TUT Research
e-Newsletter from Toyohashi University of Technology
No.15 Nov 2018

FEATURE STORY

Toward development and mass production of all-solid-state lithium Ion batteries

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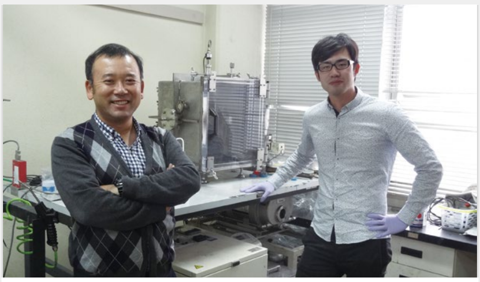
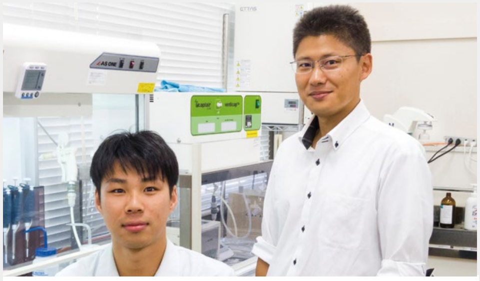
Research Highlights

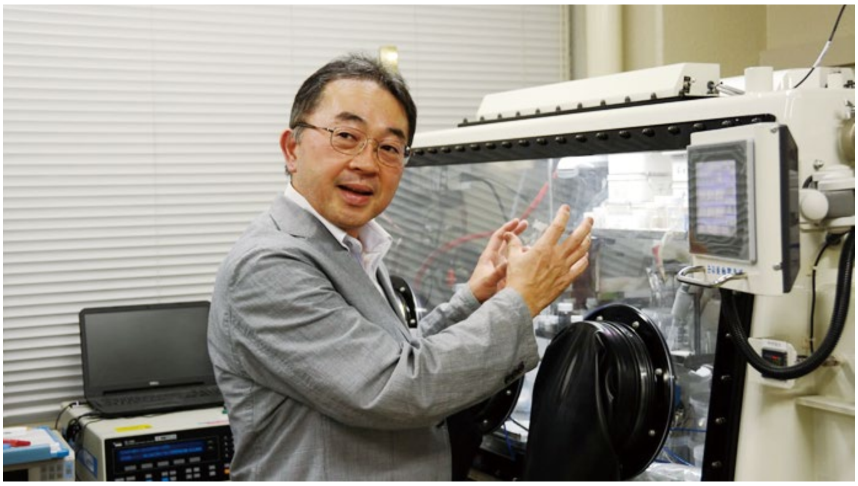




Pick Up

Toward development and mass production of all-solid-state lithium Ion batteries

Atsunori Matsuda



Lithium ion batteries (LIBs) are widely used as power sources for smartphones and laptop computers. They are also essential for certain types of transport such as electric vehicles (EVs) as well as for emergency power supplies in the event of a disaster. Unsurprisingly then, there is fierce global competition to develop LIBs with even higher energy density and better performance. However, there is a major drawback with the current generation of LIBs, in that a flammable organic electrolytic solution is used for the electrolyte, creating is a risk of leakage and ignition. Due to this, the drive to develop safer materials has become an urgent matter.
It is in this context that the next-generation LIBs are being developed as all-solid-state batteries using flame-retardant solid-state electrolytes and boasting excellent stability. As a part of this drive, Professor Atsunori Matsuda has proposed a "liquid-phase shaking method" synthesis process. Since this method allows for solid-state electrolytes to be easily produced in large quantities, it has been widely recognized as a major contribution to the development and mass production of all-solid-state LIBs.

Interview and report by Madoka Tainaka

Expectation for all-solid-state lithium ion batteries is increasing against the backdrop of the uptake of EVs

Currently, the rapid uptake of EVs is driving the urgent need for practical all-solid-state LIBs that realize both high energy density and safety. Toyota stated that it will replace all its models with hybrid cars or EVs by the end of 2025, and it is expected that the shift to EVs will advance rapidly all over the world in the future.

In light of these circumstances, in June 2018, the New Energy and Industrial Technology Development Organization (NEDO) launched a research and development project on the early realization of all-solid-state LIBs. In addition to solving issues for the commercialization of all-solid-state LIBs, topics such as development of mass-production processes and evaluation of suitability for onboard batteries, etc. will be tackled.

The project is being carried out by 23 major companies in Japan such as automobile, battery, and material manufacturers, 15 universities and public research institutes including Toyohashi University of Technology (TUT), and will be based at the Consortium for Lithium Ion Battery Technology and Evaluation Center (LIBTEC). It is an "All Japan" initiative that will strengthen links between industries.

Professor Matsuda of TUT, who is involved in the development of solid-state electrolytes - the key material for batteries - explains the advantages of all-solid-state LIBs.

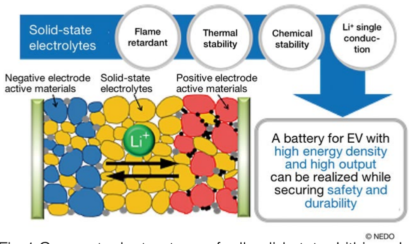


Fig.1 Conceptual structure of all-solid-state Lithium Ion battery

"It is not easy to move ions with large mass in solids. However, if the electrolyte that is sandwiched between the positive and negative electrodes can be made into a solid, the thermal and chemical stability increases, and safety is dramatically improved since the battery becomes more difficult to burn. Moreover, sulfide-type solid-state electrolytes, which use lithium sulfide (Li2S) as the main component, demonstrate high conductivity comparable to that of an organic electrolyte and are capable of a lithium ion transference ratio of 100%. In other words, because we can carry only the ions that we want, we can make a big contribution to improving the energy density."

"All Japan" initiative for early practical application

This NEDO project is the successor to the ALCA-Specially Promoted Research for Innovative Next Generation Batteries (ALCA-SPRING) project, which was implemented by the Japan Science and Technology Agency (JST) under the Ministry of Education, Culture, Sports, Science and Technology, and ran from 2013 to 2017. Under ALCA-SPRING, all activities were focused on the goal of developing next generation batteries. These ranged from battery design and material development for positive and negative electrodes and electrolytes, to evaluation and analysis. The new project has been transferred to NEDO under the auspices of the Ministry of Economy, Trade and Industry. This exceptional initiative is being framed as a second phase project on all-solid-state LIBs, with the goal of putting the research to practical use.

While Toyota was the only company that participated in the first phase, several major Japanese manufacturers have come together for the second phase, demonstrating the enthusiasm for betting on this research as an "All Japan" national effort.

"Japanese manufacturers used to hold more than 90% of the global LIB market share, but this figure has currently dropped to one third. The collective will to avoid the same thing happening with all-solid-state LIBs explains the strong backing for the research. That's why, for this project, we are not only pursuing technology and manufacturing processes, but also working on battery testing and evaluation methods so that Japanese methods will become international standards."

"Liquid-phase shaking method" opens the way to practical use and mass production

One of the most significant challenges to the practical application and upsizing of all-solid-state LIBs is production of solid electrolytes at large scale and low cost.

Responding to this challenge, Professor Matsuda succeeded in preparing lithium thiophosphate (LPS) by mixing the starting material in ester organic solvent using the liquid-phase shaking method, performing centrifugation, and then reducing the pressure and drying. Previously, it was necessary to synthesize solid electrolytes by stirring a powder for a long time using a planetary ball mill.

"With this method, it becomes possible to synthesize sulfide-based solid electrolytes in a short time and with less energy. In addition, the particles of the obtained solid electrolyte are extremely small "nano size" (about 50 to 100 nm), whereas those produced with a conventional planetary ball mill are about 5 μm. By sandwiching this electrolyte between the positive and negative electrode active materials and press molding to form a compact, it mixes moderately with the active materials of both electrodes and a good interface is obtained," says Professor Matsuda.

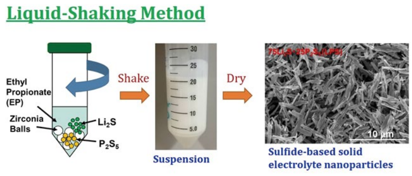


Fig.2 Liquid-shaking method

To synthesize LPS using the conventional milling method, it is necessary to continue mixing with high energy for a long time. It is also difficult to synthesize in large quantities at once. But with the liquid-phase shaking method, LPS can be prepared in a suspended state, so it can be cheaply produced in large quantities in existing chemical plants in the future.

As many countries struggle to develop sulfide-based all-solid-state LIBs, the particular reason why Professor Matsuda's manufacturing process is drawing attention is said to be its low total cost and high efficiency.

Professor Matsuda summarized his outlook on the challenges ahead as follows, "Of course, many countries are seeking mass production using the liquid-phase method, but as an academic, I want to challenge myself to do everything I can. By pursuing this principle, I hope to contribute to making better quality electrolytes and safe, high-performance all-solid-state batteries."

Perfecting the liquid-phase method for future batteries

According to the market research company Fuji Keizai, mass production of all-solid-state batteries for EVs will begin in the 2020s, and by 2035 the world market will grow to 2,787.7 billion yen. Within this market, the market for sulfide-based all-solid-state batteries will account for the majority at 2,120 billion yen. This analysis backs up the government's decision to support this project on a national basis.

Meanwhile, Professor Matsuda is looking even further into the future of batteries.

"Metal-air batteries are one of the possibilities to come after LIBs. Compared with sulfide, they can be made of more stable materials, but at present they are difficult to manufacture, and we cannot yet see a path to their widespread use. However, it would be easy to manufacture an electrolyte that makes and moves OH- (hydroxide ions) from air if the liquid-phase method is used. In fuel cells, protons (H+) need to be moved, and the liquid-phase method also holds the key to this. I expect that I will be able to utilize my experience as a specialist in materials who has developed functional materials using liquid-phase in various ways from now on."

If the performance of batteries improves, it will not only help to make EVs widespread but will also enable distributed power generation and storage, which will contribute to solving the global energy problem. We are looking forward to the further progress of Professor Matsuda's future research.

[Reporter's Note]

Professor Matsuda says that he is proud of his 6th Dan level in kendo. When he was in elementary school, he watched the TV drama "Ore Wa Otoko Da!" (I am a man!) and admired Kensaku Morita who portrayed the captain of a kendo club, and so he started kendo as a club activity from junior high school. After that, he belonged to his high school and university kendo clubs, and after getting a job he was involved in the Tsukuba University friends of kendo association and the kendo club alumni group at Osaka Prefecture University, his alma mater. Currently, he serves as an advisor to the Toyohashi University of Technology kendo club. He also taught kendo to his three children.

"Something you cultivate for over 40 years will not decline easily. I think it is meaningful to persevere at something. Currently, I am challenging myself to reach 7th Dan," says Professor Matsuda enthusiastically.

Professor Matsuda also began synthesis of functional materials using the liquid-phase method as his graduation research when he was an undergraduate. He has worked on various themes, but by tackling problems based on liquid-phase, it has led to significant research results. This is truly "the power of perseverance." Please do your best to reach 7th Dan!

Fig.3 Prof. Matsuda (left) performed Nihon Kendo Kata with his research colleague at an international conference dinner excursion.

全固体リチウムイオン電池の開発と量産化をめざして

スマートフォンやノートパソコンなどの電源として広く普及しているリチウムイオン電池（Lithium Ion Battery=LIB）。電気自動車（Electric Vehicle=EV）などの移動体の電源や災害時の非常用電源としても不可欠であり、さらなる高エネルギー密度化・高性能化をめざして、世界中で開発競争が過熱している。しかし、現状のLIBには、電解質に可燃性の有機電解液が使用されていて、液漏れや発火の危険性が伴うことから、より安全な材料への転換が急務となってきた。
そこで現在、次世代のLIBとして開発が進められているのが、難燃性の固体電解質を用いる安定性に優れた全固体LIBだ。特に、松田厚範教授が提案する合成プロセス「液相加振法」を用いれば、固体電解質が簡易な方法で大量に製造することが可能になるため、全固体LIBの開発と量産化に寄与するとして大きな注目を集めている。

EVの普及を背景に、全固体リチウムイオン電池への期待が高まる

現在、高いエネルギー密度と安全性の両方を実現する全固体LIBの実用化が急がれる背景には、EVの急速な普及がある。トヨタ自動車が2025年の終わりまでに全車種をハイブリッドカーないしはEVに置き換えると宣言したように、今後は世界中で急速にEVシフトが進むと予想される。

こうした状況を受けて、2018年6月、新エネルギー・産業技術総合開発機構（NEDO）は、全固体LIBの早期実用化に向けて、研究開発プロジェクトをスタートした。全固体LIBの製品化に向けた課題解決に加え、量産プロセスの開発、車載用電池としての適合性の評価などを実施するという。

参画するのは、自動車メーカーのほか、蓄電池・材料メーカーなどの日本の主要企業23社と、豊橋技術科学大学をはじめとする大学・公的研究機関15法人で、技術研究組合リチウムイオン電池材料評価研究センター（LIBTEC）を拠点に、業種を超えた連携を強化しながらオールジャパンで進めている。

当プロジェクトにおいて、電池のキーマテリアルである固体電解質の開発を手がける本学の松田教授は、全固体LIBのメリットを次のように説明する。

「質量の大きいイオンを固体の中で動かすのは容易ではありません。しかし、正極と負極に挟まれた電解質が固体になれば熱的にも化学的にも安定性が高まり、燃えにくくなることから安全性が格段に上がります。しかも、硫化リチウム（Li2S）を主成分とする硫化物系固体電解質であれば、有機電解液に匹敵する高い導電率を示し、リチウムイオン輸率は100%。つまり、欲しいイオンだけを運ぶことができることから、エネルギーの高密度化に大きく貢献できるというわけです」

早期実用化に向けた、オールジャパンの取り組み

実は当プロジェクトは、文部科学省所管の科学技術振興機構（JST）で実施された先端的低炭素化技術開発 - 次世代蓄電池（ALCA-SPRING)研究開発プロジェクト（2013～2017年）を引き継いだものなのだという。ALCA-SPRINGでは、次世代蓄電池の開発で、電池設計から正極・負極・電解質の材料開発、評価解析まで含めた電池システムの開発を実施。その中で、とくに実用化に期待がかかる全固体LIBについて、第2期プロジェクトとして経済産業省所管のNEDOに研究が移管されたという異例の取り組みなのだ。

第1期の参画がトヨタ自動車1社だけであったのに対して、第2期では、日本の主要メーカーが勢揃いしたように、国を挙げてオールジャパンでこの研究に賭ける意気込みが伝わってくる。

「かつて日本のメーカーは、LIB世界シェアの9割以上を占めていましたが、現在では3分の1まで落ち込んでいます。全固体LIBでは同じ轍を踏むまいと、皆が強い思いで研究に臨んでいます。だからこそ、プロジェクトの中では、たんに技術や製造プロセスを追求するだけでなく、日本の方式が国際規格になるよう、電池の試験・評価方法まで手がけているのです」

「液相加振法」で実用・量産化への道をひらく

とりわけ、全固体LIBの実用化や大型化の重要な課題の一つとなってきたのが、固体電解質の量産と低コストでの製造である。

そうした中、松田教授は、これまで遊星型ボールミルを用いて粉体同士を長時間かき混ぜて合成していた固体電解質を、液相加振法という方法により、出発物質をエステル系有機溶媒中で混ぜ、これを遠心分離したのち、減圧、乾燥することでチオリン酸リチウム（LPS）を作製することに成功した。

「これにより、短い時間と少ないエネルギーで硫化物系固体電解質を合成することが可能になりました。しかも、得られる固体電解質の粒子は、従来の遊星型ボールミルでつくるものが5μm程度であるのに対して、ナノサイズ（100～50nm程度）と非常に小さい。これを負極活物質と正極活物質の間に挟んで、加圧成形して圧粉体にすることより、両極の活物質と適度に混ざり、良好な界面が得られます」と松田教授は話す。

LPSをつくる場合、従来のミリング法で合成しようとすると、長時間、高いエネルギーをかけながら混ぜ続ける必要がある。また、一度に大量に合成することも難しい。一方、液相加振法であれば、懸濁液の状態で調製できるため、将来、既存の化学プラントで安価で大量につくることができるのだという。

各国が硫化物系全固体LIBの開発にしのぎを削るなか、とくに松田教授の製造プロセスが注目される理由は、トータルコストの安さと効率の良さだという。

「もちろん、各国が液相法による量産化を模索していますが、やはりアカデミアだからこそできることにチャレンジしたい。原理を追究することで、より良質な電解質と安全で優れた全固体電池をつくることに貢献できればと思っています」と、松田教授は展望を語った。

未来の電池へ向けて、液相法を究める

ところで、市場調査会社の富士経済によれば、全固体電池はEV向けに2020年代から量産が始まり、2035年には2兆7877億円まで一気に世界市場が膨らむと予測している。うち、硫化物系全固体電池は2兆1200億円とその大半を占める。今回のプロジェクトに、国を挙げて取り組むのも頷ける。

一方で、松田教授は、さらにその先の電池の未来まで視野に入れている。

「ポストLIBの一つに金属空気二次電池があります。硫化物に比べて、より安定した材料でつくることができますが、現状は製造が難しく、普及の見通しは立っていません。しかし、空気からOH－（水酸化物イオン）をつくって動かす際の電解質も液相法であればつくりやすい。また、燃料電池ではプロトン（H＋）を動かす必要がありますが、これも液相法がカギを握ります。これまで、材料屋として、液相で機能性材料を開発してきた経験が、今後もさまざまに活かせるでしょう」
蓄電池の性能が上がれば、EVの普及のみならず、発電や蓄電の分散化を可能にし、地球規模のエネルギー問題の解決にもつながる。今後の松田教授のさらなる研究の進展に期待したい。

（取材・文＝田井中麻都佳）

取材後記

剣道六段の腕前を誇るという松田教授。小学生の頃、テレビドラマ『おれは男だ！』で森田健作が扮する剣道部キャプテンの主人公に憧れ、中学から部活で剣道を始めたという。以来、高校、大学と剣道部に所属して、就職後も筑波大学剣友会や母校・大阪府立大学剣道部OB会で活動。現在も豊橋技科大剣道部顧問を務める。三人のお子さんにも剣道を教えた。

「40年以上かけて培ったことは簡単には衰えません。続けることに意味があるということでしょうか。現在、七段に挑戦中です」と松田教授は意気込む。

液相法による機能性材料の合成も卒業研究として学部生の頃から始めた。テーマはさまざまだが、液相をベースに一途に取り組むことで、大きな研究成果に結びついてきた。まさに「継続は力」。七段への挑戦、がんばってください！

Researcher Profile

Dr. Atsunori Matsuda
Dr. Atsunori Matsuda studied until master's course at Osaka Prefecture University, Japan. After graduate from the university, started his career at Nippon Sheet Glass Company Ltd., and received his PhD. degree in 1992 from Osaka Prefecture University. Then, he was engaged in a research as a lecturer at Osaka Prefecture University from 1997 to 2000. Currently, he is a professor in the Department of Electrical & and Electronic Information and a vice president at Toyohashi University of Technology. His research interests are Inorganic Materials Science, Sol-Gel Method, and All-solid-state battery.

Reporter Profile

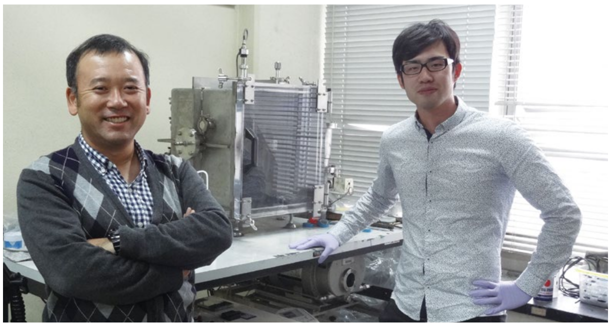
Madoka Tainaka is a freelance editor, writer and interpreter. She graduated in Law from Chuo University, Japan. She served as a chief editor of "Nature Interface" magazine, a committee for the promotion of Information and Science Technology at MEXT (Ministry of Education, Culture, Sports, Science and Technology).

Challenges for the development of oxide-based all-solid-state batteries

Thick-film cathode solidified on garnet-type oxide solid electrolyte at room temperature

By Ryoji Inada

A research group led by Associate Professor Ryoji Inada have successfully fabricated a lithium trivanadate (LVO) cathode thick film on a garnet-type oxide solid electrolyte using the aerosol deposition method. The LVO cathode thick-film fabricated on the solid electrolyte performed well, achieving a capacity of up to 300 mAh/g for both reversible charge and discharge, as well as a good cycling stability at 100℃. This finding may contribute to the realization of highly safe and chemically stable oxide-based all-solid-state lithium batteries.



Associate Prof. Ryoji Inada (left) and his student, Shunsuke Kito

Rechargeable lithium-ion batteries (LiBs) have been widely utilized globally as a power source for mobile electronic devices such as smart phones, tablets, and laptop computers because of their high-energy density and good cycling performance. Recently, the development of middle- and large-scale LiBs has been accelerated for use in automotive propulsion and stationary load-leveling for intermittent power generation from solar or wind energy. However, a larger battery size causes more serious safety issues in LIBs; one of the main reasons is the increased amount of flammable organic liquid electrolytes. The research results were reported in Materials on September 1st, 2018.

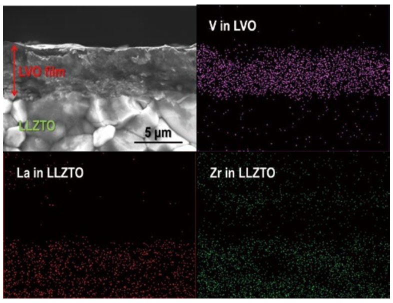


Fig.1 SEM image of a fractured cross-sectional surface of the LVO electrode fabricated on LLZTO garnet by AD. Corresponding elementary mapping for V, La, and Zr is also shown.

All-solid-state LiBs with nonflammable inorganic Li-ion (Li+) conductors as solid electrolytes (SE) are expected to be the next generation of energy storage devices because of their high energy density, safety, and reliability. The SE materials must have not only high lithium-ion conductivity at room temperature, but also deformability and chemical stability. Oxide-based SE materials have a relatively low conductivity and poor deformability compared to sulfide-based ones; however, they have other advantages such as chemical stability and ease of handling.

The garnet-type fast Li+ conducting oxide, Li7-xLa3Zr2-xTaxO12 (x = 0.4-0.5, LLZTO), is considered as a good candidate for SE because of its good ionic conductiivity and high electrochemical stability. However, high-temperature sintering at 1000-1200℃ is generally needed for densification, and this temperature is too high to suppress undesired side effects at the interface between the SE and the majority of electrode materials. Therefore, there are currently few options when it comes to electrode materials that can be used for solid-state batteries with garnet-type SEs developed by the co-sintering process.

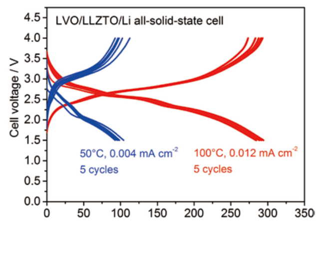
Ryoji Inada and his colleagues at the Department of Electrical and Electronic Information Engineering, Toyohashi University of Technology, succeeded in fabricating a lithium trivanadate (LiV3O8, LVO) thick-film cathode on garnet-type LLZTO by means of the aerosol deposition (AD) method. All-solid-state cell samples were prepared and tested using the fabricated composite.

The AD method is known to be a room-temperature film-fabrication process, which uses the impact-consolidation of ceramic particles onto a substrate. By controlling the particle size and morphology, dense ceramic thick films can be fabricated on various substrates without thermal treatment. This feature is attractive in the fabrication of oxide-based solid-state batteries because various electrode active materials can be selected and formed on SE without the need for thermal treatment.

LVO has been studied at length as a cathode material for Li-based batteries because of its large Li+ storage capacity of approximately 300mAh/g. However, the feasibility of LVO as a cathode for solid-state batteries has not yet been investigated. The reaction of LVO initiates at the discharging (i.e., Li+ insertion) process, which differs from that of other conventional cathode materials of LiBs such as LiCoO2, LiMn2O4, and LiFePO4. Therefore, graphite anodes, which are widely used in current LiBs, are difficult to use in batteries with LVO cathodes. In solid-state batteries with garnet-type SEs, Li metal electrodes may potentially be used as anodes; thus, LVO would become an attractive candidate for high-capacity cathodes.

To fabricate a dense LVO film on an LLZTO pellet, the size of the LVO particles was controlled by ball-milling. As a result, an LVO thick film with a thickness of 5-6 μm was successfully fabricated on LLZTO at room temperature. The relative density of the LVO thick film was approximately 85%. For the electrochemical characterization of the LVO thick film as a cathode, Li metal foil was attached on the opposite end face of the LLZTO pellet as an anode to form an LVO/LLZTO/Li structured solid-state cell. The galvanostatic charge (Li+ extraction from LVO) and discharge (Li+ insertion into LVO) properties in an LVO/LLZTO/Li all-solid-state cell were measured at 50 and 100℃.

Fig.2 Comparison of the galvanostatic charge and discharge curves for the LVO/LLZTO/Li solid-state cell at 50 and 100℃. The measurements at each temperature are repeated for five cycles.



Although the polarization was considerably high at 50℃, a reversible capacity of approximately 100 mAh/g was confirmed. With an increase in temperature to 100℃, the polarization reduced and the capacity increased significantly to 300 mAh/g at an averaged cell voltage of approximately 2.5 V; this is a typical behavior of an LVO electrode observed in an organic liquid electrolyte. In addition, we confirm that the charge and discharge reactions in the solid-state cell are stably cycled at various current densities. This can be attributed to the strong adhesion between the LVO film fabricated via impact consolidation and the LLZTO and LVO particles in the film.

These results indicate that LVO can potentially be used as a high-capacity cathode in an oxide-based solid-state battery with high safety and chemical stability, even though additional investigation is needed to enhance the performance. Researchers have carried out further studies to realize oxide-based solid-state batteries at lower operating temperatures.

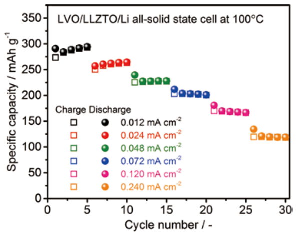


Fig.3 Cycling performance for the LVO/LLZTO/Li solid-state cell at 100℃ and different current densities from 0.015 to 0.240 mA/㎠.

This work was partly supported by Grant-in-Aids for Scientific Research (C) (Grant No. 16K06218) and Fund for the Promotion of Joint International Research (Fostering Joint International Research) (Grant No. 16KK0127) from the Japan Society for the Promotion of Science (JSPS).

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Ryoji Inada, Kohei Okuno, Shunsuke Kito, Tomohiro Tojo and Yoji Sakurai (2018). Properties of Lithium Trivanadate Film Electrode Formed on Garnet-type Oxide Solid Electrolyte by Aerosol Deposition, Materials 11(9), 1570, 2018. https://doi.org/10.3390/ma11091570

Can we have a fire in a highly-vacuumed environment?

Towards better fire safety strategies for manned space missions

By Yuji Nakamura

Yuji Nakamura and his research team at Toyohashi University of Technology have discovered that non-flaming combustion (smoldering) of a porous specimen can sustain itself, even at around less than 1 % of atmospheric pressure. The thermal structure of a 2-mm-diameter smoldering specimen, at a condition close to extinction, was successfully measured using an embedded ultra-fine thermocouple, clarifying the key issues that lead to fire extinction at low pressures. The outcome of this research will contribute to improved space exploration fire safety strategies.

Non-flaming combustion (i.e., smoldering) is an extremely slow burning process that emits toxic gas and white smoke during the burning event. This corresponds to the pre-flaming stage of burning a porous specimen, during which the blackened part grows, continuing the slow exothermic process. It eventually generates a flame that quickly accelerates the fire damage. Flaming combustion can be suppressed by reducing the pressure to nearly 1/3 of standard pressure (~30 kPa). Nevertheless, non-flaming combustion can sustain even at 1/100 of standard pressure (~1 kPa) if the ambient gas is fully-oxygenated. Extension of the critical pressure has been pointed out as an experimental fact; however, the actual reason is not known because it is extremely difficult to investigate the thermo-chemical status of near-critical conditions. Because the combustion intensity is very weak, sensor insertion may affect the status, resulting in failure to capture the actual physics.

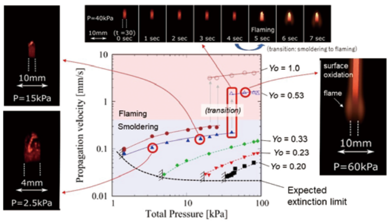

Fig.1 Smoldering limit observed in low pressure. Effects on smoldering speed (propagation velocity) and extinction relative to the pressure at various adopted O2 conditions.

A research group led by Professor Yuji Nakamura, from the Department of Mechanical Engineering at Toyohashi University of Technology, took on the challenge of measuring the temperature distribution of a smoldering thin rod in a pressure-controlled chamber at near-critical conditions. To make this possible, special care was taken to adjust the sensor while avoiding the potential failure described above. A tiny hole of 0.2-mm diameter was drilled through the fragile specimen. Then, a 50-micron R-type thermocouple was embedded into the hole. By achieving steady-state burning, even near the critical condition under a well-controlled experimental environment, a repeatable 1-D temperature profile was obtained along the axis.

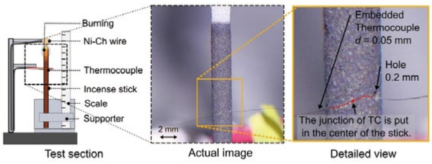

Fig.2 Temperature measurement device: fine thermocouple installed in 0.2-mm diameter hole in the specimen

The first author, Takuya Yamazaki, a PhD candidate, said, "The idea of drilling a miniscule hole into a small (2-mm) and fragile specimen such as the one we used, and then manually inserting a tiny thermocouple had never previously been considered. No doubt this was due to the high level of difficulty of such a procedure, which requires considerable patience and effort. Indeed I must admit that it was really exhausting to complete this task. Nevertheless, ultimately this process provided us sufficient insights into the near-critical condition thermal status to thoroughly understand the extinction mechanism. For instance, combustion heat is first transferred along the axis by radiation. After that, part of the transferred heat is lost to the ambient environment via natural convection when the total pressure is in the order of tens of kilo-pascals. Because the convective heat loss tends to be suppressed when the total pressure decreases, the heat transferred by radiation could remain in the specimen and so avoid extinction. Our success in being the first to demonstrate this fact by such a procedure is the fruit of our willingness to take on the 'super' challenge of measuring the precise temperature distribution of a smoldering specimen at near extinction."

"The present results will make a contribution to fire safety basically thanks to Takuya's personal devotion. This outcome suggests that the vacuumed operation to extinguish fire in space may fail unless the proper condition is achieved. Otherwise, smoldering may survive, causing a fire which may result in secondary damage to the cabin. This work is just the first step in constructing a tentative fire safety (regulation) strategy for outer space habitats in this age of privatized space development", explains Professor Yuji Nakamura.

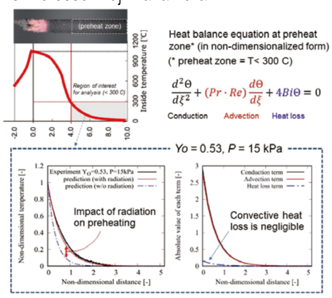

Fig.3 Heat balance analysis in the preheat zone. Thermal status during smoldering under low pressure: radiation heat transfer becomes significant, whereas convective cooling (i.e., heat loss) to ambient is negligible in the preheat zone.

We use the term "smoldering" frequently, but, in reality, no one knows how a specimen burns to generate heat locally. It has been considered that surface oxidation is the source of heat generation, and that gas-phase reaction is not required to be considered. However, based on recent numerical predictions by a Chinese research team (a member of an international collaboration team led by Prof. Nakamura), it was found that a gas-phase gentle heat generation can support or promote surface oxidation. To further the cause of understanding smoldering at low pressures, another international collaboration team in the United States, also led by Prof. Nakamura, will assume the challenge of experimentally identifying the reactivity in the gas-phase. This is a crucial step, because up to now scant attention has been paid to the reaction status of the micro-pores of a burning specimen.

Funding agency: JSPS program "Overseas Challenge Program for Young Researchers"

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New Ultrasonic Wave Phenomenon leads to Improved Safety for Society

Nondestructive testing for earlier assessment of damage to structures

By Yosuke Ishii

A research group led by Assistant Professor Yosuke Ishii at Toyohashi University of Technology has unraveled the phenomenon of a new “third ultrasonic wave” being generated when two ultrasonic waves intersect within a plate. This wave exhibits varying intensity in response to material damage and can therefore be used for nondestructively testing thin plate structures. This new technology surpasses conventional technology, enabling precise and nondestructive detection of fatigue and early damage.

Yosuke Isii (top left corner) with his lab member

Humans are unable to see the inside of an object with the naked eye unless that object is transparent. Using ultrasonic waves, however, can afford us that ability. Ultrasonic waves reflect any defects present within a material. Therefore, measuring these waves reflected from defects can tell us if a material is damaged in any way. In other words, we can “examine” materials without having to break them open. This is the principle behind nondestructive testing using ultrasonic waves. We need nondestructive testing to improve our safety in various situations, so methods for increasing testing accuracy are currently being studied around the world.

Currently, testing the state of a material that is not damaged but has some wear is a particularly hot topic of research in the field of nondestructive testing. In particular the current focus is on testing for fatigue. Like humans, materials also become fatigued. Even a small amount of load is enough to cause material fatigue when repeatedly applied. Fatigue creates minute amounts of damage in a material, which then become bigger and eventually cause the material to break. Thin plate materials are widely used in large-scale structures such as power plants built during Japan’s period of high economic growth after World War II. Now that these structures are aging, it is imperative to use nondestructive methods to test their degree of fatigue. With current technology, we are unable to detect damage unless a large amount of damage (damage that can reflect ultrasonic waves) has already occurred in materials. Because of this, it is of paramount importance to establish a technology that can accurately evaluate material fatigue in its early stages, in fact, the earlier the better.
With this in mind, the research group turned its attention to “three-wave interaction.” This is a phenomenon whereby two intersecting ultrasonic waves produce a third small ultrasonic wave within a plate. Through conducting numerical simulations and theoretical calculations, the research group succeeded in uncovering the mechanism behind how this third ultrasonic wave is generated by a three-wave interaction. The third ultrasonic wave contains a large amount of information of the properties of a material, potentially making it possible to accurately test the early stages of material fatigue (before a large amount of damage occurs).

The research team aims to experimentally verify this new technology to create a new nondestructive testing method for thin plate materials which employs three-wave interaction. Establishing such a technology will make it possible to accurately evaluate material damage far beyond the range of existing technology. This new technology is expected to improve the safety and reliability of socially important structures such as power generation plants and airplanes, and ultimately, to contribute to the safety of all of us.

This work was supported by JSPS KAKENHI Grant No. JP17K14557.

Reference

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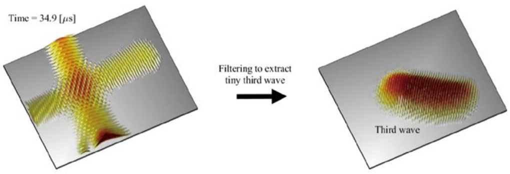


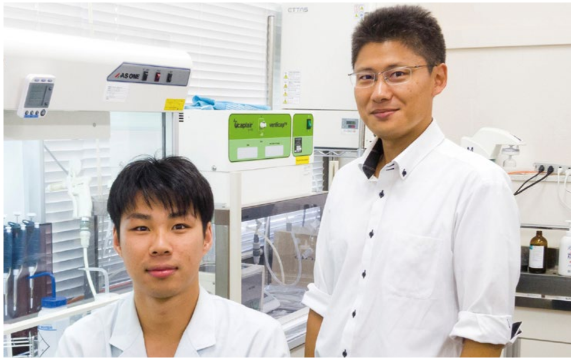
Mov1. Nonlinear three-wave interaction in plate. Two ultrasonic waves intersecting in a plate (left). Third ultrasonic wave extracted by filtering (right).

Assembly of fluctuating molecules in artificial cell membranes

Domains of hydrophilic-polymer-modified lipids in lipid bilayer membranes

By Ryugo Tero

Ryugo Tero at Toyohashi University of Technology has, in cooperation with Kanazawa University, discovered the aggregates of a hydrophilic-polymer-modified lipid in a lipid bilayer membrane. An unexpected phenomenon whereby the aggregated bulky polymer appeared lower in the atomic force microscope topography was discovered, and the related causes were revealed. These findings will lead to further understanding of the function of glycolipids and membrane proteins.



First author Yasuhiro Kakimoto (left) and research team leader Assoc. Prof. Ryugo Tero (right).

Lipids and membrane proteins existing in cell membranes, which form the outermost layer of cells, are responsible for recognizing extracellular environments and transferring that information inside the cell. Due to their deep relation to bacterial and viral infection, immunological response and neural transmission, they are important research topics in the fields of biology, medicine and drug development. In the reaction process of both external recognition and signal transfer, the formation of two-dimensional aggregates of lipids with bulky hydrophilic groups, such as sugar chains or inositol rings, are considered necessary in cell membranes. Small aggregates of up to 10 molecules are called clusters, while aggregates with more molecules and further growth are called domains.

Lipids are amphiphilic molecules derived from organisms, and have both hydrophilic and hydrophobic properties within their molecules. Many past studies have shown that interactions with the hydrophobic part, such as the phase transition and miscibility of hydrocarbon chains, play an important role in domain formation in lipid bilayer membranes. On the other hand, interactions with the hydrophilic part of lipids have not yet been widely researched, with many factors still remaining unclear. Interactions become complicated because of repulsion occurring through the fluctuation of hydrophilic properties in the water, particularly at bulky hydrophilic parts like sugar chains. The repulsion caused by such fluctuation also affects measurements via atomic force microscopy (AFM) that can detect even the tiniest amount of force.

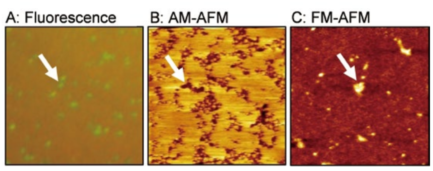


Fig.1 Lipid bilayer domains rich in polyethylene glycol (PEG)-modified lipid.
(A) Fluorescence image, (B) amplitude modulation (AM) AFM topography, and (C) frequency modulation (FM) AFM topography.

A research team helmed by Ryugo Tero, Associate Professor in Toyohashi University of Technology, has used fluorescence microscopy and AFM to examine in detail artificial lipid bilayer membranes containing lipids modified by the hydrophilic polymer, polyethylene glycol (PEG) (Fig.1). The results revealed that two types of aggregates, clusters and domains, form depending on the concentration of PEG-modified lipids, and that the there is almost no fluidity in the domains that appear due to high concentration. These aggregates are formed through the interaction not with lipids' hydrophobic part, but rather with their hydrophilic part. Interestingly, when observed with AFM, the PEG-modified lipid domains that should have been bulky, were observed at a lower level than the surroundings (Fig.1B).

Associate Professor Tero implemented a joint experiment with Professor Takeshi Fukuma in Kanazawa University to determine the reasons for this. By utilizing frequency modulation AFM (FM-AFM), and accurately controlling the force between the sample and the probe, they were able to observe the PEG-modified lipid domain at a higher level than the lipid membrane area, without the application of any amount of force (Fig.1C). Since repulsions will change due to the fluctuation of hydrophilic polymer chains dependent on the force applied, it has been found that a reverse image of the true three-dimensional structure can always be observed during an amplitude modulation AFM (AM-AFM) observation (Fig.2).

"In order to establish an experimental method for examining glycolipids'aggregate state and function, we utilized PEG-modified lipids that are easy to obtain at the very beginning. We struggled to find the most suitable conditions for sample preparation and AFM observation of the lipid bilayer membrane containing PEG-modified lipids. The results differed greatly in comparison to expectations, especially due to the fact that the recessed areas grew relative to the increase in concentration of PEG-modified lipids. Thinking there might have been a mistake, we repeated the experiment and confirmed its reproducibility. Intuitively, it may seem unlikely that the region with bulky molecules appears lower with AFM, but when the assembled state of the polymer and the basic principles of AFM are considered, this is actually very reasonable.

"The Eureka moment for our joint experimental group with Kanazawa University came when we observed how the concave-convex properties of the surface reversed after switching to FM-AFM" explains the main author, Yasuhiro Kakimoto. Mr. Kakimoto is currently enrolled in a doctoral course at Toyohashi University of Technlogy, as a part of the Program for Leading Graduate Schools organized by the Ministry of Education, Culture, Sports, Science and Technology.

The research team leader, Associate Professor Ryugo Tero said "In order to understand the functions of biomolecules at a molecular level, it is vital to comprehend the appearance of soft molecules, such as lipids and proteins, which fluctuate in water. In fact, some evidence from experimental areas containing many glycolipids being observed at a lower level with AM-AFM has been obtained over roughly the past 10 years in several systems. Although repulsion due to fluctuation of hydrophilic parts was only a hypothesis, this study has confirmed its validity. The crucial breakthroughs in this study were achieved thanks to Professor Fukuma's state-of-the-art FM-AFM instrument (Fig.2), which made a key contribution to this joint research accomplishing magnificent results."

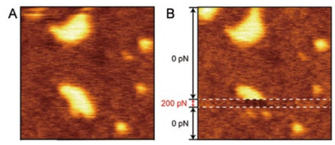


Fig.2 Force-dependent topography of the PEG-lipid-rich domain.

The principle of domain formation due to interactions with hydrophilic polymer chains identified as a result of this research has been found to share commonalities with glycolipids in the cell membrane. Our research team is of the opinion that this principle will assist with the understanding of the mechanism of cell recognition and signal transfers related with the aggregate state of glycolipids and membrane proteins. Furthermore, the findings from the experiments, in which bulky objects can appear sunken-in depending on the conditions, will be valuable for the many researchers analyzing biological molecules underwater through atomic force microscopy. In addition, PEGs have the effect of suppressing nonspecific adsorptions such as proteins, etc., and can also be utilized in bio-interfaces and drug delivery. The formation and force response of PEG-rich clusters and domains are expected to have a pervasive effect also in these fields.

This work was supported by the Japan Society for the Promotion of Science KAKENHI Grant Numbers JP15H03768 and JP15H00893; CREST, Japan Science and Technology Agency (JST) Grant Number JPMJCR14F3; A-STEP, JST. The first author Yasuhiro Kakimoto also received a grant as part of the Program for Leading Graduate Schools run by the Japan Society for the Promotion of Science.

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https://doi.org/10.1021/acs.langmuir.8b00870

酸化物を用いて超安全な電池の実現をめざす

常温で固めた酸化物全固体リチウム電池用正極の特性

稲田 亮史

豊橋技術科学大学の稲田准教授らの研究グループは、エアロゾル・デポジション(AD)法を用いてガーネット型酸化物固体電解質上にバナジウム酸リチウム(LVO)正極を常温で作製することに成功しました。対極を金属リチウムとして構成した全固体電池を100°Cで動作した結果、300mAh/g(LVO単位重量当たり)の充放電容量を確認しました。本成果は、高い安全性と化学的安定性を備えた酸化物全固体リチウム電池の実現に役立つものです。

現在、リチウムイオン電池はスマートフォンやタブレット、ノートパソコン等の小型電子機器用電源として世界中で使われています。最近では、プラグイン・ハイブリット車や電気自動車用車載電源や太陽光発電や風力発電で得られる電力を貯蔵する蓄電システム等への応用も進んでいます。電池の大型化に向けて、その安全性の確保は非常に大切ですが、現行のリチウムイオン二次電池には燃えやすい電解液が使われており、電池内で異常が発生した際に破裂や発火を引き起こす原因となります。

燃えやすい電解液の代わりに燃えない固体電解質(固体のリチウムイオン伝導体)を用いた全固体リチウムイオン電池は、高いエネルギー密度と高安全性・信頼性を同時に達成できる蓄電デバイスとして期待されています。固体電解質として使われる材料には、高いイオン伝導率の他に、成型性や化学的安定性といった多くの要件が求められます。酸化物系固体電解質は硫化物系固体電解質と比較してイオン伝導率や成形性は劣りますが、化学的安定性や取扱いの簡単さといった利点があります。

ガーネット型結晶構造を持つリチウム含有酸化物Li7-xLa3Zr2-xTaxO12(x = 0.4-0.5, LLZTO)は、優れたイオン伝導特性と電気化学的安定性を示すため、全固体電池用固体電解質として有望視されています。本材料の高密度化には一般に1000-1200°Cでの焼結が必要ですが、電極材料と接合した際の副反応を防ぐにはこの温度は高過ぎます。これが一因で、電極と固体電解質間の接合に有効な共焼結プロセスが使える電極材料は限られています。

豊橋技術科学大学電気・電子情報工学系の稲田亮史准教授と同准教授の研究グループのメンバーは、高容量正極材料として知られているバナジウム酸リチウム(LiV3O8, LVO)を、常温成膜プロセスの一つであるエアロゾル・デポジション(AD)法を利用して固体電解質上で電極化することに成功しました。また、作製した試料を用いて全固体リチウム電池を試作し、その電気化学特性を評価しました。

AD法はセラミックス粒子の常温下での衝撃固化現象を利用した成膜技術です。原料となるセラミックス粒子の形状やサイズをうまく制御すれば、高密度な厚膜を熱アシストなしで様々な基板の上に作ることができます。この特徴により、様々な電極材料と固体電解質材料の一体化が可能になるので、酸化物全固体電池を作製する上で魅力的なプロセスです。

LVOは大きな充放電容量を示すリチウム二次電池用正極材料として古くから研究されてきましたが、全固体電池用正極としての研究例はありませんでした。また、現行のリチウムイオン電池で使われているLiCoO2やLiMn2O4, LiFePO4といった正極材料とは違って充電状態で作製されるため、現行電池に使われている黒鉛を負極とする電池にLVO正極をそのまま使うのは困難です。ガーネット型固体電解質を用いた全固体電池では金属リチウムを負極に使える可能性があり、LVOは魅力的な正極材料の候補となり得ると考えられます。

同研究グループは、ボールミル処理により粒子サイズを調整したLVO粉末を用いて、LLZTO上にLVO厚膜(厚さ5-6µm、相対密度85%)を常温で固化することに成功しました。作製したLVO電極の特性を評価するために、金属リチウムをLLZTOの片端面に圧接し、LVO/LLZTO/Li積層構造を持つ全固体リチウム電池を試作し、50°Cおよび100°Cにおける充放電試験を行いました。

50°Cでは過電圧がかなり大きいものの、約100mAh/gの可逆容量が得られました。測定温度を100°Cに上げると、過電圧の低下と充放電容量の増加が見られ、300mAh/g程度の大きな可逆容量とLVOに特有な充放電曲線が得られました。更に、電流密度を0.012-0.240mA/㎠(LVOあたり15-300mA/g)に相当)の範囲で変えた条件においても、良好なサイクル安定性を確認できました。以上の結果は、LVO厚膜と固体電解質間、および厚膜内のLVO粒子間の結着力が強いためと考えられます。

本研究の成果は、LVOが酸化物全固体電池用高容量正極として適用できる可能性を示すものですが、その一方で、電池性能の向上に向けては更なる研究が必要不可欠です。同研究グループでは、酸化物系全固体電池の低温動作に向けた様々な検討を現在進めています。

本研究の一部は日本学術振興会(JSPS)科学研究費助成事業(基盤研究(C)16K06218および国際共同研究加速基金(国際共同研究強化)16KK0127)の支援の下で実施されたものです。

極低圧下でも火種は消えない？

地球外空間での防災戦略への提言

中村 祐二

豊橋技術科学大学機械工学系の中村教授らの研究チームは、極端に減圧した環境下でも炎を出さない燃焼が持続することを実験的に示すとともに、その理由を解明するための詳細計測に世界で初めて成功しました。低圧環境は宇宙船内や月面基地など、地球外環境の閉鎖空間の標準設定条件として頻繁に用いられるため、本研究成果は近い将来の有人ミッションにおける防災戦略に不可欠となる基盤情報を提供するものです。

線香やたばこのように、空隙を多く持つ固体物質は炎を出さずに緩慢な燃焼を実現することができます。この現象を「くん焼(燻焼．無炎燃焼。スモルダリング)」と呼びます。布団に火種が与えられると、暫く「くすぶり状態」が続き、その後、突然炎が立ち上がって火災が急速に拡がりますが、くん焼とはこの「くすぶり状態(の燃焼)」に相当します。通常、炎を出して燃える場合、ある程度の酸素を遮断すると炎が保てなくなって消えてしまいます。そのためせいぜい大気圧の1/3程度(～30kPa)まで減圧すれば炎は消失します。ところがくん焼の場合、遥かに低い圧力まで消えることはなく、純酸素(酸素100%)条件では、大気圧の1/100程度(～1kPa)でもくすぶりが続きます。くん焼は「しぶとい」ことは経験的に知られているものの、なぜそのような悪条件でも燃え続けられるのかは未解明のままでした。その主な理由は、消える直前での燃焼強度は著しく弱く、温度センサを挿入するとそれがきっかけで燃焼状態を変えてしまうからです。

本研究では、その未解明な問題に挑戦すべく、センサ挿入に伴う熱影響が無視できる条件を抽出し、消える直前の温度分布を高精度で計測することに世界で初めて成功しました。具体的には線香に直径0.2mmの穴をあけ、そこに極細の温度センサ(自作)を埋め込み、消炎限界付近でも定常燃焼させるような安定性の高い空間を設けることでそれを実現しています。

「脆い2mmの線香にドリルで0.2mmの穴を空けること自体、容易ではありませんが、さらにその中に極細の温度センサを埋め込み、試験チャンバ内部に正しく配置することは、表現し難い苦労を伴います。実際、1度の計測準備に相当時間がかかります。温度計測をしないと燃えた・燃えないという事実しかわかりませんが、限界近くの温度計測を成功させたことで、線香のような粒度の細かい材質で構成された多孔質材であっても、発熱部の数mmにある予熱部まで輻射による熱輸送がありそこから周囲空気に対して熱が逃げて消炎に至ること、減圧すると熱の逃げが少なくなり、予熱分はそのまま燃焼促進をもたらす可能性を指摘しました。たかが温度分布、されど温度分布です」と筆頭著者である博士後期課程の山崎拓也は説明します。

研究チームのリーダーである中村祐二教授はこう結びます。「世界に相当数の燃焼研究者がいても、わずか直径2mmの脆い燃焼試料に極細穴を開け、そこに極小センサを埋め込んで消炎状態を直接計測しようとする人はおらず、ましてや、それを実現した人はいない。他の人がやら(れ)ないことに挑戦しない限り、誰よりも先の結果を知ることができない。山崎くんの好奇心、職人ばりの技術、くじけない根性はそれを実現してくれました。宇宙空間での消火対策として、キャビン内のガスを機外に出し、内圧を低下させて消火させる防災対策が検討されていますが、減圧してもくん焼状態を持続していた場合、消えたと思って圧力回復したときに突然炎が立ち上がるという火災の二次被害がもたらされる可能性があります。そのため、くん焼が持続できない条件を明確にすることは、宇宙での防災戦略にとても重要な意味を持ちます。今後、民間主導で宇宙開発が進むと期待されていますが、低圧火災の研究を通じて想定外の事故を未然に防ぐことに貢献したいと考えています。」

くん焼は空隙の中で緩慢に化学反応が進行するとされていますが、実はそれがどのようになっているのか誰も見たことがありません。このように、現象は馴染みがあるものの、実は発熱機構すら十分にわかっていないのが実体です。最近、共同研究先の海外研究チームが「空隙内のごく弱い気相反応が空隙表面での酸化反応を強化する」可能性を数値解析にて予測しました。果たしてこれが正しいか否か、これから米国の共同研究チームと連携して空隙内での反応状況のセンシングを試みる予定です。もちろん、そのようなマイクロメータオーダの空隙の中での反応状況を検知しようとする発想は斬新であり、「誰もやら(れ)ない新たな課題への挑戦」は続きます。

超音波の新現象が社会の安全性向上につながる

構造物の損傷をより早い段階で非破壊的に評価可能に

石井　陽介

豊橋技術科学大学機械工学系の石井陽介助教らの研究グループは、「板の中で二つの超音波を交差させたときに新しい三つ目の超音波が発生する現象」を初めて解明しました。この「三つ目の超音波」の強さは、材料の損傷状態に対して極めて敏感に変化するため、飛行機や発電所といった薄板構造物の非破壊損傷評価への応用が期待されています。特に、従来の技術では検出が難しいとされる材料疲労や損傷の初期段階などを高感度に非破壊検出できる可能性を秘めています。

私たちは、材料が透明でない限りその内部を直接目で見ることができません。しかし超音波を使えば、見えないものも見えるようになります。もし材料内部に傷があれば、そこで超音波が反射します。そのため、傷からの反射波を測定することで、我々は傷の存在を認識することができます。つまり、材料を壊さずに内部を「診る」ことができるのです。これが超音波を用いた非破壊評価の基本原理です。非破壊評価は我々人類の安全を守るうえで必要不可欠な技術であり、評価精度のさらなる向上に向けて今なお世界中で研究がなされています。

現在、非破壊評価の中でも特に問題にされているのが「傷は無いが材料が劣化している状態」の評価です。その代表例として、疲労が挙げられます。人間と同じく材料にも疲労がたまります。たとえ小さな力でもそれを繰り返し受け続けると材料に疲労がたまり、やがて微小な傷が発生します。そして、それが大きな傷へと成長し、最終的に破壊に至ります。高度経済成長期に建設された発電所などの大形構造物には薄板材料が広く使用されており、それらの高経年化に伴う疲労状態の非破壊評価が重要とされています。特に、現在の技術では大きな傷（超音波を反射させる傷）が発生してからでないとそれを検知できないため、微小な傷が発生した段階、さらにはその前段階で疲労状態を精度よく評価できる技術の確立が課題とされています。

そこで、研究グループは超音波の非線形現象である「三波相互作用」に着目しました。これは、板の中で二つの超音波を交差させると三つ目の小さな超音波が発生する現象です。研究グループは数値シミュレーションや理論計算を行い、三波相互作用で生じる三つ目の超音波の発生メカニズムの解明に成功しました。この三つ目の超音波は材料特性の情報を豊富に含むため、この波を測定することで疲労の初期段階（大きな傷が発生する前段階）を感度良く評価できるのでないかと期待されています。

研究チームは、今後実験的検証を行い、最終的に三波相互作用を用いた新しい薄板材料の非破壊評価法を確立したいと考えています。これにより従来は検知できなかった材料のほんのわずかな損傷でさえも感度良く評価できるようになり、発電所や飛行機といった社会的に重要な構造物の安全性・信頼性の向上、つまり社会の安全性向上につながると期待されます。

本研究は、JSPS科研費JP17K14557の助成によって実施されたものです。

揺らぐ分子が細胞膜モデル内で作る集合体

親水性高分子修飾脂質が作る脂質二重膜内ドメイン

手老　龍吾

豊橋技術科学大学の手老准教授らは金沢大学と共同で、親水性高分子鎖を持つ脂質分子が脂質二重膜に作る集合体とその物性を明らかにしました。また、かさ高い高分子鎖の集合体が原子間力顕微鏡で低く観察される反転現象を見出し、その原因を明らかにしました。これらの知見は、感染や免疫反応に関連する糖脂質や膜タンパク質の働きを理解し、そのための実験手法を開発することにつながります。

細胞外部の環境を認識してその情報を細胞内に伝える役目は、細胞の最外層に位置する細胞膜に存在する脂質と膜タンパク質が担っています。これらは細菌やウイルスの感染、免疫反応、神経伝達などに深く関わることから、生物学・医療・創薬分野での重要な研究対象です。外部認識や信号伝達の反応過程においては、糖鎖やイノシトール環などのかさ高い親水基を持つ脂質が細胞膜上で2次元的な集合体を形成することが必要であると考えられています。この集合体は10分子程度までの小さい物はクラスター、より多くの分子が集まり広く成長したものはドメインと呼ばれます。

脂質は生体に由来する両親媒性分子であり、分子内に親水的な部分と疎水的な部分を持ちます。脂質二重膜内でのドメイン形成において疎水性部位での相互作用、例えば炭化水素鎖の相転移や混和性（miscibility）、が主要な役割を果たすことが過去の多くの研究により示されてきました。一方、脂質の親水性部位の相互作用については研究が少なく、不明な点が多いです。特に糖鎖などのかさ高い親水性部位では、親水基が水中で揺らぐことで生じる斥力が生じるため、相互作用が複雑になります。この揺らぎによる斥力は、原子間力顕微鏡（AFM）のように微細な力を検出する計測手法にも影響を及ぼします。

豊橋技術科学大学の手老龍吾准教授のグループは、親水性高分子のポリエチレングリコール（PEG）で修飾した脂質を含む人工脂質二重膜を、蛍光顕微鏡およびAFMを用いて詳細に調べました。その結果、PEG修飾脂質の濃度に依存してクラスターとドメインの2種類の集合体が形成されること、高濃度で現れるドメインにはほとんど流動性が無いことを明らかにしました。これらの集合体は、脂質の疎水性部位ではなく親水性部位の相互作用で形成されていることを示しました。興味深いことに、AFM観察において、かさ高いはずのPEG修飾脂質ドメインは周囲よりも凹んで観察されました。この理由について、手老准教授は金沢大学の福間剛教授と共同実験を行いました。周波数変調型AFM（FM-AFM）を用い、試料と探針の間の力を精密に制御することで、ほとんど力を印加せずに観察すればPEG修飾脂質ドメインが周囲の脂質膜領域よりも高く観察されることを明らかにしました（図1）。印加される力に依存して親水性高分子鎖の揺らぎによる斥力が変化するため、一般的な振幅変調型AFM（AM-AFM）観察の条件では真の立体構造とは反転した像が現れることが示されました（図2）。

「糖脂質の集合状態と機能を調べるための実験手法を確立するために、まずは入手が容易なPEG修飾脂質を用いました。PEG修飾脂質を含む脂質二重膜は、試料調製やAFM観察の最適な条件を見つけるのに苦労しました。特にPEG修飾脂質の濃度を増やすほど凹んだ領域が増えるのは予想とは全く違っていました。何かの間違いではないかと思い、実験を繰り返して再現性を確かめました。直観的には、かさ高い分子が多い場所がAFMで低く見えるとは考えられませんが、高分子の状態やAFMの原理についてよく考えると、実は非常に理にかなっているのです。金沢大学での共同実験で、FM-AFMに切り換えて表面の凹凸が反転した時にはとても興奮して、"やっぱりそうだ!"と叫んでいました。」と筆頭著者である博士後期課程の柿本恭宏（文部科学省博士課程教育リーディングプログラム履修生）は説明します。

研究チームのリーダーである手老龍吾准教授は、「脂質やタンパク質のようにやわらかい分子が水中で揺らぐ姿を捉えるのは、生体分子の機能を分子レベルで理解するために重要なことです。実は、糖脂質を多く含む領域がAM-AFMで低く観察されるという実験結果は、約10年前からいくつかの系で得られていました。親水性部位の揺らぎによる斥力が原因だろうと推測していましたが、この研究で裏付けられました。決定的だったのはやはり、福間教授の最先端のFM-AFM装置を用いた結果（図2）であり、素晴らしい共同研究成果だと思っています。」と話しています。

本研究成果によって得られた親水性高分子鎖の相互作用によるドメイン形成の原理は、細胞膜中の糖脂質などにも共通するものであり、糖脂質や膜タンパク質の集合体形成が関わる細胞認識や信号伝達の仕組みを理解するのに役立つと研究グループは考えています。さらに、かさ高いはずの物が条件によって凹んで見えうる、という実験上の知見は、原子間力顕微鏡で水中の生体分子を観察している多くの研究者にとって有用です。また、PEGはタンパク質などの非特異的吸着を抑制する作用があり、バイオインターフェースやドラッグデリバリーにも用いられています。PEG-richなクラスターおよびドメインの形成と力応答はこれらの分野にも波及効果があると期待されます。

本研究は、日本学術振興会（JSPS）科研費JP15H03768、JP15H00893、科学技術振興機構（JST） CREST （JPMJCR14F3）、JST A-STEPからの支援を受けて行われました。また、筆頭著者の柿本は文部科学省・日本学術振興会の実施する博士課程教育リーディングプログラムの支援を受けました。

Pick Up

TUT Global House is a hub for multicultural events enjoyed by Japanese and international students alike

The TUT Global House is an on campus shared-house style student accommodation facility, where international and Japanese students live together. By living and learning in such a multicultural environment, students can nurture some of the essential skills required by today's globalized society.

Over the past eighteen months, the students who live in Global House have hosted a wide range of multicultural activities. It represents a successful first step on the road towards realizing the vision of TUT as a multicultural global campus.

Reference

- One milestone toward TUT Multicultural Global Campus, TUT Research No.9,May,2017
- News from TUT Multicultural Boarding House http://www.sgu.tut.ac.jp/eng/student-life/

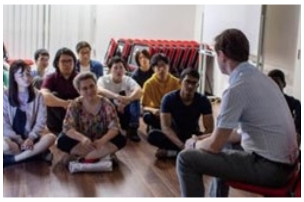
2018 Key activities hosted by the TUT Global House students

BBQ Party: Students in TUT Global House get to know each other better (September 21)

"TUT Summer Festival" hosted by the TUT Global House students (July 15)

TUT EXPO 2018, organized and run in partnership with an executive committee formed by the Global House students (July 6)

A series of "International Understanding Forums" looking at various themes, beginning with "Discover Japan, from the inside and the outside" (June 13)



Welcome Party: TUT Global House starts 2018 in a great spirit of friendship! (April 7)

"TOYOHASHI VEGE-night" : Social gathering with one of Japan's leading agricultural companies in Toyohashi (February 16)

TUT Research

e-Newsletter from Toyohashi University of Technology

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