AMERICAN CERAMIC SOCIETY

bulletin

emerging ceramics & glass technology

JANUARY/FEBRUARY 2023

Glassy solid-state electrolytes for all-solid-state batteries

Optical-grade ceramics | Federal FY23 budget proposals | Meet ACerS president

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January/February 2023 • Vol. 102 No.1

feature articles

Glassy solid-state electrolytes for all-solid-state batteries

Glassy solid-state electrolytes present several advantages over other classes of solid-state electrolytes, but some material and design challenges must be overcome prior to commercialization.

by Jacob Wheaton, Madison Olson, Victor M. Torres III, and Steve W. Martin

With safety and performance, ceramic batteries are in the works

Substantial ceramics research projects are looking to address issues with current lithium-based battery technologies. A selection of recent papers in ACerS journals highlights some of the efforts toward new electrolyte, cathode, and anode materials.

by Jonathon Foreman

Optical-grade ceramics: Historical turning point for the design of optical elements

Though traditionally believed impossible, polycrystalline ceramics can achieve optical properties on par or superior to those of single crystals—and may lead to a historical turning point in the design of optical elements.

by Akio Ikesue

Correction to the December 2022 *ACerS Bulletin*

In the December 2022 *ACerS Bulletin*, the one-inch Orton ad that appeared on pages 99 and 100 was incorrect. The correct one-inch ads are displayed above. The left ad should have appeared on page 99, while the right ad should have appeared on page 110.

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AMERICAN CERAMIC SOCIETY
bulletin

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As seen on *Ceramic Tech Today*...


Credit: Travis Nep Smith, Flickr (CC BY-NC 2.0)

A 'brake' from tradition: Glass fibers improve friction performance and wear rates of train brake shoes

Cast iron blocks and steel fibers are the dominant materials used for brake shoes in the railway industry. Researchers from a Spain-based friction materials manufacturer found that the addition of glass fibers could improve the shoes' friction performance and wear rates.

Read more at www.ceramics.org/train-brake-shoes

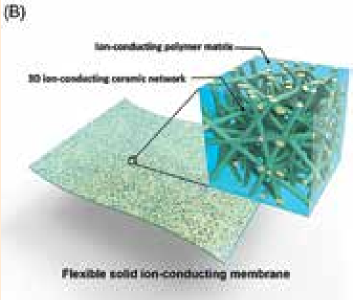
Also see our ACerS journals...

Overview and perspectives of solid electrolytes for sodium batteries
By S. Vasudevan, S. Dwivedi, and P. Balaya
International Journal of Applied Ceramic Technology

Correlating structure with mechanical properties in lithium borophosphate glasses
By P. Liu, R. E. Youngman, L. R. Jensen, M. M. Smedskjaer
International Journal of Applied Glass Science

Fe_2O_3 powder modified with $Ce_{0.6}Mn_{0.3}Fe_{0.1}O_2$ and Cr_2O_3 prepared by spray pyrolysis method for rechargeable Fe–air cell
By T. Ishihara, H. Kim, Y. Inoishi, and J. Matsuda
Journal of the American Ceramic Society

Electronic and ionic properties of sintered cathode of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NCM622)
By K. Waetzig, J. Huettl, D. Goedeke, et al.
International Journal of Ceramic Engineering & Science



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Read more at www.ceramics.org/journals

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ACSBA7, Vol. 102, No. 1, pp. 1–48. All feature articles are covered in Current Contents.

news & trends

Federal budget 2023—Targets in the CHIPS and Science Act loom over budget negotiations

By Lisa McDonald

In a familiar occurrence, the United States fiscal year 2023 began with most science programs operating on stopgap funding that extends previous budget levels until Congress passes appropriations legislation for the full year.

However, unlike the last fiscal year, looming over budget negotiations is the CHIPS and Science Act, which sets budget targets for the National Science Foundation, Department of Energy Office of Science, and National Institute of Standards and Technology. These budget targets, which have bipartisan buy-in, are much higher than the current proposed appropriations. Congressional leaders have offered few hints as to whether they will press to meet the targets quickly, defer any increases to fiscal year 2024, or even abandon the targets altogether.

Several programs outlined in the CHIPS and Science Act are not dependent on the appropriations process because they were funded through other pathways, namely the Infrastructure Investment and Jobs Act, Inflation Reduction Act, and the semiconductor provisions of the CHIPS and Science Act.

A few highlights from the proposals

Department of Defense

Following a string of budget increases, funding across the Department of Defense's research, development, test, and evaluation (RDT&E) accounts increased 11% in fiscal year 2022 to a new record of nearly $123 billion. That is nearly $50 billion more than those accounts stood just five years earlier.

For fiscal year 2023, the House and Senate proposed increases of 10% and 12%, respectively, for the RDT&E budget. However, appropriators split ways in their proposals for funding the Department of Defense's Science and Technology portfolio under RDT&E, with the House proposing a 3% cut and the Senate a 9% increase.

National Science Foundation

While House appropriators propose increasing the current $8.8 billion budget of the National Science Foundation by 9%, Senate appropriators propose a 17% increase to $10.3 billion, nearly matching the 19% increase requested by the White House.

A significant fraction of the budget would go toward funding NSF's newest directorate, the Directorate for Technology, Innovation, and Partnerships (TIP), which was officially established in March 2022. The White House seeks $880 million for the TIP Directorate in fiscal year 2023, with roughly 40% of the total coming from existing programs transferred into the directorate.

Department of Energy

The White House requested to increase DOE's budget from $44.9 billion to $48.2 billion. Both the House and Senate proposals are in line with the request, with recommended increases bringing the total budget to $48.2 billion and $49.3 billion, respectively.

Office of Science: House and Senate appropriators propose raising the DOE Office of Science budget 7% and 8%, respectively, to $8.0 billion and $8.1 bil-

lion. These proposals are notably above the White House request to increase the budget by 4% to $7.8 billion, which supporters in Congress say fall short of the targets laid out in the CHIPS and Science Act. The Office of Science already received an influx of more than $1.5 billion from the Inflation Reduction Act for labs that it oversees.

Applied energy: Like last year, the White House again requests large increases for some applied energy programs, especially those in the Office of Energy Efficiency and Renewable Energy (increase of 54%). However, unlike last year, the White House also seeks a major expansion of the Advanced Research Projects Agency–Energy and proposes that it house efforts previously envisioned for a separate climate-oriented ARPA, which Congress ultimately declined to create. The White House and Congress both seek to significantly increase the budget of the new Office of Clean Energy Demonstrations, which was launched in December 2021 to support a burgeoning portfolio of large-scale technology projects funded by the Infrastructure Investment and Jobs Act.

National Nuclear Security Administration: The NNSA budget would slightly increase from the current $20.7 billion under the various spending proposals for fiscal year 2023, with the White House and House proposing increases to just over $21 billion and the Senate proposing an increase to $22.1 billion. A goal for the White House is to restore the Stockpile Responsiveness Program's budget to $69 million. This program, which focuses on maintenance of warheads rather than design and production, was cut from $70 million to $50 million in fiscal year 2022.

National Institute of Standards and Technology

House and Senate appropriators propose increasing the $1.2 billion annual budget of the National Institute of Standards and Technology by 20% and 38%, respectively. The increases are in addition to billions of dollars for semiconductor R&D funded through the CHIPS and Science Act, which will be provided over several years as a mandatory appropriation outside of the annual budget process.

During fiscal year 2022, Congress brought back earmarks after a decade-long moratorium. This change resulted in NIST's budget becoming a repository for earmarked projects unrelated to the agency's mission, creating an apparent increase that actually left funding almost flat for its core activities. NIST will likely absorb further earmarks in fiscal year 2023, but the proposed budgets would leave core programs with a sizeable increase.

National Aeronautics and Space Administration

House and Senate proposals for NASA's fiscal year 2023 science budget are in near agreement with the White House's proposal to increase the budget from $7.61 billion to $7.99 billion.

Among science agencies, the picture for NASA's budget is relatively straightforward. However, there is some question about whether Congress will follow the White House's plan to control the multiyear expansion of NASA's planetary science program. The White House proposed delaying the Near Earth Object Surveyor mission, but asteroid detection has strong support in Congress and increased salience in view of NASA's recent successful mission to alter the dynamics of a double-asteroid system.

National Institutes of Health

Senate appropriators propose a 4% increase to $47.96 billion for the National Institutes of Health while the House proposes an even larger boost of 9% to $50.21 billion.

While the House and Senate proposals are relatively in line with the White House, they diverge regarding the recently established Advanced Research Projects Agency for Health (ARPA–H). In fiscal year 2022, House and Senate appropriators initially put forward spending proposals that made funding for ARPA–H contingent on Congress passing separate legislation establishing the agency. While several such bills were introduced, none were passed by either chamber. So, Congress ultimately provided a smaller sum of $1 billion to get ARPA–H started as debate continues over authorization.

One sticking point is whether to establish ARPA–H within NIH or as an independent agency in the Department of Health and Human Services (HHS). The White House strongly advocates housing ARPA–H within NIH to take advantage of NIH's administrative capacity, but some members of Congress and other advocates argue that administrative independence is necessary to fostering a distinctive culture of risk-taking innovation.

In its appropriation, Congress skirted the issue by granting HHS authority to transfer ARPA–H funds to NIH or another agency within the department. On March 31, 2022, HHS secretary Xavier Becerra announced he would transfer the funds to NIH but that the ARPA–H director will report directly to him.

For more information on the federal budget, visit the American Institute of Physics FYI "Budget Tracker" at https://www.aip.org/fyi/federal-science-budget-tracker. ■

Table 1. FY23 budget proposals ($ in millions)

	DOD S&T total	NSF	DOE Office of Science	NIST	NASA (science)	NIH
FY22 appropriation	18,892	8,838	7,475	1,230	7,614	45,959
White House	16,455 (-13%)	10,492 (19%)	7,799 (4%)	1,468 (19%)	7,988 (5%)	48,957 (7%)
House	18,324 (-3%)	9,631 (9%)	8,000 (7%)	1,474 (20%)	7,905 (4%)	50,209 (9%)
Senate	20,532 (9%)	10,338 (17%)	8,100 (8%)	1,696 (38%)	8,046 (6%)	47,959 (4%)

business and market view

A regular column featuring excerpts from BCC Research reports on industry sectors involving the ceramic and glass industry.

Battery recycling: Global markets

By BCC Publishing Staff

The global battery recycling market was valued at $9.6 billion in 2021 and is estimated to grow at a compound annual growth rate (CAGR) of 7.4% to reach $14.3 billion by 2027.

There are four types of battery recycling methods.

- **Mechanical treatments** involve crushing and physically separating the components and recovering the black matter, which contains important metals such as cobalt, nickel, manganese, and lithium.
- **Pyrometallurgical procedures** treat spent batteries at high temperatures without mechanical pretreatment, as batteries are put directly into the furnace. This recycling method recovers cobalt, nickel, copper, and iron as metal alloys. Aluminum, manganese, and lithium are all lost in the slag, while plastic and other organic materials are burnt.
- **Hydrometallurgical processes** include mechanical pretreatment and metal recovery from black material via leaching, precipitation, solvent extraction, ion-exchange resins, and bioleaching. Hydrometallurgical methods enable the high-purity recovery of lithium, along with cobalt, nickel, copper, and iron.
- **Thermal pretreatment followed by hydrometallurgical processes** is used to remove organic compounds and graphite that impede the recycling process's leaching and solid–liquid separation phases.

Most battery types can be recycled. However, some batteries are recycled more frequently than others, such as button cells and lead-acid car batteries (almost 90% are recycled because of the value and toxicity of their chemicals). In contrast, currently less than 5% of used lithium-ion batteries get recycled, with the majority ending up in landfills.

The low rates of lithium-ion battery recycling are concerning given the rapid growth in demand for electric vehicles, which rely on this kind of battery. A deluge of retired electric vehicle batteries is expected over the next decade. A few companies already began recycling lithium-ion batteries on a limited scale (Table 1).

About the author

BCC Publishing Staff provides comprehensive analyses of global market sizing, forecasting, and industry intelligence, covering markets where advances in science and technology are improving the quality, standard, and sustainability of businesses, economies, and lives. Contact the staff at Helia.Jalili@bccresearch.com.

Resource

BCC Publishing Staff, "Battery recycling: Global markets" BCC Research Report AVM233A, September 2022. www.bccresearch.com.

Further reading

BCC Publishing Staff, "Electric Vehicle Charging: Infrastructure and Global Markets" BCC Research Report FCB045B, November 2022. www.bccresearch.com. ■

Table 1. Worldwide lithium-ion battery recycling projects

Company	Description
American Battery Technology	In December 2021, as part of its focus on mining, extracting, and recycling lithium and other battery materials, the company said it intends to open a battery-metals recycling plant in Incline Village, Nevada, with a capacity of 20,000 metric tons of scrap materials and end-of-life batteries per year.
Brunp Recycling Technology Co.	In late 2020, Brunp, Asia's largest recycler of lithium-ion batteries, said its new plant in China's Hunan region can recycle 100,000 metric tons of lithium-ion battery trash annually.
Ganfeng Lithium	In 2021, this Chinese lithium-ion battery manufacturer said it aims to develop a battery recycling operation in Mexico to sell minerals to electric vehicle manufacturers and suppliers, including Tesla and LG Chem of South Korea.
Green Li-ion	In early 2021, this Singapore start-up opened its second recycling factory, focusing on recycling "99.9% pure" lithium-ion battery cathodes.
Li-Cycle	In January 2021, this Canadian company began constructing a $175 million recycling factory in Rochester, New York. When completed, it will be the largest lithium-ion battery resource recovery facility in North America.
Northvolt	Founded in 2016 by former Tesla executives, this Swedish battery firm already operates an experimental recycling plant and is partnering with aluminum producer Hydro to establish an 8,000-metric-ton-per-year recycling factory in Norway in 2021.
SMCC Recycling	A joint venture between South Korea's SungEel HiTech Co. and Metallica Commodities Corp., the business hopes to establish a 5,000-metric-ton lithium-ion battery recycling plant in Endicott, New York, in 2021.
Tesla	In Tesla's 2021 Impact Report, it released an update on its battery recycling effort. In 2021, Tesla increased its battery material recycling to 1,500 tons of nickel, 300 tons of copper, and 200 tons of cobalt.
Umicore	In June 2022, Umicore announced that it wants to build the world's largest battery recycling facility. The $525 million plant, to be built somewhere in Europe, would be capable of processing 150,000 metric tons per year of battery materials.

Each month, we will be highlighting articles from different areas of glass science in the online blog *Ceramic Tech Today.*

International Year of Glass comes to a spectacular conclusion

By Eileen De Guire

Alicia Durán, IYOG chair (left of center) on the IYOG reception red carpet with IYOG sponsors and participants.

What a year this has been for the global glass community!

Glass scientists, engineers, artists, museum curators, educators, and so many others around the world came together to celebrate glass and the many ways it enhances human life during this International Year of Glass.

IYOG held its Closing Conference in Tokyo, Japan, at the University of Tokyo, Dec. 8–9, 2022. The two-day conference mirrored February's opening ceremony and conference in Geneva, Switzerland, with presentations from academia, industry, and cultural organizations. In both cases, the talks were forward-looking, focused on what the future holds. This theme has resonated throughout the year, hinting that glass has much yet to reveal about its structure, properties, applications, and artistic expression.

A closing debriefing was held at the United Nations in New York City, Dec. 13–14, 2022, and IYOG leaders gave a multimedia presentation highlighting the best of the many hundreds of IYOG activities in every continent. The celebration began with a reception on December 13 followed by a debriefing at the UN Headquarters on December 14.

▲ L. David Pye (center, ACerS DLM) had the original vision for an International Year of Glass and helped craft the proposal to the United Nations for the Spanish Mission to present. The proposal was sponsored by Spain, Egypt, and Turkey, and adopted unanimously by the full UN delegation. With Pye are Erik Muijsenberg (Glass Service, Czechia) and Kathleen Richardson (ACerS DLM, University of Central Florida).

Participants gather around the *Wildfire* sculpture after the debriefing event. About 120 people from around the globe participated.

Katy Devlin (center, NGA *Glass Magazine*) led a panel discussion on what the future holds for glass. Panelists included Teresa Medici, Cultural Department of the Regional Government of Lombardy, Italy; Urmilla Jokhu-Sowell, National Glass Association, USA; Andrew Page, *Glass: The Urban Glass Art Quarterly*; Himanshu Jain, Lehigh University; Bertrand Cazes, Glass for Europe; and Erik Muijensenberg, Glass Service, a.s., Czechia.

Wildfire glass sculpture on display through December 2022 outside the UN Headquarters building. From left: Kathy Jordan (The American Glass Guild), Natalie Tyler (sculpture artist), Mark Mecklenborg (ACerS), Scott Cooper (Owens-Illinois), Manoj Choudhary (IYOG North America chair); Beth Dickey (Carnegie Melon).

▲ Alicia Durán welcomes 120 glass enthusiasts to the closing debriefing. The Spanish ambassador, Augustín Santos Maraver, is to her right, and the plenary speaker, Fernando Vallardares, sits left. Vallardares is research professor at CSIC in Spain and a leading scientist in understanding the impact of human activity on ecosystems and climate change.

Artist Natalie Tyler, who lives and works in the Berkshire Mountains of Massachusetts, loaned her sculpture *Wildfire* for display outside the UN during the month of December. The sculpture evokes the impact of climate change on the environment, which dovetails with the UN's 17 strategic development goals and the IYOG.

It has been an extraordinary year that brought diverse, global communities together and built new synergies. Already, many follow-up activities and collaborations are in the works, powered by the momentum of IYOG connections begun in 2022.

IYOG chair Alicia Durán says it best—**"Goodbye IYOG. Welcome to the Age of Glass!"** ■

▲ Discovering synergies between glass arts and glass sciences, technology, and manufacturing was one highlight of IYOG, and collaboration has begun on follow-up activities. From left: Megan McElfresh Augspurger, Stained Glass Association of America; Natalie Tyler and Larry Sibrack, Art Alliance for Contemporary Glass.

A toast to glass!

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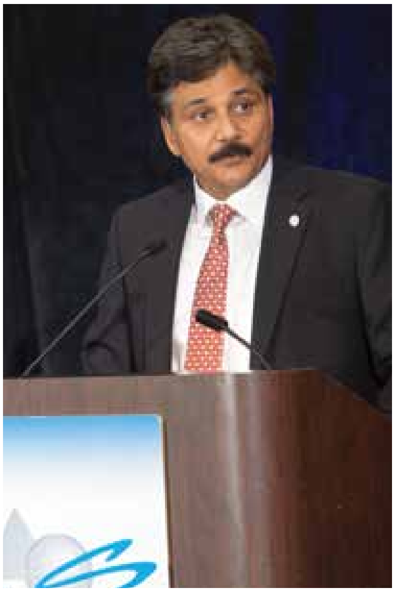

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Colorado School of Mines to launch ceramic engineering degree

Colorado School of Mines announced plans to launch a new bachelor's degree in ceramic engineering next fall. With the new degree offering, Mines will be home to one of only three ABET-accredited ceramic engineering programs at the undergraduate level in the United States. Alfred University and Missouri University of Science & Technology also offer bachelor's degrees in the discipline.

"The specialty in ceramics has been lost in the U.S. with a couple of exceptions, but it is definitely needed again," says Brian Gorman, professor of metallurgical and materials engineering at Mines. "There is a huge need for ceramic engineers, and demand is significantly outpacing supply."

Founded in 1874 with specialties in mining and metallurgy, Mines' scope and mission expanded over the years to meet the needs of industry and society. The ceramic engineering program at Mines will build on the university's long-standing expertise in materials science and engineering, as well as Mines' cutting-edge ceramics research and facilities and strong relationships with industry, including CoorsTek, which is also headquartered in Golden, Colo., and endows a graduate fellowship in ceramics at Mines.

Developed in consultation and partnership with industry, the Mines program will have a strong focus on the newer technical ceramics and glass, but the knowledge and experience gained by students in the program will prepare them for careers in both technical and traditional ceramics.

Students will receive hands-on training in ceramic processing; sintering; glass science; and mechanical, electrical, and thermal properties. Four core laboratory classes starting in a student's second year will ensure robust hands-on experience with this family of materials. Students will also have access to innovative undergraduate research opportunities and makerspaces, including Mines' on-campus glass hot shop.

"This new degree program fits well within our mission to train students for the industrial workforce," says Ivar Reimanis, professor and head of the Metallurgical and Materials Engineering Department at Mines. "Our current hands-on, laboratory-based curriculum produces graduates who know how to make things, and ceramic engineering will dovetail nicely with our existing metallurgy-focused program and strong connections to materials manufacturing. Targeted industries include semiconductors and electronics, defense, renewable and traditional energy, healthcare, household goods, automotive and aerospace, and many more. We are looking for new opportunities to engage the ceramics industry."

For more information about Mines' bachelor of science in ceramic engineering, contact Brian Gorman at bgorman@mines.edu. ■

Names in the news

Members—Would you like to be included in the Bulletin's Names in the News? Please send a current head shot along with the link to the article to mmartin@ceramics.org. The deadline is the 30th of each month.

Santokh Badesha, adjunct professor for innovation at Purdue University Elmore Family School of Electrical and Computer Engineering, was awarded the Mountbatten Medal from The Institution of Engineering and Technology. ■

Korea Chapter welcomes new leadership

Congratulations and welcome to the new leadership of the Korea Chapter!

Chair: **Hui-Suk Yun**, Korea Institute of Materials Science
Secretary: **Miso Kim**, Sungkyunkwan University
Advisory Board: **Weon-Ju Kim**, Korea Atomic Energy Research Institute
Young-Wook Kim, University of Seoul ■

Volunteer spotlight

ACerS Volunteer Spotlight profiles a member who demonstrates outstanding service to the Society.

Rodney Trice works in the School of Materials Engineering at Purdue University and has focused on many fundamental and applied research topics over the last 25 years. He currently studies ceramic processing topics on hypersonic-related materials including high-temperature high-emissivity coatings, processing of ceramic infrared and radiofrequency windows, additive manufacture of C/C composites, direct ink write of carbon fiber/SiC composites, digital light projection of ultrahigh-temperature ceramics, and powder-processing schemes to fabricate ceramics into complex shapes.

His receives support from ONR, ARPA-E, BETO, Draper Labs, AFRL, MDA, and industrial sources. He manages ceramic-related manuscript submissions to *Additive Manufacturing and Materials Research Letters* and is the Ceramic Thrust Lead for the recently funded Hypersonic Advanced Manufacturing Technology Center.

Trice is a Fellow of The American Ceramic Society and has volunteered in the Society for more than 22 years at many different levels. He is a member of both the Basic Science Division and the Engineering Ceramics Division. Trice recently served four years as chair of the Meetings Committee, where he led a subgroup of this committee to establish guidelines for the new travel scholarship fund that supports graduate and undergraduate attendance at MS&T.

We extend our deep appreciation to Trice for his service to our Society! ■

Carolinas Section plans Annual Meeting in March 2023

Sponsored by The American Ceramic Society's Carolinas Section and the Department of MSE at Clemson.

Theme: "Advances in Processing and Performance of Functional Ceramics"

When: March 30, 2023, 1–7 p.m.

Where: Advanced Materials Research Lab, Clemson University, Clemson, S.C.

Agenda includes speakers, posters, Section business meeting, laboratory tours, and networking reception.

Free if registered by **Jan. 31, 2023**. Visit the Carolinas Section webpage at https://ceramics.org/members/member-communities/sections/carolinas-section for more information and to register. ■

IN MEMORIAM

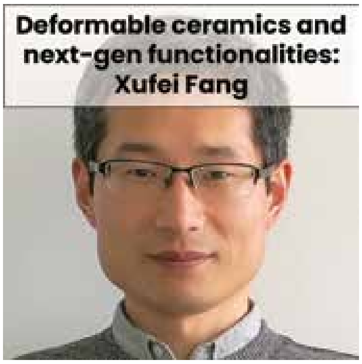
Hermann Rittler

Some detailed obituaries can also be found on the ACerS website, www.ceramics.org/in-memoriam.

more SOCIETY DIVISION SECTION CHAPTER NEWS

Ceramic Tech Chat: Xufei Fang

Hosted by ACerS Bulletin editors, Ceramic Tech Chat talks with ACerS members to learn about their unique and personal stories of how they found their way to careers in ceramics. New episodes publish the second Wednesday of each month.



In the November episode of Ceramic Tech Chat, Xufei Fang, junior group leader in the nonmetallic inorganic materials research group at the Technical University of Darmstadt, shares how his background in metals positioned him to pursue the study of dislocations in ceramics, reviews his current research in the TU Darmstadt group led by Jürgen Rödel, and describes initiatives underway to educate the larger ceramics community about this research field. Check out a preview from his episode, which features Fang describing why it is so much harder to plastically deform ceramics than it is metals.

"Very often in ceramics, because of the conventional high-temperature sintering, we do not have many dislocations to start with compared to metals. … That means if we wanted to plastically deform ceramic materials, we have to overcome the nucleation barrier, which very often is very high because of the strong ionic and covalent bonding. The second difference there is the mobility.

AWARDS AND DEADLINES

Last call for 2022 award nominations

Nominations for most ACerS Society and several Division awards are due **Jan. 15, 2023**. Nominations are encouraged for deserving candidates from groups that have been underrepresented in ACerS awards relative to their participation in the Society, including women, underrepresented minorities, industry scientists and engineers, and international members.

For more information, visit www.ceramics.org/awards or contact Erica Zimmerman at ezimmerman@ceramics.org. ■

ECD best poster awardees from ICACC 2022

The ECD announced the Best Poster awardees from the ICACC 2022 virtual meeting held last January. The awardees will be honored during the plenary session at ICACC 2023 in Daytona Beach, Fla. Congratulations to the authors of these award-winning posters!

2022 Best Poster Awards

1st place

Effect of eutectic reaction on RE-silicate formation by surface modification of SiC–**Hiroyuki Sakai et al.**, Kyoto University, Japan

2nd place

Self-supporting carbon-rich SiOC ceramic electrodes for lithium-ion batteries and aqueous supercapacitors–**Shakir Bin Mujib et al.**, Kansas State University

3rd place (tie)

Design and development of biomass-based scaffolds for multifunctional applications–**Negin Zia Mahmoodi et al.**, University of North Dakota

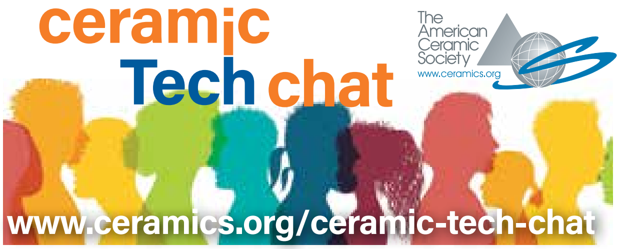
Design of electrode structure by utilizing one-dimensional carbon derived microspheres for high-areal-capacity lithium-sulfur batteries–**Sung Jin Yang et al.**, Korea Advanced Institute of Science and Technology, South Korea

FOR MORE INFORMATION:

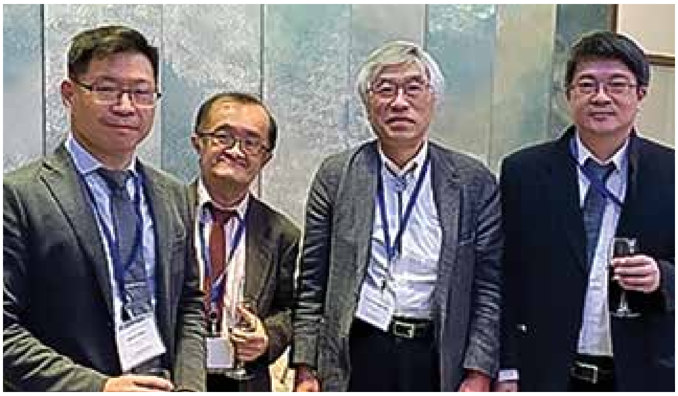
ceramics.org/members/awards

So basically, we would like to move the dislocations easily if we wanted to have a good ductile ceramic material, as in the case of metals. But the case again is because of the strong bonding, very often we have very limited mobility in ceramic materials. Another interesting feature I would say is because of the ionic and covalent bonding, the dislocations in ceramic materials can carry charge in the dislocation cores. And this also is a huge difference compared to the dislocations in metals."

Listen to Fang's whole interview—and all our other Ceramic Tech Chat episodes—at http://ceramictechchat.ceramics.org/974767. ■



Members attend dual conference in Japan



ACerS members Wei-Hsing Tuan, National Taiwan University (second from left) and Nobuhito Imanaka, FACerS, Osaka University (second from right) attended Japan's 7th International Conference on the Characterization and Control of Interfaces for the High-Quality Advanced Materials and the 57th Summer Symposium on Powder Technology in November 2022.

Trustee awards

Design and development of hydroxyapatite-based scaffolds from bioplastics—**Mackenzie Geigle et al.**, University of North Dakota

Fabrication of fiber-reinforced polymer ceramic composites by wet electrospinning—**Yunzhi Xu et al.**, Northwestern University, Evanston, Ill.

Near-infrared scintillation properties of Nd-doped $Bi_4Ge_3O_{12}$ *single crystals*—**Kai Okazaki et al.**, Nara Institute of Science and Technology, Japan

Thixotropic, shear thinning and Bingham fluid properties of geopolymer pastes—**Allison Brandvold et al.**, University of Illinois at Urbana-Champaign

Effects of aliovalent substitution in argyrodite $Li_{6+x}P_{1-x}Si_xS_5Cl$ *solid electrolytes for all-solid-state batteries*—**Jung Hwan Song et al.**, Korea Advanced Institute of Science and Technology, South Korea ■

more AWARDS

Nomination deadline: Jan. 15, 2023

Society awards will be presented at ACerS Annual Awards Banquet at MS&T in October 2023.

Contact: Erica Zimmerman | ezimmerman@ceramics.org | 614.794.5821

Society Awards	Description
Distinguished Life Membership	ACerS' highest honor, given in recognition of a member's contribution to the ceramics profession. Nominees must be current members who have attained professional eminence because of their achievements in the ceramic arts or sciences, service to the Society, or productive scholarship.
Fellows	Recognizes outstanding contributions to the ceramic arts or sciences through broad and productive scholarship in ceramic science and technology, by conspicuous achievement in ceramic industry, or by outstanding service to the Society.
W. David Kingery Award	Recognizes distinguished lifelong achievements involving multi-disciplinary and global contributions to ceramic technology, science, education, and art.
John Jeppson Award	Recognizes distinguished scientific, technical, or engineering achievements in ceramics.
The European Ceramic Society-American Ceramic Society Joint Award	Recognizes individuals who foster international cooperation between The American Ceramic Society and the European Ceramic Society, in demonstration of both organizations' commitment to work together to better serve the international ceramics community.
The Rishi Raj Medal for Innovation and Commercialization Award	Recognizes one individual whose innovation lies at the cusp of commercialization in a field related, at least in part, to ceramics and glass.
Medal for Leadership in the Advancement of Ceramic Technology	Recognizes individuals who, through leadership and vision in an executive role, made significant contributions to the success of their organization and in turn significantly expanded the frontiers of the ceramics industry.
Corporate Environmental Achievement Award	Recognizes an outstanding environmental achievement made by an ACerS corporate member in the field of ceramics.
Corporate Technical Achievement Award	Recognizes an outstanding technical achievement made by an ACerS corporate member in the field of ceramics.
Richard M. Fulrath Awards	Promote technical and personal friendships between Japanese and American ceramic engineers and scientists, as well as recognize individuals for excellence in research and development of ceramic sciences and materials. Nominees must be 45 or younger at the time of award presentation.
Karl Schwartzwalder-Professional Achievement in Ceramic Engineering Award	Recognizes an outstanding young ceramic engineer whose achievements are significant to the profession. A nominee must be between 21 and 40 years of age, and must be a member of EPDC and ACerS.
Robert L. Coble Award for Young Scholars	Recognizes an outstanding scientist who is conducting research in academia, industry, or at a government laboratory. Candidates must be an ACerS member and must be 35 years old or younger.
Du-Co Ceramics Young Professional Award	A young professional member of ACerS who demonstrates exceptional leadership and service to ACerS.
Frontiers of Science and Society - Rustum Roy Lecture	Given each year by a nationally or internationally recognized individual in the area of science, industry, or government. Generally the committee selects the lecturer, but suggestions from membership are invited.
Edward Orton, Jr. Memorial Lecturer	Selection is based on scholarly attainments in ceramics or a related field. Generally the committee selects the lecturer, but suggestions from membership are invited.
The Navrotsky Award for Experimental Thermodynamics of Solids	Awarded biennially to an author who made the most innovative contribution to experimental thermodynamics of solids technical literature during the two calendar years prior to selection.
Ross Coffin Purdy Award	Given to the author(s) who made the most valuable contribution to ceramic technical literature during the calendar year two years prior to the year of selection. The 2023 Purdy award is for the best paper published in 2021.
Richard and Patricia Spriggs Phase Equilibria Award	Given to the author(s) who made the most valuable contribution to phase stability relationships in ceramic-based systems literature during the previous calendar year (2022).
Morgan Medal and Global Distinguished Doctoral Dissertation Award	Recognizes a distinguished doctoral dissertation in the ceramics and glass discipline.

2021–2022 Global Ambassador awardees

The Global Ambassador Program recognizes dedicated ACerS volunteers worldwide who demonstrate exceptional leadership and/or service that benefits the Society, its members, and the global ceramics and glass community.

ACerS 2021–2022 president Elizabeth Dickey presented the Global Ambassador Award to the following volunteers.

Michelle Korwin-Edson, Owens Corning
Irene Peterson, Corning Inc.
Armin Feldhoff, Leibniz University Hannover, Germany
Kathryn Goetschius, Corning Inc.
Josh Pelletier, Imerys
Zhaoju Yu, Xiamen University, China
Olivier Guillon, Institute of Energy and Climate Research: Materials Synthesis and Processing, Germany
Jon Hinton, Orton Ceramic Foundation
Mark Losego, Georgia Institute of Technology
Rishabh Kundu, Technische Universität Darmstadt, Germany
Glenn Gates, Johns Hopkins, Germany
Denise Silva, Oak Ridge National Laboratory ■

STUDENTS AND OUTREACH

Attention students and young professionals: Going to EMA23 or ICACC23? Check out these events offered especially for you!

Make sure to attend the student and young professional activities being offered at the Electronic Materials and Applications (EMA 2023) conference and the 47th International Conference and Expo on Advanced Ceramics and Composites (ICACC 2023).

EMA 2023 student events

- Industry panel for students and young professionals (organized by ACerS PCSA), Wednesday, Jan. 18, 12:30–2 p.m. Preregistration is required.
- Student and young professional networking mixer, Thursday, Jan. 19, 5:30–6:30 p.m.

Register for EMA student events at https://ceramics.org/student-events-ema23

ICACC 2023 student events

- Journal Publishing Workshop, presented by Ricardo Castro, editor-in-chief of the *International Journal of Ceramic Engineering Science*. Sunday, Jan. 22, 4–5 p.m. Register for the workshop at https://ceramics.org/event-subpage/journal-publishing-workshops.
- Industry panel for students and young professionals (organized by ACerS PCSA), Monday, Jan. 23, 12–1:20 p.m. Preregistration is required.
- Student and young professional networking mixer (co-sponsored by ACerS YPN and ECerS YCN), Monday, Jan. 23, 7:30–9 p.m.
- Shot Glass Competition (organized by ACerS PCSA), Tuesday, Jan. 24, 6:45–8 p.m.

Register for ICACC student events at https://ceramics.org/student-events-icacc23

Share your comments, photos, videos, selfies, and other shareworthy content on Facebook or Twitter using the hashtag #ICACC23, and you will be entered to win a $50 gift card! We will be giving away a total of three gifts cards, one per day, from Jan. 23–25, 2023. ■

FOR MORE INFORMATION:

www.ceramics.org/students

more STUDENTS AND OUTREACH

ASSOCIATE MEMBERSHIP

ACers offers complimentary Associate membership to students who are completing their education, and to young professionals who have never before been an ACerS member.

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Collaborate and inspire with ACerS through a free Associate membership!

Are you transitioning from the hallowed halls of university to the corporate "jungle"? If you just completed your education, The American Ceramic Society can help you succeed by starting you off with a complimentary Associate membership.

Additionally, your second year of Associate membership will be offered to you for only $40. Associate membership is also available to those who have not previously held ACerS Individual membership.

Associate members have access to leadership development programs, special networking receptions, volunteer opportunities, and more.

Also, see current featured jobs at careers.ceramics.org. Post your resume and check out current openings.

Apply for Associate membership at ceramics.org/associate. ■

CERAMICANDGLASSINDUSTRY FOUNDATION

ScholarSHPE recipient is making her medical research dreams come true

While many children with an itch for hands-on activities reach for LEGOs or Lincoln Logs, a young Lilly Garcia often opted for building IKEA furniture, according to her mom Chris Garcia. Originally from Arizona, Garcia grew up with a competitive spirit and a high-performance mindset—which could be why she grew up building furniture instead of little log houses.

Now at age 20, Garcia uses her hands-on mindset to study chemical engineering as a rising junior at the University of California, Los Angeles.

"When I chose my major, I knew I wanted to end up doing medical research," Garcia says. "I didn't know how to really get there, and I knew that chemical engineering was really broad. Everyone tells you if you get a degree in chemical engineering, you could do anything, because people just want your problem-solving skills and your critical thinking skills."

She is involved in the Society of Latinx Engineers and Scientists, which is the university's student chapter of the Society of Hispanic Professional Engineers (SHPE). Recently, Garcia received a scholarship through the CGIF and ACerS in conjunction with SHPE.

Although she pursues a dream of conducting medical research someday, Garcia approaches her academic career with a calm focus and strong will.

"I like the things I'm doing," she says. "I think maybe that's what motivates me to keep doing all these things … It just doesn't feel like work, it feels interesting and fun."

Aside from building the occasional IKEA piece, Garcia also grew up an avid reader and indulged in math puzzles. While it was not always clear that Garcia would pursue chemical engineering specifically, it helps that there is already one in the family: her older brother.

"I think she could see that this degree was very flexible and would allow her to fine tune her academic interests down the line, in terms of picking a career as a chemical engineer," Chris, Garcia's mom, says.

After Garcia graduates from UCLA, she plans to narrow down a specific area of medicine to pursue as she decides her future plans.

"I don't know if that'll be, go to graduate school directly after my undergrad or maybe go into industry, find a niche that I like and go back and study more so I can be an expert in drug delivery, or be an expert in molecular interactions," Garcia says. "It's very broad still."

For now, Garcia plans to stay open minded and feels thankful to have the support of a scholarship as she completes her undergraduate journey.

"I really enjoy the feeling of support, that someone chose you," she says. "'You seem to have promise, you have potential, we want to support you.' And that's what I feel like is helping me (and) pushing me forward." ■

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Meet ACerS president Sanjay Mathur

By Eileen De Guire


Credit: ACerS

“My personal journey has taught me that things connect to each other,” says ACerS president Sanjay Mathur.

That journey began as a child in India, where he credits his grandmother for his first introduction to ceramics. She would take him to visit potters who moved from town to town creating ceramic artefacts, usually in conjunction with special festivals, such as Diwali, the Indian Festival of Light. As a boy, he was intrigued to realize that through potters, “human fingers do additive manufacturing.”

He was educated in India, ultimately earning a Ph.D. in inorganic chemistry. After a brief stint working at a pharmaceutical company, an Alexander von Humboldt Fellowship took him to Saarland University in Germany. He completed his Habilitation at Saarland University in 2004, and in 2008 he joined the faculty of the University of Cologne in Germany. Today, he chairs the Department of Inorganic and Materials Chemistry and is director of the Institute of Inorganic and Materials Chemistry. His research group grew to 40–50 students, plus a corps of group leaders that guide day-to-day research.

Mathur’s research program focuses on functionalization of nanocrystalline powders for energy and drug delivery applications. He views chemistry as fundamentally intrinsic to materials development and performance enhancement.

“I think from that viewpoint, I’ve stayed very, very loyal to my training as a sol-gel chemist, and I often use that path to develop new materials. … that bridge of connecting small molecules to an extended material like a solid nanoparticle or a macroparticle is a hybrid interface where a lot of new properties are generated,” he says. (Mathur describes his research program in detail in the December 2023 episode of Ceramic Tech Chat, accessible at https://ceramics.org/publications-resources/ceramic-tech-chat.)

He finds his career path as a university educator highly rewarding and a source of happiness.

“All those who are able to interact with younger minds, and these minds are getting younger every year, find that it’s a recalibration process. It keeps you mentally fit, first thing. And second thing, when you see how your students or your mentees are succeeding, it gives you such a satisfying feeling that that you cannot gain or get from other professional accolades,” he says.

Mathur first encountered the Society when he heard about the “Cocoa Beach” meeting, and assumed it was popular for its Florida location. Quickly, he experienced the energy and interaction of the meeting that has evolved into the Engineering Ceramics Division’s International Conference on Advanced Ceramics and Composites in Daytona Beach. He got involved in organizing symposia and eventually the officer chain of the ECD.

“We need to have a plan for members of tomorrow.”

He says, “The Society has given me a real professional identity because coming from the chemistry background, and being engaged in new materials and ceramics processing, it was always a challenge.”

As he enters his presidential year, Mathur is thinking about the lingering impact of the COVID-19 pandemic on the Society and other factors affecting the Society.

“The aftereffects of the pandemic are still being felt, and that’s why this year is going to be a turning point. Lot of things are changing, not only for pandemic-related reasons but due to the fact the geopolitical situation has also changed in the last three years,” he says. “We need to have a plan for members of tomorrow,” which will require ACerS to sharpen its value proposition and find ways to connect to younger demographics.

One way ACerS can connect to younger communities is by staying alert to new interdisciplinary approaches, Mathur says.

“The time has come where we have to reach out and start building communities outside the conventional or classical domains,” Mathur says. That will include continuing to work with international partner societies, but it could extend to working with nongovernmental organizations to hasten use of ceramic and glass materials to address grand challenges such as climate change, for example.

Mathur speaks fluent Hindi, German, and English, and is proficient in Punjabi and Rajasthani. He and his wife have two grown sons, who have often accompanied him to ACerS conferences. In his free time, Mathur cooks and plays badminton, and enjoys a Bollywood movie now and then. ■

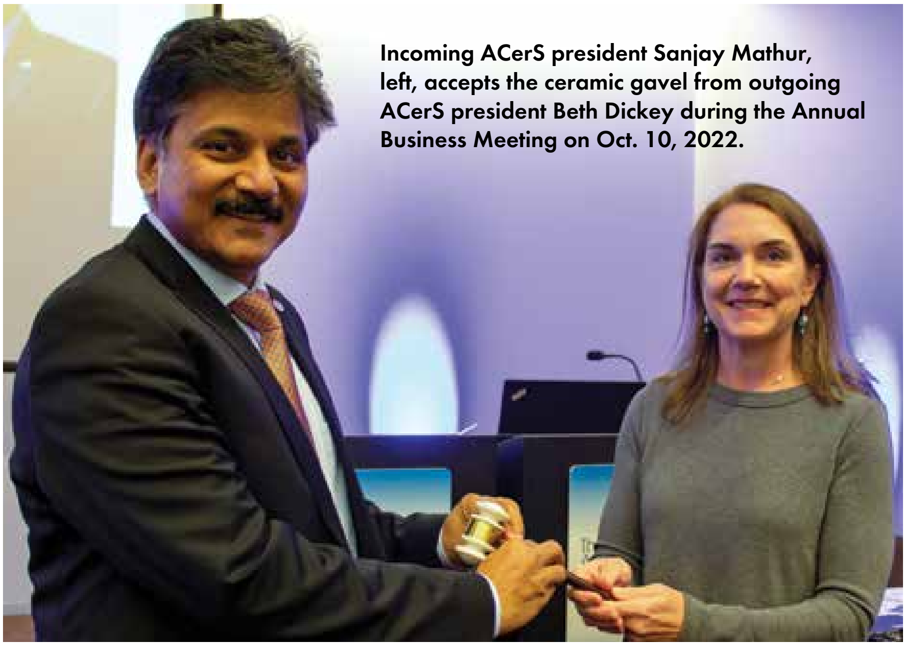
Establishment of the ACerS Germany Chapter and inaugural symposium at University of Cologne, Germany, in September 2018. Sanjay Mathur is front row, center.

Credit: Sanjay Mathur

Highlights from

ACerS 124th Annual Business Meeting

By Lisa McDonald



Incoming ACerS president Sanjay Mathur, left, accepts the ceramic gavel from outgoing ACerS president Beth Dickey during the Annual Business Meeting on Oct. 10, 2022.

Credit: ACerS

This year, The American Ceramic Society held its 124th Annual Business Meeting in-person on Monday, Oct. 10, during ACerS Annual Meeting at MS&T22 in Pittsburgh, Pa. ACerS Annual Meeting at MS&T brings together members from the whole Society as the meeting's technical content spans all aspects of ceramic and glass science, from energy applications and communications to bioceramics and more.

At the Annual Business Meeting, the ACerS president reports on the state of the Society, and the new president outlines plans for the coming year. President Beth Dickey summarized the Society's 2021–2022 accomplishments, including helping to coordinate and support International Year of Glass celebrations both domestically and abroad, as well as beginning implementation of the new strategic plan that was completed last year. (View the strategic plan at https://ceramics.org/about/acers-governance/strategic-plan.)

Treasurer Stephen Houseman reported that the Society's balance sheet remains "extremely healthy" despite the challenges brought on by the COVID-19 pandemic. This year was Houseman's last term as treasurer, with Daniel Tipsord stepping into the role for 2022–2023.

New officers were sworn-in, and out-going officers were recognized and thanked for their service. Incoming president Sanjay Mathur outlined his vision and goals for his year as president (see details on previous page). During his opening speech, Mathur noted that he believes 2023 will be a turning point for the Society following the pandemic.

The Annual Awards Banquet took place that night at the Omni William Penn Hotel. This year's awardees included 19 members elevated to Fellow Status and three members awarded the distinction of Distinguished Life Member.

In addition to the Annual Business Meeting, other events that provide updates on different parts of the Society took place during MS&T, including meetings of the Board of Directors, Division executive committee and business meetings, and meetings of ACerS working committees and subcommittees. The Society's student leadership group, the President's Council of Student Advisors, also held its annual meeting. This year, the PCSA includes 46 students from 28 universities, representing eight countries.

View pictures from ACerS 124th Annual Business Meeting at https://bit.ly/MST22photos.

ACerS 125th Annual Meeting at MS&T23 will take place Oct. 1–5, 2023, in Columbus, Ohio. ■

Hollow silica particles could form the basis of next-generation thermal insulation systems

In two recent studies, researchers explored combining hollow silica particles with other materials to create next-generation thermal insulation systems.

Hollow silica particles have fairly low thermal conductivities (0.02–0.03 W m^{-1} K^{-1}) and can be easily synthesized by several low-cost strategies. However, hollow silica particles alone can be a health hazard, so researchers are pursuing the combination of these particles with other materials to mitigate the risk of exposure as well as make it easier to transport.

In the first open-access study, researchers at Oak Ridge National Laboratory freeze-dried a mixture of hollow silica particles with cellulose fibers and carbon black to create a highly hydrophobic but structurally stable composite.

The thermal conductivity of the composite was ~0.025 ± 0.003 W m^{-1} K^{-1}, which was lower than both the cellulose fibers (0.05 W m^{-1} K^{-1}) and hollow silica particles (0.028 ± 0.002 W m^{-1} K^{-1}) alone.

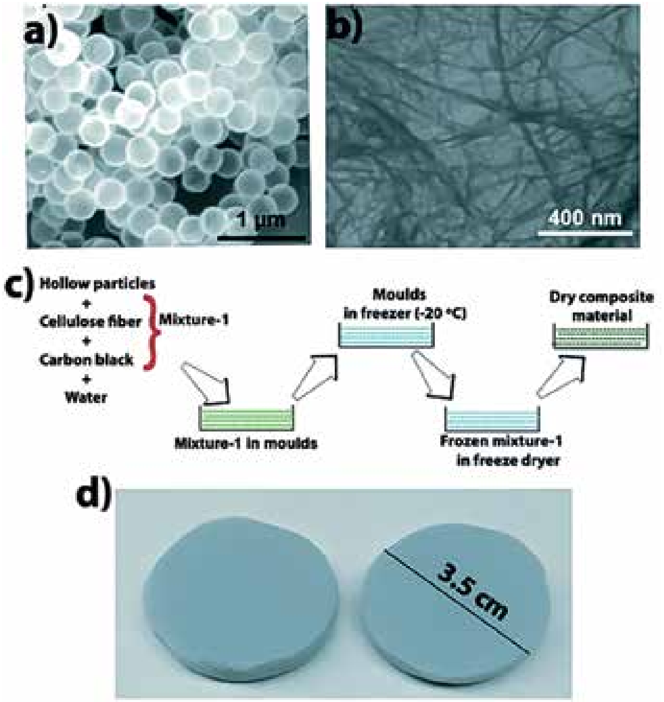
This finding was surprising because "In all other composites reported to date, the thermal conductivity of the composite is always higher than the thermal conductivity of [hollow silica particles]," the researchers write.

They suggest the heterogenous interfaces within the composite play a role in lowering the heat transfer.

In the second study, researchers at University at Buffalo and Lawrence Berkeley National Laboratory employed high-shear mechanical mixing to fabricate hollow silica–fiberglass composites.

The hollow silica particles were created via two low-cost synthesis routes. The gas-phase synthesis method generated hollow shells by a droplet surface precipitation mechanism in a flame aerosol reactor. The liquid-phase synthesis method formed hollow shells by removal of a carbon template, which was produced by hydrothermal reaction of glucose.

The composite with the lowest thermal conductivity (0.023 W m^{-1} K^{-1}) contained 60 wt.% of gas-phase SiO_2. Composites containing liquid-phase SiO_2 obtained their lowest thermal conductivity (0.026 W m^{-1} K^{-1}) at 50 wt.%. Both gas-phase and liquid-phase SiO_2 composites provided better thermal insulation performance than composites created using commercial silica gel (0.033 W m^{-1} K^{-1}).



Credit: Sharma et al., *RSC Advances* (CC BY 3.0)

(a) SEM image of hollow silica particles, (b) SEM image of cellulose fibers, (c) schematic showing the composite fabrication, and (d) photo of the composite material.

In addition to low thermal conductivity, the hollow silica–fiberglass composites demonstrated robust mechanical flexibility. Specifically, the Young's moduli of the gas-phase SiO_2, liquid-phase SiO_2, and commercial-SiO_2 composites were 35 kPa, 30 kPa, and 15 kPa, respectively.

The first open-access paper, published in *RSC Advances*, is "A lightweight thermally insulating and moisture-stable composite made of hollow silica particles" (DOI: 10.1039/D2RA01561G).

The second paper, published in *Chemical Engineering Journal*, is "Creation of hollow silica–fiberglass soft ceramics for thermal insulation" (DOI: 10.1016/j.cej.2022.140134). ■

Research News

Martian rock-metal composite shows potential of 3D printing on Mars

A small amount of simulated crushed Martian rock mixed with a titanium alloy resulted in a strong high-performance material in a 3D-printing process that could one day be used on Mars to make tools or rocket parts. Materials were developed by Washington State University researchers with as little as 5%, and up to 100%, Martian regolith, a black powdery substance meant to mimic the rocky, inorganic material found on the surface of Mars. While parts made with 5% Martian regolith were strong, 100% regolith parts proved brittle and cracked easily. But even high-Martian content materials would be useful in making coatings to protect equipment from rust or radiation damage. For more information, visit https://beta.nsf.gov/news. ■

Revealing the complex magnetization reversal mechanism with topological data analysis

Tokyo University of Science researchers used topological data analysis to develop a super-hierarchical and explanatory analysis method for magnetic reversal processes. According to the researchers, super-hierarchical means the connection between micro and macro properties, which are usually treated as isolated but, in the big scheme, contribute jointly to the physical explanation. The ability to connect magnetic domain microstructures and macroscopic magnetic functions enables the detection of subtle microscopic changes and subsequent prediction of stable/metastable states in advance. For more information, visit https://www.tus.ac.jp/en/mediarelations. ■

Planning for Mars: Thermal properties of cermet fuel for future nuclear propulsion systems

Researchers from Missouri University of Science and Technology and NASA Marshall Space Flight Center, including ACerS Fellows Bill Fahrenholtz and Greg Hilmas, used a surrogate material to explore the thermal properties of a cermet fuel that may be used in future nuclear thermal propulsion (NTP) systems.

In general, NTP systems work by having a “hot rock” of uranium atoms release high-energy neutrons to create heat. This heat is used to heat up hydrogen propellant, which is then expelled through a nozzle to produce thrust.

The extreme conditions within an NTP reactor—elevated temperatures up to 2850 K (~4,700°F or ~2,600°C), high-energy ionizing radiation, and flowing hydrogen propellant—requires the reactors to be fabricated from materials that can withstand these conditions.

Ceramic–metal (cermet) composites are candidate materials for NTP reactors. These composites consist of ceramic fuel particles, such as uranium dioxide or uranium mononitride, embedded in a metal matrix, which is typically tungsten due to its high melting point and excellent compatibility with hot hydrogen.

To model accurate reactor and fuel performance, researchers must have access to material property databases containing experimentally validated property models. But such databases are incomplete or missing for many NTP cermets. Even where the models can qualitatively predict effective properties, experimental data is lacking for operation at temperatures above 2000 K (~3,100°F or 1,700°C).

In the recent study, the researchers characterized the high-temperature thermal properties of molybdenum tungsten–hafnium nitride (MoW-HfN) cermet, a nonradioactive surrogate material for uranium mononitride.

The researchers used the laser flash method, differential scanning calorimetry, and push rod dilatometry to measure the thermal diffusivity, specific heat capacity, and coefficient of thermal expansion (CTE) of MoW-HfN, respectively. They used these values to calculate the cermet’s thermal conductivity.

Based on the experiments, diffusivity values ranged from about 0.18 cm^2/s at 200°C to 0.15 cm^2/s at 1,800°C. The CTE was measured up to 1,600°C, giving values between 6.0 and 9.0 µm/m. Measurement of the specific heat capacity was limited to temperatures less than 600°C, but it was validated by the rule-of-mixtures (ROM) model, which subsequently was used to calculate the value at higher temperatures.

Following the experiments, the researchers compared these various property values to ones calculated by different property models to determine which model(s) best represents the system.

As noted above, the ROM model did a good job calculating the specific heat capacity. Meanwhile, the Bruggemann model, which is based on the idea that a composite can be constructed incrementally by making small changes to the material, showed reasonable quantitative agreement with the calculated thermal conductivity.

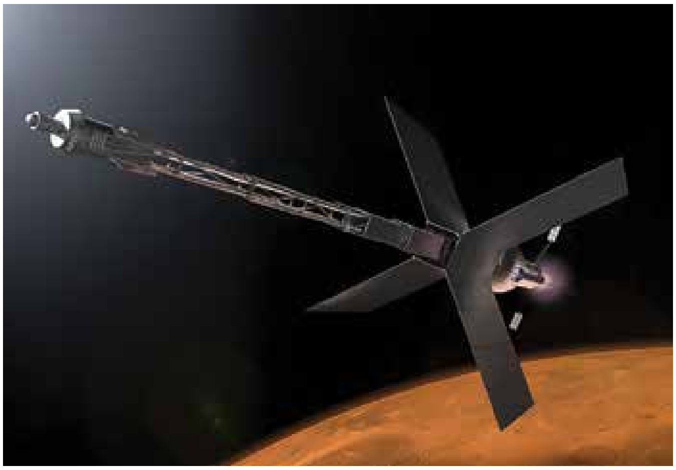
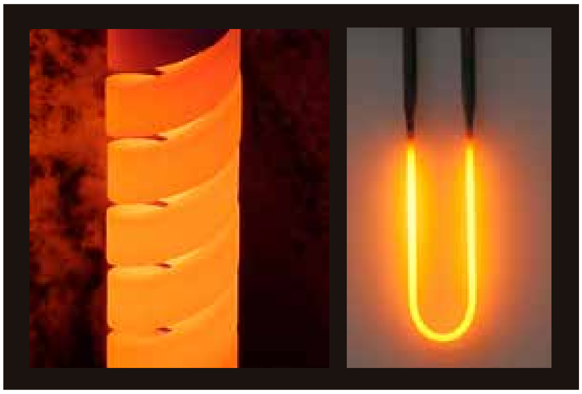


Illustration of a Mars transit habitat and nuclear propulsion system that could one day take astronauts to Mars.

Credits: NASA

However, none of the property models considered in this work could satisfactorily predict the CTE for HfN-MoW.

The paper, published in *Journal of the American Ceramic Society*, is “Thermal properties of HfN-MoW surrogate cermet fuel for nuclear thermal propulsion” (DOI: 10.1111/jace.18870). ■



ZrO_2 thin films on silicon show ferroelectricity down to 5 angstroms

For the first time, university and government researchers demonstrated that ZrO_2-based thin films with fluorite structure can demonstrate ferroelectric behavior on the atomic scale.

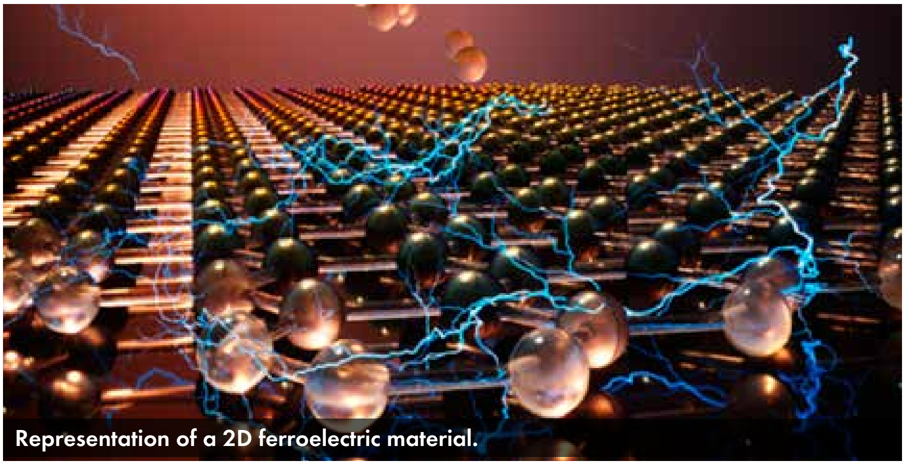
In recent years, researchers have pushed up against fundamental limits in the miniaturization of transistors to improve efficiency of electronic devices. So, they have turned to other techniques, such as materials innovations (e.g., strain engineering) and new device concepts (e.g., fin field-effect transistors), to improve efficiency.

Negative capacitance electronics is one concept receiving much attention lately. By replacing the conventional gate oxide layer in a transistor with a ferroelectric material, researchers can surpass the limits of a traditional system.

Currently, hafnium dioxide and zirconium dioxide-based thin films with fluorite structure are the focus of negative capacitance research due to these materials already being compatible with contemporary electronics manufacturing processes and machinery. Researchers have demonstrated ferroelectricity down to a sub-2-nm thickness in epitaxial and polycrystalline $Zr:HfO_2$ films. But they hope to achieve this behavior on even smaller scales as it could further improve the energy efficiency of electronics.

The researchers of the new study are led by the University of California, Berkeley, along with colleagues at The Pennsylvania State University, Lawrence Berkeley National Laboratory, and Argonne National Laboratory. They attempted to achieve atomic-scale ferroelectricity by converting the conventionally antiferroelectric tetragonal phase (t-phase) of ZrO_2 to the ferroelectric orthorhombic phase (o-phase) of ZrO_2 through reduced dimensionality.

As they explain in the paper, "The reduced dimensionality stabilizes the pressure-induced ferroelectric o-phase in fluorite-based oxides—conventionally achieved through hydrostatic pressure, chemical pressure, or epitaxial strain—in the ultrathin regime."



Representation of a 2D ferroelectric material.

Credit: Suraj Cheema, UC Berkeley

They used atomic layer deposition to grow the ZrO_2-based thin films on SiO_2-buffered silicon. To study the thickness dependence of the antiferroelectric–ferroelectric transition, they investigated the structural signatures of the respective t-phase and o-phase using synchrotron in-plane grazing incidence diffraction.

Spectra results confirmed the expected t-phase (101) reflection in thicker ZrO_2 films (3–10 nm) and the emergence of the o-phase (111) reflections for ultrathin films (2 nm) down to a thickness of 5 angstroms (0.5 nm). Local oxygen atomic imaging further distinguished between the polar o-phase and nonpolar t-phase structural polymorphs.

To characterize the electrical behavior of the ZrO_2 films, the researchers fabricated metal-insulator-metal (MIM) capacitors with varying ZrO_2 thicknesses. MIM polarization-voltage loops for 5- and 10-nm-thick ZrO_2 demonstrated a signature antiferroelectric-like double hysteresis.

Conventional polarization-voltage probes could not be applied to the ultrathin regime. So, they fabricated interdigitated electrodes to facilitate in-plane polarization switching, which allowed them to confirm the expected field-induced nonpolar-to-polar phase transition below the critical 2-nm thickness.

Plus, the polarization switching for 5 angstrom-ZrO_2 film was maintained beyond 125°C (257°F), which makes this material additionally promising for electronic applications.

"This work takes a key step towards integrating ferroelectrics into highly scaled microelectronics," says Suraj Cheema, first author and postdoctoral researcher at UC Berkeley, in an Argonne National Laboratory press release.

The paper, published in *Science*, is "Emergent ferroelectricity in subnanometer binary oxide films on silicon" (DOI: 10.1126/science.abm8642). ■

One-step process turns fish waste into functionalized carbon nano-onions

Researchers at Nagoya Institute of Technology in Japan produced highly crystalline carbon nano-onions (CNOs) using a one-step microwave pyrolysis of fish scales obtained from black snapper.

CNOs are a newer carbon nanostructure consisting of fullerenes and multiwalled nanotubes that form a concentric structure of spherical shells. The graphitic layers in the structure contain many defects and holes, which can be filled with other atoms or molecules to endow the material with different properties. Because of this versatility, CNOs show potential in a wide range of applications, including electronics, photovoltaics, catalysis, and biomedical diagnostics.

The first large-scale synthesis method for CNOs was developed more than a decade after CNOs were first discovered in 1980 as a byproduct of making carbon black. The method involved vacuum annealing a nanodiamond precursor under high temperatures (1,500°C–2,000°C). Although this method became widely used, the resulting CNO cannot be dispersed in either polar or nonpolar solvents, which is required for many applications.

Other CNO fabrication methods include arc discharge, chemical vapor deposition, ion implantation, laser ablation, and liquid phase-thermal pyrolysis. In addition to high temperatures, many of these methods require high-cost carbon sources, additional catalysts, hazardous acids or bases, and post-treatments to improve properties. Other disadvantages include contamination and low crystallinity.

The Nagoya researchers' new one-step synthesis process avoids most of these drawbacks by taking advantage of the fish scale composition. After a complex cleaning process to remove unwanted fat, color, and calcium, the fish scales are converted to CNOs within 10 seconds using similar frequencies as conventional home microwaves. This fast conversion rate is attributed to the collagen in the fish scales, which absorbs microwaves quickly and results in an extremely rapid increase in temperature.

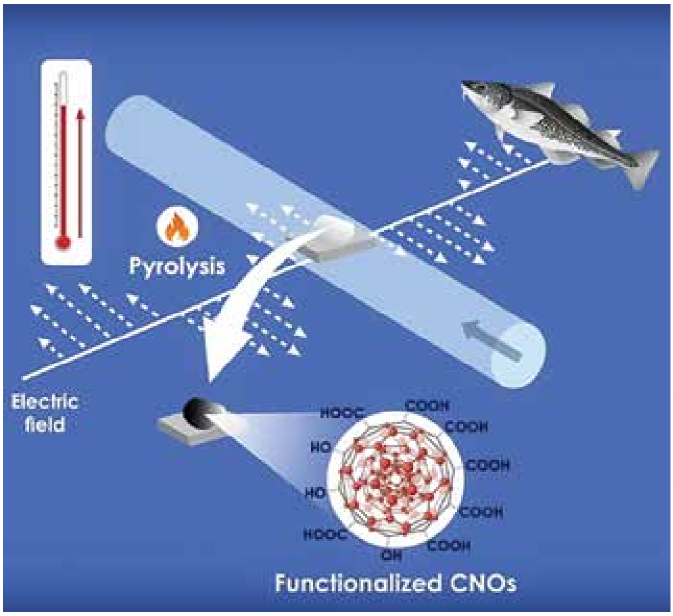
In addition to yielding CNOs with very high crystallinity, this process causes the CNO surface to be selectively and thoroughly functionalized with (−COOH) and (−OH) groups. When the CNO surface is not functionalized, the nanostructures tend to stick together, making it difficult to disperse them in solvents. However, because the proposed synthesis process produces functionalized CNOs, it allows for an excellent dispersibility in various solvents.

Another advantage of the functionalization and the high crystallinity is exceptional optical properties. The waste-derived CNO demonstrated a visible photoluminescence with a narrow emission width less than 90 nm and a superior quantum yield of 40% (i.e., the probability that a molecule will fluoresce or phosphoresce). This yield is 10 times higher than existing CNOs conventionally prepared using more complicated approaches.

To showcase some of the many practical applications of their CNOs, the researchers used a simple three-step tape casting process to create a flexible film that emitted blue light. Bright solid-state emission under ultraviolet irradiation occurred even at a low concentration of CNOs (2 mg/ml). They then turned the film into an LED that still emitted blue light, which was attributed to the active CNOs.

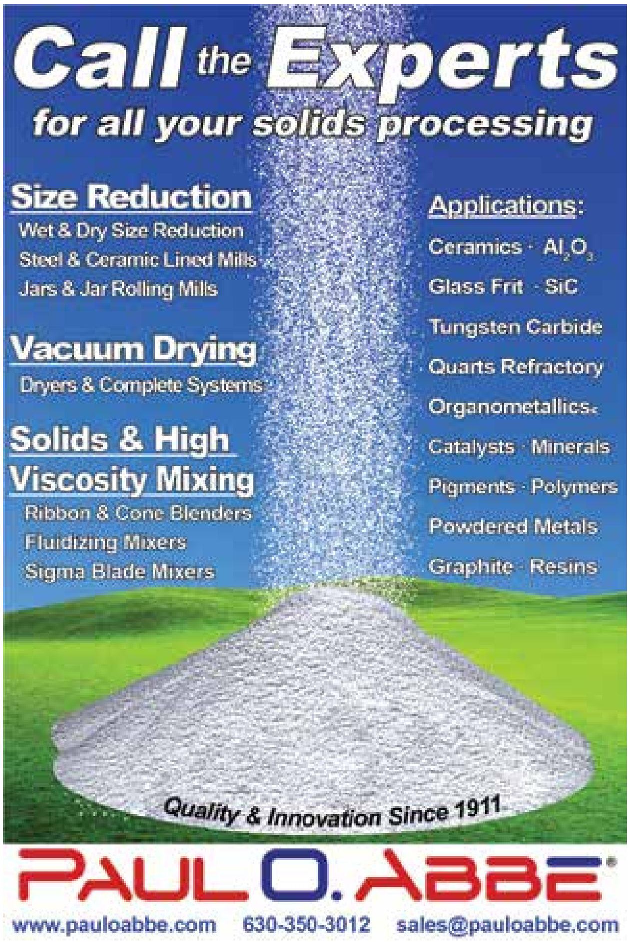
In a *Cosmos Magazine* article, coauthor Takashi Shirai, associate professor at Nagoya Institute of Technology, concludes, "These findings will open up new avenues for the development of next-generation displays and solid-state lighting."

The paper, published in *Green Chemistry*, is "Fabrication of ultra-bright carbon nano-onions via a one-step microwave pyrolysis of fish scale waste in seconds" (DOI: 10.1039/D1GC04785J). ■



Credit: Nagoya Institute of Technology, YouTube

Illustration of the one-step microwave pyrolysis process to turn fish scales into carbon nano-onions.



Reducing waste in manufacturing—conversion of silicon cutting waste into high-value silicon nitride

A group of researchers from Northeastern University (Shenyang, China) have published several papers on converting diamond wire silicon cutting waste into high-value silicon nitride.

Silicon waste is a major byproduct from solar cell production. To create solar cells, silicon is doped, melted, and extracted into a round block (ingot). The ingot is cut into thin square wafers using, conventionally, multiwire slurry saws but more recently diamond wires.

Though diamond wires cut more precisely than the slurry method, the cutting process still leads to nearly 35–40% of the silicon being thrown away because the diameter of the diamond wires is close to the thickness of the silicon wafers.

The ultrafine silicon waste particles can cause secondary pollution to soil, air, and water resources, resulting in safety and environmental concerns. So, finding ways to recycle or reuse this silicon is a benefit to manufacturers and the environment.

Several studies determined that silicon nitride (Si_3N_4) created out of diamond wire silicon cutting waste is a promising reuse method. Silicon nitride is an important high-temperature structural ceramic used in a wide variety of fields, including as engine core components, cutting tools, ball bearings, and gas turbines. It is typically prepared through direct nitridation of silicon powder, i.e., a heat-treating process that diffuses nitrogen into the surface of a material.

The fine particle size of diamond wire silicon cutting waste makes it favorable to nitridation. However, this waste powder has a different phase composition and microstructure than pure silicon powder. So, while the nitridation process of pure silicon powder is regarded as a simple gas-solid reaction, the kinetics and phase evolution are more complex when nitriding silicon waste powder from diamond wire cutting.

In a paper published October 15, the Northeastern University researchers looked to clarify the complex nitridation mechanism of the silicon waste powder.

Analysis revealed that out of three reaction models often used to describe the dynamics of gas-solid reactions, the grain model—which regards each silicon waste particle as a compact grain—did a good job explaining the results.

Essentially, the nitrogen would first react with the external grains in the accumulated silicon waste powder, then diffuse through the pores and react with the internal grains, and finally diffuse through the product layer and react with the remaining unreacted grains. The morphology and composition of the resulting silicon nitride were primarily influenced by the nitriding temperature and holding time.

Pure silicon nitride powders were obtained by nitriding at 1,550°C for 10 hours. However, particles with Si_3N_4-Si_2N_2O core-shell structure were obtained by nitriding at 1,450°C for 10 hours, "which would be a good raw material for preparing the Si_3N_4–Si_2N_2O composite ceramics with special performances," the researchers write.

In a second paper published October 18, they explored the effects of yttrium oxide (Y_2O_3), a common sintering aid, on nitridation.

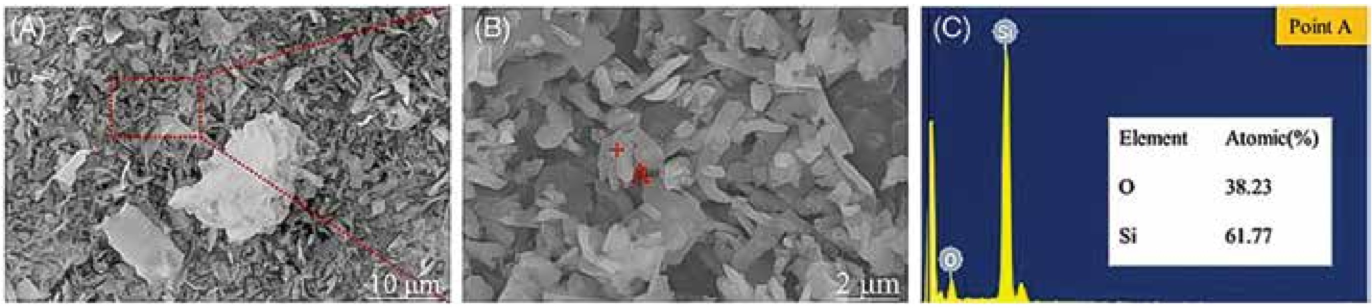
Using a variety of characterization tools, they found yttrium oxide does aid nitridation of diamond wire silicon cutting waste. Specifically, it can disrupt the native silica film, which causes many cracks to appear on the surface of the cutting waste particles.

"Thus, the good channel is provided for the diffusion of SiO and N_2, the resistance of gas phase diffusion is reduced, and the overall conversion of cutting waste is improved," they write.

To illustrate this point, consider that it required nitriding at 1,550°C for 10 hours to obtain pure silicon nitride powders in the previous paper. In this case, complete nitridation of the powders containing 8 wt.% yttrium oxide was achieved at 1,350°C in 2 hours.

The October 15 paper, published in *Journal of Cleaner Production*, is "Recycling the diamond-wire saw silicon powder for preparing the regulable Si_3N_4 materials by non-catalytic nitridation" (DOI: 10.1016/j.jclepro.2022.133656).

The October 18 paper, published in *International Journal of Applied Ceramic Technology*, is "Effect of Y_2O_3 additive on nitridation of diamond wire silicon cutting waste" (DOI: 10.1111/ijac.14242). ■



Element	Atomic(%)
O	38.23
Si	61.77

Scanning electron microscopy-energy-dispersive spectrometry analysis (A), (B and C) of diamond wire silicon cutting waste.

Credit: Wang et al., *International Journal of Applied Ceramic Technology*

ceramics in the environment

Ceramic-based nesting boxes offer cool haven for African penguins

In South Africa, the African Penguin Nest Project is relying on ceramics to provide homes for the endangered African penguin.

The African penguin, also known as Cape penguin or South African penguin, is a species of penguin confined to southern African waters. They are the only species of penguin found in Africa.

Their numbers have plummeted over the past two centuries—from more than 4 million in the 1800s to less than 50,000 today—due to the destruction of nesting sites, egg poaching, oil spills, climate change, and competition for food resources with commercial fishing.

Regarding the destruction of nesting sites, the African penguin traditionally burrowed into the deep layers of guano that had built up over centuries of habitation. However, in the 1800s, a profitable trade opened for guano as fertilizer, and almost all the guano was removed from the African penguins' breeding grounds. Without guano, the African penguins were left to nest in the open under the hot sun—which has only gotten hotter in recent decades.

Since 2009, artificial housing units ("nest boxes") have been installed at various African penguin breeding sites to provide shelter from predators and the sun. However, current nesting boxes yielded variable success. Concrete nesting boxes provided protection from predators but sometimes trapped heat, causing prolonged high daily nest temperatures. Meanwhile, some fiberglass models were consistently rejected by the African penguins.

In March 2016, members of numerous conservation organizations, governmental offices, zoological facilities, and field researchers came together to develop, test, and install a new and more effective nesting box for African penguins.

After much study, the researchers decided on a new nesting box design that is similarly shaped to the natural burrows. The double-layered boxes are hand manufactured by applying several layers of slurry-soaked geotextile over a mold. The slurry consists of a ceramic powder, water, and a waterproofing agent.

During initial data collection, monitoring of the new nesting boxes was complicated by the appearance of highly pathogenic avian influenza (HPAI strain H5N8) in several coastal areas of South Africa. This virus restricted access to the colonies and monitoring of the nests due to the risk of cross-contamination.

However, in 2021, the team successfully completed a study on Bird Island between February and March. (Bird Island and its surrounding areas in Algoa Bay host nearly half of the global population of African Penguins.) This study culminated in an open-access paper published in October 2022.

The paper states the double-layered ceramic nests outperformed all other tested nest types (exposed surface nests, cement pipe nests, natural burrows) by remaining cooler throughout the day. Temperatures never exceeded 36.7°C, in contrast to all other nest types, which experienced multiple episodes where temperatures exceeded 40°C.

African penguins check out the ceramic-based nesting box.

Credit: The African Penguin Nest Project

Additionally, the double-layered ceramic nests maintained constant levels of high humidity. (Increased humidity is necessary to prevent the egg membranes from drying out.)

Those who want to support this project may either sponsor the creation of a nest or purchase a product from the project's shop at https://www.savingpenguins.org.

The open-access paper, published in *Bird Conservation International*, is "Nest microclimate and heat stress in African Penguins Spheniscus demersus breeding on Bird Island, South Africa" (DOI: 10.1017/S0959270922000351). ■

Casting of a ~150 g NaPSON GSE preform on a preheated brass annealing mold to be reheated and drawn into a thin film for use in solid-state batteries.

Credit: Ryan Riley, College of Engineering, Iowa State University

Glassy solid-state electrolytes for all-solid-state batteries

By Jacob Wheaton, Madison Olson, Victor M. Torres III, and Steve W. Martin

Glassy solid-state electrolytes present several advantages over other classes of solid-state electrolytes, but some material and design challenges must be overcome prior to commercialization.

The introduction of the lithium-ion battery (LIB) to the market in 1991 revolutionized the energy storage field and enabled the development of portable electronic devices and electric vehicles that are widely available today. The improved energy density and cycle life compared to previous rechargeable batteries, such as lead-acid or nickel-metal-hydride, allowed for their widespread adoption.

Though these batteries revolutionized energy storage, current LIBs present several issues, mainly due to their reliance on carbonaceous anodes and organic liquid electrolytes. Their use of carbon, typically low-cost graphite, decreases the energy density on the anode to values usually one-tenth that of a pure lithium metal anode.

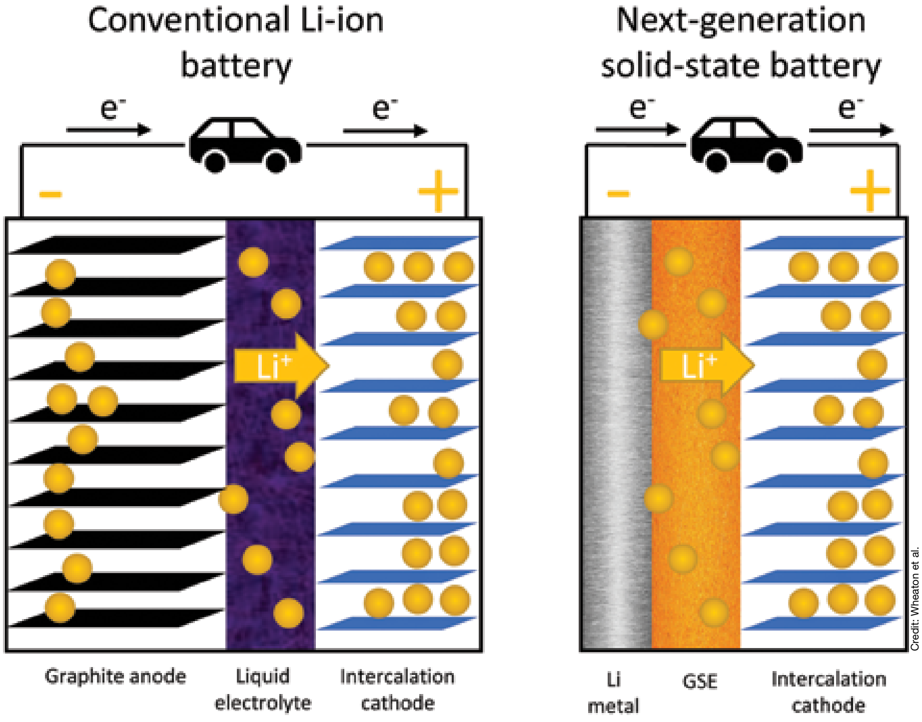
Likewise, organic liquid electrolytes can accommodate the volume expansion of the intercalation and deintercalation processes of lithium during discharge and charge processes, plus allow for simple, low cost, and rapid assembly and processing.

However, their inherent flammability reduces their safety in small-scale applications, such as smartphones and laptop computers. Their use in larger scale applications, such as battery packs in electric vehicles, requires active cooling systems to prevent thermal runaway, which can lead to dangerous fires.

With demand for more energy dense, more reliable, and safer batteries sure to increase in the future, new energy storage materials, designs, and solutions must be developed.

Solid-state batteries (SSBs), which rely on solid-state rather than liquid electrolytes, are a favored solution to not only improve the safety of LIBs but also to enhance the gravimetric energy density by enabling the use of higher voltage cathodes and lithium metal anodes. SSBs with solid electrolyte separators and glassy solid-state electrolytes (GSEs) are one class of solid-state electrolytes (SSEs) that present several advantages over other classes of SSEs, such as polycrystalline ceramics or polymers. These advantages include lower processing temperatures, greater resistance to dendrite formation, and more tunable chemistries.

This brief overview summarizes the development and current status of GSEs, along with their challenges and future prospects.



Credit: Wheaton et al.

Figure 1. Schematic of a conventional lithium-ion battery (left) and a next-generation solid-state battery (right) with a glassy solid-state electrolyte (GSE). Solid-state batteries can achieve the same capacities as conventional batteries but with a more compact—and potentially safer—design.

Benefits of all-solid-state batteries

Commercially available LIBs contain a cathode, an organic liquid electrolyte, and an anode. Typical cathode materials include $LiFePO_4$, which is commonly used in some electric vehicles, or $LiCoO_2$. While $LiCoO_2$ possesses a higher capacity than $LiFePO_4$, cobalt remains expensive and difficult to ethically source.

The anode typically is graphitic carbon, which forms LiC_6 upon charging. Lithium metal anodes offer higher energy density than graphite anodes, but they are also prone to dendrite formation in liquid electrolyte cells, which in turn leads to short-circuiting. Short-circuiting can further cause the liquid electrolyte to increase in temperature, and eventually lead to fires and explosions. Graphitic carbon anodes help mitigate these safety hazards of the organic liquid, but they do so at the expense of reduced energy density relative to the lithium metal anode.

SSBs are seen as a potential solution to this performance compromise due to their less flammable nature, which would enable the use of lithium metal anodes possessing a gravimetric energy density more than an order of magnitude greater than graphite anodes (3,860 mAh/g vs. 330 mAh/g). This dramatic increase in energy density makes lithium metal anodes highly desired. Implementation, however, requires design of a compatible SSE.

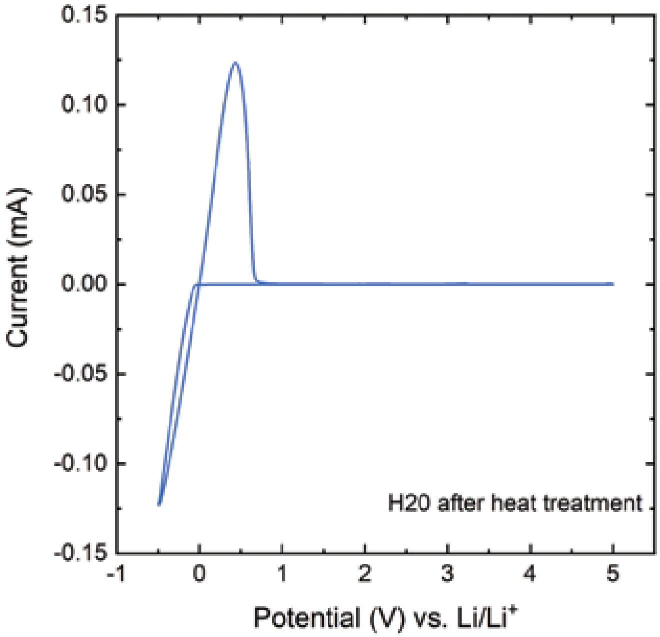
Figure 1 shows a schematic illustrating the differences between conventional LIBs and newer SSBs. While the benefits of next-generation SSBs spur research, there are still many material and design challenges that must be overcome prior to commercialization.

Requirements for SSEs in SSBs

Prior to discussing the specific qualities of GSEs, it is important to define requirements that are necessary for SSEs to be used in SSBs.

First, SSEs should have a high ionic conductivity approaching that of liquid electrolytes, about 10^{-3} S/cm, coupled with a low electronic conductivity, below 10^{-9} S/cm.[1] The combination of high ionic conductivity and low electronic conductivity is necessary to sufficiently reduce the internal resistance of the electrolyte and allow for higher discharging and charging rates and to prevent premature failure of the cell. A large electrochemical stability window, from 0 V to more than 4 V vs. Li/Li^+, is also important to prevent the electrolyte from decomposing in contact with either lithium metal or high-voltage cathodes.

An example of a cyclic voltammogram for a glass in the $Li_2S–SiS_2–LiPO_3$ compositional space is shown in Figure 2, where the GSE is stable up to 5 V vs. Li/Li^+, as no reduction or oxidation peaks are present. The peaks centered around 0 V are attributed to lithium plating and stripping behavior. Electrolyte decomposition can lead to lower efficiency when charging and discharging. Typically, a stability window from 0 V



Credit: Zhao et al., *ACS applied materials & interfaces*

Figure 2. Cyclic voltammogram showing the electrochemical stability of a $Li_2S-SiS_2-LiPO_3$ glass. No redox peaks are seen above 0 V, indicating good stability of the GSE against lithium metal. This data was obtained using a stainless steel | GSE | Li asymmetric cell design. Adapted with permission from Ref. 3. Copyright 2021 American Chemical Society.

to 5 V against lithium metal is sufficient for usage of novel cathode materials.

SSEs should also be easy to process into films with thicknesses less than 100 µm to reduce internal resistance of the cell and be competitive with organic liquid electrolytes.[2]

There are many classes of GSEs. However, so far, none of them meet all the above requirements perfectly. The most well-studied GSE types will now be discussed, beginning with the first ionically conductive glasses researched: alkali ion doped oxide glasses.

Oxide glasses

Oxide glasses were the first glasses developed for their ionic conduction properties. First studied in the late 19th century, it was not until the 1930s that efforts were made to attempt to maximize the ionic conductivity of sodium silicate glasses by increasing the concentration of Na_2O in the glass forming melt, achieving a maximum room temperature conductivity of about 10^{-9} S/cm.[4] Even with additional Na^+ added into the glass network through dopant salts such as NaCl, the conductivity only increased to about 10^{-6} S/cm.

The highest lithium ion conductivities reported in oxide glasses are typically about 10^{-5} S/cm, while sodium ion conductivities are normally even lower.[5] These low ion conductivities remain one of the greatest issues with oxide GSEs: While they are easily processed and are very low cost, they possess intrinsically low ionic conductivities even at high alkali ion concentration due to the strong ion trapping behavior of oxide anions, which significantly limits their ionic conductivities.[5]

Researchers have conducted many studies on oxide glasses to determine the effect of different alkali ions and glass-forming systems on the ionic conductivity of glasses. The results of these studies indicate that larger alkali cations consistently exhibit lower conductivities while silicate glasses typically display higher conductivities than germanate, phosphate, or borate glasses.

Significantly, however, the ionic conductivities of AgI doped oxide glasses are some of the highest conductivities reported in glasses, approaching or often even surpassing 10^{-2} S/cm.[6] This high conductivity of the Ag^+ cation is believed to be due to its high ionic polarizability. While this conductivity is well above the minimum desired conductivity of solid electrolytes, the voltage of silver batteries is limited, and the cost and density of silver limits its use.

Oxide glasses possess several desirable properties of SSEs, including a wide electrochemical stability window, relatively good atmospheric stability, high shear modulus (which is correlated with resistance to dendrite formation), and relative ease of processing. While the composition of oxide glasses can be optimized by using complex systems, such as multiple glass-forming cations and multiple ionic salt dopants, to increase conductivity, the low ionic conductivity of these glasses, at best 10^{-5} S/cm at 25°C, often makes them nonstarters for use in SSBs. A simpler method of increasing the conductivity of the glass is to replace the deep trapping energy of oxygen anions with a lower field strength, weaker trapping energy anion, such as sulfur.

Sulfide glasses

In the 1980s, several sulfide-based glass systems were found to have conductivities approaching that of organic liquid electrolytes. The higher polarizability and lower charge density and field strength of sulfide anions reduces the Coulombic attraction between the mobile cations and the sulfur anion, which in turn allows for the alkali ion conductivity to increase relative to oxygen analogues.

While sulfide glasses often present high conductivities, they also typically have several disadvantages, including their hygroscopic nature, lower resistance to crystallization, and lower electrochemical stability compared to oxide glasses. However, many of these issues can be overcome through use of controlled atmospheres and processing.

Binary alkali thiophosphates were some of the first sulfide glasses studied, particularly glasses based on $Li_4P_2S_7$ or $Na_4P_2S_7$.[7] While melt-quenched samples typically have had issues with volatilization of P_2S_5 during melting, large additions of modifying sulfides, such as Li_2S or Na_2S, can help to prevent sublimation of P_2S_5 during melting due to the increased ionic nature of the glass system.[5] These binary alkali thiophosphates typically present ionic conductivities 2–4 orders of magnitude higher than their oxide counterparts, with lithium ion conductivities often approaching 10^{-3} S/cm.[5] Figure 3 is an Arrhenius plot showing typical ranges of conductivities for oxide, sulfide, and mixed oxysulfide glasses.

In addition to phosphate glasses, alkali thiosilicate glasses (Li_2S-SiS_2) have also been extensively studied because these glasses have fewer issues with sublimation of starting materials during melting, and therefore can be easily synthesized in open crucibles without significant mass loss. Still, these glasses are typically only moderately glass forming and as such they often require fast quenching rates to prevent crystallization and reach the glassy state. For example, Pradel and Ribes used twin-roller quenching to rapidly cool glass melts and extended the glass-forming region of the $Li_2S–SiS_2$ system to produce glasses with conductivities approaching 10^{-3} S/cm.[8]

Further, it is often advantageous to combine desirable properties from multiple glass-forming systems. As such, mixing of the glass-forming cations silicon, phosphorous, and boron can be a valuable tool to improve the properties of a glass.

Mixed glass former glasses

Mixing glass-forming cations can add to the disorder of the system, leading to both positive and negative effects on the glass properties. For instance, substitution of B_2O_3 for P_2O_5 in sodium systems shows an increase in the ionic conductivity over that of binary phosphate and borate glasses, with the conductivity three orders of magnitude higher than the phosphate glass and one order of magnitude higher than the borate glass. This phenomenon is often referred to as a positive mixed glass former effect.[5]

Negative mixed glass former effects also are encountered in certain glass systems, such as in the $0.5Na_2S + 0.5[xGeS_2 + (1–x)PS_{5/2}]$ system, where the conductivity decreases with addition of a second glass forming cation.[9]

Mixing glass-forming cations can be a valuable technique to improve the glass-forming nature, stability, and conductivity of glass systems with minimal detrimental effects. Along the same lines, mixing anions in glass can also lead to similar desired property changes.

Mixed anion glasses

Mixed anion glasses have been studied in recent years by a few different groups, primarily at Osaka Prefecture University (Sakai, Japan) and Iowa State University (Ames, Iowa), with the goal of merging the high ionic conductivity of sulfide glasses with the good chemical stability of oxide glasses. These mixed oxysulfide glasses were studied with the expectation of finding an optimized compromise between chemical, electrochemical, and thermal stabilities and conductivity, but frequently, these glasses are also found to exhibit a mixed anion effect.

Small introductions of oxygen in a primarily sulfide glass system, typically less than 10 to 20 at%, will actually increase the conductivity above that of the parent pure sulfide glass. Tatsumisago et al. discovered this phenomenon in several glass systems, including in $Li_2S + SiS_2 + Li_4SiO_4$ and in $Li_2S + P_2S_5 + P_2O_5$ systems.[10] Often, the addition of oxygen helps retain the high conductivity of the sulfide glass while greatly improving the chemical durability and the electrochemical stability. Martin and Kim also demonstrated this effect with glasses in the $0.5Li_2S + 0.5(xGeO_2 + (1–x)GeS_2)$ system that exhibit a conductivity nearly a full order of magnitude higher at the $x = 0.05$ composition compared to that of the pure sulfide $x = 0$ glass.[11]

While germanium-based glasses often exhibit high conductivities, especially when paired with another glass-forming cation, the high cost of germanium often limits their viability in practical applications.

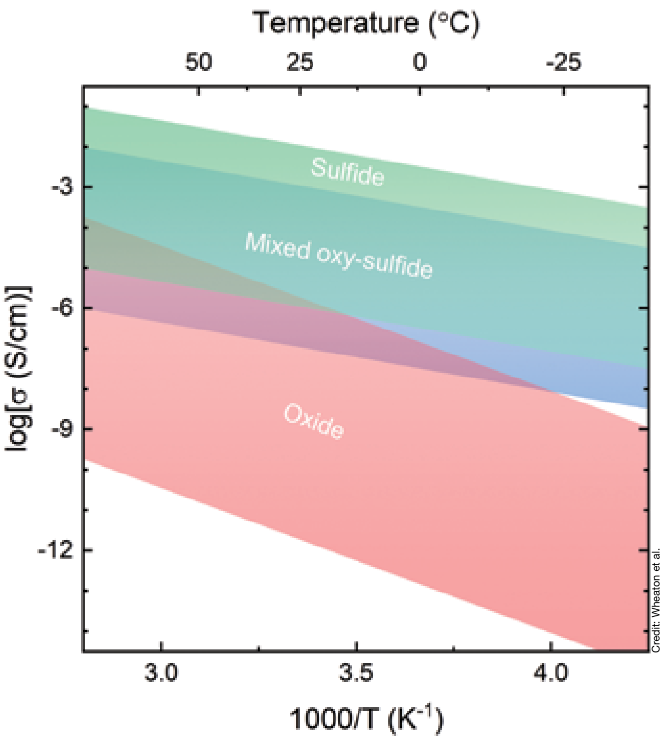


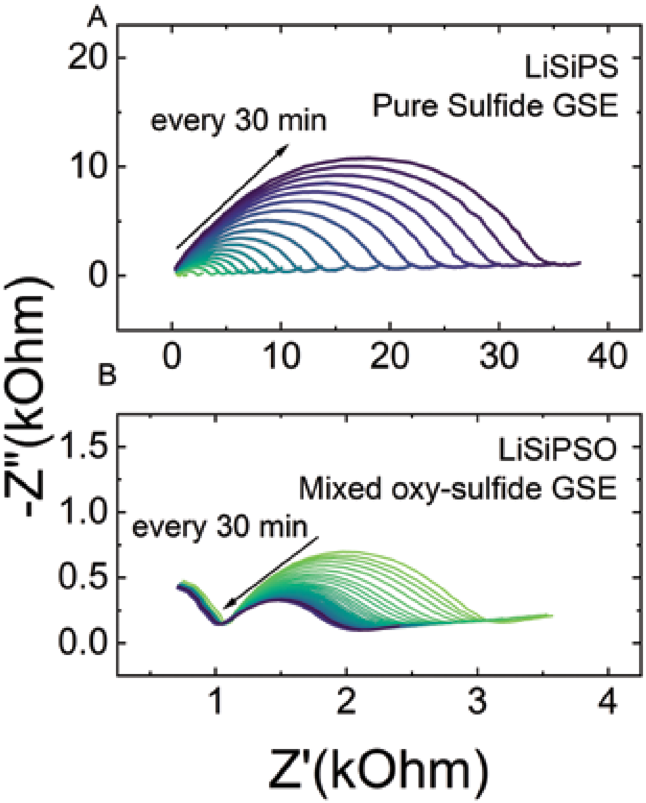
Figure 3. Arrhenius plot showing typical conductivity ranges for three composition families of glasses. The green shaded region corresponds to sulfide, the blue to mixed oxysulfides, and the red to oxides.

Mixed anion glasses in the $Li_2S + SiS_2 + Li_xMO_y$ system also show promise for improving the chemical and electrochemical stability of the GSE against lithium metal. A Nyquist complex impedance plot (Figure 4A) of a symmetric cell of a typical pure sulfide GSE sandwiched between two pure lithium metal electrodes shows that the interfacial impedance grows strongly over time. This growth in the resistance of the cell arises from the persistent reaction of the pure sulfide glass with the lithium metal anodes. Because the resistance continues to grow with time, no passivation layer (i.e., stable solid electrolyte interphase) forms to stabilize the interface.[12]

Figure 4B, on the other hand, shows a Nyquist plot of a mixed oxysulfide GSE that was doped with oxygen to stabilize the interface between the GSE and lithium metal. The interfacial impedance decreases over time after fabrication of the cell until it stabilizes. This decrease is believed to be due to creep of the lithium metal filling voids at the interface while under moderate pressure in the coin cell.[13]

Perhaps one of the most successful and well-studied mixed anion GSE materials is LiPON, first studied at Oak Ridge National Laboratory in the early 1990s.[14] Nitrogen was studied as a dopant in lithium orthophosphate (Li_3PO_4) with the hope of increasing the electrochemical potential stability window and conductivity of the base oxide.

LiPON was successfully developed and used in thin film microbatteries. Thin film LiPON is synthesized through radio-



Credit: Zhao et al., *Batteries & Supercaps*

Figure 4. (A) Nyquist plot showing the unstable nature of a sulfide GSE against lithium metal. (B) Nyquist plots showing the stable behavior of mixed oxysulfide GSE against lithium metal. Top plot reproduced with permission from Ref. 12.

frequency magnetron sputtering of a crystalline Li_3PO_4 target in a vacuum lightly backfilled with nitrogen gas. The sputtering process promotes replacement of oxygen with nitrogen up to a few atomic percent into the short-range structure of the material, altering the properties of the glass. The resulting film is typically amorphous, no thicker than a few microns, and exhibits a conductivity that is often more than an order of magnitude higher than the base Li_3PO_4, even at low concentrations of nitrogen (N/O ratio less than 0.1).

The conductivity of LiPON is nevertheless rather low, at best about 10^{-6} S/cm. This low conductivity is typically not a major issue in solid-state microbatteries, however, as 1-µm-thick radiofrequency magnetron sputtered films are durable enough to prevent short circuiting.

It was recently suggested the highly modified structure of LiPON and other weakly networked, ionic glasses can allow for enough ductility to prevent cracking of the GSE during cycling, preventing the growth of lithium metal dendrites.[15] The uses of LiPON as a thin film GSE are limited in smart sensors, RFID cards, and similar applications.[16] Typically, these thin film batteries are only 10–15 µm thick with capacities ranging from 0.1–5 mAh. LiPON thin film batteries are also limited by high processing costs, low deposition rates, and high processing temperatures.

Further mixing of anions was attempted based on the promising results of nitrogen doping in stabilizing and increasing the conductivity of oxide glasses, such as LiPON. Our group at Iowa State developed several compositions that combine some of the above strategies to optimize GSEs that show promising behaviors for use as SSEs. For example, the mixed glass former mixed oxysulfide-nitride GSE $0.95(0.67Li_2S + 0.264SiS_2 + 0.066P_2O_5) + 0.05(LiPO_{2.2}N_{0.54})$, while possessing a lower conductivity than the base pure sulfide GSE, achieved a critical current density of 1.76 mA/cm^2 at 100°C (i.e., the current density below which the SSE does not short due to lithium dendrites). This achievement indicates that the GSE inhibits the growth of lithium dendrites up to this current density. Cyclic voltammetry of the GSE also shows that the glass is stable against lithium metal up to at least 5 V, allowing for the use of novel high-voltage cathodes without electrolyte oxidation.[12]

Even with such progress, mixed anion glasses for use as SSEs are still an understudied area of glass research, with more work needed to fully understand the property changes associated with addition of other anions to the glass network.

Mechanochemically milled glasses

While melt-quenched samples can be preferable for eliminating grain-boundary impedance, high-energy mechanochemically milled (MCM) samples also present several advantages.

MCM is an interesting technique that is used to produce glasses without material loss due to volatilization and is easily scalable. The resultant powders are easily processible using common ceramic processing techniques already used in battery manufacturing, such as tape casting.

MCM glasses are typically milled at high speeds, often more than 400 rpm, for more than 20 hours, with X-ray diffraction patterns showing an amorphous halo, indicating the loss of crystalline order in the material. These materials exhibit similar thermal behavior to glasses, going through a glass transition in differential scanning calorimetry experiments. Also, recent work showed that MCM samples and melt-quenched samples with similar compositions are often structurally equivalent when compared using techniques such as Raman and magic-angle-spinning nuclear magnetic resonance spectroscopies.[5]

Recently, our group and collaborators showed a MCM $Na_3PS_{3.4}O_{0.6}$ glass can be formed into a fully dense material free of pores through simple cold uniaxial pressing.[17] This GSE showed excellent rate capabilities for sodium systems, demonstrating stable cycling for hundreds of hours at 0.5 mA/cm^2 at 60°C. The sodium-sulfur full cell produced with this pressed electrolyte also exhibited excellent behavior with a specific capacity of 1,116 mAh/g at 0.1 mA/cm^2 with the cell cycling for 150 cycles consistently.

While this study is the first report of a fully dense pressed glass, many MCM GSE materials present excellent processing behavior, and future work may reveal more glass systems that can exhibit similar behavior.

Glass-ceramic solid-state electrolytes

Glass-ceramic solid-state electrolytes (GCSEs) are a relatively new type of GSE with several advantageous properties. These GCSEs are synthesized by partial crystallization of a GSE and often exhibit ionic conductivities higher than that of the parent glass.

This phenomenon was discovered when a thiophosphate GSE was overheated during temperature-dependent conductivity measurements, where the resulting GCSE exhibited a significantly higher ionic conductivity after cooling to room temperature compared to the as-prepared GSE at the same temperature. In lithium thiophosphate GCSEs, the increase in conductivity is nearly a full order of magnitude.[5] Lithium thiosilicate GSEs exhibit the opposite behavior, where the ionic conductivity decreases by more than two orders of magnitude on partial crystallization.

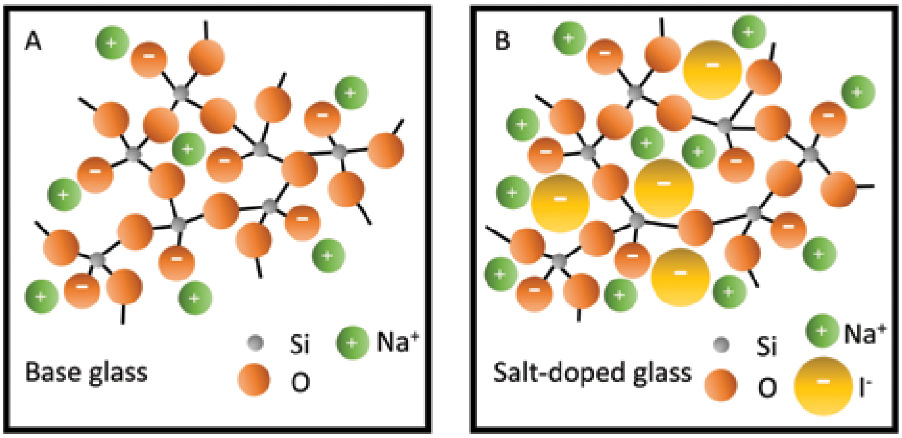
Many of the studied GCSEs are synthesized from a parent glass formed through MCM. To our knowledge, the studied GCSEs in the literature are primarily lithium-ion conductors; very few studies on other alkali ion conductors, such as Na^+ GCSEs, have been performed. Even among the lithium SSEs, GCSEs are not widely studied nor is the mechanism behind their occasionally higher conductivity fully understood.

Salt doping strategies

GSE conductivity can be improved through dissolution of dopant salts into the glassy network, much like salt doping aqueous and nonaqueous solvents. However, while dopant halide salts help improve the conductivity, they can degrade other desired properties of a GSE, such as resistance to crystallization and electrochemical stability.

Typically, the salt contains the desired conductive cation and a large, low field strength anion. For example, alkali halides, especially LiI, are used due to the low mobility of the large halide anion in the glassy network.

Often, high concentrations up to 30 or 40 mol% of halide salts can be doped into a glass without precipitation of the dopant salt on cooling to the glassy state. Typically, the dopant salt is chosen such that the field strength of the counter anion (for example, Cl^-, Br^-, or I^-) is low enough to not change the fraction of bridging/nonbridging anions, i.e., it does not react with the host glass network structure. Rather, the dopant salt anion introduces more free volume into the glass by increasing the space between the tetrahedral units of the glass structure, effectively acting as a plasticizer, weakening the glass forming ability and network connectivity, as shown in Figure 5.



Credit: Wheaton et al.

Figure 5. (A) Schematic showing a base glass with no salt doping and cations such as sodium, lithium, or potassium loosely bonded to nonbridging sulfur or oxygen. (B) Schematic showing a salt-doped glass with the same network but more spread out due to the salt dopant.

This change in the glass structure can significantly impact the properties of the glass, including a reduction in the glass transition temperature, reduced resistance to crystallization, and a significant increase in the conductivity. For example, the $0.3LiI + 0.7LiPO_3$ glass has a room temperature ionic conductivity more than two orders of magnitude higher than that of the base $LiPO_3$.[5] The change in conductivity is more pronounced in oxide glasses than in the already higher conducting sulfides. Salt doping can be problematic, however, as many of the salts used can be electrochemically unstable when in contact with lithium metal.[5]

Recent developments in glass-forming techniques for GSEs

While the electrochemical properties of a glass are important to its success as a GSE, the formability of the glass into thin separators is also crucial in moving from lab-scale to large-scale synthesis.

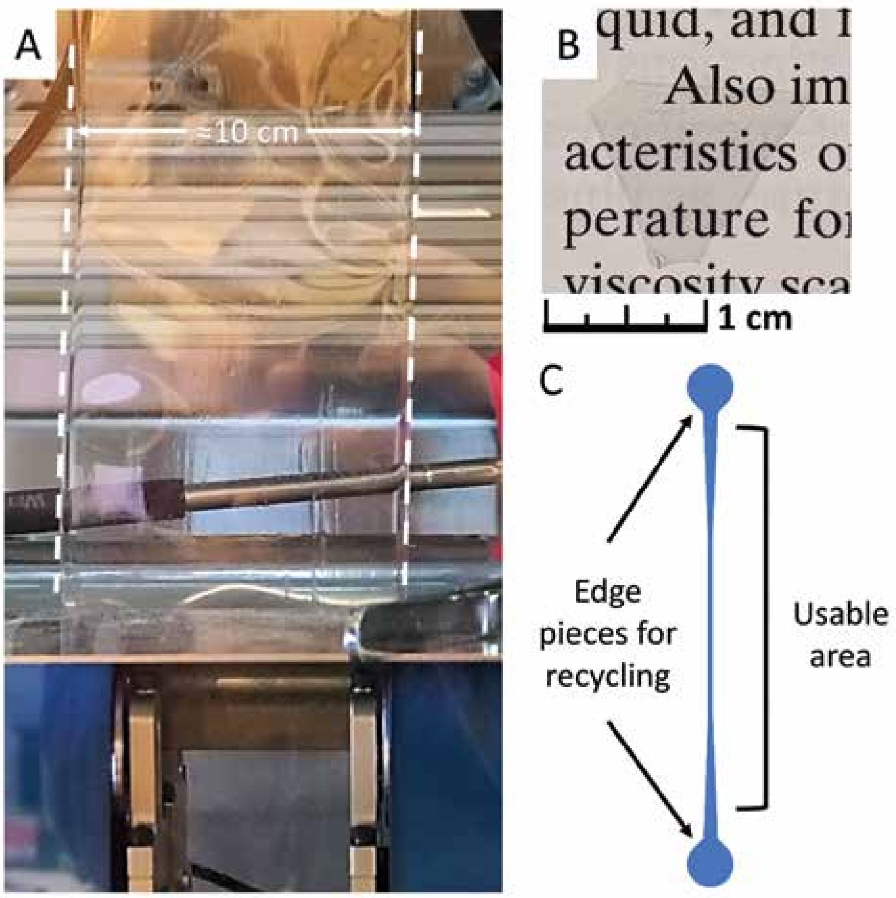
As mentioned earlier, films of 100 µm in thickness or less are necessary to be competitive with current LIBs; however, processing glasses into durable thin films can be a challenging task. General Motors developed a process of hot pressing thiosilicophosphate glasses into a low-density fiberglass mesh achieving relative densities of around 93% with films around 150 µm thick, while still preserving a conductivity of 7×10^{-4} S/cm.[18] While the film thickness still needs to be further reduced, this technique is an interesting approach to processing glass powders into a thin film.

Our group recently reported the drawing of thin-film monolithic lithium metaphosphate ($LiPO_3$) glass down to about 50 µm in thickness, as shown in Figure 6.[19] $LiPO_3$, as an oxide glass, has a conductivity of only 10^{-9} S/cm at room temperature, which is too low for use in SSBs. However, thin film drawing can be used with other much higher conductivity GSEs, such as mixed oxy-sulfide glasses, with reports being prepared on highly conducting sodium and lithium glasses being drawn into thin films through this process.

Performance of solid-state batteries using glassy electrolytes

In the past decade or so, several groups started testing their GSEs in full cell batteries. As described previously, LiPON full cells can perform well, at high currents; however, their energy densities typically only reach 2–3 mWh/cm^2 with cycling efficiencies typically between 80–99%.[14]

Recently, General Motors tested a Li–S hybrid full cell with their previously described GSE. In use for 300 cycles, their cell demonstrated a Coulombic efficiency of more than 98%, using a small amount of liquid electrolyte to improve surface contact between the electrolyte and the electrodes.[18] While



Credit: Wheaton et al., ACS Applied Energy Materials

Figure 6. (A) Image of $LiPO_3$ thin film during the drawing process. (B) Image of a 45 μm thin film for use in testing. (C) Diagram of a cross-section of the drawn thin film showing the usable area. Reprinted with permission from Ref. 19. Copyright 2021 American Chemical Society.

lithium batteries are the most studied, in the past few years, our group collaborated to produce highly energy dense Na–S full cell batteries that offer specific capacities of greater than 1,100 mAh/g at 0.1 mA/cm^2 for more than 150 cycles.[17]

While there has been some progress in using these GSEs in full cell configurations to create solid-state batteries in the past couple decades, much work is still required prior to moving beyond the laboratory setting.

Challenges and perspectives

GSEs have several unique characteristics that make them desirable materials to replace flammable organic liquid electrolytes. While oxide-based GSEs and sulfide-based GSEs each have desirable properties, they both present drawbacks—low conductivity and high reactivity, respectively—that reduce the likelihood of their use in this application.

The cost of sulfide materials and their processing is also a challenge to their use, as they require atmospheres of less than 5 ppm O_2 and H_2O to prevent degradation. The synthesis costs of some sulfide materials are higher than $10 per gram.

While still in the early stages of development, it seems that mixed anion glasses, such as the mixed oxysulfide and mixed oxysulfide-nitride GSEs, may be able to offset material costs while reconciling the low conductivity of oxides and the high reactivity of sulfides to form glasses that are highly conductive and stable against alkali metals, such as sodium or lithium.

Prior to commercialization of GSEs, several challenges need to be addressed and solved. Along with many other ceramic materials, glasses remain brittle materials and are typically mechanically fragile when reduced to the thicknesses required for use as an SSE. Small defects, such as bubbles or surface flaws, can lead to fracture of the GSE during use, leading to a potentially dangerous short circuit. Many engineering controls must be developed to eliminate flaws and reduce the risk of fracture. Additionally, as with all classes of solid-state electrolytes, large interfacial impedances between the electrodes and the GSE remain a critical issue. Researchers are working to reduce these impedances to less than 10 Ω–cm^2.

Currently, GSEs are being studied on the laboratory scale, with very few materials in commercial production. Other electrolyte materials, such as lithium lanthanum zirconium oxide, receive more attention in literature, but glassy materials are quickly gaining attention with their improved processability relative to hard and brittle ceramic powders, such as the garnet-structured electrolytes.

Acknowledgements

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With safety and performance, ceramic batteries are in the works

By Jonathon Foreman

Substantial ceramics research projects are looking to address issues with current lithium-based battery technologies. A selection of recent papers in ACerS journals highlights some of the efforts toward new electrolyte, cathode, and anode materials.

Governments around the world are pouring funding and resources into building up renewable energy infrastructure to reduce reliance on greenhouse-gas-emitting fuels.

However, relying solely on wind and solar power is challenged by the fact these technologies cannot provide a reliable baseload, which is the constant minimum flow of energy required to fulfill basic electricity demands.

Nuclear and fossil fuel power plants readily provide baseloads while fuel is supplied. But the latter option recently is less reliable in areas that depend on natural gas from Russia.

Hydroelectric power plants, which generate electricity using flowing water, can also provide reliable baseloads. For example, Canadian electricity company Ontario Power Generation maintains a storage pond near Niagara Falls that has reversible pumps. During the night, they widen the water intake gates above the falls, which increases power generation and reduces water to the falls. The excess power is used to fill the reservoir, which then delivers energy as it is emptied during the day when the hydroelectric inlet flows are reduced and the falls are brought back to their splendor.

But hydroelectric is in jeopardy now as well. Rising temperatures and rainfall changes are shrinking the reservoirs behind the hydroelectric dams. Lake Mead, the largest reservoir in the United States and where Hoover Dam is located, has fallen 158 feet in the last two decades (Figure 1). The lake's water level currently measures 1,041 feet, and the Bureau of Reclamation says the lake levels must stay above 1,000 feet to continue operating the dam's hydropower turbines.

Batteries are another energy storage technology that make relying on solar and wind for baseloads more achievable. They can provide baseload support by being charged using renewable energy sources during periods of low electricity usage or high production and by discharging into the grid as needed.

Instead of pumping and discharging water like hydroelectric power plants, batteries charge and discharge by the motions of ions and electrons. In a typical battery, the metal in the anode gives off electrons during discharge to form positive ions. The electrons flow through the external circuit while the ions migrate through the electrolyte and are deposited in the cathode and reunited with electrons to reform the metal.

In primary batteries, this flow of electrons and ions only happens once and then the battery is spent. In contrast, a reverse polarity voltage applied to rechargeable batteries drives the metal ions and electrons back to the anode, much like electricity runs the pumps to lift water into the reservoir near Niagara Falls. The batteries can then repeat the discharge/charge process.

There are other types of battery systems, but all involve the internal flow of ions and the external flow of electrons. Fuel cells work similarly, though they use fuel such as hydrogen at the anode and oxygen at the cathode. Electrolyzers generate hydrogen or other useful chemicals by essentially running a fuel cell in reverse.

The lead-acid rechargeable battery has been around for more than 150 years. It is the most reliable and cost-effective device for transportation (auxiliary systems and small-scale motive) and stationery (e.g., backup power) applications.

However, lead-acid batteries are heavy and bulky and do not work for portable electronics or large-scale transportation, such as electric vehicles and airplanes. Plus, they contain toxic and corrosive materials and release hydrogen off-gassing during recharge, posing explosion hazards that must be addressed.

Lithium-based batteries are the best energy storage solution presently for portable and transportation applications, offering high energy in compact and lightweight packages.

Figure 1. Left, Lake Mead water levels in 2012. Right, Lake Mead water levels in 2021.

Credit: (Left) Tony Webster, Flickr (CC BY 2.0); (Right) 北纬的星空, Wikimedia (CC BY-SA 4.0)

Unfortunately, lithium batteries have some substantial shortcomings. The issue with greatest notoriety is the fire hazard that plagued toys and phones and even the Boeing 787. Other issues include uncertainty in the supply and pricing of cobalt and lithium and various performance parameters, such as longevity and costs.

Substantial ceramics research projects are addressing these issues by improving or replacing lithium battery technology. A quick search for "lithium" and "battery" on https://ceramics.onlinelibrary.wiley.com reveals more than 200 entries since 2017 alone.

A selection of recent papers in The American Ceramic Society journals highlights some of the efforts toward new electrolyte, cathode, and anode materials.

Oxide coatings for cathodes

The key goal for cathode research is reducing or eliminating the cobalt used. Lithium cobalt oxide cathodes have good performance, but they are expensive. Other technologies include replacing some cobalt with manganese, aluminum, and/or nickel.

Two cobalt-free options include lithium iron phosphate (LFP) and lithium manganese oxide (LMO). Both have good qualities, with LMO being used in the Nissan Leaf. The biggest downside of LMO is loss of capacity with charge–discharge cycling.

Authors of the recent I*nternational Journal of Applied Ceramic Technology (ACT)* paper "Improved cycling stability of V_2O_5 modified spinel $LiMn_2O_4$ cathode at high cut-off voltage for lithium-ion batteries" note that the mechanisms leading to reduced capac-

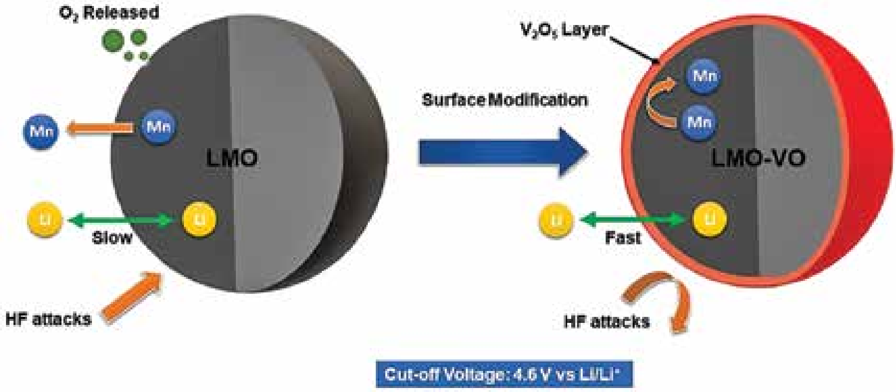
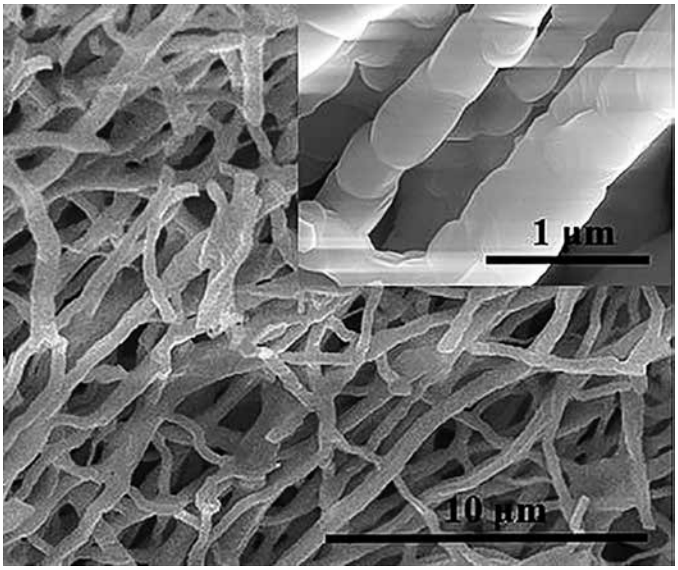


Figure 2. Schematic illustration of the functioning mechanism of V_2O_5 coating layer.[1]

Credit: Radzi et al., *International Journal of Applied Ceramic Technology*



Credit: Su et al., *International Journal of Applied Ceramic Technology*

Figure 3. SEM of electrospun high-entropy oxides calcined for 2 minutes at 850°C.[3]

ity are initiated by loss of surface oxygen at high voltage. To avoid this loss, they tried coating an LMO cathode with vanadium oxide (V_2O_5).[1]

The V_2O_5 coating strengthened the oxygen bonding to the manganese and weakened the bonding to lithium (Figure 2). This chemistry resulted in higher rates of charge transfer and lithium diffusion into and out of the spinel structure, along with stabilizing capacity over many charge–discharge cycles.

While the coating did improve these parameters, the initial capacity and cutoff voltage (high voltage on recharge) were lower than for samples featuring some other coating materials, such as SiO_2 and TiO_2. However, the other coatings resulted in higher capacity losses with cycling.

High-entropy materials for electrolytes

One approach for improving the safety of lithium-based batteries is replacing the highly flammable organic liquid or polymeric electrolytes with solid-state ceramics.

Electrolytes based on lithium lanthanum metal oxides (LLMO) show promise due to high lithium-ion conductivity, wide operating voltages, and good mechanical properties. The choice and amount of the metal dopants influences these properties, and research is being performed on a wide range of metals including zirconium, tantalum, niobium, aluminum, tellurium, and tungsten, along with mixtures of these metals and others.

High-entropy materials garnered much attention recently due to the stabilizing effect of having multiple metals with ranges of sizes and oxidation state occupying crystal sites. As the name of a recent *Journal of the American Ceramic Society* (*JACerS*) article suggests, "Processing and characterization of an $Li_7La_3Zr_{0.5}Nb_{0.5}Ta_{0.5}Hf_{0.5}O_{12}$ high-entropy Li–garnet electrolyte," the authors synthesized LLMO with equimolar amounts of zirconium, niobium, tantalum and hafnium.[2] The ceramic electrolyte was sintered at 1,100°C to 94% density with small grains and homogenous distribution of the elements.

Electrochemical testing showed high ionic conductivity (4.67×10^{-4} S/cm) and extremely low electronic conductivity ($\sim 10^{-8}$ S/cm). Low electronic conductivity is necessary to minimize leakage currents/self-discharge while the battery is idle. They attribute the high ionic conductivity to the different dopant radii stabilizing the cubic structure and maximizing the lithium-ion disorder and vacancies.

Oxides and glass-ceramics for anodes

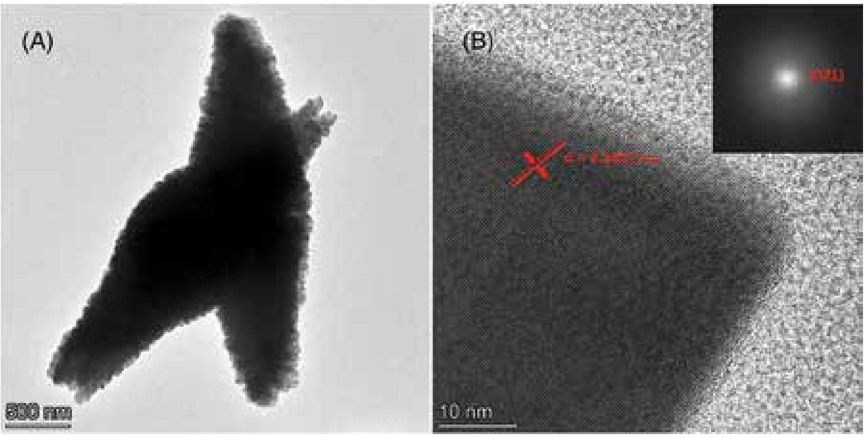
Like with cathodes, structure stabilization and increased capacity are goals for new anode materials as well. Lithium batteries mostly use graphite for the anode. While graphite easily accommodates intercalation and release of the lithium ions during the charge–discharge cycle, its total charge capacity is rather low. Lowering the cost of batteries and extending the range of electric vehicles both depend upon increasing the charge (energy storage) capacity.

As with the cathodes, anodes must conduct both electrons and ions while minimizing the distance the lithium-ions must diffuse into the structure. The authors of the *ACT* article "High entropy oxide nanofiber by electrospun method and its application for lithium battery anode material" combined the structural integrity of high-entropy magnesium–cobalt–nickel copper–zinc oxides with low-cost electrospinning process (Figure 3).[3]

Prior studies showed this oxide has good properties, particularly with nanoscale particles. The keys to this study are the format, which accommodates electrical conduction along the fiber direction while the lithium enters and exits radially, and the stability achieved using a proven, scalable fabrication method.

Their results are promising, with high stability of capacity over many cycles. However, the low initial capacity indicates more work is needed for commercialization.

Another study in *JACerS* also focuses on facile fabrication of distinctively structured crystalline materials for high stability and high capacity. In the article "Micro/nanostructured $Bi_2Mn_4O_{10}$ with hierarchical spindle morphology as a highly efficient anode



Credit: Cheng et al., *Journal of the American Ceramic Society*

Figure 4. TEM of spindle-shaped particles of nanocrystalline bismuth manganate.[4]

material for lithium-ion batteries," the title material is synthesized via hydrothermal methods without surfactants or templates.[4] The resulting materials have nanoscale crystals agglomerated into ovoid (egg or spindle-shaped) particles that are about 0.9 µm in diameter and 2.95 µm in length (Figure 4).

The materials showed high initial capacity, high stability of the reversible (usable) capacity, and good electrode kinetics. The authors attribute the material's performance to the pores and the nanoscale crystals accommodating the volume change and shortening the lithium diffusion paths, and the spindle shape providing electrical connectivity.

A third approach uses glass iron phosphate for the anode material. The loose network structure of glass readily accommodates insertion and removal of lithium during charging and discharging. However, the glassy state has insufficient electronic conductivity to be a good electrode material.

The authors of "Iron-phosphate glass-ceramic anodes for lithium-ion batteries," appearing in the International Year of Glass special issue of *International Journal of Applied Glass Science*, found that reducing the iron phosphate and allowing it to partially crystallize created a glass-ceramic with promising performance characteristics.[5]

While the capacity dropped by 50% initially during cycling, after about 50 cycles the capacity began growing, reaching close to the original value at around 700 cycles. After that point, capacity fell again but more slowly.

The authors showed that the crystals in the material experienced an order–disorder transition. The resulting material was in an amorphous state, although with no glass transition when measured by DSC.

In summary, ceramics research for the next generation of lithium-ion batteries is robust. New materials are being developed while manufacturing studies are being performed on some of the more promising ones. With many predictions of electric vehicles comprising half or more of the new vehicles manufactured or sold by 2030, the enabling technology of ceramic battery components cannot be brought to market soon enough.

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Optical-grade ceramics:

Historical turning point for the design of optical elements


Credit: Ikesue

By Akio Ikesue

Though traditionally believed impossible, polycrystalline ceramics can achieve optical properties on par or superior to those of single crystals—and may lead to a historical turning point in the design of optical elements.

When observing the microstructure of ceramics, researchers frequently see residual pores and structural defects, such as segregation at grain boundaries. These defects serve as scattering sources of incoming light, which affect the optical properties of ceramics and make them inferior to single crystals in optical applications.

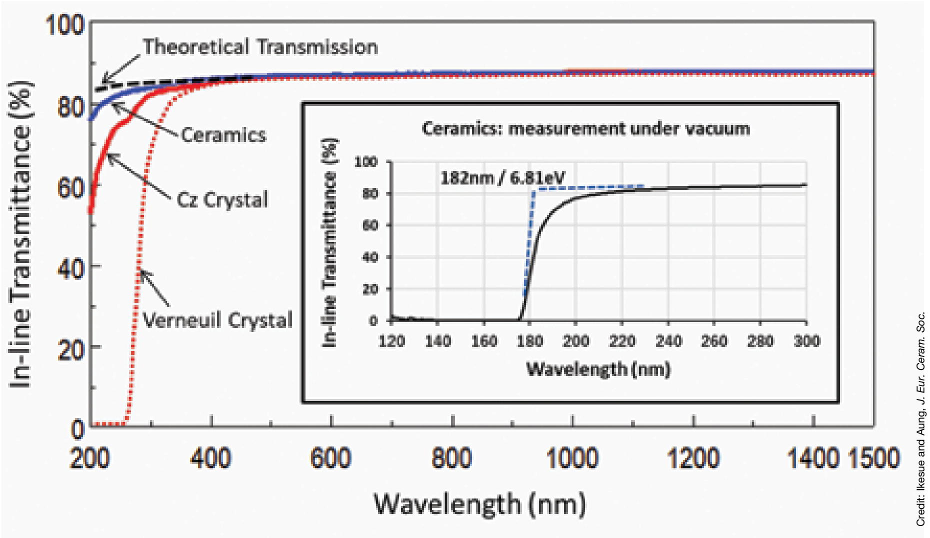
But what if these defects are removed? Could ceramics that contain pristine grain boundaries achieve optical properties similar to single crystals without grain boundaries?

Traditionally, the answer to this question is no. In the 19th century, Lord Rayleigh was awarded the Nobel Prize in Physics for constructing his own scattering theory based on computational science. According to his theory, even if these micrometer- to nanometer-scale defects are removed from the ceramic, scattering from grain boundaries (subnanometer scale) cannot be avoided.

Therefore, most materials scientists believed that the scattering of ceramics with grain boundaries would always be much larger than that of single crystals. For this reason, until the 1990s, there were very few studies on developing optoceramics for solid-state laser gain media, an application in which optical homogeneity is extremely important to ensure high beam quality of the generated laser light.

However, in 1995, the author and his colleagues successfully fabricated a polycrystalline yttrium aluminum garnet ($Y_3Al_5O_{12}$, or YAG) ceramic with optical properties on par with single crystals.[1] They demonstrated highly efficient laser oscillation using this ceramic as the laser gain media. Since then, they also reported on Faraday rotator ceramics with performance exceeding that of single crystals.[2,3] Furthermore, in 2020, they demonstrated spinel ceramics with performance that cannot be achieved with single crystals.[4]

How did they achieve these results? Low optical loss and high optical uniformity are requirements for optical



Credit: Ikesue and Aung, *J. Eur. Ceram. Soc.*

Figure 1. In-line transmittance curves of polycrystalline spinel ceramics and spinel single crystals synthesized by Verneuil or Czochralski methods, measured under air. Inset shows transmittance at ultraviolet region measured under vacuum atmosphere. Republished with permission from Reference 4.

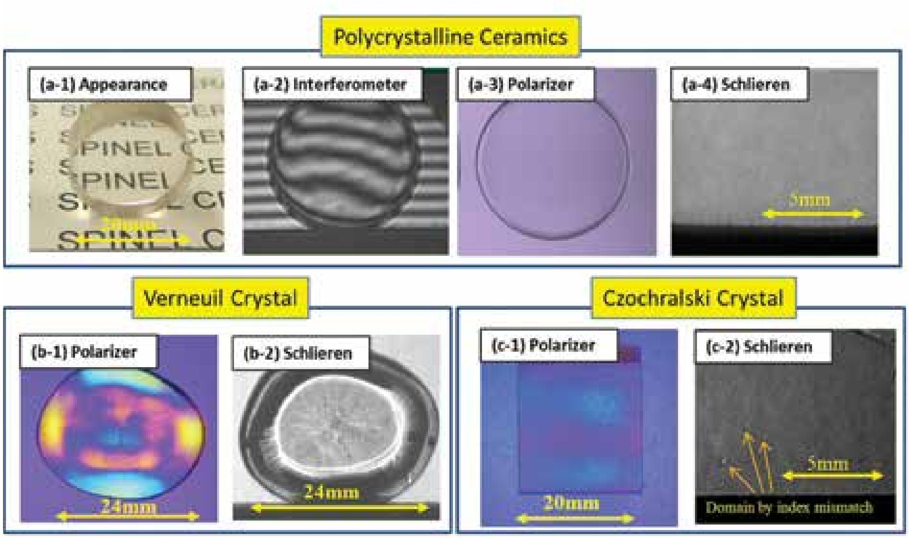
materials. They discovered ceramics obtained from a solid-state reaction process can overcome obstacles faced by single crystals when pursuing these characteristics.

Single crystals are grown using the melt-growth method, which generally causes optical distortion and segregation at the solid–liquid interface where the single crystal is grown. On the other hand, the solid-state reaction process allows for the fabrication of ceramics without segregation and with defect-free (barring dislocations) grain boundaries. While the scattering from the grain boundaries has not completely disappeared, the scattering properties and optical uniformity is superior to that of single crystals synthesized by the conventional melt-growth method.

Figure 1 compares the transmission spectra of polycrystalline spinel ceramics to the transmission spectra of spinel single crystals with a thickness of 10 mm synthesized by Verneuil or Czochralski methods. Only one residual pore of about 2 μm was detected in the spinel ceramic, so the calculated porosity is as low as 10^{-13}.[4] Therefore, if there is scattering, it must be due to grain boundaries only.

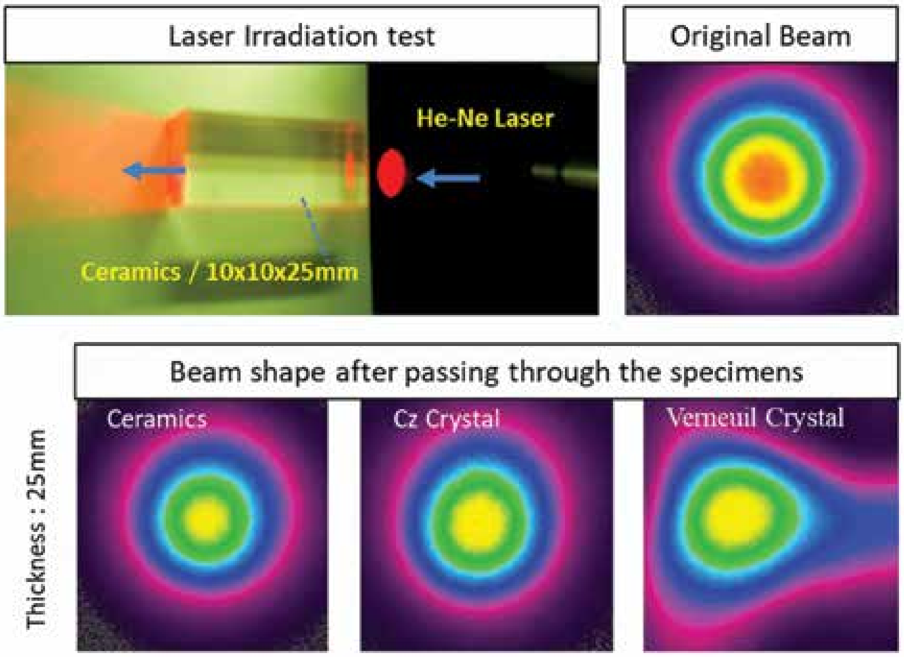
In the visible to infrared wavelength region above 400 nm, the properties of each material look similar, but the optical loss of spinel ceramics was the smallest at 0.07%/cm. In contrast, optical losses of Czochralski and Verneuil single crystals are 0.12 and 0.28%/cm, respectively.

The major difference between ceramics and single crystals, based on the measurement results, is that the transmission characteristics of ceramics with grain boundaries in the short wavelength region (vacuum ultraviolet region) are close to the calculated theoretical transmission characteristics, and the optical bandgap is 6.81 eV. According to Rayleigh's scattering theory, grain boundaries are expected to cause large scattering at short wavelengths. But the measurement results overturned the conventional concept.



Credit: Ikesue and Aung, *J. Eur. Ceram. Soc.*

Figure 2. Optical inspection of polycrystalline spinel ceramics produced by sintering method and spinel crystals by Verneuil and Czochralski methods. Republished with permission from Reference 4.



Credit: Ikesue and Aung, *J. Eur. Ceram. Soc.*

Figure 3. He-Ne laser irradiation test and change of beam pattern after passing through various specimens. Republished with permission from Reference 4.

Figure 2 shows the optical quality of the polycrystalline ceramic and the spinel single crystals. As can be seen in the figure, the most uniform material is the ceramic. Even for the single crystal produced by the Czochralski method, which generally is used to produce high-quality single crystals, birefringence and a domain structure with mismatched refractive indices are observed.

It should be noted that spinel belongs to the cubic crystal structure, and in principle there is no birefringence in materials with the cubic crystal structure. However, when observed with a polarizing plate, the commercially available single crystals still have significant birefringence. In contrast, ceramics are free of birefringence and have an extremely high extinction ratio of more than 40 dB. Furthermore, grain boundary scattering, which was measured using laser tomography with a wavelength of 633 nm, was not detected in the ceramics.

Figure 3 shows the beam shape of a He-Ne laser ($\lambda = 633$ nm) that passed through each material with a thickness of 25 mm. The single crystal material distorted the beam significantly, while the beam transmitted through the ceramics with high optical homogeneity (i.e., it retained its original shape).

Because of the long-held belief in Rayleigh's scattering theory, investigation of ceramics as an optical material has been hampered to date. However, now can be a historical turning point when optical elements will shift from single crystals to polycrystalline ceramics.

About the author

Akio Ikesue is president of World-Lab. Co., Ltd. in Nagoya, Japan. Contact Ikesue at poly-ikesue@s5.dion.ne.jp.

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'Transparent' ceramics versus 'optical-grade' ceramics

Transparent ceramics do not necessarily have excellent optical quality. In general, transparent ceramics are of a quality level that allows the surrounding scenery to be clearly observed through the material, and most transparent ceramics have a scattering loss that is 10^2 to 10^6 times larger than that of single crystals.

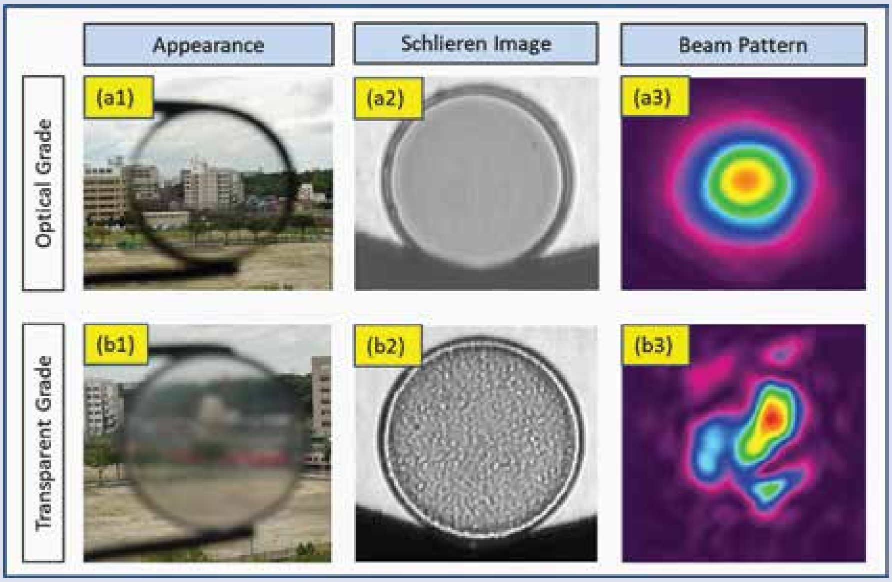
Optical-grade ceramics are ceramics with an optical loss of about 0.1%/cm, excellent uniformity, and optical performance equal to or greater than that of single crystals.

In the figure, images (a1) and (b1) demonstrate the difference between two Y_2O_3 ceramics with a thickness of 20 mm: an optical-grade sample and a transparent sample with low optical loss but poor optical homogeneity. (Y_2O_3 is a promising laser material, and research on laser oscillation from this transparent polycrystalline ceramic has been actively carried out.) The surrounding scenery can be clearly observed through the optical-grade ceramic sample (a1), while for the transparent ceramic with insufficient uniformity, the image of the surrounding scenery is blurry and distorted (b1). However, if the thickness of this transparent ceramic is reduced to less than 5 mm, the surrounding scenery can be observed clearly through the sample.

Many researchers may think that because Y_2O_3 ceramics have a single composition, they do not show nonuniformity after sintering. However, birefringence (optical distortion) occurs in the material due to insufficient grinding or ball milling conditions during the processing of the material. Therefore, although pristine Y_2O_3 has a cubic crystal structure in which birefringence does not exist, due to a slight mismatch in processing conditions, birefringence can generate in the material.

Images (a2) and (b2) show Schlieren images of optical grade and transparent grade Y_2O_3 ceramics, respectively. The Schlieren image allows accurate detection of the refractive index distribution inside the material by passing parallel light source with the same phase. The optical-grade sample has no detectable nonuniformity, whereas the transparent grade has significant nonuniformity.

Images (a3) and (b3) show the beam shapes of the 1,064 nm Nd:YAG laser transmitted through each material. The laser beam transmitted through optical-grade Y_2O_3 ceramics maintains high beam quality, similar to the high-quality spinel shown in Figure 3 (see main text). On the other hand, although the intensity of the laser transmitted through the transparent Y_2O_3 ceramics with insufficient uniformity and residual birefringence is high, most of the beam is diffused and the center part is remarkably distorted.[5] ■



Credit: Aung and Ikesue, *J. Eur. Ceram. Soc.*

Appearance (a1)(b1), Schlieren image (a2)(b2), and transmitted beam pattern (a3)(b3) for optical-grade and transparent Y_2O_3 ceramics. Republished with permission from Reference 5.

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Interfacial transitions at grain boundaries

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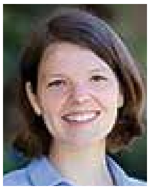

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Title: *Testing and design of ceramic structural materials and components at NASA*

GLOBAL YOUNG INVESTIGATOR AWARD

Chenxu Wang, assistant professor in the School of Physics, Peking University, China

Title: *MAX phases in extreme environments*

BRIDGE BUILDING AWARD

Paolo Colombo, professor of materials science and technology, Department of Industrial Engineering, University of Padova, Italy

Title: *Additive manufacturing of ceramics from liquid feedstocks*

PLENARY SPEAKER

Rita Baranwal, chief technology officer, Westinghouse Electric Company LLC, USA

Title: *Westinghouse fuel innovation leveraging advanced ceramics*

PLENARY SPEAKER

Huisuk Yun, Korea Institute of Materials Science (KIMS) Department Head of Advanced Biomaterials Research, and Professor of Materials Science, University of Science & Technology (UST), Korea

Title: *New challenges for ceramic additive manufacturing*

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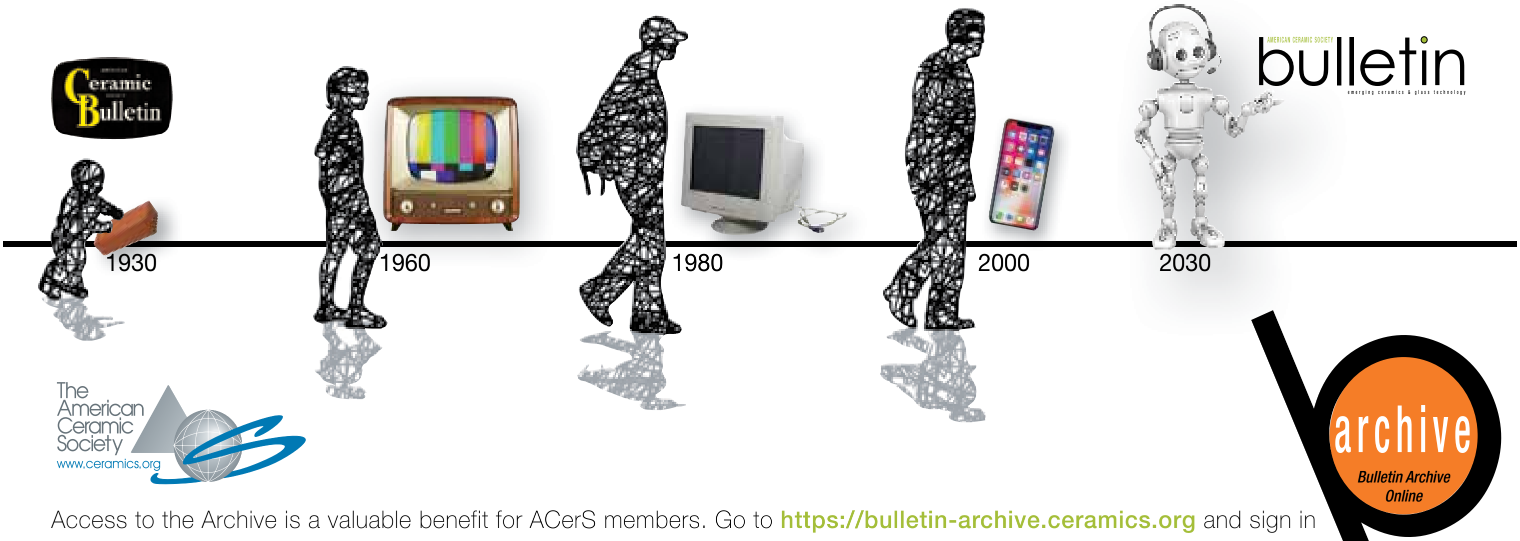

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22–27 47th International Conference and Expo on Advanced Ceramics and Composites (ICACC 2023) – Hilton Daytona Beach Oceanfront Resort, Daytona, Fla.; https://ceramics.org/ICACC23

March 2023

19–24 ➨ ECI – Electric Field Enhanced Processing of Advanced Materials III: Complexities and Opportunities – Hotel dos Templários, Tomar, Portugal; http://engconf.us/conferences/materials-science-including-nanotechnology/electric-field-enhanced-processing-of-advanced-materials-iii-complexities-and-opportunities

28–30 56th Annual St. Louis Section/Refractory Ceramics Division Symposium on Refractories – Hilton St. Louis Airport Hotel, St. Louis, Mo.; https://ceramics.org/event/56th-annual-st-louis-section-refractory-ceramics-division-symposium-on-refractories

May 2023

1–3 8th Ceramics Expo co-located with Thermal Technologies Expo – Suburban Collection Showplace, Novi, Mich.; https://www.ceramicsexpousa.com

17–19 ➨ 8th Highly-functional Ceramic Expo Osaka – INTEX Osaka, Osaka, Japan; https://www.ceramics-japan.jp/en-gb.html

30–June 1 MagForum 2023 – Grand Hotel Dino, Baveno, Lake Maggiore, Italy; http://imformed.com/get-imformed/forums/magforum-2023

June 2023

4–9 ACerS Glass & Optical Materials Division Annual Meeting (GOMD 2023) – Hotel Monteleone, New Orleans, La.; https://ceramics.org/gomd2023

5–8 ACerS 2023 Structural Clay Products Division & Southwest Section Meeting in conjunction with the National Brick Research Center Meeting – Omni Austin Hotel Downtown, Austin, Texas; https://ceramics.org/SCPD2023

14–16 13th Advances in Cement-Based Materials – Columbia University, New York, N.Y.; https://ceramics.org/event/13th-advances-in-cement-based-materials

August 2023

21–24 Materials Challenges in Alternative & Renewable Energy 2023 (MCARE 2023) combined with the 6th Annual Energy Harvesting Society Meeting (EHS 2023) – Hyatt Regency Bellevue, Bellevue, Wash.; https://ceramics.org/mcare-ehs-2023

27–31 ➨The International Conference on Sintering 2023 (Sintering 2023) – Nagaragawa Convention Center, Gifu, Japan; https://www.sintering2021.org

September 2023

26–29 ➨ Unified International Technical Conference on Refractories (UNITECR) with 18th Biennial World-wide Congress on Refractories – Kap Europa, Frankfurt am Main, Germany; https://unitecr2023.org

October 2023

1–5 ACerS 125th Annual Meeting with Materials Science & Technology 2023 – Columbus Convention Center, Columbus, Ohio; https://matscitech.org/MST23

November 2023

5–10 ➨ 15th Pacific Rim Conference on Ceramic and Glass Technology – Shenzhen World Exhbition & Convention Center, Shenzhen, China; https://ceramics.org/event/15th-pacific-rim-conference-on-ceramic-and-glass-technology

July 2024

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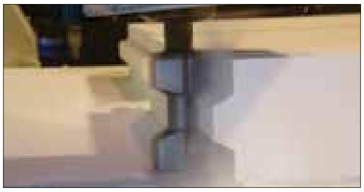

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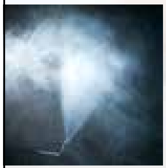

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Hugh Smith

Guest columnist

Sodium-ion batteries as the future solution to grid-scale energy storage

Numerous economic sectors (e.g., agriculture, industry) produce carbon emissions in a variety of ways (e.g., chemical processes, waste management). But most emissions can be traced back to energy generation. Carbon dioxide from fossil fuel combustion accounted for 75.3% of the global warming potential-weighted total of U.S. gross emissions between 1990–2020.[1]

Rather than fossil fuel combustion, energy can be provided by electricity generated through renewable sources, such as solar and wind. However, for this option to be an economically viable choice, there must be a way to store the generated electricity for days when the sun does not shine and the wind does not blow.

Grid-scale energy storage systems help overcome the reliability issues of renewables by storing excess energy production for later usage. Large, stationary batteries are a main energy storage method being investigated for grid-scale systems. While batteries do not deliver as much energy as some methods, such as pumped hydro, they can be called into action and modulated very easily. Further, they can be placed wherever there is space, including underground, and have no moving parts.

The cost of batteries is a practical constraint on their widespread usage. This constraint is due to the use of scarce metals like cobalt, nickel, and lithium in battery components. So, a materials solution is needed to make batteries more cost effective while still performing as required.

Sodium-ion batteries (NIBs) are a promising answer (Figure 1).[2] Sodium is more than one thousand times more abundant in Earth's crust than lithium, and it is cheaper to purify, leading to an overall much lower cost. Though the energy density of NIBs is lower than that of lithium-ion batteries (LIBs), energy density does not need to be as optimized for stationary applications as it is for mobile applications.

Credit: Hwang et al., *Chemical Society Reviews* (CC BY 3.0)

Figure 1. Overview of potential sodium-ion battery systems.

Notably, this performance difference between NIBs and LIBs is not an insurmountable barrier. Through improving the electrolyte, researchers at Pacific Northwest National Laboratory made NIBs at equivalent voltages to LIBs and improved on previous NIB metrics for cycle life and energy density. This electrolyte was also nonflammable, which is a considerable safety improvement over mainstream LIBs.[3]

To effectively implement NIBs at a large scale, high-voltage and high-energy transition metal oxide cathodes made with abundant elements must be developed. Fortunately, sodium can still perform well when paired with more abundant and environmentally friendly transition metals, in contrast to cobalt and nickel.[4]

Cathodes based on manganese oxide are cheap and environmentally friendly while demonstrating high voltage and decent energy density when compared to common LIB cathode materials. New understandings of the redox mechanism of this material open the door to further development in optimizing properties such as cycle life and energy density.[5] My graduate work will build off these new findings to make those advances.

Even when batteries are the best choice for energy storage, the optimal battery type depends on the specific application. Given its anticipated low costs and adequate performance, NIB technology is on its way to becoming the prime solution for easily controllable grid storage. Further down the line, it may even replace LIBs in small electric vehicles.

Whatever the future may hold, NIBs, and novel energy storage solutions in general, play a crucial role in reducing our future reliance on fossil fuels.

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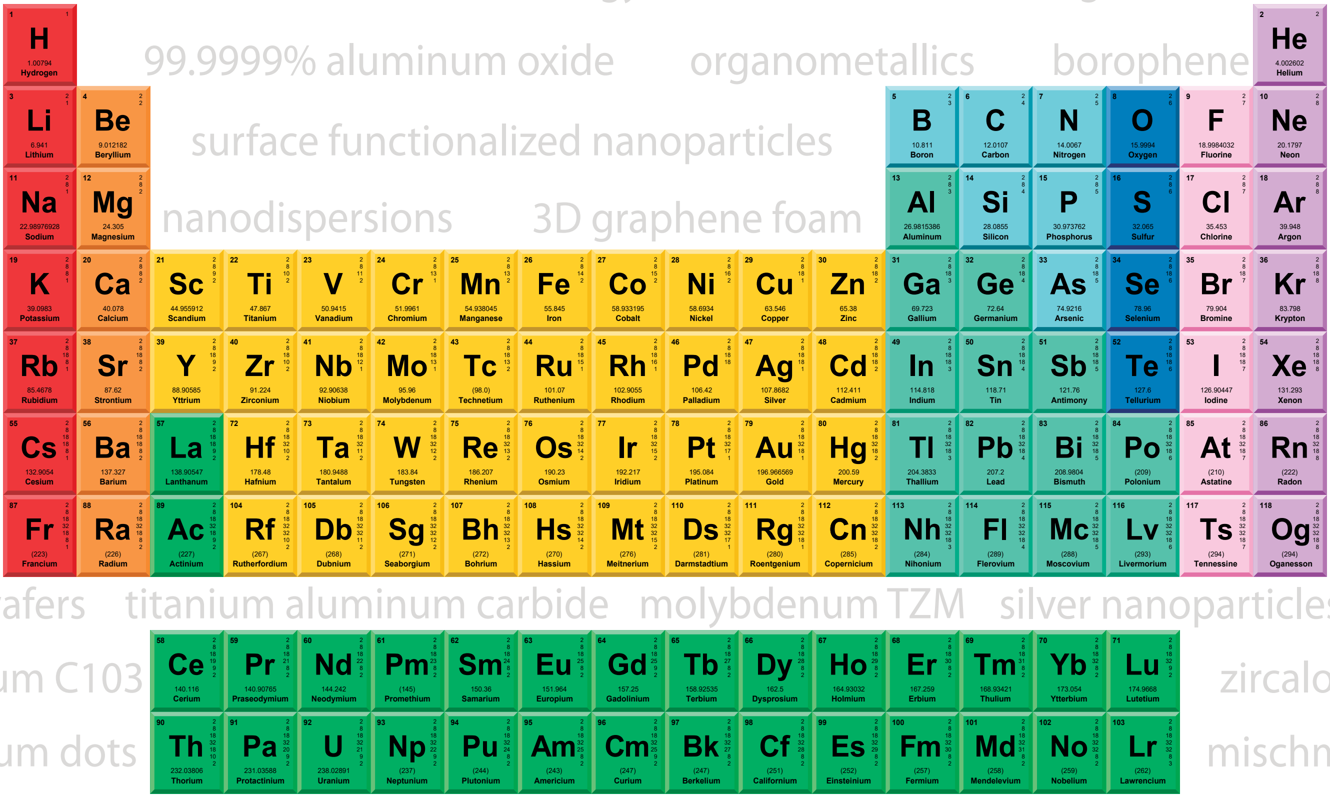

1 **H** 1 1.00794 Hydrogen																	2 **He** 2 4.002602 Helium
3 **Li** 2 1 6.941 Lithium	4 **Be** 2 2 9.012182 Beryllium											5 **B** 2 3 10.811 Boron	6 **C** 2 4 12.0107 Carbon	7 **N** 2 5 14.0067 Nitrogen	8 **O** 2 6 15.9994 Oxygen	9 **F** 2 7 18.9984032 Fluorine	10 **Ne** 2 8 20.1797 Neon
11 **Na** 2 8 1 22.98976928 Sodium	12 **Mg** 2 8 2 24.305 Magnesium											13 **Al** 2 8 3 26.9815386 Aluminum	14 **Si** 2 8 4 28.0855 Silicon	15 **P** 2 8 5 30.973762 Phosphorus	16 **S** 2 8 6 32.065 Sulfur	17 **Cl** 2 8 7 35.453 Chlorine	18 **Ar** 2 8 8 39.948 Argon
19 **K** 2 8 8 1 39.0983 Potassium	20 **Ca** 2 8 8 2 40.078 Calcium	21 **Sc** 2 8 9 2 44.955912 Scandium	22 **Ti** 2 8 10 2 47.867 Titanium	23 **V** 2 8 11 2 50.9415 Vanadium	24 **Cr** 2 8 13 1 51.9961 Chromium	25 **Mn** 2 8 13 2 54.938045 Manganese	26 **Fe** 2 8 14 2 55.845 Iron	27 **Co** 2 8 15 2 58.933195 Cobalt	28 **Ni** 2 8 16 2 58.6934 Nickel	29 **Cu** 2 8 18 1 63.546 Copper	30 **Zn** 2 8 18 2 65.38 Zinc	31 **Ga** 2 8 18 3 69.723 Gallium	32 **Ge** 2 8 18 4 72.64 Germanium	33 **As** 2 8 18 5 74.9216 Arsenic	34 **Se** 2 8 18 6 78.96 Selenium	35 **Br** 2 8 18 7 79.904 Bromine	36 **Kr** 2 8 18 8 83.798 Krypton
37 **Rb** 2 8 18 8 1 85.4678 Rubidium	38 **Sr** 2 8 18 8 2 87.62 Strontium	39 **Y** 2 8 18 9 2 88.90585 Yttrium	40 **Zr** 2 8 18 10 2 91.224 Zirconium	41 **Nb** 2 8 18 12 1 92.90638 Niobium	42 **Mo** 2 8 18 13 1 95.96 Molybdenum	43 **Tc** 2 8 18 13 2 (98.0) Technetium	44 **Ru** 2 8 18 15 1 101.07 Ruthenium	45 **Rh** 2 8 18 16 1 102.9055 Rhodium	46 **Pd** 2 8 18 18 106.42 Palladium	47 **Ag** 2 8 18 18 1 107.8682 Silver	48 **Cd** 2 8 18 18 2 112.411 Cadmium	49 **In** 2 8 18 18 3 114.818 Indium	50 **Sn** 2 8 18 18 4 118.71 Tin	51 **Sb** 2 8 18 18 5 121.76 Antimony	52 **Te** 2 8 18 18 6 127.6 Tellurium	53 **I** 2 8 18 18 7 126.90447 Iodine	54 **Xe** 2 8 18 18 8 131.293 Xenon
55 **Cs** 2 8 18 18 8 1 132.9054 Cesium	56 **Ba** 2 8 18 18 8 2 137.327 Barium	57 **La** 2 8 18 18 9 2 138.90547 Lanthanum	72 **Hf** 2 8 18 32 10 2 178.48 Hafnium	73 **Ta** 2 8 18 32 11 2 180.9488 Tantalum	74 **W** 2 8 18 32 12 2 183.84 Tungsten	75 **Re** 2 8 18 32 13 2 186.207 Rhenium	76 **Os** 2 8 18 32 14 2 190.23 Osmium	77 **Ir** 2 8 18 32 15 2 192.217 Iridium	78 **Pt** 2 8 18 32 17 1 195.084 Platinum	79 **Au** 2 8 18 32 18 1 196.966569 Gold	80 **Hg** 2 8 18 32 18 2 200.59 Mercury	81 **Tl** 2 8 18 32 18 3 204.3833 Thallium	82 **Pb** 2 8 18 32 18 4 207.2 Lead	83 **Bi** 2 8 18 32 18 5 208.9804 Bismuth	84 **Po** 2 8 18 32 18 6 (209) Polonium	85 **At** 2 8 18 32 18 7 (210) Astatine	86 **Rn** 2 8 18 32 18 8 (222) Radon
87 **Fr** 2 8 18 32 18 8 1 (223) Francium	88 **Ra** 2 8 18 32 18 8 2 (226) Radium	89 **Ac** 2 8 18 32 18 9 2 (227) Actinium	104 **Rf** 2 8 18 32 32 10 2 (267) Rutherfordium	105 **Db** 2 8 18 32 32 11 2 (268) Dubnium	106 **Sg** 2 8 18 32 32 12 2 (271) Seaborgium	107 **Bh** 2 8 18 32 32 13 2 (272) Bohrium	108 **Hs** 2 8 18 32 32 14 2 (270) Hassium	109 **Mt** 2 8 18 32 32 15 2 (276) Meitnerium	110 **Ds** 2 8 18 32 32 17 1 (281) Darmstadtium	111 **Rg** 2 8 18 32 32 18 1 (280) Roentgenium	112 **Cn** 2 8 18 32 32 18 2 (285) Copernicium	113 **Nh** 2 8 18 32 32 18 3 (284) Nihonium	114 **Fl** 2 8 18 32 32 18 4 (289) Flerovium	115 **Mc** 2 8 18 32 32 18 5 (288) Moscovium	116 **Lv** 2 8 18 32 32 18 6 (293) Livermorium	117 **Ts** 2 8 18 32 32 18 7 (294) Tennessine	118 **Og** 2 8 18 32 32 18 8 (294) Oganesson
			58 **Ce** 2 8 18 19 9 2 140.116 Cerium	59 **Pr** 2 8 18 21 8 2 140.90765 Praseodymium	60 **Nd** 2 8 18 22 8 2 144.242 Neodymium	61 **Pm** 2 8 18 23 8 2 (145) Promethium	62 **Sm** 2 8 18 24 8 2 150.36 Samarium	63 **Eu** 2 8 18 25 8 2 151.964 Europium	64 **Gd** 2 8 18 25 9 2 157.25 Gadolinium	65 **Tb** 2 8 18 27 8 2 158.92535 Terbium	66 **Dy** 2 8 18 28 8 2 162.5 Dysprosium	67 **Ho** 2 8 18 29 8 2 164.93032 Holmium	68 **Er** 2 8 18 30 8 2 167.259 Erbium	69 **Tm** 2 8 18 31 8 2 168.93421 Thulium	70 **Yb** 2 8 18 32 8 2 173.054 Ytterbium	71 **Lu** 2 8 18 32 9 2 174.9668 Lutetium	
			90 **Th** 2 8 18 32 18 10 2 232.03806 Thorium	91 **Pa** 2 8 18 32 20 9 2 231.03588 Protactinium	92 **U** 2 8 18 32 21 9 2 238.02891 Uranium	93 **Np** 2 8 18 32 22 9 2 (237) Neptunium	94 **Pu** 2 8 18 32 24 8 2 (244) Plutonium	95 **Am** 2 8 18 32 25 8 2 (243) Americium	96 **Cm** 2 8 18 32 25 9 2 (247) Curium	97 **Bk** 2 8 18 32 27 8 2 (247) Berkelium	98 **Cf** 2 8 18 32 28 8 2 (251) Californium	99 **Es** 2 8 18 32 29 8 2 (252) Einsteinium	100 **Fm** 2 8 18 32 30 8 2 (257) Fermium	101 **Md** 2 8 18 32 31 8 2 (258) Mendelevium	102 **No** 2 8 18 32 32 8 2 (259) Nobelium	103 **Lr** 2 8 18 32 32 8 3 (262) Lawrencium	

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