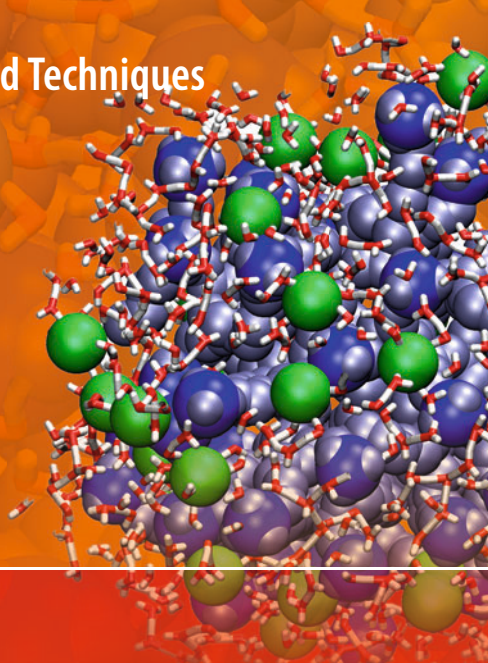


Neutron Scattering Applications and Techniques

Gordon J. Kearley
Vanessa K. Peterson
Editors



Neutron Applications in Materials for Energy

 Springer

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Preface

Neutron scattering has grown from being a physics and chemistry centred technique in which lattice dynamics and crystallography were the mainstays, to a more interdisciplinary field which includes areas as diverse as engineering, archaeology, food, plastics and all manner of nanostructured materials. The study of sustainable-energy materials is highly cross-disciplinary in nature, with the diverse activities frequently having some background in neutron-scattering techniques, which reflects the innate applicability of neutron scattering in this area. It is not surprising to find that many neutron-scattering centres are supporting an “energy project” of some description that brings together the in-house and user activities. It is refreshing to see scientists with widely-varying expertise making a joint approach to understanding and improving energy materials. Progress is made through a number of avenues:

1. Increasing performance of neutron sources and their associated instrumentation.
2. Improvement of specialised instrumentation, sample environments, and ancillary equipment (such as in situ cells), aided by collaboration, workshops, and conferences.
3. Computational resources and algorithms adapted to modelling structure and dynamics in increasingly complex materials are being both validated and used in the study of sustainable energy with neutrons.
4. Studentships and fellowships in the field are increasing, bringing fresh ideas and new approaches to the way neutron scattering is used and the data analysed.
5. Increasing awareness of the importance of sustainable energy in society, and the role that neutron techniques of analysis plays, helping to increase the resources that are allocated to this area.

This book brings together some of the core aspects of sustainable-energy materials that can be studied with neutrons, but there are obviously many other important neutron-based studies in the area that fall outside this core, for example in the fields of wind, hydro, and biomass. Similarly, a large number of non-neutron techniques are used to study the materials that we discuss in this book, and it is

frequently the combination of information from a number of techniques that leads to the final understanding.

Although the book does not contain dedicated theory or instrumental sections, the volume is aimed at those who have little or no knowledge of neutron-based techniques of analysis, and instead we refer to an earlier volume in this series in which these topics are presented in detail. The contents of this book are aimed at professionals at all levels in the field of sustainable energy, to show the types of question that can be addressed using neutrons. Some chapters in the book take the form of a review, whilst others use case studies to provide a more targeted approach. The book is structured chronologically, beginning with energy generation, moving onto storage, and then to use, although each chapter can be read independently of the others. The loose theme of application of sustainability-materials in transport applications that runs through many of the chapters is rather artificial, because each chapter has at least some bearing on stationary applications.

We are sincerely grateful to all the authors for their willingness to find the time to provide their chapters. They are all active in research and can only make their contribution to this book by taking time away from their research projects. We do understand.

Lucas Heights, NSW, Australia, October 2014

Gordon J. Kearley
Vanessa K. Peterson

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Chapter 1

Neutron Applications in Materials for Energy: An Overview

Vanessa K. Peterson and Gordon J. Kearley

Abstract Creating a global energy-system that is both environmentally and economically sustainable is one of the largest challenges currently facing scientific and engineering communities. Alternative energy-technologies and new materials have risen as a result of the combined needs for energy and environmental sustainability, with the focus moving increasingly away from fossil fuels. Neutron-based techniques of analysis play a role in almost all aspects of sustainable-energy materials research, and the chapters of this book will enlarge on these studies using examples and case studies to illustrate research approaches, methods, and outcomes.

1.1 Introduction

Research on renewable materials of relevance for environmentally benign energy-technologies is one of the most rapidly-growing research areas in materials science. The primary challenge in this research is the development of materials for such technologies that are viable in competition with existing energy-technologies, responding to application requirements such as efficiency, durability, and cost. Understanding the fundamental properties of materials and their functionality at the atomic and molecular level is crucial in addressing the global challenge of cleaner sources of renewable energy.

This book is divided into three main parts: materials for energy production, storage, and use. The central theme is identifying where the energy carrier is in the material and its interaction with its immediate environment so that these can be tailored to increase the concentration and/or transport of the carrier, which may be electrons, ions, atoms, or molecules. The theory of neutron scattering and analysis techniques, as well as the

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associated instrumentation, are explained elsewhere in the “Neutron Scattering Applications and Techniques” book series [1] and we particularly refer the reader to Chaps. 2 and 3, respectively, in the “Neutron Applications in Earth, Energy and Environmental Sciences” edition of this series [2] which are available on-line [3].

1.1.1 The Need for Neutrons

Despite the superficial similarity of the application of neutrons with those of photons, neutrons have some key differences to photons that enable neutron-based techniques to play a particularly important role in the sustainable-energy area. A full account of neutron theory and techniques is given elsewhere in this series [1] with key methods prevalent in this book outlined here. For our purposes we can regard all of the advantages and disadvantages of neutron scattering as having a single origin: neutrons interact with, and are sometimes scattered by, atomic nuclei. In all neutron-scattering methods this leads the following advantages:

- i. The scattering characteristics of each type of isotopic nucleus are well known, but vary almost randomly from one isotope type to another (scattering-lengths are shown in Fig. 1.1). This provides considerable scope for measuring light nuclei in the presence of very heavy nuclei, and also changing the scattering length by using a different isotope of the same element. For materials such as lithium-ion battery electrodes, where lithium must be probed in the presence of transition metals (see Chap. 7), this is a considerable advantage over other techniques where the scattering arises from electron density.
- ii. Incoherence arises when scattering from the nuclei do not interfere constructively. The random relation between the nuclear spins of hydrogen and neighbouring atoms contributes to the extreme incoherent neutron-scattering cross-section of the ^1H nucleus, which can be turned off by simple deuteration. Hydrogen is probably the most important element in sustainable energy-materials and it is very convenient that neutron scattering provides this selectable sensitivity for this element.
- iii. Neutron-scattering cross sections are in general quite small, so neutrons are relatively penetrating, where measurements (reflection is an exception) occur for the bulk of the sample. This penetration alleviates the need for special window materials in difficult sample environments and in situ studies. There are good examples of this in Chap. 7 for lithium-ion batteries in which the composition of the electrodes can easily be measured in an operating battery.
- iv. Neutron-absorption cross sections are also normally quite low, contributing to the high penetration of neutrons, but some isotopes have very large absorption. Lithium is perhaps the second most important element in sustainable-energy materials, so it is again convenient that ^6Li has high absorption, whilst ^7Li does not. Consequently, either radiography (and other bulk techniques) or normal neutron-scattering experiments can be made using the appropriate isotopic composition.

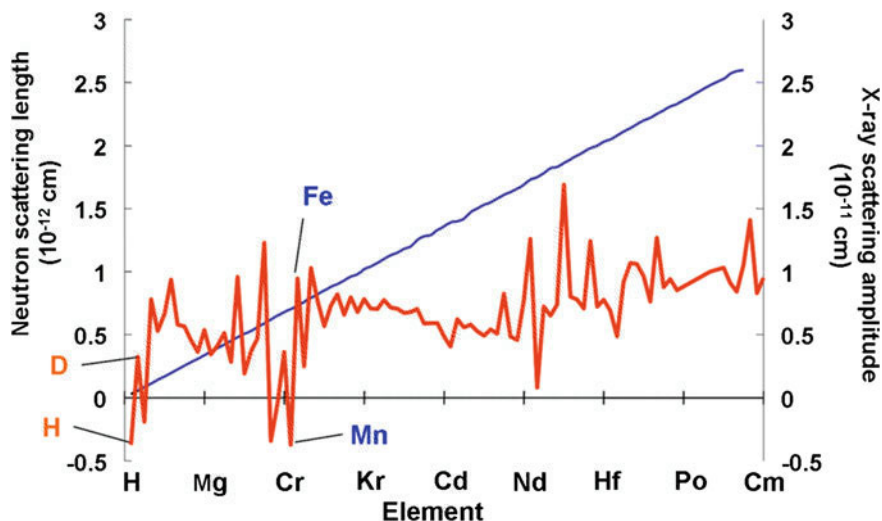


Fig. 1.1 Neutron-scattering lengths and X-ray scattering amplitudes for various isotopes (neutrons based on naturally-abundant isotopes unless specifically identified) and elements (X-rays)

The list above shows that neutron scattering is well suited to the study of sustainable-energy materials, but there are other important considerations to be made before undertaking a neutron experiment. Firstly, neutrons are difficult to produce in high quantities with the correct energies for the studies in this book, and consequently, virtually all experiments require a central facility and associated logistics. Secondly, even at the most powerful sources the neutron beams are weak when compared with photons or electrons, so the samples and the counting times for neutrons are correspondingly greater. Consequently, neutron scattering is rarely used when the desired information can be obtained by another means, and maximum use of complementary techniques (most frequently X-ray) and computer-modelling methods is common.

1.2 Neutron-Based Analysis of Energy Materials

In the next sections we will outline the basics of the neutron techniques of analysis that underpin the chapters that follow. Neutrons have the same principle attributes as photons for the study of a wide range of materials. Neutrons can be diffracted giving information about atomic position, scattered inelastically giving information about atomic (or molecular) motion, and neutrons can be absorbed giving spatial information concerning material composition through radiography and tomography. The instrumentation for photons is well known, but for neutrons there is an almost analogous group of techniques that together cover length scales from fractions of an

Å to microns (and up to many centimetres for radiography) and timescales that cover from femtoseconds to hundreds of nanoseconds. The generic properties of neutrons lead to the recurrent use of particular neutron scattering and neutron-based analysis throughout this book, and this section explains the rudiments of these.

1.2.1 Structure

Structure is determined using neutron diffraction (ND). The structure factor, $S(Q)$, describes scattered neutrons of the beam in terms of the wave-vector transfer, Q , where $Q = 4\pi\sin\theta/\lambda$, and θ is the angle of the scattered neutrons with λ being the incident-neutron wavelength. For a single crystal, the scattering will consist of Bragg peaks. In an ideal powder sample, small crystallites are randomly oriented and scattering from a particular set of lattice planes corresponds to the scattering obtained by turning a single crystal. In powder samples, Debye-Scherrer cones are obtained in place of Bragg peaks, where intensity from the cones can be determined simultaneously using large-area detector arrays.

1.2.1.1 Neutron Powder Diffraction

The workhorse of ND is powder diffraction, which has been developed to the point where complete structural information can be obtained from polycrystalline samples. Even modest dynamical information, such as diffusion pathways, can be deduced from atomic displacement parameters. The technique relies on the well-known coherent-interference pattern that is scattered from well-defined lattice planes, which, due to rotational averaging in a powder, collapse to a simple one-dimensional powder pattern. The level of detail that is available from this pattern is largely dependent on the resolution and range of the diffractometer, plus the availability of refinement algorithms, all of which continue to improve. The technique is not limited to a single compound, and measured diffraction patterns are often used to establish the phase composition in complex materials, for example where doping is used to modify electronic structure in solar-cell materials (such as in Chaps. 5 and 6).

Although very detailed structural information can be obtained from powders, the comparative simplicity of the technique also makes it the prime candidate for in situ studies, which also profit from the penetration and isotope selectivity of neutron scattering. In the context of this book, the technique is commonly used to follow the evolution of structure with temperature, or composition, for example in charging and discharging electrodes (such as in Chap. 7).

The main constraint on neutron powder diffraction (NPD) is the larger samples required compared with X-rays, and the large incoherent neutron-scattering from

the ^1H nucleus that causes a high background. In general this background can be eliminated by deuteration, with the added advantage that the crystallographic positions of these atoms can then be more-easily established.

1.2.1.2 Pair-Distribution Function Analysis

Disordered materials often provide mechanisms for improved diffusion and transport, which is desirable for many sustainable-energy materials. Pair-distribution function (PDF) analysis is becoming increasingly important in studying these materials as it provides local structure, interatomic distances, bond-angles and coordination numbers in disordered materials such as glassy and amorphous materials. The essential difference between conventional ND and PDF (linked to the neutron total-scattering experiment) is that while in ND only the Bragg peaks are considered, neutron total-scattering means that also the diffuse, weaker, scattering present between the Bragg peaks is analysed, where deviations from the average can be measured. It is this “extra” scattering that provides information about the structure on a local scale and is therefore of high importance for structural studies when the material is not fully periodic.

The PDF, or, $G(r)$, is obtained from the structure factor, $S(Q)$, via a Fourier transformation,

$$G(r) = \frac{2}{\pi} \int_0^{\infty} S(Q - 1)(Qr)QdQ \quad (1.1)$$

It is the analysis of this quantity that gives information about the local structure of the material. The Fourier transform requires data over a large Q range to avoid truncation effects, so the technique typically uses rather short-wavelength neutrons, either at the hot-end of reactor sources or at spallation sources.

1.2.1.3 Neutron Reflection

The structure and kinetics at, and close to, interfaces is of importance in many sustainable-energy devices (e.g. electrolytes and electrodes, see Chap. 7), but these properties are difficult to establish. Within certain constraints, the neutron reflection (NR) experiment can establish the scattering characteristics beneath a surface by measuring the reflected intensity as a function of angle. Above a critical angle (representing Q), total reflection occurs, but below this each layer interface produces an oscillating reflected amplitude with period $\Delta Q = 2\pi/T$, where T is the thickness of the layer. However, the measured reflected intensity is the total from all interfaces present, and because phase information is lost, the usual way forward is

to fit the measured signal with models. In practice it is the variation of sample composition within the depth of the sample that is of interest, and this is characterized as the scattering-length density (SLD) profile, which is the sum over the number density of each isotope at a given depth, z , times its bound coherent neutron-scattering length. The essential advantages of neutron measurement of reflection is the variation of scattering length with isotopic nuclei, which allows contrast variations, measurement of buried layers, and favours the light elements in the presence of heavier ones found in energy materials.

The main constraints in NR are the comparatively large and atomically-flat surface that is required, and establishing suitable models for analyzing the results.

1.2.1.4 Small-Angle Neutron Scattering

Small-angle neutron scattering (SANS) is a well-established characterization method for microstructure investigations, spanning length scales from \AA to micron sizes. Within the SANS approximation, Q simplifies to $Q = 2\pi\theta/\lambda$. The SANS Q range is typically from 0.001 to 0.45 \AA^{-1} . For example, scattering from a simple spherical system in a solvent yields a SANS coherent macroscopic neutron-scattering cross section (scattering intensity in an absolute scale) of:

$$\frac{d \sum_c(Q)}{d\Omega} = \frac{N}{V} V_P^2 \Delta_{\rho^2} P(Q) S_I(Q) \quad (1.2)$$

where (N/V) is the number density of particles, V_P is the particle volume, Δ_{ρ^2} the contrast factor, $P(Q)$ is the single particle form factor, and $S_I(Q)$ is the inter-particle structure factor. $S_I(Q)$ has a peak corresponding to the average particle inter-distance.

1.2.2 Dynamics

The dynamic structure-factor, $S(Q, \omega)$, describes scattered neutrons in terms of the wave-vector transfer Q and the neutron energy-transfer $\hbar\omega$, where $\hbar = h/2\pi$ and h is Planck's constant. The timescales and corresponding energies of the processes that are accessed by neutron scattering from energy materials are illustrated in Fig. 1.2. A particular strength of neutron scattering is that the size and geometry of the volume explored by the dynamic process is also available, and is shown on the horizontal axis of Fig.1.2.

This is particularly useful when measuring local or long-range diffusive processes, for example in fuel-cell electrolytes (see Chaps. 9 and 10).

Fig. 1.2 The frequency (E), time (t), and space (Q) domains in which the dynamics of energy materials are typically studied using neutron scattering

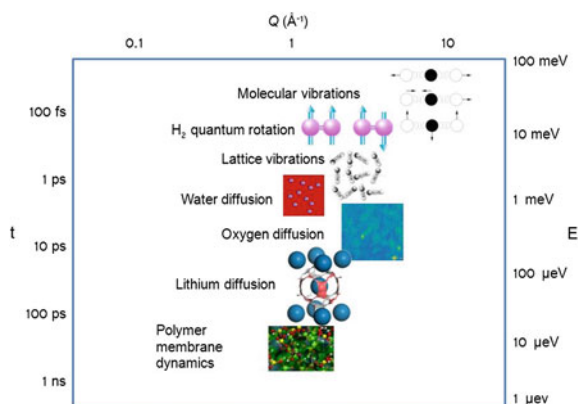
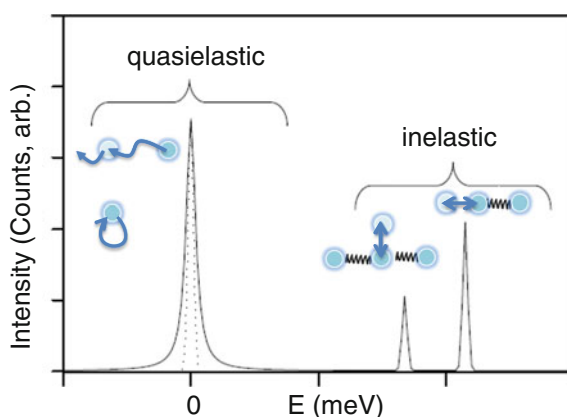


Fig. 1.3 Representative inelastic and quasielastic signals from some idealized motions that give rise to them. Reprinted from (H. Jobic and D.N. Theodorou, Microporous Mesoporous Mater **102**, 21 (2007)) [4]



Inelastic peaks usually arise from a periodic motion, and the forces controlling this motion are stronger than those that would define a more diffusive motion. Correspondingly, inelastic peaks usually arise at higher energy than the quasielastic broadening, as illustrated schematically in Fig. 1.3.

1.2.2.1 Inelastic Neutron-Scattering

Inelastic neutron scattering (INS) is crucial in the study of hydrogen storage where the neutron can excite the quantum motion of the H_2 molecule, and measure the transition energies directly (see Chap. 8). However, in the more general case INS amounts to “vibrational spectroscopy with neutrons” and in the present book is used to study local structure, vibrational dynamics, and the nature of hydrogen-bonding interactions. The main strength of the technique arises from the large neutron-scattering cross section of hydrogen, which causes vibrations involving hydrogen to dominate the spectra. This domination, particularly when combined with selective deuteration, is very powerful for providing assignment of the observed peaks to specific

vibrational-modes. In addition, it is now straightforward to calculate the INS directly from a molecular model which is not only an aid to assignment, but also a validation procedure for the model. The technique is comparable to infra-red and Raman spectroscopy, which have better resolution, but lack the hydrogen selectivity and simplicity of assignment. Incoherent INS has no selection rules and even modes that are silent in both infra-red (IR) and Raman can have significant INS intensity.

1.2.2.2 Quasielastic Neutron-Scattering

The term quasielastic neutron-scattering (QENS) can be used to describe any broadening of the elastic peak regardless of its origin, but use of the term in this book is always with reference to a stochastic or diffusive non-periodic motion. The technique is important for energy materials because it provides the relevant time and length scales on which the atomic-scale dynamics of protons and small molecules typically occur, for example in proton-conducting perovskites (Chap. 9). Various molecular processes can be distinguished from the data, which can be quite straightforward, although in systems of any complexity it is now common to use molecular-dynamics simulations from which it is now easy to produce a calculated QENS spectrum.

1.3 In Situ

Function is of great importance to the study of energy materials. At the heart of the application of neutron-based techniques of analysis to the study of energy materials is the understanding of structure- and dynamic-function relations. Comprehending the working mechanism, at the atomic and molecular scale, is the key to progressing alternative and sustainable-energy technologies, and fundamental to this is the study of the materials during operation. As such, in situ and even operando studies are commonplace and necessary in energy materials research. The in situ technique, often applied to materials under equilibrium, has been extended in recent years to operando studies, where the materials are studied under non-equilibrium conditions whilst performing their function. The advent of new-generation reactor and spallation neutron sources, as well as associated faster instrumentation, has greatly assisted in facilitating such research.

1.4 Perspectives

Whilst the difficulties of realising sustainable energy are decreasing, the difficulties of fossil-fuel based energy are increasing and the point will inevitably arrive when sustainable energy is not only socially and environmentally more favourable, but also makes economic sense in its own right. Sustainable-energy materials will

develop over the long run, and the role of neutron-scattering techniques in the understanding of these is almost certain to develop in parallel. Generic improvement in neutron sources and instrumentation will enable smaller samples to be measured in shorter times, and this is part of the wider scientific agenda. However, there are also specific improvements that will benefit the study of energy materials.

In situ and operando experiments are crucial for “close to market” studies, and whilst these are not simple with neutrons, they are generally more straightforward than with other methods. Perhaps ironically, it is now possible to construct real lithium batteries that are optimised for operando neutron-diffraction measurements, where the optimisation may affect cost, but has little or no effect on the actual operation. Often the modification for operando neutron scattering amounts to deuteration of materials and neutron-scattering centres are increasingly housing specialised deuteration facilities, capable of deutering complex molecules.

The complex systems that characterise the development of energy materials give complex neutron-scattering signals, from which it can be difficult to deconvolve unambiguous information. However, the rapid increase in computer hardware and software is enabling the experiment, data treatment, theory, and modelling to be brought together to provide consistent interpretation of the neutron-scattering data. Although at present this is the domain of specialists, considerable efforts are being made throughout the neutron-scattering community to bring this type of approach within the reach of non-specialist users. Although previously the multiprocessor computer hardware required for this type of work was only available at central-computing establishments, it is now becoming ubiquitous in universities and neutron-scattering centres where there is generally good local support.

The experimental programme at neutron-scattering centres has to strike a balance between scientific, societal, commercial, and national interests, the details of which depend on the strategy and “terms of reference” of the centre. Sustainable-energy materials are almost equally important in all aspects of this balance, which provides a unique opportunity for communication and collaboration across these aspects and between neutron-scattering centres. Although this type of initiative has yet to occur, there have been a large number of conferences and workshops at the purely scientific level that have been funded from a diverse range of sources. Larger gatherings, specifically highlighting neutron scattering, would provide an overarching description of problems, bottle-necks, and resources, from industry, strategists, and through to experimentalists.

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Part I

Energy Generation

Energy generation is not only important for meeting the requirements of consumers and industry, but is crucial for national security and economic competitiveness. Environmental sustainability is a global issue that needs to respond to existing damage from direct emissions as well as unplanned future events such as spills and leakages. Neutron techniques of analysis play some role in progressing all technologies for renewable-energy generation, although this may be limited to structural materials for wind, marine and hydro energy generation, whilst neutron scattering in earth sciences plays a significant role in geothermal energy. Chapters in Part 1 concentrate on those aspects of energy generation that are mainstream for neutron-based methods, but are nevertheless relevant to the more general sustainable-energy technologies in energy generation.

Catalysis (Chap. 2) not only plays a central role in sustainable-energy generation where renewable feedstocks are used, but also plays a more general role in increasing efficiency, reducing energy consumption, and producing cleaner targeted products from fossil-based sources such as oil, natural gas, and coal. Active sites in catalysis are often present in only trace quantities, and characterizing these with neutrons is usually limited to model compounds. However, almost the whole range of neutron techniques of analysis have been used to help in the design, characterisation and optimisation of catalysts by measuring the structure of the catalysts themselves, and following the dynamics of the reactants and products. The hydrogen economy requires an efficient means of generating, storing, and using hydrogen, all of which involve some catalysis. However, because the most important role of catalysis is in energy generation, we gather all aspects of the topic in Chap. 2.

Although global CO₂ emissions threaten today's way of life, cost-effective methods to separate, capture, store, or use CO₂ from fossil fuels represent a major challenge. As existing technologies use solvents that impose a heavy energy-penalty (about 30 % of the energy generated by the plant), a key scientific challenge is the development of materials that can interact with flue-gas streams to capture and concentrate CO₂ with lower energy requirements. Porous materials such as

coordination polymers offer a new way to address this in that they not only possess the highest surface area of any known materials, but they can be engineered to be selective for CO₂. Therefore, solid porous hosts represent one of the most promising technologies for separating and storing gases of importance in the generation and use of energy. Studying the uptake of CO₂ in such materials at the fundamental level is required to progress these towards commercialisation, with such studies allowing direct feedback into the synthesis of materials with enhanced CO₂ uptake, selectivity, and chemical stability. Neutron scattering is essential in this research with in situ studies involving pressure and/or temperature being of particular importance. Both structural and dynamical information is important in this area in order to establish the gas–host interaction, and forms the basis of Chap. 3.

Structural materials are important to all forms of sustainable-energy production and neutron scattering is increasingly being used to characterize and understand fatigue and failure, and in this context we concentrate on materials for nuclear-energy applications in Chap. 4. Nuclear materials are particularly demanding because they must meet the mechanical demands not only under pressure, temperature, and chemical environment, but also under the effects of irradiation. Neutron-based characterisation of such materials mainly takes the form of neutron diffraction to understand how the microstructure and crystal structure characterize bulk material-properties. Superficially, this is a straightforward measurement, but in practice we need to understand how crystal structure, microstructure, chemical composition, and orientation are all coupled, and how these can be controlled to obtain (or avoid) particular properties. Major neutron-scattering centres now have at least one instrument that is conceived specially to do these types of experiment.

One of the greatest contributions neutron scattering has made in the study of sustainable energy-materials is in solar cells, which are divided into inorganic and organic in Chaps. 5 and 6, respectively. Photovoltaics (PV) is required for each of them, and is the direct conversion of light into electrical energy, the first PV device having been built by Edmond Becquerel who discovered [R. Williams, *J. Chem. Phys.* **32**, 1505 (1960)] the PV effect in 1839. The operating principles of this effect are based on a sequence of light–matter interactions that can be summarized as follows:

- (i) Absorption of photons with a given energy matching the semiconducting properties of the device (band gap and intrinsic coefficients);
- (ii) Free charge-carrier generation in inorganic semiconductors and bound exciton (pair of electron-hole) creation in the case of the organic analogous and exciton [E.A. Silinsh, V. Capek *Organic Molecular Crystals -Interaction, Localization and Transport Phenomena* (American Institute of Physics, New York, 1994)] dissociation;
- (iii) Charge transport via relevant pathways;
- (iv) Charge collection at dedicated electrodes and photocurrent generation.

PV solar cells convert solar energy into electricity via the PV effect in a variety of strategies that can be classified as (Fig. 1): Multijunction, single-junction GaAs, crystalline Si, thin-film, as well as organic and emerging (including hybrids).

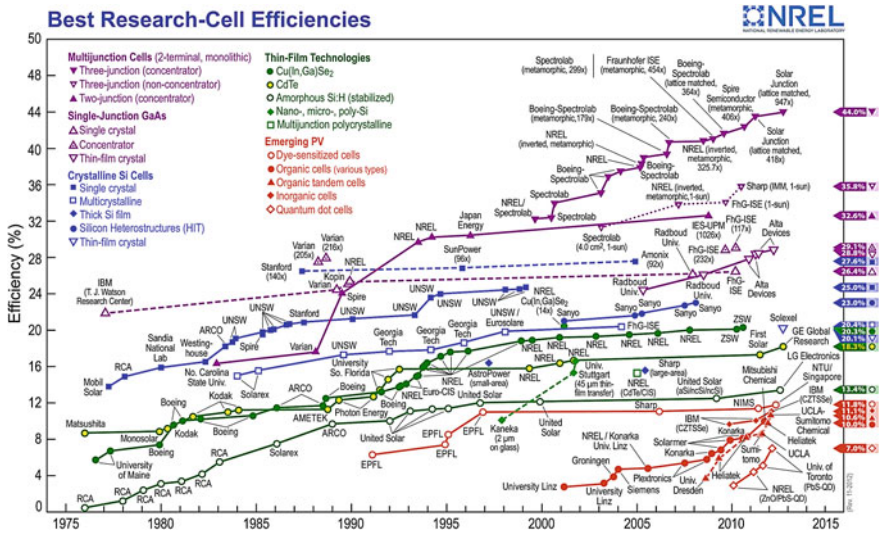


Fig. 1 Power conversion efficiency (PCE) of various solar cells showing their recent performance. Source: National Renewable Energy Laboratory

Sustained development has been achieved for each of the PV strategies over the past decades (Fig. 1). It is important to notice that step changes in efficiency mainly arise with the discovery of a new strategy, but that this is not always upwards. This is because many factors contribute to the cost per Watt, and low efficiency may be counterbalanced by overall cost, which is composed of:

- (i) Energy pay-back time;
- (ii) Stability and lifetime;
- (iii) Environmentally friendly materials and production;
- (iv) Cost and supply of materials;
- (v) Adaptability of shape/form;
- (vi) Size/weight.

For PV materials there is a convenient separation of the materials in the broader classification of inorganic and organic. More attention has been devoted to inorganics, which have been known for well over a century and promise very high efficiency. In contrast, the first organic PV (OPV) was crystalline anthracene [H. Kallmann, M. Pope, J. Chem. Phys. **30**, 585 (1959)], this having been first observed in 1959. OPVs have only been only attracting significant attention in the past decade (Fig. 2), at least in part as a result of robust concepts and principles for organic semiconductors set up around 1970 by Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa, who were awarded the Nobel Prize in 2000 for this contribution. This paved the way for the use of organic materials as PV devices, inducing and stimulating a tremendous interest in research on OPVs for both fundamental and technical purposes.

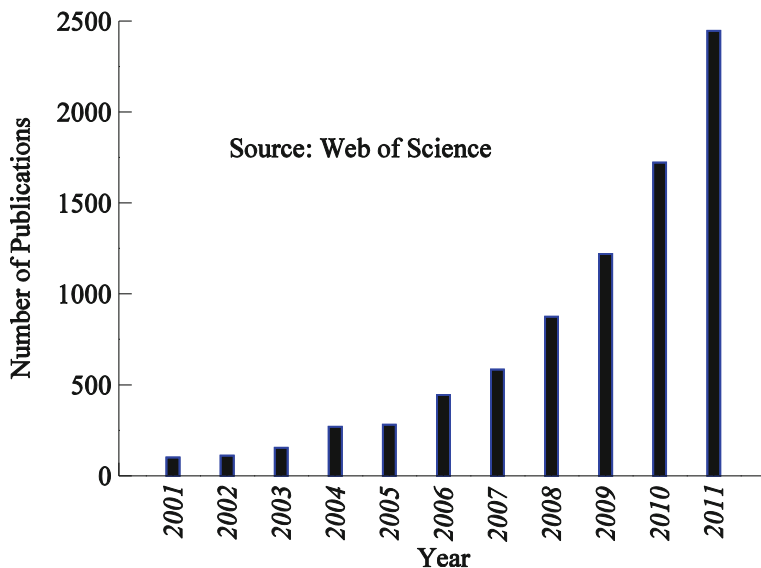


Fig. 2 Approximate number of publications per year for the last 10 years with the topic organic solar cells

In inorganic (thin film, Chap. 5) and organic (Chap. 6) solar cells we focus our attention on case studies of model systems with the aim of showing how neutron techniques of analysis in combination with other techniques contribute to our understanding and resolution of specific challenges in PV materials. The failure of one of the earliest cells, $\text{Cu}_2\text{S-CdS}$, due to Cu^+ to Cu^{2+} conversion, illustrates the importance of understanding functional properties of PV materials at a number of levels. PV materials cover a vast range, from soft, almost liquid materials through to hard crystalline materials, with local and large-scale structure, interfaces, and dynamics over a wide range of timescales also being important. The challenge for diffraction is that the required semi-conductors are usually not only non-stoichiometric (due to doping), but also composed of elements with similar atomic numbers. The non-stoichiometry can lead to structural defects that affect the material and electronic properties so it is essential to have a method for identifying and characterising these differences. Chapter 5 shows how the neutron scattering cross-sections enable not only neighbouring elements to be distinguished, but also the study of defect non-stoichiometric structures. Chapter 6 concerns investigating the comparatively weak forces holding the organic and polymeric molecules together, these being both advantageous and disadvantageous for PV applications. Hence, whilst for inorganic PV materials the atoms can be regarded as localized, for organic PV materials molecular dynamics plays at least an equally important role as time-average atomic position. Dynamics on different timescales is responsible for

recombination, charge-transfer, processing, and ultimately ageing, all of which are important to the PV's function.

Chapter 6 shows not only the use of neutron diffraction, but also how different neutron spectroscopies can be used to unravel the dynamics that helps or hinders different aspects of the PV process.

Chapter 2

Catalysis

Hervé Jobic

Abstract Catalysis helps to save energy and to produce less waste. Hydrogen will possibly be the energy carrier for the future, but it will not replace oil before several decades so the efficiency of the catalytic processes in petroleum refinery and petrochemistry still has to be improved. Numerous physical techniques are being used to follow catalytic processes. The samples can be subjected to several probes: electrons, photons, ions, neutrons; and various fields can be applied: magnetic, electric, acoustic, etc. Apart from the basic catalyst characterization, the various methods aim to observe surface species (intermediate species are much more tricky), the reaction products, and the influence of diffusion. Coupling of two, three, or more techniques is now common and very powerful. The biggest challenge has always been to perform measurements during the reaction, the term *in situ* being sometimes replaced by the more recent one *operando*, when the catalyst is under working conditions of pressure, temperature, flow, and avoiding diffusion limitations.

2.1 Catalysis and Neutron Scattering

The main classes of heterogeneous catalysts are: (i) metals and alloys (supported or not), (ii) metallic oxides (including mixed oxides, heteropolyacids, superacids), (iii) zeolites and molecular sieves in general, and (iv) sulfides. It will take some more years before deciding if metal-organic frameworks (MOFs) become a new member of the catalysts family.

Several neutron techniques are used to study catalytic systems: neutron diffraction (ND), small-angle neutron scattering (SANS), inelastic neutron scattering (INS), and quasi-elastic neutron scattering (QENS). We will limit ourselves here to INS and QENS of hydrogen species and dihydrogen molecules adsorbed on the surface of catalyst particles or inside porous materials.

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Hydrogen has recently been associated with the words fuel cells and energy storage, but it is also an essential component in catalytic reactions and the hydrogen produced is mainly used in petroleum refining and ammonia production for fertilizer. Nowadays, about 90 % of the H_2 production comes from catalytic steam reforming of natural gas at high temperatures (subsequent reactions of water–gas shift and preferential oxidation are required to decrease the CO level of the gas mixture to a few ppm before it can be used in a fuel cell). At the time being, one is facing a huge increase of H_2 needs (with related CO_2 emissions), so that until Jules Verne’s predictions are realized (water: the coal of the future), we may reach an H_2 deficit, as predicted by some experts.

The applications of INS to catalysis have been mainly focused to systems which are either difficult or impossible to study by other spectroscopies such as transmission or reflection–absorption infrared, and Raman. The kind of catalyst which is studied in INS has generally an inhomogeneous surface, e.g. oxides, sulfides, and metals, although zeolites, which are well-crystallized materials, are well suited. These substrates can be almost transparent to neutrons if they contain a small quantity of hydrogen, in which case the neutron spectrum will be fairly flat and it will be possible to observe all the vibrational modes of the adsorbate.

QENS has been mainly used to measure the diffusion of H or hydrogenated molecules, although the transport of deuterated molecules and of molecules which do not contain hydrogen atoms can now be followed. The dimensionality of diffusion has been studied, even if the samples are in powder form. On zeolites [1], MOFs [2], or clays [3], anisotropic diffusion (one or two dimensional) has been evidenced. The technique allows us to probe diffusion over length scales ranging from an Å to hundreds of Å. The mechanism of diffusion can thus be followed from the elementary jumps between adsorption sites to Fickian diffusion.

2.2 Neutron Spectroscopy of Hydrogen-Containing Materials

There are very few works on atomic-hydrogen diffusion on catalysts by QENS, the H species resulting from H_2 dissociation have been predominantly studied by INS. When hydrogen is bonded to metal atoms, the heavy atoms can be considered as fixed during the local modes of hydrogen. A consequence is that the mean-square amplitudes for the hydrogen atoms will be generally small so that the sample temperature will be of small influence on the INS intensities. Another consequence is that the nondegenerate modes of hydrogen will have nearly the same intensity and an E mode will be twice as intense as an A mode. The INS spectra can thus be fitted and the relative intensities of the bands yield the populations of the various sites.

INS studies of the adsorption of H_2 on various materials, to observe rotational transitions, and of various hydrogen species present on metal and sulfide catalysts were previously reviewed [4, 5]. Only recent work will be considered here.

2.2.1 Sorption of H_2 During the Reduction of Copper Chromite

The activation of a copper–chromium system in H_2 is accompanied by an accumulation of H_2 , which can become active for hydrogenation reactions, in the absence of H_2 in the gas phase. This sorption of H_2 is due to a specific mechanism of Cu^{2+} reduction from the $CuCr_2O_4$ structure, a reaction which does not release water. The reduction leads to the formation of metallic copper and to protons substituting for copper cations in the vicinity of O^{2-} anions. INS spectra of copper chromite as prepared and reduced at various temperatures are shown in Fig. 2.1. The initial catalyst shows bands at low frequencies, due to the mass of the atoms, these bands having a low intensity because no proton motion is involved. Upon reduction, a large intensity

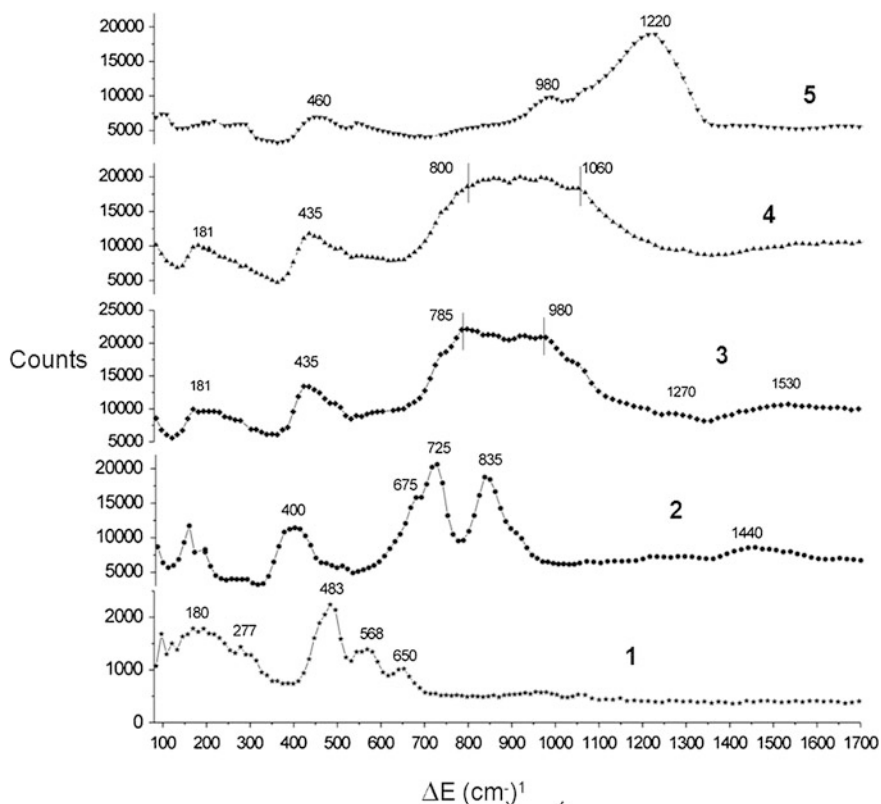


Fig. 2.1 INS spectra of as prepared and reduced samples of copper chromite. 1 Initial spectrum, 2 reduced with hydrogen at 250 °C, 3 at 290 °C, 4 at 320 °C, 5 at 450 °C. The data were obtained on the instrument IN1BeF at the Institut Laue–Langevin (ILL). Adapted with permission from (A.A. Khassin, G.N. Kustova, H. Jobic, T.M. Yurieva, Y.A. Chesalov, G.A. Filonenko, L.M. Plyasova, V.N. Parmon, *Phys. Chem. Chem. Phys.* **11**, 6090 (2009)) [6]

increase can be measured and OH-groups bending modes are observed in the energy range displayed in Fig. 2.1. Increasing the reduction temperature yields a shift of these bending modes to higher frequencies (from 700–800 to 1,220 cm^{-1}), while the stretching modes shift to lower energy. This indicates that hydrogen bonding strength with neighbouring anions increases with the rise in temperature. The band around 400 cm^{-1} was assigned to librations of two geminal protons (i.e. HOH-groups) [6].

2.2.2 Dissociation of H₂ on Ceria-Supported Gold Nanoparticles

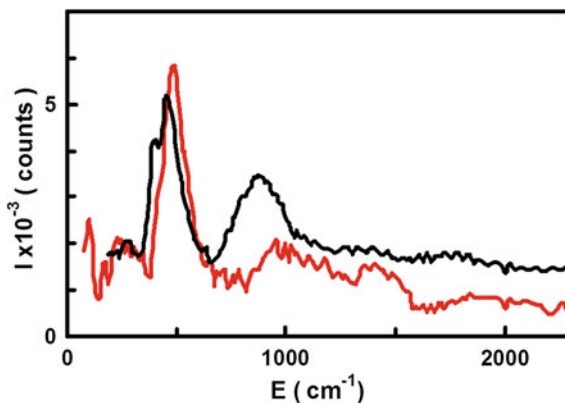
Catalysis by Au nanoparticles has attracted considerable attention since it was discovered that Au particles, with a size less than a few nm, are active. Au nanoparticles deposited on oxides can dissociate H₂ heterolytically on sites involving one Au atom and a nearby surface oxygen atom. This is in contrast with other metals such as M = Ni, Pd, Pt, etc., where H₂ is dissociated homolytically (in a symmetric fashion). The relatively poor activity of Au for hydrogenation reactions was attributed partly to the inability of Au to break the H–H bond and to the instability of Au hydrides (Au–H species), while various M–H species have been clearly evidenced by INS.

The INS spectra obtained after chemisorption of H₂ on 3–4 nm Au particles supported on nanoparticulate ceria (5 nm) show a peak at 400–600 cm^{-1} accompanied by a broad band from 750 to 1,200 cm^{-1} . The first peak was assigned to bridging hydroxyl groups, and the second band to librational modes of water present on the catalyst surface and resulting from the reaction of hydrogen with oxygens of ceria [7]. The lack of observation of Au–H species by INS can be explained by the low percentage of Au on the sample (Au loading: 0.48 wt%). On the other hand, the formation of Au–H could be observed by Fourier-transform infrared (FT-IR) spectroscopy, which seems to indicate a greater sensitivity of IR spectroscopy for this sample.

2.2.3 Hydride Species in Cerium Nickel Mixed Oxides

Bio-ethanol obtained from biomass has been suggested as a promising renewable source of H₂. It is a challenge to find low-cost catalysts (without noble metals) able to break the C–C bond of ethanol at low temperature. A CeNiH_ZO_Y catalyst was recently found to convert ethanol at 60 °C only, by steam reforming coupled with partial oxidation [8]. The distribution of products is similar to what is obtained by steam reforming at high temperatures: H₂ (about 45 %) and mainly CO₂ and CO. The reaction is initiated at 230 °C, but the temperature increases after a short induction period so that a temperature of 60 °C is sufficient to maintain the reaction. This is explained by the occurrence of two exothermic reactions: (i) between hydride species

Fig. 2.2 INS spectra of CeNi_1O_Y (black) and $\text{CeNi}_{0.5}\text{O}_Y$ (red/grey) after a treatment at 250 °C under H_2 (the INS spectrum of the solid treated in vacuum at 200 °C was subtracted). The data were obtained on the instrument IN1BeF at the ILL



of the catalyst and O_2 , and (ii) between ethanol and O_2 (partial oxidation). The reaction is sustainable because hydride species are replaced and provided by ethanol.

A pre-treatment at 250 °C under H_2 is necessary to obtain the active catalyst, which is an oxyhydride. As in the case of copper chromite, large quantities of hydrogen can be stored in CeNi_XO_Y mixed oxides. H_2 is heterolytically dissociated at an anionic vacancy and an O^{2-} species of the catalyst. The insertion of hydride species in the solid was evidenced by INS. The spectra of CeNi_1O_Y and $\text{CeNi}_{0.5}\text{O}_Y$ are shown in Fig. 2.2. The INS spectrum of the solid treated in vacuum at 200 °C, which contains OH groups, has been subtracted. The peak at about 460 cm^{-1} was assigned to hydrides and the band around 870 cm^{-1} to H adsorbed on metallic Ni particles, because the band intensity decreases when the Ni loading is decreased. While the assignment of the first peak appears to be reliable (after re-oxidation, this peak disappears whereas a band corresponding to OH groups emerges around 630 cm^{-1}), the assignment of the higher frequency band to $\mu_3\text{-H}$ species on Ni^0 particles is less certain, and the contribution from OH groups cannot be excluded.

2.3 Dihydrogen

In the long term, H_2 is envisaged as a potential energy carrier. However, one of the issues for portable applications of this energy vector relies on its economic and safe pressure storage under the conditions of transport. Although the targets set for 2015 by the U.S. department of energy (DOE) are difficult to reach, several options are extensively investigated. Compressed or liquefied H_2 is not suitable for mobile applications, because of low volumetric energy density and safety problems. A promising way for mobile applications is solid state storage. One can differentiate physisorption in porous materials, including zeolites, MOFs and different types of carbons, and chemisorption resulting in the formation of hydrides. INS has been used to characterize various hydrides, starting from transition-metal hydrides, up to complex hydrides composed with light elements (lithium, boron, sodium or aluminium),