temperature induction furnace. In our syntheses we have encountered problems in keeping a stable, homogeneous melted zone, but zone melted materials with Cd and Mg have been produced. As a reference, aCd and Mg doped materials have been produced by the quench method. In order to quantify possible impurity phases the compounds were investigated by powder diffraction at the Japanese Synchrotron Radiation Facility Source SPring 8. This facility is the world's most powerful X-ray source, and impurity phases may routinely be determined down to ca. 0.3%. The figure shows an example of data collected at SPring8 of 1% Cd doped Zn4Sb3 prepared by the quench method.

Data analyses show that the material has an yet unknown impurity (less than 1% weight). Data were measured also at high temperatures in order to examine the thermal decomposition, and analysis of these data is in progress. Preliminary results indicate that Cd has a positive influence on the thermal stability, and even materials synthesized by the quench method are far more stable than undoped materials. Technically, it would be a great advantage if stabile materials could be prepared by a fast quench method in contrast to a comprehensive zone melting method.

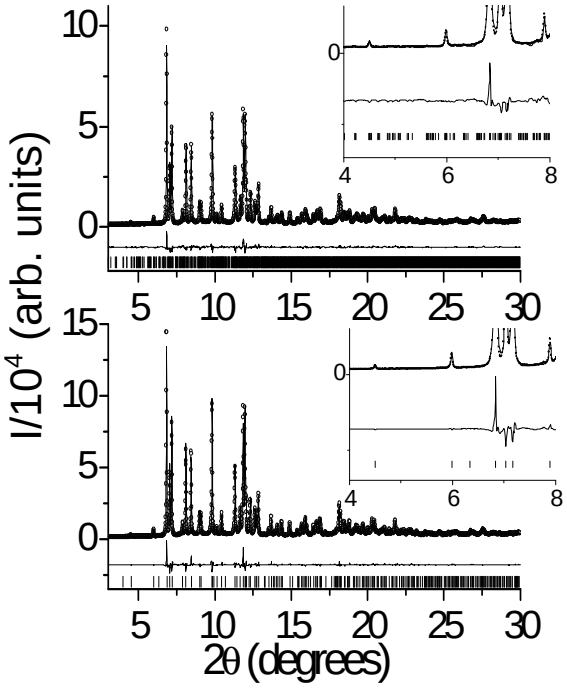
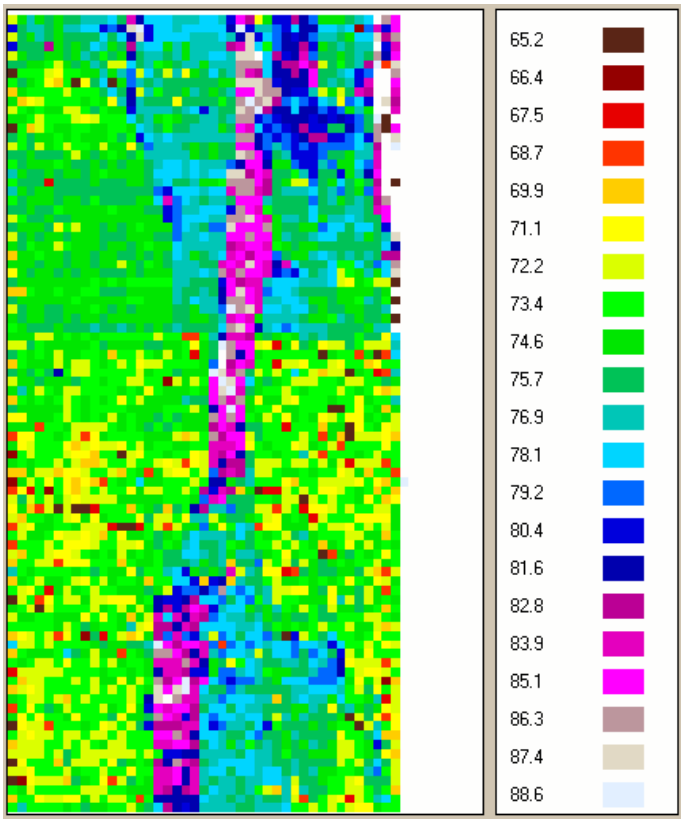


Figure 2. A plot of the spatially resolved thermopower.

Thermal stability has been examined by means of TGA/DSC measurements. The homogeneity has been examined using a Seebeck microprobe which measures spatially resolved thermopower.



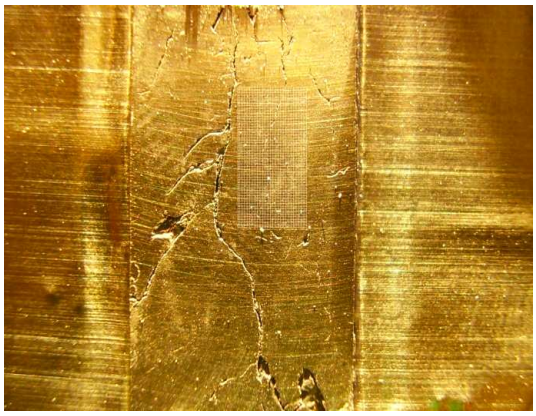


Figure3. Spatial Seebeck scan of 2% Cd doped Zn4Sb3

As can be seen in Figure 3 the thermopower of the Cd doped sample is only about 75 □V/K, which is significantly smaller the 120 □V/K observed for dense undoped samples. Earlier we have shown (B. L. Pedersen et al, *Appl. Phys. Lett.* 2006, 89, 242108) that the density of Zn4Sb3 samples is critical for obtaining a good thermoelectric performance and the poor performance of the present samples most likely is due incomplete compaction. However, since the PXRD data show that the samples are somewhat impure we want to pursue improved compaction on more pure samples. New materials synthesis therefore is in progress. Comprehensive thermoelectrical properties will also be measured using our Quantum Design instrument of the University of Aarhus.

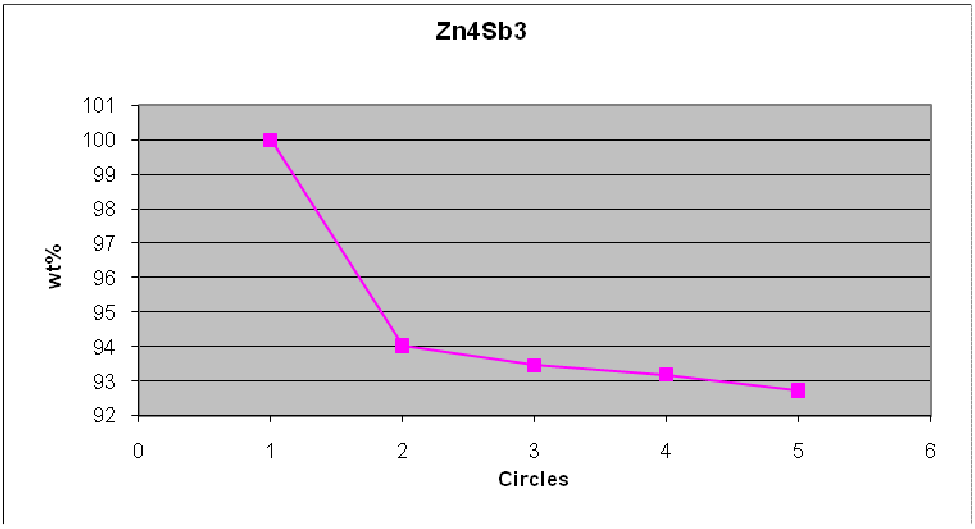
Stability of Zn4Sb3 under inert atmosphere

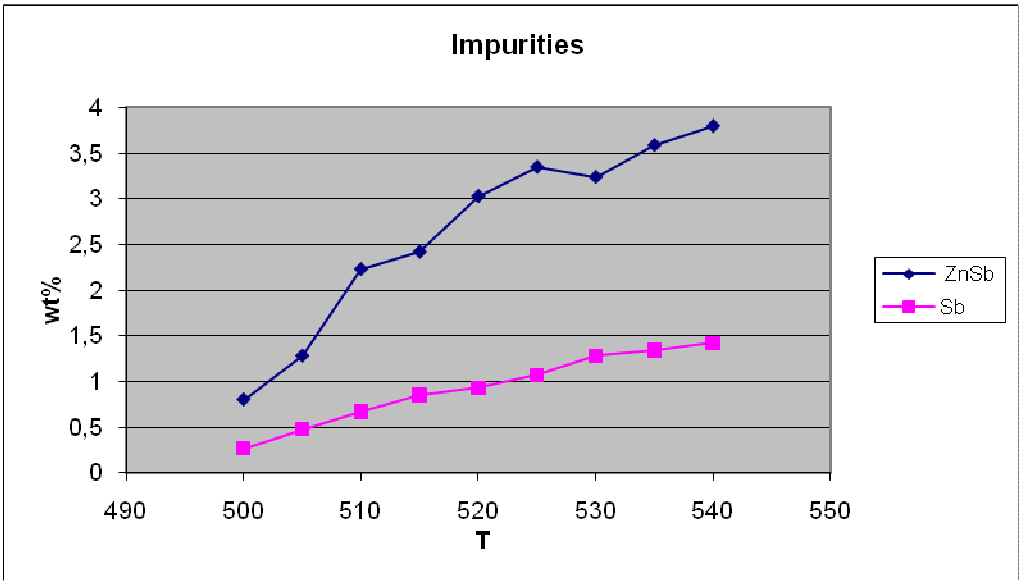
In the final period of the project the focus has been on determining the stability of Zn4Sb3 under inert atmosphere condition as well as quantifying the effect of Cd doping on the thermal stability. In earlier work (B. L. Pedersen and B. B. Iversen, *Appl. Phys. Lett.* 2008, 92, 161907) we quantified the thermal decomposition of undoped quench and zone-melted samples during heating in air. To find out whether the Zn4Sb3 phase intrinsically is thermodynamically unstable it is important to repeat such studies in an inert atmosphere. If adequate stability is observed in an inert atmosphere it may be possible to process the material so that it can be used in actual devices "as is". This would be a great advantage in industrial processing of the materials. We have therefore measured synchrotron powder diffraction data on capillaries sealed under argon of pure quench and zone melted materials. The data were measured at Spring8 in Japan, which is the world's most powerful X-ray source. Data were measured during heating to 625 K and then during thermal cycling five times between room temperature and 625 K. The data have been analyzed with the Rietveld refinement method to quantify the impurity phase content as a function of temperature.

The upper plot reveals that the thermal stability is significantly improved in Argon, and less than 10% of the sample degrades compared with more than 50 % when heating in air. Moreover, it seems that the sample reaches a stable plateau where there is only modest further degradation. As seen in

the lower plot the impurity phases do not include oxides when heating takes place in air, and the most significant impurity is the ZnSb phase, which also has reasonable thermoelectric properties. The new data suggest that implementation of Zn4Sb3 in thermoelectric modules also could be attempted based on material protected from air by some coating or enclosure.

In order to check the effect of Cd doping on the thermal stability new zone melted and quench samples have been synthesized, and multi-temperature synchrotron data have been measured at Spring8. The data analysis is in progress, but preliminary results suggest a clear positive effect of Cd doping on the thermal stability of quench samples. It appears, however, that one critical sample parameter, the grain size, so far has not been adequately controlled. There are indications that samples with larger grains sizes possess better thermal stability, and this aspect deserves further study.




Impurities
wt%
4
3,5
3
2,5
2
1,5
1
0,5
0
490
500
510
520
530
540
550
T
ZnSb
Sb