Nanotechnology and materials

5 Recent Trends in Neutron Beam Assisted Material Analysis Technology

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Neutron beams have a peculiar characteristic among the classes of quantum beams: they interact only with the atomic nucleus and, because they have no electrical charge, are not affected by the electrons inside substances. Application of the neutron beam in material analysis enables detection and analysis of light elements, such as hydrogen and lithium, which are mostly beyond the reach of traditional X-ray and electron beam methods. The electrical neutrality of the neutron made it difficult to create and control a neutron beam by means of electrical force, i.e. an electrical field, and has resulted in a high level of technical difficulties in the development of high-intensity sources, resulting in a delay in practical applications in comparison with other quantum beams such as X-rays and electron beams. In recent years, however, many large-scale facilities capable of producing high-intensity, high-quality neutron beams have came into operation in various countries, including the Japan Phroton Accelerator Research Complex (J-PARC) that allows access to neutron beams with the world’s highest level of intensity. This trend has helped in stepping up material research using neutron beams in various countries.

The achievements in recent years include detailed structural analysis of lithium-ion battery electrodes and proteins with rich hydrate contents using a high-intensity, high-quality neutron beam. The usefulness of these techniques is somewhat limited, however, by the prolonged measurement time and the need for a large crystal sample. Substantial effort is being made to increase the beam intensity to a level that will enable shorter measurement time and smaller samples. Future availability of more accurate analysis of lithium and hydrogen, and structural analysis of a wider variety of biological materials will provide an essential infrastructure for the development of new energy devices and pharmaceutical agents. Through the use of the neutron’s excellent capacity to penetrate through materials, future development of small sources can increase the possibility of neutron beam applications in such areas as structural defect detection (e.g. structural objects made of metal and ceramic) and security purposes (e.g. baggage inspection).

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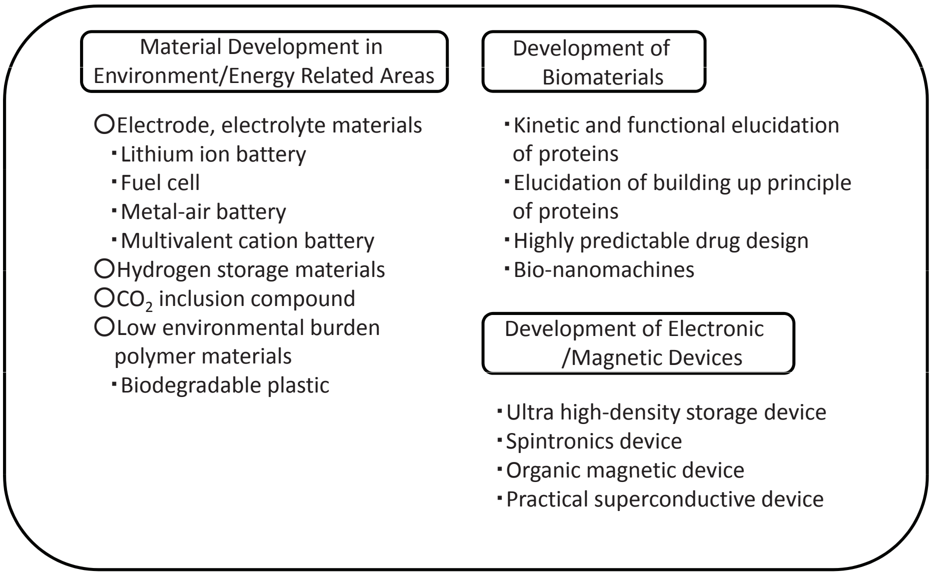

Figure : Areas of Material Analysis Where the Neutron Beam Can Play an Important Role

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5

Recent Trends in Neutron Beam Assisted Material Analysis Technology

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1 Introduction

We have witnessed, in recent years, substantial and rapid growth in technologies for high-precision generation and control of particle beams (electron, ion, and neutron) and radiation (X-ray), accompanied by ramifications thereof in such areas as high-precision analysis and material processing, taking full advantage of the technologies. These developments have worked to now collectively establish a research domain called "quantum beam technology." Utilization of quantum beams enables us to analyze the atomic-level structure of metallic-, ceramic- and biological materials. The quantum beam technologies are expected to lay the foundation for the future development efforts of new energy materials and novel pharmaceuticals.[1]

Among the classes of quantum beams, neutron beams have a peculiar characteristic in that they are electrically neutral – entirely void of electric charge – and interact solely with atomic nuclei without interference from the surrounding electrons. Application of the neutron beam in material analysis enables detection and analysis of light elements that are mostly beyond the reach of traditional X-ray and electron beam methods.

This report presents the mainstream trends in this research area, mainly from the viewpoint of material analysis, including an introduction to the characteristics of neutron beams and some cases of practical material analysis. It also includes a discussion on the future perspective.

2 Characteristics of the neutron used for material analysis, and method for its creation

2-1 Characteristics and properties of neutron

The neutron was first discovered by J. Chadwick in 1932, and later, W. Heisenberg theoretically predicted that the atomic nucleus consisted of protons and neutrons.[2] The neutron has a mass comparable with that of the proton (1.675×10^{-27} kg) and is characterized by its electrical neutrality: it has neither positive nor negative charge. The neutron cannot occur in nature by itself and only escapes as a single particle when an atomic nucleus decays. It has an average lifetime of around 15 minutes, and undergoes spontaneous decay resulting in such elementary particles as protons, electrons, and anti-electron neutrinos. Because it is entirely free of electrical charge, the neutron interacts only with atomic nuclei when it travels inside a material, without interference from electrons. The neutron, after its creation, can travel at an average distance of around 220m before it collides with other atomic nuclei (mean free path). The neutron has a spin – an intrinsic characteristic of an elementary particle that exhibits magnet-like properties – therefore, it behaves like a tiny magnet (Figure 1).

2-2 Characteristics of material analysis by means of a neutron beam

The neutron beam represents a collimated bundle of neutrons traveling in one direction, and belongs to the class of particle beams such as the electron beam and ion beam. It also belongs to the class of radiation such as α-rays (helium nucleus), β-rays (electron) and γ-rays (electromagnetic radiation): discovered by A. Becquerel.[2]

At present, X-rays (electromagnetic wave) and electron beams (charged particle) are widely used as tools for material analysis, taking advantage of their properties, capable of exerting electric force through electric fields and electrical charge. Namely, they interact with the electric charge (i.e. electrons) distributed inside the material. The interaction is weak in light elements, such as hydrogen, because of the small number of electrons: the signal available for analysis becomes faint or totally imperceptible.

The charge-free neutron beam, on the other hand, does not interact with the charged electrons when a material is irradiated with one. As a result, interactions between atomic nuclei become more outstanding in comparison with that with electrons, making it a helpful tool to elucidate material structures that lay beyond the reach of X-rays and electron beams. A variety of methods and devices have been developed to utilize the neutron beam for material analysis, and these are broadly classified into two categories: neutron diffraction and transmission (Figure 2).

Table 1 summarizes the characteristics of neutron-beam-based material analysis in comparison with those of the X-ray method. As interference of waves (Bragg diffraction[5]) is used in structural analysis, the wavelength range employed corresponds to the interatomic distances in a crystal (i.e. 0.1-0.2 nm). The wavelength of an X-ray, a type of electromagnetic wave, is determined by its energy, and neutron wavelength can be adjusted by controlling its traveling velocity. As the typical neutron velocity in thermal equilibrium (2,200 m/sec) approximately corresponds to the energy level of atomic vibration (25.3 meV), the neutron can also be used to obtain information regarding the vibrating atoms.

2-3 Creation of neutron beam

To perform a highly sensitive measurement with high resolving power in a short period of time, a

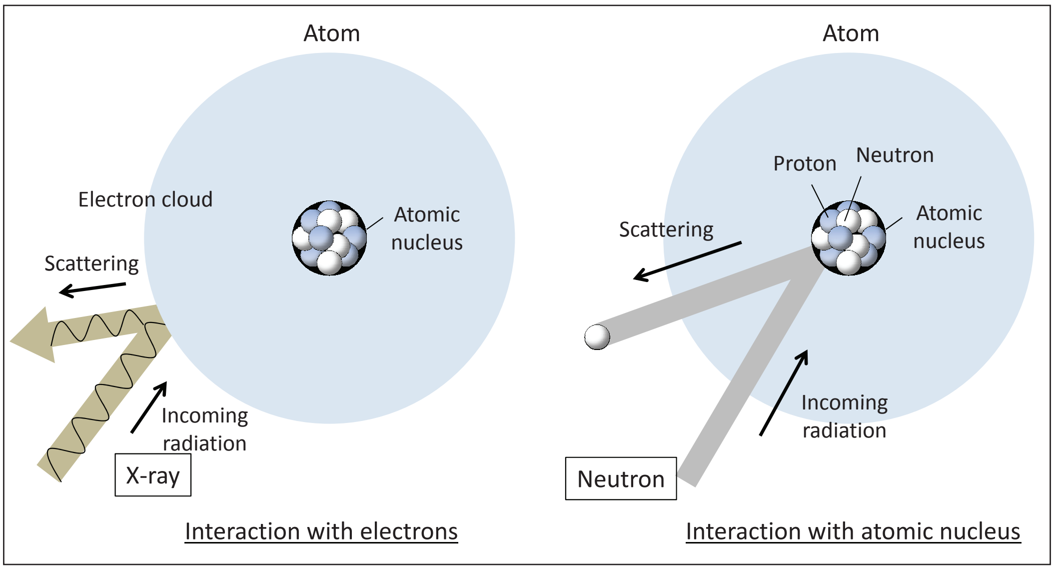

Figure 1: Interaction with the Atomic Nucleus: X-ray vs. Neutron
Prepared by the STFC based on reference[3]

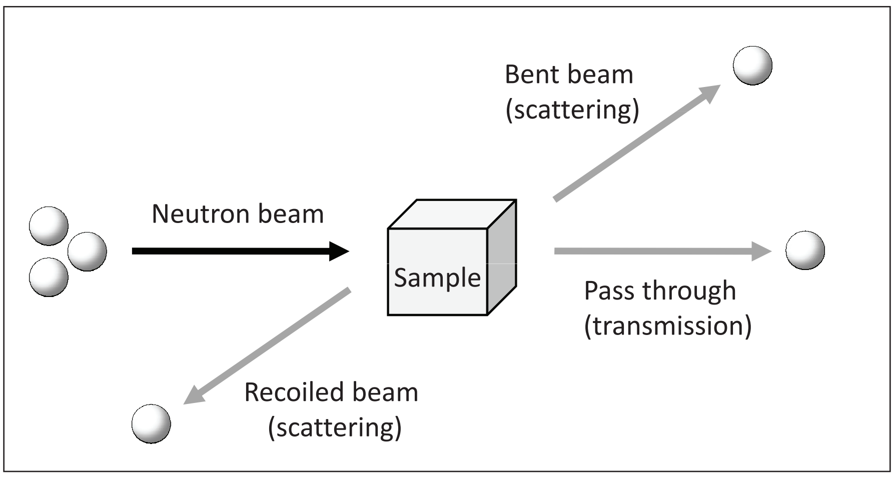

Figure 2: Material Analysis Using Neutron Scattering and Transmission
Prepared by the STFC based on reference[4]

Table 1: Comparison of X-ray and Neutron

Source	X-ray	Neutron beam
Physical state	Electromagnetic wave (photon)	Neutral particle (material wave)
Wavelength *	0.1-0.2 nm	0.1-0.2 nm
Energy *	6-12 keV	10-30 meV
Scattering application (e.g. crystal structure analysis)	Interaction with electrons (suited for electron-rich elements)	Interaction with atomic nuclei (not affected by the number of electrons) (capable of analyzing spin and magnetism)
Transmission application (e.g. nondestructive analysis)	Projects electron-rich materials (advantageous for analysis of metals and ceramics)	Projects materials with fewer electrons (advantageous for analysis of light elements and organic substances)

* Energy and wavelength range commonly used for crystal structure analysis

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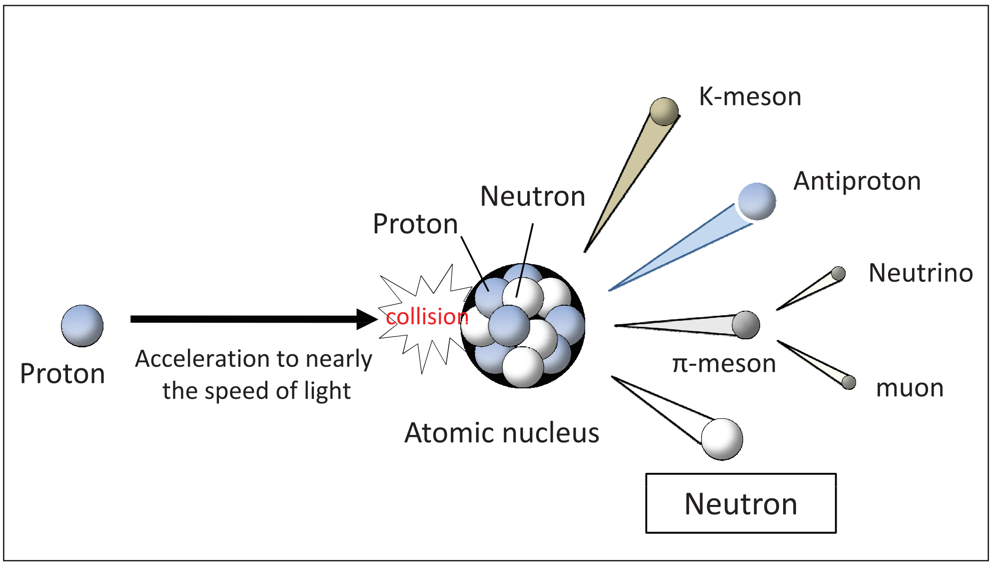

Figure 3: Neutron Creation Using an Accelerator: Nuclear Breakdown

Prepared by the STFC based on reference[4]

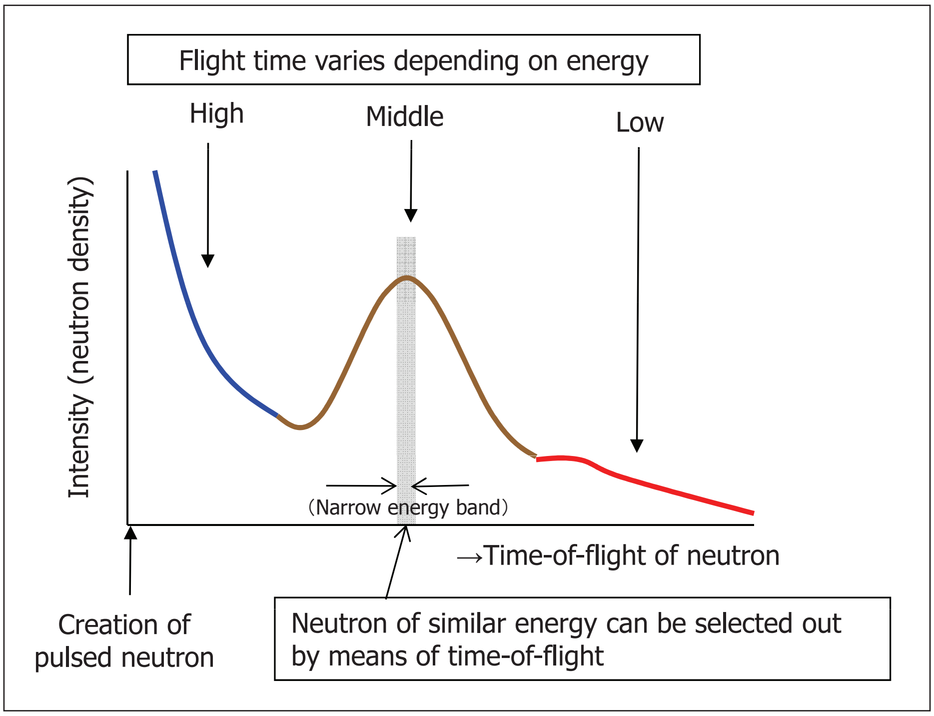

Figure 4: Energy Selection Method for Pulsed Neutrons

Prepared by the STFC based on reference[6] neutron beam with high intensity (high neutron density) and uniform energy (narrow energy width) is required. As a neutron source, nuclear fission or breakdown can be used for producing them.

Nuclear fission taking place inside a nuclear reactor can provide neutrons. Low energy thermal neutrons – those that have attained equilibrium with the thermal agitation of surrounding molecules through multiple collisions with nuclei – are used for material analysis. Thermal neutrons, however, have a somewhat blurred range of energy, making it difficult for them to be used in a high-resolution material analysis. Another method of neutron creation makes use of nuclear breakdown: a proton (hydrogen nucleus) accelerated to nearly the speed of light by the accelerator is slammed into target atoms (e.g. Hg atom), breaking down the nucleus and emitting secondary particles. This process creates elementary particles such as muons and neutrinos, as well as neutrons (Figure 3). The neutrons thus created are characterized by a very high level of energy, and are moderated by passing them through hydrogen or light hydrogen to an energy level comparable with thermal neutrons, or several tens of meV. This method is also characterized by pulse bombardment: pulsed protons are slammed into the target atoms creating a train of narrow-width pulsed neutrons, enabling energy level selection by measuring the time-of-flight – from the time of neutron creation until its arrival at the detector. This method allows obtaining a neutron beam with a very narrow energy width (Figure 4). With the increasing number of facilities that provide access to a high-quality pulsed neutron beam, and with the availability of ever increasing beam intensity, this technique is receiving attention in recent years in view of material analysis.

2-4 Large-scale accelerator facilities for neutron beam creation

In recent years, large-scale neutron beam facilities are being constructed in succession in major research countries around the world. The facilities usually include accelerators that produce high-quality, high-intensity beams of pulsed neutrons. At present, high-power (0.1-1 MW) accelerator facilities are in operation in three countries: ISIS[7] at Rutherford-Appleton Laboratory (UK), SNS[8] at Oak Ridge National Laboratory (USA), and J-PARC[9,10] (Japan). Other ongoing undertakings include the ESS (European Spallation Source) project (EU)[11] and CSNS (China Spallation Neutron Source) project (China).[12]

J-PARC, located in Tokai village (Ibaraki Pref.), is a facility jointly owned by the Japan Atomic Energy Agency (JAEA) and High Energy Accelerator Research Organization (KEK), and provides, as of 2010, one of the world's highest levels of high-intensity (in terms of neutron number) and high-quality neutron beams. J-PARC has 23 beam lines to be used for research in material and life science: each of these beam lines provides services for research mainly related to the evaluation method development for a variety of advanced devices in such domains as: functional materials, structural materials, high-efficiency batteries, fuel cells, catalysts, and engines.

Among them, the following two beam lines are owned by Ibaraki prefecture and are made available for supporting industrial use by private sector enterprises: BL-03 (for structural analysis of life substances: iBIX), BL-20 (for crystal structure analysis of materials: iMATERIA).

3 Neutron Beam Applications in Material Analysis Technology

The neutron beam as used in material analysis technology has a range of promising applications in a variety of research areas as shown in Figure 5. This report introduces some of the representative neutron beam applications in material analysis centered in the following two areas: crystal structure analysis using neutron beam diffraction (scattering) and neutron radiography (transmission).

3-1 Crystal structure analysis using neutron beam scattering

As described in Chapter 2-2, the neutron exhibits a wave-like nature, enabling its use as a tool for crystal structure analysis just as X-ray is used for that purpose – the principle of Bragg scattering (diffraction).[5] The neutron diffraction method is especially useful for analyzing crystals that contain light elements such as hydrogen, lithium, oxygen, and nitrogen. Neutron beam diffraction is one of the classical methods, and it found new applications as a tool for material development, triggered by the high-temperature superconductivity fad around 1990. In the material development effort for use in high-temperature superconductivity, the method was

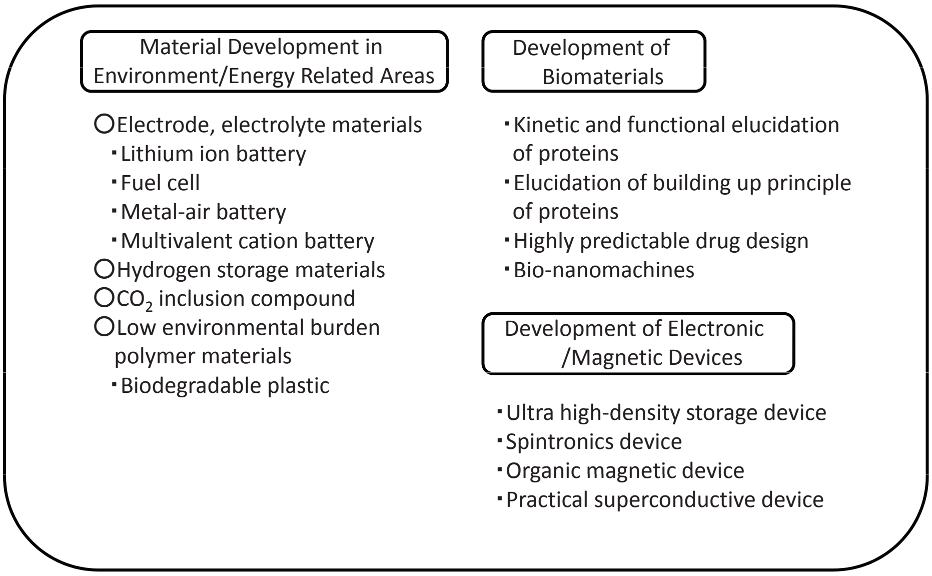

Figure 5: Areas of Material Analysis Where the Neutron Beam Can Play an Important Role

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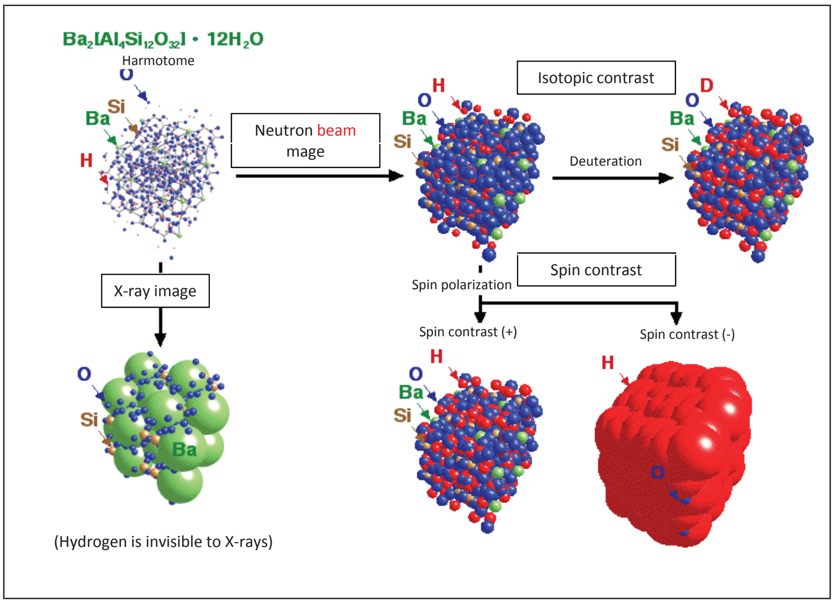

Figure 6: Schematic Representation of Structural Analysis Using Neutron Beam

Source: reference[13]

used to determine locations of oxygen (or oxygen vacancy) and light elements (e.g. boron and carbon) contained in a rare-earth element matrix, as well as for determining magnetic structure. More recently, research is underway to expand the applicability of neutron diffraction in such areas as: behavior observation of light elements – lithium and hydrogen – in lithium-ion battery and fuel cell matrixes, and structure determination of hydrate-containing proteins and DNA.

Figure 6 schematically represents the approaches taken by three study examples for the structural analysis of $Ba_2[Al_4Si_{12}O_{32}]$•$12H_2O$ (hydrate).[13] Note that, in this figure, the geometrical cross-sections of the spheres are sized so that they are proportional to their scattering cross-section.

1) Neutron beam vs. X-ray: Characteristics in structural analysis

While X-ray analysis generally provides clear signals from electron-rich elements, i.e. Ba, it provides only faint signals from elements with fewer electrons, i.e. hydrogen (H) and oxygen (O). In contrast, analysis using a neutron beam produces clear images of H and O.

2) Analysis using isotopic contrast

The strength of neutron-nebulous interaction depends on the structure of the atomic nucleus. Substitution of hydrogen (H) with deuterium (D) will enhance the signal from the hydrogen position. Therefore, subtraction of the original image from the deuterated one will leave only the information related to the substituted hydrogen atoms. This technique is called isotopic contrast, and can be an effective approach for other atomic species other than hydrogen.

3) Analysis using spin contrast

Because the neutron has a spin, the interaction with the atomic nucleus spin can be used to enhance the image contrast for better analysis. An image with highly enhanced contrast can be obtained by controlling the neutron spin and nucleus spin separately, i.e. a comparison of a parallel spin image and an anti-parallel image.

3-1-1 Analysis of lithium-ion battery electrode materials

The development of lithium-ion batteries – the major rechargeable battery for portable devices and next generation automobiles - is now energetically underway. The behavior of lithium ions between the anode and cathode has a significant influence on battery performance. Figure 7 shows the results of structural analysis of $LiMn_2O_4$ (cathode material). While the results obtained using X-rays include blurred images of oxygen (O), that obtained using the neutron beam presents clear oxygen images and even the lithium images are visible. This is a promising achievement for the future crystal structure elucidation of battery electrodes.

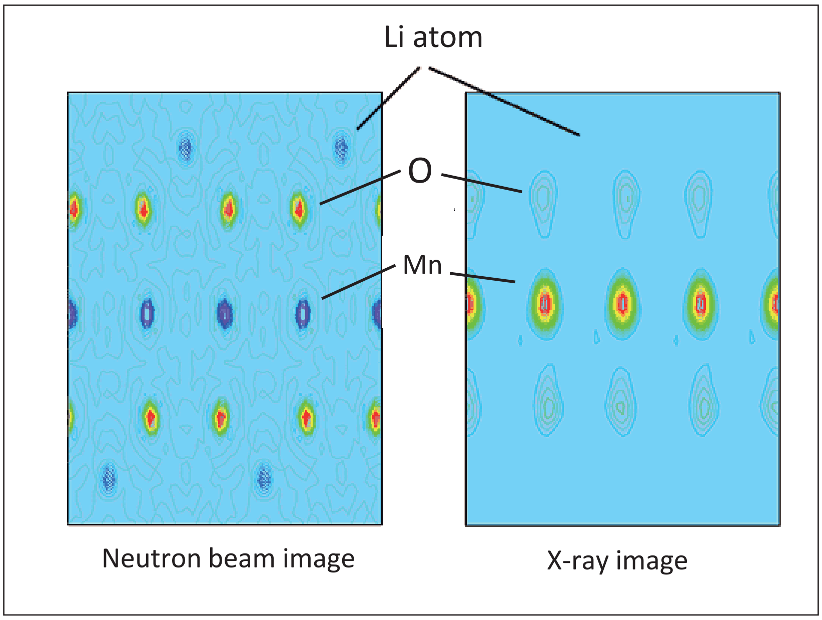

Figure 7: Structural Analysis of Lithium Ion Battery Cathode Material

Source: reference[14]

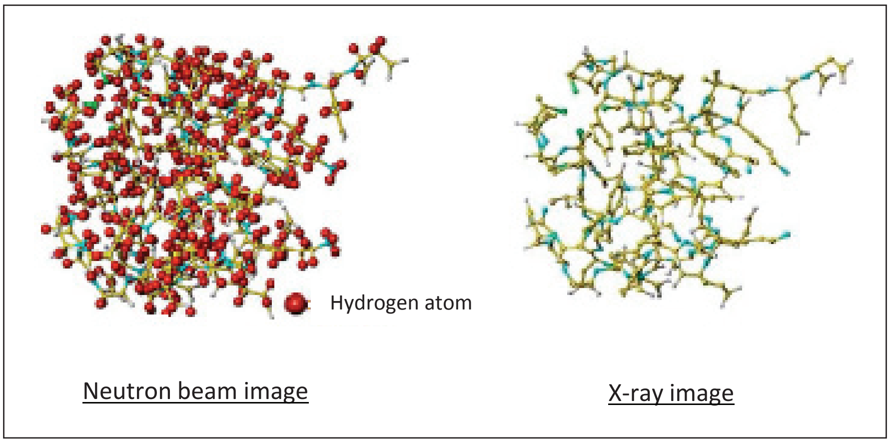

Figure 8: Structural Analysis of Protein

Source: reference[15]

3-1-2 Structural analysis of biological materials

Biological materials, such as proteins and DNA, are surrounded by a host of hydrates. Structural analysis using the neutron beam can reveal the positions of water molecules – hydrogen and oxygen. These light elements are almost invisible to X-ray (Figure 8). At present, preparation of large crystals presents a huge challenge for the technique to be useful in the analysis of organic materials. Still, the neutron beam has the potential to become a practical method for pharmaceutical and cosmetic product development in the future.

3-2 Interior observation of materials: transmission of neutron

X-rays are easily absorbed by many-electron elements such as metals. The neutron beam shows good transmittance through metallic elements, and is absorbed relatively easily by light elements such as hydrogen, water, oxygen, and nitrogen (Figure 9). Neutron radiography is a measurement method taking advantage of these characteristics, and allows us to observe the distribution of water, fuel, and organic materials inside metallic/ceramic structural objects (Figure 10, 11).[16] This analysis technique has been applied in nondestructive inspection – for example, soot deposition distribution inside the exhaust treatment catalyst of diesel engine automobiles.[17] In addition, research is underway to use this technique for the observation of water inside fuel cells.[18] Device research is also underway: small and movable neutron sources are being developed that can be used in on-site inspection of degraded/damaged components in architectural structures (e.g. bridges).[19]

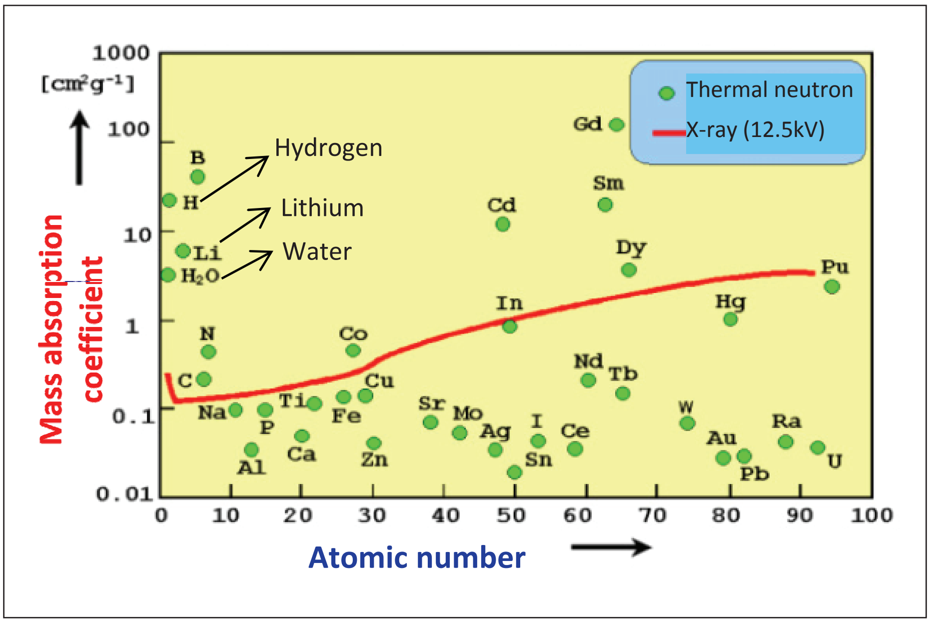

Figure 9: Absorption Coefficient of X-ray and Neutron Beam: Dependence on Atomic Number

Source: Reference[16]

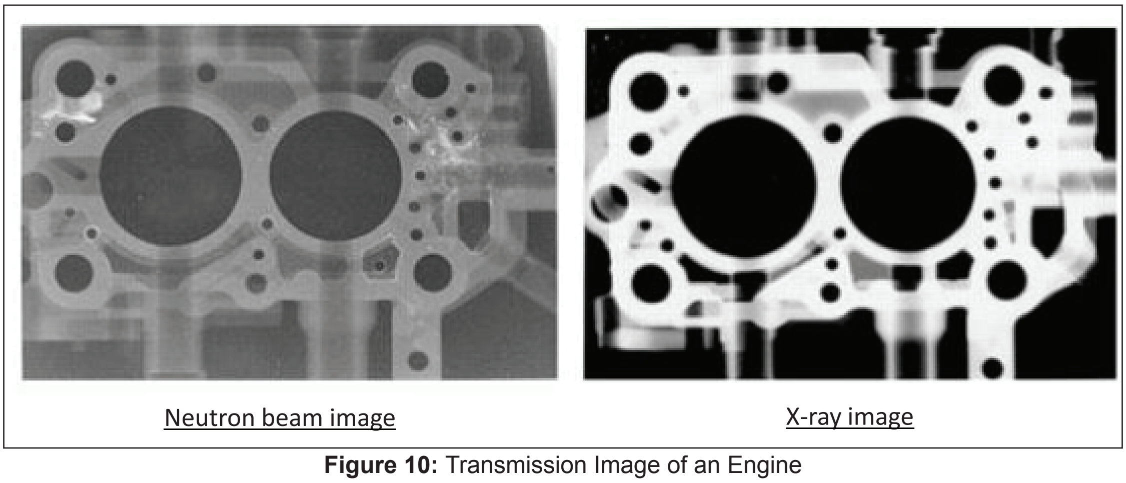

Figure 10: Transmission Image of an Engine

Source: Reference[16]

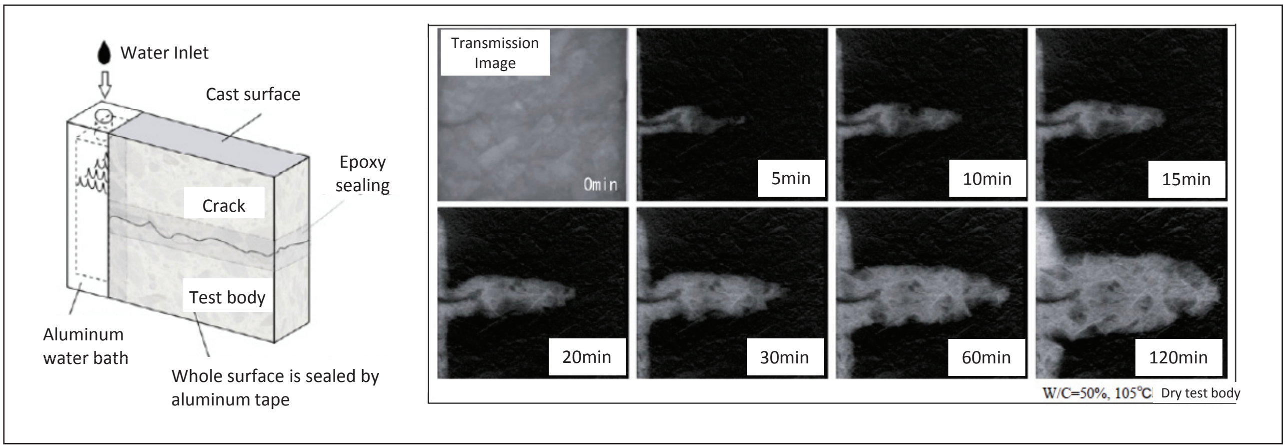

Figure 11: Infiltration of Water Through Concrete Cracks (Time Change)

Source: Reference[16]

Table 2: Typical Cases of Neutron Beam Application Study

Material	Method	Cases of analysis
Inorganic functional material	Powder neutron beam diffraction	Structural analysis of: nitride fluorescent substance, lithium-ion battery cathode material, lithium battery ionic conductive body, oxide/magnetic material, hydrogen trapping mechanism of hydrogen storage material, ceramic material.
Bio-polymer material	Neutron beam diffraction	Structural analysis of: glycoenzyme in plant tissues, proteins, organic compound crystals.
Magnetic/polymer material	Neutron small angle scattering	Magnetic structure analysis of nanomagnetic particles and crystals, magnetic domain analysis of perpendicularly magnetized films, quantitation of rust growth in anticorrosion steel, analysis of molecular chain distribution in rubber bulk matrix, structural analysis of fillers in rubber material, particle size analysis of crosslinked rubber.
Industrial material	Neutron beam diffraction (residual stress measurement)	Internal strain measurement of welded bodies, strain and stress distribution measurement of carburized carbon steel, stress measurement inside reinforced concrete blocks.
	Neutron radiography	Flow property evaluation of a powder used as the developer for electrophotographic system, evaluation of bubbles in inks, evaluation of subcutaneous defects of steel, visualization of flow inside welded bodies and hydraulic valves, Inspection of liquid fuelled rocket combustors, deformation visualization of magnetic valve seals.
Thin-film material	Neutron reflectance measurement	Surface/interface structural analysis of: optical memory, magnetic bodies, dielectrics, condensers, multi-layer reflective coating, steel material, battery electrodes, and polymer thin-film
Semiconductor	Neutron doping	Nuclear transformation from ^{30}Si (approx 3% of Si) to ^{31}P
	Prompt γ-ray analysis, activation analysis*	Impurity evaluation of semiconductors
Agricultural crops	Neutron radiography	Distribution and behavior of water in plants and fruits, perspective visualization of soil and plant roots.
	Prompt γ-ray analysis, activation analysis*	Heavy metal detection in agricultural crops, Hg detection in soil, production region identification of beef.
Cultural assets0	Neutron radiography	Nondestructive analysis of pearls embedded inside a bronze mirror.
Others (nondestructive inspection)	Neutron radiography	Water content analysis of rocks, properties analysis of scallop shells as asphalt material.
	Prompt γ-ray analysis, activation analysis *	Production region identification of stone materials, heavy metal analysis of scallops, hazardous substance analysis of construction waste materials, component analysis of cosmetic products, chloride analysis of concrete, nitride analysis of explosives and waste chemical weapons, elemental analysis of optical components.

* Prompt γ-ray analysis: a method of elemental (isotope) analysis based on the measurement of γ-ray spectrum emitted when a neutron is absorbed by an atomic nucleus. Activation analysis: a method of elemental analysis based on the detection of disintegration γ-ray spectrum emitted from radioactive nuclides, which are created when a neutron is absorbed by an atomic nucleus.

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3-3 Cases of neutron beam application in material research

Table 2 summarizes the cases of material research conducted using the JAEA's thermal neutron source (JRR-3). These studies are listed in the case report[20] of the "Transfer Promotion Program of Neutron Utilization Technology" – a program conducted as a part of a project sponsored by MEXT starting in 2007.

4 The Challenges We Are Facing, and the Future Prospects

The introduction of neutron beam technology has enabled us to conduct detailed analysis of battery materials and biological materials. As affairs now stand, researchers still have such challenges as the long analysis time that renders dynamic observation difficult, and the need for larger crystal samples. In J-PARC, output power upgrading of neutron sources (～ 1 MW) and proliferation of various experiment devices are currently underway. These efforts are expected to help boost the experimental conditions in the future: more accurate and speedy material analysis using a smaller amount of samples. Enhanced output power of the neutron source will enable, for example, the behavioral observation of hydrogen atoms inside the electrolyte membrane (fuel cell development), as well as the rapid and dynamic conformation analysis of proteins that contain hydrogen and hydrates. The sample sizes required may be reduced to a level comparable to those for X-ray analysis. These developments will enable, for example, magnetic structure analysis of novel high-temperature superconductivity materials and low-dimensional organic magnetic materials. Other possibilities include in-process, time-split measurement of steel materials.

Analysis of materials that contain light elements requires a high-intensity neutron source, resulting in the need for large-scale common facilities such as J-PARC. For a better utilization of these common facilities, establishment of a user-friendlier environment is highly desirable both in terms of technological and administrative aspects, accompanied by enhanced collaboration among industry, academia and government. Another noteworthy trend is the development of small-sized portable/moveable neutron sources: these are used, for example, in on-site inspection of defective components in architectural structures made of concrete and ferrous materials, as well as in nondestructive inspection of industrial products and security screening of baggage, whereby the experimental results obtained through the use of large-scale neutron sources will be of help. The global trend in the material analysis technologies using neutron beams deserves continuous monitoring into the future.

The facilities in J-PARC, located in Tokai village, Ibaraki Prefecture, suffered severe damage due to the 2011 Tohoku Earthquake, and research activities there are halted as of the time of this writing. As a closing remark, the authors would like to extend their deepest sympathies for those working in the facilities, and wish for the earliest possible recovery and revitalization.

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Profile

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Dr. Gamo acted as a researcher in a private sector enterprise research laboratory, and engaged in the areas of carbon nanotubes, micro-machined electron source and display (application of semiconductor films), and application of illumination devices. During these periods, he did collaborative research at AIST (Advance Industrial Science and Technology), NIMS (National Institute of Material Science) and universities as a visiting fellow. He joined STFC in April 2010. He is a member of the No.158 committee (vacuum nanoelectronics) of the Japan Society for the Promotion of Science, and a science fellow of the Surface Finishing Society of Japan. PhD in engineering (Kyoto University).

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She was born in Okinawa. She is a master in science and joined STFC after research in a private sector company and a university. She was strongly interested in the mismanagement problem of used automobiles in her teens, and has been engaged from her university years in statistical survey of metallic resource recycling. She was strongly inspired by some of the materials she encountered during the survey activities. Her current interest is to convey the same "inspiration and excitement" of material research to others.

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