Overview of Progress in R&D for Thermoelectric Power Generation Technologies in Japan

Takenobu Kajikawa
Shonan Institute of Technology
Fujisawa, Kanagawa, Japan
Outline

• Background
• Government-funding Projects
• Private Companies’ Activities
• Future Prospects
• Concluding Remarks
Background

- Urgent Reconstruction of Overall Energy Policy in Japan due to Fukushima Nuclear Power Station Disaster  ➔ Urgency of the establishment of renewable energy tech.

- Enforcement of Take-up Regulation of entire electric power from renewable energy conversion system such as PV and wind power  ➔ Acceleration of growing the renewable energy tech.

- ICT2013 (June 30 – July 4, 2013) will be held in Kobe, Japan.  ➔ Stimulation to R&D activities on TE
Ongoing Government-funding R&D Projects

• NEDO project / Development of Nano-Structured Thermoelectric Materials using Clathrates

• JST project / Development of High-Efficiency Thermoelectric Materials and Systems
Project Goal; $ZT=1.3$ at 200-300 °C

Design of novel clathrates by first-principle calculations
Yamaguchi Univ.

Synthesis of single crystals toward higher ZT
Hiroshima Univ.

Synthesis of bulk materials for modules by sintering technique
Yamaguchi Univ.

Optimization of Segmented TE modules
AIST, KELK

Design & demonstration of TE power generation unit for waste heat recovery in the furnaces
DENSO 160W/unit
Enhancement of TE Performance for Nano-structured Clathrates

- **BGS**: $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$
- **BGCS**: $\text{Ba}_8\text{Ga}_{16-x}\text{Cu}_x\text{Sn}_{30}$

**Advantage**

Both p- and n-type legs for a module can be made from the same material. No degrading by thermal hysteresis.
There are large differences between experimental results and calculations based on TE material performance. This discrepancy is attributed to the imperfection in electrode technology for this material system mainly.
Development of High-Efficiency Thermoelectric Materials and Systems
(2008.10-2014.3)


Nagoya University, Japan
CREST, Japan Science and Technology Agency, Japan
*** AIST, Japan
**** Hokkaido University, Japan
***** Tokyo University of Science at Yamaguchi, Japan

Development of Novel TE Materials of Non-toxic, Non-rare, Cheap, and Usable in Air for wide temperature range

Design/Development of TE Modules and Systems
### Development of Novel TE Materials (JST-CREST)

<table>
<thead>
<tr>
<th>LT 300-500 K</th>
<th>LT~MT 300-700 K</th>
<th>MT 500-800 K</th>
<th>HT 800-1000 K</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>3D SL STO</strong></td>
<td><strong>TiS(_2) NSL</strong></td>
<td><strong>Mn(_3)Si(_4)Al(_3)</strong></td>
<td>Siクラスレート</td>
</tr>
<tr>
<td>Goal : (ZT=0.8)</td>
<td>Goal : (ZT=0.6)</td>
<td>Goal : (ZT=0.6)</td>
<td>Goal : (ZT=0.5)</td>
</tr>
</tbody>
</table>

- **3D SL STO** realizing \(ZT\sim1@300\text{K}\) was proposed.
- **Energy filtering effect** at grain boundaries was verified.
- First succeeded in **La-STO nanocubes**.
- **3D SL ceramics** of STO are under development.
- **TiS\(_2\)**-based NSL gave world record : \(ZT=0.37@700\text{K}\) for sulfides. (ICT2010 Best Scientific Paper Award, ICT2011 Outstanding Poster Award)
- Proposed quantum confinement effect in **TiS\(_2\) nanosheets**.
- **TiS\(_2\)/Organic Hybrid SL** is now under investigation.
- **Mn\(_3\)Si\(_4\)Al\(_3\)** phase was found to give \(ZT\sim0.2@800\text{K}\)
- High oxidation resistance (<800 K in air)
  - Verified the ability to generate high power with a test module.
  - **Basic research** is underway among CREST Team.
- **Ba\(_8\)Al\(_{16}\)Si\(_{30}\)** gave world record : \(ZT=0.4@900\text{K}\)
- **Ba\(_8\)Ga\(_{16}\)Si\(_{30}\)** ⇒ discovery of phonon-scattering enhancement by guest atoms in Si nanocages.
- Challenging to improve TE properties of **Ba\(_8\)Al\(_{16}\)Si\(_{30}\)**.
## Design/Development of TE Modules/Systems

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>LT Heat</td>
<td>LT~MT Heat</td>
<td>LT~HT Heat</td>
</tr>
</tbody>
</table>

### DSSC/SSA/TE Hybrid Device

- **Power Generation System (1):** Water lens concentrates sunlight.

### MT TE module

- **p-MnSi\textsubscript{x}/ n-MnSiAl**

### Power Generation Systems (2):

- Concentrated sunlight directly irradiates TE converter.

---

Ongoing Developments of Thermoelectric Applications promoted by private companies

- **Waste Heat Recovery Systems**
  - Industrial furnaces (Komatsu/KELK, Showa Cable Systems, TEC New Energy)
  - Motorcycles/Automobile (Atsumitec, Komatsu)
  - Incinerator (Showa Denko/PLANTEC, ACTREE)

- **Renewable Energy Sources**
  - Solar thermal energy (TDS group, JAXA)
  - Hot springs TEG (Toshiba)

- **Energy Harvesting TEG**
  - Monolithic micro TE Generator (Murata Manufacturing Co.Ltd.)
  - Mini-size TEG system (YAMAHA, KELK)
A 200 W class TEG system recovering the exhaust heat from a gas carburizing furnace was installed in the large gear manufacturing process.

Sixteen thermoelectric modules were mounted in the test facility.

The burning power depends on flow rate of carburizing gas. One Case: 10 m³/h in flow rate, 21 kWt in thermal power.
Configuration of main part for TEG system

Temperature dependence of power output
Results for duration test

Sample data on time dependence of power output and hot side temperature for long duration test

Long run test has been carried out since 2010.

Operation time without maintenance has reached more than 12,600 h at the present stage.

TEG system will be installed to all carburizing furnaces in the factory step by step in future.

2012.03.20
EGR Cooler combined with TEG by KOMATSU

Structure of Cooler with TE modules

High temp. heat exchanger plate
Spring
TE modules
Low temp. heat exchanger plate

Air
Turbocharger
Engine
Rejected gas

Coolant

EGR Gas

2012.03.20

Experimental facility
Test results show the good agreement of experiment with calculation.
Solar powered desalination system combined with TEG by TDS Group

Major components for the proposed concept to produce electricity, fresh water and heat
Energy balance & temperature allocation for a conceptual design

Assumptions for fresh water production cost estimation:

Capacity: 10,000 t/d, Plant availability: 0.9, Site: the Middle East, Plant Life: 20 years, Inflation rate: 2.0%, Construction year: 2010, Efficiency of TEG: 7%, Efficiency of PV: 20%
Fresh water production cost competitiveness with others

Proposed System

PV: Photovoltaic, TE: Thermoelectric Generator, ST: Steam turbine Cycle
Assumptions
Direct Normal Irradiance: 2,500 kWh/m², Plant availability: 90%
Operation period: 20 years, Inflation rate: 2.0%, Cost index: based on year 2010,
Cost of TE modules, CSP and PV: based on mass-production volumes,
All the utilities except for sea water are self-sufficient
Proof-of-Concept Experiment

- Design of steam generator combined with TEG
- Overall heat balance
- TEG characteristics
- Dynamic mass balance and control in variation of temperature
- Design of Proto-type Solar Desalination System combined with TEG
Monolithic oxide-metal composite micro TEG for energy harvesting
by Murata Manufacturing Co., Ltd.

- TEG modules have been made based on multilayer ceramic capacitor technology.
- The p- and n-type layers printed on insulators are stacked and co-sintered.

\[ \text{p: } (\text{Ni-Mo}) + (\text{La}, \text{Sr})\text{TiO}_3 \]
\[ \text{n: } (\text{La}, \text{Sr})\text{TiO}_3 \]
Performance of TE materials and device

Power output is obtained about 100μW at 10K in ΔT.

Devices can be mass-produced with MLCC process at low cost.

V-I characteristics of the device

Performance of TE element
Future Prospects

• New projects started in 2011
  1) NEDO project / R&D program for Innovative Energy Efficiency Technology
  2) JST projects / Advanced Low Carbon Technology R&D Program

• Academic Roadmaps revised in TSJ
  TE Materials
  TE Applications
New NEDO Project

Development of Thermoelectric Generation Technology for Steel Plant Waste Heat Recovery

Team: JFE Steel Corporation, KELK,Ltd., Hokkaido University

Term: 2012.1-FY2015
New JST Project:

Fabrication of Solar-Heat Thermoelectric Materials by Controlling Ordered Structures and Phase Interfaces

October 2011 ~

Goal: Solar-heat TE power generation system

High potential TE materials are required for the temperature range: 650~1000 K (above Bi-Te) using environmentally friendly TE materials.

P.L.: Yoshisato Kimura
Associate Professor
Tokyo Institute of Technology
Materials Science & Engineering
1. Controlling Ordered Structures based on Half-Heusler system

Heusler (FH)

Half-Heusler (HH)

A(Zr) B(Ni,Co) X(Sn) Vacancy Vacant-site

Occupation(+Co)

Zr-Co-Zr

Sn Ni

ZrCo2Sn

Zr-Ni-Co-Sn

ZrNi3Sn (HH)

Zr(Ni,Co)2Sn (FH)

ZrNi2Sn (FH)

Lattice Defects
Structural vacancy, Anti-phase domain, etc

Band structure
Conversion of p-n
Peak temperature

Seebeck coefficient

\[
S = -\frac{\pi^2}{3} \frac{k_B^2 T}{e} \frac{1}{N(E_F)} \left[ \frac{\partial N(E)}{\partial E} \right]_{E=E_F}
\]
2. Controlling Phase Interfaces

**Phase Interfaces**
- Phase separation
- Precipitation
- Cluster
- Grain Boundary etc.

**Scattering effect**
- Lattice thermal conduction
- Seebeck coefficient

**Nano clustering**

**HR-TEM**
Hf(Ni,Co)Sn

**FFT**

**STEM-DFI**
Hf(Ni,Co)Sn

**HH matrix**
001
010

**FH precipitates**
50nm

**TiNiSn(HH)**
8.5 at.%Hf

**TiNi2Sn(FH)**
Phase separation

**Solubility**
9.0 at.%Zr

**Miscibility gap**
1373 K

**Phase separation**

**ZrNi2Sn**
- (FH)
- (HH)

**ZrNiSn**
- (HH)

**HfNiSn**
- (HH)

**All proportion miscible**
New JST Project:

Development of High Efficient Silicon Thermoelectric Materials using Nanostructure Control

PL: Professor S. Yamanaka, Osaka Univ.

Team: Osaka University and AIST

Term: 2012-2017

Goal:
ZT~1 at RT-600K for Nanostructured Si
Approaches to the Goal

- Silicide nanocomopite in Si
- Nanopillar on the surface of Si by chemical processing
- Vacancy control in nonstoichiometric Silicide etc.
Academic Roadmap on TE Materials  
by TSJ

1st Generation  
ZT=1~2 in bulk

- Bi-Te
- Pb-Te
- SKD
- Heusler
- Oxide
- Silicide
- Clathrate
- Cluster
- Organic

2nd Generation  
ZT=2~3 in bulk

- Self assembled
- Nanostructure built-in
- Non-(Bi-Te)
- Hybrid inorganic/organic

3rd Generation  
ZT>3 in bulk

- Fusion/Synergy Effect
- Atomic Network structure control
- Novel Condense Materials
- Novel Conduction mechanism for organic materials
Research distribution of kinds for thermoelectric materials presented at TSJ 2011

- 72 papers
- nano/thin film
- clathrate
- oxide
- Heusler
- sulfide
- SKD
- silicide
- Boron
- Te
- other
- Organic

2012.03.20

31
Concluding remarks

• The enhancement of TE performance for nano-structured Clathrate system has been achieved. ZT value could be obtained more than 1.3 around 500K. The demonstration test of Clathrate-based modules was successful in NEDO project.

• Four novel approaches for high-efficiency TE materials have been intensively challenged in JST project.

• The progress of three kinds of TEG applications such as waste heat recovery, solar energy and energy harvesting have been introduced as private companies’ activities.

• It is noteworthy that TEG system has been operated for more than 12,600 h without maintenance using a practical unstable heat source such as industrial furnaces.

• Two 5-year JST projects have just started to enhance the TE module efficiency from the viewpoints of nano and environmentally friendly technologies.

• The Thermoelectrics Society of Japan is active to promote and enlighten the thermoelectric technology in the society through the proposal of academic roadmaps of thermoelectric technology.
Acknowledgments

The speaker would like to express his hearty gratitude to Prof. T.Takabatake (Hiroshima Univ.), Prof. K.Koumoto (Nagoya Univ.), Dr.H.Hachiuma and Dr.H.Kaibe (KELK Ltd.), Dr.Y.Kimura (Tokyo Inst. of Technology), Prof. Y.Horita (Tokyo Inst. of Technology), Mr.K.Nakajima (Showa Denko), and Dr.T.Nakamura (Murata Manufacturing Co.Ltd)

for their cooperation and sincere support.
Thank you for your kind attention!