Material Property Simulations for Efficient Design of Environmentally Conscious Functional Materials

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OVERVIEW: With the aim of realizing a sustainable society, Hitachi has formulated an Environmental Vision directed toward overcoming the challenges facing the global environment, and based on the three pillars of Prevention of Global Warming, Conservation of Resources, and Preservation of Ecosystems. Applying this initiative in the field of material development, Hitachi is developing simulation technology that works from first principles at the level of electrons and atoms to provide comprehensive predictions of chemical properties, such as reactions involving the formation and breaking of chemical bonds; physical properties, such as optical electromagnetic, and diffusion characteristics; and mechanical properties, such as breaking strength and deformation characteristics. Through the application of this technology, Hitachi is working on material designs for the three pillars of its Environmental Vision. In the future, Hitachi intends to utilize this technology for the efficient design of a wide range of different environmentally conscious high functional materials that will enhance the products it develops.

INTRODUCTION

AS global environmental problems become more severe, there is a growing need to develop environmentally conscious materials, including materials that can help reduce emissions of carbon dioxide (CO_2) and other greenhouse gases, high functional materials that do not contain lead or other substances that are harmful to human health or the ecosystem, and materials that can be broken down and recycled after use. In the past, the development of new materials such as these often involved repeated trial-and-error testing of prototypes. However, because this approach was very time consuming, it was considered desirable to shift to an analysis-based approach to material design by using computer simulations to perform design efficiently. Against this background, Hitachi has developed simulation technology able to predict the physical properties of materials from first principles at the level of the electron and atom (see Fig. 1).

This article describes three examples of the application of material property simulation to environmentally conscious materials that support Hitachi's Environmental Vision: (1) anode material for lithium-ion batteries that help reduce exhaust gas emissions and fuel consumption in automobiles such as hybrid electric vehicles (HEVs), (2) piezoelectric materials that do not contain lead or other substances that are harmful to human health or the ecosystem, and (3) plastics that can be broken down and recycled after use.

PRINCIPLES OF MATERIAL PROPERTY SIMULATION

As macro-scale simulation based on continuum mechanics is insufficient on its own for the combined prediction of the chemical, physical, and mechanical properties of a material, analysis of the movement of each of the atoms is also required. When designing plastics that can be broken down after use to allow for recycling, for example, it is necessary to determine whether the chemical bonds between atoms (the overlap of electron clouds) will break or not, and this requires solving the equations of motion for the atoms.

As atoms are made up of a nucleus and its surrounding electrons, simulation involves calculating the states of the nucleus and electrons. While the atomic nucleus follows Newton's equation of motion (force = mass × acceleration), the fundamental equation of classical mechanics, it was determined in the early 20th century that this equation could not be used for the electron, which has a mass of less than a thousandth that of a nucleus. Instead, the more fundamental principles of quantum mechanics are required. In fact, like the electron, the physical properties that follow classical mechanics, such

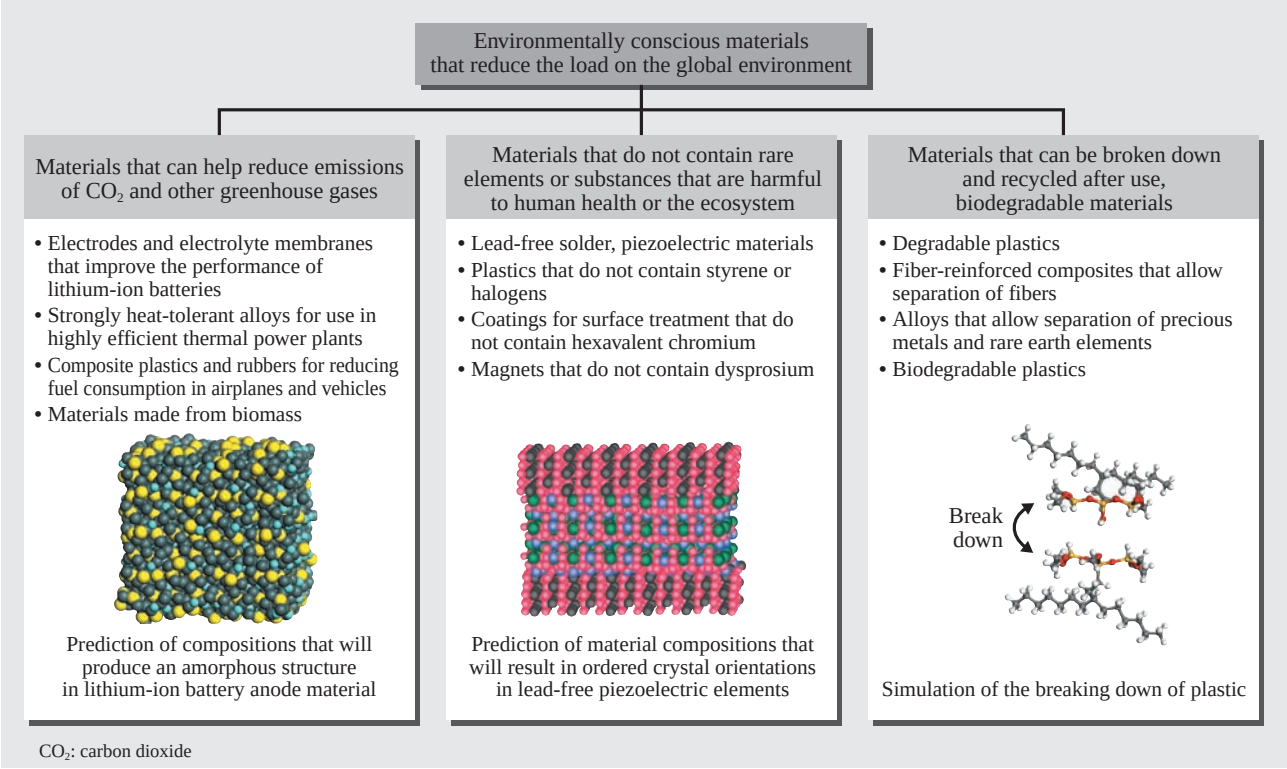

Fig. 1—Overview of Material Property Simulations for Efficient Design of Environmentally Conscious High Functional Materials. These are examples of materials that reduce the load on the environment include materials that help reduce emissions of CO_2 and other greenhouse gases, materials that do not contain lead or other substances that are harmful to human health or the ecosystem, materials that can be broken down and recycled after use, and biodegradable materials.

as the atomic nucleus and the objects visible in the world around us, can also be described by the Schrödinger equation (the fundamental equation of quantum mechanics). However, when realistic approximations are made for objects with masses several thousand times or more that of an electron, it frequently turns out that Newton's equation of motion closely approximates the Schrödinger equation and therefore that behaviors can be adequately expressed by classical mechanics.

The Schrödinger equation can be written as follows, where the states of electrons and other particles are represented as waves and described by a wave function, $\psi(r, t)$.

$$\{-\hbar^2/(2m)\}\partial^2\psi/\partial r^2+U\psi=i\hbar\partial\psi/\partial t \quad \ldots(1)$$

Here, m represents mass, r represents spatial coordinates, t represents time, U represents potential energy, i is the imaginary unit (square root of −1), and $\hbar$ is Planck's constant ($\hbar=1.05457\times10^{-34}$ J·s). Omitting details, it can be demonstrated that the wave for a particle with a mass m that is several thousand times that of an electron can be represented as a spatially localized wave packet, and that the motion of this wave packet can be approximated by Newton's equation of motion. This means that an atomic nucleus or objects visible in the world around us can be represented using Newton's equation of motion. Even though we now understand that quantum mechanics provides the fundamental underpinning, Newton's equation of motion from classical mechanics still retains an important role in describing the behavior of physical objects.

The following sections describe examples of the design of environmentally conscious materials based on predictions of their physical properties obtained by using molecular simulation technology. This technology determines the overall material behavior by combining the use of quantum mechanics to solve for electron behavior with the use of classical mechanics to solve for atomic nuclei behavior (see Fig. 2)[1].

DESIGN OF ANODE MATERIAL FOR NEXT-GENERATION LITHIUM-ION BATTERIES

The most common anode materials currently used in lithium-ion batteries are graphite and amorphous carbon. Commercial lithium-ion batteries that mix additives such as tin (Sn) alloy or silicon into carbon anodes to achieve higher capacity[2] are also available,

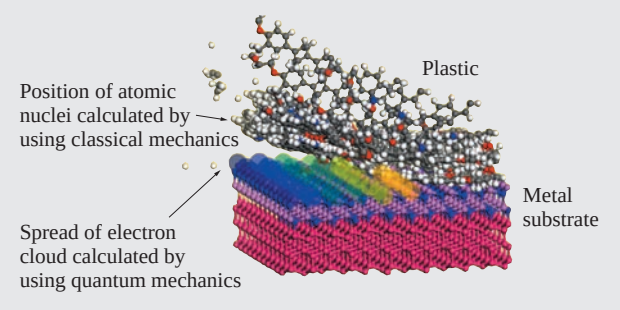

Fig. 2—Overview of Molecular Simulation.
This overview of molecular simulation shows an example of a peel test in which an external force is applied to peel off a plastic material bonded to a metal substrate.

and studies are being carried out on materials that use carbon nanotubes (see "Low-energy Electron Diffractive Imaging for Three-dimensional Light-element Materials" in this issue). To provide these batteries with the performance and reliability for use in future HEVs or electric vehicles (EVs), they will require both higher capacity and longer life. However, if their atomic arrangements retain a regular crystalline state, new materials such as Sn alloys are prone to degrading due to the large expansion and contraction strains that result from the absorption and release of lithium during charging and discharging, and this makes extending their operating life more difficult (see "Lifetime Prediction for Heavy-duty Industrial Lithium-ion Batteries that Enables Highly Reliable System Design" in this issue for an explanation of battery life prediction technology when using carbon).

Therefore, to prevent the generation of the large strains associated with the absorption and release of lithium, it is necessary to transform the alloy into an amorphous state (in which the atomic arrangement is disordered). Normally, metal alloys tend to adopt a crystalline state and often will not adopt an amorphous state even if melted and rapidly cooled. In response, Hitachi applied the molecular simulation technology described above to analyze what alloying elements should be added to achieve an amorphous state alloy capable of being used as the anode material in a lithium-ion battery.

Fig. 3 shows the atomic arrangement obtained by a simulation of the rapid cooling of a molten alloy consisting of equal quantities of Sn, cobalt (Co), and bismuth (Bi). The figure shows an ordered atomic arrangement indicating that the alloy has adopted a crystalline state. Fig. 4, meanwhile, shows the atomic arrangement obtained by a simulation of the rapid cooling of a molten alloy consisting of equal quantities of Sn, Co, and zirconium (Zr). Unlike in Fig. 3, no ordered arrangement of atoms is evident, indicating that an amorphous state has been achieved.

In this way, the mix of elements needed to produce an amorphous state alloy suitable for use as an anode material in next-generation lithium-ion batteries can be calculated based on knowledge from simulations.

DESIGN OF LEAD-FREE PIEZOELECTRIC MATERIAL

Uses for piezoelectric elements made from piezoelectric material sandwiched between electrodes include actuators that convert voltage into force and sensors that convert force into voltage. Currently, lead zirconate titanate [$Pb(Zr,Ti)O_3$, also known as PZT] is used as the piezoelectric material, and palladium (Pd) or platinum (Pt) are used as the electrodes. However, because lead is harmful to human health and the ecosystem, work is in progress on developing alternative lead-free piezoelectric materials. Examples include the development of materials made by

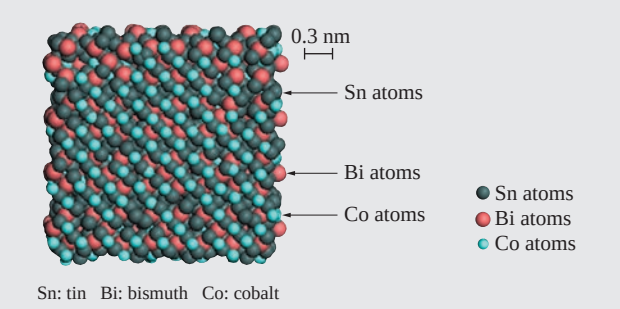

Fig. 3—Atomic Arrangement Obtained by Simulation of Rapidly Cooled Molten SnCoBi Alloy.
The alloy adopts a crystalline state characterized by an ordered atomic arrangement, making it unsuitable for use as the anode material in a lithium-ion battery.

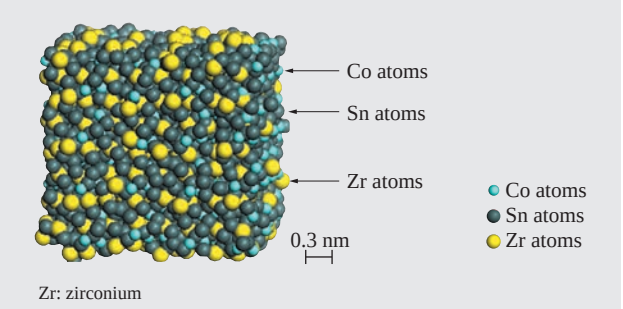

Fig. 4—Atomic Arrangement Obtained by Simulation of Rapidly Cooled Molten SnCoZr Alloy.
The alloy adopts an amorphous state characterized by a disordered atomic arrangement, making it suitable for use as the anode material in a lithium-ion battery.

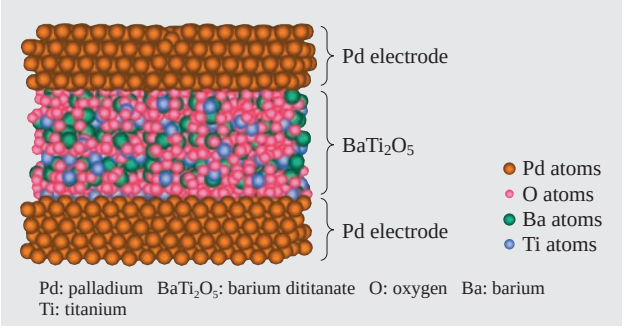

Fig. 5—Atomic Arrangement of $BaTi_2O_5$ Sandwiched between Pd Electrodes.
The disordered atomic arrangement of $BaTi_2O_5$ indicates it will not have adequate piezoelectric properties.

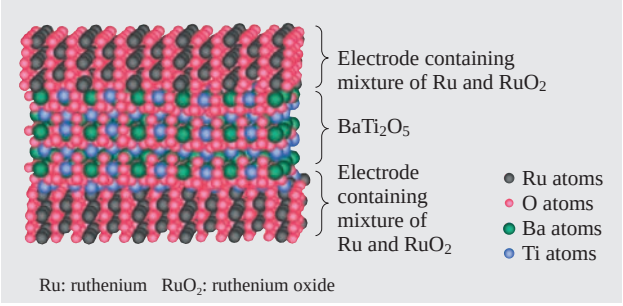

Fig. 6—Atomic Arrangement of $BaTi_2O_5$ Sandwiched between Electrodes of Mixed Ru and RuO_2.
The ordered atomic arrangement of $BaTi_2O_5$ indicates it will have excellent piezoelectric properties.

adding iron (Fe) to the currently used barium titanate ($BaTiO_3$), or materials in which another form of barium dititanate ($BaTi_2O_5$) or a niobium oxide such as (potassium, sodium) niobium oxide [(K, Na) NbO_3] are the main components. However, it remains unclear whether these materials can exhibit a higher level of piezoelectric properties than lead zirconate titanate (which contains lead). In response, studies are currently being conducted aimed at improving the level of piezoelectric properties by changing not only the piezoelectric material but also the material used for the electrodes between which the piezoelectric material is sandwiched.

$BaTi_2O_5$ is being studied as a potential lead-free piezoelectric material. Fig. 5 shows the analysis result for a molecular simulation of the atomic arrangement when this material is used with conventional Pd electrodes. The atomic arrangement of $BaTi_2O_5$ is disordered causing the force generated by the voltage to be dispersed and resulting in inadequate piezoelectric properties. In contrast, Fig. 6 shows the analysis result for a molecular simulation of the atomic arrangement when $BaTi_2O_5$ is sandwiched between electrodes made of a mixture of ruthenium (Ru) and ruthenium oxide (RuO_2). Unlike in Fig. 5, the material has an ordered atomic arrangement. Without going into details, this ordered structure means that the force generated by the voltage will not be dispersed and the material will have a high level of piezoelectric properties.

This shows how the piezoelectric properties of a material are determined in combination with the electrode material and not by the piezoelectric material alone, and indicates that an electrode material made from a mixture of Ru and RuO_2 is suitable for use with $BaTi_2O_5$.

In this way, molecular simulation can be used to identify lead-free piezoelectric materials that exhibit a high level of piezoelectric properties in conjunction with their electrode material.

DESIGN OF PLASTICS THAT CAN BE BROKEN DOWN FOR RECYCLING

The use of plastics to reduce weight in airplanes, vehicles, and other machinery has become common as a way of cutting their exhaust gas emissions and improving fuel consumption. Plastics are often reinforced by incorporating ceramic, carbon, or other types of fibers to produce composites, and there is a growing need to design plastics capable of being broken down to extract the plastic raw material and fiber for reuse. As producing prototypes and then conducting experiments to determine whether the material can be broken down is very time consuming, the molecular simulation technique described above provides an effective alternative means for achieving this.

Fig. 7 shows the use of methanol (CH_3OH) at high temperature and pressure to break down a polyethylene containing siloxane (Si-O-Si) bonds. As indicated by the figure, the equation for the bond

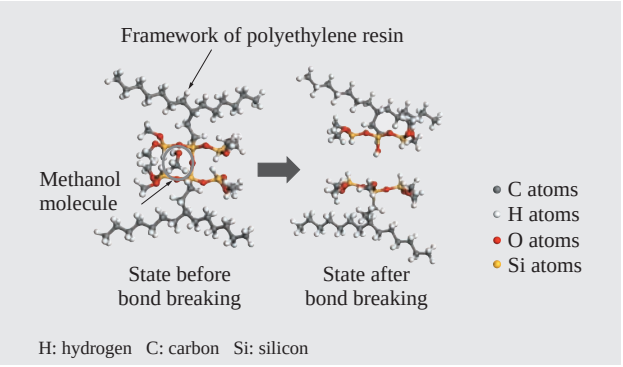

Fig. 7—Plastic being Broken Down by Methanol Molecule.
The figure shows how the siloxane bond is broken by methanol at high temperature and pressure, causing the plastic to break down.

breaking reaction is as follows.

$\text{-Si-O-Si-} + CH_3OH \rightarrow \text{-Si-}OCH_3 + \text{HO-Si}$

In this way, molecular simulation can be used to determine whether a plastic can be broken down, enabling the design of materials that are easy to recycle.

CONCLUSIONS

This article has described material property simulation technology for designing environmentally conscious high functional materials, using as examples an anode material for lithium-ion batteries, a lead-free piezoelectric material, and plastics that can be broken down and recycled after use.

This technology is also suitable for use with a wider range of other environmentally conscious materials, including the design of materials that do not contain rare elements, such as magnets without dysprosium or transparent electrodes without indium, and of strongly heat-tolerant materials able to withstand high steam temperatures to improve the efficiency of thermal power plants. In the future, Hitachi plans to apply this technology in the design of a wide range of materials with the aim of improving the reliability and performance of various different products.

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