MATERIALS FOR THE ENERGY TRANSITION

THERMOELECTRIC ENERGY CONVERSION MATERIALS

This publication forms part of the 'Materials for the Energy Transition' series. The Henry Royce Institute in collaboration with the Institute of Physics and the Institute for Manufacturing have convened the academic and industrial materials research communities to explore opportunities for materials to support the UK's net-zero by 2050 target.

HENRY ROYCE INSTITUTE

IOP Institute of Physics

IfM MANAGEMENT TECHNOLOGY POLICY

MATERIALS FOR THE ENERGY TRANSITION ROADMAP:

MATERIALS FOR DECARBONISING HEATING AND COOLING THROUGH THERMOELECTRIC MATERIALS

SEPTEMBER 2020

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INTRODUCTION

The Challenge: Materials for the Energy Transition

Following release of the Committee on Climate Change (CCC) 2019 Report[1], the UK is committed to a new greenhouse gas emissions target: net-zero emissions by 2050.

The Executive Summary of the **2019 Committee on Climate Change Report** states:

> ***"Delivery must progress with far greater urgency.***
>
> - ***2040 is too late for the phase-out of petrol and diesel cars and vans, and current plans for delivering this are too vague.***
> - ***Over ten years after the Climate Change Act was passed, there is still no serious plan for decarbonising UK heating systems and no large-scale trials have begun for either heat pumps or hydrogen.***
> - ***Carbon capture (usage) and storage, which is crucial to the delivery of zero GHG emissions and strategically important to the UK economy, is yet to get started. While global progress has also been slow, there are now 43 large-scale projects operating or under development around the world, but none in the UK.***
> - ***However, falling costs for key technologies mean that the future will be different from the past: renewable power (e.g. solar, wind) is now as cheap as or cheaper than fossil fuels in most parts of the world."***

In response, the Henry Royce Institute (the Royce), in collaboration with the Institute of Physics (IOP), has engaged with academic and industrial materials research communities to explore solutions to the grand challenge of **"Materials for the Energy Transition"**. Through roadmapping workshops and associated community-led activities, technologies were identified where materials research can make a significant impact on greenhouse gas emissions.

The key drivers for this work have been (1) the pathways to net-zero emissions suggested in the CCC report, and (2) Royce-supported community workshops undertaken in 2019 to identify areas where investment in UK materials science can generate impact and contribute to the UK's energy transition. These included the "Atoms to Devices" workshop in Leeds (May 2019); the "Operando and In Situ Characterisation of Energy Materials" workshop at the Diamond Light Source in Harwell (July 2019); and, the "Multi-Modal Characterisation of Energy Materials" workshop in Cambridge (November 2019).

As a consequence, the following four areas were identified where materials science is critical to enabling a step-change in greenhouse gas reduction:

1. Materials for photovoltaic systems
2. Materials for low-carbon methods of hydrogen generation
3. Materials for decarbonisation of heating and cooling
    I. Thermoelectric energy conversion materials
    II. Caloric energy conversion materials
4. Materials for low loss electronics

[1] Committee on Climate Change Report: Net-Zero, January 2019, https://www.theccc.org.uk/publication/net-zero-the-uks-contribution-to-stopping-global-warming/

Materials Roadmaps

In 2020, the Royce together with the respective research communities explored the various materials challenges, targets, and timescales required to support the achievement of net-zero greenhouse emissions by 2050 of the four research areas outlined above. The CCC report and the related materials community engagement emphasised that these four areas are components of a broader ecosystem of materials technologies which together contribute to the UK's goals to deliver net zero by 2050. These roadmaps form the basis for bringing scientific research communities, industry and government together to address immediate and long-term requirements for the development of a suite of energy materials to replace fossil fuel-based energy technologies. The Royce collaborated with the Institute of Physics (IOP) to set out the programme of work and ensure community-wide feedback and engagement. Skills and expertise from the Institute for Manufacturing (IfM) were commissioned to ensure a robust roadmapping methodology, throughout the series of online roadmapping workshops, and to support community discussions.

Roadmap Objectives and Methodology

The main objectives for the five materials roadmaps at the outset were as follows:

- To understand the current state-of-art for each topic
- To define the most significant technical challenges for each area that are providing barriers to impact on net zero targets
- To define the anticipated future challenges for each area in contributing to net zero targets
- To identify solutions to these challenges that can make step-changes in delivery of technologies to contribute to net zero targets
- To identify the desired performance targets of such solutions

The methodology adopted was based on wide-ranging engagement with research communities to define the roadmap objectives and expectations, to design and customise the strategic framework for the roadmapping, to develop questionnaires for the research communities involved, and to modify workshop process steps to ensure participation of the entire research community. The workshops brought together academic and industrial experts in the four respective technology areas and involved both offline and online data collection phases. The offline phases were used for data collection from individual participants and publicly available research sources, followed by data consolidation and, where necessary and appropriate, prioritisation. The online workshops were used for data review, analysis and deeper exploration of essential issues. The quality and reliability of the process was maintained by a Steering Committee involving roadmapping facilitators and technical leads from each of the four research communities.

In total, 26 workshops sessions were held across the four technology areas between March 2020 and June 2020. These revealed several materials sub-topics of particular interest for contribution towards the net-zero targets, as well as highlighting important fundamental research and commercial technology enablers that need to be established. These outputs significantly aided research communities' understanding of the future direction of energy materials research, towards the achievement UK's net-zero emission targets by 2050.

Between March and June 2020, over 220 participants contributed to the creation of these five roadmaps from the UK academic and industrial materials communities. The outcomes are:

(1) an **executive summary** report, highlighting the main findings of the four roadmapping activities, published in July 2020;

(2) five **materials development roadmaps** towards net-zero emissions for 2050, published for research communities, funding bodies, government, policy-makers and industry leaders.

The five materials roadmaps generated are living documents, and Royce will engage with research communities regularly to review these documents and to develop further roadmaps as new materials systems and technologies emerge. We would like to thank all who have participated in these activities through the roadmapping workshops, interviews, surveys and research summaries.

Oversight of these community activities was through the “Materials for the Energy Transition” Steering Group: Professor Neil Alford, (Imperial College London), Professor Manish Chhowalla (University of Cambridge), Professor Richard Curry (University of Manchester), Professor Edmund Linfield (University of Leeds).

Programme management, reporting, and community engagement was undertaken by Royce and IOP: Mia Belfield (Royce), Ellie Copeland (IOP), Anne Crean (IOP), Isobel Hogg (IOP), Judith Holcroft (Royce), Professor David Knowles (Royce), Dr Amy Nommeots-Nomm (Royce), Dr Suman-Lata Sahonta (Royce), Professor Philip Withers (Royce), Dr Katharina Zeissler (Royce).

Roadmapping activities were coordinated by IfM: Dr Nicky Athanassopoulou, Dr Diana Khripko, Dr Imoh Ilevbare, Dr Arsalan Ghani, Andi Jones, Rob Munro.

Technical oversight of roadmaps was undertaken by Dr Oscar Cespedes (University of Leeds), Dr Katharina Zeissler (University of Leeds), Dr Oliver Fenwick (Queen Mary University of London), Dr Robert Hoye (Imperial College London), Dr Xavier Moya (University of Cambridge), Dr Ifan Stephens (Imperial College London), Dr Sam Stranks (University of Cambridge).

EXECUTIVE SUMMARY

The UK government is committed to achieving net-zero greenhouse gas emissions by 2050. For this to occur, we must demonstrate significant reductions in emissions by 2035. As can be seen in figure 1 below, space heating and cooling contributes to 17% of the UK's CO_2 emissions, mostly by burning natural gas.

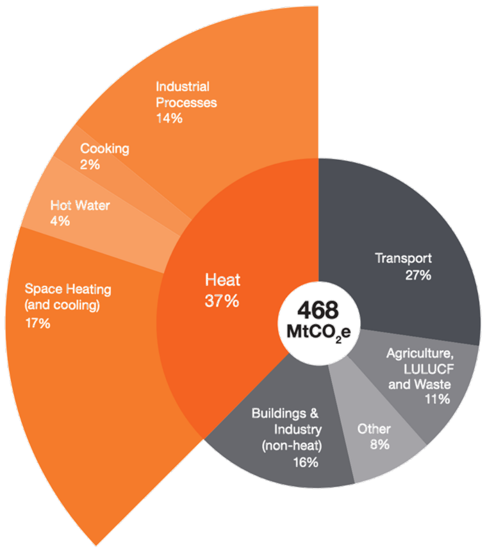

Figure 1: UK CO_2 emissions in 2016 attributable to heating[2]

The UK gas grid supplies 84% of UK homes, with unconnected districts being supplied by propane and kerosene deliveries.[3] The electrification of home heating, cooling and hot water will significantly reduce the UK's greenhouse gas emissions, and will reduce reliance on the UK gas grid.

In nations with no access to natural gas for heating, home water and space-heating is typically through electrically-powered air-source heat pumps, in which most heat exchange systems are vapour compression-based combined refrigeration or heating units. There is increasing interest in air-source heat pump systems in the UK to replace natural gas. It is predicted that by 2040, around 3.6 GW of heat pumps may be installed in the UK, requiring 11 TWh per year of electricity demand, but offsetting 50 TWh per year of natural gas demand.[4]

One scenario for the UK in 2050 would be homes with solar-integrated heat pumps for providing UK space heating and domestic hot water with reduced draw from the National Grid. However, given that refrigerants such as HFCs are powerful greenhouse gases, heat pumps that use thermoelectric or magnetocaloric, electrocaloric, elastocaloric, and barocaloric materials are being investigated as alternatives to vapour compression technology.

The Henry Royce Institute brought together UK academic experts from different research fields related to caloric and thermoelectric materials. This report refers to the roadmapping activities undertaken by the thermoelectric materials community. A separate report is available for caloric materials.

The aims of this activity were to provide answers to the following questions:

- Why should the UK take the initiative to expand research into this class of materials?

[2] BEIS Report: Clean Growth – Transforming Heat, December 2018 https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/766109/decarbonising-heating.pdf
3 Dodds, McDowall, Energy Policy 60 (2013) 305–316 DOI: http://dx.doi.org/10.1016/j.enpol.2013.05.030
[4] National Grid Report: Future Energy Scenarios, 2016 URL: http://fes.nationalgrid.com/media/1363/fes-interactive-version-final.pdf

- Which materials systems in this field show the most promise for viable energy-saving applications towards net-zero emissions by 2050, and what is the current state of the art?
- What are the current materials challenges that limit deployment of this technology?
- What performance could be achieved with current materials, and what could be achieved by 2025, and by 2050?
- How can improvements be made in the characterisation of these materials?
- How can improvements be made in provision of advanced facilities required for industry scale-up and commercial testing, in comparison to the availability of suitable lab-scale tools?

In line with the aim to decarbonise UK heating and cooling aim, focus was placed on materials and material systems for the temperature range < 500K. There is value in exploring materials and devices for high temperature industrial waste heat recovery, such as certain oxides and chalcogenides, but this is not covered by this report.

The **current state of the art** is:

- Bi_2Te_3 is used in current commercial devices but has limitations as regards:
    - Abundance – Tellurium is relatively scarce
    - Performance – current figure of merit, ZT, at ambient is around 1.

- New materials discovery is key to making step-changes to reach the 2050 targets.

Materials identified that have the potential to reach the 2050 targets, or get closer to them were identified and grouped as follows:

- **Ceramic Thermoelectrics:**
  Chalcogenides; Mg_3Sb_2 / MgAgSb and Zintl phases; Chlathrates; Skutterudites; Nanostructured Si-based materials; Half-Heuslers; Topological and Weyl based materials, Silicides (including SiGe)

- **Emerging and Lower TRL Materials:**
  2D materials (not just graphene); Organic (small molecule + polymer) and carbon nanotube; Composites (organic/inorganic/others); Combination materials and composites; Film coatings; Halide perovskites; Metal-organic frameworks; Conformable/flexible thermoelectric and periphery materials; Printable thermoelectric materials; Molecular junctions.

It was recognised that a materials discovery program could add more materials to this list.

Some important **research and technology enablers** are required across all these topics for their successful development. These are:

A. Materials Discovery and Optimisation

For Ceramic Thermoelectric Materials:

- Accelerated materials discovery programme
- Establish if sulphides can perform well at room temperature
- Design interfaces to boost performance, including energy-filtering barriers
- Use of modulation doping to create high-mobility regions
- Alloy engineering to improve performance of known materials
- Enhance understanding of band engineering and band alignment

- Development of computational tools for calculating accurate electrical and thermal transport in disordered and nano-structured materials (e.g. simulations on micron length sales)
- Translation of nanostructuring and materials engineering approaches demonstrated on Si thermoelectrics to other thermoelectric materials
- Develop materials with resonant energy levels to boost the Seebeck coefficient
- Material properties by design
- Investigate how to relax the relationship between thermal and electrical conductivity (i.e. search for non-Wiedemann-Franz materials)
- Investigate how to relax the interdependence of conductivity and Seebeck coefficient
- Use of computational tools for predictive modelling
- Development of hierarchical nanostructures to improve performance
- Use of topological states to improve thermoelectric properties

For Emerging / Lower TRL Thermoelectric Materials:

- Understand structure-property relationships and optimal morphologies
- Development of new (stable) dopants for organic materials
- Standardisation of characterisation of thermoelectric properties
- Development of computational tools to simulate morphology, disorder and interfaces
- Development of computational tools for accurate band structure calculations
- Effort to predict non-Wiedemann-Franz materials
- Modelling of disordered and dynamic interfaces
- Stabilisation of morphologies
- Establish microscopic understanding of control of physical properties
- Conduct predictive modelling to direct molecular synthesis and processing
- Predictive modelling of thermal properties
- Characterisation of disordered and dynamic interfaces
- Understand fundamental performance limits of emerging thermoelectric materials
- Produce optimised materials with high performance

B. Integration into Devices

- Development of n-type and p-type pairs of materials
- Development of interface materials
- Consider the ease of combining materials and their interface
- Improve Coefficient of Performance of cooling systems when operating at high current

- Development of low power electronics that can be powered from harvested waste heat
- Design and integration of effective heat exchangers
- Examine how energy harvesting devices can compete with piezoelectric technology
- Understand how to maintain material performance when processing into a device, including obtaining optimal morphologies
- Understand interface properties at electrodes and how to optimise these

C. Scale-up

- Consider availability of compounds
- Ensure thin-film and interface science is scaled to the bulk material
- Identify niche sector(s) where value proposition can be demonstrated
- Develop approaches to reduce cost of material production at scale
- Life cycle analysis to understand viability of scaling up new materials
- Engagement of Research and Technology Organisations (e.g. Centre for Process Innovation) to provide trials of scale-up
- Development of process technology to synthesise materials at >kg scales

In conjunction with the research developments, several **competences and resources** are needed to accelerate the deployment and adoption of these technologies. These are:

- Tools to accurately model density of states
- Investment in characterisation facilities to accelerate development, including characterisation of disordered interfaces
- National-level rapid screening approaches
- Improved interdisciplinary collaboration in the UK including funding for exchange between UK thermoelectric community researchers
- Continuity of funding for The UK Thermoelectric Network
- Use of online tools to increase dialogue in the UK community
- Mechanisms to collaborate with other communities (e.g. batteries, photovoltaics and fuel cells)

- Industry input to focus research on needs of end users
- Address knowledge and skills gap between small-scale materials research and large-scale applications
- Increased size of the UK community including modelling, device engineering and synthetic chemistry
- Life cycle thinking and sustainability
- More PhD funding for emerging thermoelectric materials research
- An established model for industrial engagement and dedicated facilities to enable engagement

- Engagement with synthesis industry to reduce costs of scaled materials production

These developments could collectively help to achieve:

- Significant incremental improvements in efficiency, allowing thermoelectric devices to take a greater market share of their current applications.
- A step change in average ZT values to >3 which will enable thermoelectric technologies to compete on efficiency with incumbent technologies, allowing thermoelectrics to expand into non-niche areas.

INDUSTRY AND MARKET OPPORTUNITY

The UK has become the first major economy in the world to pass a net zero emissions law. The ambitious target is to bring all greenhouse gas emissions to net zero by 2050, compared with the previous target of at least 80% reduction from 1990 levels[5].

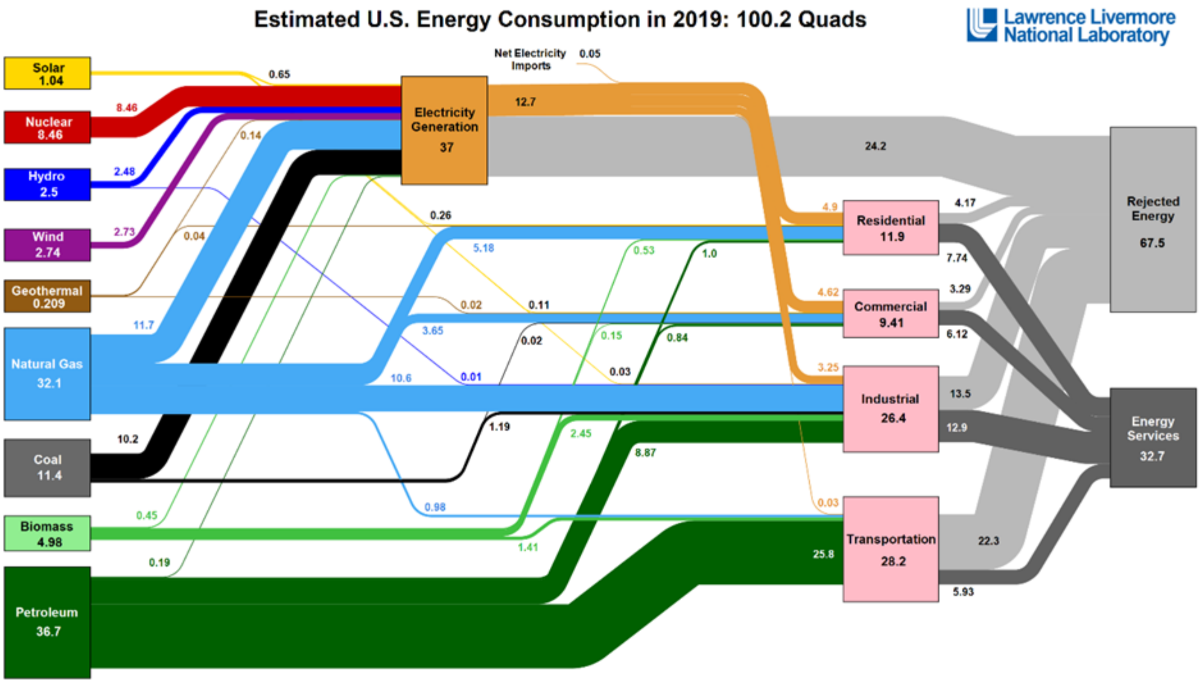

Figure 2: Estimated U.S. Energy Consumption in 2019: 100.2 Quads

Figure 2 shows the different ways that energy is both produced and used. It indicates that about 2/3 of primary energy is wasted as heat. This makes technologies that can recover this waste heat, such as thermoelectrics, important for achieving the UK's 2050 net-zero emissions goal. Furthermore, the global market for waste heat recovery systems is estimated to be $58bn, growing to $107bn by 2027.[6]

Thermoelectric materials may also be used in Peltier-based heat pumps, which have the advantages of a lack of moving parts, small size, and flexible form factor, compared to vapour-compression pumps. Thermoelectric refrigerators and air-to-air coolers are on the market,[7] whilst thermoelectric heat pumps for homes based on bismuth telluride have been assessed,[8] and commercial demonstrators are available,[9] suggesting potential for a rapidly-growing new market. The UK market for Heating, Ventilation and Air Conditioning (HVAC) is estimated to be worth approximately £17bn.[10]

As well as in heat exchange systems in the built environment, thermoelectric materials may be used to shift energy draw from automotive engines to other uses in a car, power wireless sensor networks,[11] and in conversion pathways in integrated solar thermal energy generation systems, for example.

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[5] https://www.gov.uk/government/news/uk-becomes-first-major-economy-to-pass-net-zero-emissions-law

[6] *Waste Heat Recovery System Market Size, Share & Trends Analysis Report By Application (Preheating, Power & Steam Generation), By End User (Petroleum Refinery, Power, Metal Production), And Segment Forecasts, 2020 – 2027, Grand View Research, May 2020.*

[7] https://www.teconversion.com/product/ac-50-45/ (Accessed 27/07/2020); https://www.europeanthermodynamics.com/products/thermoelectric-assemblies/air-to-air-thermoelectric-assemblies (Accessed 27/07/20).

[8] Kim *et al*., Energy and Buildings 70 (2014) 106–116. DOI: http://dx.doi.org/10.1016/j.enbuild.2013.11.021
EDF-funded analysis of optimum thermoelectric modules required for temperature control in a French home.

[9] European Commision: Enterprise Network licencing https://een.ec.europa.eu/partners/air-handling-unit-thermoelectric-heating-and-cooling-offered-licensing

[10] Sector Report: Heating, Ventilation & Air Conditioning (HVAC) Industry, Hallidays Group Lt., 2019. https://www.hallidays.co.uk/pdf/hvac.pdf

[11] D. Narducci, *J. Phys.: Energy* **2019**, *1*, 024001

PROBLEM STATEMENT

The main challenge with thermoelectric devices for applications heating and cooling is their low efficiency, with the ultimate limit set by the thermoelectric figure of merit, ZT, of the thermoelectric material. An average ZT value > 3 over the temperature range of the application would be required to be competitive in efficiency with traditional devices in most applications. However, no known thermoelectrics operating under device conditions have ZT > 3, with the highest ZT values around 2 for p-doped bismuth chalcogenides i.e. only about 10-15 % Carnot efficiency c.f. 40-60 % for vapour compression cycle systems[12]. Peak ZT values up to 2.8 have been reported for tin selenides,[13] but only at high temperatures (>500 ºC) which are outside of the scope of this roadmap.

Currently, thermoelectric generators serve application niches where efficiency and cost are less important than reliability, light weight, and small size, in comparison to vapour cycle heat pumps. The scarcity of Tellurium (Figure 3), widely used in current thermoelectric devices, also drives the need to develop new materials from abundant elements to enable thermoelectric technology to be deployed at larger scales. The full list of challenges for thermoelectric technology, as determined from preliminary work by our attendees is listed in Appendix IV.

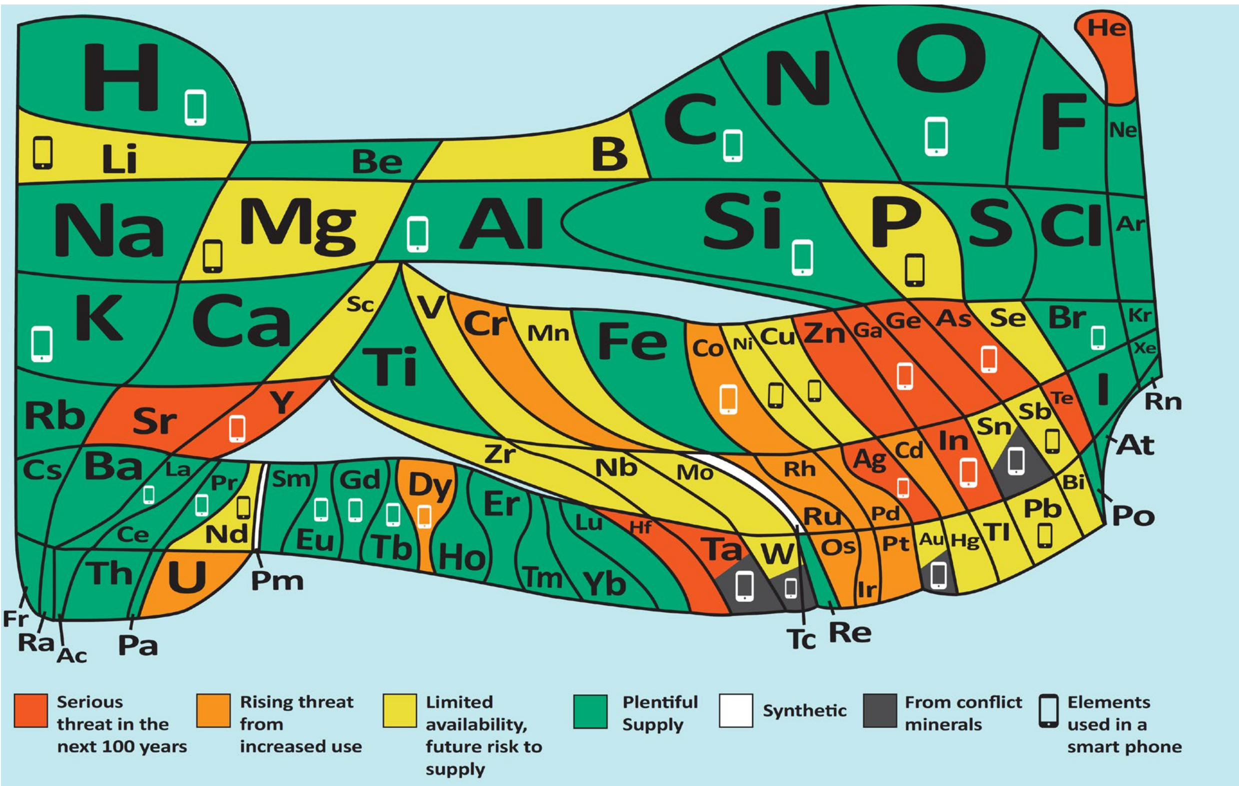

Figure 3: Periodic table of elemental scarcity (produced by The European Chemical Society[14])

[12] Venkatasubramanian, Rama; Siivola, Edward; Colpitts, Thomas; O'Quinn, Brooks (2001). "Thin-film thermoelectric devices with high room-temperature figures of merit". Nature. 413 (6856): 597–602. doi:10.1038/35098012.
[13] L-D. Zhao et al. *Nature* **2014**, *508*, 373-377; C. Chang et al. *Science* **2018**, *360*, 6390, 778-783.
[14] https://www.euchems.eu/euchems-periodic-table/ (accessed 27/7/2020)

WORKSHOP AIMS

There are specific research questions and challenges that need to be addressed in order to enable the development and adoption of existing or new materials that have the potential to make disruptive technological changes to reach UK 2050 targets. For thermoelectrics, the main questions that were investigated were:

- Why should the UK take the initiative to expand research into this class of materials?
- Which materials systems in this field show the most promise for viable energy-saving applications towards net-zero emissions by 2050, and what is the current state of the art?
- What are the current materials challenges that limit deployment of these materials?
- What performance could be achieved with current materials, and what could be achieved by 2025, and by 2050?
- What should be the key standards and metrics for performance of materials and devices?
- How do we combine these metrics to establish a single figure of merit, in particular for device applications?
- How can improvements be made in the characterisation of these materials?
- How can improvements be made in provision of advanced facilities required for industry scale-up and commercial testing, in comparison to the availability of suitable lab-scale tools?

The overall objective of this project is to develop a preliminary roadmap that can be used to guide discussions with the scientific and research communities, industry and government. Specifically, Royce and the research community would like to:

- Understand the current state-of-art in each area of interest
- Define in detail the key current challenges for each area that present barriers to meeting UK's net zero targets
- Define in detail the anticipated future challenges for each area that present barriers to meeting UK's net zero targets
- Identify and prioritise the best materials and materials systems to meet these challenges that can make step-changes in research to reach 2050 targets
- Identify the desired performance targets of these materials

Twenty participants attended the workshop and made a high-value contribution to the content and discussions. There was representation from 13 academic institutions and 1 company. The full participant list is shown in Appendix I.

WORKSHOP OUTPUTS

CURRENT STATE-OF-THE-ART

Thermoelectric generators made with different materials are available over a temperature range from >1000K down to room temperature, noting that the demand for domestic heating and cooling is located at the low temperature end of this range, and is also where the largest amount of waste heat is generated.[15] The theoretical maximum heat-to-electricity conversion efficiency of a thermoelectric generator is determined by the figure of merit, ZT, of the thermoelectric material it is made of. Device design considerations also contribute to the final conversion efficiency.

ZT, is a material property which has proven challenging to optimise, despite the fact that there is no known theoretical limit of ZT. Current production-scale materials have ZT of around 1, putting devices made from these materials close to the lowest efficiency curve shown in figure 4. With this performance, energy conversion efficiencies of only a few percent can be achieved at moderate temperatures. To have conversion efficiencies competitive with other technologies, materials with average ZT>3 over the temperature range of application need to be developed.

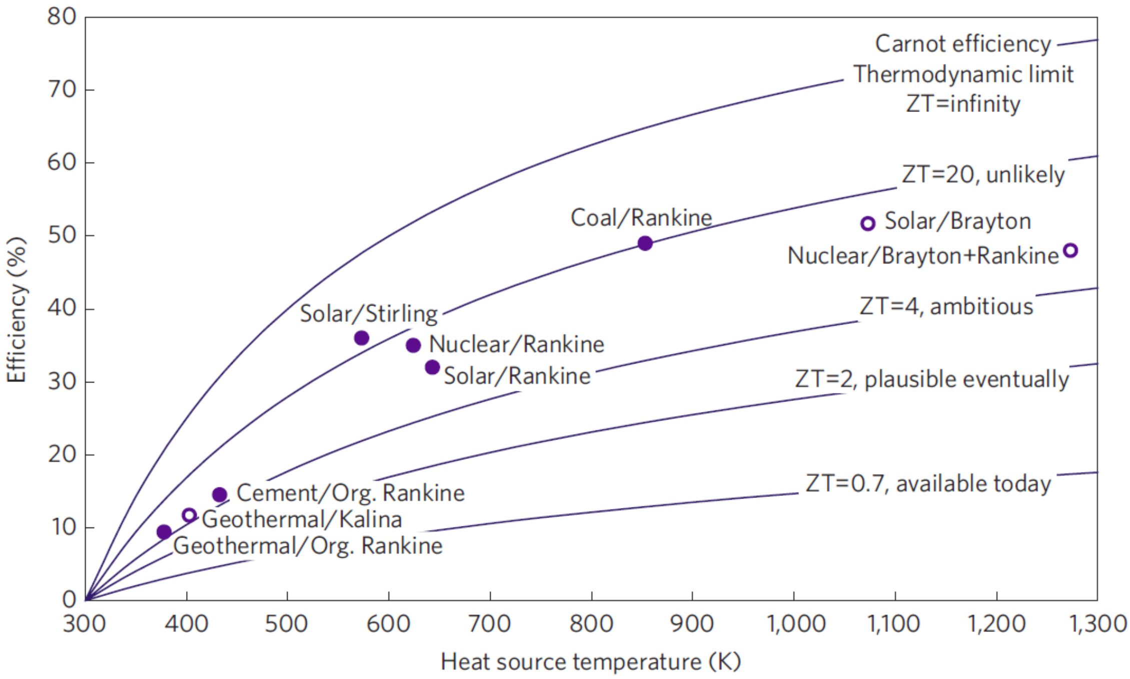

Figure 4: Heat -to-electricity conversion efficiency, Vining, Nat.Mat. 8, 83 (2009)

Despite their relatively low efficiency at present, there are already applications for thermoelectrics in Peltier cooling devices, which are refrigerant-free and have no moving parts. There are also applications for recuperating industrial waste heat, and the concept has been explored in the automotive sector to improve fuel efficiency by a few percent.[16]

Since the turn of the century, there has been a rapid improvement in thermoelectric materials performance as the understanding of thermoelectric materials has developed, and the highest reported lab-scale ZT values are now over 2.5. In addition, a number of other classes of thermoelectric materials are rapidly emerging,[17] and there have been promising breakthroughs in performance, processing and cost.

[15] Schierning et. al, *Nature Energy* **2018**, 3, 92–93.
[16] Zhang et al. *Ener. Conv. Management* **2015**, 105, 946.
[17] Beretta et al., *Mater. Sci. & Eng.* **2019**, 138, 210–255.

POTENTIAL MATERIALS AND DEVICE SYSTEMS IDENTIFIED

In total, 27 potential materials and device systems were identified during the workshop. In line with the UK's net-zero goals, a strong focus was placed on materials and material systems for the temperature range < 500K. The full list of potential solutions is shown in Appendix V.

The following measures were identified as criteria for the assessment of mature materials and devices:

Reward:

- Coefficient of performance (CoP, for cooling)
- $/Watt (for energy harvesting)

Feasibility:

- Availability and sustainability of materials
- Low cost of manufacturing
- Confidence level that the material system / device design concept will be sufficiently reliable to suit the application need (e.g. reliability over the required lifetime)

However, these measures cannot easily be used to assess the potential of materials which are not yet fully understood. The metrics used in the workshops to assess materials in the development stage were the figure of merit, ZT, which determines the theoretical limit of efficiency of a thermoelectric module, and also the power factor, which determines the maximum power output from a device. The target values for ZT and power factor are the average values over the temperature range of the application.

The materials were not prioritised, but were grouped into two areas for exploration of strategic research outlooks:

- **Ceramic Thermoelectrics:**
  Chalcogenides; Mg_3Sb_2 / MgAgSb and Zintl phases; Chlathrates; Skutterudites; Nanostructured Si-based materials; Half-Heuslers; Topological and Weyl based materials, Silicides (including SiGe)

- **Emerging / Lower TRL (Technology Readiness Level) Materials:**
  2D materials (not just graphene); Organic (small molecule + polymer) and carbon nanotube; Composites (organic/inorganic/others); Combination materials, composites, 2D; Film coatings; Halide perovskites; MOFs Material; Conformable/flexible thermoelectric and periphery materials; Printable thermoelectric materials; Molecular junctions.

It was recognised that a materials discovery program could add more materials to this list.

STRATEGIC RESEARCH OUTLOOKS

Generic strategic outlooks were developed for each of the following top-level groups:

- Ceramic Thermoelectrics
- Emerging / Lower TRL Thermoelectric Materials

Specific topic roadmaps were developed initially for *Chalcogenides*, and *Organic (small molecule + polymer) and carbon nanotube*. It was subsequently decided to create a separate topic roadmap for *Molecular junction devices* as this was not well covered by the top-level groups. The three specific topic roadmaps are shown in Appendix VI.

The two generic strategic outlooks are described in the next section. The following fields are included:

- Target metrics for each group of materials/ material systems
- The R&D required in terms of materials discovery and optimisation, integration into devices and scale-up
- The required competences and resources for the development of the solution
- The key enablers, barriers and risks in the further development and commercialisation of the research

Three time periods are covered: short term (next 5 years i.e. up to 2025), the medium term (next 15 years, i.e. up to 2035) and the long term (next 30 years, i.e. up to 2050).

TOPIC 1: CERAMIC THERMOELECTRICS

Topic summary

Current thermoelectric technology is serviced entirely by ceramics as the active thermoelectric material. These materials are generally quite stable and often have good thermoelectric performance. It is therefore no surprise that this topic contains established materials, such as bismuth telluride, that have been studied and exploited for decades, but there are also a number of other classes of ceramic that show promise and are at various stages of development.

The classes of ceramics that were discussed as part of this topic are:

- Clathrates
- Skutterudites
- Nanostructured silicon-based materials
- Mg_3Sb_2 / MgAgSb and Zintl phases
- Half-Heuslers
- Silicides
- Chalcogenides

It was acknowledged that a materials discovery program could add new materials to this list. It was also acknowledged that there are more ceramics, such as the oxides which are technologically interesting, but perform best at high temperatures so are not covered by this roadmap. Materials using spin-Seebeck effects were also identified as potentially high performing ceramic thermoelectric materials, but they were not included due to a lack of expertise within the workshop participants.

The workshop concluded that the chalcogenide bismuth telluride should not be the focus of a future materials research programme. Bismuth telluride has been the champion thermoelectric material for room temperature applications for many years and it was felt that further materials research on this material was unlikely to yield significant improvements in performance. Nonetheless the chalcogenides remain an active research area, as demonstrated in recent years by the advances made in tin selenide, the chalcogenide with the highest peak ZT of any bulk thermoelectric material to date.

The state-of-the-art material performance varies according to the group. Chalcogenides lead the field with many materials with peak ZT>1, and the maximum for tin selenide of 2.8 at >500ºC.[18] Zintl materials[19] and skutterudites[20] have also shown peak ZT ≈1.8-1.9 in the laboratory. In fact, all the classes listed have achieved peak ZT of at least 0.4.

[18] L-D. Zhao et al. *Nature* **2014**, *508*, 373-377; C. Chang et al. *Science* **2018**, *360*, 6390, 778-783.
[19] J. Zhang et al., *npj Comput. Mater.* **2019**, *5*, 76.
[20] G. Rogl et al. Acta Mater. **2015**, *95*, 201–211; *Novel Thermoelectric Materials and Device Design Concepts*, Springer, **2019**, 177-201.

Strategic research outlook

The targeted areas for research and development suggested by the workshop attendees are:

- Materials discovery and optimisation
    - An accelerated materials discovery programme
    - Establish if sulphides can perform well at room temperature
    - Design interfaces to boost performance, including energy-filtering barriers
    - Use of modulation doping to create high-mobility regions
    - Alloy engineering to improve performance of known materials
    - Enhance understanding of band engineering and band alignment
    - Development of computational tools for calculating accurate electrical and thermal transport in disordered and nano-structured materials. [Simulations on micron length sales
    - Translation of nanostructuring and materials engineering approaches demonstrated on Si thermoelectrics to other thermoelectric materials
    - Develop materials with resonant energy levels to boost the Seebeck coefficient
    - Material properties by design
    - Investigate how to relax the relationship between thermal and electrical conductivity (i.e. search for non-Wiedemann-Franz materials)
    - Investigate how to relax the interdependence of conductivity and the Seebeck coefficient
    - Use of computational tools for predictive modelling
    - Development of hierarchical nanostructures to improve performance
    - Use of topological state to improve thermoelectric properties

- Integration of materials into devices:
    - Development of n-type and p-type pairs of materials
    - Development of interface materials
    - Examine how energy harvesting devices can compete with piezoelectric technology
    - Consider the ease of combining materials and their interfaces
    - Improve Coefficient of Performance of cooling systems when operating at high current
    - Development of low power electronics that can be powered from harvested waste heat
    - Design and integration of effective heat exchangers

- Scale up:
    - Consider availability of compounds
    - Develop methods to ensure thin-film and interface science can be scaled to the bulk material

Required competences/resources

The following required competences and resources were identified by workshop attendees for a successful research programme:

- Tools to accurately model density of states
- Continuity of funding for The UK Thermoelectric Network
- Improved interdisciplinary collaboration in the UK (increasing numbers of modellers and device engineers)
- Address knowledge and skills gap between small-scale materials research and large-scale applications
- Mechanisms to collaborate with other communities (e.g. batteries, photovoltaics and fuel cells)
- Industry input to focus research on needs of end users

Enablers

It was also acknowledged that environmental issues would limit the development of certain materials, and that development of low environmental impact materials from abundant elements would enable wider deployment of the technology.

Figure 5 (on the next page of this report) shows the summarised strategic research outlook for ceramic thermoelectrics.

<table>
<tr><th colspan="2"></th><th>Short term
2025</th><th>Medium term
2035</th><th>Long term
2050</th></tr>
<tr><td colspan="2">Target Metrics</td><td>–</td><td>–</td><td>ZT(average): 4-5
(but could be higher if non-Wiedemann Franz materials can be developed)
[For 1mm^3 of material]</td></tr>
<tr><td rowspan="24">Research and technology challenges</td><td rowspan="15">Materials discovery and optimisation (theoretical and experimental)</td><td colspan="2">Accelerated materials discovery programme</td><td></td></tr>
<tr><td>Establish if sulphides can perform well at room temperature</td><td></td><td></td></tr>
<tr><td>Design interfaces to boost performance, including energy filtering barriers</td><td></td><td></td></tr>
<tr><td>Use of modulation doping to create high mobility regions</td><td></td><td></td></tr>
<tr><td>Alloy engineering to improve performance of known materials</td><td></td><td></td></tr>
<tr><td>Enhance understanding of band engineering and band alignment</td><td></td><td></td></tr>
<tr><td>Development of computational tools for calculating accurate electrical and thermal transport in disordered and nano-structured materials. [Simulations on micron length sales]</td><td></td><td></td></tr>
<tr><td>Translation of nanostructuring and materials engineering approaches demonstrated on Si thermoelectrics to other thermoelectric materials</td><td></td><td></td></tr>
<tr><td></td><td>Develop materials with resonant energy levels to boost the Seebeck coefficient</td><td></td></tr>
<tr><td></td><td>Material properties by design</td><td></td></tr>
<tr><td></td><td colspan="2">Investigate how to relax the relationship between thermal and electrical conductivity (i.e. search for non-Wiedemann-Franz materials)</td></tr>
<tr><td></td><td colspan="2">Investigate how to relax the interdependence of conductivity and Seebeck coefficient.</td></tr>
<tr><td></td><td>Use of computational tools for predictive modelling</td><td></td></tr>
<tr><td></td><td>Development of hierarchical nanostructures to improve performance</td><td></td></tr>
<tr><td></td><td></td><td>Use of topological state to improve thermoelectric properties</td></tr>
<tr><td rowspan="7">Integration of materials into devices</td><td colspan="3">Development of n-type and p-type pairs of materials</td></tr>
<tr><td>Development of interface materials</td><td></td><td></td></tr>
<tr><td>Examine how energy harvesting devices can compete with piezoelectric technology.</td><td></td><td></td></tr>
<tr><td>Consider the ease of combining materials and their interfaces.</td><td></td><td></td></tr>
<tr><td colspan="2">Improve Coefficient of Performance of cooling systems when operating at high current</td><td></td></tr>
<tr><td colspan="3">Development of low power electronics that can be powered from harvested waste heat.</td></tr>
<tr><td colspan="2">Design and integration of effective heat exchangers</td><td></td></tr>
<tr><td rowspan="2">Scale up</td><td>Consider availability of compounds</td><td></td><td></td></tr>
<tr><td>Ensure thin-film and interface science is scaled to the bulk material</td><td></td><td></td></tr>
<tr><td colspan="2" rowspan="6">Required competencies and resources</td><td colspan="3">Tools to accurately model density of states</td></tr>
<tr><td colspan="3">Continuity of funding for The UK Thermoelectric Network</td></tr>
<tr><td colspan="3">Improved interdisciplinary collaboration in the UK (increasing numbers of modellers and device engineers)</td></tr>
<tr><td colspan="3">Address knowledge and skills gap between small-scale materials research and large-scale applications</td></tr>
<tr><td colspan="3">Mechanisms to collaborate with other communities (e.g. batteries, photovoltaics and fuel cells)</td></tr>
<tr><td colspan="3">Industry input to focus research on needs of end users</td></tr>
<tr><td colspan="2">Enablers</td><td colspan="3">Environmental issues will limit development of certain materials.</td></tr>
</table>

Figure 5: Ceramic Thermoelectrics Strategic Research Outlook

TOPIC 2: EMERGING AND LOWER TRL MATERIALS

Topic summary

Recent trends in thermoelectric research have seen the emergence of new classes of non-ceramic materials which each offer potential advantages in one or more of the categories of elemental abundance, processability, cost, performance and toxicity. However, these materials have only been partly explored for thermoelectric applications and are at a low technology readiness level. The group of materials explored in this topic are typically organic materials, carbon materials or hybrid materials.

The full list of materials that were discussed as part of this topic is:

- Organic semiconductors (small molecule and polymers)
- Carbon nanotubes
- 2-Dimensional materials (but not just graphene)
- Composites (except composites of ceramic thermoelectric materials)
- Halide perovskites
- Metal-organic frameworks

It was recognised that a programme of materials discovery could add new classes of materials to this list.

The majority of these materials have a complex morphology at the nanoscale and in all cases there is an incomplete theoretical understanding of the limits of their thermoelectric performance. Understanding what is the optimal morphology and realising this in devices is a focus for these materials, with the hope that the new physics arising from these complex morphologies might allow high *ZT* to be achieved.

Nonetheless, issues of long-term stability, poor understanding of interfaces in devices, and cost-effective synthesis at scale, remain significant barriers to deployment of these materials. Due to the low technology readiness level, devices based on these materials are not likely to be deployed in the short term, but could create an impact in the medium to long term.

The state-of-the-art material performance depends on the material group:

- For polymers, peak $ZT \approx 0.2$ has been demonstrated for PEDOT[21] and metal co-ordination polymers,[22] and power factors > 1 mW/mK^2 [23] have been demonstrated in thin films.
- For composites of polymers with carbon nanotubes and graphene, power factors of >1 mW/mK^2 [24] have been demonstrated.
- For halide perovskites, peak $ZT > 0.1$[25] has been achieved.
- Amongst 2D materials, TiS_2 has shown $ZT = 0.8$.[26]

In all cases, computational modelling has predicted that significant improvements in performance should be possible. A large proportion of materials falling within this category remain unexplored for thermoelectrics, so materials discovery will need to be included as part of a research programme.

Strategic research outlook

The targeted areas for research and development suggested by the workshop attendees are:

[21] O. Bubnova et al. *Nat. Mater.* **2011**, *10*, 429 ; G. H. Kim et al., *Nat. Mater.* **2013**, *12*, 719.
[22] Y. Sun, et al. *Adv. Mater.* **2016**, *28*, 3351.
[23] V. Vijayakumar, et al., *Adv. Energy Mater.* **2019**, *9*, 1900266.
[24] C. Cho et al., *Adv. Energy Mater.* **2016**, 6, 1502168.
[25] T. Liu et al., *Nat. Commun.* ***2019***, *10*(1), 5750; M. Haque et al., *Adv. Sci.* **2020**, *7*, 1903389.
[26] Y. Wang et al. *J. Mater. Chem. C* **2018**, *6*, 9345.

- Materials discovery and optimisation
  - Understand structure-property relationships and optimal morphologies
  - Development of new (stable) dopants for organic materials
  - Standardisation of characterisation of thermoelectric properties
  - Development of computational tools to simulate morphology, disorder and interfaces
  - Development of computational tools for accurate band structure calculations
  - Effort to predict non-Wiedemann-Franz materials
  - Modelling of disordered and dynamic interfaces
  - Stabilisation of morphologies
  - Establish microscopic understanding of control of physical properties
  - Conduct predictive modelling to direct molecular synthesis and processing
  - Predictive modelling of thermal properties
  - Characterisation of disordered and dynamic interfaces
  - Understand fundamental performance limits of emerging thermoelectric materials
  - Produce optimised materials with high performance

- Integration of materials into devices:
  - Understand how to maintain material performance when processing into a device, including obtaining optimal morphologies
  - Understand interface properties at electrodes and how to optimise these

- Scale up:
  - Identify niche sector(s) where the value proposition can be demonstrated
  - Develop approaches to reduce the cost of material production at scale
  - Life cycle analysis to understand the viability of scaling up new materials
  - Engagement of Research and Technology Organisations (e.g. Centre for Process Innovation) to provide trials of scale-up
  - Development of process technology to synthesise materials at >kg scales

Required competences/resources

The following required competences and resources were identified by workshop attendees for a successful research programme:

- Increased size of the UK community in this area
- Increased synthetic chemistry capability in this area
- Use of online tools to increase dialogue in the UK community
- Investment in characterisation facilities to accelerate development
- National-level rapid screening approaches
- Development of characterisation tools for ordered and disordered interfaces
- Life cycle thinking and sustainability
- More PhD funding for emerging thermoelectric materials research
- Funding for exchange between UK thermoelectrics community researchers
- Funding to maintain the UK Thermoelectric Network
- An established model for industrial engagement and dedicated facilities to enable engagement
- Engagement with synthesis industries to reduce costs of scaled materials production

Enablers

The community identified a number of factors that would enable the success of this R&D programme:

- Technology pacing items:
  - Availability of rapid characterisation and prototyping tools
  - Development of tools to understand the relevant physics
  - Theoretical property prediction and techniques for characterisation of interfaces.
  - Control of structure-property relationships

- Commercial pacing items:
  - Reduction of the cost per kg of many materials in this class
  - Progress in delivering cost and performance needs of end users for devices produced at scale
  - Industrial Strategy Challenge Fund type of funding could unlock commercial potential

It was also identified that mechanisms to engage the UK research community with the international community would be useful.

Figure 6 (on the next page of this report) shows the summarised strategic research outlook for emerging/ lower TRL thermoelectric materials.

<table>
<tr><td colspan="2"></td><td>Short term
2025</td><td>Medium term
2035</td><td>Long term
2050</td></tr>
<tr><td colspan="2">Target Metrics</td><td>ZT(average): 1
Power Factor (temp average): 2 mW/mK2
Reliability/stability: ~few months for most of these materials
Coefficient of performance (COP): 0.4</td><td>ZT(average): 2
Power Factor (temp average): 5 mW/mK2
Reliability/stability: 3-5 years
COP: ~0.4</td><td>ZT(average): >3
Power Factor (temp average): >10 mW/mK2
Reliability/stability: >10 years
COP: ~0.4</td></tr>
<tr><td rowspan="22">Research and technology challenges</td><td rowspan="14">Materials discovery and optimisation (theoretical and experimental)</td><td>Understand structure-property relationships and optimal morphologies.</td><td></td><td></td></tr>
<tr><td>Development of new (stable) dopants for organic materials.</td><td></td><td></td></tr>
<tr><td>Standardisation of characterisation of thermoelectric properties</td><td></td><td></td></tr>
<tr><td>Development of computational tools to simulate morphology, disorder and interfaces.</td><td></td><td></td></tr>
<tr><td>Development of computational tools for accurate band structure calculations.</td><td></td><td></td></tr>
<tr><td colspan="2">Effort to predict non-Wiedemann-Franz materials.</td><td></td></tr>
<tr><td colspan="2">Modelling of disordered and dynamic interfaces .</td><td></td></tr>
<tr><td>Stabilisation of morphologies.</td><td></td><td></td></tr>
<tr><td></td><td>Establish microscopic understanding of control of physical properties.</td><td></td></tr>
<tr><td></td><td colspan="2">Conduct predictive modelling to direct molecular synthesis and processing.</td></tr>
<tr><td></td><td>Predictive modelling of thermal properties.</td><td></td></tr>
<tr><td></td><td>Characterisation of disordered and dynamic interfaces.</td><td></td></tr>
<tr><td></td><td></td><td>Understand fundamental performance limits of emerging thermoelectric materials</td></tr>
<tr><td></td><td></td><td>Produce optimised materials with high performance.</td></tr>
<tr><td rowspan="3">Integration of materials into devices</td><td colspan="3">Understand how to maintain material performance when processing into a device, including obtaining optimal morphologies.</td></tr>
<tr><td>Understand interface properties at electrodes and how to optimise these.</td><td></td><td></td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td rowspan="5">Scale up</td><td>Identify niche sector(s) where value proposition can be demonstrated.</td><td></td><td></td></tr>
<tr><td>Develop approaches to reduce cost of material production at scale.</td><td></td><td></td></tr>
<tr><td>Life cycle analysis to understand viability of scaling up new materials.</td><td></td><td></td></tr>
<tr><td colspan="2">Engagement of Research and Technology Organisations (e.g. Centre for Process Innovation) to provide trials of scale-up.</td><td></td></tr>
<tr><td></td><td colspan="2">Development of process technology to synthesise materials at >kg scales.</td></tr>
<tr><td colspan="2" rowspan="12">Required competencies and resources</td><td colspan="3">Increased size of the UK community</td></tr>
<tr><td colspan="3">Increased synthetic chemistry capability in this area</td></tr>
<tr><td colspan="3">Use of online tools to increase dialogue in the UK community</td></tr>
<tr><td>Investment in characterisation facilities to accelerate development</td><td></td><td></td></tr>
<tr><td colspan="3">National-level rapid screening approaches</td></tr>
<tr><td>Development of characterisation tools for ordered and disordered interfaces</td><td></td><td></td></tr>
<tr><td colspan="3">Life cycle thinking and sustainability</td></tr>
<tr><td colspan="2">More PhD funding for emerging thermoelectric materials research</td><td></td></tr>
<tr><td colspan="3">Funding for exchange between UK thermoelectric community researchers</td></tr>
<tr><td colspan="3">Funding to maintain the UK Thermoelectric Network</td></tr>
<tr><td></td><td colspan="2">An established model for industrial engagement and dedicated facilities to enable engagement</td></tr>
<tr><td></td><td colspan="2">Engagement with synthesis industry to reduce costs of scaled materials production</td></tr>
<tr><td colspan="2">Enablers</td><td colspan="3">Technology pacing items: Theoretical property prediction and techniques for characterisation of interfaces; Control of structure-property relationships; Development of tools to understand the relevant physics; Availability of rapid characterisation and prototyping tools.
Commercial pacing items: Cost per kg of scaled material is too high for many materials in this class. Significant progress needs to be made to deliver cost and performance needs of devices at scale; Industrial Strategy Challenge Fund type funding could unlock commercial potential.
Other: Mechanisms to engage UK research community with international community</td></tr>
</table>

Figure 6: Emerging/ Lower TRL Thermoelectric Materials Strategic Research Outlook

CONCLUSIONS AND RECOMMENDATIONS

This report, commissioned by the Henry Royce Institute, has presented the outputs of a consultation with experts in the field of thermoelectrics. It presents some of the key opportunities and challenges for thermoelectric technology in the decarbonisation of heating and cooling. The research and development activities required to capture the opportunities have been identified.

The ability of thermoelectric materials to contribute to the government's zero-carbon targets has been presented. Thermoelectric modules are semiconductor devices that can convert an electrical current into a temperature gradient or vice versa. They can therefore provide fully electric heating and cooling technology without moving parts or refrigerants. They can also be used to harvest waste heat from other processes and convert it directly into electricity. These devices are robust and the technology is mature in certain niche applications within, for example, the aerospace and refrigeration sectors. However, there remain certain factors that are holding back wider adoption of this technology. A key limiting factor identified was the low efficiency of current thermoelectric devices, as well as the sustainability of current state-of-the-art materials. This report comes at a time when a large number of new thermoelectric materials are being discovered, and the market for thermoelectric technology is growing. It is therefore timely to consider how to capture this momentum and expand the role of thermoelectric technology in society. The opportunity for the UK in this sector is huge, with 17% of our CO_2 emissions coming from space heating and cooling[27]. Furthermore, the Heating, Ventilation and Air Conditioning (HVAC) UK market is estimated to be worth approximately £17bn.[28] Stimulating innovation in this sector would therefore provide energy security, job security and environmental security for the UK.

The community split the discussion into two classes of thermoelectric materials and their embodiment in devices: *Ceramic materials* and *Emerging / low TRL materials*.

The *ceramic* category encompasses the current state-of-the-art materials and mature device technology, but also includes many emerging sub-classes whose full potential has not yet been realised. The *Emerging / Low TRL materials* is a category for materials which have shown initial potential, but require significant further research to understand their full potential. This category includes organic, hybrid, carbon and 2-dimensional materials. The Strategic Research Outlook developed in this process reflects the mix of mature and emerging materials technologies and the need for a parallel materials discovery programme.

The community identified the following broad areas where action could be taken by policy makers to unlock the potential for thermoelectric technology in the decarbonisation of heating and cooling:

- *Development of tools and facilities.* These include computational facilities for accurate band calculations, and both experimental and computational tools to characterise disordered materials and interfaces. National-level facilities for rapid screening, and for scale-up of processing and manufacturing were also called for.
- *Facilitation of networking activity.* This would be between researchers and engineers within the UK as well as with international partners. Enhanced funding for The UK Thermoelectrics Network[29] was identified as one mechanism for this.
- *Filling skills gaps.* Skills gaps were identified in materials modelling as well as device engineering which bridges the gap between academic materials research and industry. The need to train more people to PhD-level was also identified.

[27] BEIS Report: Clean Growth – Transforming Heat, December 2018 https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/766109/decarbonising-heating.pdf
[28] Sector Report: Heating, Ventilation & Air Conditioning (HVAC) Industry, Hallidays Group Lt., 2019. https://www.hallidays.co.uk/pdf/hvac.pdf
[29] www.thermoelectricnetwork.com

- *Targeted R&D funding.* It was felt that sustained targeted research funding could help unlock the potential of this technology, with the Industrial Strategy Challenge Fund cited as a model for this.

APPENDICES

APPENDIX I: PARTICIPANTS/ CONTRIBUTORS

PARTICIPANT	AFFILIATION
Prof. Henning Sirringhaus	Cambridge
Prof. Gao Min	Cardiff
Dr Yimin Chao	East Anglia
Dr Jan-Willem Bos	Heriot-Watt
Prof. Simon Woodward	Nottingham
Dr Oliver Fenwick	Queen Mary University of London
Dr Iris Nandhakumar	Southampton
Profs K de Groot	Southampton
Prof. R Dorey	Surrey
Dr Neophytos Neophytou	Warwick
Prof. Jon Goff	Royal Holloway
Prof Robert Freer	Manchester
Prof Richard Curry	Manchester
Dr Jan Mol	Queen Mary University of London
Professor Colin Lambert	Lancaster
Dr Andrew Knox	TEConversion
Prof. Neil Alford	Imperial College London
Manish Chhowalla	University of Cambridge
Isobel Hogg	Institute of Physics
Amy Nommeots-Nomm	Imperial College London
Nicky Athanassopoulou	IfM ECS (Facilitator)
Diana Khripko	IfM ECS (Facilitator)
Imoh Ilevbare	IfM ECS (Facilitator)
Arsalan Ghani	IfM ECS (Facilitator)
Andi Jones	IfM ECS (Facilitator)
Rob Munro	IfM ECS (Facilitator)

WORKSHOP DETAILS

The workshop was commissioned by Henry Royce Institute and delivered by IfM Education and Consultancy Services Limited.

Dates

First Session: 20 March 2020, 14.00 – 16.00
Second Session: 27 March 2020, 11.00 –12.00
Third Session: 27 March 2020, 15:30 – 17.30
Fourth Session: 29 April 2020 09:30 – 10.30 and 10:30 – 12:00
Fifth Session: 12 May 2020 14:00 – 15:00

Scientific Co-ordinator

Dr Oliver Fenwick, Queen Mary University of London

Facilitators

Online moderation by
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IfM Education and Consultancy Services

Dr Arsalan Ghani
Industrial Associate
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Mr Rob Munro
Industrial Associate
IfM Education and Consultancy Services

Topic 1 - Ceramic Thermoelectrics Participants: Prof. Richard Curry, Dr Neophytos Neophytou, Dr Jan-Willem Bos, Prof. Neil Alford, Dr Iris Nandhakumar, Dr Oliver Fenwick, Prof. Kees de Groot, Prof. Gao Min

Topic 2 - Emerging and Lower TRL Materials Participants: Prof. Henning Sirringhaus, Prof. Simon Woodward, Dr Neophytos Neophytou, Dr Jan-Willem Bos, Dr Iris Nandhakumar, Dr Oliver Fenwick

APPENDIX II: WORKSHOP METHODOLOGY

The roadmapping workshop methodology consisted of three parts: design, the workshops, and reporting of the workshop outcomes.

Design

During the design phase, the following activities took place:

- Discussing and designing in detail the workshop methodology and process. The workshop used the **S-Plan** framework developed by the IfM over a period of several years [30, 31, 32]. The framework has been configured to help universities and research organisations align their research activities with industry needs, supporting decision-making and action;
- Designing the templates necessary to support the workshop activities;
- Agreeing the detailed workshop agenda;
- Agreeing the desired workshop outputs.

Workshops

The roadmapping workshop process brought together twenty participants from the research community and industry and had the following structure:

- First Session on 20 March 2020 14.00 – 16.00
  - To review the content submitted through delegate pre-work and the IOP survey
  - To identify and fill in any gaps
  - To review and feedback.
  - *Following this session it was agreed to split out the Caloric and Thermoelectric streams for the subsequent workshops.*

- Second Session on 27 March 2020 11.00 –12.00
  - To review the outputs from workshop 1
  - To identify which materials systems show the most promise for viable energy-saving applications towards net-zero emissions by 2050

- Third Session on 27 March 2020 15:30 – 17.30
  - To identify key material systems for the decarbonisation of heating and cooling
  - To explore selected key material systems
  - To map the research and development path (in terms of materials discovery and optimisation, integration of materials into devices and scale-up) and required resources
  - To describe the required technological and commercial enablers

- Fourth Session on 29 April 2020 09:30 – 10.30 and 10:30 – 12:00

[30] http://www3.eng.cam.ac.uk/research_db/publications/rp108
[31] Phaal, R., Farrukh, C.J.P., Probert, D.R. (2004). "Customizing Roadmapping", *Research Technology Management*, 47 (2), pp. 26–37.
[32] Phaal, R., Farrukh, C.J.P., Probert, D.R. (2007). "Strategic Roadmapping: A workshop-based approach for identifying and exploring innovation issues and opportunities", *Engineering Management Journal*, 19 (1), pp. 16–24.

    - Additional topic roadmapping sessions
    - To explore two identified key material system generic groups
        - Ceramic Thermoelectric materials
        - Low TRL (Emerging) Thermoelectric materials
    - To map the research and development path (in terms of materials discovery and optimisation, integration of materials into devices and scale-up) and required resources
    - To describe the required technological and commercial enablers

- Fifth Session on 12 May 2020 14:00 – 15:00
    - Additional topic roadmapping session
    - To explore additional identified material system
        - Molecular Junction Thermoelectrics
    - To map the research and development path (in terms of materials discovery and optimisation, integration of materials into devices and scale-up) and required resources
    - To describe the required technological and commercial enablers

Reporting of outcomes

Finally, the IfM ECS transcribed all of the output from the workshop in electronic format, drafted the current report and distributed it to Royce for review and wider circulation.

APPENDIX III: WORKSHOP AGENDAS

Session 1	
14:00 – 14:05	Welcome from HRI
14:05 – 14:20	Introductions, objectives and workshop 1 process
14:20 – 14:30	Discussing the content collected so far (data provenance and review process)
14:30 – 15:30	Review pre-work and identify gaps for materials and systems (in small groups)
15:30 – 15:55	Feedback review of group review (5 minutes presentation)
15:55 – 16:00	Wrap-up, next steps and process feedback

Session 2	
11:00 – 11:05	Introductions, objectives and overall process (split into Thermoelectrics/Calorics streams)
11:05 – 11:15	Introduction and workshop 2 process
11:15 – 11:45	Review the consolidated outputs from workshop 1
11:45 – 11:50	Prioritisation process and scoring criteria
11:50 – 11:55	Voting
11:55 – 12:00	Wrap-up

Session 3	
15:30 – 15:40	Introductions, objectives and workshop 3 process
15:40 – 16:00	Select priority ideas for exploration and set up small groups
16:00 – 17:00	Group discussion of key priorities
17:00 – 17:25	Presentation and review
17:25 – 17:30	Wrap-up and feedback

APPENDIX IV: DETAILED CHALLENGES COLLATED THHROUGH PRE-WORK

Overall, eleven challenges were identified from the participants that have or may have an impact on the development and implementation of thermoelectric materials for heating and cooling. These are shown below.

	Challenges
C1	Increase the coefficient of performance
C2	Insufficient materials performance
C3	Non-toxic high ZT Materials and alloys
C4	Materials with ease of system integration
C5	Replace Bi_2Te_3 as the best near room temperature TE material
C6	Accuracy of measurements
C7	Relating microscopic transport processes to device performance
C8	Funding
C09	New material discovery for ZT >2
C10	Ability to scale-up
C11	Cross-sector, multi-disciplinary collaboration on technologies and processes

APPENDIX V: PROPOSED MATERIAL AND DEVICE SYSTEMS GROUPED BY TEMPERATURE RANGE

Material Systems Innovations / solutions	Low temp materials/ devices (<500 deg K)	T1, T4, T6, T8, T11, T12, T13, T14, T15, T16, T17, T18, T19, T20
	Med temp materials/ devices (500 - 900 deg K)	T2, T3, T5, T7, T8, T10
	High temp materials/ devices (>900 deg K)	T7, T8, T9, T10
	Devices	T21, T22, T23, T24, T26, T27

T1	Mg3Sb2 / MgAgSb and Zintl phases	T15	Organic (small molecule + polymer) and carbon nanotube
T2	Chlathrates	T16	Composites (organic/inorganic/others)
T3	Skutterudites	T17	Combination materials, composites, 2D, e.g. Film coatings
T4	Nanostructured Si-based materials	T18	Molecular junction thermoelectric
T5	Half-Heuslers	T19	Halide perovskites
T6	Topological and Weyl based materials	T20	MOFs Material
T7	Silicides (including SiGe)	T21	Thermo Batteries - liquid and solid electrolyte thermoelectric cell
T8	Chalcogenides (PbTe, SnSe, Bi2Te3, Sulfides etc.)	T22	Conformable/flexible thermoelectric generators
T9	Oxides	T23	Printed thermoelectric generators
T10	Functionally graded materials	T24	Solar thermoelectric generator
T11	Spin-caloritronic materials	T25	Fluids (liquid crystal)
T12	Spin Seebeck	T26	Thermoelectric refrigerators
T13	Thermoelectric film coatings for glasses	T27	Domestic heating/cooling
T14	2D materials (not just graphene)		

APPENDIX VI: RAW WORKSHOP OUTPUTS

Topic Roadmap 1: Chalcogenides (PbTe, SnSe, Bi2Te3, Sulphides etc)

	New materials system innovations/ solution:		**T8 - Chalcogenides (PbTe, SnSe, Bi2Te3, Sulphides etc)**	**Roadmap Layer:** Low/Med/High Temp/ Device — Low/ Med/ High	**Participants:** Kees, Gao, Richard, Phytos
			Material/ Device Metrics		
			Short term	**Medium term**	**Long term**
Step 1	Please specify, if possible, the targets for this material system or device		*ZT (average):* *Power Factor (temp average):* *Reliability/stability:* *COP:* *$/Watt???*	*ZT(average):* *Power Factor (temp average):* *Reliability/stability:* *COP:* *$/Watt???*	*ZT(average): currently highest target 4/5 unless*** *Size of material: 1mm cubed* *Power Factor (temp average):* *Reliability/stability:* *COP:* *$/Watt???*
Step 2	Material system description/scope what are the potential applications?		Where are we now? State of art Sulphides - low mobility Only Bi2Te3 addresses heating and cooling Tellurium too rare and expensive - cannot be scaled Competing materials contain heavy metals - environmental issues	Scope What's IN: Selenides and Sulphides Energy harvesting Energy scavenging? Low carbon requires this to address heating and cooling What's OUT: Bi2Te3 - S/T removes cooling?	Desired future. What success would look like. What are the key performance characteristics / parameters (e.g. flexibility, transparency, durability? Selenides/ sulphides working at room temp? No sign at present that this is possible
Step 3			**Short term 2020 - 2025**	**Medium term 2025 - 2035**	**Long term 2035 - 2050**
	R&D required Please describe the research and development path towards the desired future. What are the key milestones?	**Materials discovery and optimisation (theoretical and experimental)**	- Accelerated materials discovery programme required - Low TRL research to find out if Selenides and sulphides can work at room temp.□ Design of material properties & Engineering of functionality and devices: - Interface issues: materials & filtering barriers - Modulation doping - can you create non-uniform dopability to create high mobility regions? (ST-MT)□	Create resonant levels which increase the Seebeck coefficient Can we "relax" the relationship between thermal and electrical conductivity - multi-band materials? phase transitions?** Relax the interdependence of conductivity and Seebeck - is this med or long term? - this could lead to ZT of 10	Topological quantum states
		Integration of materials into devices	* Ease of putting materials together * N-type and p-type with high electrical and low thermal conductivity * Interface materials - high electrical and high thermal conductivity		
		Scale-up	Availability of compounds Need to scale up from thin film interface science side to bulk		
	Required competences and resources (finance, people, knowledge, partnerships)				
Step 4	Technology pacing items:		What Technology Issues will determine the deployment? If using Chalcogenides - need to make alloys with them Environmental issues mean heavy metals should not be avoided - even with doping		
	Commercial pacing items:		What non-Technology Issues will determine the deployment?		
	Other enablers/ risks:		Standards? Policy?		
	Link to challenges		Does this link to any challenges identified in pre-work? Does this address any current material challenges? C6, C10, C11		

Topic Roadmap 2: Organic (small molecule + polymer) and carbon nanotube

	New materials system innovations/ solution: Organic (small molecule + polymer) and carbon nanotube (T15)					**Roadmap Layer: Low temp materials/ devices (<500 deg K)**		**Participants: Simon, Henning, Oliver,**
Step 1			**Material/ Device Metrics**					
			Short term			**Medium term**		**Long term**
	Please specify, if possible, the targets for this material system or device. NOTE Guided by Bismuth Telluride		*ZT(average): 1* *Power Factor (temp average): 1mW/mK2* *Reliability/stability: ~few months (little work done)* *COP: ~0.4* *$/Watt???* **COP, cooling out / electrical power* *Ref Simon for $/W*			*ZT(average): 2* *Power Factor (temp average): ~5mW/mK2* *Reliability/stability: 3-5yrs (ask into OLED display community)* *COP: ~* *$/Watt???* *NOTE: Performance comes mainly from very low thermal conductivity*		*ZT(average): >3* *Power Factor (temp average): 10mW/mK2* *Reliability/stability: 10 years+* *COP: ~* *$/Watt???*
Step 2	Material system description/scope what are the potential applications?		Where are we now? State of art Pedots ZT ~0.2, N-type ZT ~0.2. metal coordination polymer Carbon nanotube / polymers		Scope What's IN: Organic (small molecule + polymer) and carbon nanotube. C based Semiconductors. Coordination polymer. Molecular or polymeric units into film and bulk materials. Composites CNTs. What's OUT: NOT the optimisation of Bismuth Telluride. Polymer ceramic composites.			Desired future. What success would look like. What are the key performance characteristics / parameters (e.g. flexibility, transparency, durability? Refrigeration at 0C with good material and 10 years life. Predictability of targeted molecular design for structure-property relationships
Step 3			**Short term 2020 - 2025**			**Medium term 2025 - 2035**		**Long term 2035 - 2050**
	R&D required Please describe the research and development path towards the desired future. What are the key milestones?	**Materials discovery and optimisation (theoretical and experimental)**	Where are we now? State of art. Ability to efficiently measure factors for electrical, thermal conductivity Understanding structure property morphologies and processing is a common challenge across all materials Identify specific material challenges e.g. new dopants is critical for organics	Standardisation of characterisation of factors, that the wide community can use. Understanding S-P relationships Need for computational tools to simulate morphology disorder and interfaces Accurate electronic band structure calculations	Development of new dopants Calculative (in silico) discovery/prediction of non Wiedemann–Franz materials would be really useful Modelling of stability and reliability of interfaces Stabilisation of optimal morphologies	Microscopic understanding and control of physical processes Predictive modelling to understand molecular structure and thermal properties Characterisation and modelling of non-crystalline (disordered) and dynamic interfaces		Understanding of fundamental limits of organic TE materials. Ability to produce optimised materials and performance characteristics.
		Integration of materials into devices	Maintaining material performance after processing into a device to give ZT	Understanding interfaces at electrodes		Morphology S-P processing think films with optimal morphology at scale		
		Scale-up	Identifying niche sector where value proposition can be demonstrated. *Ask industry	Pedot at scale - HOW? Cost of scaled material	CPI or similar RTO to provide scale testing Understand viability of scaling up new materials due to availability of raw material or carbon footprint or other factors	Good process technology to make at >kg scales. DITTO for Materials Discovery	Development of growth and processing techniques at scale. Manufacturing processes are distinct for different materials and	Add in a $x/te
	Required competences and resources (finance, people, knowledge, partnerships)		The organic community in the UK is critically small and needs to be scale-up. Synthetic chemistry capability to aid exploration of new materials Mechanisms e.g. online for increasing the size of the thermoelectric community in the	Characterisation facilities to speed up development. National level rapid screening approaches. Development and/or access to characterisation tools for interfaces especially disordered ones	Industrial innovation policy stimulation. Build in life cycle / sustainability thinking PhDs in organic thermoelectrics More exchanges between the thermoelectric community researchers	Small scale applications in a relevant context Maintain the UKs thermoelectric network especially with industry participation	Industrial engagement model and facilities Also need engagement with organic industry outside pharmaceuticals	
Step 4	Technology pacing items:		What Technology Issues will determine the deployment? Theoretical property prediction and techniques for characterisation of interfaces, Structure-Property relationships. Tools to understand the relevant physics, accelerators.					
	Commercial pacing items:		What non-Technology Issues will determine the deployment? Cost of scaled material: $20/g for Pedots --> significant progress needs to be made to deliver cost, performance needs of devices at scale. ISCF mechanism to funding.					
	Other enablers/ risks:		Standards? Policy? Need to list the small community in the UK but the potential to engage other communities					
	Link to challenges		Does this link to any challenges identified in pre-work? Does this address any current material challenges?					

Topic Roadmap 3: Molecular junction thermoelectric

	New materials system innovations/ solution: Molecular junction thermoelectric			**Roadmap Layer:** Low/Med/High Temp/ Device	**Participants: Jan Mol, Colin Lambert, Olly F**
			Material/ Device Metrics		
			Short term	**Medium term**	**Long term**
Step 1	Please specify, if possible, the targets for this material system or device		*ZT (average): ZT=1 in research-level devices* *Power Factor (temp average):* *Reliability/stability:* *COP:* *$/Watt???* *Current figures of merit: Seebeck & Electrical conductance*	*ZT(average):ZT>10 for single molecule and SAMs at room temperature* *Power Factor (temp average):* *Reliability/stability:* *COP:* *$/Watt???*	*ZT(average): ZT>10 at room temperature in stable technological-relevant devices* *Power Factor (temp average):* *Reliability/stability:* *COP:* *$/Watt???*
Step 2	Material system description/scope what are the potentail applications?		Where are we now? State of art At a research stage - developing strategies for increasing the Seebeck coefficient of molecules Room temperature quantum effects have been demonstrated at single molecule level and shown to improve the thermoelectric performance of single molecules. Signatures of these quntum effecst in electrical conductance have been shown to translate into self-assembled monolayers. Strategies for utilising phonon interference to reduce thermal conductance have been identified, but not yet demonstrated exoperimentally. Current at miliKelvin temperature (unpublished, Delft University of Technology): S up to 414 microvolts/K ZT est. >10 Current at 4-77 K (published, Oxford/QMUL): S up to 450 microvolts/K PF: ~ 100 fW/K^2 for a single molecule Current at 300 K (published, U Michigan): S up to 50 microvolts/K PF: ~ 100 fW/K^2 for a single molecule	**Scope** What's IN: Start with a single molecule whose properties have been optimised for thermoelectricity, utilising room-temperature quantum interference. Translate functionality into self-assembled monolayers or nanoparticle molecular networks. Demonstrate an ability to cross-link molecule in a SAM to improved stability. There is a need to demonstrate experimentally that phonon interference effecst can reduce thermal conductance in both single molecules and SAMs.	Desired future. What success would look like. What are the key performance characteristics / parameters (e.g. flexibility, transparency, durability? At least 2D - potentially 3D & bulk Price competitive Non-toxic, flexible, wearable, stable Powering the IOT
			Short term **2020 - 2025**	**Medium term** **2025 - 2035**	**Long term** **2035 - 2050**
Step 3	**R&D required** Please describe the research and development path towards the desired future. What are the key milestones?	**Materials discovery and optimisation (theoretical and experimental)**	Where are we now? State of art * Measuring the thermal conductance of single molecule junctions * Applying strategies to molecules and synthesising - *what are the synthetic challenges?* *Optimising the electrodes (single molecules)	* Contacting to molecules to be routine and reproduceable * Optimal designs for molecules with minimal thermal conductance (computational activity) *Identify optimal anchor groups	Ultra-high purity molecules combined with defect-free electrodes.
		Integration of materials into devices	* Development of methods to make highly ordered SAMs * Integrating single molecules into devices * Develop a CMOS compatible single molecule junction	* Larger scale structures in which electrode materials and molecules are combined to optimise thermoelectric performance and reduce thermal conductance, for example by phonon scattering at the molecule-electrode interface.	* Nano fabrication techniques improve so that atomically precise structures can be made
		Scale-up	* CPI or similar RTO to provide scale testing * Understand viability of scaling up new materials due to availability of raw material or carbon footprint or other factors * Integrate organics with CMOS for temperature sensing & thermal management	* Reproducible arrays of single molecule junctions, combined with an ability to dope or electrostatically gate the arrays.	* Large scale manufacturing of atomically-precise molecular junctions (single-molecule device arrays, SAMs, molecule-nanoparticle networks)
	Required competences and resources (finance, people, knowledge, partnerships)		* Chemistry expertise in synthesis * Modelling requirements to predict trends in properties * State of the art nano-fabrication facilities * Capability to routinely measure ZT for thin films (perpendicular to the plane) * Extend capability to gate single molecules to thin films amd metallic break junctions	* Capability to measure the thermal conductance of single molecules * Capability to develop electrodes which are atomically well-defined. * Capability to routinely measure ZT for single molecules	Partnerships between chemists, physicists and engineers will be needed to deliver integrated devices.
Step 4	Technology pacing items:		Most likely the ability to create SAMs on electrodes and surfaces, which are defect-free on an atomic scale.		
	Commercial pacing items:		The pace of climate change and the price of oil will have a major influence on the level of investment.		
	Other enablers/ risks:		The target molecules should be non-toxic and therefore able to meet required standards for commercial deployment. At present there are no restriction on freedom to operate.		
	Link to challenges		Does this link to any challenges identified in pre-work? Does this address any current material challenges?		

APPENDIX VII: LIST OF FIGURES