EUROPEAN ENERGY RESEARCH ALLIANCE

Description of Work (DoW) of the Joint Programme
AMPEA: Advanced Materials and Processes for Energy Applications

Version: 3
Last modification date: November 12th 2018

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SUMMARY OF THE EERA JP Advanced Materials and Processes for Energy Applications [AMPEA]

Implementing a basic science programme for energy is one of the key roles assigned to EERA by the European Commission in the frame of the European Strategic Energy Technology Plan (SET-Plan). The EERA comprises 17 Joints Programmes (JP) of areas relevant to energy challenges. Basic science is often presented as crucial in generating the breakthroughs needed to bring new generations of technologies to the market. The aim of the EERA-JP AMPEA is to foster a truly multi-disciplinary approach to develop enabling tools and new concepts for future emerging energy technologies.

The mission statement of AMPEA states that it has to develop new horizons for science for energy, visible in Europe at the industrial and political level. Thus, the main objective is to harness and integrate materials science and process innovation for high performance sustainable energy technologies, in order to enhance the long-term competitiveness of European Industry. AMPEA aims at working in close coordination with other EERA-JPs and with Universities (European Platform Of Universities Engaged In Energy Research - EPUE) to bridge fundamental and applied research fields. The contact with industry is done through a partnership with EMIRI, the Energy Materials Industrial Research Initiative (http://emiri.eu/). EMIRI gathers industrials active in the field of energy materials as well as RTOs and brings thus the voice of the industry to AMPEA about the needs in terms of innovative energy materials. AMPEA and EERA signed a Memorandum of Understanding with EMIRI in 2015 and they have had ongoing cooperation activities since 2014. Presently, AMPEA gathers 34 public research organizations and universities from 13 European countries. Participation of new organizations is under discussion.

In order to fulfill his missions, AMPEA is organized in a matricial way with the aim of applying the capacity of 3 "*Tools*" sub-programmes (SPs) corresponding to generic research areas to "applications" SPs related to known emerging energy challenges and domains (see Figure). There are presently 3 identified "*Applications*" SPs, the first being artificial photosynthesis, *i.e.* the ability to efficiently convert large amounts of solar energy into easily usable and storable chemicals, by mimicking nature or by plain engineering. Other application SPs will be added as they are identified and defined by the AMPEA and more generally by the EERA members. Below are given summaries of the different existing SPs of AMPEA.

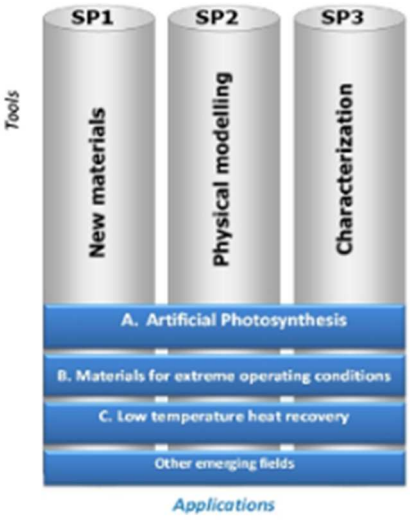

Figure 1: AMPEA sub-programmes (SPs) structure into a matrix of "*Tools*" and "*Applications*"

- **Sub-Programme Tool 1 "*Materials sciences*" (SP1)**:

Energy applications demand materials systems with a large range of functionalities and stability often in stringent operating conditions. New tools and innovative design's possibilities emerging from the utilization of micro-/nanotechnologies and more recently of additive manufacturing processes or other new innovative processing methods have the potential to create breakthroughs in today's energy conversion processes. This can be achieved (objectives) via

- the development of entirely new (designed) bulk/coating materials presenting improved functionality and/or stability in operation;
- the utilization of nano-/microstructures as well as additive or other innovative manufacturing processes to design materials properties and device functionality while reducing energy demand, waste materials and CO_2 emission for their production;
- engineering the interfaces to minimize the loss contributions that currently limit the device performance;
- the development of material synthesis techniques that allows the upscaling to large quantities for powder production.
- cooperating with the other modelling and characterisation sub-programs of AMPEA to benefit from the knowledge gained with advanced characterisation and multi-scale modelling to drive novel concepts of materials and devices.

The ambition of SP1 is to promote non-specific cutting-edge materials developments with a potential for high efficiency energy applications. On one hand, SP1 addresses innovative approaches for the synthesis of materials and their assemblies at various scales (atomistic, microscopic, macroscopic). These encompass for example: i) new routes to synthesis multi-cation oxides with fast transport properties, high entropy alloys, etc. ii) new fabrication routes to produce advanced multi-layered systems with tailored compositions and microstructures etc.; iii) new reactor concepts with innovative geometry (*e.g.* multichannel systems, tubular reactors, etc,); iv) novel approach and design of sealing technologies, etc. On the other hand, SP1 explores promising phenomena, in particular related to mass and/or charge transport, and establish sound strategies to eliminate bottle-necks to the exploitation of these phenomena in energy applications. Bottle-necks and loss mechanisms are often related to

interfacial effects. This sub-program addresses active materials present in various energy technologies (catalysis, photovoltaics, fuel cells, electrolysers, batteries, photocatalysis, thermoelectrics, gas separation membranes, membrane reactors, materials for fusion devices, materials for power plants, etc.), as well as those materials necessary in relevant key enabling technologies, *e.g.*, refractive and protective coatings, light weight composites, and alloys. This interaction enables further improvements in conventional and new energy processes that currently have practical limitations in temperature, corrosive environments etc.
Materials of interest have been divided into the following categories according to their function and application: "Materials for catalysis and photocatalysis", "Materials for Power Plants", " Materials for CO_2 capture and production of synthetic fuels (energy carriers) or commodity chemicals", "Thermoelectric materials", "Large scale synthesis of nano and micropowders", "Advanced thin film processing", and "Plasma Facing Materials".

- **Sub-Programme Tool 2 *"Multiscale modelling of materials, processes and devices"* (SP2)**:

The goal of this "Sub-programme 2" is to coordinate a concerted effort in AMPEA to identify current challenges and forthcoming trends in multiscale modelling and simulation. This effort is critically important in advancing materials, processes and devices for energy applications, while ensuring sustainable production route and fostering circular economy: firstly, innovative energy materials are often complex structures or "high technology" products (multi-functional), which cannot be described by basic models; secondly, the formation and application of such structures are very much dependent on conditions of processing and utilisation; and thirdly, the integration of such materials in devices is intricate and thus requires careful design and optimisation. All of these issues encompass multiscale spatial and temporal dimensions of tens of magnitudes, where cross-disciplinary work is a necessity.
Furthermore, during the recent years with the rapid evolution of computing resources and the related advances in programming a new paradigm related to artificial intelligence, machine learning and cloud computing arises. This new way to think informatics is about to revolutionize our methods in designing, modelling and describing material properties and use. The latter, which is probably the most salient advanced of the past years is detailed in the updated content of the DoW of SP2.

- **Sub-Programme Tool 3 *"Characterization"* (SP3)**:

Advanced experimental characterization and analysis are considered absolutely essential for significant advancing of materials and processes for energy applications. Development of today and tomorrow's key experimental techniques is complex, requires multidisciplinary skills, is costly and takes long time. Consorted efforts involving teams of technique experts, material scientists and engineers are thus required and a joint European program is considered an optimal route towards this goal. Furthermore synergetic use of multiple techniques is in most cases beneficial which underpin the need for joint European actions even more.
SP3 establishes a characterization platform for the other sub-programs. As AMPEA deals with new, sophisticated materials in inorganic and organic fields with some of them are applied under extreme conditions also sophisticated characterization techniques and strategies are necessary. Therefore a network of facilities with sophisticated instrumentation is established in this sub-programme. In addition the joint actions of the platform include the improvement and development of techniques and instrumentation in the areas of *in situ* and *operando* characterization in the time scale and nanometer resolution in 2D and 3D at a wide range of temperatures and pressures.
The objective of SP3 is twofold:
- to create a forum which can help the experimental experts to be world leading in developing the best possible new advanced characterization techniques for the scientific problems in mind. This will include meetings and workshops focusing on technique aspects, platforms for exchange of analysis and imaging software, and dedicated meetings between technique experts and scientists within the other subprograms to quantify optimal technique parameters, *e.g.* spatial and time resolutions, penetration depths, temperatures etc.
- to provide one entry point to the suite of advanced techniques and thus help the users to get an overview of experimented possibilities. This will be addressed in the future via a dedicated web page.
This subprogram represents a European added value in the sense that it is expected to lead to:
- Synergy in developments of advanced experimental techniques with special attention to *in situ* and *operando* techniques,
- Further use of multiple complementary techniques,
- Establishment/consolidation of European networks for technique developments,
- Cross fertilisation between technique experts and materials scientist,
- Time and money savings.

- **Sub-Programme Application A *"Artificial Photosynthesis"* (SPA)**:

The generation of fuels from sunlight and water is considered as a task of paramount importance for a sustainable energy supply in the future. Decomposition of water by a photoelectrochemical process is a possibility to store solar energy in form of hydrogen on a large scale. Alternatively, the electrons and protons recovered from water can be used for CO_2 reduction and hydrocarbon production. In both cases the catalysts for the oxidation and reduction half-reactions have to be developed and the two processes combined in a suitable device.

For a **direct photochemical energy conversion**, two main approaches can be distinguished. **Molecular approaches** using a plethora of catalysts for oxidation and reduction interfaced with different chromophores for their activation by visible light. Similarly a broad range of **materials** have been developed based on low-bandgap semiconductors and co-catalysts. For a practical use, these photocatalytic systems can be incorporated in a photoelectrochemical cell (PEC) device rather than be used in homogeneous phase. A third approach is based on an **indirect conversion** process by combining solar cells with electrolysis systems. For these systems, different degrees of integration can be envisioned and their advantages and disadvantages discussed. Examples for a highly integrated system are multi-junction photovoltaic devices with catalyst layers for oxidation and reduction on both surfaces, frequently addressed as an artificial leaf.
Independent of the chosen approach it became clear that any economically viable solution for solar fuel production has to meet three essential criteria: high efficiency, high robustness and low cost. The latter criterion is sometimes replaced by "scalability" to take into account elemental abundance, raw material cost, and capital costs.
To establish research activities on an European level from basic aspects to working devices, a Description of Work and Roadmap on this topic within the AMPEA EERA Joint Programme addressing molecular, inorganic and hybrid approaches is formulated.

- **Sub-Programme Application B *"Materials for Extreme Operating Conditions"* (SPB)**:

The transition to a low carbon future is a big challenge, which requires innovative materials, technologies and systems. Emerging energy technologies require materials combining properties such as high thermal stability, corrosion resistance, sufficient strength and creep resistance at extreme temperatures, thermomechanical stability, specific thermal conductivity, etc. Cost effectiveness of these materials, on the other hand, is another key issue. Among others, long-term stable materials for the following applications are considered:

- Demanding combustion processes including new fuels and higher process temperatures for significant increase of Carnot-based efficiency;
- Carbon capture, utilization and storage (CCUS) technologies to strike global warming;
- Concentrated solar power;
- Facing Plasma Components (FPCs) in fusion reactors (Tokamaks).

The AMPEA sub-programme "Materials for extreme operating conditions" will focus on three activity areas:

- Materials development,
- Characterization and testing of materials and devices in operating conditions,
- Development of multiscale simulation and modelling approaches for sound life time predictions.

- **Sub-Programme Application C *"Advanced Materials for Heat Exploitation and Energy Conversion"* (SPC)**:

The SPC relates to research, development and testing in *operando* conditions of materials for intensified temperature heat exploitation. Five focus areas are considered:

- Energy harvesting materials;
- Polymer nano-composites for intensified heat transfer;
- Micro- and nano-structured heat exchange surfaces;
- Nanofluids,
- Materials for thermochemical energy storage.

Each of these focus areas is characterised with quantified research targets to be achieved in a five year time perspective by resorting the tools made available by the TOOLS subprogrammes of AMPEA. Tight connection with the relevant EU initiatives (*e.g.* ICT-Flagship, SPIRE) and associations (*e.g.* EMIRI, CEFIC) are desirable, as well as with other EERA joint programmes (*e.g.* Energy storage, Concentrated Solar Power, Hydrogen and Fuel Cells, Geothermal Energy).
The research efforts carried out should be capable of generating new devices based on the advanced materials developed (thermo-electric modules, polymer heat exchangers, innovative heat exchange and storage) by 2020.

General comment:
AMPEA was launched in November 2011 and the Description of Work (DoW) was released in March 2012. The JP at that time included 5 sub-programmes (SPs). Following a Steering Committee in November 2012, AMPEA was re-organized in a matricial way with 6 with 3 "Tools" and 3 "Application" SPs (see Figure above). The second version of the DoW was prepared in February 2014 with the first review of AMPEA. This 3rd version of the DoW has been revised according to the new insights of participants in view of the second review of the JP. The amount of changes as compared to version 2 are very different from one sup-programme to the other due to in part to the evolution in the topic and depending on the feedback of the participants to the JP.
In the future, further evolution of the JP and its sub-division into SPs can be further envisioned with the evolution of the field of energy materials, the changing general European and international context (e.g. Mission Innovation, FET Flagships) and with game changing techniques and methodologies such as high performance computing and artificial intelligence. These aspects have already are currently discussed and will be also the aim of forthcoming steering committees and might lead to further changes in the sub-programme structures and the DoW.

Background

The SET-plan as well as the EU energy Roadmap have defined clear and demanding goals for 2020 and 2050, respectively. Although the scenarios are still debated and will remain hypothetical, it is clear that a revolution in energy systems is needed to reach the ambitious objective of reducing by 2050 greenhouse gas emissions to 80-95% below 1990 levels. This revolution certainly requires that present technologies be improved. But it also calls for breakthrough in concepts, materials, processes and finally energy devices. The 17 EERA Joint Programmes already implemented and focusing energy technologies aim at improving renewable energy harnessing, storage, transport and distribution technologies and help their deployment. These JPs, particularly well-suited to take up 2020 challenges, tackle the technical difficulties on an extended value chain, from basic knowledge to industrial type questions.
However, for most of them, even though they are already installed in the field, hard barriers remain : for ex. Adequately and precisely forecasting turbine interaction in wind farms, reaching a >50% efficiency for PV cells ; developing oxygen / carbon dioxide filters able to withstand 850°C or higher temperatures. Some of these barriers may prevent the reaching of crucial 2020 objectives.
Moreover, some very hard challenges cannot yet be viewed from the application side, since too high scientific problems remain to be solved: for example, this is the case for high performance nanostructured thermoelectric materials or for artificial photosynthesis. The mastering of these future emerging technologies is one of the ultimate goals of AMPEA [*Advanced Materials and Processes for Energy Applications*] Joint Programme launched in November 2011.
Turning to the energy efficiency objectives, very important to achieve SET-plan policy, they are usually thought of as being short term issues. However, the harnessing of the wasted thermal energy can be implemented at many length scales, from the nanoworld to the machine or industrial process scale. The science of these multiscale multidisciplinary processes requires the basic tools to be developed, basic phenomena to be further explored.

Added value of the Joint Programme

This Joint Programme (JP) brings four types of added values:

- The objective and scientific challenges of the European Energy Roadmap will be made visible to the scientific community. This visibility will be instrumental in driving new interest and new capacities into the questions treated by EERA JPs. The transverse position of EERA JP AMPEA is an efficient way to nurture technology-oriented programmes with scientific inputs.
- By uniting materials research and processes science, AMPEA creates the multi-disciplinary frame for innovating designs and concepts to appear.
- The characterisation and simulation tools will be developed with a clear vision of needs from energy scientists. These two activities usually define ambitious goals, easier to pursue for large teams: the JP will be their cement, providing them with the valuable resources of both materials and processes SP.
- In the frame of AMPEA, future emerging technologies will find the scientific base and the powerful tool to grow in strength and efficiency: a first example of this has been *artificial photosynthesis*. In November 2012, 16 new partners have joined AMPEA to participate more specifically to the SP on Artificial Photosynthesis: presently 27 participants or associate participants have some commitment in this SP including some of the major players in Europe. Following the same line, end of 2012 and 2013, two other new applications SPs were launched, namely SPB "*Materials in extreme operating conditions*" and SPC "*Low temperature heat recovery*".
- **Connection between AMPEA and industry:** during the 5th AMPEA JPSC (Jülich, May 2014), the JPSC agreed to have **EMIRI** (Energy Materials Industrial Research Initiative, http://emiri.eu/) as a partner organization within AMPEA with an observer status within AMPEA. This scheme was also validated by the EERA and the formalization of this observer status for EMIRI within AMPEA was done through a Memorandum of Understanding (MoU) signed in April 2016 in Brussels. Besides, joint AMPEA-EMIRI actions were initiated, *e.g.* the organization of a side event (The role of advanced materials as enablers in tackling the EU Energy challenges) during the SET Plan conference in Rome in December 2014 and the Joint participation to FET Flagship proposal (call FETFLAG-01-2018).

Structure of the Joint Programme and existing Sub-Programmes

Since the last review, there has been no changes in the structure of AMPEA in terms of Sub-Programmes (SPs). To date is organized in a matricial way with the aim of applying the capacity of 3 "*Tools*" sub-programmes (SPs) corresponding to generic research areas to "applications" SPs related to known emerging energy challenges and domains (see Figure 1). There are presently 3 identified "*Applications*" SPs, the first being artificial photosynthesis, *i.e.* the ability to efficiently convert large amounts of solar energy into easily usable and storable chemicals, by

mimicking nature or by plain engineering. Other application SPs will be added as they are identified and defined by the AMPEA and more generally by the EERA members. Below are given summaries of the different existing SPs of AMPEA.
An overall view of the Structure of AMPEA for the period 2014-2018 in terms of management and Sub-Programmes with the coordination is presented in Figure 2.

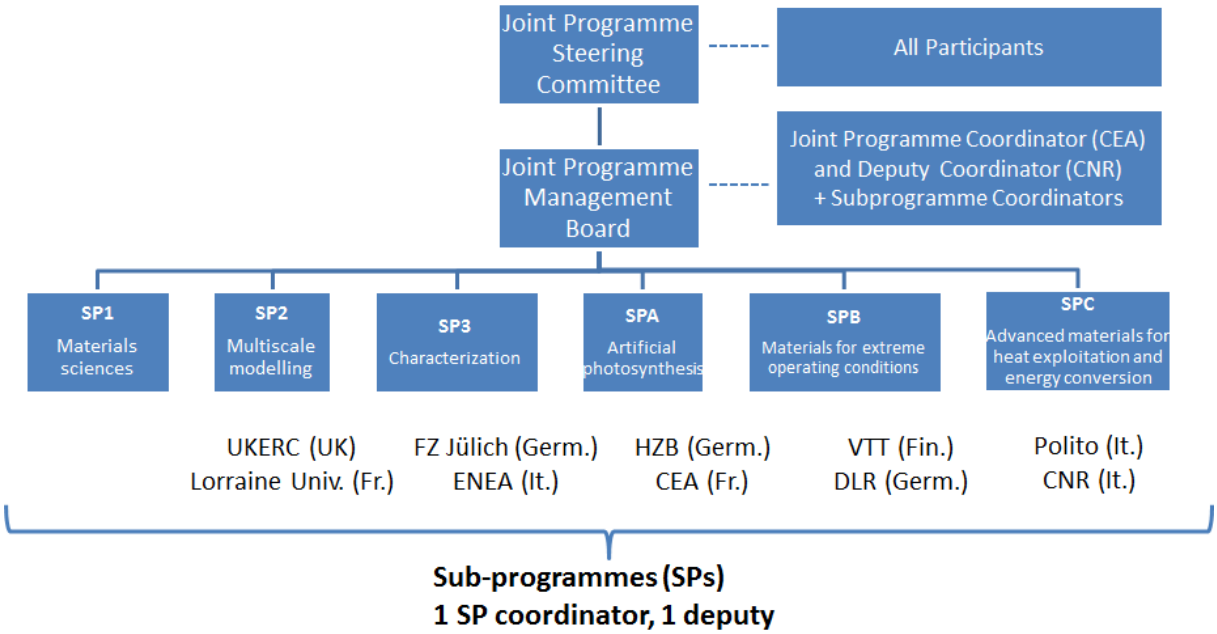

Figure 2: Overall structure of AMPEA during the period 2014-2018 with the different governing bodies and the sub-programmes.

Milestones for the management of the Joint Programme

The table below lists the Milestones related to the management of the Joint Programme as defined in the 2nd version of the DoW (February 2014) with the indication of the planned achievement and the status. This list has been extended with new Milestones for the next 4 years (which corresponds to the average duration between two reviews). Further technical milestones are indicated for the different sub-programmes and can be found in the relevant sections.

***Table 1**: List of the milestones for the AMPEA JP Management*

Selected Milestones	Measurable Objectives	Project Year	Status
M0.1	Updated AMPEA webpage	**2014**	**To be done**
M0.2	5th AMPEA JPSC with scientific session FZ Jülich, Workshop "Materials for Energy Devices I"	**2014**	**Done (May 2014)**
M0.3	Action plan to promote AMPEA joint proposals within H2020	**2014**	**Done**
M0.4	Formalize connection of AMPEA with EMIRI	**2014**	**Done Principle of cooperation achieved in 2014 - Memorandum of Understanding (MoU) signed with EMIRI in April 2016**
M0.5	6th AMPEA JPSC with scientific session Polytechnic University of Valencia, Workshop "Materials for Energy Devices II"	**2014**	**Done (November 2014)**
M0.6	Networking proposal submitted (*e.g.* COST action)	**2014**	**Done (2015) ITN proposal (ACES-TE Materials)**
M0.7	7th AMPEA JPSC with scientific session UCL, Workshop "Modelling of materials for Energy Devices	**2015**	**Done (June 2015)**
M0.8	Networking proposal submitted (*e.g.* COST action)	**2015**	**Done (2016) ITN proposal (ACES-TE Materials) resubmitted**

M0.9	8th AMPEA JPSC with scientific session PoliTO Workshop "Low temperature heat recovery"	**2015**	**Done (November 2015)**
M0.10	EERA-AMPEA dissemination event	**2015**	**Done** **Inter-JP cross fertilization workshop in April 2015 + side event co-organized with EMIRI at the SET-Plan conference (December 2015)**
M0.11	9th AMPEA JPSC with scientific session University of Lorraine Workshop "Power to chemical technologies"	**2016**	**Done (June 2016)**
M0.12	10th AMPEA JPSC with scientific session SINTEF, Workshop "Materials for membranes in energy applications: gas separation membranes, electrolysers and fuel cells"	**2016**	**Done (February 2017)**
M0.13	EERA-AMPEA dissemination event	**2016**	**Done** **Presentations of the Joint Programme by the coordinator**
M0.14	11th AMPEA JPSC with scientific session J. Heyrovský Institute, Workshop "Photo- and Electro-Catalysis in Energy Conversion"	**2017**	**Done (November 2017)**
M0.15	12th AMPEA JPSC with scientific session EERA Office, Joint EoCoE and AMPEA Workshop "Accelerating the energy transition: challenges in materials design enabled by recent advancements in high performance computing"	**2017**	**Done (June 2018)**
M0.16	13th AMPEA JPSC with scientific session HZB Bessy II "Synchrotron Radiation and Neutron Scattering for Energy Materials"	**2017**	**Done (November 2018)**
M0.17	EERA-AMPEA dissemination event	**2017**	**Done** **- 2016: Book on Artificial Photosynthesis with several chapters from members of the JP including the Joint Programme coordinator** **- 2017: article on SPA in the journal Pan European networks**
M0.18	IRP AMPEA proposal (provided a suitable call appears)	**2016-2017**	**Done (2018)** **AMPEA was involved in Joint proposal for a FET Flagship (Call FETFLAG-01-2018)**
M0.19	Review of AMPEA – Updating of the DoW and revision (if needed) of the Sub-Programme structure	**2018**	
M0.20	AMPEA JPSC with scientific session	**2019**	
M0.21	AMPEA JPSC and cross EERA JP workshop	**2019**	
M0.22	Dissemination event	**2019**	
M0.23	AMPEA JPSC with scientific session	**2020**	
M0.24	AMPEA JPSC and cross EERA JP workshop	**2020**	
M0.25	Networking proposal submitted (*e.g.* COST action)	**2020**	
M0.26	AMPEA JPSC with scientific session	**2021**	
M0.27	AMPEA JPSC and cross EERA JP workshop	**2021**	
M0.28	Dissemination event	**2019**	
M0.29	AMPEA JPSC with scientific session	**2022**	
M0.30	AMPEA JPSC and cross EERA JP workshop	**2022**	
M0.31	Networking proposal submitted (*e.g.* COST action)	**2022**	

Participants and human resources:

Acronym	Full name	Country	Role	Associated to	HR committed (py/y)
CEA	Commissariat à l'énergie atomique et aux énergies alternatives	FR	JP coordinator SPA coordinator		45
CIEMAT	Centro de Investigaciones Energéticas, Medioambientales y Tecnologicas	ES	Participant		9
CNR	Consiglio Nazionale delle Ricerche	IT	SPC coordinator (deputy)		21
CSIC	Agencia Estatal Consejo Superior de Investigaciones Científicas	ES	SP1 coordinator (deputy)		35
CVR	Centrum vyzkumu Rez s.r.o. - J. Heyrovsky Institute of Physical Chemistry of Academy of Sciences Czech Republic	CR	Participant		11
DIFFER	Dutch Institute for Fundamental Energy Research / FOM-institute	NL	Participant		6
DLR	Deutsches Zentrum für Luft- und Raumfahrt EV	DE	SPB coordinator (deputy)		8
DTU	Danmarks Tekniske Universitet	DK	Participant		5
ENEA	Italian National Agency for New Technology, Energy and Sustainable Economic Development	IT	SP3 coordinator (deputy)		25
Franuhofer	Fraunhofer Gesellschaft	DE	Participant		6
FZJ	Forschungszentrum Jülich GmbH	DE	SP1 and SP3 coordinator		40
HGF	Helmholtz-Gemeinschaft Deutscher Forschungszentren e.V.	DE	Participant		67
HZB	Helmholtz-Zentrum Berlin (HZB)	DE	SPA coordinator		19
ICIQ	Institut Català d'Investigació Química	ES	Participant		12
IFPEN	Institut Français du Pétrole Energies Nouvelles	FR	Participant		13
IK4	Association IK4 Research Alliance	SP	Participant		10
IMDEA Ener	IMDEA Energy	SP	Associate	**CSIC**	5
IREC	Fundacio Institut de Recerca en Energia de Catalunya	ES	Associate	**CSIC**	5
MPI CEC	Max Planck Institute for Chemical Energy Conversion	DE	Participant		6
NERA	Netherlands Energy Research Alliance	NL	Participant		10
Polito	Politecnico de Torino	IT	Participant		12
PSI	Paul Scherrer Institute	CH	Participant		10
SINTEF	SINTEF	NO	Participant		6
Tecnalia	Fundacion Tecnalia Research & Innovation	ES	Associate	**CIEMAT**	3
TU Delft	Technical University Delft	NL	Full		24
UKERC	United-Kingdom Energy Research Center	UK	SP2 coordinator		7
ULi	University of Limerick (UL)	IE	Participant		5
ULo	University of Lorraine	FR	Participant		46
UMU	Umea University	SE	Participant		10
UniBo	University of Bologna - Alma Mater Studiorum (UniBo)	IT	Participant		10
Unito	Università degli studi di Torino (Unito)	IT	Participant		10
UPV	UNIVERSITAT POLITÈCNICA DE VALÈNCIA	SP	Associate	**CIEMAT**	5
UU	Uppsala University	SE	Participant		10
VTT	Technical Research Centre of Finland	FI	SPB coordinator		5
				Total	**567**

***Table 2**: List of participants and associated participants to AMPEA with the corresponding human resources (status November 2018 on the EERA participant portal)*

In november 2018, the Joint Programme AMPEA hosts **34 partners** in total including **30 full partners** and **4 associate participants** from **13 member states and associated countries** (data from the EERA participant portal)**.** The total commitment in terms of human resources is **567 py/y**. These numbers correspond to persons working in the fields covered by AMPEA and that can "*participate in joint activities and share their work to the extent possible within the limits of prior obligations to funders of ongoing projects*". They were indicated in the initial application form of each participant to the JP and have not revised since then. This is something which shuld be done in the future.

The list of participants with the involvement for each partner is given in the table above. The present of status of involvement per country in the JP is given below. For each country, the first number is the number of organizations involved in the JP (participant and associated participants) whereas the second one is the total human resources py/y per country:

- Czech Republic: 1 organization 11 py/y
- Denmark: 1 organization 5 py/y
- Finland: 1 organization 5 py/y
- France: 3 organizations 104 py/y
- Germany: 6 organizations 146 py/y
- Irland: 1 organization 5 py/y
- Italy: 5 organizations 78 py/y
- Netherlands: 3 organizations 40 py/y
- Norway : 1 organization 6 py/y
- Spain: 6 organizations 84 py/y
- Sweden: 2 organizations 20 py/y
- Switzerland: 1 organization 21 py/y
- United-Kingdom: 1 organization 52 py/y

Compared to the previous DoW (February 2014), the total number of participants has decreased from 44 to 34 participants. This can be explained by several reasons. Some participants left the Joint Programme due to changing interests and new ones entered such as **IMDEA Ener**, **IREC**, **IK4**, **NERA**, **TU Delft**, **Unito**. One major reason for the change was when the EERA turned to a legal entity with new rules for organizations to participate to EERA with a revised fee for EERA which adds to the fee of the Joint Programme. Presently, there is no fee to participate to AMPEA but to still be part of AMPEA, the organization have to pay the EERA fee. Some participants left the JP and EERA on this occasion and others chose to appear under the umbrella of one organization. This is the case of **UKERC** which represents the interest of five british organizations (University College London, Imperial College London, University of Cambridge, University of Glasgow and University of Nottingham).

There also 3 pending applications under discussion/examination to join AMPEA: CNRS, Lepaja University (Latvia), Norwegian University of Science and Technology (NTNU).

Infrastructures and facilities

The efficient use of infrastructures and facilities is at the heart of sub-programme 3, devoted to characterisation and demonstration platforms of energy materials and devices. This subprogram has two objectives, both able to improve the utilisation of large scale facilities:

I) To create a forum which can help the technique experts to be world leading in developing the best possible new advanced characterization techniques for the scientific problems in mind.
II) To provide *one* entrance point to the suite of advanced techniques and thus help the users to get an overview of experimented possibilities. This will be addressed via a dedicated homepage.

Doing this, the aim is to seek a synergy in developments of advanced (in particular *in situ* and *operando*) experimental techniques and analysis software, we will try to establish or consolidate European networks for advanced technique developments. During the period 2014-2018, several workshops addressing advanced characterization issues were organized to allow networking. The DoW on SP3 lists the techniques and facilities that could be of interest to the AMPEA community. Gathering and keeping updated all this information on an AMPEA webpage still has to be done.

Management of the JP AMPEA

Governance structure

The EERA JP AMPEA is currently organized into 6 sub-programmes and has been discussed above (see Figures 1 and 2). This structure allows efficient management of the JP activities. In the future, new subprogrammes may be added or the existing sub-programmes. In this sense, a first discussion on having a new "*application*" sub-programme took place during the 13th JPSC organized in Berlin in November 2018. This sub-programme would

be on "*Autonomous Materials Development Platform*" and is related to the use of new digital techniques and artificial intelligence for the development of energy materials.

JP membership

Public body or/and recognised as non-profit research organisation by European Commission can join the program as *Participants* if they commit more than 5 person years/year (py/y) to the program. Other organisations or those committing less than 5 py/y to the program can join as *Associates*. The contributions of an Associate, both in terms of human resources and R&D work, are consolidated with those of the Participant that the Associate has chosen. Several small members may associate and name one of them as representative, becoming a Participant if the consolidated contribution surpasses 5 py/y. The Participant will represent the interests of the Associates that are linked to it. Any agreements governing the relationship between Participants and Associates are to be set up by the respective Participants and Associates. In the case of institutions not fill in the first two criteria its participation into the JP as Associate is mandatory and has to be approved by the Executive Committee (after being accepted by the JP Management Board and the JP Steering Committee).

EERA membership is formalized by signing a Declaration of Support, JP membership (either as participant or as associate) is formalized by signing program-specific Letter of Intent. The participation to the JP furthermore requires for the Applicant to fill in an application form describing the scientific interest to join AMPEA as well as resources which could be made available. After approval of the application by the JPMB, a representative of the applying organization is invited to present the application during the next JPSC and by providing necessary material relevant to the application (application form, presentation of the applicant, web page, etc). During the JPSC, a vote regarding the application is done provide there is the quorum for the vote (2/3 of the JP participants taking into account power of attorneys) and if this quorum is not reached, the vote can be done electronically (yes or no to the application) with a suitable delay (typically 2 weeks), a lack of answer corresponding to yes.

JP Steering Committee

The JP Steering Committee is composed of one representative of each institute participant. The JP Steering Committee:

→ selects the Joint Programme Coordinator and its deputy
→ selects the Sub-programme coordinators
→ reviews the progress and achievements of the JP
→ provides strategic guidance to the management board
→ approves new JP members (participants or associates)
→ approves updates of the Description of Work of the JP.

The JP Steering Committee is chaired by the JP Coordinator and the Deputy; the sub-programme coordinators participate as observers in the Committee. It convenes twice a year. The JP coordinator and the sub-programme coordinators cannot act as representatives of their respective R&D organisation in the Steering Committee.

JP Management Board

The JP Management Board is the executive body of the JP and is composed of the JP Coordinator (chair), the Deputy JPC and the sub-programme coordinators and deputies.

Tasks and responsibilities:

→ Financial management of the JP budget (if applicable)
→ Contractual oversight
→ IP (intellectual property) oversight
→ Scientific co-ordination, progress control, planning on programme and subprogrammes
→ JP internal communication
→ External communication with other organisations (European Commission, ZEP, EII, EPUE.....)
→ Reporting to Steering Committee and EERA ExCo

The JP Management board meets approximately approximately once per month or every two months depending on needs and period of the year. Two of these JPMBs meetings are physical ones coupled to a JPSC whereas the other ones are done by teleconference to avoid costly and time consuming travels.

JP Coordinator

The JP Coordinator (JPC) is elected by the JP steering committee for a mandate of four years. The mandate can be renewed. The JP Coordinator chairs the Steering Committee and the Management Board.

Tasks and responsibilities:

→ Coordination of the scientific activities in the joint programme and communication with the EERA ExCo and the EERA secretariat.
→ Monitoring progress in achieving the sub-programmes deliverables and milestones.

→ Reporting scientific progress and unexpected developments to the EERA ExCo.
→ Propose and coordinate scientific sub-programmes for the joint programme.
→ Coordinate the overall planning process and progress reporting.

JP Deputy Coordinator
The Deputy JP Coordinator (JPC) assists the JPC in all tasks relevant to the coordination of the Joint Programme (see above). The JP Deputy Coordinator (JPC) is elected by the JP steering committee for a mandate of 4 years.

Sub-programme coordinator and deputies
The Sub-programme coordinators (SPC) are selected by the JP steering committee for a mandate of four years. The mandate can be renewed. The sub-programme coordinator takes part in Steering Committee meetings, is a member of the management board and chairs the sub-programme execution team. In addition, a deputy is appointed to support the SP coordinator in managing the corresponding SP.
Tasks and responsibilities:
→ Oversee the sub-programme projects
→ Coordination of the scientific activities in the sub-programme to be carried out by the participants according to the agreed commitment. The SPC communicates with the contact persons to be assigned by each participant.
→ Monitoring progress in achieving the sub-programmes deliverables and milestones.
→ Reporting progress to joint programme coordinator
→ Propose and coordinate scientific actions for the sub-programme
→ Monitor scientific progress and report unexpected developments
The Deputy SP Coordinator assists the SP coordinator in all tasks relevant to the coordination of the SP (see above). The Deputy SP Coordinator is elected by the JP steering committee for a mandate of 4 years.

Interface with other EERA Joint Programmes

Considering the transverse nature of AMPEA, the interface treatment is especially important and demanding. Nearly all activities shall create interest or consequences in some JP or the other. But interfaces will be as important with academic laboratories, where a fundamental research relevant to our energy goals is performed. Thus, every actor of AMPEA is in charge of making contacts, bringing in new ideas or concepts and new questions, but also disseminating to the more technological JPs the usable results and making the necessary interfaces. The goal will be to create the conditions for the long-term development and enlargement of the energy research facilities, as well as to establish common R&D programmes, exchange researchers and creating synergies between the partners of the EERA joint research programmes in the field of energy technologies.
The specific objectives of AMPEA in terms of dissemination and interface treatments are:
1) Implementation of dissemination activities on advanced materials for energy, dedicated to the related industrial community, policy makers as well as scientific community including people of other JPs.
2) Training of young researchers on synthesis of novel materials, new synthesis methods (SP1), new physical or chemical transport processes (SP2) and on advanced characterization techniques (SP3)
3) To allow an easy access and/or collaboration to people of other JPs to the advanced characterization methods addressed in SP3.
4) To interact with the other Joint programmes in order to provide inputs and output, to avoid overlapping and to create synergy for the development of energy technology.
On the occasion of the previous review (in 2014), a mapping of the potential connection of AMPEA with other EERA Joint Programmes was undertaken and is summarized in the Table below.

Interface with JP on…	**Interface description**
Bioenergy	Application SPA
Carbon Capture and Storage	Tools SP2
Concentrated Solar Power (CSP)	Tools SPs, SP1 to 3 Applications SPB, SPC
Energy storage	Tools SPs, SP1 to 3 Applications SPA, SPC
Fuel cells and hydrogen technologies	Tools SP1, SP3 Application SPA
Geothermal	Application SPC
Nuclear materials (NM)	Tools SPs, SP1 to 3 Application SPB
Solar Photovoltaic	Tools SPs, SP1 to 3

Smart cities	Applications SPA, SPB
Smart grids	Application SPB
Wind energy (WE)	Application SPB

***Table 6**: List of potential interfaces between AMPEA sub-programmes and other EERA Joint Programmes.*

As the other materials focussed EERA Joint Programme, privileged contacts were established with the Joint Programme Nuclear Materials (JPNM) and several joint actions were launched. This includes the joint organization of the EERA inter-JP cross-fertilization workshop on "Materials for energy applications and technologies", ENEA Brussels Office, Brussels, April 28-29, 2015. The aim of this workshop was to discuss and address common issues in EERA around materials for energy applications. 11 Joint Programmes in total were represented during this meeting.
In the future, such cross EERA Joint Programmes will be promoted.

Risks

Three major risks need to be managed. First, AMPEA, by its nature, encompasses a wide scope: the objectives and paths to follow have to be made precise enough to permit the work to be focused, and the progress to be correctly assessed. A second type of risks comes from the fundamental type of research, which will be the business of AMPEA, but which is also the business of many labs in the universities and RTOs: AMPEA shall not work isolated, knowing the efficiency of competition among many teams, for new ideas to appear. An open-minded relation shall develop especially with the European Platform of Universities engaged in Energy research (EPUE). Thirdly, by pursuing long term technological goals, we will take the risk that our research be made obsolete by new progress in already industrialised techniques. A way to avoid this is to look for enabling capacities, applicable to many fields, beside the technological goals: AMPEA is made of both basic cross-cutting subjects of generic interest, and long term applied goals.

Intellectual property rights of the JP AMPEA

Joint Program AMPEA will adhere to the IPR policy of EERA. As it is agreed amongst participants and associates of the EERA JP AMPEA, the IPR will be handling at the project level in respect with the EERA IPR policy.

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EERA
EUROPEAN ENERGY RESEARCH ALLIANCE

SUB-PROGRAMME TOOL 1: Materials Sciences

A sub-programme within AMPEA

Description of Work

Subprogram coordinator:
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Last modification date: November 12th, 2018

All scenarios about the future global energy requirements anticipate an increasing demand for electricity, which in 2030 is predicted to double. Increasing global population and fast growing economies especially in developing countries are identified as main drivers for this development. The development of advanced functional materials for energy devices is a key issue to reach the most important properties such as long-term stability, high efficiency, easy manufacturability with low waste to further handle and limited or none CO_2 footprint, low price, non-toxicity and public acceptance.
Energy applications demand materials systems with a large range of functionalities and stability often in stringent operating conditions. New tools and innovative design's possibilities emerging from the utilization of micro-/nanotechnologies and more recently of additive manufacturing processes or other new innovative processing methods have the potential to create breakthroughs in today's energy conversion processes. This can be achieved (objectives)

- by the development of entirely new (designed) bulk/coating materials presenting improved functionality and/or stability in operation;
- by the utilization of nano-/microstructures as well as additive or other innovative manufacturing processes to design materials properties and device functionality while reducing energy demand, waste materials and CO_2 emission for their production;
- by engineering the interfaces to minimize the loss contributions that currently limit the device performance;
- by the development of material synthesis techniques that allows the upscaling to large quantities for powder production.
- by cooperating with the other modelling and characterisation sub-programs of AMPEA to benefit from the knowledge gained with advanced characterisation and multi-scale modelling to drive novel concepts of materials and devices.

The ambition of SP1 is to promote non-specific cutting-edge materials developments with a potential for high efficiency energy applications. On one hand, SP1 addresses innovative approaches for the synthesis of materials and their assemblies at various scales (atomistic, microscopic, macroscopic). These encompass for example: i) new routes to synthesis multi-cation oxides with fast transport properties, high entropy alloys, etc. ii) new fabrication routes to produce advanced multi-layered systems with tailored compositions and microstructures etc.; iii) new reactor concepts with innovative geometry (*e.g.* multichannel systems, tubular reactors, etc,); iv) novel approach and design of sealing technologies, etc. On the other hand, SP1 explores promising phenomena, in particular related to mass and/or charge transport, and establish sound strategies to eliminate bottle-necks to the exploitation of these phenomena in energy applications. Bottle-necks and loss mechanisms are often related to interfacial effects. This sub-program addresses active materials present in various energy technologies (catalysis, photovoltaics, fuel cells, electrolysers, batteries, photocatalysis, thermoelectrics, gas separation membranes, membrane reactors, materials for fusion devices, materials for power plants, etc.), as well as those materials necessary in relevant key enabling technologies, *e.g.*, refractive and protective coatings, light weight composites, and alloys. This interaction enables further improvements in conventional and new energy processes that currently have practical limitations in temperature, corrosive environments etc.
Materials of interest have been divided into the following categories according to their function and application: “Materials for catalysis and photocatalysis”, “Materials for Power Plants”, " Materials for CO_2 capture and production of synthetic fuels (energy carriers) or commodity chemicals", “Thermoelectric materials”, “Large scale synthesis of nano and micropowders”, “Advanced thin film processing”, and "Plasma Facing Materials".

Materials with specific properties are at the focal point of every new technology, and are the bottleneck for almost all energy technologies aiming for high efficiency and low cost. Hence the design and development of new materials integrated into processes is critical to future specific needs in energy applications. In the following we propose materials-related research fields that are important for cost-effective energy production/conversion and storage in the future and that should be part of an EERA Joint Program for basic science. Materials specifically for nuclear applications, photovoltaics, wind power, CSP, CCS, fuel cells, membrane reactors and batteries as well as materials for the light-induced fuel production are also topics of separate joint proposals. However, computational design, synthesis methods and scalable manufacturing processes applicable to several of the above mentioned applications are included in the AMPEA JP.

In the fields of "Materials for catalysis and photocatalysis", new long term stable materials will be developed to increase the stability and selectivity in the production of different advanced fuels and especially focus will be given on conversion of renewable and fossil sources to H_2, syngas, methane methanol and liquid fuels. In the field “Materials for Power Plants” thermal barrier coatings also with new integrated sensor functionalities, ceramic matrix composites and new stable metal super alloys (Ni-base alloys) will be developed to increase the efficiency of the fossil power plants by increasing the operation temperature.
In the fields of Materials for CO_2 capture and production of synthetic fuels (energy carriers) or commodity chemicals, new materials and stable thin film membranes with activated catalytic surfaces delivering higher flux,

better selectivities and high mechanical strength will be developed for CO_2 capture technologies (CCS) and other energy intensive technologies to strike the global warming. Also the optimisation of support structures including transport modelling is required to enhance the performance and life time of the layered arrangements. Similarly, novel electrolyte materials and composite electrodes operating at intermediate temperature will be integrated in new cell's designs for fuel cell and electrolyser technologies. Novel high temperature sorbents for CO_2 capture and possibly sulphur removal will be investigated to improve the efficiency of gas cleaning.
"Thermoelectric materials" with improved conversion efficiency and materials stability will be developed and integrated for either solid state refrigeration or energy conversion applications.
The topic "Plasma Facing Materials" is dealing with metallic and ceramic materials (bulk and protective coatings) under extreme quasi-stationary and transient thermal loads as well as severe particle exposure such as H, He and Neutrons which are needed in future fusion reactors.
The two last topics apply to-, but are not limited to-, all materials listed above.
- "Large scale synthesis of nano and micropowders" will improve the production techniques and the standardization of nano and micro powders with multiple applications including speciality powders for additive manufacturing, catalysts, coatings, battery and hydrogen storage materials, polymer fillers or raw materials for powder metallurgical and ceramic processes.
- "Advanced thin film and 3D processing" will develop flexible and scalable deposition processes and systems, including 3D techniques that require specific material design, that deliver a high-level control of the process parameters to generate high performance materials, coatings and products with tuneable and controllable composition, microstructure and reduced residual stress. This topic will also pay attention to material precursor /solvent/additives selection to avoid use of toxic or scarce product, and to reduce waste amount and energy consumption, *e.g.* by means of integrated multi-technique and multi-scale procedure.

Materials for catalysis and photocatalysis

In these topics the development of non-noble catalysts aims to increase the stability and selectivity in the production of different advanced fuels and focuses on conversion of biomass, waste products and fossil sources and CO_2/water to H_2, syngas, methane and liquid fuels. Processes for fuel production often require extreme conditions, such as high temperature and/or hydrothermal biomass conversion and solar-thermal fuel synthesis. New stable materials, structured at the nano-, micro-, and mesoscale, will be developed.
The number of (photo) catalysts in use for fuel production is rather limited and the materials are expensive. Promising candidates, such as metal oxides (*e.g.* doped or alloyed Mn_xO_y, $Ni_{1-x}O$, Fe_2O_3, WO_3 and $BiVO_4$ electrodes) and photovoltaic hybrid systems using amorphous catalysts layers (*e.g.* MoS_2 for hydrogen evolution), will be investigated in form of nanostructured powders and layers. These materials are much less expensive than RuO_2, IrO_2 and Pt.
Among biomimetic approaches using inorganic systems mimicking photosynthesis, one possible solution is the conversion of sunlight into chemical energy via photonic excitation of a photovoltaic thin film, directly combined with corrosion-stable layers at its front and back surface of electro catalysts allowing water electrolysis at the electrode-electrolyte-interfaces. Generated hydrogen can be stored as compressed gas, liquid H_2, metal hydride or methanol. Alternatively, CO_2 reduction and hydrocarbon production can be achieved on the cathode side of the device. In both cases, noble metal-free catalysts are needed to develop electrodes for a mass market with respect to oxidation/reduction of water and reduction of CO_2, respectively. Another approach is the development of molecular systems close to the conditions in the thylakoid membrane in green algae and plants.
The research will be focused on:

- Detailed understanding of the relation between material characteristics (as expressed in charge carrier kinetics, crystal structure and nanostructure etc.) and conversion rate and selectivity;
- Development of computational tools supporting the evaluation and selection of materials for the catalysis for fuel production in collaboration with SP2;
- Experimental investigation and evaluation (electrochemistry will be largely used) combined with in situ / operando characterization of catalysts in view of quantifying efficiency and stability in collaboration with SP3;
- Optimization of the coupling of photovoltaics to fuel production using photocatalysts directly converting solar energy into fuels (monolithically or otherwise) or by coupling photovoltaics to a fuel producing unity (hybrid electrolyser etc.);
- Catalysts for fuels synthesis (CO_2 fixation and reduction), membranes, solid oxide fuel cells, solid oxide electrolysers and solar- and hydrothermal- and other energy applications.

Great challenges "Materials for catalysis"

Challenge
Non-noble metal catalysts for electrochemical reactions

Advanced catalysts for thin films to activate the surface (development of nano-composites) of gas separation membranes and membrane reactors Tailored microstructures and *in situ* characterisation
Long term stable catalysts at high temperatures and under harsh environments Multiscale modelling for catalyst design
Catalysts for fuel production from H_2O, CO_2 and renewable sources (photolysis of water, electrolysis and CO_2 reduction)
Highly efficient sustainable catalysts for fuel production from H_2O, CO_2 and renewable sources

Great challenges "Materials for photocatalysis"

Challenge
Solar hydrogen from inorganic systems with 5% STH efficiency Solar hydrogen from molecular systems with 1% STH efficiency hybrid systems up to STH 3%
Inorganic systems with up to 8% efficiency on a m^2 scale molecular based systems of 3% STH efficiency Hybrid systems of 5% STH efficiency
Integrated inorganic systems with up to 15% efficiency on m^2 scale molecular based systems with up to 5% STH efficiency Hybrid systems with up to10% STH efficiency CO_2 fixing systems of 10% STH efficiency

Materials for Power Plants

In the field **"Materials for Power Plants"** environmental barrier coatings, ceramic matrix composites and new stable metal super alloys (Ni-base alloys) are needed to increase the efficiency of the fossil power plants by increasing operation temperature. It is interesting to note that such a kind of materials can be profitably used for both structural and functional components in the field of energy (stationary turbines, power and solar plants) as well as in that of aerospace (jet propulsion, sensors, and thermal protection). Improved characteristics are essential concerning strain tolerance, low thermal conductivity, sintering resistance, phase stability, reflectivity, fatigue strength, abradability, corrosion resistance, and fitness for alternative burning gases. Furthermore, new functionalities e. g. sensor structures should be integrated to exploit the potential of such innovative thermal barrier coatings exhaustively. The research will focus on:

- Life time models need to be established to explain damage mechanisms and to optimize coating characteristics systematically.
- For steam turbine and boiler applications new high strength ferritic- martensitic, austenitic steels and nickel base alloys with improved creep strength and high resistance against steam oxidation are of major relevance.
- For combustion chambers and hot gas conducting parts liners made of ceramic matrix composites (CMC) are taken into account. If fiber reinforced ceramics replace air-cooled metallic parts in gas turbines significant saving of cooling air will be possible. On one hand this will lead to a significant increase in efficiency. On the other hand the saved cooling air can be used to realize lean combustion reducing CO_2 and NO_x emissions drastically. CMCs were developed since late 1990´s and a high stage of development is achieved empirically. Introduction of novel Ox/Ox materials to industrial processes, however, requires better computability and predictability.

Great challenges "Materials for Power Plants"

Challenge
Functional graded Coatings for Advanced Power Plants and new Power Plant Concepts (*e.g.* IGCC, Oxyfuel) and the relevant fabrication processes Advanced surface engineering methods (*e.g.* to improve internal oxidation resistance)
Materials modelling capabilities to reduce time to market for new alloys Integrated sensor technology to increase performance and integrity
Long term stable materials for highly efficient multi fuelled zero emission power plants Materials for new generation high efficient fossil power plants Joining and fabrication of new materials (redesign of components) Lightweighting of gas turbine blading
Ultrahigh temperature materials for direct electricity generation and fuel production in a greenhouse gas emission free society

Materials for CO_2 capture and production of synthetic fuels (energy carriers) or commodity chemicals

Advanced materials designed as granulates and multichannel systems (sorbent technologies) and stable thin dense film membranes with activated catalytic surfaces for separation of gases (membrane technologies) are needed for CO_2 capture technologies (CCS) to strike the global warming. Their implementation demands the use of new separation devices such as Oxygen transport membranes (O_2/N_2 Oxyfuel process), Hydrogen separation membranes (H_2/CO_2 Pre combustion) or CO_2 selective membranes (CO_2/N_2 Post combustion separation; H_2/CO_2 Pre combustion). In addition synthetic fuels as energy carriers or commodity chemicals can be produced by membrane reactors with thermal energy from renewable processes. An alternative to use of carbon based resources could be based on the deployment of steam electrolysis, whose reversible operation may be considered as novel pathway for energy storage. These devices use multi-layered thin film components whose functionalities and stability are strongly challenged by interfacial reactions and diffusion processes.
All these materials and the necessary thin film structures required to ensure high functionality must be stable at high temperatures in harsh environment of power plants and energy intensive industries (steel, cement plants, etc.). In the AMPEA basic transport phenomena in different material classes are studied and the scale up and device fabrication are handed over to the CCS JP. Further goals are:

- Study the main degradation phenomena with specific focus at the interfaces of multi-layered systems;
- Develop life time models needed to establish the feasibility and efficiency of these processes;
- Develop flexible manufacturing routes enabling to tailor materials functionalities at all length scales (atomistic, macroscopic, interfaces)
    - Investigate novel membranes design, *e.g.*, liquid/solid dual phase membranes, graded layers, asymmetric membranes with low cost support, membranes alternatives to Pd for H_2 separation etc.
- For Pressurized Pulverized Coal Combustion (PPCC) technologies sorbents are needed which lower the alkali metal concentration in the hot flue gas at 1400 °C to levels according to gas turbine specifications.

Great challenges "Materials for Power Plants"

Challenge
Novel membrane systems with high flux combined with high stability demonstrated at laboratory scale in relevant operating conditions Advanced surface engineering methods to improve electro-catalytic activities Themomechanical and chemical stable support structures
Reliable and thin film graded membranes with high flux and selectivity demonstrated at pilot scale (TRL 6) Novel high temperature sorbents for hot flue gas cleaning (TRL5)
Long term stable materials for highly efficient multifuelled zero emission power plants Materials for new generation in high efficient fossil power plants Development of novel integrated processes using membrane technologies for CCS in energy intensive industries
Ultrahigh temperature materials for direct electricity generation and fuel production in a greenhouse gas emission free society

Thermoelectric materials

Topic **"Thermoelectric materials"** is focused on the development of advanced materials for either solid state refrigeration or energy conversion applications. The improvement in conversion efficiency, materials stability and integration and finally reduction of fabrication cost of the thermoelectric devices are the main challenges to be overcome in the next decades. In a thermoelectric (TE) generator (TEG), electricity can be generated by the direct action of heat on the constituting materials (n- and p-type semiconductors). These systems are simple, compact, silent and highly reliable (no moving parts). The efficiency of a TEG is related to the dimensionless figure of merit ZT ($ZT = S^2/\rho\lambda$, where S is the Seebeck coefficient, ρ the electrical resistivity and λ the total thermal conductivity). Large amounts of waste heat are produced by industrial processes, stationary and mobile energy applications. For remote and low-power electric consumers, the major fraction of energy is lost in transmission. An approach to reduce resource consumption and to slow the man-made greenhouse effect caused by CO_2 emission is the generation of useful electricity from waste heat. The prospect of thermogenerators turning from auxiliary to primary sources of energy is highly envisaged at the light of the development of self-powered autonomous systems contributing to the growth of a distributed energy production scenario. Thermoelectric (TE) power generation based on the Seebeck effect may find their potential applications in self-sustainable technical systems acting remote or independently of electrical mains connection, including autarkic heating systems, usage of geothermal and solar thermal heat, energy harvesting for self-sustainable sensing and data acquisition, control and data transfer. TE micro-generators also may play an important role.
Main research fields are e. g.

- Decentralized use of waste heat for electrical supply to autarkic low power consumers for system control and data acquisition,
- Conversion of waste heat of energy machinery and industrial processes by means of low-cost TEG,
- Development of autarkic heating systems which cover the electrical consumption of their functional components independently of an external source as mains connection, by conversion from system immanent heat flow
- Increase of reliability in supply, improvement of system functionality and simplification of system design by reduction of cabling and installation effort,
- Increase of efficiency in hybrid energy systems: SOFC + TEG, solar thermal systems + TEG, CHP + TEG
- Development of new materials concept and systems exhibiting high Z factor and conversion efficiency, respectively

From the thermoelectric materials side, two routes should be investigated: materials with a complex and/or open crystalline structure and nanostructured materials. It will be necessary to conduct extended research, both experimental and theoretical, to determine the influence of different factors on the electron and phonon TE transport properties in these two classes of materials and on the magnitude of ZT. In this framework, some of the main tasks are:

- To identify efficient strategies and processing routes to produce advanced n and p type materials. This includes thin films for autonomously working low-power, low cost systems.
- To investigate the TE materials joining (metal-n and p legs) at the operating temperature, their protection against thermal and chemical degradation (bi-functional coatings, graded composition TE materials), their integration for the suitable TE module engineering.
- To develop theoretical approach exploring new mechanisms for improving ZT (engineering of the thermal conductivity and the thermopower).

Such a technology can be effectively exploited for micro-harvesting applications like sensoring, IoT, etc. In this field, the attention focuses on polymeric composites working at low/mid temperatures. They are very attractive due to its easy fabrication processes and low material cost. Promising strategies include the addition of carbon nanostructures and semiconductors or metals. Before real engineering of polymer-based thermoelectric devices, there is reasonable advance to be achievedPolymers are made of low cost raw materials and possess a remarkably low thermal conductivity.

Great challenges "Thermoelectric materials"

Challenge
Integration of the current advanced materials in thermoelectric devices
Development of stable and sustainable thermoelectric materials with ZT = 1.5 for power generation
Development of stable and sustainable thermoelectric for micro-harvesting
Integration of thermoelectric devices in every day life to reduce CO_2 emission and to produce electrical generation with ZT = 2. Highly efficient green solid state cooling devices alternative to heat pumps
With ZT = 3-3.5, Recover of waste heat for stationary power supply

Large scale synthesis of nano and micropowders

Topic **"Large scale synthesis of nano and micropowders"** is focused on production techniques for obtaining different nano and micro structures and morphologies with multiple applications including specialty powders as feedstock for additive manufacturing, catalysts, coatings, battery and hydrogen storage materials, polymer fillers or raw materials for powder metallurgical and ceramic processes. The synthesis method may include micelle preparation, spray-pyrolysis, rapid cooling techniques or electrospinning, condensation of metallic vapours in inert or reactive gas atmosphere, mechano-synthesis through high- or low-energy ball millling, depending on common interests of the partners.

A second aspect of the processing chain is related to maintain the original structure of powders in the bulk materials from sintering and compaction of ceramic/composite powders. Nowaday SPS is the principal available technique, but it is expensive and up to a point suitable for large-scale samples.

Great challenges "Large scale synthesis of nano and micropowders"

Challenge

Low-cost and high-yield production methods Surface passivation methods for safe handling of nanomaterials
Low-cost and low-energy production methods
Closed-loop synthesis of nanomaterial containing product starting from non-nano raw materials without the need of human contact during the manufacturing process
Closed-loop recycling of nanopowders and nanocomposites facilitating the separation of raw materials with zero emissions to environment
Maintain nanostructured features in bulk materials obtained from powder sintering/compaction

Advanced thin film and 3D processing

The use of high performance functional coatings/thin film/3D materials system requires a deep understanding (at different length scales) of the relation with the adjacent layer (interfaces), the mechanical properties of surfaces (*e.g.* surface stiffness and hardness, residual stress and surface roughness) and how these properties are influenced by the material microstructure and process parameters. Today there is still a lack of knowledge in correlating nano/micro/structure and tribological-mechanical properties, affecting the in-service behaviour and durability of thin film based systems, due to the deposition process. Among the major goals there are:

- to develop deposition systems, that deliver a high level control of the process parameters to generate high performance coatings with tunable and controllable microstructure and residual stress.
- to develop integrated multi-technique and multi-scale procedure for the measurement and control of tribological and mechanical properties of nano-structured materials as well as small-scale device techniques with high resolution characterization methods.
- to develop materials whose properties will be tailored to enable their use as feedstock in additive manufacturing processes (flowability, granulometry, refractive index etc.) so as to promote new routes for materials engineering and assemblies

Great challenges "Advanced thin film and 3D processing"

Challenge
Low cost high yield deposition methods available Novel feedstock for additive manufacturing available
nanostructure-property relations established based on high resolution characterisation methods including 3D techniques Full understanding of properties of thin film structures e. g. mechanical aspects
Deposition systems developed enabling high level control of process parameters
Large area of defect free thin film structures produced

Plasma Facing Materials

The topic **‚Plasma Facing Materials'** is dealing with metallic and ceramic materials under extreme quasi-stationary and transient thermal loads as well as severe particle exposure such as H, He and Neutrons in future fusion reactors. Synergistic effects resulting from simultaneous degradation and embrittlement of the wall materials induced by hydrogen, helium and neutron bombardment need to be taken into consideration. Activities in this field are mainly focussed on plasma compatible materials, preferentially with low-atomic numbers (low-Z) such as beryllium and monolithic carbon based materials but also on high-Z refractory metals with predefined microstructures and alloying partners. It is interesting to remark that many materials among "Plasma Facing Materials" can profitably used in other technological applications in plasma environment like plasma torch for waste incinerator.

The lifetime of plasma-facing and structural components strongly depend on the operation conditions. Exposure with high fluxes of ions, neutrals, and neutrons and subsequent material degradation pose specific challenges. High heat loads and environmental (particle) loads require generic material developments and solutions also relevant for other fields of energy research. Main issues to be treated in the frame of sub programme 1 are the determination of load limits under stationary and transient exposure, damage mapping under transient thermal loads including composites and coatings with different micro structure and chemical composition. The simulation of fusion relevant loading scenarios shall be performed in (linear) plasma devices and electron, ion or laser beam based high heat flux test facilities. In these tests also synergistic loading combining thermal loads with plasma exposure and neutron induced material degradations need to be studied to provide realistic assessment of the component lifetime. Beside the above mentioned candidate materials improved grades and newly developed classes of materials shall be investigated. The implementation of hydrogen diffusion barriers, development and testing of self-passivating alloys to overcome accidental conditions with air or steam ingress, fibre or layered composites with improved

mechanical properties as well as nano-structured composites with improved recrystallization performance form additional key issues.

Great challenges "Plasma Facing Materials"

Challenge
Newly developed plasma compatible plasma facing components for ITER
Demonstration of the technical feasibility of actively cooled wall armour for DT-burning magnetic confinement experiments
Prototypes of actively cooled first wall components for commercial power plants
Highly efficient plasma and neutron resistant plasma facing components for future fusion power plants

Materials for Photovoltaic Devices with JP CSP

In the topic "Materials for Photovoltaic Devices" the specific challenges are the increase of the device efficiency beyond the Shockley-Queisser-limit by using new concepts and the use of abundant elements in thin film devices". Concepts to increase the efficiency of PV devices involve extended nanostructures, intraband absorbers, hot-carrier absorbers, impact ionization absorbers, absorbers with tuned band gaps for multijunction cells, plasmonic scattering through nanostructured coatings, materials for thermo-photovoltaic devices or materials for photon enhanced thermionic emission (PETE). In all of these cases new materials have to be developed.

Silicon/silicon dioxide (Si/SiO_2) nanostructures are potential building blocks for further improving the efficiency of silicon based solar cells and have the potential to exceed the Shockley–Queisser limit of 32.7% for single-junction solar cells by exploiting quantum size effects. As a short term goal, such structures represent promising hetero-contacts and passivation layers for Si-based wafer and thin-film solar cells.

One realization for such a functional element is a Si/SiO_2 hetero-emitter consisting of silicon nanodots embedded in a silicon dioxide matrix. The hetero-emitter must be capable to passivate the underlying absorber material, to induce a band bending (*e.g.* by doping) and to have a sufficient conductivity.

Currently we are following 2 routes to grow the hetero-emitter: first by decomposition of SiOx layers and secondly by a self-assembled growth based on the dewetting of a thin amorphous Si-layer (a-Si).

Nanostructured materials and solar cells

Silicon nanowire-based solar cells have been recently proposed. It has been shown that the use of Si nanowire-based solar cells provides an efficiency entitlement on the order of 15–18% depending on nanowire size (diameter and length) and quality (carrier lifetime). One of the key aspects of such all-inorganic Si nanowire solar cells is that it is possible to form p–n junction conformally about the nanowire surface in a high-density array. This has the benefit of decoupling the absorption of light from charge transport by allowing lateral diffusion of minority carriers to the p–n junction, which is at most 50–200 nm away, rather than many microns away as in Si bulk solar cells. Furthermore, the optical properties of Si nanowire arrays are significantly different from those of solid thin films of the same thickness in that the optical absorption is dramatically increased across the spectrum. The nanowires may be synthesized using standard techniques such as chemical vapor deposition (CVD), with the possibility of direct growth on flexible substrates such as metal foils.

Materials for Fuel Cells and electrolysers with JP FC and H_2

The topic "Materials for Fuel Cells and electrolysers" is focused on the material development for high temperature cells with oxygen ion electrolyte (SOFC/SOEC) or proton conducting electrolyte (PCFC/PCEC) and low temperature fuel cells (PEM). For the high temperature cells new materials for the electrolyte and electrode materials with high performance at a lower operation temperature are required. The activities starting from basic materials research concerning catalytic and electrochemical characteristics, followed by powder processing and manufacturing of components. Also sealing concepts and materials which are mechanical stable during thermal cycling are needed. In addition catalysts for direct hydrocarbon fuelling are required.

For the Polymer Electrolyte Membrane Fuel Cells (PEMFC) new catalyst materials have to be developed or alternatively the Pt utilization and activity has to be improved, in order to reduce the amount required. This last issue can be addressed by achieving a greater selectivity in the placement of the platinum particles onto the porous substrate, such as Electrodeposition (ELD) or Physical Vapor Deposition (PVD) or by optimizing the carbon-based materials used as catalyst support. For PEM fuel cells also a major focus lies on bio inspired catalysts and in improving of carbon supports for electrodes. The optimization of the bipolar plates is needed for these fuel cells. Materials development for increased temperature operation (up to 200°C) is necessary especially for decentralized stationary energy supply devices such as combined heat and power fuel cell systems. That is, materials for Membrane Electrode Assemblies (catalysts and supports, membranes, gasket materials) as well as cell hardware composite materials are needed for successful technical implementations.

The following topics are covered in other EERA JPs but are mentioned to address their importance regarding material development:

Materials for Batteries and Supercapacitors

In topic "Materials for Batteries and Supercapacitors" materials with higher capacities (charge density) are required. Also structural stability of material, good ion-conducting electrolytes under application conditions is needed. In addition to the classical battery types a strong activity in all solid state batteries are required due to their safe operation mode.

There exists significant political and industrial interest in the development of batteries in particular for transport applications and energy storage from renewable power sources. Among the different battery concepts (*e.g.* Li-S, Zn-air, etc.), Li-ion batteries are currently preferred and these comprise three components: a cathode material, which is typically a Li containing material such as $LiFePO_4$ or $LiCoO_2$; an anode material such as graphite; and an electrolyte such as a lithium salt in an organic solvent. The benefits of Li ion systems are that there is no memory effect, low self-discharge levels and good portability. Current efforts in battery research focus on overcoming some important limitations: over-discharge causes formation of Li_2O; aging (especially with charge/discharge cycles) leading to capacity decrease; recyclability; toxicity and manufacturing issues; and safety, since under certain conditions the batteries may explode on mistreatment.

Silicon is an attractive anode material for lithium batteries because it has a low discharge potential and the highest known theoretical charge capacity (4,200 mAh g^{-1}). Although this is more than ten times higher than existing graphite anodes and much larger than various nitride and oxide materials, silicon anodes have limited applications because silicon's volume changes by 400% upon insertion and extraction of lithium, which results in pulverization and capacity fading. Silicon nanowire battery electrodes have been shown to be able to circumvent these issues as they can accommodate large strain without pulverization, provide good electronic contact and conduction, and display short lithium insertion distances.

Goals for work in this area are therefore to decrease cost and improve safety of Li batteries and also increase cycling tolerance, stability, capacity, operation temperature, increase output power and material recyclability. In order to attain this goal, the application of nanoscale engineering, nanochemistry and multidoping strategies and controlled modification of the crystalline structure is crucial. It is also of utmost important the exploration of low cost manufacturing routes for scale up of the most successful materials identified in the most fundamental activities.

Materials for Hydrogen Storage

In the topic "Materials for Hydrogen Storage", nanostructured materials with high hydrogen capacity for mobile and stationary applications, with a good cyclability and fast sorption kinetics at near application temperature are needed. The tailoring of the material properties involves the development of new synthetic techniques.

Hydrogen is an important alternative to the traditional energy carriers, even in the near future. It can be produced from a variety of sources and is extremely environmentally benign since water is the only exhaust product when energy is derived from electrochemical reaction with oxygen. While hydrogen production is already technologically feasible, hydrogen storage is a major bottleneck to overcome technological limits, especially for mobile applications and distribution of renewable energy, in order to support a wide diffusion of this energy carrier. As the chemical storage of hydrogen involves significant heat of reaction to be removed from the storage reactor during loading as well as sufficient heat supply for release of hydrogen during discharge thermal management of the storage reactor is a key issue.

Nanostructured materials are able to improve the kinetics and thermodynamics of H-sorption of solid-state hydrogen storage. The development of novel lightweight nanostructured materials will be the focus of this activity using synthesis techniques, complete characterization and computational modelling. Different classes of materials will be investigated, including metallic and salt-like hydrides, complex borohydrides, and highly porous materials.

Milestone	Measurable Objectives	Project Year
M1	*"Materials for catalysis": Non noble metal catalyst for water splitting and catalytic conversion*	*2*
M2	*"Materials for catalysis": Detailed understanding of transport properties and electrochemical reactions at atomistic level towards design of new (electro)catalysts*	*10*
M3	*"Materials for Power Plants": Long term stable and materials for high combustion temperatures*	*5*
M4	*"Materials for Power Plants": Joining methods for new and dissimilar materials*	*15*

M5	*"Thermoelectric materials": Fabrication of more effcicient and stable thermoelectric devices than the current devices at a cost as low as possible*	*5*
M6	*"Thermoelectric materials": Based on theoretical background, found new efficient and stable thermoelectric materials*	*5*
M7	*"Large scale synthesis of nano and micropowders": Production of metal and metal-composite NPs 5000 kg/month with production cost less than 200 €/kg.*	*2*
M8	*"Large scale synthesis of nano and micropowders": Maximum 100 % additional costs to decrease particle size from 100 µm to 100 nm*	*5*
M9	*"Advanced thin film processing":*	*5*
M10	*Full characterization of materials for advanced first wall components (thermal and mechanical properties incl. plasma and neutron environments)*	*5*
M11	*Actively cooled components for DEMO based on improved plasma facing and structural materials (implementation of new composites, self passivating alloys and diffusion barriers)*	*15*

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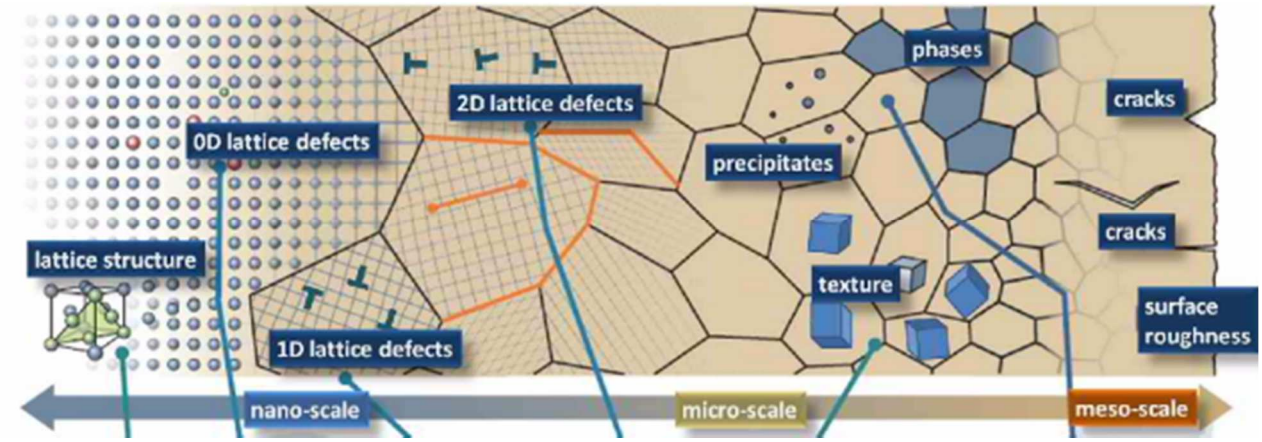
EERA
EUROPEAN ENERGY RESEARCH ALLIANCE

SUB-PROGRAMME TOOL 2: ***Multiscale Modelling of Materials, Processes and Devices***



A sub-programme within the
AMPEA EERA Joint Programme

Description of Work

Sub-programme coordinators:
David LACROIX, UL

Last modification date: November 12th, 2018

The goal of the AMPEA "Sub-programme 2" is to coordinate a concerted effort in AMPEA to identify current challenges and forthcoming trends in multiscale modelling and simulation. This effort is critically important in advancing materials, processes and devices for energy applications, while ensuring sustainable production route and fostering circular economy: firstly, innovative energy materials are often complex structures or "high technology" products (multi-functional), which cannot be described by basic models; secondly, the formation and application of such structures are very much dependent on conditions of processing and utilisation; and thirdly, the integration of such materials in devices is intricate and thus requires careful design and optimisation. All of these issues encompass multiscale spatial and temporal dimensions of tens of magnitudes, where cross-disciplinary work is a necessity.
Furthermore, during the recent years with the rapid evolution of computing resources and the related advances in programming a new paradigm related to artificial intelligence, machine learning and cloud computing arises. This new way to think informatics is about to revolutionize our methods in designing, modelling and describing material properties and use. The latter, which is probably the most salient advanced of the past years is detailed in the updated content of the SP2 sub-programme of AMPEA.
In the following, important issues about multiscale modelling are presented, milestones and interactions with other AMPEA sub-programmes and EERA join-programmes are also addressed.
In order to develop and deploy efficient materials and processes in energy applications, an integrative approach that combines theory, models, simulations, fabrication and characterization should be considered. Among these research areas, "modelling and simulations" are a powerful toolbox, which can open the way to innovative design of new materials and new production routes for energy applications. However, conventional tools and models developed to address to date are often confined within small-scale domains and inadequate to materials that involve nanostructures, microstructures, composite and alloy phases. Similarly, they are not suitable to investigate intensified processes that combine heat and mass flow transfers, electronic and chemical transports, mechanical loads, transient operations, etc. For such complex but real-time applications, multiscale modelling could bring critical insight in materials and processes limitations, and thereby, open routes for optimization. Hence, dedicated numerical simulations need to be established to address these specific requirements. Besides, in what concerns new materials and processes for energy a cross-disciplinary approach is essential. As discussed in the following, models and tools developed to predict transport properties of innovative materials are interdisciplinary and more and more used for research and engineering purposes. Similarly, integrating processes e.g. with process intensification in the field of energy applications often requires competences and technologies in several domains such as catalysis, chemistry, electronics, materials and process engineering, mechanics, etc. Therefore, this "tool" sub-programme on multiscale modelling will strongly interact with other "tool" and "application" sub-programmes as well as with other EERA Joint Programmes as it is at the crossroads of theory, measurements and practical applications.

In this framework, several actions have been achieved in AMPEA and examples of integrated computational material engineering such as the development of the VTT Propertune TM environment [1] will be discussed hereafter. Besides, a common reflection with the European Center of Excellence dedicated to the computation in the field of Energy (EoCoE [2]) has started to identify common interest that might foster interaction between two different communities, i.e. the physic and computational ones.
The main goal is to provide tools that can support research and developments in the identified application sub-programmes (Artificial photosynthesis, Advanced materials for heat exploitation and energy conversion, Materials for extreme operating conditions) as well as for the other Emerging fields or other EERA Joint Programmes where materials and processes challenges are important. Therefore, simulation tools devoted to the specific length scales of interest, which can address several physical phenomena, are necessary. Between material atomistic properties and its application in a process or a device several problems must be investigated:

1. Identify what are the relevant models to be applied from the atomic scale that characterize the material to the system scale related to its integration in an energy production device.
2. Relate models and numerical simulation tools; find the most efficient solving techniques and quantify their reliability and their accuracy, for example by defining and using benchmark test cases to address models and tools exactitude. Use of small-scale prototypes to compare simulations and experiments.
3. Discover and investigate through data mining and machine learning new materials for energy applications, especially taking into consideration raw material abundance, toxicity, availability, etc.
4. Considering a bottom-up modelling approach, identify the key properties that rule the functionality of the whole device and find the most appropriates techniques to minimize the impacts of the involved parameters in the numerical solution of a given problem, *e.g.* using effective medium theory, or model reduction techniques.
5. Propose efficient techniques to achieve the coupling between different physics such as heat and mass transport, chemical and biological or mechanics and electric interactions, *etc.*
6. Consider the crosscutting issues between this sub-programme and the other joint programmes dealing with energy applications (*e.g.* Fuel Cells and Hydrogen, Energy storage, Photovoltaic, *etc.*).

Numerical simulation in physics, mathematics, engineering and even in biology or medical sciences is now commonly used. This situation is related to the rapid evolution of computing sciences and technologies. Calculations, which were done on personal computers a decade ago, are now routinely done on super-calculator, PC clusters or in the frame of grid and even cloud computing. This allows achieving calculations involving complex models and boundary conditions but also very thin meshes and small time steps. Among the recent progress done in this field, very fast phenomena occurring at atomic scale can now be addressed or complex interactions at macroscale in realistic engineering devices and processes. **Thus, one purpose of this work-programme is to make a detailed survey of the existing tools that can be applied to the Joint Programme objectives and to anticipate the arising of new the ones, like the one related to artificial intelligence, at once**.

In the frame of material modelling a broad range of numerical tools presently exist. From the atomic scale to the microscopic one, an incomplete list could be; *ab-initio* techniques, Molecular Dynamics, Monte Carlo models, discrete element methods. These simulation tools have in common to make few (or no) assumptions and are frequently identified as reference techniques. However, their implementation is often delicate and strongly dependent of the considered problem. These techniques belong to the family of "discrete methods" and get their name from the small scales for which they apply.
Oppositely, when system size becomes larger or when several physical coupling should be taken into account these methods are no longer applicable with the current numerical resource and other techniques must be used. The latter ones belong to "continuum methods" and the material is considered as an equivalent media with homogeneous and averaged properties. These methods are commonly used for engineering purposes; the widely known are the finite volume methods, the finite elements, the meshless methods, etc. They are very often employed for computational fluid dynamics, heat transfer, solid mechanics etc. However, a comprehensive outlook of models and simulation tools shall also include the mesoscopic scales, at the intersection between discrete and continuous behaviour. They explain the transition of fundamental transport properties of materials when characteristic size of the system becomes of the same order as the associated mean free path of energy carriers; *e.g.* phonons in nanostructures, electron transport, ions in membranes and fuel cells, complex fluids, etc. For such applications, models and simulation tools are not well established and are frequently a compromise of discrete and continuous approaches.
On this basis, important challenges of this sub-programme will be:

1) Propose a global and versatile methodology to address and bridge atomistic and microscale features (transport properties calculation and tailoring, nanostructuration effect, interfaces, volume/surface effect, microkinetics, etc.) for innovative materials intended for energy applications;
2) Identify clearly the new ways to achieve large-scale calculations (including data mining) through Exascale High Performance Computing, machine learning and artificial intelligence.
3) Define properly mesoscales related to the applications of interest and identify the key parameters which allow the coupling between discrete and continuous modelling;
4) Work on integrated multiphysic modelling and simulation to address engineering problems related to devices and processes in connection with energy issues.

This can be considered as a possible updated roadmap to succeed in efficient modelling and simulation of materials, processes and devices. In the following, these four main challenges are listed. Each of them is subdivided into workpackages that detail the problematic, the state of the art, current progress and research efforts. We also point out their advantages and their limitations. Beside, connection and cross-cutting with the other sub-programmes, especially the application ones, is discussed.

Grand Challenges
Grand challenges were identified four years ago, parts of them were in the core of some AMPEA actions and lead to specific events such as workshop and dedicated Joint Program Steering Committee (JPSC).

Year	Challenges
5	Objective: Propose a global and versatile methodology to predict and bridge atomistic and microscopic features (transport properties calculation, nanostructuration effect, role of interfaces, volume/surface effect, microkinetics etc.) to design innovative materials with improved functionality and/or lifetime.
7	Objective: Define properly mesoscales related to the applications of interest and identify the key parameters, which allow the coupling between discrete and continuous modelling.
10	Objective: Work on integrated multiphysic modelling and simulation to address engineering problems related to devices and processes in connection with energy issues.

10	Objective: Identify the next-generation technologies (artificial intelligence, Exascale computing, etc.) which will allow breakthroughs in designing and modeling new materials for energy. This point shall address material optimal properties identification as well as in-operando behavior of new materials.
2015-2018	Achievements: • Co-organization of the joint AMPEA-EoCoE workshop entitled: "*Accelerating the energy transition: challenges in materials design enabled by recent advancements in high performance computing [3]*", Brussels June 7th, 2018. • Organization of a roundtable. • Participation to the "*EoCoE Workshop on HPC for Energy Applications* [4]", Brussels June 15th, 2017. • Organization of the Workshop entitled: "*Modeling on materials for energy devices*", University College London, June 17th 2015 • Participation to the "*EERA Inter-JP cross-fertilization workshop on materials for energy applications and technologies*", Brussels April 28th-29th, 2015.

In order to pursue the achievement of these challenges, it is necessary to differentiate the research activities and also to continue encouraging cross-fertilization events to share ideas, methods and tools.
The formerly suggested workpackages (three WP) addressing issues ranging from the small scales, which are related to the material itself, to the large scales, which characterize the devices and the processes, are recalled and updated with the achievement of the last four years. Furthermore, a supplementary WP dedicated to the new computing paradigm discussed above (AI, Exascale, Machine Learning) is added. In the latter emphasis is put on the synthesis of joint reflection between AMPEA and EoCoE.

1.1. Small scales models and tools – materials

Small scale modelling is fundamental to study and predict physical properties of materials. For the lowest scales, electrons which are responsible for the chemical bonds between atoms, govern these materials properties. Thus, the determination of the electronic structure of the considered materials and an intelligent transfer of its characteristics to higher-order scales using multidisciplinary schemes is a crucial issue. The latter one can be obtained with quantum mechanics using the first-principles, or *ab-initio* methods. These models often lie on the Density Functional Theory (DFT) which provides with very few assumptions the electronic properties of a material. Using these data one can recover various properties such as: dispersion properties, band gap in semiconductors, optical absorption spectra, thermal expansion properties, Young's modulus, *etc*. However, *ab-initio* techniques remain quite difficult to implement and are limited to atomic structures which are not too large (roughly hundreds of atoms). Therefore, they are useful to provide reliable inputs to models and simulation tools operating at "larger" small scales such as molecular dynamics or Monte-Carlo methods.
For structures such as nanowires, nanofilms, quantum dots, superlattices, *etc*. other modelling tools like molecular dynamic are well suited and allows the determination of thermal and mechanic properties. This technique lies on the monitoring of the displacement of an ensemble of atoms due to interacting forces. The latter ones usually derive from (conservative) "potentials that can be obtained either by *ab-initio* calculations or through empirical considerations. Different kind of molecular dynamic methods exists according to the targeted application. For instance, one can cite the equilibrium molecular dynamic (EMD) and the non-equilibrium molecular dynamic (NEMD). They are usually considered for thermodynamic parameters assessment and especially the thermal conductivity which is a key parameter for the design of new thermoelectric materials. Yet, it should be noted that several other techniques similar to MD exist, among them there is Monte-Carlo molecular modelling.

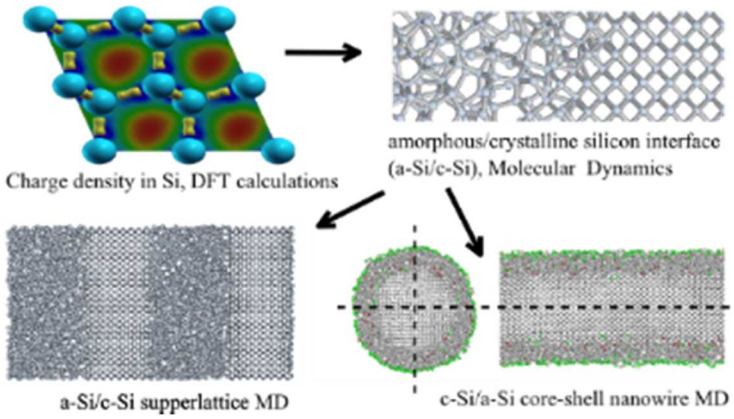


Figure 1 – ab-initio and molecular dynamics calculations for silicon

3.2 Mesoscales and large scales models and tools – devices and processes

When the characteristic size of studied material becomes large regarding to the atomic or molecular scales, small scale modelling previously discussed is no longer possible. The first reason is that computing requirement is not today available. Moreover, for mesoscales and large scales, materials are usually not perfect and it exists structures such as defects, cracks, grain boundary, *etc*. According to the parameters of interests, modelling and simulation can be carried out at mesoscales, considering local effects, or at large scales assuming homogeneous properties. In the frame of material design for energy application, techniques such as Monte-Carlo solution of transport equations can be very efficient for mesoscales, whereas numerical tools like finite volume methods, finite elements, etc are often used to solve coupled transport equations at large scales.
For mesoscale modelling it is often complex to find the "good" physics and its limits. In such a case, simulation parameters often lie on the small scale modelling results which provide the laws and/or the material constitutive relation that shall be considered. On the other hand, in the case of large scale simulations there is a plethora of numerical tools that can be used to study solids and fluids energy materials. Integrated tools like Comsol Multiphysics [5] (finite elements) or ANSYS Fluent [6] (finite volumes) can even address complex engineering problems where dedicated parameters and behaviour law appraised by small and mesoscale models can be possibly implemented. Besides, in some cases, these tools can also address chemical or species transport occurring in devices or processes. Whatever will be the chosen tools, there is often large user community involved in the development of the applied physic's softwares. This point must be kept in mind before developing new models and tools for processes and devices modelling.

An example of this type of multiscale achievement including modelling stages ranging from the microstructure description to the design of product and their in-operando use can be found in the VTT Propertune tools dedicated to encompass the concept of "factory of the future". This computing environment developed by colleagues of VTT, involved in AMPEA, is an advanced computational modelling-based material design environment. ProperTune optimises material design, replacing expensive, time consuming testing and shortening time-to-market for new products.

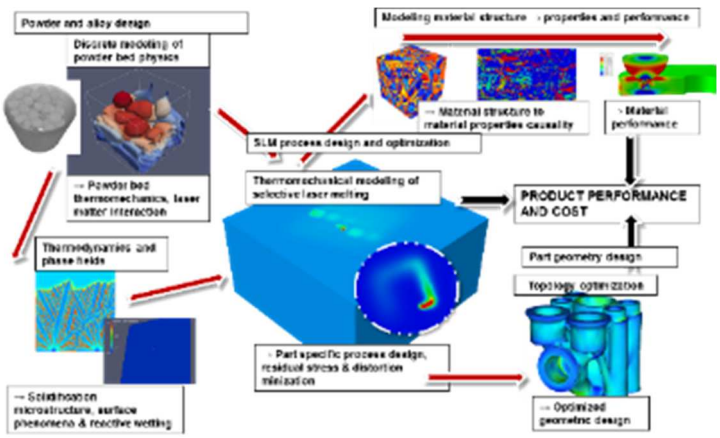


Figure 2 – Multiscale modeling for metal additive manufacturing [7]

3.3 Integration, model order reduction and applied tools

Efforts for integration of different simulation platforms will be carefully considered both in terms of prediction accuracy and capability. In several practical cases, indirect coupling or interfacing is sufficient, at least as a first attempt, to achieve data and information passing across different simulation platforms. In others, direct integration may be more valuable, but will require much more dedicated resources and advances in methodologies and simulation schemes. Some initial case studies will be considered under this WP2, as specified in the following.
In what concerns model order reduction [8] (MOR), such an approach becomes unavoidable when models and simulations point to describe the dynamical behaviour of a complex system. In this case, even if the small and large scales physics are well understood, the number of involved parameters is simply too large to be handled by the current computational devices. For this problematic, model order reduction is a way to preserve the accuracy of calculations and to decrease the computational time. There are several mathematical techniques to achieve model order reduction, the most commonly used lies on proper orthogonal decomposition methods [9] (POD). On this basis, a physical system, which is characterized by a set of partial differential equations (PDEs), is first discretized to obtain a system of ordinary differential equations (ODEs) that model the system. Then, MOR techniques can be used to reduce the number of ODEs, preserving the system original input-output behaviour. For such an approach two major issues must be considered: firstly, the reduced model must be stable to ensure numerical simulation convergence and secondly the quantification of the error generated by the model reduction needs to be evaluate. Yet, this technique can be applied to numerical prediction in a broad range of application including: fluid dynamics, material deformation, structure vibrations, etc. It could be also used for active control or optimization in process monitoring.

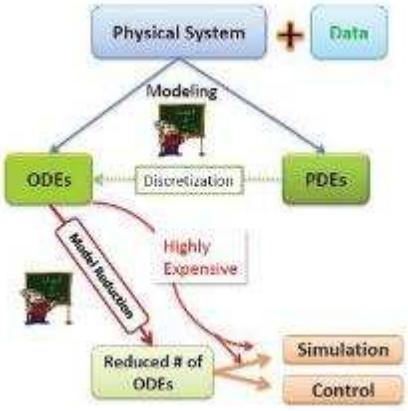


Figure 3 – Model order reduction philosophy [10]

3.4 New paradigm related to artificial intelligence, machine learning and exascale

During recent workshops hold in 2017 and 2018, and more specifically after fruitful exchanges with EoCoE representatives, several issues about new computation paradigm were raised. In the following, a non-exhaustive list of the latter is given. They are not ordered in terms of importance but shall retain attention as they could drastically change our way of designing and modeling materials for energy.

- **Material simulation is now often based on small-scale approaches, *i.e.* considering atoms and electron interactions (as discussed in 3.1)**. These so-called DFT (Density Functional Theory), Quantum Monte Carlo, Molecular Dynamics, etc. are very promising and give a very accurate understanding of phenomena that underlie material properties (*e.g.* organization of ionic liquid in pores, amorphization of thin layers on solar cells, impact of defects and substitutions in the elaboration of new catalysts, *etc.*). Yet, all these methods need important (considerable) computing resources that are not always available or remain expensive.
  Even if those methods are mostly mature, there is still work to do to increase their accurateness and to catch physical phenomena on larger systems: **exascale supercomputers could significantly play a role.**

- **Databases and material screening**. To create breakthroughs in new material discovery with the availability of HPC computing platform, numerical screening of existing material databases is very promising and is a pillar of “Mission Innovation [11]” MI-C6, through “Inverse Design”. In this approach

well-chosen descriptors can help identifying the relevant material with the expected properties. Here the following is needed:

- Standardization for information classification and data structure is needed in databases for materials science.
- The access to databases to the existing modeling tools should be improved and supported.
- Classification of descriptors in database analysis needs to be improved and new descriptors are needed to optimize material search

- **Machine learning and artificial intelligence (AI)**. If AI can appear as a complicated tool to manage for new materials exploration, especially in a whole integrated process (simulation, elaboration, characterization & feedback) suggested by MI-C6, machine learning is a key tool to accelerate computational design of materials on an integrated platform:
  - The energy material sector could largely benefit by such approaches. Indeed it could be interesting to develop materials knowledge repository for energy materials and devices (enough feedback, data to develop appropriate algorithms).
  - Issue of trial/error approach. In order to succeed in the development of a machine learning process, not only experimental/numerical techniques are needed. Errors and misleading attempts are also useful to develop a critical reasoning. New knowledge must be fed back to the scientific community and stakeholders by reporting problems, coding new types of analyses and applications, and proposing new but reliable materials for computation.

- **Exascale**. Exascale is at the core of several projects and Centers of Competences within Europe. Presently, the technology seems not to have reached enough maturity to induce a new way of designing materials, nevertheless it is undisputable that in few years, it will be available. For example, in exascale computing has just proven its efficiency in the frame of climate analytics [12]; giving an undisputable proof of the interest of this new computing architecture. Questions are now about:
  - Material design for energy is a vast area: accurate analysis is needed in order to optimize investments to be ready for the new technology. Similarly, a discussion needs to be opened in order to classify in which material science domains this technology leads to real breakthroughs. **Clear objectives** are to be defined to succeed in this evolution.
  - Not many numerical codes are ready to be ported on the new exascale architectures. A clear assessment is needed.
  - Not many scientists in materials science for energy are ready to exploit the new possibilities offered by exascale technologies. Scientific collaborations with HPC experts and communities, like EoCoE, should be largely supported.

3.5 Cross-linking with "Applications"- SP's

3.5.1 Models for artificial photo-synthesis

The simulation efforts here will be directly associated with SPA, where there is a critical need to identify mechanisms of charge-transfer and reaction pathways, in order to design and develop effective catalyst systems. Besides, the collection of light in the larger, as possible, spectrum range is mandatory to increase the performance of artificial leafs. Thus, models and simulations should take into account at small scales the interaction between photons and the absorbing materials. For these issues atomic scale modelling should provide answers concerning photon-electron interaction, electronic properties and charge transport. A peculiar attention should be paid to the design of highly efficient material in term of catalysis and light absorption. Microkinetic modelling allows estimation of kinetic parameters and identify the limiting processes at electrochemical interfaces. This is of utmost interest in this field, since by identifying the limiting processes at the electrochemical interface, new design rules for interfaces can be set-up which will allow for significantly increase performance of electrochemical devices. At mesoscales artificial photo-synthesis technology also needs models and simulation to characterize the transport properties of semiconductors which are often used to ensure the light harvesting. In this field, models and tools widely developed for photoelectric materials design (III-V semiconductors) could be useful. For example several nanostructures based on thin films, mesoporous materials or even single and coated nanowires (core-shell) are currently investigated for such application and have been already studied for electronic application. Finally, at larger scale, light collection is also an engineering problem that has been addressed by several groups and for which several simulation tools exist. They use techniques such as ray tracing, Monte Carlo solution of the radiative transfer equation *etc*. to model and optimize solar illumination on a sample or a device. A particular attention could be paid on models develop for photo-bioreactors where the optimisation of light absorption by microalgae cultures is close to the current problematic in what concerns the development of industrial solar fuel reactors.

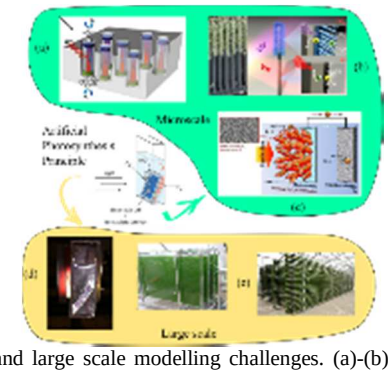


Figure 4 – Artificial photo-synthesis, micro and large scale modelling challenges. (a)-(b) Si/TiO2 core/shell nanowire arrays[13-14], (c) Schematic diagram for a photoelectrochemical cell with an hematite photoanaode [15], (d) artificial leaf prototype, (e) plate and tubular photo-bioreactor for microalgae cultivation.

3.5.2 Models for materials operating under extreme conditions

Future energy technologies place increasing demands for materials performance in terms of extremes in temperature, pressure, stress, strain, strain rate, chemical activity, electromagnetic flux and fields. Often materials fail at one-tenth or less of their intrinsic limits. Materials failure poses severe limits to efficiency, durability and operating conditions of energy devices and systems. Simulations will consider the effects of high pressures and/or high temperatures on electronic and microstructural and structural changes that lead to large variations in their integrity and functionality (e.g. physical, electro-chemical and mechanical properties). These can range from quantum mechanical, molecular dynamics, phase field and finite element approaches to tackle relevant issues at the appropriate scale domain of materials and components. Particularly for "extreme" conditions, simulation is a cost-effective tool to understand the effects of temperature and/or pressure that are hard to access or even inaccessible by experimental means.
One of the initial focusses is to look into the need for materials to withstand thermo-mechanical extremes, *i.e.* a combination of high pressure and/or high/low temperature, and high rate of impact, such as steam turbines and large wind turbine blades. Simulations can guide the design of new structures and new materials with targeted properties to withstand the extremes. Such designs require both the fundamental understanding of electronic densities, atomic structures, grain boundaries and interfaces, and more importantly, how these features change, move and interact in relation to the variation of the conditions. It is also important to develop advanced tools or simulation platforms to couple or interface simulation methodologies at the scales of interest and relevance.

Membranes for selective gas separation is another topic where efficient computational techniques along with the associated theoretical consideration and experimental results are key issue that can be usefully exploited for shortening the time from research to engineering. Theoretical analysis of target process; numerical screening approach to understand physically realistic and technologically suitable properties of membranes; atomistic modelling for the optimal material design from known materials can provide with the interfacial energetics and electronic properties, performance indicators of new materials.

3.5.3 Models for heat recovery

In the framework of heat recovery there are several challenges. The first entails optimizing existing materials, while the second encompasses finding new thermoelectric materials (composites, high temperature oxides, inter-metallics (possibly from the family of high entropy alloys)). Both are done in order to increase the conversion efficiency, determined by the so-called dimensionless figure-of-merit. Material such as bismuth-telluride (Bi_2Te_3) is presently available in thermoelectric modules and its figure-of-merit (ZT) is around unity, which leads to a thermoelectric conversion efficiency below 10%. It is believed that a ZT of 3-4, or a significant reduction in cost at ZT of 1 would lead to large-scale industrial applications.
Other challenges are related to fluids mechanics with microstructured surfaces and nanofluids that can enhance heat transfer.
One traditional way to increase ZT and thus the efficiency is to increase phonon scattering and thus reduce the overall thermal conductivity. Typically this is done through nano-structuring as illustrated in Figure 5 for a polyaniline/carbon-nano-tube composite. However, understanding and predicting the outcome of such, and more complicated concepts are difficult, both from experiments and theory. This mainly originates from the interwoven nature of transport of charge and heat, in addition to the complexities involved when describing such transport phenomena.
For instance, for oxide and intermetallic based thermoelectric, efficient thermoelectric material must have a low thermal conductivity in order to have high conversion efficiency. On the contrary, in the case of polymers heat

transport is weak as in the majority of amorphous or disordered materials. Thus, to improve heat exchange, doping with small amounts of highly conductive materials is a promising way. In this case, one as to find solutions to preserve phonon transport in channels that can be also organized at micro and nanoscales.
Multiphysics modelling applied to TEG elements is a powerful tool for materials and modules design and limits the number of experiments; numerical analysis can contribute to find the optimal geometry for the module; to solve the mechanical problem of coupling elements with different coefficient of thermal expansion; to localize the tensile stresses, etc.

Nanostructuration is one of the proposed solutions to improve materials properties (see Figure 5). However, elaboration and experimental characterization of nanostrucured thermoelectric material is not simple, and this makes the multiscale modelling a valuable way to investigate these new materials.
An important requirement for a thermoelectric material is, given a high Seebeck coefficient, a high electrical conductivity. This poses particular challenges when discovering new oxides, composites and polymers. Particularly the two latter suffers from lack of stability when doped or not reaching high enough electrical conductivity. These problems are not to such an extent present for the intermetallics, where the conversion efficiencies are presently significantly higher (but still too low for large scale applications). For the intermetallics, focus is on how to reduce the lattice thermal conductivity and optimizing the doping level to reach maximum conversion efficiency at the operating temperatures.
In all essence optimizing all these materials, independent of their type is a matter of knowing the details of all transport coefficients at different temperatures; the electrical conductivity, the Seebeck coefficient, the Hall coefficient, the lattice thermal conductivity and the thermal conductivity associated with the electrons. Usually, the problem, after performing electronic and phononic structure calculations, condenses down to determining the scattering properties of electrons and phonons. This is still a largely unresolved issue and significant approximations are made at this step, which in many cases renders direct comparisons with experiments or indications of conversion efficiencies not so convincing. However, these studies are still somewhat useful, if one is set to compare rather similar materials.
These issues are further magnified by the fact that there is no unified theory or understanding of transport, particularly electron transport of inter-metallics, metals and semiconductors, and oxides, composites and polymers. Typically two different viewpoints are used; transport by free carriers, or transport by transfer of charge, for the latter and former class, respectively.
There is no denying that solving these issues would greatly magnify the predictability in material science, as most functional materials utilize transport of charge or heat in some way or another.

Multiscale modeling is in addition to solving the problems above, a necessary tool to investigate these materials. It is particularly important when we start to investigate amorphous, heavily distorted materials, interfaces etc., where standard crystal theory hardly can be used.

For microstructured surfaces and nanofluids, multiscale modelling is also essential. For such problematic common large scale laws, that are usually considered to predict heat exchange coefficient, are no longer valid, especially when the size of fluid channels is below the millimetre. On the other hand when looking at the nanofluid properties, constitutive relations that define the viscous behaviour or the thermal properties need to be reconsidered.

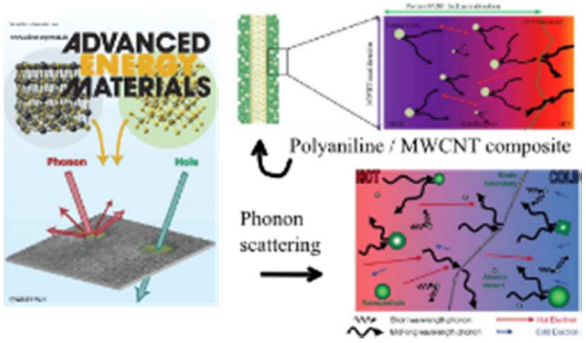


Figure 5 – Tuning phonon properties in materials. Cover of Advanced Energy Material (Vol. 2, No. 9, September 2012). Polyaniline / MWCNT composite [15]. Phonon scattering mechanisms [16]

Main Milestones and deliverables for this activity

Period 2014-2018 (in DoW 2014)

MS number	*Title*	*Time*
M2.1	*Sub-programme 2 objectives and contents*	*Year 1 (2014)*
M2.2	1st Workshop on materials for energy and tools used to model them. Inventory of the existing tools and identification of the reliable techniques. Determination of one (or more) reference material for benchmarking in connection with the EERA JP.	*End of Year 1 (2014)*
M2.3	Identification of working groups. Task sharing on model evaluation (benchmark cases) and suggested SP applications modelling and simulations actions.	*Year 2 (2015)*
M2.4	Implementation of 3 pilot projects on the identified actions, at least one per Application SP and possibly with other JPs according networking actions.	*Years 2-4 (2015-2017)*
M2.5	2nd Workshop, presentation and evaluation of the collaborative works achieved on benchmarks and applications. Updating the SP2 DoW and related action plan.	*End of Year 3 (2017)*
M2.6	Organization of an international summer school on modeling issues on materials and processes for energy	*Year 4 (2018)*

Achievements:

	Title	*Year*
	Participation to the "*EERA Inter-JP cross-fertilization workshop on materials for energy applications and technologies*", Brussels April 28th-29th, 2015	*2015*
	Organization of the Workshop entitled: "*Modeling on materials for energy devices*", University College London, June 17th 2015	*2015*
	Participation to the "*EoCoE Workshop on HPC for Energy Applications* [4]", Brussels June 15th, 2017	*2017*
	Co-organization of the joint AMPEA-EoCoE workshop entitled: "*Accelerating the energy transition: challenges in materials design enabled by recent advancements in high performance computing [3]*", Brussels June 7th, 2018. Organization of a roundtable.	*2018*

The efforts here are in close association with those in other EERA JPs. Several discussions have been held with JP on Nuclear materials (Professor James Marrow), JP on Energy storage (Professor Peter Hall), and JP for CO_2 capture and storage (the UIK partner - UK CO_2 capture network). Such interactions will lead to joint workshops and project applications in the near future.

One successful example has been the award of a recent grant under FP7 on Multiscale Simulation Platform for CO2 capture in Chemical Looping Processes. This is led by one of the AMPEA partners, SINTEF, in collaboration with AMPEA members and those outside the consortium. Such an example offers worked experience for consortium proposals in the future, particularly under the Horizon 2020 programmes.

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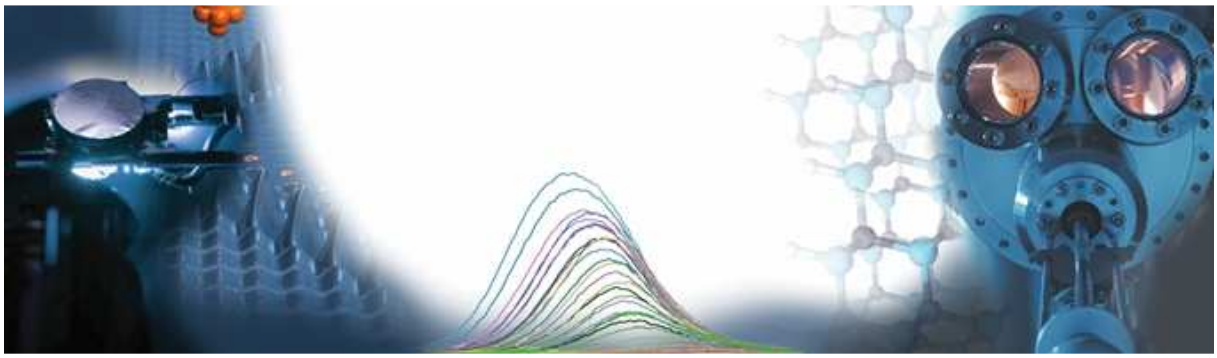
EUROPEAN ENERGY RESEARCH ALLIANCE



SUB-PROGRAMME TOOL 3: *Characterization*

A sub-programme within the
AMPEA EERA Joint Programme

Description of Work

Sub-programme coordinators:
Astrid Besmehn, FZ Jülich and Amelia Montone, ENEA

Last modification date: *November, 12th 2018*

Advanced experimental characterization and analysis are considered absolutely essential for significant advancing of materials and processes for energy applications. Development of today and tomorrow's key experimental techniques is complex, requires multidisciplinary skills, is costly and takes long time. Consorted efforts involving teams of technique experts, material scientists and engineers are thus required and a joint European program is considered an optimal route towards this goal. Furthermore synergetic use of multiple techniques is in most cases beneficial which underpin the need for joint European actions even more.
SP3 establishes a characterization platform for the other sub-programs. As AMPEA deals with new, sophisticated materials in inorganic and organic fields with some of them are applied under extreme conditions also sophisticated characterization techniques and strategies are necessary. Therefore a network of facilities with sophisticated instrumentation is established in this sub-programme. In addition the joint actions of the platform include the improvement and development of techniques and instrumentation in the areas of *in situ* and *operando* characterization in the time scale and nanometer resolution in 2D and 3D at a wide range of temperatures and pressures.
The main objective of SP3 is twofold:
I) to create a forum which can help the experimental experts to be world leading in developing the best possible new advanced characterization techniques for the scientific problems in mind. This will include meetings and workshops focusing on technique aspects, platforms for exchange of analysis and imaging software, and dedicated meetings between technique experts and scientists within the other subprograms to quantify optimal technique parameters, *e.g.* spatial and time resolutions, penetration depths, temperatures etc.
II) to provide one entry point to the suite of advanced techniques and thus help the users to get an overview of experimented possibilities. This will be addressed in the future via a dedicated web page.
This subprogram represents a European added value in the sense that it is expected to lead to:
- Synergy in developments of advanced experimental techniques with special attention to *in situ* and *operando* techniques,
- Further use of multiple complementary techniques,
- Establishment/consolidation of European networks for technique developments,
- Cross fertilisation between technique experts and materials scientist,
- Time and money savings.

Clean and sustainable energy is one of the major challenges that European society has to face in the coming decades. The AMPEA EERA Joint Programme covers some of the most innovative elements to approach this challenge. It includes the immensely promising field of artificial photosynthesis, wherein chemically-stored fuels, such as methanol and hydrogen, are synthesized directly using the energy originating from the sun. But most innovative also means highly challenging. Materials for extreme conditions, and responsive nanostructures for direct conversion by photocatalysis are only two examples that demonstrate both aspects, and it is not only the challenge to invent something but also the necessity to develop these materials and systems in order that they become marketable. Multilayered systems encountered in e.g. gas separation membranes, fuel cells and electrolysis technologies bring new challenges to determine and tailor contribution of interfaces to their functionality. These interfaces could be solid/solid, solid/liquid or even solid/gas and demand a complete understanding of physical and chemical processes involved. In addition the structure/function relationship is not only important for materials development (materials by design) but it demands analytical tools which could gain the relevant information on all length (nano to macro) and time scales (seconds to years). Typically energy generation systems have life time between 20-50 years. On this time scale degradation processes especially for energy generation in harsh environments (e.g. high temperatures or corrosive gas) play an important role. Materials development for such conditions need the help of life time predictions by simulation but also a complete understanding of the degradation processes involved. Therefore accelerated aging testing methods are needed to support materials optimization and modeling of such systems.

The challenges regarding characterization in the above mentioned topics are manifold and depend strongly on the energy generation techniques. Therefore analytical tools are needed, which deliver a complete understanding of the physical and chemical processes involved in materials/interfaces systems close to operation conditions. In conclusion there is a demand for in-situ, operando experimentation and testing, on all length- and timescales relevant for understanding the mechanisms as well as the processes associated with energy generation (and storage) in real operating conditions during device life time.

Materials used for devices in energy generation and direct conversion by e.g. electrocatalysis, photocatalysis or photoelectrochemistry have to deal with chemical reactions occurring on the nanoscale at ambient pressure in different gas atmospheres and a wide range of temperatures (room temperature up to 1000°C and more). In order

to optimize these materials a complete understanding of all involved processes at the molecular level in the timeframe of individual chemical conversions is required. This includes transport mechanisms in bulk materials (e.g. grain boundary segregation) as well as at interfaces (e.g. gas adsorption at and gas diffusion in surfaces), which is also relevant for advanced functional materials for electrochemical based technologies. To imitate nature's success in photosynthesis, we need to be able to design responsive matrices: components that are out of equilibrium in a controlled manner and use a combination of classical and quantum coherence for providing fast and efficient channels to thermodynamic irreversibility in photocatalysis.

Therefore when developing materials for energy applications we need *in-situ* and *operando* characterization techniques to understand the processes involved, supply data for modeling and support the supply chain from basic understanding to market.

Presently lots of focus is on developing tools for 3D, in-situ/operando characterizations of materials and complete devices as well as on imaging techniques for nanoscience. In addition methods, which allow to determine the structure/function relationship on a very local scale, gain more attention. This is due to the fact that many critical processes are governed not by the average behavior but by "the weakest link". Examples of the latter are formation and development of cracks as well as interface problems in e.g. batteries or fuel cells. Natural systems are the product of historical contingency in the biological evolution and exploit well-defined chemical paradoxes induced by folding and self-assembly of nanostructured molecular complexes, on a scale of 1-100 nm. Underpinning of the design of such dynamic materials with complex energy landscapes for artificial photosynthesis applications will require 3D volume reconstruction methods based on computational integration of diffraction, spectroscopy and imaging data across length scales, and with sub-Angstrom resolution in essential details.

The idea of this sub-programme (SP) on *"Characterization"* is to create a European platform to benefit of technique development and scientific use of the advanced experimental techniques available in the partner's laboratories and facilities. It will supplement other large scale European initiatives, as it will contain more experimental techniques. The focus is on synergetic use of multiple techniques and will be driven by the specific scientific needs in the other sub-programmes. Close coordination between activities in the various initiatives shall however, be assured.

The scope of the SP is broad as the applications are broad and involves different subfields:

1. development of entirely new (designed) materials
2. behavior of materials under extreme conditions
3. molecularly designed systems
4. solid-state components
5. nature guided designs
6. nano-/microstructures to design materials properties and device functionality
7. interfaces to minimize loss contributions that currently limit device performance

Numerous breakthroughs lie in the collaboration between the subfields. In another dimension the development will be driven by understanding.
In some cases experiments may document behaviors quite different from model predictions. Examples of this are in-situ non-destructive 3D experiments, which have revealed phenomena which could never have been predicted based on traditional 2D static characterizations and therefore not by the theoretical models developed based on the 2D data. The new experimental observations in this case stimulate new generations of models. Especially for aging and for complex process understanding like for example in solar energy conversion to solar fuels there is a need for structural, chemical and physical information with high lateral resolution *in-situ* and *operando*.

A network of advanced characterization platforms dedicated to studying materials and processes for energy will be needed to support this work for the *in-situ* and *operando* characterization by methods from laboratory scale and large scale instrument facilities (*e.g.* synchrotron and neutron reactor facilities). There is definitely a need for a European initiative to support the research on such complex topics.

Finally this also fits into the framework of joint development of new approaches on the EMIRI roadmap and will therefore support the European approach. It is well in agreement with other European approaches of using large scale infrastructures, here ESFRI, where a close collaboration is necessary. The platforms developed will of course support many other EU programs in more conventional approaches to solve the energy challenge of the European society.

We propose a joint use of available specific characterization techniques as well as the development of dedicated experimental characterization techniques defined by the application platforms, in improved as well as new energy systems and materials. This subprogram will be developed in synergy with the other subprograms. This should cover the whole experimental range including beamlines and instruments at international large scale facilities, as well as auxiliary equipment for example test of specific systems on existing instruments, advanced electron microscopy, and techniques for measurements of physical properties and chemical conversions under the relevant conditions. One Focus will be on developing advanced tools for *3D, in-situ* and *operando* measurements as well as tools for mapping/imaging the structure or properties on the relevant *time and local* scales.

Another focus will also be on *synergetic* use of multiple techniques to provide complementary views of a single structure, process or component in special or multi-sites within the European Science community. The future of characterization is proposed to be one where not only individual techniques are pushed to their limits but where the community devises strategies of technique synergy to address complex multiscale problems in materials and systems, covering length scales from the dimensions of atoms to macroscopic engineering components and for time scales ranging from sub-picoseconds to hours and beyond.

The present activity will support analytical instrumentations, which are non-common (and mostly not commercially available) and of general importance for many institutes either as they are only available in few sites or are part of large scale facilities.

The work program of the AMPEA-EERA sub-programme 3 *"Characterization"* lists available technologies, which are already in use for the joint work as well as technologies currently under development/construction. Finally a top down process from challenges to milestones shows the next steps. At the end there is an outlook of future demands for supporting the other programs of AMPEA-EERA.

Existing advanced techniques will be made available to the JP and synergetic use will be discussed and facilitated for the various scientific challenges. So far the available techniques include:

Technique	**Place**	**Description**	**Keywords**
3DXRD	ESRF, SLS, CELLS (ALBA Synchrotron)	Fast structural characterization of materials in 3D. Good for in-situ measurements of structural changes in the bulk of relatively large samples during exposure to external stimuli such as strain and temperature. Spatial resolution in µ m range	In-situ / in-operando (small systems) 3D Local measurements
In-situ SANS and SAXS	LLB, ILL, ESRF, SLS, HZB SINQ	In situ and behavior study of water management in fuel cells by small- angle neutron and X-ray scattering	In-situ behavior Time resolved Spatially resolved
In-situ XRD, SAXS	SINTEF	XRD equipped with a PIXcel3D detector. Measurements in both reflection and transmission mode. A hybrid monochromator can be used for SAXS. A XRK 900 reactor cell from Anton Paar for in situ measurements. In-situ measurements can be performed in various gas flows, steam or vacuum at 20- 900° C and pressures up to 10 bar.	In-situ/operando XRD
In-situ neutron diffraction	ILL, SINQ, TUD	In-situ determination of Li or H2 diffusion in solid materials such as insertion electrode or metal hydrides	In-situ
In-situ NDP	TUD	Neutron Depth Profile for in-situ determination of Li profile in operating batteries	In-situ / operando

In-situ thermochemical XPS	SINTEF, SLS, CELLS (ALBA Synchrotron), CSIC	In-situ and near in-situ thermochemical treatment of surfaces (-150 °C to +600 °C in UHV conditions, +25 °C to 1000°C at 1bar inert, oxidizing or reducing atmospheres) during or prior to analysis with x-ray photoelectron spectroscopy	(near) in-situ, XPS, surface/interface chemistry
In-situ X-ray absorption and emission spectroscopy	SLS / ESRF, CELLS (ALBA Synchrotron), CSIC	Element-specific electronic and geometric structure determination of functioning materials; solid, liquids, gases, pressure up to 100 bar; temperature up to 1000ºC. Time-resolution in 100 msec range. Space-resolution in µm range.	In-situ, time- and space-resolved; XAS, XES; combined methods

3D XRF / tomography	SLS	3D chemical speciation and sample density	
AP-XPS	FZJ	temperature up to 900 °C with corrosive gases under oxidative conditions - monitoring of chemical conversions on surfaces	In-situ characterization of chemical reactions at ambient conditions
TR-AP-XPS	FZJ	temperatures up to 1200°C in various gaseous environments with 1s time resolution	In-situ study of catalytic processes
High resolution X-ray Computed Tomography (CT)	ENEA	High resolution, high accuracy Non-destructive testing and failure analysis	Internal structure Geometrical information Failure analysis

IBA	DIFFER	IBA techniques yield quantitative, isotope-sensitive and depth resolved compositional (stoichiometric) analysis of materials, up to micrometers deep into the material. Typical methods: Rutherford Backscattering Spectrometry (RBS), Elastic Recoil Detection (ERD), Elastic Backscattering Spectrometry (EBS), Particle Induced X-ray Emission (PIXE), Particle Induced Gamma-ray Emission (PIGE) and Nuclear Reaction Analysis (NRA)	quantitative and qualitative material analysis, stoichiometry of complex oxides, thickness and interface characterization
Micro-IBA	Saclay	Light element (H, He, Li, C, …) distribution in solid materials with isotopic sensitivity	IBA keywords + operando analysis, isotopic tracers
INA	TUD	Activation analysis, quantitative distribution in solid materials with isotopic sensitivity	
ToF-SIMS	SINTEF	Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) (instrument Trift V nano TOF from Physical Electronics) allows detection of small amounts (down to 1 ppm) of any element (including H) or molecule on a surface. The lateral resolution is below 1 µm, so chemical maps can be made, showing where a certain element or molecule is present. The instrument has a built-in Focused Ion Beam (FIB) which can cut into the sample surface and reveal the three-dimensional structure of the material. In situ heating/cooling.	High sensitivity, ppm level surface analysis, 3-D information
Helium Ion Microscope (HIM) Orion Plus Zeiss	ENEA	microstructural and microanalytical	high resolution characterization
In-situ TEM	DTU	High resolution characterization of TEM foils. Good for in-situ measurements during loading in Hysitron stage and in natural gas flows	In-situ Local measurements
3DTEM	CEA-PFNC	Structural characterization of materials in 3D by transmission electron microscopy used in many domains of materials for energy (Fuel cells, batteries, PV,…)	3D TEM

HREM	HZB	High resolution analytical TEM with < 0.8 Angstrom resolution, equipped with advanced EDX system as well as energy loss detection system	Local measurements
HREM, in-situ thermal and electrothermal analysis at ambient apressure and high temperatures	SINTEF	0.2 eV energy resolution in EELS (at 200 kV) •Aligned for 60, 200, and 300 kV accelerating voltages 0.8 Å spatial resolution in STEM (at 300 kV) •Super-X EDS detector: 0.7 srad collection angle. Windowless design allows superior light element detection •High brightness XFEG 2.0 Å spatial resolution in TEM (at 300 kV) Protochips Fusion 500 Double tilt holder with MEMS-based E-chips for in-situ thermal and electrothermal TEM analysis. Heating up to 1200 °C Protochips Atmosphere gas cell system: allows high spatial resolution S/TEM imaging, EELS and EDS at ambient pressure and high temperature. Supplies experiment gases at pressures up to 1 atm, temperature between room temperature and 1000 °C at any pressure within operating range	Local measurements, atomic resolution structural and chemical resolution, in situ thermochemical analysis, ambient pressure
Probe and image corrected HREM	SINTEF	Cold field emission gun with energy spread of < 0.3 eV Fully aligned at 80 and 200 kV Cs-probe corrector (Resolution in HAADF < 1Å) Cs-image corrector (Resolution in HRTEM < 1 Å) Holders: single tilt holders, single tilt reinforced, double tilt holders (+- 30 degrees), double tilt reinforced, cold stage holder, heating holder, enviromental cell/transfer holder, tomography holders and a rotation holder.	Local measurements, atomic resolution
HR FEG-SEM	SINTEF	STEM FEI Nova NanoSEM 650, with large sample chamber (up to 15 cm in length), high throughput EDS, EBSD analysis, in-situ tensile testing.	Versatile SEM, high throughput EDS, in-situ mechanical testing.
3D EBSP	HZB	3 D tomography based on EBSD and (new 3 D EDX analysis system) based on Auriga Zeiss FIB equipment Gold based sputtering source for Auriga FIB system to prepare TEM samples based on Li- Ion storage devices as well as Al- based alloys	3D, local measurements
Ultra-high- resolution on the Titan PICO TEM	FZJ	structural and chemical characterization	Resolution to atomic scale
Titan HOLO TEM Titan ChemiSTEM TEM	FZJ	in situ electrical biasing of photovoltaic devices Equipped with a four-quadrant EDX detector	In-situ with high resolution Chemical information
3D Laser flash at High Temperature (H.T.)	LEMTA, Nancy CNR ICMATE Padova ENEA	3D Laser Flash method thermal characterization of solids from 300K up to 1300K. Thermal diffusivity measurement of anisotropic materials in its 3 directions. Iverse technique and a 3D theoretical model Heat pulsed by CO_2 laser beam (130 Watts). The temperature field recorded through a fast FPA cooled Broad-Band Infrared camera with a very high sensitivity (InSb 1.5µm-5.5µ m). Thermal diffusivity measurement up to 1600°C	Thermal diffusivity Thermal conductivity Specific heat values High temperature Inverse technique Infrared Camera

USC Autoclaves	VTT, Espoo	Autoclave for USC conditions up to 695°C/420 bar and for doped steam environments up to 400°C/150 bar • Computerized water chemistry control with high temperature pH, conductivity, corrosion and redox potential monitoring • Novel high accuracy bellows e.g. for fatigue and creep-fatigue crack growth testing in demanding simulated or actual service environment • Impression creep testing facilities for determination of local creep properties, such as heat affected zones in welded joints • Electrochemical corrosion monitoring and surface characterization, e.g. EI/CEI/CDE measurements for in-situ characterization of surface films at high pressure and temperature • High temperature probes for continuous boiler fouling, heat balance and electrochemical corrosion monitoring	Corrosion, creep
Pressurised LN_2 characterization 64-124K	University of Cambridge	Electric transport measurements in magnetic field in liquid nitrogen in the range of temperatures 64K-124K • Cryosorption • I-B characterization at extreme cryogenic conditions	Pressurized Liquid nitrogen , Cryogenics
Ultra high magnetic field transport characterization facilities "CryoB-Impulse"	University of Cambridge	Electric transport measurements at 32Tesla using 16 ms pulsing facilities. Pulsed transport current 1kA. • Materials ehavioursation, • Magnetisation, • Transport properties at low temperatures	High magnetic field, cryogenics, high current, Pulse magnetic field
3D Volume reconstruction	Leiden NECEN uNMR	Computational integration of MAS NMR and TEM with modeling from sub-Angstrom to the mesoscale level. characterization of fast channels to thermodynamic irreversibility in photocatalysis	Characterization of responsive matrices
Photochemistry analysis platform	Leiden NECEN uNMR	Computational integration of optical spectroscopy, magnetic resonance, Mossbauer and other spectroscopic methods for determining optimal mechanisms for chemical energy conversion	Characterization of responsive matrices
Liquid and solid-state NMR	SINTEF	Instrument for liquid samples (9,4 Tesla magnet, 400 MHz) Instrument for solid samples (11,7 Tesla magnet, 500 MHz) Most NMR active nuclei can be studied Possibilities for variable temperature experiments (77K – 623K) A gas flow probe can be used to study gas-solid reactions up to about 623 K at 1 atm pressure.	In-situ solid & liquid state NMR
WLI	SINTEF	Performances vertical axis: Scanning range:>7300 µm(PSI-mode:130nm). Resolution: 10 nm (PSI-mode: 0,5nm). Scanning speed:~ 5s for 50 µm scanning depth. Performances lateral dimensions: Measurement area: from 62 µm x 46 µm to 4.5 mm x 3.4 mm depending on magnification. Resolution: Down to ~0,5 µm (near optical limit resolution). Pixels / image: 640 x 480 pixels. Maximum sample size: 700 mm (or more) x 300 mm x 100mm (x-y-z). Maximum coverage: 200 mm x 200 mm. Sample weight: <30kg. Reflectance >2%,	Surface topography
Micro Material Tester (UMT-2)	CNR ICMATE	Reciprocative Tests (ASTMG133) Rotary Tests (ASTMG99) Tribocorrosion Tests (ASTMG119) Scratch Test under constant or progressive load (UNIEN1071-3)	Wear, Scratch, Tribocorrosion

Impedance Spectroscopy	CNR ICMATE	Electrical characterizations of ionic conductive materials (up to 1100°C)	Electrical characterization
Thermoelectric characterization	CNR ICMATE	Simultaneous determination of thermal conductivity and electric properties (conductivity, thermoelectric power or Seebeck coefficient) up to 800°C	Thermal conductivity Electric properties
4-wire technique Van-der-Pauw technique	CNR ICMATE	Measurement of contact resistance and dielectric constant	Contact resistance Dielectric constant
Thin Film Analyzer (TFA)	ENEA	Electrical, thermal, and thermoelectrical characterization (-170°C up to 300°C) Thermal conductivity, electrical resistivity, Hall coefficient, Seebeck coefficient, power factor, thermoelectric figure of merit, Van-der-Pauw method 3ω in-plane and cross-plane characterization	Thin films Sheet resistance Seebeck coefficient Hall coefficient Thermoelectrical characterization

A series of new techniques will be developed in the near future by various partners in this JP. Moreover, instrumentation to enable in-situ and in-operando characterization, such as under (extreme) pressure and controlled temperature will be developed and made available. Here an expert forum will contribute with technical discussions advices and exchange of expertise and dedicated meetings between technique experts and scientists within the other sub-programmes shall facilitate quantification of optimal techniques parameters. The techniques presently in preparation are:

- **EMIL (HZB):**

This set-up will be a dedicated analysis system for solar energy materials and catalysts involving two beamlines at the BESSY II synchrotron facility in Berlin, Germany. A cluster tool for the deposition of thin film solar cell materials and the preparation of catalysts will be combined with state-of-the-art X-ray and electron spectrometers in a single UHV- environment. The unique feature of this set-up will be the availability of brilliant X-ray x-radiation from 60 eV to 10 keV, allowing depth-dependent PES measurements in an unprecedented energy range. Furthermore, the in-system preparation will allow step-by-step deposition and analysis of thin film devices and their components without contamination by air. The same set-up will also be used for *in-situ*, high pressure PES on catalytic surfaces, allowing the monitoring of chemical reactions at surfaces under realistic operating conditions.
The EMIL laboratory was opened in October 2016 with a core instrumentation for thin film deposition and laboratory X-ray sources for photoelectron spectroscopy. These facilities have been usede extensively since then, with continuous addition of instrumentation. The UE48 undulator for soft X-rays delivered the first light in October 2017 while the hard X-ray CPMU17 undulator, which is a specially developed in-vacuo, liquid nitrogen cooled insertion device, was installed in summer 2018. First light is expected early in 2019 and first “friendly users” at the end of 2019.

- **Photoacoustic device (CNR ICEMATE)**

For a more precise determination of the thermal diffusivity of liquids, a photoacoustic device has been designed and realized. This system allows measurements up to 75 ° C and turns out to be more sensitive compared to more traditional techniques. In fact, the measure of the thermal diffusivity is not related to the absolute measurement of the thickness of the liquid, but depends on its variation during the measurement. The detector is a photoacoustic chamber to which a high-sensitivity microphone is connected. The device is operative (2018).

- **XPS spectrometer coupled with (near)- in-situ thin film deposition (SINTEF, Norway):**

Near in-situ deposition of thin films via sputtering and evaporation techniques will enable the study of chemistry, composition and electronic structure as well as the growth mechanism of thin films and the formation of interfaces via X-ray photoelectron spectroscopy without samples getting in contact with ambient (vacuum/controlled atmospheres). The deposition apparatuses will be connected to a ThetaProbe XPS instrument capable for parallel angle resolved analysis (depth resolution of ~ 1nm), series elemental and chemical state imaging (spatial resolution ~3µm3 ~µm). The technique is designed for in-situ, gas-solid liquid/solid interaction, nanoscale and is expected to be operative by 2020. Micro- X- ray synchrotron analysis up to 800 to 900 °C and resolution

of < 50 nm and of high resolution localized in situ stress analysis of high temperature materials and composites.

- **Probe corrected TEM/STEM (*SINTEF/NTNU*):**

"Built in" correction for the spherical aberrations of the condenser system allowing for sub- Ångstrom resolution in scanning mode (atomic resolution in crystalline materials), has become operative in part.

- **Remote Scanning Electron Microscopy (SEM)**

A remote control system for SEM through internet is available at ENEA Casaccia laboratory. A SEM ZEISS EVO MA 15 equipped with EDS microanalysis can operate in high vacuum and in variable pressure operation is used. Collaborations and training are easily possible by WEB-SEM.

- **HEMCP (Helmholtz society):**

The Helmholtz Energy Materials Characterization Platform (HEMCP) is designed as an infrastructure platform for 4D information (space and time) on structural, electrical and chemical properties under preparation and operating conditions (in-situ / operando) of materials related to energy research. HEMCP will focus on materials characterization, exploring the following issues:

- In-situ characterization of chemical and electronic properties of thin films, surfaces and interfaces
- Structural characterization and multiscale simulation of functional nanostructured materials for energy applications
- Characterization of materials for extreme thermal and mechanical loading conditions
- Development and utilization of sophistically combined and in situ-characterization methods during materials processing and operation.

Grand Challenges:

Grand challenges were identified about four years ago, parts of them were in the core of some AMPEA actions and lead to specific events such as workshop and dedicated Joint Program Steering Committee (JPSC).

Year	Challenge
2020	In-situ, operando characterization of materials and individual molecules
2025	In-situ, operando characterization of systems and devices
2025	In-situ, operando accelerated testing of materials, devices and systems
2030	new products entering the market, support for industry in real world challenges

In order to pursue the achievement of these challenges, it is necessary to differentiate the research activities and also to continue encouraging cross-fertilization events to share ideas, methods and tools.
Achievements with regard to the Grand Challenges are listetd below.

Achievements:

Title	*Year*
Talk on HEMCP on the 5th AMPEA JPSC with scientific session FZ Jülich, Workshop "Materials for Energy Devices I"	*2014*
Organization of one session dedicated to advanced characterization techniques on the7th AMPEA JPSC with scientific session UCL, Workshop "Modelling of materials for Energy Devices	*2015*
Organization of the "Materials" session on the EERA Conference, Birmingham, UK	*2016*
Co-Organization of the scientific session on the 13th AMPEA JPSC with scientific session; HZB Bessy II "Synchrotron Radiation and Neutron Scattering for Energy Materials"	*2018*

Discussions during the above mentioned workshops and conference still show the importance to go for suitable *in-situ* or even better *operando* analytical techniques.
Development of such tools is a cost- and time-consuming task. Therefore SP3 would provide a forum for discussion in tool development, drawbacks and new outcome with respect to *in-situ / operando* characterization. On the other hand the needs of material scientist must be identified and addressed by the experimental scientist. Cross fertilisation workshops, which were already organized in the past, will be organized in the future. These workshops could either be material or analytical driven or even both. A combination with JPSC meetings are favourable.

AMPEA-EERA joint program consists of sub-programmes with a stronger application focus and subprogrammes with a strong of focus on methods, like SP3 with its focus on characterization. The interface description is given in the table below. In-situ and operando characterization with a focus on high resolution materials and time and temperature variation is essential for the work of the application driven sub-programmes.

The provided characterization tools support always at least two mainly all other application sub-programmes as given by the table:

Sub-programme	X-Ray/ Neutrons	EM	NMR/MRI	High Temp, Charact.	Low Temp. electromag.	Special (Ions, Nuclear)
A	X	X	X		X	X
B	X	X	X	X		X
C	X	X			X	X
Other emerging fields	X	X	X	X	X	X

A: Artifical Photosynthesis, B: Materials for Extreme Conditions, C: Advanced Materials for Heat Exploitation and Energy Conversion

In management the coordination of the joint sub-programmes and the programme is performed by a series of workshops and by routinely meetings, and video- and telephone conferences, respectively. The joint understanding which has been formed during many interpersonal exchange during recent years will be transferred to a webpage for additional colleagues within the European Scientific community to enter the process, the establishment of an expert forum to discuss the development of new technologies, their possible synergies and make the joint knowledge available for the scientific community. Joint characterization of materials bringing together the knowledge of the characterization expert on one hand and the application expert on the other hand are the next step in the process.

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3. ESFRI: European Strategy Forum on Research Infrastructures, http://ec.europa.eu/research/infrastructures/index_en.cfm?pg=esfri
4. HEMCP: Helmholtz Energy Materials Characterization Platform www. hemcp.de

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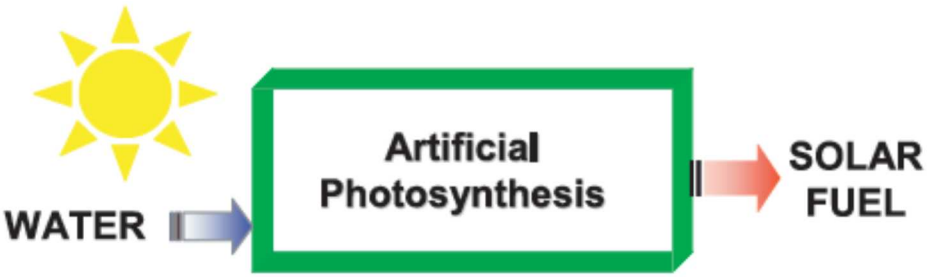
EUROPEAN ENERGY RESEARCH ALLIANCE



SUB-PROGRAMME APPLICATION A: *Artificial photosynthesis*

A sub-programme within the
AMPEA EERA Joint Programme

Description of Work

Sub-programme coordinators:
Sebastian Fiechter, HZB and Winfried Leibl, CEA

Last modification date: *November, 12th 2018*

Abstract sub-programme A ”Artificial Photosynthesis”

The generation of fuels from sunlight and water is considered as a task of paramount importance for a sustainable energy supply in the future. Decomposition of water by a photoelectrochemical process is a possibility to store solar energy in form of hydrogen on a large scale. Alternatively, the electrons and protons recovered from water can be used for CO_2 reduction and hydrocarbon production. In both cases the catalysts for the oxidation and reduction half-reactions have to be developed and the two processes combined in a suitable device.

For a **direct photochemical energy conversion**, two main approaches can be distinguished. **Molecular approaches** using a plethora of catalysts for oxidation and reduction interfaced with different chromophores for their activation by visible light [Ashford CR 2015]. Similarly a broad range of **materials** have been developed based on low-bandgap semiconductors and co-catalysts [1]. For a practical use, these photocatalytic systems can be incorporated in a photoelectrochemical cell (PEC) device rather than be used in homogeneous phase. A third approach is based on an **indirect conversion** process by combining solar cells with electrolysis systems. For these systems, different degrees of integration can be envisioned and their advantages and disadvantages discussed [2]. Examples for a highly integrated system are multi-junction photovoltaic devices with catalyst layers for oxidation and reduction on both surfaces, frequently addressed as an artificial leaf.

Independent of the chosen approach it became clear that any economically viable solution for solar fuel production has to meet three essential criteria: high efficiency, high robustness and low cost. The latter criterion is sometimes replaced by “scalability” to take into account elemental abundance, raw material cost, and capital costs [3].

To establish research activities on an European level from basic aspects to working devices, a Description of Work and Roadmap on this topic within the AMPEA EERA Joint Programme addressing molecular, inorganic and hybrid approaches is formulated.

1. Introduction

Technologies leading to efficient conversion and storage of sunlight energy into chemical energy open the unique possibility of providing a renewable and sustainable energy supply in Europe based on the nearly infinite radiation energy of the sun. While the availability of renewable energy sources is highly fluctuating – depending on the presence of sunlight or wind – this converted energy can be used as a power source for all kind of applications with no constraints in time. For this purpose, it is envisioned, in the framework of an AMPEA application [4], to develop a device which is able to split water into hydrogen and oxygen when illuminated by sunlight. Such a device should - from an economic and environmental point of view - consist of cheap, abundant and non-toxic elements featuring a Solar-to-Hydrogen (STH) efficiency > 10% and achieve a price of ~3-5 €/kg H_2 (DOE and EU target, resp.) Fuels, which are necessary to provide mobility, can be obtained either by replacing the proton reduction by CO_2 reduction catalysis or by converting the hydrogen harvested from sunlight into hydrocarbons in a second step.

Among biomimetic approaches using inorganic systems, one possible solution is the conversion of sunlight into chemical energy via photonic excitation of a photovoltaic thin film, directly combined with corrosion-stable layers of electrocatalysts at its front and back surface allowing water electrolysis at the electrode-electrolyte-interfaces. To increase the catalytic activity of these surfaces microstructured materials is of special interest. Generated hydrogen can be stored as compressed gas, liquid H_2, or in form of a metal hydride. Alternatively, CO_2 reduction and hydrocarbon production can be achieved on the cathode side of the device utilizing the electrons and protons recovered from water oxidation on the anode side. In both cases, noble metal-free catalysts are needed to develop electrodes for a mass market with respect to oxidation/reduction of water and reduction of CO_2, respectively.

2. Previous work and present status

The effect of photoelectrochemical water splitting was initially described by Fujishima and Honda in 1972 investigating a TiO_2 single crystal electrode [5]. In the following decades, researchers especially from the United States of America were the first to demonstrate a Solar-To-Hydrogen (STH) efficiency > 10% [6].
However, this device, described by Khaselev and Turner in 1998, based on a p-nGaAs/p-$GaInP_2$ tandem solar cell, failed to meet both the stability and scalability requirements [6]. In the same year, a more economical solution was presented by Rocheleau et al. using a triple junction amorphous Si-based solar cell demonstrating a STH efficiency of 7.8% [7]. Since then, different systems have been reported which addressed these criteria, in particular proposing catalysts with earth-abundant metals [8].

Reece, Nocera *et al.* [9] presented a water splitting device using again an amorphous silicon-based triple junction solar cell, but deposited on a steel foil whereas front and back contact of the membrane were covered by cheap catalysts (amorphous CoO_x and a NiMoZn alloy) and the artificial leaf was totally immersed in an electrolyte of pH 7. Recently, Abdi *et al.* developed a water oxidizing device combining a silicon tandem solar cell with a photoelectrochemically active $BiVO_4$ layer harvesting an STH efficiency of nearly 5% [10] (see also Fig. 2). Later this value was improved to 7.7% using a combination of Fe_2O_3, $BiVO_4$ and silicon [11]. An extensive overview of stand-alone water splitting systems was reported in 2015 by Ager *et al.* [12]. Despite good progress, however, such integrated systems so far are still facing scalability and especially durability issues [13].

Parallel to these attempts to design integrated direct water splitting devices, exclusively driven by sunlight, water electrolysis has also been investigated by combining a conventional alkaline electrolyser with traditional photovoltaic arrays as power supply. However in the case of a coupled system using individual components, separated stands, frames, wiring and electronic control are necessary while a photoelectrochemical system has a simple design and should be adaptive to bright sunlight as well as applicable under diffuse and even fast changing light

conditions without degradation of the electrodes. Another important advantage of PEC systems is thermal management; in a PV-driven electrolysis system the PV panel heats up and decreases the overall efficiency of the system, whereas in a PEC system the heat automatically transported to the solid/liquid interface where it is used to enhance the electrochemical reaction rates [14]. A 2013 study of the US Department of Energy and several follow-up studies suggest that PEC-based solutions could produce hydrogen at lower costs than coupled PV-electrolysis systems and may have more favourable net energy balances under the right conditions [15].
A study of the US Department of Energy claims that this solution could produce hydrogen at lower costs than the coupled system.
Besides these material-based approaches the design of molecular catalysts and sensitizer-catalyst ensembles to perform the light-driven multi-electron catalytic transformation using water as electron and proton source, which is a major theme on the agenda of chemists. This research is on a more fundamental level, often inspired by the structure and function of highly efficient natural enzymes [16]. The advantage of a molecular approach to photocatalyst design is the possibility of virtually unlimited rational variation of the molecules synthesized [17]. Advanced techniques for functional characterization allow to identify performance-limiting features and reaction pathways and provide information necessary for optimization of the systems in a rational, iterative process. Photoelectrochemical cells based on molecular components interfaced with semiconducting electrode surfaces have been reported, often realized as variants of Grätzel's sye-sensitized solar cells [18]. Possibly the intrinsically lower stability of molecular systems compared to solid-state devices makes this approach less promising for large-scale solar energy conversion. However, such systems give precious insight into the mechanism of catalyst activation and catalytic reaction mechanisms, potentially of great importance for the other systems. It cannot be excluded that hybrid systems, combining the best of both worlds, will emerge as a promising option.

3 Research strategies and international activities

The development of a water splitting membrane whose function is similar to the role of the thylakoid membrane of the photosynthetic apparatus in green algae and plants is motivated by the awareness that hydrogen will play a key role in a sustainable energy economy because hydrogen produced from water and renewable energy sources will – as a low carbon technology - not contribute to a CO_2 accelerated climate change. From an economy – and strategic – point of view, mass production of hydrogen from water will lower the dependency of Europe from foreign fossil oil and gas deposits.

Since 2007, the European Parliament acknowledged this situation in enacted directives, describing it as a comprehensive, eco-friendly hydrogen economy [19]. In the framework of the European Research and Innovation programme HORIZON 2020, the topic hydrogen and fuel cells therefore became one of five Joint Technology Initiatives.

On the basis of orientation documents authored by national and international experts, the American Department of Energy (DOE) started funding of a series of so-called Energy Frontier

Research Centers of which several have large solar fuels activities. The DOE also created Energy Innovation Hubs in 2010. Among them, the Joint Center for Artificial Photosynthesis (JCAP), which has been established at two locations, the California Institute of Technology (CALTECH) and the Lawrence Berkeley National Laboratory (LBNL) in California, is the world's largest research programme in Artificial Photosynthesis. In Europe, the Swedish Consortium for Artificial Photosynthesis (CAP) was set in 1994 and is since 2005 concentrated at Uppsala University as the largest initiative in Europe. Other European initiatives in the field of artificial photosynthesis have been launched in Great Britain (SolarCAP), Italy, Germany (a new Solar Fuels programme has been started at the Helmholtz Centre in Berlin), Switzerland (EPFL) and The Netherlands (BioSolarCells consortium). Elsewhere in the world, in Japan (OCARINA), Korea (KCAP), China and Australia, ambitious programmes have been initiated. This burgeoning activity reflects that the solar driven conversion of abundant resources (e.g. CO_2, water) to chemical fuels is one of very few truly sustainable pathways that combine solar energy production and its long-term storage with compatibility with the current energy infrastructure. Since many fundamental and technological hurdles still need to be overcome, the development of 'solar fuel' pathways is an urgent matter if it is to contribute to the envisioned sustainable energy infrastructure for the 9–10 billion people anticipated to be living on the planet by the year 2050.

The proposed AMPEA initiative fits seamlessly with the goals of the International Energy Agency (IAE) Hydrogen Implementing Agreement (HIA). Hydrogen is the one essential ingredient for all chemical fuels and the importance of its sustainable production cannot be overstated. The IEA-HIA pursues collaborative hydrogen research and development and information exchange among its member countries, in order to accelerate hydrogen implementation and its widespread utilization for optimal environmental protection, energy security and international economic development, while establishing the HIA as a premier global resource for expertise in hydrogen.

4. Objectives

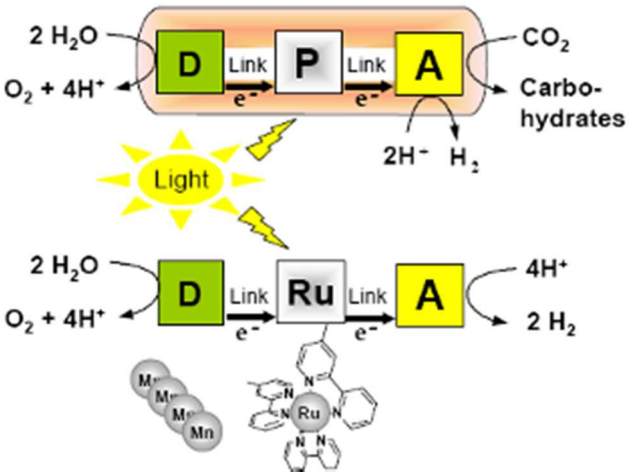
The aim of the AMPEA sub-program Artificial Photosynthesis is at first to decipher fundamental mechanisms underlying water splitting with the objective to develop a device producing hydrogen with high efficiency at low cost. In a simplified scheme as shown below (Figure 1) such a device, immersed in an electrolyte, consists of a light trapping molecule or a semiconducting layer "P", performing the transfer of charge from a water oxidizing catalyst "D", where oxygen evolution occurs, to a reducing catalyst "A", which evolves hydrogen or which, in the presence of CO_2, protons, and electrons, produces carbohydrates (Figure 1). In the planned artificial system, dye molecules will be used as light trapping elements, manganese or cobalt complexes as oxidizing catalysts, and bio-inorganic molecules, alloys or different inorganic compounds comprising transition metals such as Mo, Ni, Fe, Co as hydrogen evolving catalysts.

Photoelectrochemical (PEC) water splitting using exclusively inorganic materials such as compound semiconductors as light absorbers and transition metals and transition metal chalcogenides as electrocatalysts is an alternative route. In an inorganic PEC device, a

photoactive semiconductor is directly immersed in water where it automatically forms a semiconductor/liquid junction (SCLJ). With this type of junction, water splitting is possible even under weak-light conditions. Moreover, due to the limited flux of solar photons, typical current densities are about two orders of magnitude lower than the ~1 A/cm^2 used for commercial electrolyzers. This relaxes the demand on the electrochemical stability of the electrocatalysts used and enables operation close to pH 7. Operation under such neutral conditions is a crucial advantage because it mitigates corrosion problems and avoids safety concerns for large-area applications.

As a mid-term goal, the aim of this program is the conversion of light into chemical energy via photonic excitation of a thin film PV structure. This requires the development of corrosion-stable layers at the front and back contact of the device catalysing water electrolysis at the related electrode-electrolyte-interfaces (Fig. 2). Since photovoltages in the range from 1.6 to 1.8 V and high photocurrent densities at U = 1.23 V are necessary to obtain high STH efficiencies new photocathode as well as photoanode materials (e.g. organohalide perovskites [20] or complex metal oxides [21]) will be explored and adapted to the needs of a light-driven water splitting device. In addition, upcoming new photovoltaic materials and hybrid device concepts (e.g. hybrid inorganic – biosynthetic systems [22]) have to be kept in mind. Due to the high overvoltages needed to reduce CO_2 under selective formation of hydrocarbons (e.g. ethylene, ethanol and aldehydes [23]), which can be used as feedstock for the chemical industry, new PV structures and new catalysts have to be developed.

These targets were discussed in an EERA JP-AMPEA cross-linking workshop on Artificial Photosynthesis, held in Wageningen, The Netherlands, from June 11 - 12th 2013. Approximately 40 experts from and outside Europe discussed the challenges and presented the views of the AMPEA EERA Joint Programme (JP) community in the field of Artificial Photosynthesis (AP) and production of Solar Fuels (SF) in connection with materials, modelling and advanced characterization issues and in line with the general philosophy of the AMPEA JP (see Figure 3). A part of the results have still been published in Green [25].



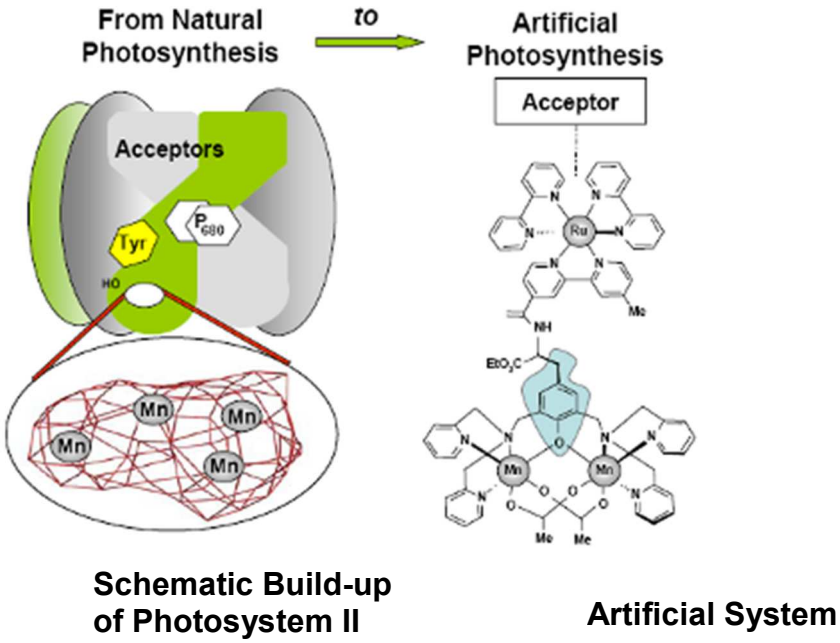


Figure **1** Schemes of artificial leaf–type systems for light induced water splitting using molecules and complexes.

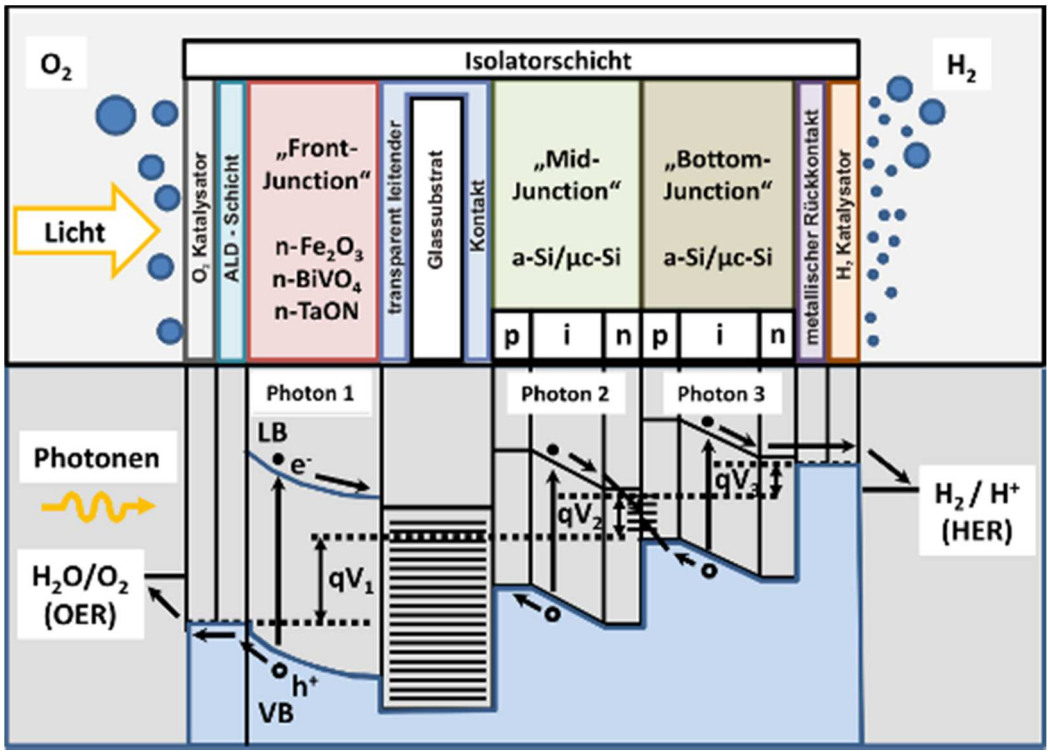


Figure 2. Scheme of a water splitting membrane in form of a thin film semiconductor device transporting excited charge carriers to back and front contact after illumination with sunlight. The charge carriers are used to split water into hydrogen and oxygen [26].

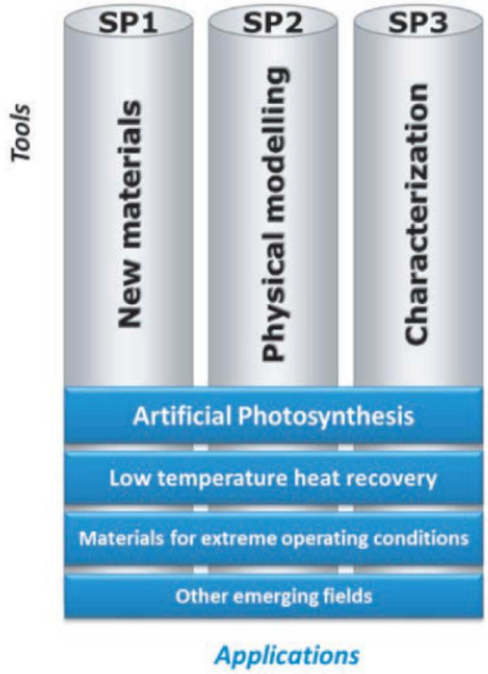


Figure 3. Structure of AMPEA and associated sub-programmes (SPs) with a matrix of tools and applications corresponding to emerging energy technology applications.

The workshop addressed the bottlenecks and grand challenges in the field of AP/SF in six work groups.
As a result of this meeting priority research should focus on the design of molecules, advanced materials and structures as well as processes for artificial photosynthesis energy conversion and production of solar fuels exhibiting

- flexibility of solar fuel device designs;
- energy transformation and fuel production efficiency;
- long-term stability;
- scalability and affordability.

A roadmap was issued together with the definition of a number of challenges, each with defined milestones and deliverables, which will be listed in the chapter below. Similarly, each AMPEA pillar designed a number of issues to be addressed for securing the roadmap (also listed below).

5. Work programme and roadmap

The work program "Artificial Photosynthesis" has the aim to develop water splitting devices in m^2 scale with STH efficiencies >10% considering three main topics:

- PEC inorganic systems,
- PEC molecular systems and
- hybrid systems.

5.1 Main challenges and roadmap

The main targets are given in Table 1.

Table 1. Goals towards water splitting devices

Year	Main targets – devices towards the artificial leaf
2020-2025	- inorganic systems with up to 8% efficiency on a m^2 scale - molecular based systems of 3% STH efficiency - hybrid systems of 5% STH efficiency - CO2 fixing systems of 5% olar-to-Hydrocarbon (STHC) efficiency
2025-2040	- integrated inorganic systems with up to 15% efficiency on m^2 scale - molecular based systems with up to 5% STH efficiency - hybrid systems with up to10% STH efficiency CO_2 fixing systems of 10% Solar-to-Hydrocarbon (STHC) efficiency

5.2 Materials issues (SP1)

To develop efficient water splitting devices interdisciplinary working research consortia belonging to AMPEA members have to be formed addressing the following work packages:

Challenges on materials for direct solar fuels production are:

- durable catalysts and light absorbing systems based on abundant, non-toxic and cheap elements,
- broadband spectrum light-harvesting systems made from abundant, cheap and non-toxic elements for efficient fuel production,
- obtaining adequate matching of electron levels at interfaces so that voltage losses are minimized,
- immobilization strategies for catalysts and light absorbing systems,
- understanding the parameters underlying control of proton transfer and vectorial electron transfer,
- catalysts for hydrocarbon production from sunlight, H_2O and CO_2 as feedstock for the chemical industry

Challenges on processes and devices are:

- light-driven devices for hydrogen and hydrocarbon production as feedstock chemicals comparing design concepts based on bio-inspired molecular and bulk semiconductor platforms,
- scalability of device design and engineering at all relevant levels,
- light management at a higher level for improved performances (*e.g.* integration of solar light concentrators),
- development of smart-responsive matrices (adapted to the working environment) and
- relevant characterization techniques for improved efficiencies and lifetimes.

Milestones and deliverables are summarized in Table 2.

Table 2. Main milestones and deliverables concerning material issues

Milestone number	Targets	Years
MA.1	selection of suited material systems (absorber systems and catalysts)	**1-3**
MA.2	selection of suited bio-inspired molecular and bulk semiconductor platforms	**3-5**
MA.3	realization of water splitting and CO2 reducing devices with an efficiency of η(STH or STHC) > 10% in m^2 scale	**10-20**

5.3 Modelling issues (SP2)

All along the current program, modelling will be needed to accelerate and guide a rational device design, based on insight and understanding of the fundamental processses rather than a pure trial-and-error approach.

Challenges on modelling for direct solar fuels production are:

- atomistic aspects (structure, mechanisms and microscopic rates),
- high throughput (rational design) aiding materials synthesis,
- meso-scale and continuum modelling optimizing nanostructures,

- bridging time and length scales reaching device level.

Modelling will focus on multiscale syntheses, simulations of nanostructures and materials for hydrogen generation, chemical/photo-electro-chemical catalysis, and chemical/ electrochemical energy storage.

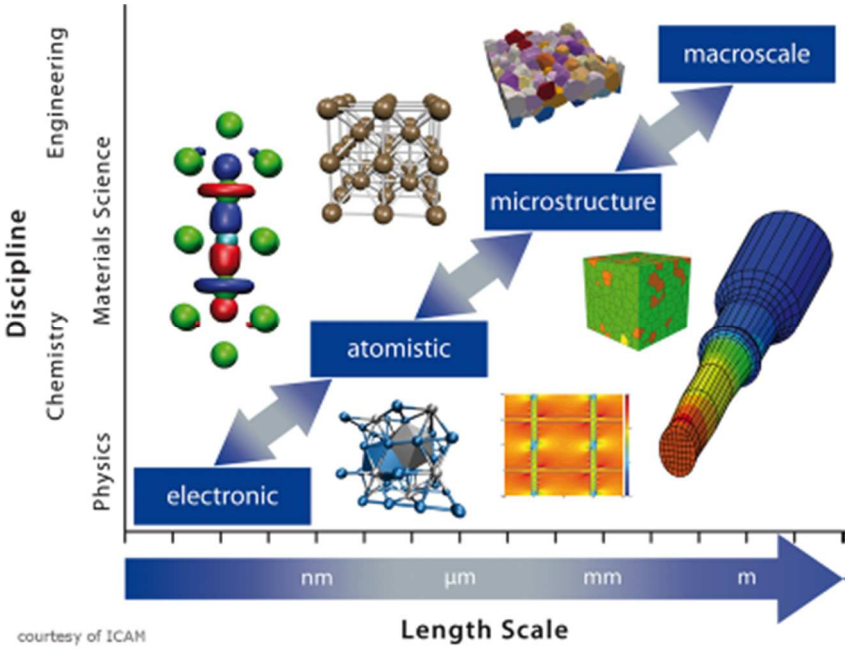


Figure 5. Multiscale analysis and modelling.

Fundamental theories to be used are coupled with ab initio, molecular dynamics, cellular automata and finite element simulations for materials design and discovery, while selected materials are synthesised by self-assembly, deposition and precipitation methods. Materials systems to be investigated cover clusters, oxides, and functional hybrid systems that show desirable properties for clean energy applications.
The overall aim is to clarify the nature of H_2, CO_2 and H_2O interactions with various host structures and surfaces, so as to identify the most-effective H-storage systems, CO_2 sorbents, water splitting catalysts [27]. Considerations are given to the influences of structural geometry, defects, charge and doping of nanostructures from first principles electronic structural simulations. Stability of nanostructures is evaluated from the electronic structures and binding energies, and energy barriers are determined from the Nudged Elastic Band method. Well-tested first principles codes, e.g., WIEN2K and VASP, are used for the studies.

Main milestones and deliverables for this activity are summarized in Table 3.

Table 3. Milestones “Modelling”

Milestone number	Targets	Years
MA.4	atomistic aspects (reactivity and structure)	**3**
MA.5	rational design/mesoscopic modelling	**5-8**
MA.6	Modelling at the device scale	**10-20**

5.4 Characterization issues

A network of advanced characterization platforms has to be built within AMPEA to study all aspects of energy conversion. Of particular interest and importance are *in-situ* and *operando* characterization methods, which allow the relevant processes to be studied under relevant (working) conditions. Such techniques have to be developed in AMPEA laboratories and at large scale instrument facilities to characterize materials, processes and systems. An example of such a facility is the Energy Materials In-Situ Laboratory (EMIL) at the Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, where solid/solid and solid/liquid interfaces can be studied under operating conditions with various forms of X-ray spectroscopy.

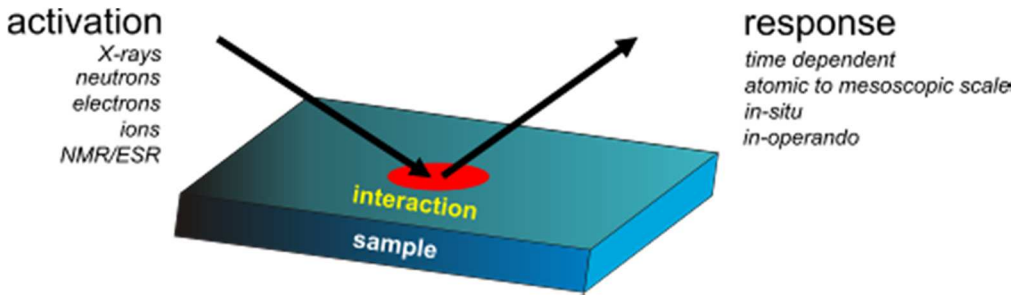
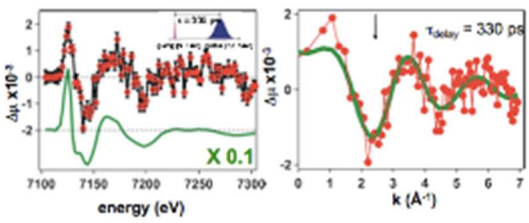
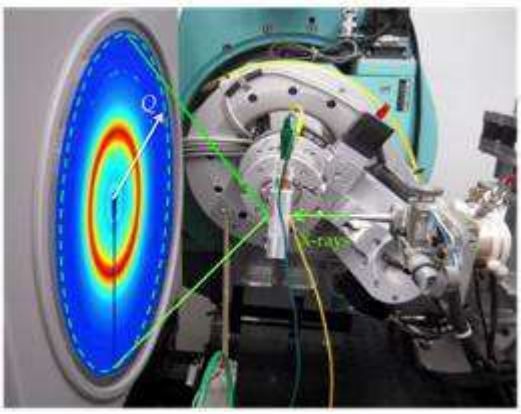
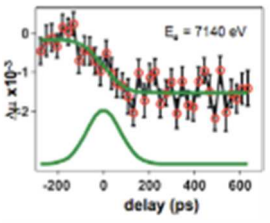


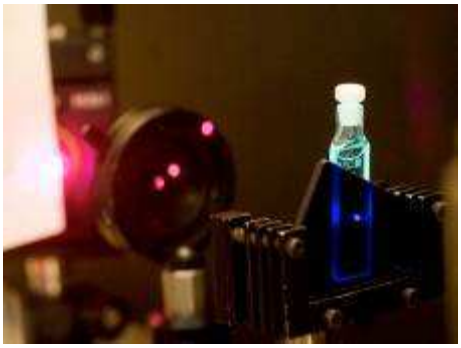
Figure 6. Scheme to generally illustrate the interaction of light, neutrons, electrons, ions, magnetic fields etc. with a sample (molecule, solid state device) to obtain data as a function of time and length scale under in-situ or in-operando conditions.

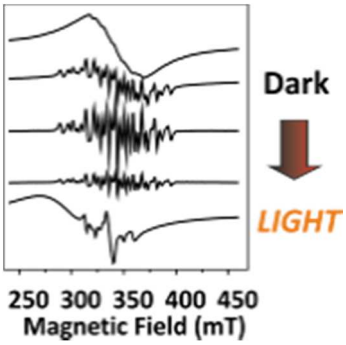
This laboratory can be used for this AMPEA application to perform materials characterization and especially *in-situ* characterization of semiconductors and catalysts in cooperation with two Max-Planck-Institutions (FHI-Berlin, CEC-Mühlheim an der Ruhr). Other centers and individual laboratories across Europe will contribute important expertise and facilities for a range of advanced spectroscopic and scattering methods (see Figures 6 and 7).











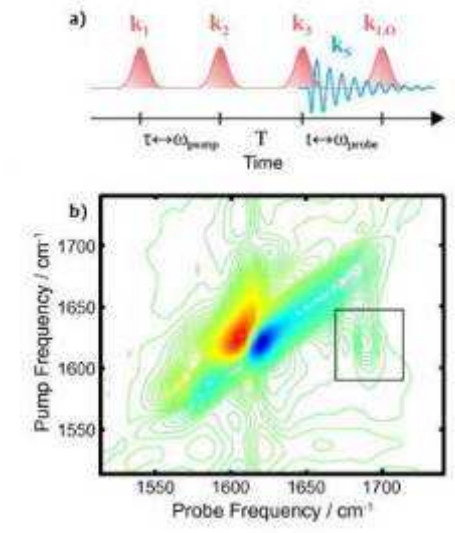


Figure 6.
Top row: in-situ X-ray FEL experiment: X-ray absorption on a transition metal complex reveal ultrafast structural dynamics;
middle row: light-driven oxidation of a water-oxidation catalyst monitored by EPR;
bottom row: ultra-fast laser experiment; example from 2D-IR data [28-30].

The activities are part of Sub-Programme 3 of the AMEPA EERA Joint Programme (see Fig. 3).

For the characterization of molecular photocatalyst systems also a wide range of electrochemical and spectroscopic methods is employed. In particular time-resolved studies using synchronization with the help of short laser flashes allows to follow the fate of the excited state, determine the rates of charge transfer reactions and identify unstable intermediates. The knowledge on a mechanistic level thereby gained is the very basis of the attempt to design and synthesize modified versions in an iterative process of improvement.

Challenges for characterization

- *Characterization of a complex system that is mesoscopic, with large solid/ liquid and molecular/solid interfaces that are crucial for device function;*
- *Characterization under in-situ and in-operandi conditions;*
- *Following the transfer and transport of excitation energy, electrons, protons and fuel products on time-scales from femto-seconds to seconds, and on length-scales from Ångströms to centimeters;*
- *Following the different mechanistic steps of catalytic cycles to identify bottle-necks.*

Table 4. Milestones "Characterization"

Milestone number	Targets	Years
MA.7	Organization of a characterization platform in AMPEA	**1-5**
MA.8	*operando* characterization tools	**1-10**
MA.9	Development of large scale facilities for energy research	**3-10**
MA.10	*In-situ* characterization on an atomic scale	**10-30**

5. Interface with SP and other JPs of AMPEA / EERA Joint Programs

The AMPEA SPA on Artificial Photosynthesis shares common scientific issues with the EERA-JPs Energy storage, Fuel Cells and Hydrogen Technologies and Photovoltaics in terms of materials (new non-noble electrocatalysts, new oxide semiconductors) and processes (rapid thermal annealing (RTP), plasma laser deposition (PLD), atomic layer deposition (ALD)). Joint coordination (*e.g.* workshops) and collaborative ones (*e.g.* joint projects) could be envisioned. Besides, the massive deployment of H_2 as an energy storage medium and a fuel for *e.g.* public transportation will require addressing the issues of production of the fuel in large scale, and its safe transportation and distribution to the end users. Such aspects could be dealt in collaboration with the Smart Cities JP. In this later case, coordination actions with this JP appears to be the best option at first.

Table 5. Milestones "Interaction"

Milestone number	***Interaction with AMPEA subgroups and other Joint Programs within*** AMPEA and EERA joint Programs	*Time*
MA.11	Identification of groups within AMPEA working on Artificial Photosynthesis	*Year 1*
MA.12	1st Workshop on results obtained by national projects Preparation of a common European research proposal	*Year 2*
MA.13	Submission of the proposal in the program HORIZON 2020	*Year 3*
MA.14	2nd Workshop, presentation and evaluation of the collaborative work achieved within the project	*End of Year 4*
MA.15	Organization of an international summer school on artificial photosynthesis	*Year 5*

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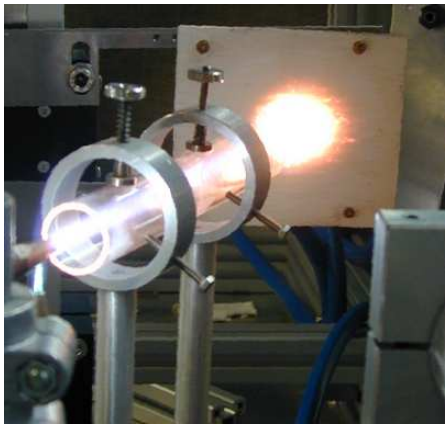

SUB-PROGRAMME APPLICATION B: ***Materials for Extreme Operating Conditions***

A sub-programme within the
AMPEA EERA Joint Programme

Description of Work

Sub-programme coordinators:
Pekka Pohjanne, VTT and Martin Schmücker, DLR

Last modification date: *November, 12th 2018*

The transition to a low carbon future is a big challenge, which requires innovative materials, technologies and systems. Emerging energy technologies require materials combining properties such as high thermal stability, corrosion resistance, sufficient strength and creep resistance at extreme temperatures, thermomechanical stability, specific thermal conductivity, etc. Cost effectiveness of these materials, on the other hand, is another key issue. Among others, long-term stable materials for the following applications are considered:
- Demanding combustion processes including new fuels and higher process temperatures for significant increase of Carnot-based efficiency;
- Carbon capture, utilization and storage (CCUS) technologies to strike global warming;
- Concentrated solar power;
- Facing Plasma Components (FPCs) in fusion reactors (Tokamaks).

The AMPEA sub-programme "Materials for extreme operating conditions" will focus on three activity areas:

- materials development,
- characterization and testing of materials and devices in operating conditions,
- development of multiscale simulation and modelling approaches for sound life time predictions.

The main drivers of the global energy systems are growth in energy demand, challenges linked to energy security and mitigation of environmental impacts. The climate change mitigation requires that the net amount of greenhouse gases released into the atmosphere is reduced. EU has introduced following key targets for the year 2030: At least 40% cuts in greenhouse gas emissions from 1990 levels, at least 27% share for renewable energy, at least 27% improvement in energy efficiency. These targets are demanding and the transition to a low carbon future is a big challenge, which requires innovative ways for the development and implementation of low carbon energy technologies and systems.

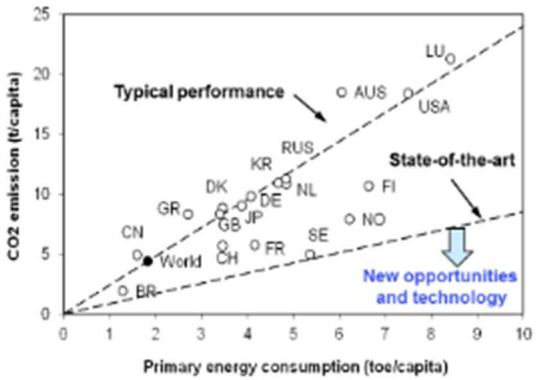

Figure 1. CO_2 emissions vs. primary energy consumption for selected countries [1]

The competitive carbon neutral combustion requires that future boilers can utilise biomass and co-firing of challenging fuels without undue compromise on the thermal efficiency. There will be significant competition on suitable renewable fuels in the future although extended biomass and other renewable fuel sources are foreseen in e.g. agricultural and process waste and sludges not forgetting new sources not considered at present. New fuels are likely to introduce more impurities that make combustion more difficult, causing fouling, slagging high temperature corrosion and erosion threatening equipment durability. On the other hand, less fuel is needed if high combustion efficiency can be achieved. This requires higher operating temperatures and pressures that are limited by materials performance under severe conditions of combustion. The continuous trend to increase steam cycle efficiency (through higher steam data) in conventional thermal power plants helps also to reduce greenhouse gas and other emissions, and to save valuable fuel resources. The high steam pressure and temperature levels will set increasingly stringent requirements for mechanical properties, like creep resistance, as well as steam side oxidation resistance even without introducing new combustion processes. The performance of the overall system is also much affected by the characteristics of the production mix, network (grid) connectivity and market positions in the system. For example the ever increasing share of variable renewable energy generation (wind & solar) will enhance the fluctuation of supply, with the consequence that other power sources has to compensate this variability by operating in more demanding load following mode, meaning in a regime of fluctuating temperature, thermal cycles and reduced operating hours. This will affect a call for new material solutions and technology.

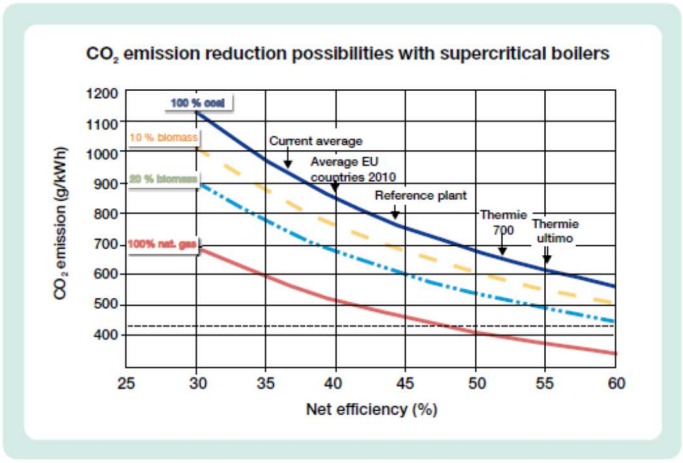

Figure 2. CO_2 emission reduction possibilities with supercritical boilers by improving efficiency and fuel selection [2].

Extreme high temperatures and aggressive environments are present also in other energy applications like in concentrating solar power (CSP) systems, where solar energy can be converted into heat to create steam to run turbines to generate electric power or to convert solar energy to fuels in thermochemical conversion. In CSP some of the components can reach extreme temperatures and present very challenging problems in terms of daily extreme thermal cycling and lifetime. The trend to increase efficiency increase temperatures further and poses new demands e.g. for salt heat transfer fluids. This will set again new demands for materials and calls for new solutions. Similar type high temperature and non-aqueous coolant challenges are faced also e.g. in fourth generation (GEN IV) nuclear systems: Gen IV sodium-cooled fast reactor (SFR), lead-cooled fast reactor (LFR) and molten salt reactor (MSR) concepts. In addition to these commonalities are found also from other clean energy technologies like deep geothermal and solid oxide fuel cells and electrolysers (SOFC/SOEC) that also operate at high temperatures and corrosive environments.

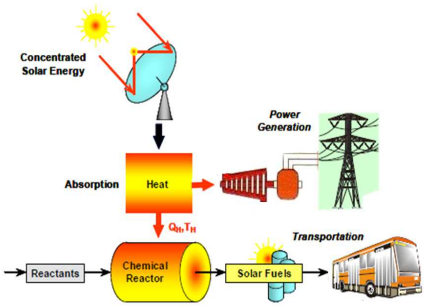

Figure 3. Schematic of solar energy conversion to fuels in thermochemical conversion modified after [3].

As shown above materials play an important role in the development and innovation of more efficient, sustainable, safe and reliable energy conversion technologies for the future. In the energy sector we are facing tighter emission standards, wider fuel spectrum, new technologies, distributed production, more demanding process conditions and increasing required efficiency. These demands lead to operation with high temperatures and severe chemical and mechanical loads. The need for economical use and high efficiencies with longer service life will also set new challenges for materials performance. Materials development for energy uses is typically a very slow process, from the time of material innovation to the material construction phase, but it can be fostered. Material development requires fundamental understanding of how the processing, microstructure, nanostructure and properties interact in order to enhance performance under more severe operating conditions. Achieving this goal will necessitate the development and adaption of new characterisation, manufacturing, modelling and validation processes.

The AMPEA Materials for extreme operating conditions sub-programme will support these goals by gathering the important players in the field of materials on a European level together and thus enabling the increase of collaboration between different players and the efficient use of infrastructures and facilities in Europe. Several experts of the field already enrolled in AMPEA stress the importance of basic work to be done in the field of materials, characterisation and modelling. Success in this requires cooperation and coordination of research activities with other interest groups and platforms like The Energy Materials Industrial Research Initiative (EMIRI), European Technology Platform for Advanced Engineering Materials and Technologies (EuMat), as well as with similar interest groups in the U.S.A. and Japan, *e.g.* Materials Genome Initiative (MGI) and global Mission Innovation (MI) initiative / Clean Energy Materials Innovation Challenge (IC6).

The expected long term impact of SP B "Materials for extreme operating conditions" sub-programme is the development of material research and related multiscale modelling, characterisation and experimental facilities to accelerate and strengthen the competitiveness of European Industry in the field of low carbon energy generation. The first mandatory step is to increase the collaboration among different players and to form a network that will establish a European plan (roadmap) on materials for extreme operating conditions.

At the beginning, the SPB will focus on the high service temperatures, new combustion or heat transfer issues and aggressive operating environments faced in the high efficiency combustion processes and in solar receivers and thermochemical reactors. In this context the sub-programme will be closely linked to the Fuel Cells and Hydrogen, Bioenergy, Carbon Capture and Storage, Geothermal and Materials for Nuclear Energy EERA joint programmes concentrating on material research.

Materials for power plant applications

Improved efficiency through higher steam values requires improved materials and coatings able to withstand increasingly aggressive process conditions at higher temperatures.

Conventional power sources (with or without carbon capture, utilization and storage - CCUS) are needed during the energy transition. In case of coal -fired plants, superheating temperatures will exceed 600°C and, further to 700°C. The basis for boiler materials remains the development of creep, creep-fatigue and thermomechanical fatigue resistant steels and stainless steels that have to meet the requirements of thick-wall pressure equipment. Most demanding applications will require Ni-based alloys that today are mainly used in gas turbines today. In contrast, smaller tubes and other boiler surfaces will suffer from fireside corrosion and erosion, and steam-side oxidation. Therefore, the number of usable materials is limited. Stress corrosion, corrosion fatigue and other more localised forms of damage may show increasing impact with newer steels.

Shift to renewable and other challenging fuels with low-melting and corrosive impurities, such as alkali and heavy metal salts, alter materials to fireside corrosion. In many cases, the best available materials have failed yielding reduction of steam conditions to a maximum of about 400–530°C, and/or shortened component lifetime. It becomes necessary to develop and produce new corrosion resistant materials, coatings as well as combustion additives to tackle the high temperature corrosion issues. These protective coatings (also with new integrated sensor functionalities), ceramic matrix composites and new high strength alloys (ferritic-martensitic, austenitics, Ni-, (Mo,Nb)-base alloys) and combustion additives will be developed.

Additional challenge will come from the increasing share of variable renewable energy (VRE) generation that requires load following mode operation from boilers, i.e. low partials loads (down to 10-25%) with fast ramping and this calls high performance materials that can withstand higher stresses in terms of mechanical and environmental loads. The same applies also to other balancing power technologies, like gas turbines and engines, suitable not only for distributed production, but also adaptable for challenging multi-/biofuel operation.

Improved characteristics concerning strain tolerance, phase stability, fatigue strength, corrosion resistance, and performance under alternative combustion gases are essential. Furthermore, new functionalities (*e.g.* sensor structures) should be integrated. Joining methods for new and dissimilar materials is needed to ensure the service reliability of advanced processes with increased service parameters. Advanced materials for separation of gases with higher flux and better selectivity will be developed for carbon capture, utilization and storage (CCUS) technologies (CCS) to strike the global warming. Especially the materials used in gas treatment plant to develop the CCS technologies should resist to corrosive condensate in long-term conditions up to several ten thousand hours.

Materials for CSP applications
To use highly concentrated solar radiation for power generation and for thermochemical processes structural and functional materials with specific properties are required.

Mirror materials
There are various approaches to optimize performance, life time and economics of mirror systems. Complex PVD coating systems are applied to increase reflectivity (λ/4-layers) and for protection against environmental attacks. The identification of degradation mechanism during service is important from technological and scientific point of view. Mechanistically data interpretation of empirical and accelerated aging tests is mandatory for reliable life time predictions. Interactions between temperature, (UV)-irradiation, corrosion, and abrasion by mineral dust must be understood for constructive optimization of reflector systems.

Absorbers
The ideal absorber for innovative high-temperature-high-efficiency solar plants merges the characteristics of high absorbance at the wavelengths of the sun spectrum and low emittance at the operating temperature, i.e. able to accumulate thermal energy with minimal loses. An absorber material which does not re-radiate heat, tends unavoidably to store thermal energy and to raise its temperature. Therefore the conditions of high temperature stability, high thermal conductivity, good mechanical properties and good resistance to oxidation are required too. Moreover, interactions between absorber materials and air-borne mineral dusts, or melts, respectively, should be investigated in detail. Another promising concept for concentrated solar technology is the so-called particle receiver. In this approach, suitable particles are used as absorber, heat carrier and heat storage media. The particles should have high spectral absorptivity together with thermal and mechanical stability against abrasion and erosion. Besides conventional silicon carbide-based ceramics, zirconium diboride represents a promising material for application as absorber. ZrB2 has the potential to address many of the issues outlined above, in view of its melting point exceeding 3000°C, good thermo-mechanical properties, coupled with intrinsic selective optical properties. R&D is currently focussing on punctual investigations on the process-microstructure-properties relationships and on efficient fabrication techniques to obtain tailored microstructure.

Heat carriers and materials for thermal thermal storage
In case of liquid heat carriers (multinary salt melts) constitutional issues (low temperature eutectics, congruent melting, and stability against decomposition) are most important as well as possible interactions with their containments. For solid particle heat carriers absorptivity, heat resistance, flow behavior, abrasion resistance and heat exchange must be optimized. Again, cost effective fabrication processes are required. Another current research issue deals with redox materials as future heat storage media making use of reversible chemical reactions with high reaction enthalpies. Molten salt heat storage is state-of-the-art but suitable salt compositions ("Solar salt") still are relatively expensive. Hence, a new approach is under development focused on the dilution of salt melts by cheap inorganic solid particles with suitable heat capacity and chemical stability.

Materials for thermochemical water/CO_2 splitting cycles
The use of redox materials for (solar)thermochemical water or CO_2 splitting to produce H_2, CO or derivates is a promising approach to produce synthetic fuels. Development of suitable redox materials is an interdisciplinary field. Beyond thermodynamics, the role of materials science covers microstructural design and stability, solid state diffusion, reaction reversibility, nucleation phenomena and transformation kinetics. Moreover, suitable containments must be provided, stable against harsh temperatures, thermal shock and water vapor.

The understanding and improvement of energy applications require powerful tools to investigate materials in their physical and chemical environment, or processes in the presence of the true materials configuration. Experimental characterisation platforms for materials and devices at laboratory and in-field scale are needed as well as multiscale modelling to reduce timescale from an idea to conception. Through fundamental process understanding, the objective would be to improve prediction capabilities as well as long-term operation assessment. Moreover, materials development can also be supported by physical model development.

Outline

The problem of materials for energy applications has already been addressed in many National, European, International initiatives and programmes. However being an enabling technology, in most cases material research has been moved to the background. In order to rapidly meet the new demands for materials, a number of aspects need to be improved. It is mandatory to understand how alloy composition, microstructure, nanostructure and processing interact and affect performance of materials in operating conditions. In this context, multiscale material modelling needs to be developed to predict and control processes to give the desired properties and to predict

lifetime. In the frame of this project, we need to identify the expertise and facilities and combine them in a new efficient way to achieve these long-term goals.

The AMPEA Materials for extreme operating conditions sub-programme will be composed of three activity areas:
materials development for extreme operation conditions,

- characterisation and testing of materials and devices in operating conditions,
- development of multiscale modelling approach, artificial intelligence (incl. data centric modelling techniques such as machine learning)

The great challenges are presented below at a general level. The time scale of basic research being generally long, this appears in the milestones of materials research, which span from 5 to 20 years. The development of enabling tools like characterisation and multiscale modelling platforms has nearer milestones, in the range of 1 to 10 years. This sub-programme will be closely interacting with AMPEA SP 1 "Materials", SP2 “Multiscale Modelling” and SP3 "Characterization”.

Grand challenges “Materials for Power Plants”

Year	Challenge
5	Functional graded coatings for advanced power plants and new power plant concepts (e.g. IGCC) Advanced surface engineering methods (e.g. to improve internal oxidation resistance)
10	Materials modelling capabilities to reduce time to market for new alloys Integrated sensor technology to increase performance and integrity
20	Materials for new generation high efficient zero emission power plants (e.g. long term stable materials for multi-fuel operation) Joining and fabrication of new materials (redesign of components) Light weighting of gas turbine blading
50	Ultrahigh temperature materials for direct electricity generation and fuel production in a greenhouse gas emission free society

Grand challenges “Materials for Concentrated Solar Power”

Year	Challenge
20	Long term stable redox materials and corresponding systems available for water splitting and CO2 splitting suitable for solar fuel production with an efficiency > 10 %.

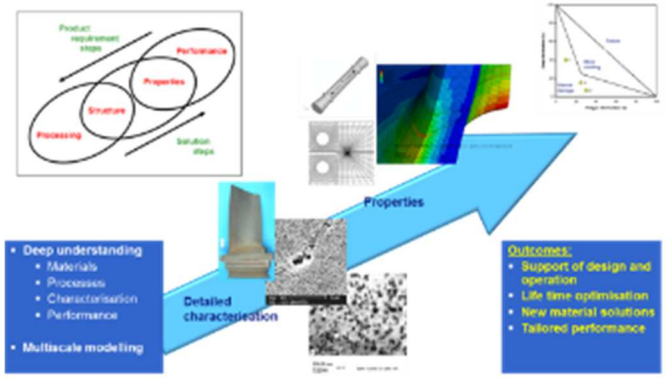

Figure 4. Illustration of processing-structure-properties-performance (PSPP) approach modified after [4], which links performance criteria to material structure and processing.

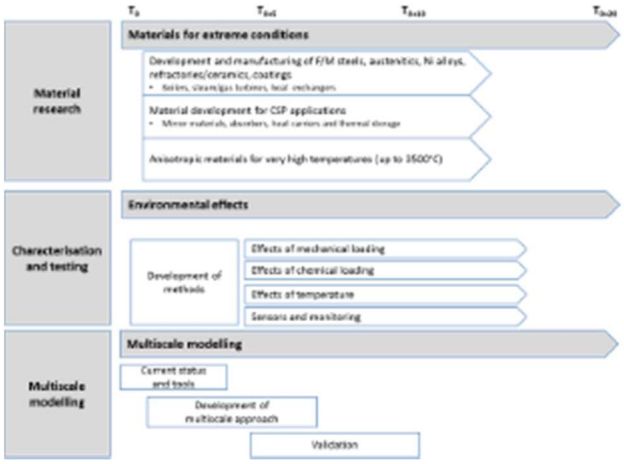

Figure 5. Illustration SP B activity areas and timeline.

- Extreme materials network and roadmap

A first workshop on this sub-programme was organized in June 2013 at VTT (Espoo, Finland). It gathered members of the Joint Programme willing to be active in SPB. On this occasion, first contacts with other EERA Joint Programmes were also made to define common interests and connections in the future. The EMIRI (Energy Materials Industrial Research Initiative) initiative was also represented to share common interests between SPB and industrials players in the field of materials research [5]. Besides networking for possible future common projects, the major outcomes of this first workshop of SPB were the outline of the strategy and roadmap of the sub-programme, its cross-linking with other SPs of AMPEA as well as with other EERA-JPs. The 2nd international workshop was in April 2014 together with experts from other EERA JP's and most important interest groups (e.g. EMIRI, EuMaT) to identify and define the critical expertise's needed and common interests and projects. This was followed by series of HT materials workshops latest being

- Materials resistant to extreme conditions for future energy systems, European Commission funded International Workshop, 12-14 June 2017, Kyiv – Ukraine
- EERA HTM workshop & EUPRO II Seminar, 20-21 November, 2017, J. Heyrovský Institute, Prague
- EERA AMPEA - EoCoE WS Brussels June 8th, 2018. Brussels

Mission Innovation / Clean Energy Materials Innovation Challenge (IC6) co-operation was started in October 2017, when our representative was participating to the "Clean Energy Materials Innovation Challenge Expert Workshop" in Mexico as official EU observer. The roadmap work is in progress, though slowly. At first phase EERA joint JP position paper "Materials for high temperature energy applications" with the contribution of EuMaT was published in June 2018 [6] and was presented to EU DG Research and Innovation in Brussels Oct 19th, 2018.

Milestone	**Measurable objective**	**Project year**
Extreme materials network and roadmap		
MB.1	Sub-programme content • Tentative definition of the sub-programme focus and interest groups	0 (completed)
MB.2	Extreme materials network • 1st workshop	0 (completed)
MB.3	Sub-programme content • SPB DoW - Sub-programme update	1 (completed 2014)
MB.4	Extreme materials network • 2nd International workshop • Definition of members and define tasks of working groups	1 (completed 2014)
MB.5	Identification of the most promising topics for the first pilot projects and propositions of calls for future H2020 work-programmes.	1 - Two brokerages in 2014 and 2015 yielding to several proposals
MB.6	European roadmap - Extreme materials	2

- Material research

The goal is to create and achieve deep fundamental understanding on the relationships between processing and properties of new generation of materials for future energy applications. At the beginning, the focus will be on high temperature and aggressive environments existing in the high efficiency combustion processes and in solar receivers and thermochemical reactors. Materials included are high strength steels/alloys, coatings, refractories/ceramics and composites. Special attention will be paid to question how composition, microstructure, nanostructure and processing interact and affect performance, not forgetting the effects of different surface treatments, fabricability and joinability of materials.

Material development needs for high temperature applications (T > 500 °C) in boilers, steam/gas turbines, heat exchangers, gas clean up devices):

- *Materials with higher high temperature strength:*

Optimization of ferritic-martensitic steels up to 650ºC and materials with higher Cr contents for operation up to 670ºC, Ni base alloys up to 800 ºC. Improvement of the microstructural stability as well as the mechanical properties, creep strength and fatigue characteristics. Deeper knowledge from strengthening mechanisms, phase stability and ageing interactions, definition of accelerated aging tests, life time predictions. Identifying the needs for new sealing and joining systems, manufacturing of components and repairing.

- *Innovative coating technologies:*

Improvement of protective coatings, overlays and thermal barriers systems for boiler components, steam and gas turbines, heat exchangers suitable to withstand cyclic operation.

- *Novel material concepts:*

New fabrication methods for oxide dispersion-strengthened (ODS) materials. Development of non oxide (C/SiC, SiC/SiC) and oxide (alumina, mullite, zirconia) ceramic matrix composites (CMC). Development of oxide fibers with higher thermal stability. Development manufacturing and repairing methods for gradient materials. New era, possibilities of high entropy alloys.

- *Environmental effects on advanced materials:*

Mechanisms and evaluation of steam side oxidation and its effects in creep, fatigue, creep assisted fatigue crack growth. Oxidation mechanisms in new combustion environments e.g. due to oxyfuel combustion or due to altered working fluids for IGCC. Development of fireside corrosion resistant alloys and coatings to meet the demands of renewable and other challenging fuels with low-melting and corrosive impurities, such as alkali and heavy metal salts.

- *Monitoring and process control:*

The use of wide fuel spectrum, higher thermal loads and cyclic operation bring the increasing need for the continuous monitoring of service conditions and fast reaction ability when unwanted critical changes, e.g. fouling, high heat fluxes and increased corrosion are observed. Advanced combustion additives, like hot corrosion inhibitors and self-cleaning additives, are developed to increase fuel flexibility. New online monitoring techniques and integrated sensor technology developed to increase performance and availability.

Material development for low temperature applications (T < 200 °C) in pipelines, heat exchangers:

- *Evaluation of materials for* carbon capture, utilization and storage (CCUS) *technologies:*

Identification of degradation mechanism in CO_2 and the effects of pressure (up to supercritical), moisture, impurities and brine. Definition of accelerated aging tests.

- *Low temperature heat exchangers:*

Acid dewpoint corrosion and the effects of deposits, inorganic and organic impurities. Definition of accelerated aging tests and development of monitoring sensors.

- *Pipelines:*

Environmentally assisted cracking (EAC) mechanisms in high strength materials and the phase stability and ageing interactions, definition of accelerated aging tests, life time predictions.

- *Novel material concepts:*

Development of coatings and surface engineering methods to mitigate dewpoint corrosion. Development of composites and hybrid materials for CO_2 storage.

Material development for CSP applications

- *Mirror materials:*

Identification of degradation mechanism during, definition of accelerated aging tests, life time predictions. Deeper insight into interactions between temperature, (UV)-irradiation, corrosion, and abrasion by mineral dust must.

- *Absorbers:*

Process technologies for cost efficient fabrication of porous SiC ceramic bodies and prevention of process-related material flaws. Life time prediction, interactions between SiC ceramics and mineral dusts or melts.

- *Heat carriers and materials for thermal thermal storage:*

Constitutional issues (low temperature eutectics, congruent melting, stability against decomposition, interactions with their containments). Optimization of absorptivity, heat resistance, flow behavior, abrasion resistance and heat exchange for solid particle heat carriers. Redox materials as heat storage media making use of reversible chemical reactions with high reaction enthalpies.

- *Materials for thermochemical water/CO_2 splitting cycles:*

Development of suitable redox materials. Thermodynamic-based materials screening, microstructural design and stability, optimization of transformation kinetics. Development of suitable containments, stable against harsh temperatures, thermal shock and water vapor.

Anisotropic materials for very high temperatures (up to 3500 °C)

- High anisotropy Carbide-Graphite composites (>3500°C) or Tungsten-Nickel-Copper alloy (>1800-2000°C) used as "Facing Plasma Components" (FPCs) in fusion reactor (Tokomaks) to face with high heat flux depositions due to the ELMs (Edge-Localized Modes) crashes in Divertor Plasma.

- Silicon carbide powder or foam (2600-2900°C) used either like energy vectors and absorbers in solar furnace in for concentrated solar energy (see above).

- Yttria-stabilized zirconia (>2000°C), nanostructured AlN coatings (2200°C), Tungsten-Carbide (2870°C), Boron Nitride (2600°C-2800°C) used as thermal shields in turbo machineries (gas turbines, turbomachines working at high temperature for improving their energy efficiency).

- Zirconium diboride (>2000°C) for reactor fuel assemblies, heaters, burners, refractory elements, reactors, gas turbine components

Material research - Main Milestones and deliverables

Milestone	**Measurable objective**	**Project year**
Material research		
M B.7	New high strength ferritic- martensitic, austenitic steels and nickel base alloys with improved creep strength and high resistance against steam oxidation	5
M B.8	Cost effective use of new and coatings to meet the demands of renewable and other challenging fuels in high efficiency boilers.	5
MB.9	New hybrid and gradient material concepts with enhanced high temperature oxidation and corrosion resistance.	10

Characterization and testing

Test facilities and best practices of characterisation are shared with the AMPEA SP 3, and round-robin tests are foreseen. The SP 3 will form experimental characterisation and demonstration platforms of energy materials and devices under operating conditions. The characterisation tools will be developed with a clear vision of needs from material and energy scientists. The research will focus on different environmental effects and multiple mechanisms, such as the influence of steam and combustion gases in creep and creep assisted fatigue crack growth and oxidation/corrosion as well as erosion-corrosion.

Characterisation and testing of environmental effects

- The effects of mechanical loads, development of standard experiments in climate chambers/autoclaves/pilot plants and on site

- Characterisation of materials behaviour under gas/steam streams (turbines, boiler components)
- Characterisation of materials behaviour under gas/steam streams in burner-rigs and pilot plants (turbines, boiler components)
- Characterization of thermal properties at very high temperatures
- Development of specific facilities for thermal characterization of anisotropic materials, coatings and deposits (anisotropic due to their elaboration processes (evaporation, sputtering, PVD or CVD)) at high temperature.
- Measurement of transient high heat fluxes and high temperatures (MegaJoule Laser, atmospheric re-entry of space vehicles) by multi-spectral methods on high reflective materials in hot environments (divertor FPCs in Tore-Supra or ITER) using electrically tunable filters or dichroic detection (pyro-reflectometry).

Characterisation and testing - Main Milestones and deliverables

Milestone	Measurable objective	Project year
Characterisation and testing		
M B.10	Identification of characterisation facilities, test-rigs, and pilot plants as well as onsite	2
M B.11	Definition of accelerated aging test requirements and development of new procedures for climate chambers/autoclaves	5
M B.12	Development of test methodologies at pilot plants and onsite	5

Multiscale modelling

Multiscale modelling will generate fundamental understanding of mechanisms that influence the durability of the different properties of construction materials, products and components. This activity is shared with the SP2. Multiscale modelling in materials technology should be fostered to reduce timescale from an idea to conception. Development and experimental validation of integrated models focussed on the material-component performance evolution during long-term service. Experimental validation should be based mainly on field data (operational data, results from materials tested in operating conditions, post-mortem analysis of critical components) to improve the prediction capability of models.

Multiscale modelling:
- Current status and collection of tools
- Selection and integration of potential models for a multiscale approach
- Computational and experimental validation of models, development of a multiscale approach
- Models based on field and laboratory data for life time prediction and assessment of critical components
- Operating conditions, kinetic and thermodynamic models for fouling/slagging/corrosion/ erosion in advanced processes.

Life time models need to be established to explain damage mechanisms and to optimize coating characteristics systematically.

Modelling - Main Milestones and deliverables

Milestone	Measurable objective	Project year
Multiscale modelling		
M B.13	Phase transformation and microstructural stability models for ageing at high temperatures	5
M B.14	Kinetic and thermodynamic models development for fouling/corrosion in combustion	5
M B.15	Validated material degradation models for multiple failure mechanisms to predict performance	10
M B.16	Multiscale modelling capabilities to reduce time to market for new alloys	10

Materials and technology developments undertaken in the AMPEA *SPB Materials for Extreme Operating Conditions* are of interest for several other JPs and particularly:

- the Carbon Capture and Storage JP, where material new material concepts for carbon capture, utilization and storage (CCUS) technologies are needed.
- the Nuclear Materials JP, with following common issues with AMPEA SPB: High temperature (HT) questions, creep-fatigue, welding and joining, material development, aggressive and corrosive environments.
- the Bioenergy JP, where verified material concepts are needed for the new aggressive bioenergy and biofuel processes.
- the Concentrated Solar Power JP.
- the Geothermal JP.

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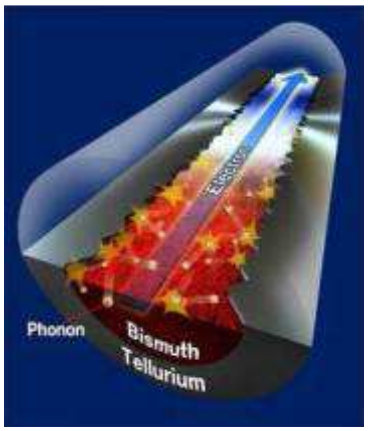
EUROPEAN ENERGY RESEARCH ALLIANCE



SUB-PROGRAMME APPLICATION C: ***Advanced Materials for Heat Exploitation and Energy Conversion***

A sub-programme within the
AMPEA EERA Joint Programme

Description of Work

Sub-programme coordinator:
Monica Fabrizio, CNR

Last modification date: *November, 12th 2018*

Abstract sub-programme C "Advanced Materials for Heat Exploitation and Energy Conversion"

This subprogram of the AMPEA EERA Joint Initiative has been revised according to the new insights of participants. Therefore, the updated subprogram includes ionic liquids with peculiar thermoelectric properties and thermoelectric materials for high temperature applications. In agreement with the new version, the title also has been updated and now it is "Advanced Materials for Heat Recovery and Energy Conversion".
Given the advancement of the state of the art, specific review concerned the "Grand challenges" that have been amended and focused on targets that appear more realistic.
Heat recovery and energy conversion topics include many applications and technologies but only few ones are considered in sub-programme. With this premise, the sub-programme C is a kind of work-in-progress that the participants will update following the evolution of their own research interests.

The SPC relates to research, development and testing in *operando* conditions of materials for intensified temperature heat exploitation. Five focus areas are considered:
- Energy harvesting materials;
- Polymer nano-composites for intensified heat transfer;
- Micro- and nano-structured heat exchange surfaces;
- Nanofluids,
- Materials for thermochemical energy storage.

Each of these focus areas is characterised with quantified research targets to be achieved in a five year time perspective by resorting the tools made available by the TOOLS subprogrammes of AMPEA. Tight connection with the relevant EU initiatives (*e.g.* ICT-Flagship, SPIRE) and associations (*e.g.* EMIRI, CEFIC) are desirable, as well as with other EERA joint programmes (*e.g.* Energy storage, Concentrated Solar Power, Hydrogen and Fuel Cells, Geothermal Energy).
The research efforts carried out should be capable of generating new devices based on the advanced materials developed (thermo-electric modules, polymer heat exchangers, innovative heat exchange and storage) by 2020.

1. Background

Introduction

A dominant fraction of the world's power, roughly 10 trillion watts, is produced by burning fossil fuels and running internal combustion engines. For every watt of mechanical power generated, almost one and a half watts are dumped as waste thermal power. This is in part due to intrinsic thermodynamic constraints and in part to techno-economic feasibility limits. Reference temperatures and cost effectiveness boundaries for heat recovery are application sensitive (building, industry, mobility, renewables sectors,…); this suggests that we can use a different indicator for heat exploitation, such as the exergy content. Heat with low exergy (i.e. related to high entropy/irreversible processes)) is indeed difficult to recover to valuable heat or mechanical work in an economic manner, mainly due to low driving forces (a typical example is the temperature difference between the fluid in the low temperature range of the energy cycle and the recipient fluid or solid at ambient temperature). Low/mid temperature (waste) heat is generated by several processes and can be derived from some renewable energy sources (geothermal, solar thermal, heat of anthropic origin, etc.) to increase their efficiency. Within this scenario Fig. 1 outlines some of the major technologies available for effective heat recovery for power applications or heat transfer purposes.

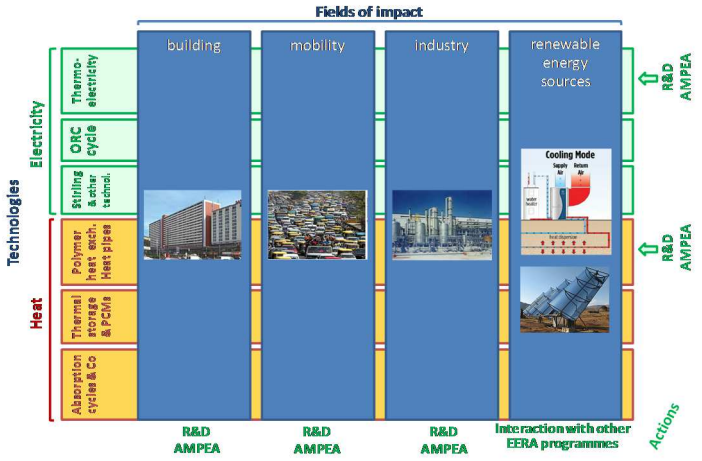


Figure. 1. Main technologies for heat recovery and energy conversion for power applications or heat transfer purposes along with their fields of impact. The main R&D focus areas within the AMPEA EERA programme are pointed out along with possible interactions with other EERA programmes on renewables.

Some technologies for heat recovery are now available in the market (e.g. absorption cycles, Stirling engines, ORC cycles, phase change materials, etc…), but further development is required, as confirmed by the high-TRL focus of Horizon 2020 calls. All the proposed technologies require significant progress in materials science and engineering to express their full potential. Moreover, some topics (thermo-electricity, polymer nanocomposites for low temperature heat exchangers, nanofluids, nanostructured surfaces for heat transfer enhancement and thermochemical energy storage) show great crosscutting application potential and limited market exploitation, which renders this overall R&D worth addressing with specific emphasis in the current basic&applied research-driven AMPEA sub-programme.

As a whole, the present AMPEA subprogramme will promote and coordinate research in the closely related fields above by the use of common methodologies and modelling tools and agreed upon roadmaps.
The main aim of this sub-programme is to establish, at EU level, a valuable connection between the researchers operating in these fields to:

→ Achieve convincing progress in these promising fields through coordinated research efforts within AMPEA and beyond.

→ Provide suitable R&D results and arguments to convince the EU stakeholders to include funding opportunities in the next biannual calls (2016-2017, 2018-2020) of the Horizon 2020 framework programme including large programme areas like the Energy section (where energy efficiency, closely related to the present subprogramme, is one of the three main challenges) or public-private partnerships like e.g. SPIRE (www.SPIRE2030.eu).

→ Pursue in the meanwhile cooperation within the currently available EU programmes in the Horizon 2020 calls[1].

→ Increase the participation to international events and initiatives centred on advanced materials for heat exploitation and energy conversion

The international R&D context of the addressed technologies

Energy harvesting materials

Thermoelectric materials. Thermoelectric power generation is based on the Seebeck effect, according to which a temperature difference generates charge displacement and consequently an electrical voltage between the hot and cold ends of the thermoelectric material. This means direct conversion of thermal into electrical energy and in effect thermoelectric generators (TEGs) show many advantages, such as the high simplicity and reliability of the system, the absence of moving parts and the long lifetime ensured. Thanks to its compactness and solid state-based static operation, TE converters are especially suitable for efficient compact portable energy sources, as well as for (static or portable) remote sensor power supply. In USA and China market, some companies have thermoelectric modules and generators in their product portfolio (www.tellurex.com, www.thermoelectric-generator.com, www.tegpower.com, etc.). Similar companies are also in Europe (OFLEXX, Grentech, Micropelt, Siemens,..). However, in spite of a number of TEG devices has been already developed in diverse technological fields (cars,

[1] e.g. Future and Emerging Technologies; European Research Grants; Graphene Flagship, www.graphene-flagship.eu, where some of the AMPEA partners are already members)

casting houses, residential boilers, wood pellet furnaces, glass manufacturing plants, chemical and process industries,...), new thermoelectric materials still miss significant market penetration.
The TEG efficiency closely depends on the figure of merit ZT of the TE materials, involving the Seebeck coefficient, the electrical conductivity and the thermal conductivity, as expressed in the following equation:

$$ZT = \frac{\alpha^2 \sigma T}{\kappa_{el} + \kappa_{ph}}$$

It is commonly accepted that a ZT higher than 1 is a recommended condition for the employ of TE materials in practical applications, giving a target conversion efficiency of 5-7%. As shown in Figure 2, the research has led to even better results than those envisaged above, with materials covering on turn various temperature ranges for different applications (Figure 2 left).

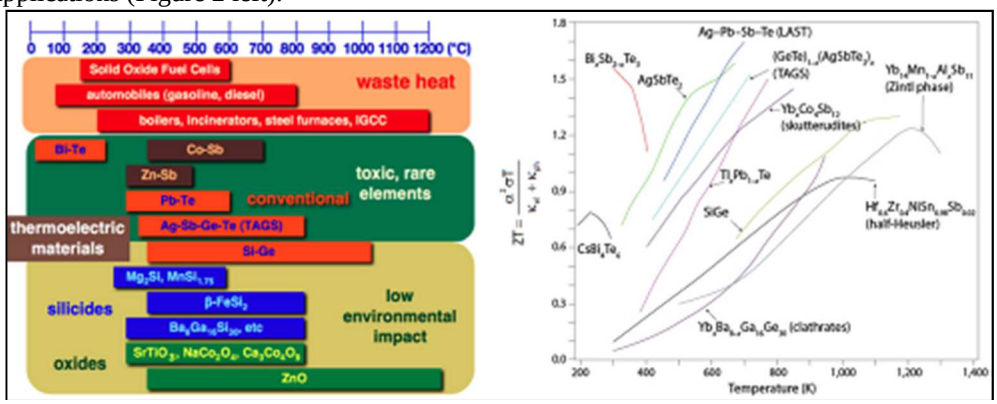


Figure 2. Highlights on thermoelectric materials and devices. See text for detailed explanation.

Semiconductors based on heavy elements (eg. Bi_2Te_3, $CoSb_3$, PbTe, Si-Ge alloys) show the highest values of ZT achievable and are at present at pre-industrial or even commercial (mainly Bi_2Te_3) level. Thus, the progress in the last 10 years has led to nanostructured semiconductors, such as filled skutterudites and half-heusler compounds allowing a significant improvement of the figure of merit and of the working temperature, as shown in Figure 2 (right). The enhancement of the thermoelectric performance in these new materials has been mainly due to the independent control of thermal and electrical conductivity. However, they show some drawbacks, like toxicity, chemical reactivity at high temperatures and presence of critical raw materials. Based on this short premise, it is immediately envisaged that practical, efficient and cheap TEGs can be engineered only if safe and non-critical materials will be developed in a wide range of temperatures. These aspects are outlined in some projects dedicated to this technology by the National Countries [2] where it is outlined the importance of widening the work temperature range of TEGs and investigating alternative material structures for new TE module design.

In recent years, large international efforts have been on new inorganic semiconductors to substitute tellurides, with the potential to achieve high-efficiency TEG based on earth-abundant, inexpensive and non-toxic elements. Particularly promising compounds can be found among half-Heusler alloys, Zintl phases, silicides like Mg_2Si and the Mn-Si system, antimonides like the Zn-Sb family, and naturally occurring tetrahedrites. Some of these alternatives are about to reach commercial maturity, so the development of these materials presently takes place at virtually all TRL levels. This involves discovery of new materials, optimization of doping regimes, development of processing and compacting routes, establishment of novel metallization and bonding technologies, introduction of new generator designs, optimization of system architecture, integration of TEG in real environments with heat exchangers and power control, etc. A small, but growing European industry is ready to employ results from this research and development.

There has also been increasing attention on polymeric composites for *IoT* thermoelectric applications. Polymers are made of low cost raw materials and possess a remarkably low thermal conductivity. Moreover, the relative ease of solution processing, their mechanical stability and flexibility together with low density make conductive polymers suitable for integration in a thermoelectric generator. Nevertheless, the effective utilization of conducting polymers is hindered by their low electrical conductivity and Seebeck coefficient, therefore an increase of the power factor has been recognized as the key strategy in enhancing the ZT of conductive polymers. These can be arranged through the selection of suitable dopants, an adequate doping level and by controlling the crystallinity

[2] in Italy the Research Program for the National Electric System 2006-2009, 2010-2012 2015-2017 of the Ministry of Economic Development, in Spain a large Project Consolider-NANOTERM 2010-2015) and in the VII Framework Programme (NANOHITEC 2011-2014; THERMOMAG 2010-2014, NEXTEC 2010-2014). In Norway, several large projects, including the researcher projects NEAT (2017-2019), HEATER (2018-2020), COMET (2017-2020), OXIPATH (2017-2020), ANSWER (2018-2021), THELMA (2013-2017), the innovation projects TESIL (2017-2019), 3D-TEM (2018-2021), THERMOMAT (2013-2016), the innovation cluster THERMIO (2016-2020).

during the synthesis process, but nanocomposite materials offer a more promising approach for preparation of effective flexible and cheap TE modules that can be assembled and engineered into a variety of desired shapes and scales.

In general, the thermoelectric conversion efficiency of most oxides is not comparable yet to that of conventional TE compounds and a major breakthrough is needed to improve their properties and make them appealing for practical applications. In the case of large temperature difference, that allows to achieve high Carnot efficiency, it is necessary to maximize the device ZT, and not just a peak materials zT. The device segmenting with different materials or functionally graded materials that have peak zT at different temperatures can be an interesting route to improve device ZT. In this view, transition metal oxides such as ZnO, $NaCoO_2$, $Ca_3Co_4O_9$, $CaMnO_3$, $LaCoO_3$, $Sr_xBa_{1-x}Nb_2O_6$, $EuTiO_3$, $BaTiO_3$ and $SrTiO_3$ have recently attracted considerable interest as alternative bulk TE materials even if oxides require a very delicate preparation since minor changes in the oxygen content may result in large changes of device properties.

Pyroelectric materials. Pyroelectric materials have the potential to complement the efficiency and effects of thermoelectric materials. Thermoelectric energy harvesting occurs when there is a temperature gradient, while pyroelectric energy harvesting needs time varying temperature. Pyroelectricity is probably one of the least-known electrical properties of solids. The pyroelectric effect refers to the so-called spontaneous polarization (P_S) in certain anisotropic solids due to temperature fluctuation, being the direct conversion of the polarization gradient to electric voltage and vice versa. At steady-state (dT/dt=0), the spontaneous polarization of a pyroelectric material is constant, and leads to a charge on each surface of the material which attracts free charges. When the material is subjected to heating (dT/dt > 0) or cooling (dT/dt < 0), the changes in surface charge cause a flow of electrons and the generation of an electric current. The current $i_p(t)$ is proportional to the rate of change of the pyroelectric material temperature, $i_p(t)=pA\ dT(t)/dt$; p is the material pyroelectric coefficient, A is the surface area of the electrode connected to the pyroelectric material during measurements with electrodes orientated normal to the polar direction, dT(t)/dt is the rate of temperature change. The pyroelectric current is independent of material thickness but to maximize it the material needs a larger effective surface, a large pyroelectric coefficient and a high rate of temperature change. Hence, the large temperature gradients that exist in car engines or power turbines make them ideal candidates for pyroelectric energy harvesting. It is worth mentioning that pyroelectric materials are also piezoelectric, and it is possible to have combined piezo-pyroelectric energy harvesting.

Thermally conductive polymer nanocomposites

With few, rather expensive exceptions (Cevallos et al., 2012; www.coolpolymers.com; www.stanyl.com; www.polyone.com; www.lati.com), polymers typically exhibit low thermal conductivity (generally below 1 W/mK). The thermal conductivity of polymers can be enhanced by the addition of thermally conductive fillers, including graphite, carbon black, carbon fibers, graphene, ceramic or metal particles which have thermal conductivities higher by orders of magnitude. Unless knowledge based innovative techniques are adopted (Fina et al., 2012; Colonna et al, 2018), high filler loadings (>30 vol.%) are typically necessary to achieve the appropriate level of thermal conductivity in thermally conductive polymer nanocomposites (PNC), which implies several drawbacks from several viewpoints: i) cost (the cost of fillers is higher than that of polymers); ii) processability (with high filler loading the polymer reological properties change significantly which, in turn, renders some moulding techniques impossible, e.g. injection moulding).

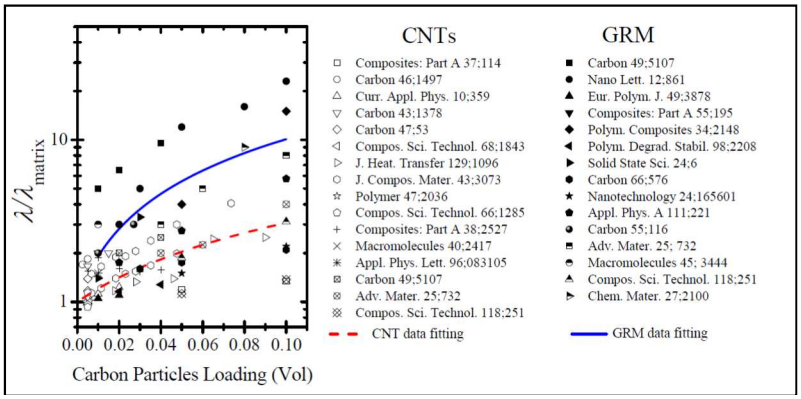


Figure 3. Normalized thermal conductivity (l) data of CNT or GRM polymer nanocomposites as function of volume carbon particle loading. Reproduced from Colonna et al, Carbon 2016.

Carbon-based fillers appear to be the best promising fillers, coupling high thermal conductivity, chemical resistance to acids and bases, and light weight, which is in line with the prevalent application fields for polymer heat exchangers (e.g. chemical processing, biomass flue gas heat recovery, marine diesel engine intercooler, etc.). Nanoparticles have also been widely investigated for exploitation in thermally conductive materials, including in combination with more conventional microparticles. In particular, graphene and related materials were recognized as the most effective nanoparticles for the enhancement of thermal conductivity in polymers (Figure 3) and attracted significant research efforts in the last 5 years. [3]

Beside the transfer to industrial application, frontier research is currently focused on the engineering of thermal interfaces for the enhancement of thermal contacts between percolative networks of conductive particles. [4] With a strong synergism with the Graphene flagship, the AMPEA consortium involved in the present proposal will develop new PNCs based on innovative nano-materials engineering, new processing route and a wider range of fillers and polymer matrixes in order to maximise the inter-filler-particles contact conditions, for building an effective phonon percolation pattern at the lowest possible filler loadings. The use of co-continuous polymer blends depicted in Figure 3, is just a possible example, other possibilities being: the processing of polymer pellet pre-coated with conductive nano-particles, the promotion of post-processing self-assembling phenomena among dispersed nanoparticles, etc. To foster these developments and provide a valuable interpretation of the achieved results specific multiscale modelling tools will be developed, as later explained. If nano-composites have provided a distinctive increase of the thermal conductivities inside solids, other nano-technologies or materials may influence the heat transfer coefficients at the fluid-solid interfaces. In the presence of low driving forces / low temperature differences across heat transfer surfaces (as in the case of low temperature heat exchangers), they may give rise to significant benefits in terms of heat transfer efficiency and heat exchanger compactness.

Micro- and nano-engineered heat transfer surfaces

Micro- and nano-engineered heat transfer surfaces have recently shown significant potential in various application fields:

- heat exchange with fluids in the turbulent regime
- heat exchange with fluids undergoing phase changes (e.g. boiling or condensation)

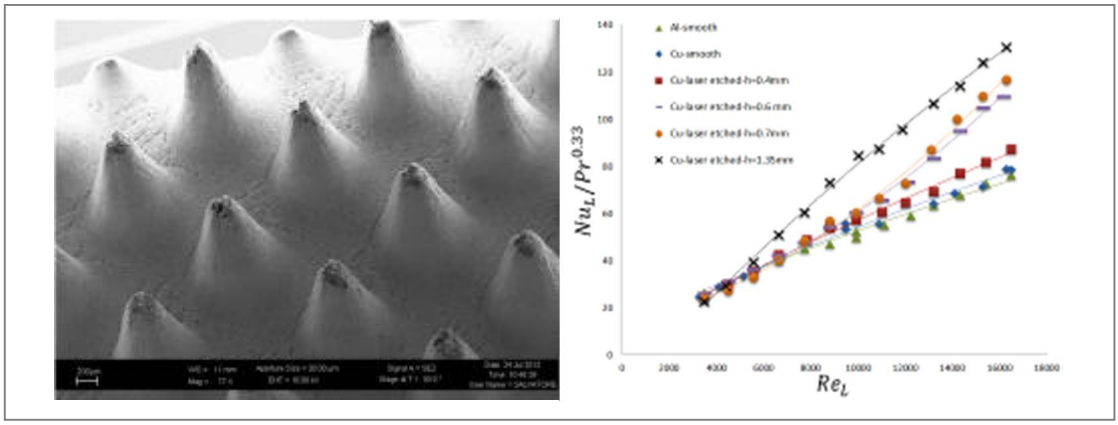


Figure 4. Highlights on nanostructured heat exchange surfaces. See text for detailed explanation.

In the first case, the heat transfer enhancement is not only due to the increase of heat transfer area entailed by the presence of ordered micro-edges over the surface, but also to appositive perturbation of the turbulent fluid pattern close to the heat transfer surface which can be already induced by rather low amounts of materials deposited over the surface. Particularly, Figure 4 shows the effect on the heat transfer coefficient of the height of Cu pillars obtained by laser etching at the premises of one of the spin-off companies incubated at the POLITO's incubator I3P. Up to 60% increase of the heat transfer coefficient could be obtained in the turbulent regime. A detailed modelling with explanation of the dominant mechanisms entailing such a performance enhancement has been provided, on the grounds of a multi-variable geometrical study validated by means of various heat transfer surfaces obtained by additive manufacturing techniques.

As confirmed by other recent studies, nanostructured surface provides a more homogeneous and concentrated pattern for the nucleation sites of steam bubbles in the boiling process or the liquid droplet in condensation ones,

[3] In fact, the exploitation of graphene and related materials for the thermal transport enhancement was part of the activities carried out within the Graphene Flagship[3], (www.graphene-flagship.eu), 1 G€ EU funded initiative started in 2014 and currently focused on the development of industrial applications for graphene and technological transfer.

[4] An ongoing project on the Design, manufacturing and control of INterfaces in THERMally conductive polymer Nanocomposites was funded by the European Research Council at Polito.

which results in twofold increases of the heat exchange coefficients and very low boiling inception superheats or condensation inception undercoolings (1-2°C).
The AMPEA partnership will make progress in this rather recent research field either in the fundamental understanding via adequate modelling tools or in the development of new micro- and nano- designed heat transfer surfaces.

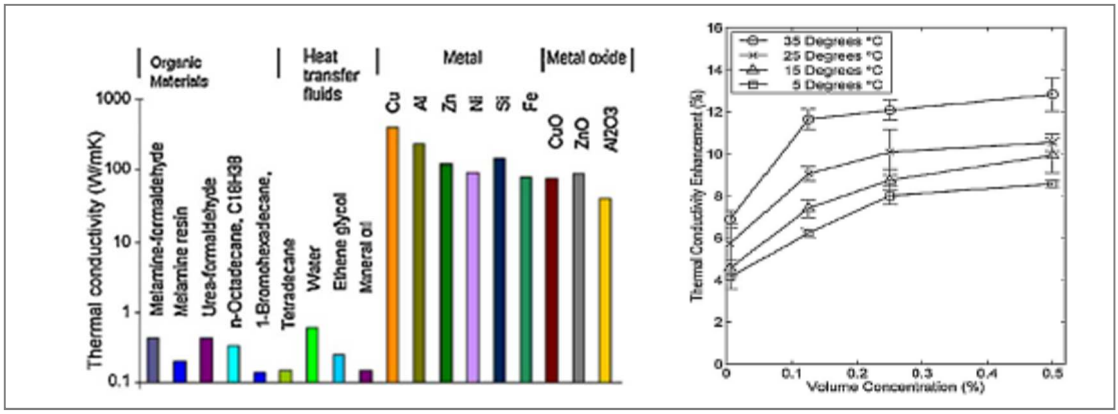
Nanofluids

Nanofluids are advanced and functionalized fluids obtained by adding nanosized solid particles in low to moderate volumetric fractions to a base fluid (Figure 5). Nanofluids can provide the following advantages: (i) nanosized particles have enhanced stability against sedimentation since surface forces easily balance the gravity force, and (ii) thermal, optical, mechanical, electrical, rheological, and magnetic properties of nanoparticles, which depend significantly on size and shape, can be customized during manufacture. Hence, nanofluids are often superior to the reference fluid alone. Since the early studies by Masuda et al. (1993) and Choi (1995), a number of research efforts have shown that the nanofluids exhibit peculiar thermal properties even at very low concentration of suspended nanoparticles, which makes them promising and cost-effective for applications in thermal management systems. Indirect advantages of enhanced heat transfer coefficients could be miniaturized (smaller and lighter) heat exchangers with reduced fluid inventory and reduced life-cycle impact.

Figure 5. Highlights on nanofluids: (right) a summary of thermal application for different nanofluids; (left) an example of the effect of the amount of suspended nanoparticles on the enhancement of the fluid thermal conductivity.

Recent experiments have also demonstrated that nanofluids have attractive properties for applications in the area of heat transfer, drag reduction, binding ability for sand consolidation, gel formation, wettability alteration, significant enhancement of boiling critical heat flux and corrosive control. The tribological performance of nanolubricants obtained with addition of carbon and metal nanoparticles can be usefully applied to refrigerating devices but also to cogeneration engines. [5]

Several industrial applications have been developed using nanofluids as cooling/heating media (Chandrasekar, 2012; Buschmann, 2013): electronic liquid cooling system, nuclear power plant cooling systems, rubber processing, public utilities, oil and gas industry, food and beverage processing industry, chemicals and plastics industry, solar energy conversion to electricity, and heating, ventilation, and air conditioning (HVAC) systems for buildings, etc. To explore just one example, let us consider the application of copper-ethylene glycol nanofluids



in a demanding automotive cooling system studied by Leong et al (2010). It was observed that, overall heat transfer coefficient and heat transfer rate in engine cooling system increased with the usage of nanofluids compared to ethylene glycol (i.e. base fluid) alone. It is observed that about 3.8% of heat transfer enhancement could be achieved and also estimated that the air frontal area could be reduced by 18.7% with the addition of 2% copper particles in a base fluid.

Moreover, nanofluids can be advantageously integrated with renewable energy sources. In particular, their use for sunlight absorption in direct-absorption solar collectors is worth of study, as black nanofluids can work both as solar absorbers and as heat-transfer media (Otanicar et al. 2010, Sani et al. 2011) and overcome several drawbacks of conventional systems.

Very recent papers also showed the significant enhancement in thermal conductivity and/or heat transfer in nanofluids based on magnetic nanoparticles, as in the recent paper on the effect of magnetic field on laminar convective heat transfer of magnetite nanofluids (Azizian et al., 2014).

Thermochemical energy storage materials

[5] Recently enlightened by POLITO for diesel engine lube oils in the EU funded ADDNANO project (Deorsola et al., 2012), by CNR for gas engine oil (Zin et al., 2013) and for air conditioning equipment oils and oil-refrigerant mixtures (Bobbo et al. 2010) in the projects funded by the National Research Program for the Italian Electric System

The possibility to store thermal energy when excess heat is available (e.g. from the environment during the day or during the summer, as well as from batch industrial processes or "waste" heat) is representing a fascinating way to enhance energy efficiency. In particular seasonal storage and controllable stored energy release are research topics currently attracting significant research efforts. In fact, the traditional phase change materials, widely exploited in daily solar energy storage, are usually not suitable for seasonal storage owing to their intrinsic low density of energy stored. Furthermore the heat discharge of PCM is triggered by temperature only, so that the discharge cannot be controlled or programmed, thus limiting their use in more flexible applications, requiring on-demand heat discharge from the storage device.
On the other hand, thermochemical Storage, based on the adsorption/desorption of water on/from hydrated salts is an excellent option for controlled storage and release of energy «on demand».

hydrated salt	Q [KJ/K g]	Dehydartion Temp [°C]	Hydration Temp [°C]	Cost [€/Kg]
$MgCl_2 \cdot 6H_2O \leftrightarrow MgCl_2 + 6\,H_2O$	2001	120-180	<70-80	0,15
$MgSO_4 \cdot 7H_2O \leftrightarrow MgSO_4 + 7\,H_2O$	1671	60-265	25	0,077
$Na_2SO_4 \cdot 10H_2O \leftrightarrow NaSO_4 + 10\,H_2O$	1749	40-100	< 20	0,056
$SrBr_2 \cdot 6H_2O \leftrightarrow SrBr_2 \cdot 1H_2O + 5H_2O$	1033	40-100°C	RT	2,4
$LaCl_3 7H_2O \leftrightarrow LaCl_3 \cdot 1H_2O + 6H_2O$	1242	50-100	RT	2,5

Figure 6: Hydrated salts examples and properties

Nonetheless, there are technological challenges associated with the use of hydrated salts include stability upon aggregation, excess water absorption, durability, which require integrated efforts to overcome the present limitations and provide industrially viable solutions for large scale applications.
In particular, the combination of hydrated salts with thermally conductive, porous and mechanically stable carbon structures have been recently explored at polito and demonstrated promising at lab scale. It is also worth mentioning that development of hydrated salt-based storage is directly linked to polymer-based heat exchangers, which are required to provide a low-cost, design-flexible and highly resistant materials in the harsh corrosive saline environment.

2. Objectives

In term of general objectives, this sub-programme aims at developing new (micro- or nano-designed) materials according to the EU scenario by the year 2020: 1) save 20% energy; 2) decrease 20% of CO_2 emission; 3) achieve 20% of renewable energies.
Each area of technological impact (Figure 1) shows however its specific own conditions, operating conditions, reference heat transfer fluids, economical constraints. Generally, the materials developed in this sub-programme are expected to be costly in comparison with conventional materials, but significantly improving the energy efficiency of benchmark applications.

In the next section, specific and semi-quantitative objectives are provided along a succinct roadmap of activities.

3. Work programme and roadmap

Coming into specific details, some grand challenges are hereafter outlined, based on a survey of the current patents and literature in the respective areas as well as on the expertise of the AMPEA partners. Timescales are different for different applications, depending on their current level of development, the further efforts required for their improvement, the respective market constraints. Therefore, along the time coordinates the table reports a number of milestones with measurable objectives for any of the technological areas of interest.
Grand challenges, defined on 2014, directed some AMPEA actions, such as the workshop "Low temperature heat recovery" held in Torino on 2015 and dedicated Joint Program Steering Committee (JPSC).

Grand challenges

topic	5 years	10 years	20 years
Energy harvesting materials	Integration of the current materials in sustainable devices	Development of stable and sustainable thermoelectric	Integration of energy harvesting devices in everyday life to reduce CO_2

		materials with ZT = 1.5 for power generation	emission and to produce electrical generation with ZT = 2. Highly efficient green solid state cooling devices alternative to heat pumps.
	3 years	**5 years**	**10 years**
Polymer nano-composites for intensified heat transfer	Exploit the potential of current compounding techniques (e.g. screw extrusion) to generate nanofilled polymer compounds with improved thermal conductivity and minimized costs at the lowest possible filler content	Significant improvement of the thermal conductivity and reduction of filler contents through new, improved compounding techniques optimised on the grounds of appropriate multiscale modeling	Develop self assembling techniques guaranteeing a further stepwise increase in thermal conductivity for an equal filler content or sufficient thermal conductivities for minimised filler contents and manufacturing costs.
	3 years	**5 years**	**10 years**
Micro/nano-designed surfaces for intensified heat transfer	Clearly demonstrate the potential of micro/nano-designed surfaces for intensified heat transfer manufactured with reproducible lab scale techniques (e.g. rapid prototyping,laser etching, etc.)	Optimise industrial cost-effective manufacturing techniques to derive marketable products and demonstrate practical applications	Optimise through a knowledge based approach self-cleaning antifouling surface expanding the potential application of these heat transfer surface to a wider span of appliances.
	5 years	**10 years**	**15 years**
Nanofluids	Repeatability and reproducibility of experimental data	Comprehension of relationship between chemical-physics characteristics of nanoparticles and lubricant properties of nanofluids	Comprehension of relationship between chemical-physics characteristics of nanoparticles and thermal properties of nanofluids
	3 years	**5 years**	**10 years**
Thermochemical energy storage materials	Lab-validated solutions for the hydrated salt stabilization upon aggregation, excess water absorption, durability	Integration of stabilized thermochemical heat storage materials into demonstration devices	System integration and control systems developed for the to management of the thermal battery charge/discharge

Milestones and Actions

Section 1 – Energy harvesting materials

Polymeric TE materials work at low/mid temperatures and are very attractive due to its easy fabrication processes and low material cost, but it is necessary to improve their electrical conductivity. Promising strategies include the addition of carbon nanostructures and semiconductors or metals. Before real engineering of polymer-based thermoelectric devices, there is reasonable advance to be achieved.

As an example of achievement in the field, doped-polyanilines composite have been studied to obtain hybrid organic/inorganic thermoelectric materials. Processing route has been set up for obtaining flexible TEG leg with state-of- the-art ZT. The best ZT was calculated for PANI-DBSA containing SWCNH 15 wt%. Preliminary encouraging results were obtained with addition of BiSeTe NMP .

New topic has been explored, not included in the initial DoW. Thermoelectric liquids (nanofluids) are under investigation containing redox couples (thermogalvanic effect) and/or charged colloidal particles (thermoelectric diffusion and adsorption) in search of novel thermoelectric phenomena.[6] The host liquids (electrolytes) include water, organic solvents, ionic liquids and their mixtures. Charge stabilized magnetic nanoparticles are found to increase the thermoelectric power-output by 100% at very low concentrations[7].

For liquids, the definition of “high temperature” is considerably lower than that of solid counterparts. That being said, instead of using aqueous electrolytes at CEA they are now integrating ionic liquids which allow the use of thermoelectric liquids at temperature much higher than 100°C. Current operational temperature range is about 200°C. This limit is expected to be increased to above 300°C by introducing suitable thermocell material.

For mid-temperature power generation (500–900 K) critical semiconductor alloys have been thoroughly studied and developed thanks to their high figure of merit. Apart from the relevant issues of chemical stability with respect

[6] H2020 FET-Proactive project MAGENTA (https://www.magenta-h2020.eu) has been successfully submitted Partnership include two AMPEA members, CNR and CEA

[7] PhD thesis of T. Salez, 2017.

to sublimation and oxidation, such materials are in conflict with clear indications of the RoHS European directive. Compared to the traditional thermoelectrics used in the same temperature range, many new materials have begun to appear, characterized by low environmental impact, by virtue of their low element toxicity, low cost, and higher natural abundances. In the medium-long term, envisaging a wider development and spread of TE converters, the switch to sustainable materials will turn out to be mandatory. They can realistically face the challenges of a real exploitation of the TEG technologies in a wide range of temperatures.
Study on ancillary materials are in progress, concerning the deposition protective coatings onto the module legs, metal connectors and joining for lowering the internal resistance.
Detailed and systematic fundamental studies are ongoing for assessing the effects of structure and dimensionality on the thermal conductivity and thermoelectric properties, together with technological research devoted to material processing.
Finally, as shown by many studies, multiphysics modelling applied to TEG elements is a powerful tool for materials and modules design and limits the number of experiments; numerical analysis can contribute to find the optimal geometry for the module; to solve the mechanical problem of coupling elements with different coefficient of thermal expansion; to localize the maximum of tensile stresses.

Table 1a

Milestone	Measurable Objectives	Project Year
Thermoelectric Materials		
M C.2	Avoidance of rare earth, noble metals or toxic materials (e.g. Pb) in the thermoelectric devices	*5*
M C.4	Achieve higher compactness and lightness of devices through adequate system engineering and process intensification (e.g. combination with other technologies of the present subprogramme)	*15*
M C.5	Expansion of the temperature range of effectiveness from 100°C (enhancement of efficiency required) to 1000°C (enhancement of durability required) through a better engineering of thermal-electrical properties of materials	*20*

Pyrolectric materials could harvest energy from naturally occurring temperature changes such as changes in ambient temperature, and artificial temperature changes due to exhaust gases, convection or solar energy. These materials can operate with a high thermodynamic efficiency and, showing an advantage over thermoelectric materials, they do not require bulky heat sinks to maintain the required heat difference. Hence, pyroelectric energy harvesting represents another potential methodology to rescue some of the enormous amount of energy wasted as heat by converting the thermal fluctuations into electrical energy.
Current activity carried out under the supervision of ENEA concerns a novel approach to the formation of ZnS wurtzite nanopowder and nanotextured wurztite ceramics which can offer new pathways in pyroelectric (and piezoelectric) energy harvesting, leading to significant breakthroughs in the development of high quality and non-toxic materials for use in ambient energy harvesting at a lower cost. The two years research project will be done in collaboration with other stakeholders. [8]

Section 2 – Polymer nano-composites for intensified heat transfer
This area of research requires both short term and medium term progresses. In the short term, the best performances achievable with commonly used compounding techniques must be assessed. Any significant progress achieved by these could possibly lead to early market products.
In the medium term, the achievement of a better fundamental knowledge of phonon transfer mechanisms, the development of accurate design tools and the promotion of self-assembling techniques to obtain the filler percolation pathways at minimal filler content, could lead to a radically innovative class of materials.
As achievements in the field, thermally conductive polymer nanocomposites were developed in terms of processing, performance and modelling.
Aiming at obtaining superior nanoparticles dispersion via an industrially viable and scalable process, reactive polymer processing was studies thoroughly. In particular , polymerization during extrusion via ring opening were found to be a convenient method to infiltrate lamellar nanoparticles (graphene nanoplatelets, reduced graphene oxide) and subsequently disperse those taking into advantage of the increasing viscosity upon polymerization. This was applied to cyclic oligomers of polybutylene terephatalate as well as lactide, to obtain nanocomposites based on polybutylene terephthalate. Isotropic thermal conductivity was obtained in the range of 1 to 2.5 W/mK, depending on the particle type and loading (<20%wt), demonstrated to possibility to produce, via melt processing in extruder, materials with thermal conductivity performance in line with the state of the art materials produced

[8] This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 797951

with thermosets solvent-assisted methods. On the other side, strong orientation and excellent dispersion obtained via a potentially scalable pressing-and-folding method demonstrated in-plane thermal conductivities >10 W/mK (i.e. >30times the pristine polymer) with particle loadings of 25%.

Table 1b

Milestone	Measurable Objectives	Project Year
Polymer nano-composites for intensified heat transfer		
M C.6	Achieve a 10-fold increase in thermal conductivity compared to the bulk polymer material with nano-filler loading < 5 wt% or at least 10 W/(mK);	*3*
M C.7	Achieve a 20-fold increase in thermal conductivity compared to the bulk polymer material with nano-filler loading < 5 wt% or at least 10 W/(mK);	*5*
M C.9	Expand the viability of these nano-composite materials up to 200°C;	*7*
M C.10	Develop self-assembly techniques for the build-up of phonon perculation activity with 20-fold increase in thermal conductivity compared to the bulk polymer material with nano-filler loading < 2 wt%	*7*
M C.12	Achieve the level of knowledge to develop multifunctional exploiting the potential of nanofillers to tune thermal, electrical and mechanical properties of polymer materials.	*15*

Section 3 – Micro/nano-designed surfaces for intensified heat transfer

Beyond the full exploitation of the potentialities of micro- and nano-structured heat exchange surface in boosting sensible and latent heat transfer the main challenges here are in the development of economic manufacturing techniques and in the development of self-cleaning surfaces to avoid fouling processes.
Beside surface top-down microstructuration, bottom-up nanostructured coatings on surfaces have aslo been explored. Indeed, some organic/inorganic coatings were demonstrated as a mechanical flexible and though alternative to high temperature inorganic insulations, especially aerogels. For instance, “brick and mortar” organic-inorganic coatings were also demonstrated able to protect bulk substate in the presence of a flame, owing to their delamination to produce multilayered porous insulating coatings.

Table 1c

Milestone	Measurable Objectives	Project Year
Micro/nano-designed surfaces for intensified heat transfer		
M C.13	50% increase of convective heat transfer coefficient by surface micro-structuring through a better engineering of wall	*3*
M C.14	push forward nanostructured surfaces in industrial applications for boosting heat transfer coefficients in the presence of phase changes (e.g. pool boiling, condensation, etc.)	*3*
M C.16	development of surface nano-patterning for electrostatic heat transfer enhancement (e.g. ionic wind).	*7*
M C.17	development of nano-structured anti-fouling coatings for heat transfer surfaces;	*10*

Section 4 – Nanofluids
In spite of this great potential, there are a number of issues which have not been fully investigated (e.g. the exact mechanism for alteration of thermophysical properties and forced convective heat transfer characteristics is still unclear) as well as technological hurdles that need to be overcome to ensure practical applications (e.g. durability of the particles suspension; avoidance of deposition of nanoparticles; safety issues related to the leakage of nanoparticles in case of defaults, increased viscosity and pumping power, field effect on magnetic nanoparticles depending on particles size, etc.). Some of the groups in AMPEA are focusing their research efforts to overcome these barriers, also on the ground of recent advances achieved in controlling the aggregation state of the suspended nanoparticles. [9]
One of the main issues in the interpretation of nanofluid thermal and lubricant properties is probably the significant differences among the conductivity values reported in the literature, even for nanofluids based on the same base

[9] The on-going European Cost Action “NanoUptake” is dedicated to developing and fostering the use of nanofluids as advanced heat transfer/thermal storage materials to increase the efficiency of heat exchange and storage systems. CEA is on the management committee, and ENEA, DUT and CNR are members. Joint events AMPEA-NanoUptake can be envisaged in the near future

fluid and on the same type of nanostructured material. Considering the same type of particles and base fluid, such variations may be due to different shapes or sizes of nanoparticles, to different stability of the suspension that could affect the properties over time, to the presence of surfactants that can alter the thermal conductivity, besides a variability of the results depending on the method of evaluation of the conductivity.
Concerning nanolubricants, although considerable efforts have been made to understand how nanoparticles work to reduce friction and wear, the friction decrease mechanism has still to be clarified. Several mechanisms have been presented to enhance the lubricant properties with different nano-oils, as rolling/sliding effect, protective film, third-body effect, and mending effect. Among available nanoparticles, carbon nanostructures, in particular fullerene and nanotubes are promising candidates as additives in lubricant oils, thanks to the ease of shearing their individual layers. However, in most cases the poor reproducibility is due to insufficient control of the synthesis process, which must ensure reproducibility in the shape, size and stability of the suspended nanoparticles. This suggests that the development of synthesis methods for nanofluids is still one of the challenges to face in this field. Same examples of the activities carried out in AMPEA are shortly described below. With commercial lubricants as base oil, nanolubricants were prepared dispersing metal/metal oxide NMPs and C nanostructures (SWCNH, graphene nanoplatelets). The validation of the efficiency and improvements of nanoparticles used as additives in conventional oils were carried out in laboratory (Stribeck test for friction coefficient and wear tests) and in working conditions on engine test bench cycle. These new lubricants containing nanoparticles were able to warrant better performances than commercial oils in terms of durability, wear resistance, friction and heat transfer. Description is in progress of the real role played by nanoparticles as additives in oils and their activity during engine working, as well as the investigation of the synergistic effect of nanolubricants and hard protective coatings.
Moreover, in order to reach an efficient management of the energy at all levels (conversion, production, transfer, transport…) basic research is required to investigate thermal processes and the different means energy is being transported and converted. Energy transfer and thermal processes should be considered in various media: in fluids (fluid, gaseous, diphasic), in solids and at different scales, up to scales of nanofluids. As many processes in energy conversion occur in turbulent conditions, it is obvious that energy efficiency will benefit a better understanding of turbulence; eventually, it is necessary to consider the complex interactions taking place in energy systems in order to maximize their efficiency, comparing liquid coolants from both a thermal and hydraulic perspective.
Finally, if the base fluid/nanoparticles system is approached in a holistic way, many applications can be envisaged. One interesting example is their possible use for increasing the overall efficiency of solar devices exploiting both optical and thermal properties of nanofluids in view of their use as sunlight absorber fluids. In particular, the use of them for direct sunlight absorption (“black fluids”) has to be explored by combining the experimental characterization of optical properties, the numerical simulation of heat transfer performances and the engineering upscaling towards real systems. With this aim, many studies have been carried out involving AMPEA and CSP JP groups and a direct absorption receiver has been designed and set up to investigate the capability of the nanofluid to absorb the concentrated sunlight. The thermo-physical properties of SWCNH suspension in water are the same as those of the base fluid, but the presence of carbon nanoparticles greatly enhances the optical characteristics. The efficiency is comparable to that obtained with a surface receiver tested in the same system, but the stability of the absorbing fluids is always a challenge.

Table 1d

Milestone	Measurable Objectives	Project Year
	Nanofluids	
M C.18	To achieve a 15% increase in thermal conductivity and no more than 5% increase in viscosity, compared to the bulk fluid, by low-cost nano-particles loading < 1 v%;	*5*
M C.19	To increase the durability of nanofluids by improving the stability, by reducing the amount of surfactants and by engineering better the nano-coated particles	*10*
M C.20	To improve of 30% the lubricant properties of nano-fluids in industrial applications (T range 80-300 °C)	*10*

Intensive cooperation have been established with the three AMPEA tool-related sub-programs on “Materials”, “Characterisation” and “Modelling”. These inter-relationships are crucial to cement and provide a cross-fertilisation among the different technological areas of the present sub-program. It is indeed evident that common materials development routes, characterisation means or modelling tools may be adopted throughout the research areas. One research line may draw inspiration from the discoveries of another one. For this reason, periodic workshops (at least one per year) are held with common participation of all the R&D performers involved in the sub-program.

Cooperation with the tool-related sub-programmes

- Materials

As mentioned in earlier sections, nanomaterials are essential for nearly all the technologies involved in the present sub-program, with the only exception concerning micro-structured surface for heat transfer enhancement in the turbulent regime (Fig. 4). For this very application field, rapid prototyping, as pioneered by Ventola et al. (2014), could provide large benefits to understand the relationship between the shape of the surface pillars and the achieved heat transfer enhancement. Moreover, nano-engineered powders for rapid prototyping could be used to enhance even further the desired features of the fluid-solid interfaces with enhanced heat transfer.
Anyway, in all fields, nanotechnologies have to be exploited keeping an eye on economic feasibility at an industrial level. In this perspective, in the area of nanocomposites with enhanced heat transfer properties, the development of self-assembling methods for the formation of percolating filler particles are as complex as potentially highly beneficial from en economic point of view, provided that no changes to the main polymer compounding industrial processes (e.g. screw extrusion) are required and rather low cost polymer matrixes are used.
By analogy, the deposition of nano-structured materials on the surface of condensers or pool-boilers will have to be cost effective to be fully justified by the enhancement of heat transfer coefficients in these two contexts.
Conversely, in the area of thermoelectricity, there is a lack of detailed and systematic studies on the nanostructuring techniques and the effect of the nanostructure on the thermal conductivity and thermoelectric properties of different materials covering the entire span from inorganic to organic ones.
In order to achieve suitable TRL for TEGs based on safe materials and components, it is necessary to integrate the material study with the design and numerical simulation of the module, considering the possibility of further optimizing the TE properties, but it is also necessary to find a so-called “killer application” injecting new enthusiasm into the research community.
Moreover, in the area of nanofluids, particular care will be taken to achieve the integration of nanofluids in different applications, as for *black fluids* in solar applications.

Beyond techno-economical issues, life-cycle assessment will be a commonly employed tool for the design of materials and synthesis/deposition processes. Moreover, as a crucial issue for any nano-material, safety analysis of both materials manufacturing processes and potential release of nanoparticles in use or after disposal will be carefully evaluated. Finally, pre-normative issues will also be considered, in line with the procedures established by the NANOfutures initiative (“European initiative for sustainable development by Nanotechnologies”) and the need of techno-economic assessment of new technologies.

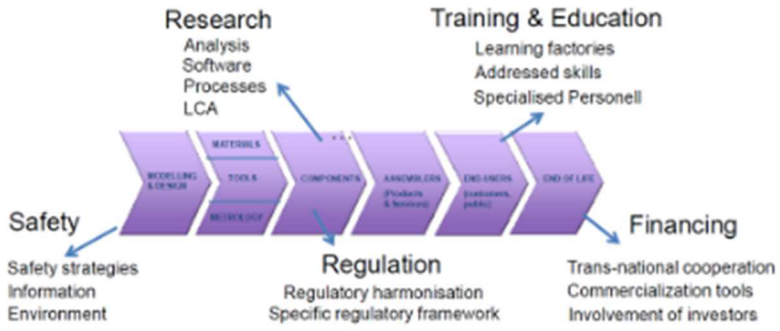


Figure 7: Route for the development of nanomaterials developed by the former NANOfutures initiative (www.nanofutures.info).

- Characterization

Beyond the overall thermal and electrical conductivities measured at a macroscale via conventional systems, the need to measure thermal conductivities at a nanoscale level to understand the effectiveness of the materials preparation routes and provide validation data for nanoscale models, may lead to further developments in the area of nano-thermal analysis (TA) and temperature mapping.
The sufficiently accurate and precise measurement of thermal diffusivity of fluids has been a major concern for several years in the past. Estimations on different fluids have been reported by authors with larger spreads than reported experimental errors. Effective results have been obtained designing and building a device based on photoacoustic effect for the estimation of the thermal diffusivity of fluids at different temperatures. The photoacustic technique demonstrated a potential for a more accurate estimates of thermal diffusivity of fluids compared to more conventional techniques such as the “HotDisk” and “Laser Flash” methods that seems more suitable for the characterization of solids and powders. This is an example of instrumental research carried out on cheap but useful instrumentation that can be replicated by the groups interested to this kind of characterization.

- Modelling

A specific thrust area of interest is the discovery of new techniques for modeling, measuring, and analyzing thermal phenomena at multiple time and length scales in emerging novel material systems with the ultimate goal of exploiting these phenomena to design future materials and components that break the paradigm of today's materials.
As for the thermoelectric applications, modelling will provide a fundamental understanding of the physical phenomena, in order to fix the requirements of the materials and to address their development in the most suitable way. DFT methods, Boltzmann transport modelling, TE continuum theory are modeling approaches of certain interest in the development of new TE materials and in the proper understanding of the physical mechanisms affecting their performance.

4. Interface with other JPs

The overall set of EERA joint programmes (JPs) can be found in http://www.eera-set.eu/.

The materials developments undertaken in the present subprogramme of the AMPEA JP can be of interest for several other JPs and particularly:

- Energy Storage JP, where a subprogramme on "Thermal storage" has been issued including phase change materials, advanced fluids and thermochemical systems for thermal storage. Any mean to transfer heat effectively to these storage media is obviously welcome and technology integrations are expected as particularly fruitful, as mentioned above.
- Concentrated Solar Power JP, where the storage of concentrated solar power deserves a specific subprogramme. It has to be mentioned to these merits that one of the most promising applications of nanofluids lies in the recovery of heat from solar thermal systems (Javadi et al., 2013).
- Geothermal Energy JP, an area where the low temperature ranges of the geothermal fluids coupled with their corrosive nature offer good application opportunities for heat recovery through polymer heat exchangers.
- Hydrogen and Fuel Cells JP, where once again polymer heat exchangers could be integrated with the polymer-electrolyte-membrane (PEM) related technologies (electrolysers and/or fuel cells) for system efficiency maximisation purposes, with no major prejudice of lightness , as highly welcome on board cars.

Specific meetings will have to be organised with the relevant persons of the above JPs for the mentioned technological challenges.

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