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

---

V.K. Peterson (✉) · G.J. Kearley
Australian Nuclear Science and Technology Organisation,
Lucas Heights, NSW 2234, Australia
e-mail: vanessa.peterson@ansto.gov.au

G.J. Kearley
e-mail: gke@ansto.gov.au

G.J. Kearley and V.K. Peterson (eds.), *Neutron Applications in Materials for Energy*, Neutron Scattering Applications and Techniques,
DOI 10.1007/978-3-319-06656-1_1

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 ^{1}H 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 ^{6}Li has high absorption, whilst ^{7}Li does not. Consequently, either radiography (and other bulk techniques) or normal neutron-scattering experiments can be made using the appropriate isotopic composition.

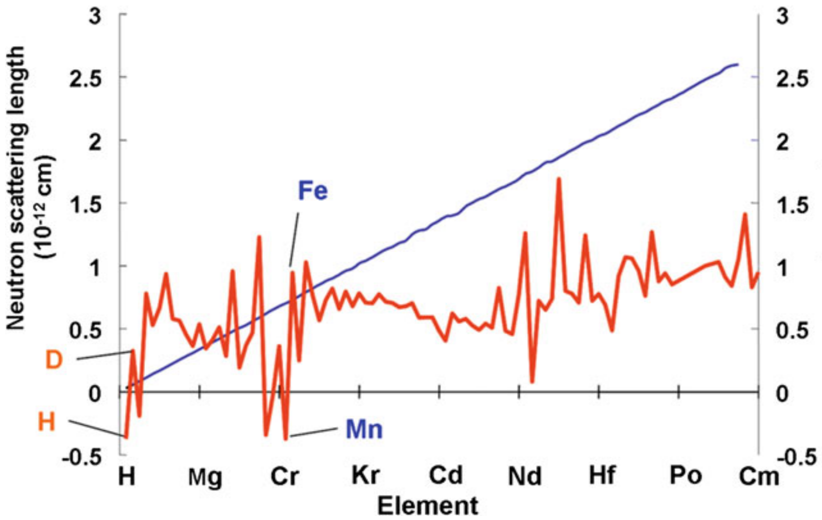

Fig. 1.1 Neutron-scattering lengths and X-ray scattering amplitudes for various isotopes (neutrons based on naturally-abundant isotopes unless specifically identified) and elements (X-rays)

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 ^{1}H 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 at 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,

$$\mathrm{G}(r) = \frac{2}{\pi}\int_0^{\infty} \mathrm{S}(Q-1)(Qr)Q\,dQ \tag{1.1}$$

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 $\Delta Q = 2\pi/\mathrm{T}$, 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 Å 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 Å^{-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:

$$\frac{d\sum_{\mathrm{c}}(Q)}{d\Omega} = \frac{\mathrm{N}}{\mathrm{V}}\mathrm{V}_{\mathrm{P}}^{2}\Delta_{\rho^2}\mathrm{P}(Q)\mathrm{S}_{\mathrm{I}}(Q) \tag{1.2}$$

where (N/V) is the number density of particles, $\mathrm{V_P}$ is the particle volume, $\Delta_{\rho 2}$ the contrast factor, P(Q) is the single particle form factor, and $\mathrm{S_I}(Q)$ is the inter-particle structure factor. $\mathrm{S_I}(Q)$ 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).

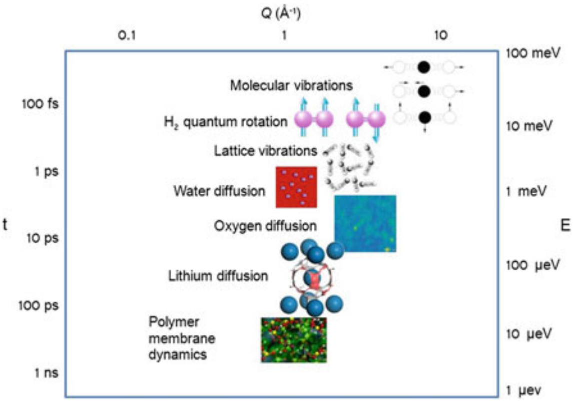

Fig. 1.2 The frequency (E), time (t), and space (*Q*) domains in which the dynamics of energy materials are typically studied using neutron scattering

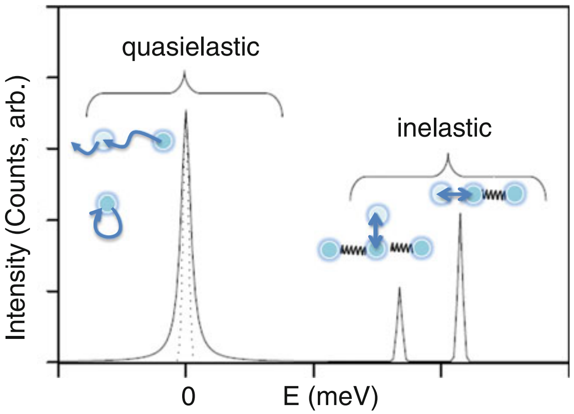

Fig. 1.3 Representative inelastic and quasielastic signals from some idealized motions that give rise to them. Reprinted from (H. Jobic and D.N. Theodorou, Microporous Mesoporous Mater **102**, 21 (2007)) [4]

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 deuterating 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.

References

1. I.S. Anderson, A.J. Hurd, R. McGreevy (eds.), *Neutron Scattering Applications and Techniques*, (Springer, Berlin)
2. L. Liang, R. Rinaldi, H. Schober. (eds.), *Neutron Applications in Earth, Energy and Environmental Sciences* (Springer, Berlin, 2009)
3. http://www.springer.com/series/8141. Accessed 4 March 2014
4. H. Jobic, D.N. Theodorou, Microporous Mesoporous Mater **102**, 21 (2007)