



UK ENERGY RESEARCH CENTRE

Accelerated Materials Discovery for Energy Storage and Conversion Devices

Meeting Report

St Antony's College, Oxford, UK, 2nd - 4th April 2007
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The Institute of Materials, Minerals & Mining



This document is a report by the organiser of a technical meeting set up as part of UKERC's research programme. It is believed to be an objective record of the meeting but has not been separately reviewed by the participants.

THE UK ENERGY RESEARCH CENTRE

Operating at the cusp of research and policy-making, the UK Energy Research Centre's mission is to be the UK's pre-eminent centre of research, and source of authoritative information and leadership, on sustainable energy systems. The Centre takes a whole systems approach to energy research, incorporating economics, engineering and the physical, environmental and social sciences while developing and maintaining the means to enable cohesive research in energy. To achieve this UKERC has developed the Energy Research Atlas, a comprehensive database of energy research, development and demonstration competences in the UK.

UKERC also acts as the portal for the UK energy research community to and from both UK stakeholders and the international energy research community. The National Energy Research Network (NERN), supported and facilitated by UKERC, acts as an umbrella network for energy researchers across all disciplines. The UKERC Meeting Place, based in Oxford, is a key supporting function of UKERC that aims to bring together members of the UK energy community and overseas experts from different disciplines, to learn, identify problems, develop solutions and further the energy debate.

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IOM3 AND THE IEA

The Institute of Materials, Minerals and Mining aims to be the leading international professional body for the advancement of materials, minerals and mining to governments, industry, academia, the public and the professions. The International Energy Agency's Office of Energy Technology and R&D (ETO) operates under the guidance of the Agency's Committee on Energy Research and Technology (CERT). The Ad Hoc Group on Science and Energy Technologies was set up by the CERT to support the development of new energy technologies by strengthening the connections between basic science and applied energy programmes.

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Foreword

Tom Kerr, Senior Energy Analyst, IEA Secretariat

The International Energy Agency (IEA) commends St. Antony's College and the United Kingdom's Energy Research Centre (UKERC) for hosting this event on advanced materials research and the development of new energy technologies. This sharing of information about basic research and energy applications is of critical importance, as it allows us to achieve the shared IEA goals of security of energy supply, economic growth and environmental protection.

Developing advanced energy technologies requires more than applied research and development. Radical innovation is also crucial. Advances in basic science will be the foundation for progress on myriad energy technologies. Electricity storage, advanced turbines, photovoltaic cells, fuel cells, CO₂ capture and sequestration, hydrogen production and storage, and bio-based fuels are just a few examples. It is creative linkages between basic research and applied technology development that will pinpoint these opportunities. But not enough is being done to foster such linkages.

To address this, the IEA's Committee on Energy Research and Technology to create the Ad-Hoc Group on Science and Energy Technologies (AHGSET). This conference, focusing on accelerated materials research and application, is the fifth event in the AHGSET network. The IEA hopes to build on these successful events with future networking, publications, and outreach, centered on increasing linkages between critical basic science and energy technology. Congratulations on a successful event.

Prof Jim Skea, Research Director, UK Energy Research centre

Putting our energy systems on a long-term sustainable path will require a step change in the performance of energy technologies. Progress in basic science has a vital role to play. Materials science in particular has been identified as key across a range of technologies including renewables, nuclear energy, fossil fuel use, energy conversion and energy storage.

At the same time, advances in the methods used by the material science community are leading to accelerated progress. Computer modelling of materials has emerged as a predictive tool for the discovery and development of new materials at all scales for the quantum to the continuum. A second key development has been the acceptance of rapid throughput screening methods for the discovery of new functional materials with enhanced properties.

The UK Energy Research Centre (UKERC) has been given the task of networking the energy research community and facilitating links between the UK and those working in other countries. With materials scientists showing a growing interest in the energy domain, UKERC was therefore pleased to collaborate with the International Energy Agency and the Institute of Materials, Minerals and Mining in

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this innovative workshop. Although the range of technologies covered in the workshop was broad, the focus on accelerated materials discovery for electrochemical devices such as fuels cells, photovoltaics and batteries provided a common theme and facilitated productive engagement between the participants. We hope that the report of the workshop will be of interest to the wider community and will stimulate others to take an interest in the energy/materials nexus.

Introduction

J A Kilner , Imperial College, London

The continued growth of carbon emissions and its effect upon global warming give rise to a set of difficult challenges for both scientists and engineers. These challenges are to provide affordable and durable methods of energy conversion that are either carbon free or that have a high efficiency for the conversion of fossil fuels into electrical energy. Most new engineering solutions present immense challenges for the materials community as many of these new technologies rely upon materials that have yet to be developed, and cover materials in all their diversity, from structural composites to novel functional materials. When these difficulties are coupled with the fact that the timescales are very short, and that to have any effect we must obtain some of these solutions within the next 10-20 years, the real scope of the task becomes apparent.

Clearly conventional methods of materials discovery are not going to meet this aggressive agenda and an accelerated form of materials discovery is needed. The important question is what type of accelerated materials development tools will become available? Much has been made of combinatorial approaches to materials discovery; however there are many barriers to the introduction of these methods, not least their suitability to all classes of materials. In addition to these limitations there is the requirement for rapid screening methods to allow combinatorial libraries to be measured in an accelerated manner. This is not always easy for materials applications that rely upon complex functionality, often in very aggressive environments.

Computer simulation offers an alternative way of providing guidelines for materials searching. Atomistic simulation of defects and transport in materials is well established however it is hardly a rapid process and much of the effort is expended in the rationalisation of existing experimental data. A change in scope is needed to exploit the potential of this technique to predictive materials screening. Multi-scale modelling is another simulation technique that has been attracting much attention recently however again the thrust has been to understand existing data rather than to work in a predictive mode.

The aim of this workshop was to bring together a group of leading workers in the fields of energy technologies, combinatorial methods and computer simulation techniques, to define target performance for materials, and to explore the best methods to discover and develop materials capable of achieving these targets. We focussed mainly on electrochemical devices in order to reduce the scope of the meeting and to obtain a more focussed view, albeit in a rather reduced materials set. The final aim was not to produce a standard proceedings volume but rather to capture the important discussions that took place between the experts in the various fields both in the sessions and in the breakout sessions that followed from the main sessions.

Day 1 – 2nd April

1. Session 1 – State of the art in electrochemical devices,

Chairs: Tatsumi Ishihara and Peter Slater

This session dealt with the problems related to the storage of energy, which is vital as is well known that the production of energy from renewable sources is intermittent (wind, solar, etc). Both talks addressed the problems associated with high-density storage of energy, mainly the need for new materials or optimisation of existing ones.

1.1 Critical materials problems in SOFC's and high temperature electrolyzers, Harumi Yokokawa (AIST, Japan)

At present, all efforts relating to the development of SOFC (solid oxide fuel cells) technology are based on the reduction of the temperature of operation, from high temperature SOFC's (800 –1000 °C) to intermediate temperature-solid oxide fuel cells (IT-SOFC's working at 500-700 °C). Companies like Kyocera (using thin YSZ, yttria stabilized zirconia, as electrolyte), Mitsubishi Materials (LSGM, strontium- and magnesium- doped lanthanum gallate) and Ceres Power (Ceria) are working on IT-SOFC obtaining efficiencies of about 42-48%.

Much work has still to be done from the development of materials, to the fabrication of the stack and finally the system design.

The most important part of a SOFC is the electrolyte. Discovery of new electrolyte materials is one of the major concerns. For example, the LSGM discovered by Ishihara (1994) is being used by Mitsubishi Materials Ltd. Proton conductors will also be relevant e.g. barium and strontium zirconates and cerates.

As regards the cathode material it is necessary to optimise performance vs. stability. The most used materials are LSM (lanthanum strontium manganite), LSCF (lanthanum strontium cobalt ferrite), and LSCo (lanthanum strontium cobaltite), but stability with the electrolyte still needs to be improved. Ceria interlayers avoid the formation of SrZrO_3 and $\text{La}_2\text{Zr}_2\text{O}_7$, but at the same time make the fabrication process difficult. Other novel cathode materials are also of interest such as the system La_2MO_4 , with $\text{M} = \text{Ni}, \text{Co}$.

Ni-YSZ, Ni-ScSZ (Scandia stabilized zirconia) and Ni-CGO (gadolinia doped ceria) are the most commonly used anode materials. The main problem relating to these is fuel flexibility, as the Ni catalyst has problems of sintering, carbon deposition, sulfur tolerance and redox-cycling. Other novel anode materials are (La, Sr)TiO₃ and (La, Sr)(Cr, Mn)O₃.

Oxide based materials (like LaCrO₃-based and titanate based) and metal based materials (like Fe-Cr ferritic and Ni-Cr) can be used for the interconnects. The main problem with the metal-based materials is oxidation (producing chemical volume expansion) and Cr diffusion to the electrodes.

Key technological issues for SOFC's are cost, reliability and efficiency. The fundamental issues to be solved are:

1. development of new electrolytes;
2. solid-gas interface: problems with diffusion in oxides;
3. equilibrium in solid- solid interface; and
4. cation diffusion in solids: surface segregation.

Prof. Yokokawa's concluding remarks were:

- Materials compatibility is important for high temperature electrochemical devices.
- Materials design approach should match with materials' thermodynamic features.
- Base-acid relation is still important at high temperatures.
- Combined considerations on mass transfer and surface reactivity will be needed.
- Local equilibrium is a strong approximation for interface chemistries.

In the following discussion, Prof. Yokokawa was asked about the different distributions for LSM, LSC and LSF of chromium poisoning that occurs on the cathode surface. His response was that the appearance of Cr poisoning is somewhat strange because the stability of LSM is the highest among the perovskites LSM, LSF and LSC, whereas the Cr poisoning is most severe. This can be explained in terms of the cathode reaction mechanism. In LSM, the three phase boundaries are the main electrochemically active sites, whereas the whole surface area is active in LSF and LSC. This gives rise to the different oxygen potential distribution in the active site vicinity. This explains the strong driving force for Cr containing vapours to be transported to the three phase boundaries and deposited at such sites.

1.2 Critical materials problems in PEMFC's, David Thompsett (Johnson Matthey, UK)

PEMFC's (proton exchange membrane fuel cells) have a very large range of applications including automotive, portable and small scale stationary (CHP)

applications. The membrane of a PEMFC can be either based on perfluorinated sulphonic acids, like nafion, or based on sulphonated partially and non-fluorinated polymers, like PEEK (polyetheretherketones) or PVDF (polyvinylidene difluoride), particularly useful for DMFC's (direct methanol fuel cells). For the catalyst, the most commonly used material is Pt in form of nanoparticles.

The materials requirements in PEMFC's are:

- limitations of current materials
- identify desired enhanced material properties
- translate component properties to MEA (membrane electrode assembly) function
- relevant testing

For example, in H_2 /air, the losses are due to the poor oxygen reduction kinetics and mass transport, and at higher currents these are the largest losses to performance. In DMFC performance, MeOH oxidation and oxygen reduction are the major significant performance losses.

Regarding the catalyst, several efforts are being made to avoid the high cost of the platinum, and it is being demonstrated that Pt alloys (with cobalt or ruthenium) can improve the activity of the catalyst.

Finally, the key challenges for PEMFC catalysts are the oxygen reduction activity, MeOH oxidation activity and the catalyst activity under dynamic conditions. For the membranes it is necessary to get higher temperature performances at lower relative humidities and also to reduce the MeOH permeability. For the optimisation of the layers it is necessary to improve H_2O transport properties, and globally the challenge is to minimise the number of MEAs required to obtain a certain power output.

In conclusion, new materials are needed for PEMFC's. They also require integration in end-use devices (e.g. MEA) and need to be tested under relevant conditions to demonstrate the benefits.

In the following discussion Dr Thompsett was asked about why only hydrogen and methanol are being considered as fuels, and whether formic acid should be considered as well as it has none of the long kinetics and storage problems nor the need for artificial humidification. He responded that the fuel cell business is very driven by consumers and as yet there has not been a significant call for formic acid. However, it is a good fuel providing high current densities. There is therefore a need to educate users to bring about use of the acid as a fuel. Dr Thompsett was also asked about the advantages of non-fluorinated polymer membranes over fluorinated materials such as Nafion and he answered that one advantage is that the non-fluorinated materials are typically higher yield as they generally have less steps in their synthesis.

The cost of the membrane material was queried. Nafion costs \$300 per m², which is expensive due to the material not being a volume product. PTFE is much cheaper due to its wider use. Another participant queried the limits to reducing the platinum particle size. Dr Thompsett said that particle size must be as small as possible to maximise the surface area however this also makes the surface more sensitive to carbon deposition and the activity of smaller particles is shown to be less. Could platinum be replaced by an oxide as for SOFC's. His response was that it comes down to catalytic activity and due to the low operating temperature of PEMFC's in comparison to SOFC's the activity of oxides would be too low to reduce oxygen.

1.3 Critical materials problems in high energy density batteries, Peter Bruce (University of St Andrews, UK)

Energy storage is more important today than ever before and Li batteries can provide a solution. However, new generations of batteries are required for new markets in order to get higher energy storage and higher power densities. This requires a step change in materials performance.

The challenges for anode materials are to achieve more Li stored per g and cc ($>300 \text{ mA h g}^{-1}$), low voltage, low cost, low toxicity, safety, higher resistivity and also a reversibility of $>99.9\%$ per cycle. Alloys containing Si or Sn can increase the capacity by up to 7 times, but this results in a problematic volume change of about 300% (problem of reversibility). Other promising novel anode materials are TiO₂ nanowires.

For the electrolyte, the most commonly used material to date is LiPF₆ in ethylene carbonate or dimethyl carbonate. The main challenges with this material are: avoid PF₆⁻ (HF formation); high conductivity over operating temperature range ($>10^{-3} \text{ Scm}^{-1}$); stability to reduction and oxidation; chemical stability; safety; low cost; and toxicity. New materials are being studied, like ionic liquids (e.g. propyl-methylpyrrolidinium FSI/LiFSI) and crystalline polymer electrolytes (e.g. PEO₆:LiXF₆, X=P).

Similar challenges need to be overcome for the cathodes, like higher energy densities ($>130 \text{ mA h g}^{-1}$), high voltage, low cost, low toxicity, safety, and achieving a reversibility of $>99.9\%$ per cycle. New intercalation compounds like Li(Co_{1/3}Ni_{1/3}Mn_{1/3})O₂ are being presented as an alternative to the traditional Li_xCoO₂. Another possibility is using the oxygen from air as an electrode in a battery/fuel cell hybrid. These systems can achieve a capacity 5-10 times higher than with LiCoO₂. Other alternatives are the mesoporous materials (e.g. LiMn₂O₄) to increase rate capability or conversion reactions Li/FeF₃.

In the discussion that followed, Prof Bruce was asked from the audience about the stability of electrolytes towards oxidation at the anode. He pointed out that present lithium-ion cells only work because of a serendipitous passivating layer that forms on the anode surface inhibiting further electrolyte oxidation. He suggested moving the

electrochemistry of the Li-ion cell along the potential scale in order to moderate this problem and to remove some of the present constraints on the materials, so allowing more space for completely new materials. This would include new electrolytes with higher stability to reduction at the cathode. The role of the noble metals was mentioned in the context of his description of the new Li/O₂ cell,. Peter stated that the classical O₂ reduction catalyst, Pt does not work well in such a cell.

1.4 Critical materials problems in supercapacitors, Peter Hall (University of Strathclyde, UK)

Batteries have high energy densities but due to mass transfer limited chemical reactions, they have low power densities. Supercapacitors store energy electrostatically and have no chemical reactions, hence higher power densities are possible.

Capacitors need to operate at high voltages and need large energy storage. Ionic liquids are the best candidates to solve this problem because they can operate at higher maximum voltages, they are large molecular, highly viscous materials and do not diffuse into carbon porosity readily. Accessible pore size needs to be increased through activation and weight minimized to reduce costs.

Supercapacitors could be used in transport applications to reduce the size of expensive batteries or fuel cells and so meet the total power requirements of automotive transport. As an example, a pure supercapacitor bus is already running in Shanghai. In order to use supercapacitors in transport applications, energy density must be maximised with respect to volume. Use of aqueous based electrolytes (high ϵ_r) is safer for transport. Accessible surface area can also be maximized on a volume basis. The end goal is a supercapacitor with an energy capacity of 80-100 kW, a low carbon cost and which is environmentally benign.

A rapid materials development is needed for supercapacitors. The possibilities are: use of commercially available polymer derived carbons; vary surface functionality by selective oxidation; and use air stable ionic liquids (more information on dielectric properties of ionic liquids is required).

During the discussion that followed, Peter was asked about the properties that ionic liquids have to have in order to give interesting results. The absence of information on the dielectric properties of these liquids was mentioned as well as other issues such as the capability of the liquid to wet the surfaces of the capacitors. There was considerable discussion relating to other types of capacitor configuration, beyond the double parallel plate. Peter was asked about the probability of using grain boundaries as charge storage since they would have a large area; this led to the discussion of whether the dielectric constant of the bulk is the same as that of the grain boundaries. The space charge in grain boundaries of BaTiO₃ and their global capacity

were discussed. In closing the discussion, Peter emphasised the necessity of using cheap, common engineering materials such as carbon instead of more expensive high tech-ceramics or noble metals as constituents of other energy storage devices.

1.5 Session 1 speakers panel discussion

During this discussion, the two chairs of the first session, Tatsumi Ishihara and Peter Slater, and the four speakers, Harumi Yokokawa, David Thompsett, Peter Bruce and Peter Hall, responded to questions from the audience.

Supercapacitors:

Peter Hall was asked if he had tried BaTiO_3 as a supercapacitor as the grain boundaries can be utilised to store charge. He answered that this must work in real life and hence carbon is currently used because it is cheap and easy to manufacture. The big advantage of supercapacitors is that the materials are sustainable, unlike fuel cell materials. Peter was also asked about the size (area, volume, mass) of supercapacitors. He explained that it is possible to buy a supercapacitor now but they are not completely optimised; performance needs to be improved in order to find a place in the market.

Batteries:

Peter Bruce was asked if platinum could be used in lithium batteries as it is commonly used in fuel cells. His response was that platinum is a poor catalyst in lithium batteries as it doesn't provide the reversibility, so transition metal oxides are better. The function of the catalyst in fuel cells is the reduction of the oxygen. He was also asked if the charge and discharge into nanowires is well known. He believes that intercalation of lithium into TiO_2 nanowires is like interstitials into the bulk structure. There was further discussion about silicon that has shown promise as an anode but for which thermal expansion may be an issue. He reported that various systems are being used. Polymer binders could withstand this expansion. The expansion could be due to particles moving within the solid so the challenge is to tether them.

Fuel cells, PEMFCs:

There was discussion on recycling platinum from fuel cells. This can be done fairly easily and it makes sense to recycle. Dr Thompsett was asked for his opinion on whether more time should be spent on researching hydrogen storage; his view is that more work should probably be invested in generation rather than storage.

There was some discussion around the use of different types of catalyst in PEMFCs. In aqueous fuel cells platinum is used because other metals would corrode. There was a suggestion that alkali fuel cells would perform well with different catalysts. Dr Thompsett said that alkali membranes with high OH conductivities are interesting but the most effective catalysts are precious metals.

SOFCs

Prof Yokokawa was asked about the mechanism of cracking as oxygen conducting materials are known to have issues with thermal cycling. He explained that the electrolyte materials used are stable enough but anode or cathode materials can have electronic changes which in turn cause changes in thermal expansion. All materials in the cell must have the same thermal expansion coefficient. In the anode the nickel can become nickel oxide (NiO) whereas in the cathode LSM does not show much change but LSC and LSF do.

Prof Yokokawa was asked for his views on the conductivity of proton conductors for SOFCs. He emphasised that stability against valence is important. BZY (yttrium stabilized barium zirconate) presents good stability but due to its low conductivity it must be used in thin layers. He was also asked about his comments on lanthanum nickelates which are used as a cathode material and for mixed conductors in general. Harumi explained that lanthanum nickelate doping with strontium decreases conductivity and also requires the use of a ceria interlayer with YSZ due to the chemical instability between zirconia and lanthanum nickelate. Doping with iron is more stable. $\text{La}_2\text{NiO}_{4+\delta}$ with YSZ has a good surface exchange coefficient but is very reactive, however it works very well with CGO. A participant asked about other electrolytes such as LSGM and if stability issues have been overcome. Harumi reported that his group is now working with LSGM as an electrolyte in a 1kW stack and that this works well and is stable. One issue relates to NiO dissolving into the LSGM. Tatsumi Ishihara added that LSGM films show no degradation on thermal cycling (anode supported fuel cell). $\text{La}_2\text{NiO}_{4+\delta}$ is a very interesting material with high mixed conductivity. It has shown promise as a cathode material with CGO however there is still some dissolution of the $\text{La}_2\text{NiO}_{4+\delta}$ into the CGO.

There was some discussion about proton conduction in barium zirconate, which has shown low grain boundary, high bulk conductivity, and has been found to have very high proton conductivities. Prof Yokokawa's thoughts are that the results depend on the synthesis process as two-phase regions tend to be formed.

When asked if enough research is being carried out on new materials, He responded that most people do not want to change from YSZ as an SOFC electrolyte material which is why a large amount of current research is focussed on producing thin films. The next steps will involve cost reduction and mass production. The main problem is that industry doesn't want to change and they are usually the driving force.

Day 2 – 3rd April

1.6 AHGSET future vision,

Tom Kerr (IEA)

The goals of the International Energy Agency are related to energy security, environmental protection and economic growth. Their activities include:

- co-ordinate efforts to ensure energy security
- conduct policy analysis
- link research activities and governmental directives
- compile energy statistics
- review energy policies & programs
- convene, mobilize science & technology experts

The IEA research groups are divided into four main areas: buildings, transport, industry (including fuel cells, advanced materials, hybrid and electric vehicles, buildings and community systems, energy storage, emissions reduction in combustion and high-temperature superconductivity); fossil fuels (clean coal science, greenhouse gas R&D); renewables (bioenergy, geothermal, hydrogen, hydropower, ocean energy systems, photovoltaic power systems, solar heating and cooling and wind energy systems) and fusion (environmental, safety, fusion materials, plasma).

An important division of the IEA is the Ad Hoc Group Science & Technology (AHGSET). Its mission is to support the development of new energy technologies by strengthening the role of science and the connections between basic science and applied energy programs. They have organised 5 workshops since 2003 and their strategic objectives are to:

- advise decision makers on the opportunities for science to contribute to energy technologies;
- link the science and energy technology communities;
- develop and share approaches and tools; and
- promote strategic international collaborations in science.

The next steps for AHGSET are to develop a two-year program strategy and organise workshops covering the remaining areas of basic science (e.g. biohydrogen, advanced biofuels and nanotechnology). It also consults IEA implementing agreements (i.e. produces case study examples of basic science/energy research linkages and identifies energy challenges where basic science research can assist). Other duties include conducting outreach to science, production of energy/environment publications, and reach out to other science/energy R&D networks (e.g. academic institutions, Government agencies and industry).

The discussion that followed focussed on how the IEA is funded whether the IEA funds research. The IEA does not have significant funding and does not fund research. However, the IEA can be part of any research proposal/project. Tom also mentioned that the IEA has established relationships with international organisations like the European Commission.

Session 2 Bulk Science: The Design of Novel Materials.

Chair: Colin Greaves

2.1 Design of ionic and mixed anion conductors, Allan J. Jacobson (University of Houston, US)

The design of ionic and mixed anion conductors involves optimizing properties for a specific application, the synthesis of a molecular structure with a specific property and also the exploration of new structures and compositions.

Mixed conductors can be divided in to: perovskite ferrites (*oxygen vacancy mechanism*) like $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-x}$; $x = 0.2, 0.3$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{3-x}$; perovskite related structures (*oxygen interstitials*) like $\text{La}_2\text{NiO}_{4+x}$ and $\text{Pr}_2\text{NiO}_{4+x}$; and perovskite oxides with ordered A cations (*2 dimensional vacancies*) like $\text{PrBaCo}_2\text{O}_{5+x}$ and LaBaCuFeO_5 .

The properties of mixed conductors are:

- electronic and ionic conductivity;
- electro(catalytic) oxygen reduction;
- interface stability;
- stability;
- thermal and chemical expansion;
- mechanical properties; and
- stable microstructure;

$\text{AA}'\text{B}_2\text{O}_5$ compounds have good properties. There are large classes of compounds with this formula and their archetypal structure is that of YBaCuFeO_5 . Their magnetic and electronic properties have been studied extensively at low temperature. Typical examples include $\text{GdBaMn}_2\text{O}_{5+x}$ (disordered when produced in air and ordered when produced in argon) and $\text{GdBaCo}_2\text{O}_{5+x}$. $\text{PrBaCo}_2\text{O}_{5+x}$ (PBCO) is also an excellent candidate because it has high electronic conductivity and a wide range of nonstoichiometry. Epitaxial thin films of PBCO, studied by surface exchange analysis revealed that:

- The very fast surface exchange for PBCO may be due to the c axis being aligned in the film plane, increasing the number of surface oxygen vacancies.
- The surface exchange is much faster than for thin films with comparable crystallinity of disordered $\text{LaSrCo}_2\text{O}_{6-x}$ on LaAlO_3
- When the LSCO film is annealed at 900 °C, the crystalline quality decreases, and the surface exchange rate increases significantly but is still lower than observed for PBCO.

Review data from other interesting compounds like $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, $\text{La}_2\text{CuO}_{4+x}$, $\text{Ba}_5\text{Ru}_2\text{O}_{10}$, $\text{Ba}_5\text{Nb}_2\text{O}_{10}$ or apatite derivatives were also presented.

In conclusion, Prof Jacobson remarked that $\text{AA}'\text{BO}_5$ are a large class of mixed conductors with high ambipolar conductivity and many design possibilities. Both theory and experiments are needed in this area in order to understand problems associated with band structures, energetics of order/disorder, cation-vacancy order and the thermodynamics of oxidation. Electro(catalytic) behavior using thin film models is also an important area of investigation.

During the discussion, he was asked about why the thermal expansion coefficient (TEC) was not ideal for most of the perovskite and apatite compounds. He argued that there is a big change in composition over a narrow P_{O_2} range.

2.2 Design of ionic and mixed cation conductors, Peter Slater (University of Surrey, UK)

Proton conductors can be used as electrodes or electrolytes in fuel cells or as hydrogen separation membranes. Li ion conductors can be used as electrolytes (ionic conduction) or as electrodes (mixed ionic and electronic conduction) in Li ion batteries.

The requirements that are needed for a good ionic conductor are:

- A large number of mobile ions, with a large number of empty sites available for the mobile ions to move into.
- The empty and occupied sites should have similar energies, with a low activation energy for jumping between neighbouring sites.
- The structure should have a framework, preferably 3D, with open channels through which ions may migrate.
- The anion framework should be highly polarisable.

Traditionally perovskite systems have been used as protonic conductors, like $\text{BaCe}_{1-x}\text{Y}_x\text{O}_{3-x/2}$, $\text{BaZr}_{1-x}\text{Y}_x\text{O}_{3-x/2}$, $\text{Ba}_3\text{Ca}_{1+x}\text{Nb}_{2-x}\text{O}_{9-3x/2}$ or $\text{La}_{1-x}\text{Ba}_x\text{ScO}_{3-x/2}$, where there is competition between the oxide ion and proton conduction. These systems need an ability to incorporate water. However, too much water incorporation can lead to instability (e. g. K_2NiF_4 systems). Stability issues must be considered. For example, $\text{BaCe}_{1-x}\text{Y}_x\text{O}_{3-x/2}$ is a very good proton conductor but in the presence of CO_2 tends to

form BaCO_3 . High sintering temperatures are required with consequent Ba losses. Possible solutions include replacing Ce by Zr (low conductivity) or co-doping with Zn.

New systems are also being explored, like the $\text{Ln}_{1-x}\text{A}_x\text{MO}_{4-x/2}$ (Ln = rare earth, A =alkaline earth, $\text{M}=\text{P}$, Nb , Ta). They have lower conductivities but excellent stability in a CO_2 atmosphere. The system $\text{Ln}_{1-x}\text{Ba}_{1+x}(\text{Ga}/\text{Al})\text{O}_{4-x/2}$ ($0 \leq x \leq 0.2$) has higher conductivities than $\text{Ln}_{1-x}\text{A}_x\text{MO}_{4-x/2}$ but lower conductivities than perovskites. When doping with Pr we can produce samples with mixed proton and electronic (p-type) conductivity.

There are also systems that work at lower temperatures ($< 400^\circ\text{C}$), like the solid acid protons conductors (e.g. CsHSO_4 , CsH_2PO_4) or metal phosphates (e.g. SnP_2O_7).

Targeted doping in perovskite systems (octahedral cations) results in some 5 coordinate cations allowing water incorporation. Doping of other new systems (e.g. $\text{La}_{1-x}\text{Ba}_{1+x}\text{GaO}_{4-x/2}$) leads to 3 coordinate cations. This may explain low solution limits for some phases. However these materials can accommodate oxygen vacancies via condensation of tetrahedral units (Ga_2O_7 units).

Peter concluded that in the study of proton conductors, significant progress has been made in optimising sintering and stability on perovskite systems. Interest in materials containing tetrahedral units (accommodation of vacancies via X_2O_7 units) is growing. Peter said it was important to note that a number of the recently reported proton conductors are well known systems so attention should be focused on other known materials.

In Li batteries the traditional cathode material is LiCoO_2 . A large amount of work involving doping of this material with Ni, Mn and other metals has been carried out. Also of interest is the replacement of Co e.g. LiMnO_2 , LiMn_2O_4 . More recently, interest has been growing in phosphate systems, like LiFePO_4 or LiVPO_4F . These materials have very good rapid charging/discharging properties but generally have poor electronic conductivity. The future target is an oxyanion system with good electronic conductivity. At present, batteries mainly use liquid electrolytes but solid electrolytes are now being used such as polymer electrolytes (traditionally amorphous systems targeted). Crystalline polymers have also been shown to have high conductivities (e.g. PEO_6 : LiXF_6 ($\text{X}=\text{P}$, As , Sb)). Other new systems include: $\text{La}_{0.67-x}\text{Li}_{3x}\text{TiO}_3$ (perovskite), nasicon, lisicon -type, garnet, or $\text{Ln}_3\text{M}_2\text{Li}_5\text{O}_{12}$ ($\text{M}=\text{Nb}$, Ta , Sb).

Future research is likely to include further studies of systems containing oxyanions (XO_4^{n-}). A greater understanding on the conduction process is also required (fundamental studies and co-operative effects are important, especially for H^+ conduction). The promising results for Li ion conducting crystalline polymers are of great interest. As regards fuel cell applications, proton conducting systems operating between $100\text{--}400^\circ\text{C}$ can develop a real niche (e.g. solid acid systems need to stabilise the superionic phase to lower temperatures). Finally, there is a need for

work into mixed proton and electronic conductors for electrode applications. Most work to date has focused on the use of traditional electrodes in SOFCs based on oxide ion conducting electrolytes.

During plenary discussion, Dr Slater mentioned that the polarisability of the whole structure rather than individual ions contributes to conductivity. In response to a question relating to the conductivity of hydrogen phosphates versus phosphoric acid He pointed out that the results are sometimes non-reproducible, and so this needs further study. He was also asked about the flexibility of those materials. He assumes that limits of structural stability, in structures without linked tetrahedral rotation, is possible. In the perovskites, structural distortions can be partially accommodated by tilting of the octahedra.

Session 3 - Nanotechnology: The Design of novel nanostructures

Chair: Elisabeth Djurado

3.1 Applications of nanomaterials and nanostructures for fuel cells, Igor Kosacki (Shell, US)

In the next 20 years energy consumption will increase by over 50%. Efforts are needed to explore new fossil resources, develop alternative forms of energy and improve energy efficiency. Hydrogen is the ultimate renewable primary energy resource because its combustion produces simply water and energy. SOFCs are presented as an interesting alternative but there are still problems with existing materials due to the high operation temperature (900-1000 °C) and the high cost of manufacture. To enhance SOFC performance at reduced temperatures it is necessary to reduce the internal resistance of the cell and improve the performance of catalytic electrodes. The design of advanced materials for SOFCs based on interface engineering using nanotechnology presents a major research challenge that needs to be tackled.

To date, the most important systems used as ionic conductors in SOFCs are: $\text{CeO}_2:(\text{Gd}, \text{Sm})$, $\text{ZrO}_2:(\text{Y}, \text{Sc}, \text{Ca})$, and LaSrGaMgO_3 . It seems conventional materials have reached a limit, so new materials with enhanced ionic conductivity and catalytic activity are needed. In conventional ceramics, ionic conductivity in solids is limited by low ion mobilities (maximum possible value of the ionic conductivity is about 10 S/cm at melting point). The use of nanoscale materials can change the diffusion mechanism which increases ionic mobility. The use of nanomaterials involves: large numbers of grain boundaries ($\sim 10^{19}\text{cm}^{-3}$); large ratio of particles in interfacial to volume area (ca. 30-60%); grain boundary impurity segregation; space charge

effects; and grain size dependent defect thermodynamics. The diffusion coefficient associated with grain boundaries is much higher compared to the coefficient due to the bulk hence higher conductivity values are obtained. In addition, faster reaction kinetics result due to an extended surface area. For example, use of nanopowders in YSZ has resulted in a 10^2 times enhancement in electrical conductivity. This effect is attributed to grain boundaries that control electrical transport. In nanocrystalline CeO_2 , the observed enhancement in electronic conductivity is even higher (10^4 times). This effect is related to a decrease in the enthalpy of the oxygen vacancy formation. Nanocrystalline ceramics applied to gas sensors also enhance protonic conductivity. The kinetics of the electrical conductivity is 10^3 faster than bulk.

Better results have been observed in nanoscale epitaxial YSZ thin films on MgO substrates. 15nm thick YSZ film exhibits the highest ionic conductivity ever reported, where the electrical conductivity of YSZ films is the superposition of grain boundary/surface and bulk contributions. Exceptionally high ionic conductivity values have been also obtained in nano-scale CeO_2 / $\text{Sm}:\text{CeO}_2$ superlattices. Those results are extending in single chamber SOFCs performances.

To conclude:

- Ultra thin, highly textured YSZ, $\text{Sm}:\text{CeO}_2$ films and heterostructures $\text{Sm}:\text{CeO}_2/\text{CeO}_2$ have been synthesised on MgO substrate by PLD (pulsed laser deposition).
- These films are free of blocking grain boundaries.
- The physical properties of nanoscale oxides can be controlled by the thickness and film texture.
- Increased conductivity was also observed in superlattice structures with alternating 30nm $\text{CeO}_2:20\%\text{Sm}$ and 20nm CeO_2 layers.
- Exceptional potential of nanocrystalline ceramics for developing advanced electrochemical devices.

There was discussion around protons delivering enhanced conductivity. Dr Kosacki's response was that protons at the interface could possibly increase conductivity. Considering the mechanical stability of the superlattice he said that they had no time to investigate chemical stability, however treatments at 400 °C for one month shows no instability. Igor was also asked if nanostructures are inherently unstable particularly if cycling Ce grains will grow in bulk materials and this is controlled in thin films by limiting thickness to 100-200 nanometres.

3.2 Applications of nanomaterials and nanostructures for batteries, Joachim Maier (Max Planck Institute, Germany)

Size effects of lithium batteries are based on cell voltage, transport and storage. For example, in transport, novel "soppy sand electrolytes" (oxide-solution composites) are being used and they present good performances. These electrolytes are formed

by different oxides ($\sim 0.3 \mu\text{m}$), such as SiO_2 , TiO_2 or Al_2O_3 , and a solution of LiClO_4 in methanol (0.1M).

Storage in Li batteries is provided by one of the following mechanisms: volume intersection (absorptive), phase formation (reactive) or interfacial insertion (adsorptive). Reversible heterogeneous Li-storage has been reported, and consists in a mechanism involving Li-insertion (discharge) and Li-extraction (charge). RuO_2 is an interesting candidate, which reacts with Li as follows: $\text{RuO}_2 + 4\text{Li} \rightleftharpoons 2\text{Li}_2\text{O} + \text{Ru}$

The challenges in materials research relating to Li-storage include finding new materials with enhanced transport properties. It is necessary to work on the variation of local transport properties by enhancing the performance of existing materials. This can be done by homogeneous or heterogeneous doping or by nano size effects. For example, it has been shown that nanoparticles of TiO_2 have better performances at high current rates. Reduction of effective diffusion length by nano-sized mixed conducting networks is also a research priority. Metalising pore channels with RuO_2 has been shown to improve performance.

In conclusion:

- Nanoionics and nanotechnology have significant potential to improve the performance of Li-based batteries, even at room-temperature, in terms of stability and activation energy;
- Improving materials parameters through application of interfacial or confinement effects provides advantages including reduced transport path lengths.
- Improvements of transport, transfer and storage.

3.2 Speakers panel discussion

The session chairs, Colin Greaves and Elisabeth Djurado, and the four speakers, Igor Kosacki, Joachim Maier, Allan Jacobson and Peter Slater, led the discussion by responding to questions put forward by participants.

Prof Maier was asked if any of the Li^+ conductor defects could be transferred to the oxide ion conduction area. He responded that the oxygen ion needs to be stabilised in some way.

A participant asked Prof Jacobson whether much is known about the surface structure or interface in materials. He replied that little is known although some studies have been done on SrTiO_3 and LaAlO_3 . Dr Kosacki added that EXAFS (Extended X-ray Absorption Fine Structure) studies have revealed that the average disorder is similar in both nano and micro crystalline ceria, and grain boundaries have not changed much. He was also asked if it is possible to make dense

nanocrystalline films. He said that they had been made using polymeric precursors and densities have been confirmed by TEM (transmission electron microscopy).

Dr Kosacki was asked to comment on CGO and whether there is improved ion or electronic conduction with varying grain size. Igor believes that the quality of CGO, in terms of Si content, is important as well as processing methods and a sensitive grain boundary area. More information was sought on Shell's strategy concerning high temperature fuel cells. He replied that Shell is taking a long term view - 100 years. He believes that gasoline provides the best means of storage for H₂ (~ 26% H₂).

Dr Slater was asked about structural stability for cation conduction. He thinks that a requirement is needed to maintain coordination, and to have the ability of polyhedral rotation is also needed.

Session 4 - Theoretical techniques

Chair: Rose-Noelle Vannier

4.1 Simulation of Materials: Fuel Cells & Lithium batteries, Saiful Islam (University of Bath, UK)

New materials are key to major developments in fuel cells and lithium batteries – this requires a step change in materials science. This also requires a combined approach of materials modelling and synthesis and characterisation (X-ray diffraction, conductivity, etc.). The simulation methods can be divided into the following:

- Atomistic (>50,000 ions)
- Molecular dynamics (>20,000 ions)
- Quantum mechanical e.g. Density Functional Theory (<200 ions)

For ionic and mixed conductors for solid oxide fuel cells and membranes, most of the research being carried out involves simulating perovskite type materials (e.g. LaGaO₃) and new structures (e.g. La-Si-O, apatite). For example, simulations on LaGaO₃ are useful for understanding the migration pathway, the defect association or clustering. In LaCoO₃ cathodes, simulations predict that at an atomic level the surface has not a bulk termination, which is consistent with low energy ion scattering of experiments on SmCoO₃. Novel apatite-type materials are also being simulated, contributing to the understanding of ion conduction paths e.g. silicates:



A radical development is required for lithium batteries (Li batteries are required in hybrid electric cars) due to the price and toxicity of the Li_xCoO₂ currently widely used. Layered LiMO₂ (M = Fe, Mn, Mn-Ni), LiMn₂O₄ spinel or LiFePO₄ olivine are

possible alternatives for the next generation of Li batteries. For example, the Li migration path in LiFePO_4 has been predicted to be non-linear (curved path with lattice relaxation). Modelling of surfaces and morphology is also consistent with the experiments. Other useful simulations are also being carried out for layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ compounds. Other recent studies include Re-doped bismuth oxide ($\text{Bi}_{28}\text{Re}_2\text{O}_{49}$), proton conductor LaBaGaO_4 in SOFCs, and LiMPO_4 and Nasicon-type in lithium batteries.

The simulation of materials is essential in order to understand the structure and properties of new materials. Atomistic-scale insight enables understanding about defects, ion transport, dopant effects, surface structures, crystal morphologies and the electronic structure. However, interaction and feedback is needed alongside the experimental work and is one of the challenges with new improved materials.

4.2 Neural networks and genetic algorithms in ceramic compound design, Steven Manos (UCL, UK)

New materials discovery can be described as a cycle, in which we start by studying the databases. The cycle continues with the neural networks, which consist in approximating relationships between composition and function. The next step involves the use of genetic algorithms (combinatorial design of new ceramic compositions), finishing with the manufacture process (rapid throughput experiments).

London University Search Instrument is adopting this process. In this project, different ceramic powders are mixed with solvents to form 'inks'. The inks are automatically mixed by an inkjet printer and printed onto slides. A robotic arm transfers these slides to the furnace for sintering. These slides are then distributed to other locations for experimental analysis (XRD, SIMS and Evanescent Microwave Probe). This data is always available to researchers at the various institutions involved via an online web interface. Databases are used to store manufacturing process details, experimental results, and literature results. The electronic properties database contains approximately 1200 materials and the ion diffusion database has approximately 1100 unique records, including temperature data. Metadata includes references, along with very basic processing data for dielectric data.

Neural networks can be used to model general non-linear relationships between input (composition) and output variables of interest. A network is 'trained' to remember the relationship between input and output variables (*back propagation*), using training data (literature datasets). The input to the network is the composition of the material and the output is (in this case) the permittivity or diffusion coefficient. This encapsulates the literature data, giving an easy way to quickly evaluate compositions.

Genetic algorithms (GAs) are optimisation and design algorithms that can be applied to a wide range of problems. Optimisation is achieved through incremental improvement of a population of designs by *selection of the fittest*. Members of the population are replaced with candidate ceramics. It is common to start off with a random population of 'parent' ceramics, then proceed to breed new *children* (new variants which are similar, yet different to parents). Design objectives are generally recombined into a single objective, often through a weighted sum ($F = w_1 * O_1 + w_2 * O_2$). This essentially means that an a-priori decision is made as to the relative importance of objectives. Multi-objective techniques involve finding a group of solutions that are trade-offs with respect to the multiple objectives considered and can often yield rich information about the trade-offs and underlying genotype (ceramic composition). A literature database and neural network predictor will be publicly available (www.foxd.org). Much computational effort, whilst carrying out a GA-related search, tends to be wasted on satisfying constraints. The searches tend to focus on particular systems of functional ceramics. Although a high dimensionality dataset, the search actually involves exploring small clusters that are a long distance from other clusters. It is also important to consider the prediction and mining of metadata as well as numerical data.

Session 5 - Accelerated Materials Discovery

Chair: John Owen

5.1 Thick-film combinatorial libraries for functional ceramics discovery, Julian Evans (Queen Mary, University of London, UK)

The different types of combinatorial library are: thin-film, thick-film, discrete, gradient and random. Previous work on solid free forming (SFF) by direct ceramic ink-jet printing prompted this approach to high throughput synthesis of thick-film, discrete, ceramic libraries. The aim of SFF is to control both external shape and the internal spatial arrangement of composition by computer. Strategies for mixing using an ink-jet printer including proximity printing and sintering, mixing behind the nozzle and mixing in front of the nozzle.

The printer has eight aspirating-dispensing nozzles each controlled by an electromagnetic valve and linear stepper acting on a 1.5 ml syringe. The nozzles first reformat well plates, then aspirate from the target wells and print onto ceramic tiles. The furnace has four large zones each independently controlled to give four separate firing schedules. The shape of the droplet relic can be adjusted by changing the composition of the vehicle and the volume fraction of the powder. The shapes made by droplet drying can even be used as well plates themselves and can hold metals or act as catalysts.

The advantages of using thick film ink-jet printed libraries are that it:

- tests the same commercial powders used in fabrication of devices.
- assembles powders by sintering processes.
- tests sintering temperatures and times for a given powder.
- tests effects of grain growth and porosity.
- allows precise composition to be attainable $\sim 1-2$ wt.% (cf. thin-film methods).
- allows bulk samples of different thickness and shape to be prepared.

In the discussion that followed, Prof Evans was asked if nitrates have been used for the synthesis. He explained that his group did not presently use nitrates and that the starting powders are either oxides or carbonates. He takes the view that combinatorial techniques are actually done in every department laboratory: students are making powders, synthesising pellets and then characterising the properties. This technique simply involves working on a larger scale by automating the synthesis. Sintering temperature is an issue, because it is not possible to predict a priori for each element of the ternary library and there is usually a large gradient between both ends of the library. Considering how thick films form by drying an ink suspension, he thinks that for well-dispersed inks, the sediment is well-packed ready for sintering. This is the opposite requirement to paint or ink suspensions made by colloidal techniques which need to be re-dispersed. During the drying process, particles tend to agglomerate less quickly. Problems are encountered when carbonates are introduced into the ink mix. During the sintering stage, carbon dioxide is expelled from bulk materials causing open porosity. Dispersants are used in ink formulation but not all powders react in the same way or with the same dispersant.

During the drying process, Marangoni flows occur at the surface, creating a depletion of the ink from the centre to the surface edge. Finally, Prof Evans remarked that combinatorial synthesis in inorganic materials has been essentially delivered by thin film techniques. However, characterising thin films brings its own problems and it is not straightforward to get back to the bulk properties. To date, thick films have not been well investigated.

5.2 High Throughput Synthesis and Screening, Brian Hayden (University of Southampton, UK)

Thin film materials are produced by high throughput synthesis using physical vapour deposition (HT-PVD synthesis). Simultaneous deposition of elements from multiple sources, with control of the "wedge" profile and rates results in thin film materials with compositional gradients. A software development for specific applications controls all the data processing, data analysis and data presentation. For example, the ternary system Ge-Sb-Te has been studied by this technique. The applications include electrochemical screening of electrocatalysis and electrochemical screening of

fuel cell catalysts, e.g. Pt-Pd-Au or Pd-M (M = Ni, Fe, Co). Other systems studied are the ternary Pt-Co-Au, carbon-supported gold or titania supported gold. HT-PVD synthesis can also be used for screening of hydrogen storage materials (like the system Mg-Ni-H) or for screening functional ceramic materials (titania supported Au particles or Pb-Zr-Ti oxides). Other applications include screening of photovoltaic materials and screening of gas sensor materials.

Prof Hayden was asked which materials had been found for the PEMFC catalyst. He thinks this is one problem with the combinatorial techniques. His research group has found quite new and interesting materials, the best of which have been patented, meaning no disclosure for ten years. Through a partnership with the Johnson Matthey Group it was possible to successfully screen the new materials.

Another question related to the differences between Prof Hayden's alternative research approach and the conventional method of research. His research group started designing an experiment to characterise what the company wanted. Analysis of the results showed they were similar and as accurate as the ones the company get in their lab. However the Southampton research group speeds up the research synthesis and decreases the composition gradient of analysis. This is also an effective way to see how the property changes within the chemical space.

Prof Hayden also mentioned that the materials department seems to be reluctant in moving to an accelerated research program. Brian believes that the major issue with high throughput screening is funding so would willingly collaborate with other partners to develop an automated technique to screen materials in any field. A possible solution is to create a combinatorial European or international committee to make a single database that would deal with all properties. This would enable exploration of trends of different properties and relationships between them. Not necessarily rationally, but for instance the use genetic algorithms will be very useful for the high throughput synthesis and screening techniques.

APPENDIX

BREAKOUT SESSION 1

Group 1A

1. Are we approaching the limits of “conventional” materials e.g. conductivity relative permittivity etc?
2. What are the major materials limitations to device development?
3. What timescale do we have for the development of new materials i.e. what are the external constraints?
4. Can we predict when new breakthroughs will occur?

First two questions were answered together. “Conventional materials” were defined in the group as materials that are in widespread use today and for which incremental improvements can be expected, but not a step-up. There was a limited discussion on SOFC materials for residential (1 to 5 kW) and stationary applications (100’s kW to MW’s). Conventional materials have already demonstrated performance and durability commensurate with commercial applications, but only in well-controlled environments. Failure and degradation mechanisms of fuel cell systems in real-life applications have not yet received the attention to deconvolute contributions from materials from other factors such as engineering and modes of operation. Future attention is therefore needed to gaining a better understanding of failure modes of SOFCs and the particular role materials are playing.

There was also limited discussion on automotive (hydrogen PEM) and portable (DMFC) applications. Conventional materials are contributing substantially to the barriers to commercialisation of these technologies. Particularly, the stability of the membrane in automotive operation (dry and hot), stability of the catalyst support and the cost of materials are cited here. DMFC has already seen introduction of commercial products, but generally it is agreed that materials cost and poor catalyst activity (resulting in low fuel efficiency) are two major components holding back widespread use. Both are tied to inadequate material properties.

In the Li-batteries field, conventional materials have a hard limit in terms of theoretical capacity, which technology improvements are forecast to approach soon. Improvements are therefore to be expected only in areas such as coulomb efficiency or rate capability. Based on conventional materials improvements are envisaged to come from new architectures (e.g. composite electrodes to enhance rate capability). Finally, in supercapacitors, conventional materials are based on high surface area carbon materials and are seen to be not limiting to the usefulness and commercial success of supercapacitors. Supercapacitors are a commercial reality today. A functionality convergence with batteries is foreseen whereby supercapacitors achieve

energy densities approaching the low end of batteries, and batteries at that low end of energy density achieve discharge capabilities approaching that of supercapacitors with acceptable capacity fade.

Answering question 3, it was discussed that generally, improvements that are incremental based on existing materials have time horizons to commercial realities measured in a small number of years (2 to 5), while step-up improvements based on new materials take a decade or longer to surface in commercial applications. There was some discussion with open end whether external stimulations (e.g. legislation, public perception) are needed/helpful to accelerate progress.

Little time was spent on the last question, and it was answered, somewhat tongue-in-cheek, that we can't predict when new breakthroughs will occur. The intention of the question was clear and very relevant and possibly leading to a workshop on just that topic.

Group 1B, 1C and 1D

Three different groups were discussing the following questions.

1. Are we approaching the limits of "conventional" materials e.g. conductivity, relative permittivity etc?
2. Can we design new materials with improved bulk properties (do we know how?)
3. Does "nano" offer the prospect of enhanced materials performance?
4. Do we know how to design nanostructures to give enhanced properties?

All groups thought that we are very close to the limit but only with the existing compositions (this is the meaning for "conventional" materials). It means that we are not approaching the limits but we have to look for other compositions. In group1D, there was a discussion about the evolution and optimisation of materials. We are not going further in the optimisation, and there is no evolution (most of the conductivity data is from 50 years ago). But it is clear that we need a revolution, and two possible solutions are: fluorite-type materials (were proposed as oxygen conductors up to 500 °C); and the use of combinatorial chemistry.

In order to design new materials with improved bulk properties, understanding of the basic properties is essential. All the groups agreed that it is possible to improve those properties but most efforts must be focused on:

- Create databases about the existing materials
- Use the high throughput synthesis
- Considering that design of materials is different from synthesis
- Use of combinatorial chemistry

- Invest on new composite materials (we also need engineering approach)
- Invest on new ways of materials preparation

Answering the question about if “nano” offer the prospect of enhanced materials performance, group 1B thought that in the batteries field, some help is needed in order to understand the smaller diffusion length. It is possible that the electrochemical sintering may limit this parameter and we still have to certify if the enhancement of the properties is correct. In HT-SOFC, an enhancement of conductivity performance has been observed with nano anode and cathode materials (going from 15 microns to 15nm we can improve 100 times the ionic conductivity), so “nano” in this field is very promising.

Group 1D considered “nano” as the revolution (the step from the microscale to the nanoscale has demonstrated that grain boundaries improve conductivity data), but lots of engineering help is needed to develop composites and matrix supported catalysts.

There were some contradictory opinions relating to whether we know how to design nanostructures to give enhanced properties. Group 1B was the most pessimistic and they thought that we don’t know yet how, although group 1C thought that recent discoveries offer good prospects about the design of nanostructures. Group 1D had mixed views and concluded that the most important fact is that we know what we need to do. So, future work has to be focused on the following:

- know what’s going on the interfaces;
- work in collaboration with simulators;
- how to produce tons of nanopowders for a real application;
- minimise the impurities in materials; and
- check the stability of the nanomaterial at 500 °C with time.

BREAKOUT SESSION 2

Group 2A

1. Does materials simulation offer a way forward to AMD?
2. What simulation methods hold the most promise? E. g. atomistic vs QM
3. Do AI and neural nets have any role in AMD? I.e. vs structure property relationships?
4. How can this field be further developed – can we predict properties of nano materials?

It was agreed that materials simulation offers a good way forward for Accelerated Materials Discovery and it is a very useful guide for experimentalists.

The big issue is how to find new materials. High throughput synthesis can be very useful in this area and it can help to create maps-prediction of materials, although in some cases we are limited by computing power/system size.

The most promising simulation methods probably are the methods for interfaces/surfaces. These methods are more complex than others (orders of magnitude or difficulty) and also depend on history of the sample, atmosphere... Other promising methods are Multiscale modelling and Monte-Carlo methods.

Neural networks in Accelerated Materials Discovery can have an important role but there are still some key points to be solved:

- Sifting and analysing vast databases
- Focussing only on naïve/simple properties is an issue
- New materials are needed quickly
- Serendipity factor – creativity vs. data mining
- Proprietary information, although here there can be commercial interests

In order to get further development in the field, we have to work on:

- Real surfaces/interfaces
- Dynamic descriptions
- Nanoparticles
- Electronic conductivity / coupled transport
- Disordered systems
- Nonequilibrium methods
- Phase stability of complex compositions / metastable phases

Group 2B

1. Do rapid throughput methods offer a way forward to AMD?
2. What methods hold the most promise? E.g. pld vs robotic?
3. Is this a plausible way forward given our basis in the materials structure property relationships?
4. How can this field be further developed?

Rapid throughput methods offer many possibilities to develop Accelerated Materials Discovery. Main difficulties are in the fields of batteries and H₂ storage. It is also important to consider intrinsic and morphological properties and there is certainly a need to move on screening techniques

Thin film methods are the most promising in order to accelerate the materials but also informatics is essential, and they have to be scientifically informed.

It was considered that the field of rapid throughput methods is a plausible way forward given our basis in the materials structure property relationships and it can be further developed although there are socio-economic barriers and they need global materials. We need standardization of databases, although we know that is particularly complicated. Funding is required. A good idea mentioned is to promote groups to make impact (CONSORTIA).

Programme

Agenda

Monday 2nd April

From 12:00 Registration and lunch at St Antony's College

14:00-14:15 Welcome and introduction

John Kilner (UKERC), Thomas Kerr (IEA)

Session 1 - State of the art in electrochemical devices

Chair: Tatsumi Ishihara

14:15-14:45 Critical materials problems in SOFC's and high temperature electrolyzers – *Harumi Yokokawa (AIST, Japan)*

14:45-15:15 Critical materials problems in PEM's – *Dave Thompsett (Johnson-Matthey, UK)*

15:15-15:45 Refreshment Break

Session 1 continued - State of the art in electrochemical devices

Chair: Peter Slater

15:45-16:15 Critical materials problems in high energy density batteries – *Peter Bruce (St Andrews, UK)*

16:15-16:45 Critical materials problems in super capacitors *Peter Hall (University of Strathclyde, UK)*

16:45-17:45 Speakers panel discussion

18:00 Pre-dinner drinks and dinner at St Antony's College

From 21:00 Bar at Lady Margaret Hall is open
(There is a cashpoint in LMH near the bar.)

Tuesday 3rd April

9:00-9:30 AHGSET future vision – *Thomas Kerr (IEA)*

Session 2 - Bulk Science: The design of Novel Materials

Chair: Colin Greaves

9:30-10:00 Design of ionic and mixed anion conductors

Allan Jacobson (University of Houston, USA)

10:00-10:30 Design of ionic and mixed cation conductors

Peter Slater (University of Surrey, UK)

10:30-11:00 Refreshment break

Session 3 - Nanotechnology: The Design of novel nanostructures

Chair: Elisabeth Djurado

11:00-11:30 Applications of nanomaterials and nanostructures for fuel cells – *Igor Kosacki (Shell, USA)*

11:30-12:00 Applications of nanomaterials and nanostructures for batteries – *Joachim Maier (Max Planck Institute, Germany)*

12:00-13:00 Speakers panel discussion
 13:00-14:00 Lunch

Session 4 - Theoretical techniques

Chair: Rose-Noelle Vannier

14:00-14:30 Simulation of Materials

Saiful Islam, (University of Bath, UK)

14:30-15:00 Neutral networks and genetic algorithms

Steven Manos (UCL, UK)

15:00-15:30 Refreshment break

15:30-17:00 **Breakout group session 1:**

Critical materials requirements for electrochemical devices

17:00-18:00 Breakout groups feedback to plenary

19:00 Conference dinner at Lady Margaret Hall

From 21:00 Bar at Lady Margaret Hall is open

(There is a cashpoint in LMH near the bar.)

Wednesday 4th April

Session 5 - Accelerated Materials Discovery

Chair: John Owen

9:00-9:30 Rapid throughput synthesis – *Julian Evans*

(Queen Mary, University of London, UK)

9:30-10:00 Rapid screening techniques – *Brian Hayden*

(University of Southampton, UK)

10:00-10:30 Refreshment break

10:30-12:00 **Breakout group session 2:** Accelerated Materials Discovery

12:00-12:45 Breakout groups feedback to plenary

12:45 – 1:00 Closing Remarks

13:00-14:00 Closing lunch

List of Attendees

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