Materials chemistry and electrochemistry have long been very active fields of research accelerated by chance discoveries, societal needs, and the ever expanding constituency of researchers around the globe. Advances in synthesis, characterisation techniques, and interdisciplinary research have caused an almost exponential growth in research where applications have been driving the focus – especially in energy related research. This is important because despite the vast increase in accessible fossil fuel reserves, expanded partly by fracking for oil and gas, we must surely stop using fossil fuels as soon as possible. Even if we burn a fraction of these reserves, then climate change leading to a rise in average global temperatures greater than 2 °C will be unstoppable, threatening not just society, but the entire global ecosystem on planet Earth. Life as we know it will surely decline. The key realisation is intimidating. Two thirds of our current fossil fuel reserves are effectively unusable if we want to preserve our climate, no matter how low the oil price. So how can the next generation of materials help solve these problems? Well, some of the most important needs in materials for energy relate not only to conversion and new energy systems, but also to the ability to store energy at high densities. Also, the need for scalable systems that are durable cannot be over emphasised and these stringent requirements will surely allow scientists to creatively rise to the challenge. At Faraday Discussion 176, I observed such a transformation, where discussions not only about scientific principles but real world applications and practical implementation were combined.

Faraday Discussions have a great tradition, but Faraday Discussion 176 marked a special development as the first time that a Faraday Discussion has been held in Asia; the venue was the University of Xiamen in China. Also, it was fitting that the topic, next generation energy materials, was discussed in a country that has recently become the largest producer and consumer of energy in the world, and is also rolling out the largest renewable energy program. However, many serious issues must be tackled beyond the science, not only economic, political, social and environmental. The role of science today has not changed. Beyond
fundamental developments, we must use our current technologies to develop next
generation technologies, established by the current energy system. There is some
urgency. This next generation of energy systems has to cope with increasing
population, climate change, the need for food and water, as well as higher living
standards. There are many questions. How can we create scalable energy systems?
Which blend of systems (wind, tidal, solar, nuclear) could help the energy mix?
How are we going to produce carbon-dense fuels? If we keep using carbon, how
can we move to a renewable carbon cycle that removes and converts carbon
dioxide at least at the rate it is produced? What are the material challenges? How
can we encourage the next generation of researchers?

In my opinion, one of the greatest challenges is how do we ensure that research
starts at the fundamental end of the spectrum, leading to application, rather than
application first. The gradual shift in publication trends to high volume and
citations is worrying. This is driven by rewarding publication volume by research
funding, which in turn serves to distort the system. This in turn reduces scholar-
ship and forces bright researchers to instead focus on the incremental. This
should be avoided at all cost. Since we all understand there is a problem, and we
all take an active role in the system to varying degrees, it is up to us to change the
status quo for the better by striving to do the best science driven by curiosity, big
challenges, and chance discoveries. Researchers need to be willing to take risks,
but all too often this risk is seen through the lens of a failed career, and this
should be highly discouraged. By celebrating the process of discovery and
encouraging researchers to explore the unknown, I think there is hope that we can
reverse this trend. Where better to discuss fundamentals to application in next
generation materials for energy than at a university that has one of the top
chemistry departments in China, and one of the top 100 chemistry departments
worldwide, Xiamen.

This Faraday Discussion had three themes, electrochemical conversion and
energy storage systems, solar cells and photocatalytic systems, and energy-related
catalytic and other materials. Whilst I will not give a lecture-by-lecture summary
(this can be gained by reading this volume), I will try and make some observations
about the current status of the field and the current perspectives and challenges
for the future. The Introductory Lecturer (Peidong Yang, University of California
Berkeley) provided an overview of the state-of-the-art in inorganic materials,
showing how control on the nanoscale allows the design of architectures with vast
potential for a range of relevant applications e.g. solar cells. Yang described how
nano-materials science has developed rapidly over the last decade with the ability
to direct the formation and faceting of nanoparticles, nanocrystals and nano-
rods/wires.¹ Three levels of control are needed: assembly, spatial and temporal
organisation. Only temporal as well as spatial organisation will yield functional
systems that can exploit the nanoscale non-equilibrium organisation.² This
requires that we understand the control parameters for the development of
electrochemical materials and appreciate that as such, non-equilibrium systems
are developed by the structural and compositional complexity increase. Maier
proposed³ that the distance from equilibrium and the complexity of the system
can be understood if one distinguishes between the intrinsic (in situ) and extrinsic
(ex situ) parameters. The control of defects, morphology and topology are also
vital in defining the properties of the system and materials science can be viewed
in terms of size and complexity, see Fig. 1. These ideas provoked discussion about
the nature of defects and pondering on the effects on a system if random defects could be ‘programmed’ intentionally into a material.

The topic then shifted to battery electrodes in electrochemical circuits, where many complex issues of stability, diffusion, and composition are highly relevant, and also in fuel cells where diffusion is vital. In the case of SOFC cathode materials, substitution reactions can be used to improve performance, for example where calcium was partly substituted with strontium in Ca$_3$Co$_4$O$_{9+\delta}$, and this may be likely due to an increase of the volume of the rock salt layers in which the conduction process takes place. The role of structural studies was discussed in understanding not only the overall structure, but also local environments, which is key to developing new materials. Griffin explained in detail how solid state NMR spectroscopy could be used to study the local environments of anions in supercapacitor electrodes and to quantify changes in the populations of adsorbed species during charging. Exploring the size of the anions absorbed within the carbon micropores of the electrode as a function of concentration, potential, and polarisation also revealed much about the mechanism, including the relationship with anion size. The role of size was highlighted again in the investigation of nickel hexacyanoferrate (NiHCFe) as a cathode material. This is a very interesting material in both aqueous and organic electrolytes due to its ease of synthesis, use of earth abundant ingredients, and framework. It is hoped that such systems will lead to long life and high performance. The recent developments of new techniques increases dramatically the amount of useful information that can be gained from electrochemical systems such as batteries and supercapacitors. For instance the use of in situ liquid cell TEM allows the imaging of electrode interfaces in liquids with high spatial resolution, and under operation. The imaging of a gold electrode–electrolyte interface with lithium during charging and discharging using an electrochemical liquid was discussed, including control experiments and how to interpret the data. Also both in situ and ex situ SEM were discussed in the context of exploring the formation of lithium dissolution and dendrite formation.

Moving to fuel cells and electrolyser, there was much discussion about the development of new electrode materials, which is currently seen as a big barrier for the wide adoption of fuel cells and electrolyser. In electrolyser, understanding the oxygen evolution reaction (OER) is important, and probing the surface chemistry of Ru oxide in acidic and alkaline environments revealed that...
the kinetics of the OER are almost entirely controlled by the stability of the Ru surface atoms. This is because during the OER, surface defects are created and the oxide is only active for OER if it is itself unstable. For the hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR), non-precious metal catalysts suitable for acidic electrolytes are vital. Several solutions were discussed including the use of graphene supported iron-based nanoparticles encapsulated in a nitrogen-doped carbon.\(^\text{10}\) Also, Co oxide (Co\(_3\)O\(_4\)) nanotubes are shown to act as efficient water oxidation catalysts when driven with a visible light sensitizer (pH 7).\(^\text{11}\) The role of inorganic membranes was also discussed for the designing of solar-fuel type devices. Nickel compounds were also found to be effective for the OER when small nanoparticles of nickel oxide and nickel hydroxide were investigated.\(^\text{12}\) The catalytic activity was comparable to that of the best mixed metal oxide catalysts under the same conditions, whereas plate-like WO\(_3\) photoanodes were discussed as being good for photoelectrochemical (PEC) water oxidation. In my own lecture I mentioned our efforts to develop a new electrolyser system based upon electron-coupled proton buffers,\(^\text{14}\) and focused on a system using a polyoxometalate redox mediator, see Fig. 2.\(^\text{15}\) In our new electrolyser system, oxygen and hydrogen production can be both spatially and temporally separated. In the first step, the polyoxometalate buffer is both reduced and protonated whilst oxygen is evolved and in the second step, on addition of the reduced POM to a catalyst, hydrogen is produced up to 30 times faster than in conventional PEME (proton exchange membrane electrolyser) systems.

Next, the discussion moved to a more bio-inspired system with a direct comparison of photoelectrochemical (PEC) water oxidation\(^\text{16}\) activity between a photosystem II (PSII)-functionalised photoanode and a synthetic nanocomposite photoanode. These systems are extremely complex, requiring supramolecular control, and this was also shown for fully synthetic systems for light driven water oxidation.\(^\text{17}\) The discussion moved to consider the oxidative stability of such systems and also suitable candidates for constructing photoanodes for light driven water oxidation\(^\text{18}\) and water splitting in dye sensitized photoelectrochemical devices. An open question at this point is how to develop modules for oxygen evolution with those for hydrogen evolution in a simple way that can efficiently allow different catalytic ‘modules’ to be swapped into the system. Designing catalyst complexes that can withstand many millions of

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Fig. 2  Schematic of our polyoxometalate-based electrolyser system; reproduced from ref. 15.
turnovers is possible, but long term issues regarding stability and possible oxidative damage need to be explored. Biology has very efficient repair and reset mechanisms and it is not clear to what extent that artificial systems will need similar levels of maintenance.

Advances in solid-state dye sensitized solar cells was one of the highlights, with much discussion about the jumps in efficiency and scope for further control and enhancement, especially with hybrid organic–inorganic metal halide perovskites and the use of double blocking layers. DSSCs are already making a big impact with the first commercial systems being produced, but the leap in efficiency that allows the cost per watt to decrease is now moving toward a level where wider adoption is possible. This is because of the extraordinary leap in the solar-to-electric power conversion efficiency of devices using CH$_3$NH$_3$PbI$_3$ as a sensitizer, which has increased from 3 to 17.9%, as described by Grätzel and others.

Cell operation of the hybrid perovskite solar cells is also an important dimension, with a liquid phase deposition (LPD) method of a TiO$_2$ nanolayer for carbon-based perovskite solar cells. In a range of other developments, materials for solid state lighting were discussed, including which target structures to use to develop phosphors. Solid state lights not only require less energy, but have longer lifetimes and could be easier to recycle. Thermoelectric materials based upon silicon were also an interesting topic. This is because silicon nanoparticle based materials show especially low thermal conductivities due to their high number of interfaces, which increase the observed phonon scattering.

Approaching the final chapter of the meeting, we discussed the catalysis of small molecules, for example the reaction of CO on Fe(OH)$_x$/Pt nanoparticles. This demonstrated that Fe(III)–OH–Pt stepped sites readily react with CO adsorbed nearby to directly yield CO$_2$ and simultaneously produce coordinatively unsaturated iron sites for O$_2$ activation. There was much discussion about the role of precious metals like Pt, and how Pt-based electrocatalysts for the oxygen reduction reaction (ORR) hinder the practical application of proton exchange membrane fuel cells (PEMFCs). In this respect it is critical to replace platinum with non-noble metal electrocatalysts. A number of options now exist, and this issue is one of the most crucial if the issue of scale is to be addressed. For example, carbonised metalloporphyrins are a good candidate for electrocatalysis, as is the more accessible hemin, where heat-treated nanoporous hemin activity can be comparable to that of commercial Pt/C in alkaline solution. Also, the study of CO adsorption at tetrahedahedral (THH) Pt nanocrystals (NCs) was explored, which showed that CO adsorbs dominantly on the (100) sites of THH Pt NCs at low CO coverage.

Finally, the perspective lecture of Wang was extremely exciting, showing how triboelectric could have literally thousands of applications. By invention of a triboelectric nanogenerator using an elastic plastic material, mechanical energy could be converted to electrical energy. This could have applications literally everywhere and the lecture highlighted almost every conceivable option! I conclude by thanking the University of Xiamen and the organising committee Zhong-Qun Tian, Kazunari Domen, Clare Grey, Galen Stucky, Dongyuan Zhao and Nanfeng Zheng for organising such a wonderful and stimulating meeting. I can confidently predict that this will be the start of many extremely important Faraday Discussions in China and Asia as a whole.
References


