Material Challenges

(in *real* devices for fuel solar production & employment)

Focus on Workshop *outcomes*, needed for

- Recommendations to CECAM, to forward to the EC For action within the FP8 (identify key themes for common bids for resources)
- Report to ICTP & to Psi-K network

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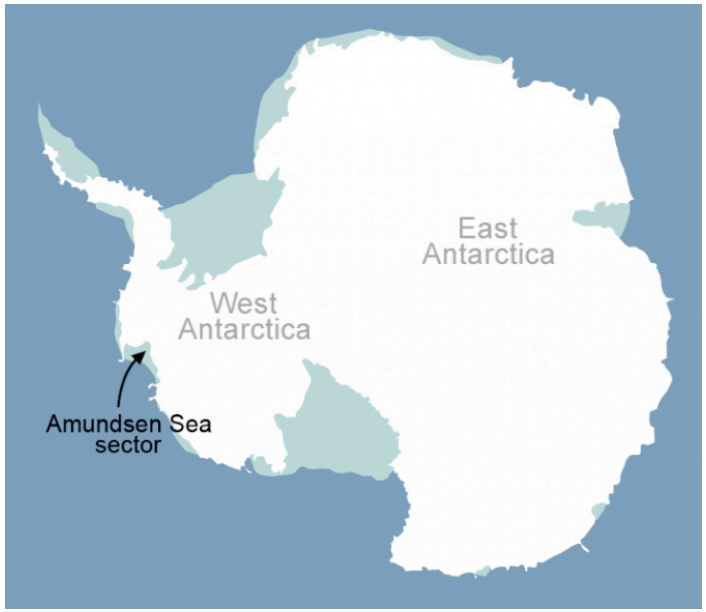
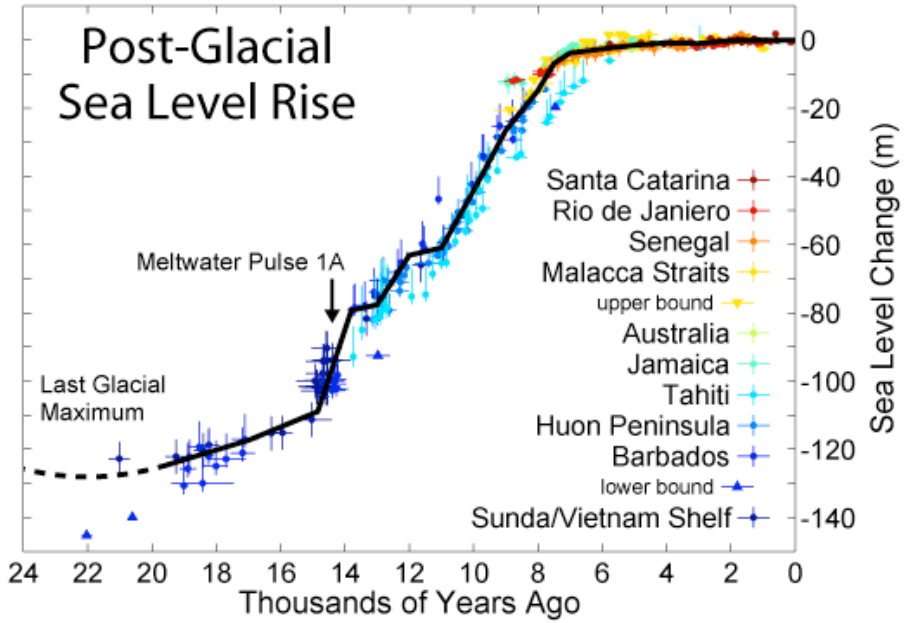
Motivation Aplenty…



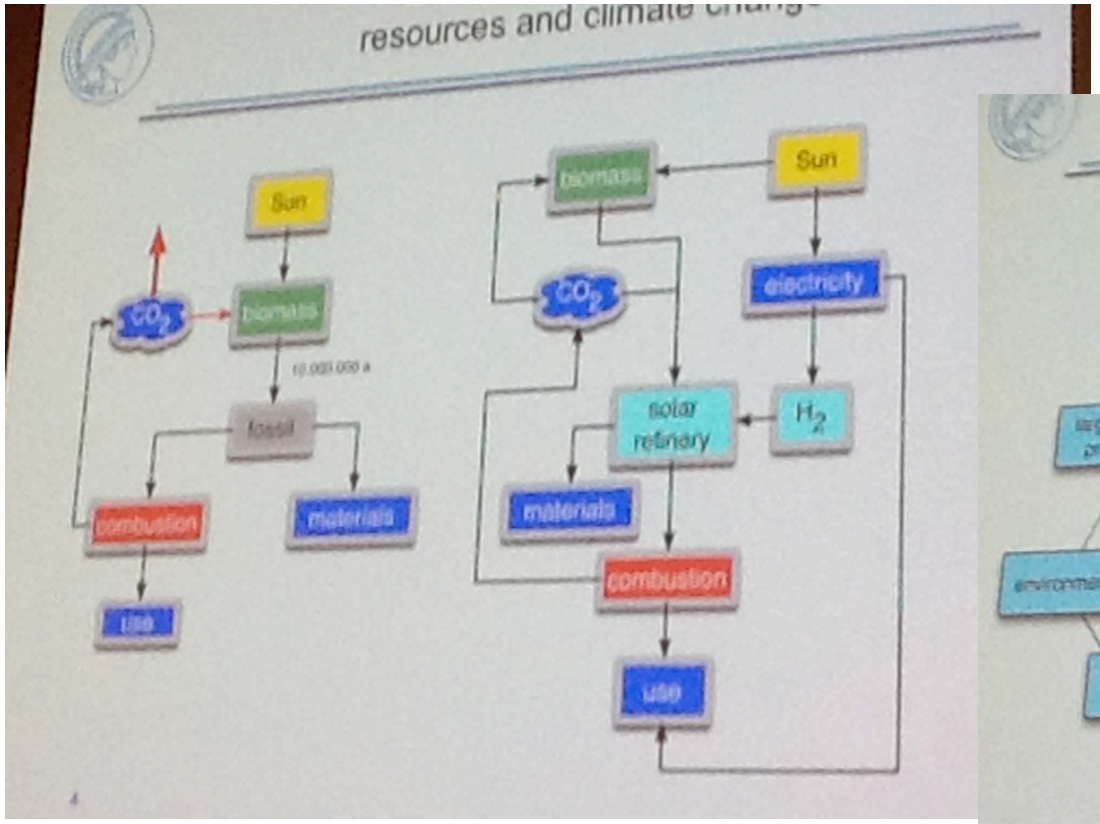


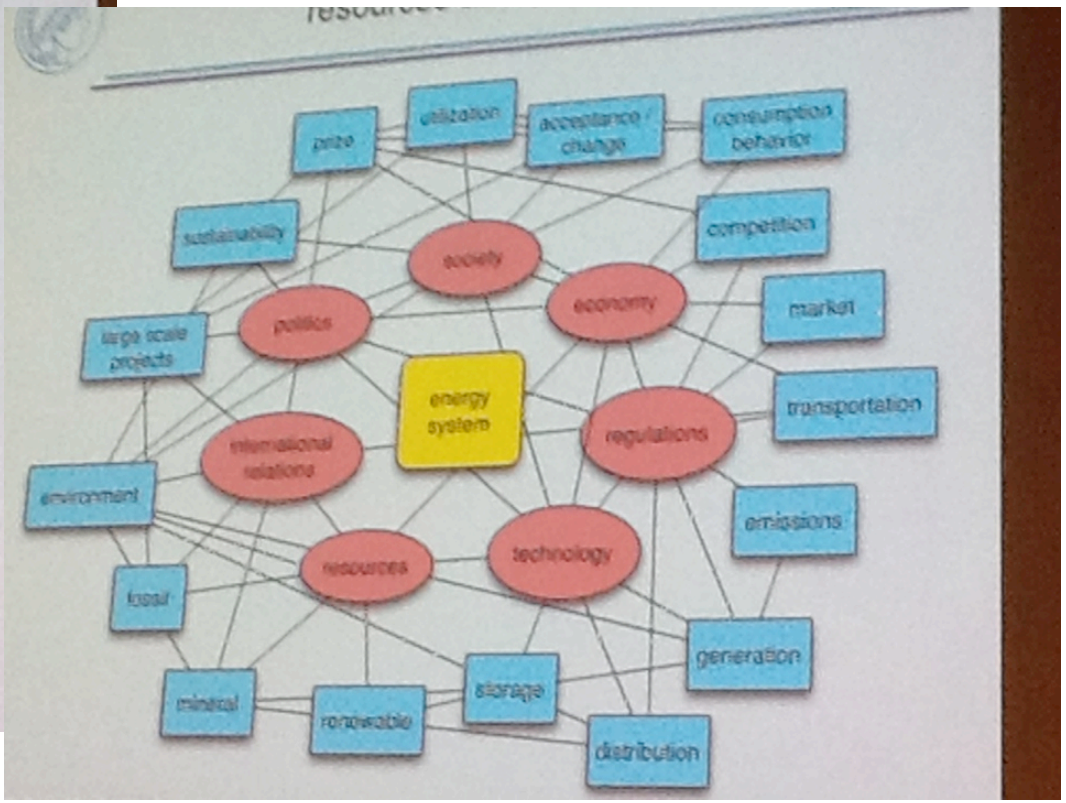
Global warming: it's a point of no return in West Antarctica. What happens next?

Last week saw a 'holy shit' moment in climate change science. A landmark report revealed that the collapse of a large part of Antarctica is now unstoppable [on its own good for about 1.2m of sea level rise]

Eric Rignot, The Observer, Saturday 17 May 2014 20.30 BST

Present, Future, *and in between…*





…background challenges

Background Challenges

- SEVERE CLIMATE CHANGES CHALLENGE
  mostly due to carbon emissions
- LOOMING SUSTAINABILITY CHALLENGE
  Fossil fuels will run out (and before that, break-even costs are bound to raise)
- GENERAL SOCIETAL CHALLENGES
  Energy production needs to factor in space and water logistics. Conflict with political agendas (Kyoto failure, fossil fuels prominence for power steering). Need for a background culture for sustainability, and generally a long term vision.
- Conversion and storage. TW-scale electrolysis already feasible, but need for new materials (perovskite solar cells): comp. and exper. Materials science: from single atoms to hierarchical architecture up to microscopic/macroscopic.
- At political level: talking to politicians; role of ICTP in developing countries; role of young people.
- Maybe right materials are yet to be discovered.

MATERIALS CHALLENGES

FUNDAMENTAL

- Need of much better understanding of the fundamental processes (catalysis steps, overpotential causes, hole/electron diffusion, …).
- Pressure to identify new, better performing materials (current performance still a way from thermodynamic limits)
- Need for better characterisation (new techniques? More experimental and theoretical)
- Need to enhance component durability (against corrosion, performance deterioration, thermal fatigue, …)

DEVICE-RELATED

- Safety (energy concentration, chemical stability)
- Cost Containing (rare materials, energy containment, distribution infrastructure)
- Coordinating research with large plants specs & logistics
- Device lifetime issues, recyclability and environmental impact
- Most importantly, an Engineering Problem: how to achieve a correct hierarchic organisation of primary, secondary, tertiary, etc., structures within a properly functioning device. Devising techniques to do this is still in its infancy…

Example: Desired Materials Properties

(Source: Karsten Albe's talk yesterday afternoon)

- 1.23 eV < band gap < 3 eV
- Engineered pathways of electron-hole pairs
- Charge transfer used for water splitting instead of corrosion
- Efficient H_2 production with low overvoltages
- Fermi level alignment issues (under illumination)
- Design of an actually working device
- Design *and implement* device assembling procedures (real life, plant scale).

SUGGESTED DIRECTIONS I: EXPERIMENT

- Characterisation: *in situ & in operando techniques*
- Enhanced photo/-electro-catalysis: *doping* to moderate overpotential and enhance conductivity [0.1nm]
- Reducing primary materials cost, enhancing performance and improving durability: *Nano-resolved control of catalyst/electrode structures* [1-100nm]
- Microstructure control (porosity, thermal stability) [1um+]
- Trends:
  - A shift to (bio)organic materials for enhanced range of functionalities
  - A shift towards mixing top down and bottom up fabrication strategies, trying to exploit supramolecular self-assembly
  - Synthesizing carbon-based fuels is a realistic option (e.g., by solar powered inverted fuel cells)
  - Throughout, tight integration of experiment and theory: catalysis is too hard to understand/conquer/control for either, taken on its own…

SUGGESTED DIRECTIONS II: THEORY

- **Dealing with open shell radicals**: exact exchange techniques, extensive validation/ calibration against higher accuracy techniques on small reference systems
- **Dealing with charged states:** non-periodic static embedding, image-charge corrections
- **Dealing with excited states:** advanced electronic structure techniques, bespoke models for transport of hole/electron conduction
- **Dealing with complex phase spaces:**
  1) Composition space: data mining search and relative heuristics, databases
  2) Structure prediction at fixed composition: heuristics for complex electrodes
  3) Modelling high barrier reactions: rare event techniques (NEB, metadynamics, …)
  4) Modelling chemically aggressive (often, hot) reactive environments: First principles molecular dynamics
  5) Modeling component chemo-mechanics: via dynamical embedding techniques (e.g., to target stress-corrosion, interface chemistry under thermal expansion mismatch, or catastrophic fracture)
  6) Beyond explicit electrons: force field potentials, cluster expansions
  7) Beyond dynamics: Kinetic Monte Carlo techniques
  8) Beyond atomistic representation: finite defects analysis, finite elements, serial embedding techniques (“message passing” multi-scale including coarse graining to bead- or grid-based finite elements).

Discussion:

-) More promising materials: organic or inorganic? Actually, currently hybrid organic-inorganic are the most recent breakthrough in the field.

-) More collaboration is needed. See best practices at Fritz Haber Institute in Berlin (Schloegl, Freund, Scheffler): sharing ideas and concepts. There are also language barriers between communities. Problem: precision at which you know to know something: e.g. theory good at calculating adsorption energies, but these are difficult to impossible to measure. On the opposite, atomic structures and spectra might be useful. Necessary to overcome technical limitations (e.g. for metal-oxide interfaces, organic-inorganic interfaces). The causality of observations must be investigated. It is possible to synthesize large systems with properties predicted by theory; e.g. MgO: idea of subsurface doping came from theory, it was followed by 4 years of experimental work. Huge increase of activity in the end.

-) Barriers for collaborations: 4 years of work without publications, this is nearly impossible in the current reward system. We must praise content over publication statistics. For this there is need of funds for blue-sky research for long-term breakthroughs as wished for by CECAM, whereas Horizon2020 seems to go in the opposite direction.

-) For the success of collaborations, two elements are fundamental: accuracy of results, and flow of ideas. Theory could also help experiments focus on most promising systems/measurements, but need clear predictions from theory. Problems of communications between theory and experiments are a major hurdle to collaboration.

-) At the nanoscale, many phenomena are new and/or uncontrolled. This is a scale that is not easy to reach by electronic-structure simulation methods. Theoretical models sometimes are far from experiment in terms of size. Sometimes, on the contrary, agreement is very good.

-) Recombination centers in oxides and origins of photocatalytic properties: still not understood, contribution of theory insufficient. We have to address the fundamental issues, also with theory, rather than just checking materials in a sequential way. We need concepts about microscopic phenomena that give insight and can guide materials search and research. On the other side, there also high-throughput calculations and data mining will be useful.

-) Some experimentalists report to have had a theoretician (postdoc) in their experimental group, and it was working. A semi-young theoretician, collaborating with other theoreticians elsewhere, interfacing with experimentalists. Also very close collaborations with external partners are possible, but it is necessary to overcome an initial barrier, to let understand what is really measured in experiments. Then it becomes extremely powerful. Ideas flow works both ways.

-) What are the requirements for a successful collaboration, e.g. for Horizon2020? Collaboration could be particularly useful to explain microscopic mechanisms, e.g. ultrafast processes like charge transfer. First on a simpler system to understand the fundamentals, and then experiments should go for an upscale in size/complexity.

-) In collaborations, having theoreticians with different expertise is very useful. It takes years for a collaboration to evolve (several years). 48-moths projects are not useful in this context, there is a need for different funding strategies, also long-term. Also some changes to projects could be useful, e.g. the definitions in milestones, and the concept of milestone itself. The European Research Council is an example of a good-working program for funding of long-term fundamental research. An ERC program for groups would be useful.

-) For projects, also an option for renewal after 48 months, upon judgement of a commission, would be a great step forward. Actually, currently there is a new kind of projects: Flagship projects, with a huge amount of money for 10 years for 100 groups or more. Energy might be a suitable topic for this kind of funding. But competition for that is huge.

-) Also, progress takes place in two steps: individuals bringing forward new ideas, and then big collaborations help the concept ripe up to practical technology.

-) For theory-experiment collaborations, it is much better when people are in one place. For example with temporary presence of scientists (1-2 years), to see how it evolves.

-) What would be a suitable topic for such a collaboration? For some, the seed should be a concept, not a product. On the other side, there is a need to solve practical materials problems, to get things real. For example, in photovoltaics. Many technologies are being invesitgated, none is fully satisfactory for real life, mainly due to lack of long-term stability of the materials (e.g. are hybrid perovskites stable?).
Still, there is a need to identify ‘simple’ general problems, grand challenges. E.g. wide-band gap semiconds are very stable, but do not absorb light. Whenever they are modified to absorb light (e.g. by H doping), the stability problem is back. There are a lot of mutual exclusion principles between desired properties.
Another possible problem of general interest with practical implications could be that of hole conduction in oxides. A big breakthrough would be to predict the lifetime of excitons in semiconductors.

-) In polymeric fuel cells, Pt is used as catalyst. It needs to be reduced. They were successful in reducing the Pt amount, but then there is peroxide formation which leads to corrosion problems for the polymers. Peroxide radicals attack the material. Corrosion in low-Pt environment is a problem that is of major importance. Platinum is there to stay.

-) Stability and reactivity are mutually exclusive. A compromise must be achieved. Stability can be thermodynamic or kinetic. To be reactive, it is important to be slightly above thermodynamic equilibrium. There are probably many states slightly above equilibrium. Materials kinetics needs to be understood to control this and to find an optimal compromise. For example, surface roughness is the main control parameter for the reactivity of MgO. This can be controlled through metal-support interaction. Synthesizing particles for catalysis and controlling the final shape under operating conditions is a very important area of research. Sometimes the only way to get different shapes is to use different synthesis methods. There is no theory guiding this process. It is important to get people interested into atomistic kinetics for synthesis and control of nanostructures, on the time-scale of vibrations of the system. Taking into account pH, potentials. It needs molecular dynamics. During reaction conditions, shape and compositions change. In fuel cells, it is not even clear whether Pt or Pt oxide is doing the catalysis.

-) There is need to know from experiment the structure *in operando*, to start to do theory. On the other side, a role of theory is also to predict what the candidate structures are that might be there under operating conditions. Currently, theoreticians still look for the most stable structures.

-) Many possible ways to have theory-experiment collaborations. Anyway, you have to start from the thermodynamics, then you can go to kinetics. Still, huge phase space. It is expensive but all tools are already there. Configuration space exploration through data mining for kinetics should be possible, e.g. in combination with kMC.

What are the grand challenges?