

Materials Science High-energy X-ray scattering and X-ray absorption fine structure (XAFS)

Visualization of large cage-like network structure of glass and solvated electrons

Generally, glass is formed by melting a raw material to a melt (liquid) state at high temperature followed by cooling. Not all materials can be made into glass; many materials form crystals instead of glass when a melt is cooled. To understand the glass formation of materials, the research group focused on CaO-Al₂O₃ systems that form or do not form glass depending on slight differences in the composition (material with a high glass-forming ability: 64 mol%CaO-36 mol%Al₂O₃; material with a low glass-forming ability: 50 mol%CaO-50 mol%Al₂O₃). To form glass using a material with a low glass-forming ability, the material was maintained as a melt without a container (containerless processing) and then rapidly cooled to form glass (Fig. 1). The atomic structures of the glasses were examined by high-energy X-ray scattering and X-ray absorption fine structure (XAFS) at SPring-8 (Fig. 2). The data were analyzed by large-scale theoretical calculations using a supercomputer to determine the atomic and electronic structures of the glasses. The results indicate that a large “cage-like network structure” (Fig. 3) forms in the materials with a high glass-forming ability. In contrast, such a structure does not exist in the materials with a low glass-forming ability. Researchers have recently reported that electrified glass can be formed by solvated electrons through the removal of oxygen in a reducing atmosphere. The solvated electrons are located in the cage-like network structure and were found to lead to an energetically stable a stable glass structure by the large-scale theoretical calculation.



Fig. 1 Oxide melt levitated at high temperature (by courtesy of Atsunobu Masuno, The University of Tokyo)

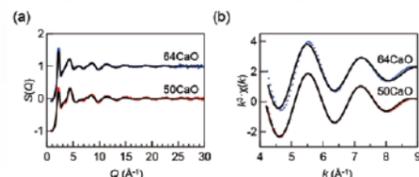


Fig. 2 Results of (a) high-energy X-ray scattering and (b) XAFS at Ca K absorption edge (blue and red dots) shown with the results of large-scale theoretical calculation (black lines)

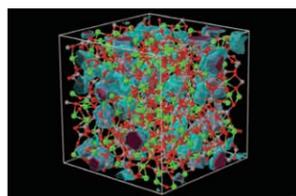


Fig. 3 Atomic arrangement of the 64 mol%CaO-36 mol%Al₂O₃ material with a high glass-forming ability

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Materials Science Hard X-ray photoemission spectroscopy (HAXPES)

Clarification of thin-film transistor properties using the transparent oxide semiconductor, indium gallium zinc oxide (IGZO)

A transparent oxide semiconductor, indium gallium zinc oxide (InGaZnO, generally abbreviated as IGZO), is optically transparent because of its wide bandgap of ≥ 3.0 eV. In addition, IGZO thin-film transistors (TFTs) with electron mobility one order of magnitude higher than that of amorphous silicon TFTs can be easily fabricated. Furthermore, IGZO has a high switching performance. Therefore, IGZO has been widely recognized as a material for realizing next-generation devices, such as high-performance transparent flexible transistors, that have been difficult to realize using conventional semiconductors (Fig. 1). In recent years, research and development for the improvement of the performance of devices and for the search of new materials has been active. The analysis of electronic states, such as the tail level, which significantly affects TFT performance and stability, has been high-priority research themes. In general, X-ray photoelectron spectroscopy (XPS) is known to be a powerful experimental tool for directly observing electronic states. However, the data obtained by general XPS using soft X-rays are affected by the surface conditions and it is extremely difficult to identify the original electronic states of the sample used as the material of an actual device because of its extremely small detection limit of 2–3 nm. Recently, hard X-ray photoemission spectroscopy (HAXPES) using high-energy X-rays (6–10 keV) as the excitation light source was developed at SPring-8 for the purpose of analyzing the electronic state of the deep region (bulk) of a sample. When the energy of the X-rays is increased to approximately 6 keV, the detection limit of photoelectrons increases to ~ 20 nm and the surface effect can be ignored. The tail states at the conduction band edge and immediately above the valence band of IGZO were examined by HAXPES (Fig. 2). The results revealed that the existence of excess electronic density of states (DOS) caused by the tail state prevents p⁻ channel operation and shifts the threshold voltage upon the application of negative bias stress under light illumination. As explained, the HAXPES results for the electronic conduction properties of a bulk are helpful in the development of mobile phones, tablet terminals, and large 55-inch organic electroluminescence televisions (EL-TVs) using the IGZO-TFT displays currently in use.

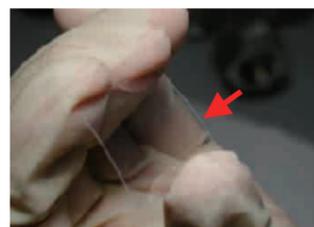


Fig. 1 High-performance transparent flexible transistor This transistor exhibits high electron mobility (~ 10 cm²/V.s), high ON/OFF ratio ($\sim 10^8$), low s value (~ 0.1 V/decade), and low driving voltage (< 5 V)

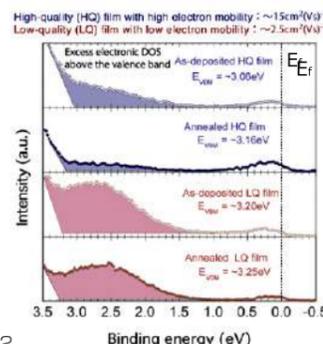


Fig. 2 HAXPES spectra in the vicinity of bandgap region and Fermi level (E_F) of high- and low-electron-mobility IGZO films with and without annealing

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Chemical Science X-ray absorption fine structure (XAFS)

Development of high-energy-density, high-safety, and low-cost magnesium rechargeable batteries

The practical use of rechargeable magnesium batteries, which are superior to lithium ion rechargeable batteries, has been expected because they have a high theoretical energy density, magnesium resources are abundant, and rechargeable magnesium batteries are safe. However, divalent magnesium ions have the drawbacks of a strong ionic interaction, difficulty of diffusion in the solid phase, and extremely slow electrode reaction compared with monovalent lithium ions. In addition, no electrolyte for stable and safe operation of magnesium batteries that enables magnesium deposition/dissolution has been found. Therefore, issues related to the cathode and electrolyte should be resolved before the fabrication of rechargeable magnesium batteries.

In this study, the research group succeeded in the synthesis of a cathode material (ion-exchanged MgFeSiO₄) in which the diffusion path of magnesium ions is secured by precisely controlling the crystal structure of the cathode material. With the use of MgFeSiO₄, the insertion and extraction of double the number of magnesium ions compared with conventional cathode materials became possible. The reason behind the stable and high-capacity reaction of MgFeSiO₄ was examined in detail by powder X-ray diffraction and X-ray absorption spectroscopy using high-brilliance synchrotron radiation X-rays. The results indicate that the three-dimensional structure of Si-O and Fe-O forms a skeleton structure and that the reaction proceeds by the single-phase reaction of the insertion and extraction of magnesium ions while maintaining the three-dimensional crystal structure [Fig. 1 (a)]. Also, the mechanism of charge compensation through the change in the iron valence along with the insertion and extraction of magnesium ions was clarified [Fig. 1 (b)]. Rechargeable magnesium batteries with the highest performance in the world were realized by combining the MgFeSiO₄ cathode, a newly developed electrolyte solution, and a magnesium metal anode (Fig. 2).

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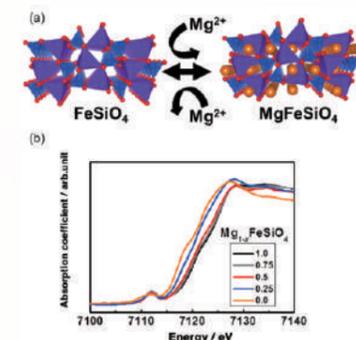


Fig. 1 (a) Structural change in cathode material owing to charge/discharge reaction and (b) XAFS spectra for Mg_{1-x}FeSiO₄

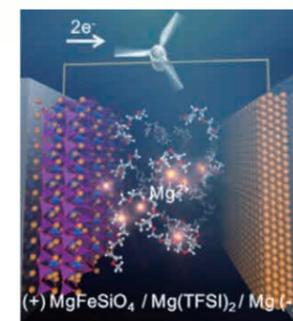


Fig. 2 Schematic of high-energy-density and highly safe rechargeable magnesium batteries

Chemical Science Imaging and spectroscopy

Shedding New Light on Efforts toward Elucidation of the Degradation Mechanism in Membrane-electrode Assembly

The fuel cell is coming into widespread use both in households (e.g., “Ene Farm” residential fuel cell) and industry (typically, commercialization for automobiles) as a next-generation energy source. Still, it faces challenges, including the upgrade of power generation efficiency and reduction of undesirable effects (e.g. elution/degradation of precious Pt catalyst on the cathode). As the fuel cell membrane-electrode assembly (MEA) is a complex heterogeneous system (Fig. 1), the development of a method to probe inside of it nondestructively in order to identify spatial locations of Pt catalyst’s leaching out and degradation has been a very challenging task. In this study, combination of a novel imaging method, X-ray laminography, and XAFS was developed in SPring-8 to obtain hitherto intangible information on cathode catalyst layers inside the fuel cell MEA, i.e. the distribution of the catalyst and the chemical state inside the fuel cell membrane and MEA, with a visual perspective. The result was the first successful visualization of Pt catalyst distribution and chemical state in the cathode catalyst layers in 3D, providing 4D visualization (Fig. 2). The results obtained are expected to shed new light on the degradation mechanism of fuel cell catalyst, and accelerate the development of materials with higher durability for use in fuel cells.

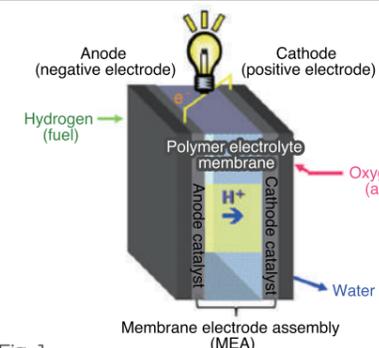


Fig. 1 Schematic diagram representing a fuel cell (hydrogen fuelled)

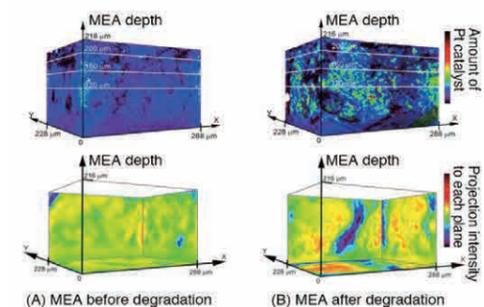


Fig. 2 3D distribution of Pt catalyst on the cathode catalyst layer in a fuel cell MEA, as revealed by X-ray laminography XAFS measurement

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