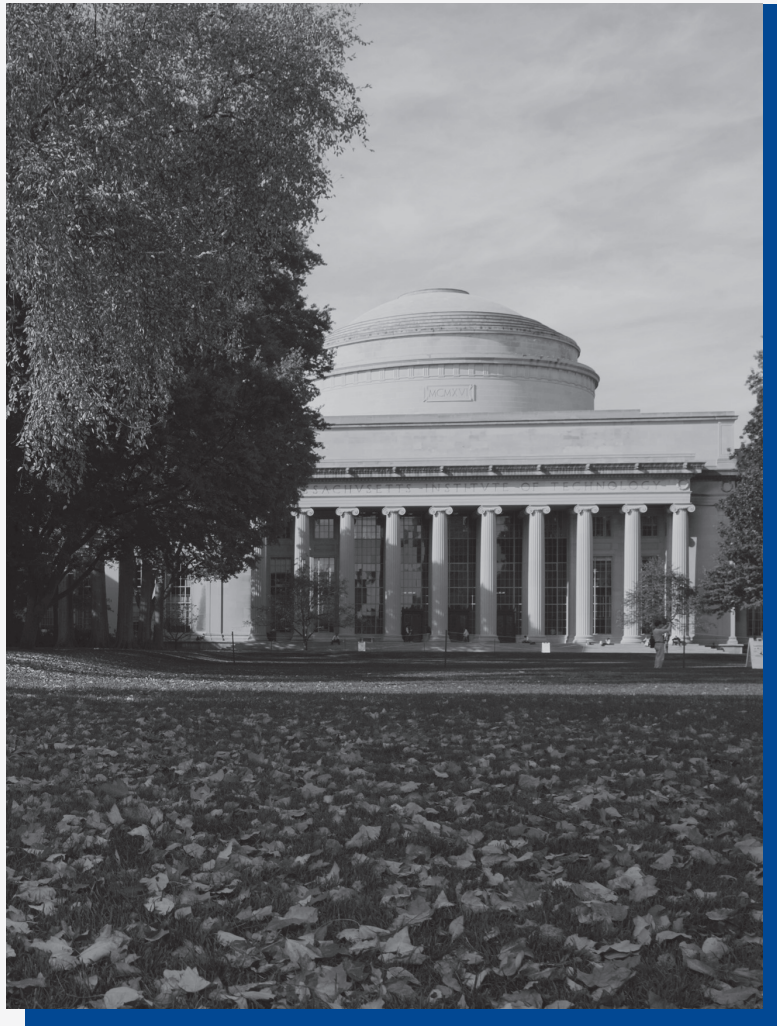


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# ENERGY STORAGE

BATTERIES, ECONOMICS, ENERGY  
 CONVERSION, ENERGY HARVESTING,  
 FUEL CELLS, THERMAL ENERGY  
 HARVESTING/STORAGE, STARTUPS



## RESEARCH SURVEY

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## Energy Storage

This survey by MIT's Industrial Liaison Program identifies selected MIT expertise and research in areas related to energy storage.

A key interest for energy storage is in its application to electricity generation, allowing for present energy production to be retained for use in the future. Power generation cannot always keep up with demand fluctuations and energy storage allows for providers to maintain a steady supply of energy during peak demand by storing electricity that is generated during off-peak times. Additionally, energy storage makes sources like solar and wind power, which are dependent on time of day and weather, more reliable.

Though energy can technically be stored in a variety of ways, the research identified in this report focuses on batteries, which is the primary method of storing energy chemically. Research on batteries include novel materials for batteries, as well as modeling and optimization of battery life cycles.

Additional topics include energy conversion and fuel cells, thermal energy storage, the economics of energy storage at the grid level and commercial applications of energy storage, and energy harvesting for electronic devices.

<b>BATTERIES – NOVEL MATERIALS, OPTIMIZATION, &amp; MODELING .....</b>	<b>7</b>
MARTIN Z BAZANT .....	7
<i>Bazant Research Group</i> .....	7
<i>Modeling the Metal–Insulator Phase Transition in <math>\text{Li}_x\text{CoO}_2</math> for Energy and Information Storage</i> .....	7
<i>Data-driven prediction of battery cycle life before capacity degradation</i> .....	8
ANGELA M BELCHER .....	8
<i>The Biomolecular Materials Group</i> .....	8
<i>Virus-Templated Nickel Phosphide Nanofoams as Additive-Free, Thin-Film Li-Ion Microbattery Anodes</i> .....	9
<i>Biotemplated Zinc Sulfide Nanofibers as Anode Materials for Sodium-Ion Batteries</i> .....	9
RICHARD D BRAATZ .....	10
<i>Braatz Group</i> .....	10
<i>Closed-loop optimization of fast-charging protocols for batteries with machine learning</i> .....	10
<i>Data-driven prediction of battery cycle life before capacity degradation</i> .....	11
FIKILE R BRUSHETT .....	11
<i>Brushett Group</i> .....	11
<i>Establishing Design Principles For Molecular Engineering Of High Concentration Redox Electrolytes</i> .....	12
<i>An investigation on the impact of halidization on substituted dimethoxybenzenes</i> .....	12
<i>Understanding the role of the porous electrode microstructure in redox flow battery performance using an experimentally validated 3D pore-scale lattice Boltzmann model</i> .....	13
<i>Engineering porous electrodes for next-generation redox flow batteries: recent progress and opportunities</i> ...	13
<i>Improved Energy Arbitrage Optimization with Detailed Flow Battery Characterization</i> .....	13
W CRAIG CARTER .....	14
<i>Phase-field model for diffusion-induced grain boundary migration: An application to battery electrodes</i> .....	14
<i>Mechanical instability of electrode-electrolyte interfaces in solid-state batteries</i> .....	15
YET-MING CHIANG .....	15
<i>Effect of Concentrated Diglyme-Based Electrolytes on the Electrochemical Performance of Potassium-Ion Batteries</i> .....	15

<i>Order-disorder transition in nano-rutile TiO<sub>2</sub> anodes: A high capacity low-volume charge Li-ion battery material</i> .....	16
<i>Electrochemical Redox Behavior of Li Ion Conducting Sulfide Solid Electrolytes</i> .....	16
<i>Stabilizing Li-S Battery Through Multilayer Encapsulation of Sulfur</i> .....	17
BETAR GALLANT .....	17
<i>Gallant Research Group</i> .....	17
<i>Chemical and Structural Design of Inorganic-Organic Layers for Stabilized Li Anodes</i> .....	18
<i>The intrinsic behavior of lithium fluoride in solid electrolyte interphases on lithium</i> .....	18
<i>Rechargeable-battery chemistry based on lithium oxide growth through nitrate anion redox</i> .....	18
<i>Governing Role of Solvent on Discharge Activity in Lithium-CO<sub>2</sub> Batteries</i> .....	19
<i>Tailoring the Discharge Reaction in Li-CO<sub>2</sub> Batteries through Incorporation of CO<sub>2</sub> Capture Chemistry</i> ....	19
<i>Conversion tech could turn CO<sub>2</sub> emissions into battery electrolytes</i> .....	20
<i>Video: Introduction, Betar Gallant, Esther &amp; Harold E. Edgerton Career Development Professor</i> .....	20
T ALAN HATTON .....	20
<i>Hatton Research Group</i> .....	20
<i>Self-assembled nanostructures in ionic liquids facilitate charge storage at electrified interfaces</i> .....	21
<i>Redox-electrolytes for non-flow electrochemical energy storage: A critical review and best practice</i> .....	21
JING KONG .....	21
<i>Nanomaterials and Electronics Group</i> .....	22
<i>Sustainable Synthesis of Biomass-Derived Carbon Electrodes with Hybrid Energy-Storage Behaviors for Use in High-Performance Na-Ion Capacitors</i> .....	22
JU LI .....	23
<i>Electrochemically Driven Mechanical Energy Harvesting</i> .....	23
<i>A Novel Moisture-Insensitive and Low-Corrosivity Ionic Liquid Electrolyte for Rechargeable Aluminum Batteries</i> .....	23
<i>A low-cost intermediate temperature Fe/Graphite battery for grid-scale energy storage</i> .....	24
<i>Li metal deposition and stripping in a solid-state battery via Coble creep</i> .....	24
<i>Optimal annealing of Al foil anode for prelithiation and full-cell cycling in Li-ion battery: The role of grain boundaries in lithiation/delithiation ductility</i> .....	25
<i>Gradient Li-rich oxide cathode particles immunized against oxygen release by a molten salt treatment</i> .....	25
New electrode design may lead to more powerful batteries .....	26
JENNIFER L M RUPP .....	26
<i>Electrochemical Materials Lab</i> .....	27
Solid State Li-Ion Batteries.....	27
Solid Oxide Fuel Cells.....	27
<i>All-Solid-State Glucose Fuel Cell for Energy Harvesting in the Human Body</i> .....	27
<i>A low ride on processing temperature for fast lithium conduction in garnet solid-state battery films</i> .....	28
<i>Building better all-solid-state batteries with Li-garnet solid electrolytes and metalloid anodes</i> .....	28
DONALD R SADOWAY .....	29
<i>Modeling discontinuous potential distributions using the finite volume method, and application to liquid metal batteries</i> .....	29
<i>A borate decorated anion-immobilized solid polymer electrolyte for dendrite-free, long-life Li metal batteries</i> .....	29
YANG SHAO-HORN .....	30
<i>Electrochemical Energy Lab</i> .....	30
<i>FSI-inspired solvent and "full fluorosulfonyl" electrolyte for 4 v class lithium-metal batteries</i> .....	31
<i>Solvent- And Anion-Dependent Li<sup>+</sup>-O<sub>2</sub> - Coupling Strength and Implications on the Thermodynamics and Kinetics of Li-O<sub>2</sub> Batteries</i> .....	31

<i>Revealing electrolyte oxidation: Via carbonate dehydrogenation on Ni-based oxides in Li-ion batteries by in situ Fourier transform infrared spectroscopy</i> .....	31
<i>Molecular Design of Stable Sulfamide- and Sulfonamide-Based Electrolytes for Aprotic Li-O<sub>2</sub> Batteries</i> .....	32
<i>Revealing Electronic Signatures of Lattice Oxygen Redox in Lithium Ruthenates and Implications for High-Energy Li-Ion Battery Material Designs</i> .....	32
<i>Enhanced Cycling Performance of Ni-Rich Positive Electrodes (NMC) in Li-Ion Batteries by Reducing Electrolyte Free-Solvent Activity</i> .....	33
CARL V THOMPSON.....	33
<i>Modeling the Effect of Lithium Superoxide Solvation and Surface Reduction Kinetics on Discharge Capacity in Lithium-Oxygen Batteries</i> .....	34
<i>Multi-cell thermogalvanic systems for harvesting energy from cyclic temperature changes</i> .....	34
BRIAN L WARDLE.....	35
<i>necstlab</i> .....	35
<i>Multifunctional nanocomposite structural separators for energy storage</i> .....	35
<b>ECONOMICS OF ENERGY STORAGE</b> .....	<b>36</b>
WILLIAM H GREEN, JR.....	36
<i>Green Research Group</i> .....	36
<i>Recharging systems and business operations to improve the economics of electrified taxi fleets</i> .....	36
<i>Learning only buys you so much: Practical limits on battery price reduction</i> .....	37
OMER KARADUMAN.....	37
<i>Economics Grid-Scale Energy Storage</i> .....	37
APURBA SAKTI.....	38
<i>Review of wholesale markets and regulations for advanced energy storage services in the United States: Current status and path forward</i> .....	38
JESSIKA TRANCIK.....	39
<i>Trancik Lab</i> .....	39
<i>Value of storage technologies</i> .....	39
<i>Storage Requirements and Costs of Shaping Renewable Energy Toward Grid Decarbonization</i> .....	39
<b>ENERGY CONVERSION AND FUEL CELLS</b> .....	<b>40</b>
YOGESH SURENDRANATH.....	40
<i>Surentranath Group</i> .....	40
<i>Oxygen Reduction Catalysis at Tunable Metal Sulfide Nanofilms</i> .....	41
<i>Graphite Conjugation Eliminates Redox Intermediates in Molecular Electrocatalysis</i> .....	41
<i>Mixed Electron-Proton Conductors Enable Spatial Separation of Bond Activation and Charge Transfer in Electrocatalysis</i> .....	42
HARRY L. TULLER.....	42
<i>Crystal Physics and Electroceramics Laboratory</i> .....	42
<i>Chemomechanics of Fuel Cell Related Materials</i> .....	42
<i>Tailoring Nonstoichiometry and Mixed Ionic Electronic Conductivity in Pr<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>2-δ</sub>/SrTiO<sub>3</sub> Heterostructures</i> .....	43
BILGE YILDIZ.....	43
<i>Laboratory for Electrochemical Interfaces</i> .....	44
<i>Solid oxide fuel and electrolysis cells</i> .....	44
<i>Solid state Li-ion batteries</i> .....	44
<i>Polar or not polar? the interplay between reconstruction, Sr enrichment, and reduction at the La<sub>0.75</sub>Sr<sub>0.25</sub>MnO<sub>3</sub> (001) surface</i> .....	45
<b>ENERGY HARVESTING</b> .....	<b>45</b>

ANANTHA P CHANDRAKASAN .....	45
<i>A Silicon MEMS em vibration energy harvester</i> .....	46
<i>A MEMS Magnetic-Based Vibration Energy Harvester</i> .....	46
SANG-GOOK KIM.....	46
<i>Park Center for Complex Systems: Micro Nano Systems Laboratory</i> .....	47
<i>Buckled MEMS beams for energy harvesting from low frequency vibrations</i> .....	47
JEFFREY H LANG .....	47
<i>A Robust Electromagnetic MEMS Vibration Energy Harvester</i> .....	48
<i>Contactless Current and Voltage Detection Using Signal Processing and Machine Learning</i> .....	48
<i>Simulation and Modelling of a Spatially-Efficient 3D Wireless Power Transfer System for Multi-User Charging</i> .....	49
<i>Co-optimization of a piezoelectric energy harvesting system for broadband operation</i> .....	49
<b>THERMAL ENERGY HARVESTING AND STORAGE .....</b>	<b>49</b>
GANG CHEN .....	49
<i>NanoEngineering Group</i> .....	50
Thermal Storage.....	50
<i>Thermal energy storage radiatively coupled to a supercritical Rankine cycle for electric grid support</i> .....	50
<i>Video: Advanced Materials and Systems at the Energy and Water Nexus</i> .....	51
JEFFREY C GROSSMAN .....	51
<i>The Grossman Group</i> .....	52
Thermal Harvesting and Storage .....	52
<i>Solvent- And Anion-Dependent Li<sup>+</sup>-O<sub>2</sub> - Coupling Strength and Implications on the Thermodynamics and Kinetics of Li-O<sub>2</sub> Batteries</i> .....	52
<i>Laser-sculptured ultrathin transition metal carbide layers for energy storage and energy harvesting applications</i> .....	53
<i>Optically-regulated thermal energy storage in diverse organic phase-change materials</i> .....	53
Saving heat until you need it.....	53
ASEGUN S HENRY.....	54
<i>Atomistic Simulation &amp; Energy Research Group</i> .....	54
Thermal Energy Grid Storage (TEGS) Concept.....	55
<i>Thermal energy grid storage using multi-junction photovoltaics</i> .....	55
“Sun in a box” would store renewable energy for the grid.....	55
ALEXIE KOLPAK .....	56
<i>Kolpak Group</i> .....	56
<i>Parameter-free model to estimate thermal conductivity in nanostructured materials</i> .....	56
EVELYN N WANG .....	57
<i>Device Research Laboratory</i> .....	57
Advanced Thermal Storage.....	57
Solar Energy: Solar Thermophotovoltaic.....	58
<i>High temperature stability of transparent silica aerogels for solar thermal applications</i> .....	58
<i>Harnessing Heat beyond 200 °c from Unconcentrated Sunlight with Nonevacuated Transparent Aerogels</i> .....	59
<b>PROGRAMS, LABS, CENTERS .....</b>	<b>59</b>
MIT CLIMATE .....	59
<i>Decarbonizing the Electricity Sector</i> .....	60
Getting the carbon out of the electricity sector .....	60
MIT ENERGY INITIATIVE .....	61
<i>Saving heat until you need it</i> .....	61
<i>Energy Storage Center</i> .....	61

Review of wholesale markets and regulations for advanced energy storage services in the United States: Current status and path forward.....	61
Energy Storage for the Grid: Policy Options for Sustaining Innovation.....	62
MATERIALS RESEARCH LABORATORY .....	62
MICROSYSTEMS TECHNOLOGY LABORATORIES.....	63
<i>High Capacity CMOS-compatible Thin Film Batteries on Flexible Substrates</i> .....	63
<i>Crystal Engineering of Mixed Cation Perovskite for Fabrication of Highly Efficient Solar Cells</i> .....	64
<i>Buckled MEMS Beams for Energy Harvesting from Low-frequency Vibrations</i> .....	64
<i>A Robust Electromagnetic MEMS Vibration Energy Harvester</i> .....	65
<i>All-solid-state Glucose Fuel Cell for Energy Harvesting in the Human Body</i> .....	65
SOLID-STATE SOLAR-THERMAL ENERGY CONVERSION CENTER (S3TEC) .....	66
TATA CENTER FOR TECHNOLOGY AND DESIGN .....	66
<i>Energy</i> .....	66
On-Demand High-Throughput Synthesis of Zeolites and MOFS For Energy, Storage, Separation and Catalysis.....	67
Solar Energy Storage for Solar Cooking: Research, Development & Market Testing .....	67
Capturing Biogas as a Sustainable Energy Source to Power Rural Communities.....	68
<b>MIT-RELATED STARTUPS.....</b>	<b>68</b>
MIT STARTUP EXCHANGE.....	68
24M TECHNOLOGIES INC. ....	68
AMBRI, INC. ....	69
ANTORA ENERGY .....	69
CADENZA INNOVATION .....	69
<i>A novel way to advance a better battery design</i> .....	70
FORM ENERGY .....	70
HEILA TECHNOLOGIES .....	70
HELIX POWER.....	70
NANORAMIC LABORATORIES .....	71
POLYJOULE .....	71
SOLIDENERGY SYSTEMS .....	71

**BATTERIES – NOVEL MATERIALS, OPTIMIZATION, & MODELING****MARTIN Z BAZANT**

Edwin G Roos (1944) Professor and Executive Officer of Chemical Engineering,

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Publications: [http://web.mit.edu/bazant/www/papers/cv\\_papers.html](http://web.mit.edu/bazant/www/papers/cv_papers.html)

Professor Bazant is broadly interested in applied mathematics and engineering physics. Research focuses on transport phenomena in microfluidics and electrochemical systems, motivated by applications in energy storage, water purification, and lab-on-a-chip technology. Current topics include nonlinear electrokinetics, "shock" electro dialysis, electrodeposition, super-hydrophobic surfaces, super-capacitors, fuel cells, and rechargeable batteries. Bazant spent his first ten years on the faculty at MIT in the Department of Mathematics, where he led the Nonlinear Electrokinetics Group, Dry Fluids Laboratory, and Applied Mathematics Computational Laboratory. Bazant joined the Department of Chemical Engineering in December 2008, while retaining a joint appointment in Mathematics. His research now combines mathematical modeling with experiments. His group has students from Chemical Engineering, Mathematics, Physics, Mechanical Engineering, and Materials Science.

**Bazant Research Group**

<http://bazantgroup.mit.edu/>

Research: <http://bazantgroup.mit.edu/research>

Publications: <http://bazantgroup.mit.edu/publications>

Our group specializes in mathematical modeling of transport phenomena, especially in electrochemical systems and micro/nanofluidic devices. We develop new models for complex nonlinear phenomena and employ both analytical approximations and computational methods to solve the models and make predictions to be compared with experimental data. In some cases, we collaborate with experimental groups at MIT and around the world, but we also have our own laboratory, focusing on electrochemical systems for environmental and energy applications.

Current research topics relate to energy (Li-ion batteries, electrochemical capacitors, fuel cells), water treatment ("shock electro dialysis", capacitive desalination, separations), and microfluidics (nonlinear electrokinetics, hydrodynamic slip, electrophoresis, nanofluidics) as well as fundamental aspects of applied mathematics, continuum mechanics, and statistical physics.

**Modeling the Metal–Insulator Phase Transition in  $\text{Li}_x\text{CoO}_2$  for Energy and Information Storage**

Nadkarni, N., Zhou, T., Fraggedakis, D., Gao, T., Bazant, M.Z.

Advanced Functional Materials, Volume 29, Issue 40, 1 October 2019, Article number 1902821,

<https://doi.org/10.1002/adfm.201902821>

An electro-chemomechanical phase-field model is developed to capture the metal–insulator phase transformation along with the structural and chemical changes that occur in  $\text{Li}_x\text{CoO}_2$  in the regular operating range of  $0.5 < x < 1$ . Under equilibrium, in the regime of phase coexistence, it is found that transport limitations lead to kinetically arrested states that are not determined by strain-energy minimization. Further, lithiation profiles are obtained for different discharging rates and

the experimentally observed voltage plateau is observed. Finally, a simple model is developed to account for the conductivity changes for a polycrystalline  $\text{Li}_x\text{CoO}_2$  thin film as it transforms from the metallic phase to the insulating phase and a strategy is outlined for memristor design. The theory can therefore be used for modeling  $\text{Li}_x\text{CoO}_2$ -electrode batteries as well as low voltage nonvolatile redox transistors for neuromorphic computing architectures.

#### Data-driven prediction of battery cycle life before capacity degradation

Severson, K.A., Attia, P.M., Jin, N., Perkins, N., Jiang, B., Yang, Z., Chen, M.H., Aykol, M., Herring, P.K., Fraggedakis, D., Bazant, M.Z., Harris, S.J., Chueh, W.C., Braatz, R.D.  
Nature Energy, Volume 4, Issue 5, 1 May 2019, Pages 383-391, <https://doi.org/10.1038/s41560-019-0356-8>

Accurately predicting the lifetime of complex, nonlinear systems such as lithium-ion batteries is critical for accelerating technology development. However, diverse aging mechanisms, significant device variability and dynamic operating conditions have remained major challenges. We generate a comprehensive dataset consisting of 124 commercial lithium iron phosphate/graphite cells cycled under fast-charging conditions, with widely varying cycle lives ranging from 150 to 2,300 cycles. Using discharge voltage curves from early cycles yet to exhibit capacity degradation, we apply machine-learning tools to both predict and classify cells by cycle life. Our best models achieve 9.1% test error for quantitatively predicting cycle life using the first 100 cycles (exhibiting a median increase of 0.2% from initial capacity) and 4.9% test error using the first 5 cycles for classifying cycle life into two groups. This work highlights the promise of combining deliberate data generation with data-driven modelling to predict the behaviour of complex dynamical systems.

#### ANGELA M BELCHER

James Mason Crafts Professor of Biological Engineering and Materials Science and Engineering,  
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Department Head / Biological Engineering (BE)  
Lab: <http://belcherlab.mit.edu/>  
Publications: <http://belcherlab.mit.edu/publications/>

Transition metal phosphides are a new class of materials generating interest as alternative negative electrodes in lithium-ion batteries. However, metal phosphide syntheses remain underdeveloped in terms of simultaneous control over phase composition and 3D nanostructure. Herein, M13 bacteriophage is employed as a biological scaffold to develop 3D nickel phosphide nanofoams with control over a range of phase compositions and structural elements. Virus-templated  $\text{Ni}_5\text{P}_4$  nanofoams are then integrated as thin-film negative electrodes in lithium-ion microbatteries, demonstrating a discharge capacity of  $677 \text{ mAh g}^{-1}$  ( $677 \text{ mAh cm}^{-3}$ ) and an 80% capacity retention over more than 100 cycles. This strong electrochemical performance is attributed to the virus-templated, nanostructured morphology, which remains electronically conductive throughout cycling, thereby sidestepping the need for conductive additives. When accounting for the mass of additional binder materials, virus-templated  $\text{Ni}_5\text{P}_4$  nanofoams demonstrate the highest practical capacity reported thus far for  $\text{Ni}_5\text{P}_4$  electrodes. Looking forward, this synthesis method is generalizable and can enable precise control over the 3D nanostructure and phase composition in other metal phosphides, such as cobalt and copper.

#### The Biomolecular Materials Group

<http://belcherlab.mit.edu/>  
Research: <http://belcherlab.mit.edu/research/>



Publications: <http://belcherlab.mit.edu/publications/>

In the Biomolecular Materials Group, we evolve simple organisms using directed evolution to work with the elements in the rest of the periodic table. We encourage these organisms to grow and assemble technologically important materials and devices for energy, the environment, and medicine. These hybrid organic-inorganic electronic and magnetic materials have been used in applications as varied as solar cells, batteries, medical diagnostics and basic single molecule interactions related to disease. In doing so, we have capitalized on many of the wonderful properties of biology—using only non-toxic materials, employing self-repair mechanisms, self-assembling precisely and over longer ranges, and adapting and evolving to become better over time.

### **Virus-Templated Nickel Phosphide Nanofoams as Additive-Free, Thin-Film Li-Ion Microbattery Anodes**

Records, W.C., Wei, S., Belcher, A.M.

Small, Volume 15, Issue 44, 1 October 2019, Article number 1903166,

<https://doi.org/10.1002/smll.201903166>

Transition metal phosphides are a new class of materials generating interest as alternative negative electrodes in lithium-ion batteries. However, metal phosphide syntheses remain underdeveloped in terms of simultaneous control over phase composition and 3D nanostructure. Herein, M13 bacteriophage is employed as a biological scaffold to develop 3D nickel phosphide nanofoams with control over a range of phase compositions and structural elements. Virus-templated Ni<sub>5</sub>P<sub>4</sub> nanofoams are then integrated as thin-film negative electrodes in lithium-ion microbatteries, demonstrating a discharge capacity of 677 mAh g<sup>-1</sup> (677 mAh cm<sup>-3</sup>) and an 80% capacity retention over more than 100 cycles. This strong electrochemical performance is attributed to the virus-templated, nanostructured morphology, which remains electronically conductive throughout cycling, thereby sidestepping the need for conductive additives. When accounting for the mass of additional binder materials, virus-templated Ni<sub>5</sub>P<sub>4</sub> nanofoams demonstrate the highest practical capacity reported thus far for Ni<sub>5</sub>P<sub>4</sub> electrodes. Looking forward, this synthesis method is generalizable and can enable precise control over the 3D nanostructure and phase composition in other metal phosphides, such as cobalt and copper.

### **Biotemplated Zinc Sulfide Nanofibers as Anode Materials for Sodium-Ion Batteries**

Zhang, G., Wei, S., Belcher, A.M.

ACS Applied Nano Materials, Volume 1, Issue 10, 26 October 2018, Pages 5631-5639,

<https://doi.org/10.1021/acsnm.8b01254>

Sodium-ion batteries (SIBs) have generated substantial interest because of the geopolitical uncertainty of the availability of lithium, as well as the potential cost savings associated with replacing lithium with sodium. One of the key technological impediments to SIBs is the availability of a high-capacity anode material. Here, we show that biotemplated zinc sulfide nanofibers, prepared using the M13 bacteriophage template, have the potential to be used for this purpose. We investigated the effect of both annealing and carbon coating on the electrochemical performance of these materials. Biotemplated zinc sulfide nanofibers, when coated with a few-nanometer carbon layer, could deliver a reversible capacity of 603 mAh/g at 100 mA/g discharge rate, even when the zinc sulfide loading is as high as 70%. The initial Coulombic efficiency reached 71%, and the electrode could be cycled for at least 100 cycles.

**RICHARD D BRAATZ**

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Publications: <http://web.mit.edu/braatzgroup/publications.html>

Richard D. Braatz is the Edwin R. Gilliland Professor at the Massachusetts Institute of Technology (MIT) where he does research in process data analytics, design, and control of advanced manufacturing systems. He received MS and PhD from the California Institute of Technology and was the Millennium Chair and Professor at the University of Illinois at Urbana-Champaign and a Visiting Scholar at Harvard University before moving to MIT.

**Braatz Group**

<http://web.mit.edu/braatzgroup/index.html>

Publications: <http://web.mit.edu/braatzgroup/publications.html>

Our research is in applied mathematics and control theory and its application to manufacturing systems where the control of events at the molecular scale is key to product quality.

Some specific applications include:

- Optimal design of pharmaceutical crystallizers that utilize process intensification to manufacture crystals of precisely controlled size and molecular structure;
- Multiscale modeling and design of nano- and microstructured polymeric materials that respond to internal or external stimuli to spatially control the release of macromolecules;
- Control of molecular systems and nanodevices, from molecular clustering on surfaces to carbon nanotube-based nanobiosensors.

**Closed-loop optimization of fast-charging protocols for batteries with machine learning**

Attia, P.M., Grover, A., Jin, N., Severson, K.A., Markov, T.M., Liao, Y.-H., Chen, M.H., Cheong, B., Perkins, N., Yang, Z., Herring, P.K., Aykol, M., Harris, S.J., Braatz, R.D., Ermon, S., Chueh, W.C.

Nature, Volume 578, Issue 7795, 20 February 2020, Pages 397-402,

<https://doi.org/10.1038/s41586-020-1994-5>

Simultaneously optimizing many design parameters in time-consuming experiments causes bottlenecks in a broad range of scientific and engineering disciplines. One such example is process and control optimization for lithium-ion batteries during materials selection, cell manufacturing and operation. A typical objective is to maximize battery lifetime; however, conducting even a single experiment to evaluate lifetime can take months to years 3–5. Furthermore, both large parameter spaces and high sampling variability necessitate a large number of experiments. Hence, the key challenge is to reduce both the number and the duration of the experiments required. Here we develop and demonstrate a machine learning methodology to efficiently optimize a parameter space specifying the current and voltage profiles of six-step, ten-minute fast-charging protocols for maximizing battery cycle life, which can alleviate range anxiety for electric-vehicle users. We combine two key elements to reduce the optimization cost: an early-prediction model, which reduces the time per experiment by predicting the final cycle life using data from the first few cycles, and a Bayesian optimization algorithm, which reduces the number of experiments by balancing

exploration and exploitation to efficiently probe the parameter space of charging protocols. Using this methodology, we rapidly identify high-cycle-life charging protocols among 224 candidates in 16 days (compared with over 500 days using exhaustive search without early prediction), and subsequently validate the accuracy and efficiency of our optimization approach. Our closed-loop methodology automatically incorporates feedback from past experiments to inform future decisions and can be generalized to other applications in battery design and, more broadly, other scientific domains that involve time-intensive experiments and multi-dimensional design spaces.

#### Data-driven prediction of battery cycle life before capacity degradation

Severson, K.A., Attia, P.M., Jin, N., Perkins, N., Jiang, B., Yang, Z., Chen, M.H., Aykol, M., Herring, P.K., Fraggedakis, D., Bazant, M.Z., Harris, S.J., Chueh, W.C., Braatz, R.D.

Nature Energy, Volume 4, Issue 5, 1 May 2019, Pages 383-391, <https://doi.org/10.1038/s41560-019-0356-8>

Accurately predicting the lifetime of complex, nonlinear systems such as lithium-ion batteries is critical for accelerating technology development. However, diverse aging mechanisms, significant device variability and dynamic operating conditions have remained major challenges. We generate a comprehensive dataset consisting of 124 commercial lithium iron phosphate/graphite cells cycled under fast-charging conditions, with widely varying cycle lives ranging from 150 to 2,300 cycles. Using discharge voltage curves from early cycles yet to exhibit capacity degradation, we apply machine-learning tools to both predict and classify cells by cycle life. Our best models achieve 9.1% test error for quantitatively predicting cycle life using the first 100 cycles (exhibiting a median increase of 0.2% from initial capacity) and 4.9% test error using the first 5 cycles for classifying cycle life into two groups. This work highlights the promise of combining deliberate data generation with data-driven modelling to predict the behaviour of complex dynamical systems.

#### FIKILE R BRUSHETT

Associate Professor of Chemical Engineering, <http://cheme.mit.edu/profile/fikile-r-brushett/>

Lab: <https://www.brushettresearchgroup.org/>

Publications: <https://www.brushettresearchgroup.org/publications-cfvg>

Fikile Brushett is an Associate Professor of Chemical Engineering at the Massachusetts Institute of Technology (MIT) where he holds the Cecil and Ida Green Career Development Chair. Since joining the institute in 2013, his research has focused on advancing the science and engineering of electrochemical technologies for a sustainable energy economy. He is especially fascinated by the fundamental processes that define the performance, cost, and lifetime of present day and future electrochemical systems. Fikile received his B.S.E. in Chemical & Biomolecular Engineering from the University of Pennsylvania in 2006 and his Ph.D. in Chemical Engineering from the University of Illinois at Urbana-Champaign in 2010, under the supervision of Professor Paul J.A Kenis. From 2010-2012, he was a Director's Postdoctoral Fellow in the Electrochemical Energy Storage group, under Dr. John T. Vaughey, at Argonne National Laboratory.

#### Brushett Group

<https://www.brushettresearchgroup.org/>

Research: <https://www.brushettresearchgroup.org/research>

Publications: <https://www.brushettresearchgroup.org/publications-cfvg>

Our mission is to develop transformative electrochemical technologies that enable a sustainable energy economy. Our approach is interdisciplinary as we draw from chemical engineering,

materials science, electrochemistry, organic chemistry, mechanical engineering, and economics to develop new materials, processes, and devices harnessing electrochemical phenomena. We are particularly interested in understanding and controlling the fundamental processes that define the performance, cost, and lifetime of present day and next-generation electrochemical systems. Presently, we are pursuing research on redox flow batteries for grid storage and on electrochemical upgrading of low-value feedstocks.

### **Establishing Design Principles For Molecular Engineering Of High Concentration Redox Electrolytes**

Principal Investigator: Fikile R. Brushett

Project Dates: August 1, 2018 – July 31, 2021

[https://www.nsf.gov/awardsearch/showAward?AWD\\_ID=1805566](https://www.nsf.gov/awardsearch/showAward?AWD_ID=1805566)

This project focuses on a type of battery called non-aqueous redox flow batteries (RFBs) that are promising for large-scale, stationary energy storage applications. RFBs have advantages for electrical grid-scale energy storage options that would reduce overall energy consumption when linked with an electrical grid. Non-aqueous RFBs that contain organic electro-active species have the following unique features relative to other RFB designs: higher operating voltages, non-corrosive electrolytes, smaller size, and use of scalable organic active materials (which are more environmentally friendly and potentially lower cost). This collaborative project addresses fundamental research to support the design of electrolytes for non-aqueous RFBs with high energy density, better stability, and acceptable fluid flow properties. This project will not only establish the foundational knowledge necessary to design electrolytes for next-generation grid storage batteries but will also provide fundamental insights into other electrochemical technologies necessary for a sustainable energy economy....

### **An investigation on the impact of halidization on substituted dimethoxybenzenes**

Kowalski, J.A., Carney, T.J., Huang, J., Zhang, L., Brushett, F.R.

Electrochimica Acta, Volume 335, 1 March 2020, Article number 135580,

<https://doi.org/10.1016/j.electacta.2019.135580>

Functionalized organic molecules are emerging as charge storage materials in electrochemical technologies as the breadth and diversity of the organic design space offers the possibility of purpose-built materials with property sets optimized for a particular application. First developed as overcharge protection materials in lithium-ion batteries, substituted dialkoxybenzenes represent a potentially promising molecular platform for advancing soluble charge storage materials. Here, we systematically substitute a series of halide groups at the 2- and 5-positions of the 1,4-dimethoxybenzene core, investigate the impact the halide groups have on molecular properties using electrochemical and spectroscopy methods, and compare these results to those of 2,5-dimethyl-1,4-dimethoxybenzene (25DDB), a previously reported derivative. In general, we observe that introduction of heavy halogen atoms leads to decreased gravimetric capacity as compared to 25DDB, but concomitantly improves solubility and redox potentials. As the halide functional group increases in size, the active material becomes less stable in its oxidized state as evinced by both cyclic voltammetry and bulk electrolysis cycling. None of the halogenated species are as stable as 25DDB indicating that these materials may be better suited for applications with more rapid cycling conditions (e.g., redox shuttling). More broadly, these results may serve as a useful data set for computational methods for materials discovery and optimization.

### Understanding the role of the porous electrode microstructure in redox flow battery performance using an experimentally validated 3D pore-scale lattice Boltzmann model

Zhang, D., Forner-Cuenca, A., Taiwo, O.O., Yufit, V., Brushett, F.R., Brandon, N.P., Gu, S., Cai, Q.

Journal of Power Sources, Volume 447, 31 January 2020, Article number 227249,

<https://doi.org/10.1016/j.jpowsour.2019.227249>

The porous structure of the electrodes in redox flow batteries (RFBs) plays a critical role in their performance. We develop a framework for understanding the coupled transport and reaction processes in electrodes by combining lattice Boltzmann modelling (LBM) with experimental measurement of electrochemical performance and X-ray computed tomography (CT). 3D pore-scale LBM simulations of a non-aqueous RFB are conducted on the detailed 3D microstructure of three different electrodes (Freudenberg paper, SGL paper and carbon cloth) obtained using X-ray CT. The flow of electrolyte and species within the porous structure as well as electrochemical reactions at the interface between the carbon fibers of the electrode and the liquid electrolyte are solved by a lattice Boltzmann approach. The simulated electrochemical performances are compared against the experimental measurements with excellent agreement, indicating the validity of the LBM simulations for predicting the RFB performance. Electrodes featuring one single dominant peak (i.e., Freudenberg paper and carbon cloth) show better electrochemical performance than the electrode with multiple dominant peaks over a wide pore size distribution (i.e., SGL paper), whilst the presence of a small fraction of large pores is beneficial for pressure drop. This framework is useful to design electrodes with optimal microstructures for RFB applications.

### Engineering porous electrodes for next-generation redox flow batteries: recent progress and opportunities

Forner-Cuenca, A., Brushett, F.R.

Current Opinion in Electrochemistry, Volume 18, December 2019, Pages 113-122,

<https://doi.org/10.1016/j.coelec.2019.11.002>

Redox flow batteries are a promising electrochemical technology for energy-intensive grid storage applications, but further cost reductions are needed for universal adoption. As porous electrodes are responsible for functions within the flow cell that impact charge transfer, ohmics, and mass transport, improvements in electrode materials and design may yield significant performance and economic benefits. This mini-review summarizes recent developments in the design and characterization of porous electrodes with a focus on understanding and controlling both the microstructure and surface chemistry, which broadly align with mass transport and reaction kinetics. Key opportunities and challenges in the science and engineering of these materials are also presented with the goal of engaging the broader community and accelerating progress towards chemistry-specific flow battery electrodes.

### Improved Energy Arbitrage Optimization with Detailed Flow Battery Characterization

Jafari, M., Rodby, K., Barton, J.L., Brushett, F., Botterud, A.

IEEE Power and Energy Society General Meeting, Volume 2019-August, August 2019, Article number 8974070, <https://doi.org/10.1109/PESGM40551.2019.8974070>

This paper elaborates on the characterization of vanadium redox flow battery (VRFB) performance for energy arbitrage optimization based on the experimental data obtained in-house. Typical figures-of-merit used for evaluating VRFBs include coulombic, voltaic, and energy efficiencies.

However, these metrics along with the deliverable power vary as a function of discharge/charge current during cycling. Thus, using a basic energy storage model with constant efficiency and fixed maximum power is not a rigorous approach for predicting the performance of VRFBs in applications with variable supply/demand of electricity. Moreover, optimization based on such an oversimplified treatment may result in inaccurate battery dispatch signal and may overestimate arbitrage profit. Here, we propose a more detailed VRFB model with dynamic efficiency and maximum power limits as a function of state of charge (SOC). These data were obtained using lab-scale VRFB cells over a range of operating conditions. The dynamic model's performance is compared to the basic model for various day-ahead electricity price profiles. Substantial difference between the predictions of two modeling approaches on the battery dispatch and profits was observed. The results indicate that the dynamic model provides more accurate predictions on the battery performance for applications with intermittent energy profile.

### W CRAIG CARTER

POSCO Professor of Materials Science and Engineering, <https://dmse.mit.edu/people/w-craig-carter>

Margaret MacVicar Faculty Fellow

Lab: <http://pruffle.mit.edu/>

Professor W. Craig Carter came to MIT with a research focus in the application of theoretical and computational materials science to microstructural evolution and the relations between material properties and microstructure. He places particular emphasis on the physical analysis of complex processes when possible and the development of numerical algorithms and codes when microstructural simulation is required, and in recent years he has brought his interests and skills to the science of battery materials and the electro-chemo-mechanics of phase transitions and fracture of battery electrodes. He and Professor Yet-Ming Chiang have developed a flow battery that utilizes co-suspensions of solid state electrode and electronically conductive particulates. They co-founded a company, 24M, to produce grid scale energy storage solutions.

### Phase-field model for diffusion-induced grain boundary migration: An application to battery electrodes

Renuka Balakrishna, A., Chiang, Y.-M., Carter, W.C.

Physical Review Materials, Volume 3, Issue 6, 25 June 2019, Article number 065404,

<https://doi.org/10.1103/PhysRevMaterials.3.065404>

Diffusion-induced grain boundary migration is a phenomenon in which a grain boundary moves in response to the driving forces generated by diffusing solute species. For example, diffusing solute species change the atomic volume in the host material, either by filling a vacancy with a misfitting solute atom or by expanding host lattices through interstitial diffusion. These volume changes are inhomogeneous and are stored as elastic energy in the material that drives grain boundaries. In this paper, we introduce our previously developed Cahn-Hilliard-phase-field-crystal model (CH-PFC) as a computational tool to investigate diffusion-induced grain boundary migration in crystalline materials. This multiscale phase-field model couples the composition field of a diffusing species with the crystallographic texture of a host material. We apply the CH-PFC model to battery electrodes and investigate whether interstitial solute diffusion induces grain growth in FePO<sub>4</sub>/LiFePO<sub>4</sub> electrodes. To this end, we compute grain growth in 60 FePO<sub>4</sub> electrodes by conducting two parallel trials: In the first trial, we cycle the electrode and calculate diffusion-induced grain growth. In the second trial, we do not cycle the electrode and calculate curvature-driven grain growth. We find a statistically significant grain growth in the cycled electrodes and

negligible grain growth in the noncycled electrodes. Overall, we show that the CH-PFC model not only predicts electrode microstructures as a function of the Li composition, but also predicts the crystallographic features of an electrode during battery operation.

### Mechanical instability of electrode-electrolyte interfaces in solid-state batteries

Bucci, G., Talamini, B., Renuka Balakrishna, A., Chiang, Y.-M., Carter, W.C.  
Physical Review Materials, Volume 2, Issue 10, 30 October 2018, Article number 105407,  
<https://doi.org/10.1103/PhysRevMaterials.2.105407>

The interfacial contact between active material and solid electrolyte in a composite electrode limits the kinetics of all-solid-state batteries (ASSB). Despite the progress in processing techniques to improve cohesion in composite electrodes, the electrochemical reactions and mechanical stresses developed during battery operation affects interface properties. Here, we propose a one-dimensional radially symmetric analytical model based on the cohesive theory of fracture, to investigate the mechanical stability of interfaces in ASSB microstructures. Using the cohesive-energy approach, we analyze the delamination criterion and derive a stability condition for fracture propagation. Furthermore, we investigate the role of particle size and material properties on delamination, and we explore the effect of delamination on area-specific impedance. We report that delamination is induced when electrode particles undergo a volumetric change of about 7.5% during (de)intercalation. Compliant electrolytes ( $E < 25$  GPa) are found to accommodate up to 25% of particle volume change and delay the onset of delamination. The study identifies geometric regimes for mechanical stability. Such regimes are based on the relative size of the damage zone with respect to the particle radius. Finally, we demonstrate that delamination can significantly influence the total charge/discharge time if highly conductive electrolytes are employed. Overall, the analyses provide guidelines for engineering electrode-electrolyte interfacial properties by controlling particle size, material stiffness, and adhesive strength and length scale.

### YET-MING CHIANG

Kyocera Professor of Ceramics, <https://dmse.mit.edu/people/yet-ming-chiang>

Prof. Chiang's research focuses on the design, synthesis, and characterization of advanced inorganic materials and related devices. Current topics include new cathode and anode materials for lithium ion batteries, phase transformations in electroactive materials, electrochemical device design, electrochemical-to-mechanical energy conversion, self-assembling colloids, and the stability and defect chemical properties of interfaces in inorganic materials.

### Effect of Concentrated Diglyme-Based Electrolytes on the Electrochemical Performance of Potassium-Ion Batteries

Katorova, N.S., Fedotov, S.S., Rupasov, D.P., Luchinin, N.D., Delattre, B., Chiang, Y.-M., Abakumov, A.M., Stevenson, K.J.  
ACS Applied Energy Materials, Volume 2, Issue 8, 26 August 2019, Pages 6051-6059,  
<https://doi.org/10.1021/acsaem.9b01173>

The effect of salt concentration in diglyme-based electrolytes on cycling performance of promising  $\text{KVOPO}_4$  and  $\text{K}_{1.69}\text{Mn}[\text{Fe}(\text{CN})_6]_{0.85} \cdot 0.4\text{H}_2\text{O}$  positive electrodes (cathodes) and a hard carbon negative electrode (anode) for next-generation potassium-ion (K-ion) batteries is investigated. A decrease in free solvent molecule number with increasing electrolyte concentration is found, which results in a better aluminum current collector stability, formation of thinner solid electrolyte interface (SEI) passivation layers, and further inhibition of solvent degradation redox processes

occurring at the electrode surface upon cycling. The  $\text{KVOPO}_4$  and  $\text{K}_{1.69}\text{Mn}[\text{Fe}(\text{CN})_6]_{0.85} \cdot 0.4\text{H}_2\text{O}$  cathodes exhibit an enhanced specific discharge capacity (54 and 105  $\text{mA} \cdot \text{h} \cdot \text{g}^{-1}$ , respectively) in K-ion cells at the highest electrolyte concentrations (2 and 2.5 M KPF6 in diglyme, respectively) at a 0.1 C rate. However, the behavior of the hard carbon anode is noticeably affected by the salt concentration over the first few cycles, a phenomenon tentatively attributed to the SEI layer formation and the presence of irreversible intercalation sites for  $\text{K}^+$  ions in the hard carbon framework. Finally, electrochemical tests on K-ion full cells consisting of the  $\text{K}_{1.69}\text{Mn}[\text{Fe}(\text{CN})_6]_{0.85} \cdot 0.4\text{H}_2\text{O}$  cathode, a hard carbon anode, and an ether-based electrolyte show capacity retention of 86% over 300 cycles at a 0.6 C rate.

#### Order-disorder transition in nano-rutile $\text{TiO}_2$ anodes: A high capacity low-volume change Li-ion battery material

Christensen, C.K., Mamakhel, M.A.H., Balakrishna, A.R., Iversen, B.B., Chiang, Y.-M., Ravnsbæk, D.B.

Nanoscale, Volume 11, Issue 25, 7 July 2019, Pages 12347-12357,

<https://doi.org/10.1039/c9nr01228a>

Nano-sized particles of rutile  $\text{TiO}_2$  is a promising material for cheap high-capacity anodes for Li-ion batteries. It is well-known that rutile undergoes an irreversible order-disorder transition upon deep discharge. However, in the disordered state, the  $\text{Li}_x\text{TiO}_2$  material retains a high reversible ion-storage capacity of  $>200 \text{ mA h g}^{-1}$ . Despite the promising properties of the material, the structural transition and evolution during the repeated battery operation has so far been studied only by diffraction-based methods, which only provide insight into the part that retains some long-range order. Here, we utilize a combination of ex situ and operando total scattering with pair distribution function analysis and transmission electron microscopy to investigate the atomic-scale structures of the disordered  $\text{Li}_x\text{TiO}_2$  forming upon the discharge of nano-rutile  $\text{TiO}_2$  as well as to elucidate the phase behavior in the material during the repeated charge-discharge process. Our investigation reveals that nano-rutile upon Li-intercalation transforms into a composite of  $\sim 5 \text{ nm}$  domains of a layered  $\text{Li}_x\text{TiO}_2$   $\alpha$ - $\text{NaFeO}_2$ -type structure with  $\sim 1 \text{ nm}$   $\text{Li}_x\text{TiO}_2$  grain boundaries with a columbite-like structural motif. During repeated charge-discharge cycling, the structure of this composite is retained and stores Li through a complete solid-solution transition with a remarkably small volume change of only 1 vol%.

#### Electrochemical Redox Behavior of Li Ion Conducting Sulfide Solid Electrolytes

Swamy, T., Chen, X., Chiang, Y.-M.

Chemistry of Materials, Volume 31, Issue 3, 12 February 2019, Pages 707-713,

<https://doi.org/10.1021/acs.chemmater.8b03420>

The lithium-phosphorus-sulfide family of solid electrolytes has attracted much attention for applications in solid-state batteries, as it exhibits some of the highest lithium ion conductivities of solid electrolytes to date. Here, we systematically assess the stability of the  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> exemplar over a wide electrochemical window, from 0 to 5 V vs Li/Li<sup>+</sup>, that encompasses the potentials of all negative electrodes and most positive electrodes of interest for high energy density lithium batteries. By use of a unique cell construction in which the solid electrolyte is fabricated as an electroactive electrode by adding carbon as an electronic conductor, redox activity is amplified. The interphase (SEI)-forming solid-state reactions at high potential are found to be irreversible and passivating, whereas those occurring at low potential are reversible. This contrasts with the irreversible anode SEI formed at low potentials in lithium ion and lithium metal batteries and the general absence of an SEI at cathode potentials. Using elemental sulfur and phosphorus as redox-



active internal standards, we show that the redox behavior of  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> upon decomposition is essentially a superposition of that of sulfur and phosphorus species formed at the interphase.

### Stabilizing Li-S Battery Through Multilayer Encapsulation of Sulfur

Ansari, Y., Zhang, S., Wen, B., Fan, F., Chiang, Y.-M.

Advanced Energy Materials, Volume 9, Issue 1, 3 January 2019, Article number 1802213,

<https://doi.org/10.1002/aenm.201802213>

Advancements in portable electronic devices and electric powered transportation has drawn more attention to high energy density batteries, especially lithium-sulfur batteries due to the low cost of sulfur and its high energy density. However, the lithium-sulfur battery is still quite far from commercialization mostly because of incompatibility between all major components of the battery—the cathode, anode, and electrolyte. Here a methodology is demonstrated that shows promise in significantly improving battery stability by multilayer encapsulation of sulfur particles, while using conventional electrolytes, which allows a long cycle life and an improved Coulombic efficiency battery at low electrolyte feeding. The multilayer encapsulated sulfur battery demonstrates a Coulombic efficiency as high as 98%, when a binder-free electrode is used. It is also shown that the all-out self-discharge of the cell after 168 h can be reduced from 34% in the regular sulfur battery to less than 9% in the battery with the multilayer encapsulated sulfur electrode.

### BETAR GALLANT

Assistant Professor of Mechanical Engineering,

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Lab: <http://gallant.mit.edu/>

Publications: <http://gallant.mit.edu/publications>

Betar Gallant joined the MIT faculty in January 2016 as an assistant professor of mechanical engineering. Gallant completed her B.S., M.S., and Ph.D. in mechanical engineering at MIT. During her graduate studies with Professor Yang Shao-Horn, she was a National Science Foundation graduate research fellow, an MIT Martin Family Fellow and an MIT Energy Initiative Fellow. Gallant was a Kavli Nanoscience Institute Prize postdoctoral fellow at Caltech, where her research focused on tuning mechanical properties via surface chemistry control in Si-polymer structures for solar fuels applications. She will develop materials and devices for energy and environmental cleanup applications including greenhouse gas and pollutant capture and conversion, which will be informed by the understanding of chemical and electrochemical reaction pathways. She plans to utilize nanoscale insights into heat and mass transfer and energy conversion to bridge molecular control of processes with scalable environmental technologies.

### Gallant Research Group

<http://gallant.mit.edu/>

Research: <http://gallant.mit.edu/research>

Publications: <http://gallant.mit.edu/publications>

Our group is developing new reactions and devices of value for a modern and sustainable society that allow us to live, make, move, and produce energy and products while minimizing environmental impact.

Currently, our focus is on two main themes. The first is the exploration of novel and primary schemes for batteries, alternative-chemistry fuel cells, and other modes of energy delivery that are

carbon-neutral. The second focus is on the capture and electrochemical conversion of greenhouse gases produced by transportation and in a wide range of industrial processes.

The essence of our group can be described as embodying a multiscale, molecular-to-device approach to technology development. We are a highly interdisciplinary group, combining chemistry, electrochemistry, materials design, transport engineering, and reaction design to achieve control over energy and mass flows in micro-to-macro-scale devices.

### **Chemical and Structural Design of Inorganic-Organic Layers for Stabilized Li Anodes**

Principal Investigator: Betar Gallant

Project Dates: September 1, 2018 – August 31, 2021

[https://www.nsf.gov/awardsearch/showAward?AWD\\_ID=1804247](https://www.nsf.gov/awardsearch/showAward?AWD_ID=1804247)

This project will generate fundamental knowledge and identify design principles for developing improved battery anodes based on lithium metal. This knowledge is critical for enabling rechargeable high energy density lithium electrode batteries for electric vehicle-based transportation and for compact storage of renewably generated electricity. This work will advance understanding of how this active material forms beneficial, ionically-conductive material films that have the potential to impart improved stability, cycling efficiency and lifetime. The insights developed in this work can be used to design new fabrication procedures and improved interfaces for lithium anodes with higher degrees of stability, which is currently a key issue with this technology. This work could lead to lighter, longer-lasting and more compact transportation batteries, which supports improved national energy sustainability, reduced air pollution, and a potential path to more widespread electric vehicle adoption....

### **The intrinsic behavior of lithium fluoride in solid electrolyte interphases on lithium**

He, M., Guo, R., Hobold, G.M., Gao, H., Gallant, B.M.

Proceedings of the National Academy of Sciences of the United States of America, Volume 117, Issue 1, 7 January 2020, Pages 73-79, <https://doi.org/10.1073/pnas.1911017116>

Lithium is the most attractive anode material for high-energy density rechargeable batteries, but its cycling is plagued by morphological irreversibility and dendrite growth that arise in part from its heterogeneous “native” solid electrolyte interphase (SEI). Enriching the SEI with lithium fluoride (LiF) has recently gained popularity to improve Li cyclability. However, the intrinsic function of LiF—whether chemical, mechanical, or kinetic in nature—remains unknown. Herein, we investigated the stability of LiF in model LiF-enriched SEIs that are either artificially preformed or derived from fluorinated electrolytes, and thus, the effect of the LiF source on Li electrode behavior. We discovered that the mechanical integrity of LiF is easily compromised during plating, making it intrinsically unable to protect Li. The ensuing in situ repair of the interface by electrolyte, either regenerating LiF or forming an extra elastomeric “outer layer,” is identified as the more critical determinant of Li electrode performance. Our findings present an updated and dynamic picture of the LiF-enriched SEI and demonstrate the need to carefully consider the combined role of ionic and electrolyte-derived layers in future design strategies.

### **Rechargeable-battery chemistry based on lithium oxide growth through nitrate anion redox**

Giordani, V., Tozier, D., Uddin, J., Tan, H., Gallant, B.M., McCloskey, B.D., Greer, J.R., Chase, G.V., Addison, D.

Nature Chemistry, Volume 11, Issue 12, 1 December 2019, Pages 1133-1138,

<https://doi.org/10.1038/s41557-019-0342-6>

Next-generation lithium-battery cathodes often involve the growth of lithium-rich phases, which enable specific capacities that are 2–3 times higher than insertion cathode materials, such as lithium cobalt oxide. Here, we investigated battery chemistry previously deemed irreversible in which lithium oxide, a lithium-rich phase, grows through the reduction of the nitrate anion in a lithium nitrate-based molten salt at 150 °C. Using a suite of independent characterization techniques, we demonstrated that a Ni nanoparticle catalyst enables the reversible growth and dissolution of micrometre-sized lithium oxide crystals through the effective catalysis of nitrate reduction and nitrite oxidation, which results in high cathode areal capacities (~12 mAh cm<sup>-2</sup>). These results enable a rechargeable battery system that has a full-cell theoretical specific energy of 1,579 Wh kg<sup>-1</sup>, in which a molten nitrate salt serves as both an active material and the electrolyte.

### Governing Role of Solvent on Discharge Activity in Lithium-CO<sub>2</sub> Batteries

Khurram, A., Yin, Y., Yan, L., Zhao, L., Gallant, B.M.

Journal of Physical Chemistry Letters, Volume 10, Issue 21, 7 November 2019, Pages 6679-6687, <https://doi.org/10.1021/acs.jpcllett.9b02615>

Non-aqueous Li-CO<sub>2</sub> batteries reported in literature have almost exclusively relied upon glyme-based electrolytes, leading to a hypothesis that they are uniquely active for CO<sub>2</sub> discharge. Here, we study the effect of electrolyte composition on CO<sub>2</sub> activity to examine whether this is the case. The results indicate that TEGDME-based electrolytes containing moderate concentrations of Li<sup>+</sup> salts (roughly within the range of 0.7–2 M examined herein) are most conducive to CO<sub>2</sub> activation, especially compared to dimethyl sulfoxide and propylene carbonate-based electrolytes. Through electrochemical, spectroscopic, and computational methods, we determine that glymes have lower desolvation energies for Li<sup>+</sup> compared to other solvent candidates, whereas high salt concentrations increase the local density of Li<sup>+</sup> surrounding CO<sub>2</sub> and reduction intermediates. These attributes collectively increase the availability of Li<sup>+</sup>, crossing a threshold necessary to support CO<sub>2</sub> activation. Discharge voltage and reaction rates are also sensitive to the alkali cation identity, further invoking its key role in enabling or suppressing reactivity.

### Tailoring the Discharge Reaction in Li-CO<sub>2</sub> Batteries through Incorporation of CO<sub>2</sub> Capture Chemistry

Khurram, A., He, M., Gallant, B.M.

Joule, Volume 2, Issue 12, 19 December 2018, Pages 2649-2666, <https://doi.org/10.1016/j.joule.2018.09.002>

The search for viable end-uses of CO<sub>2</sub> has motivated considerable research into CO<sub>2</sub> utilization in energy storage devices such as alkali metal-based O<sub>2</sub>/CO<sub>2</sub> and -CO<sub>2</sub> batteries. However, efforts have been stymied by the low electrochemical activity of CO<sub>2</sub> in most organic media. In this work, we report a mediated CO<sub>2</sub> capture and conversion process, based on amine (e.g., 2-ethoxyethylamine) chemisorption, which provides a new electrolyte system for facilitating the discharge reaction in Li-CO<sub>2</sub> batteries. Our results indicate that electrochemical reduction of CO<sub>2</sub>-loaded amines proceeds at significantly higher discharge potentials (~2.9 V versus Li/Li<sup>+</sup>) compared with physically dissolved CO<sub>2</sub>, which is inactive in the amine's absence. The discharge reaction forms solid-phase Li<sub>2</sub>CO<sub>3</sub> as the primary discharge product and yields high discharge capacities (>1,000 mAh/g), highlighting the coupling of CO<sub>2</sub> capture chemistry to nonaqueous batteries as a promising approach for the design and manipulation of CO<sub>2</sub> conversion reactions.

### Conversion tech could turn CO2 emissions into battery electrolytes

**The accelerating effects of climate change have led to growing agreement that carbon capture sequestration and storage (CSS) will need to be part of the solution, Yet, so far attempts to capture CO2 from power plants have proven too expensive from both a dollar and carbon footprint perspective.**

Eric Brown, ILP Institute Insider, February 19, 2019, <http://ilp.mit.edu/newsstory.jsp?id=25539>

Researchers around the world are exploring solutions to simplify and reduce the energy cost of CO2 capture for storage or transformation into useful products. At MIT's Gallant Research Group, Mechanical Engineering Assistant Professor Betar Gallant has demonstrated promising results for an electrochemical conversion technology that could directly add value to CO2 waste by enabling its use in an energy storage device.

As detailed in an Oct. 2018 paper in *Joule* co-authored with doctoral student Aliza Khurram and postdoc Mingfu He, Gallant's technique pre-activates the CO2 in an aqueous amine solution before further converting it within a solid phase electrolyte environment. The resulting carbamate solution can then be used as an electrolyte to drive a CO2 battery. Alternatively, it could be used for continuous power generation within the power plant.

"We'd like to capture CO2 and ideally recycle it and convert it to something valuable," says Gallant. "If we can convert CO2 to a solid that could be used for energy storage we could close the carbon cycle."...

### Video: Introduction, Betar Gallant, Esther & Harold E. Edgerton Career Development Professor

ILP Video, February 19, 2019, <http://ilp.mit.edu/videodetail.jsp?confid=null&id=2745#>

### T ALAN HATTON

Ralph Landau Professor of Chemical Engineering, <http://cheme.mit.edu/profile/t-alan-hatton/>  
Director, David H Koch School of Chemical Engineering Practice School (Cambridge)  
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Publications: <https://hattongroup.mit.edu/daj-publications/>

T. Alan Hatton is the Ralph Landau Professor and Director of the David H. Koch School of Chemical Engineering Practice at MIT. Research interests include exploitation of structured fluids in chemical processing operations with a recent focus on the use of tailored solvents, and of surface-modified magnetic fluid nanoparticles, to enhance reaction and separation processes to minimize pollution.

### Hatton Research Group

<https://hattongroup.mit.edu/>  
Research: <https://hattongroup.mit.edu/research-2/>  
Publications: <https://hattongroup.mit.edu/daj-publications/>

Our research focuses primarily on the development of electrochemical processes to facilitate chemical separations and to mediate the transformation of captured waste to useful commodity chemicals. The electrochemically-mediated separation processes that are currently under development and investigation in our group can primarily be divided into two areas: carbon capture

(particularly for post-combustion carbon dioxide capture at coal-fired power plants) and water purification (including decontamination of wastewater and desalination).

### Self-assembled nanostructures in ionic liquids facilitate charge storage at electrified interfaces

Mao, X., Brown, P., Červinka, C., Hazell, G., Li, H., Ren, Y., Chen, D., Atkin, R., Eastoe, J., Grillo, I., Padua, A.A.H., Costa Gomes, M.F., Hatton, T.A.  
Nature Materials, Volume 18, Issue 12, 1 December 2019, Pages 1350-1357,  
<https://doi.org/10.1038/s41563-019-0449-6>

Driven by the potential applications of ionic liquids (ILs) in many emerging electrochemical technologies, recent research efforts have been directed at understanding the complex ion ordering in these systems, to uncover novel energy storage mechanisms at IL–electrode interfaces. Here, we discover that surface-active ILs (SAILs), which contain amphiphilic structures inducing self-assembly, exhibit enhanced charge storage performance at electrified surfaces. Unlike conventional non-amphiphilic ILs, for which ion distribution is dominated by Coulombic interactions, SAILs exhibit significant and competing van der Waals interactions owing to the non-polar surfactant tails, leading to unusual interfacial ion distributions. We reveal that, at an intermediate degree of electrode polarization, SAILs display optimum performance, because the low-charge-density alkyl tails are effectively excluded from the electrode surfaces, whereas the formation of non-polar domains along the surface suppresses undesired overscreening effects. This work represents a crucial step towards understanding the unique interfacial behaviour and electrochemical properties of amphiphilic liquid systems showing long-range ordering, and offers insights into the design principles for high-energy-density electrolytes based on spontaneous self-assembly behaviour.

### Redox-electrolytes for non-flow electrochemical energy storage: A critical review and best practice

Lee, J., Srimuk, P., Fleischmann, S., Su, X., Hatton, T.A., Presser, V.  
Progress in Materials Science, Volume 101, April 2019, Pages 46-89,  
<https://doi.org/10.1016/j.pmatsci.2018.10.005>

Over recent decades, a new type of electric energy storage system has emerged with the principle that the electric charge can be stored not only at the interface between the electrode and the electrolyte but also in the bulk electrolyte by redox activities of the electrolyte itself. Those redox electrolytes are promising for non-flow hybrid energy storage systems, or redox electrolyte-aided hybrid energy storage (REHES) systems; particularly, when they are combined with highly porous carbon electrodes. In this review paper, critical design considerations for the REHES systems are discussed as well as the effective electrochemical characterization techniques. Appropriate evaluation of the electrochemical performance is discussed thoroughly, including advanced analytical techniques for the determination of the electrochemical stability of the redox electrolytes and self-discharge rate. Additionally, critical summary tables for the recent progress on REHES systems are provided. Furthermore, the unique synergistic combination of porous carbon materials and redox electrolytes is introduced in terms of the diffusion, adsorption, and electrochemical kinetics modulating energy storage in REHES systems.

### JING KONG

ITT Career Development Professor of Electrical Engineering,

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Lab: <http://nmelab.mit.edu/>

Publications: <http://www.rle.mit.edu/nmeg/publications/>

Professor Jing Kong is a principal investigator in the Research Laboratory of Electronics (RLE) at the Massachusetts Institute of Technology (MIT). She received the B.S in chemistry from Peking University in 1997 and the Ph.D. in chemistry from Stanford University in 2002. From 2002 to 2003, she was a research scientist at NASA Ames Research Center, and from 2003 to 2004, she was a postdoctoral researcher at Delft University. She joined the MIT faculty in 2004 in the Department of Electrical Engineering and Computer Science.

Professor Kong's research interests focus on the problem of combining the synthesis and fabrication of individual carbon nanotubes, and integrating them into electrical circuits. Applications of her research include the use of carbon nanotubes as extremely sensitive chemical sensors to detect toxic gases.

### Nanomaterials and Electronics Group

<https://www.rle.mit.edu/nmeg/>

Research: <https://www.rle.mit.edu/nmeg/research/>

Publications: <https://www.rle.mit.edu/nmeg/publications/>

We are designing new strategies to make graphene, MoS<sub>2</sub>, h-BN and other novel 2D materials with desired physical, chemical qualities. The in-depth understanding in how to make those materials is enabling us to develop brand new architectures for high-performance electronics and energy conversion.

### Sustainable Synthesis of Biomass-Derived Carbon Electrodes with Hybrid Energy-Storage Behaviors for Use in High-Performance Na-Ion Capacitors

ACS Applied Energy Materials, 2020, Article in Press, <https://doi.org/10.1021/acsaem.9b02166>

Although there have been many efforts to improve the performance of electrical energy storage devices by preparing electrode materials with nanostructures and specific chemical compositions, most of the synthetic pathways developed have not addressed issues of safety, cost, and sustainability. Herein, we have simultaneously realized the sustainable synthesis, nanostructure engineering, and heteroatom doping of two carbon materials by separate tailored strategies using gelatin and phytic acid as biomass precursors. These-together with all the other reagents employed-have high terrestrial abundance with low cost and low toxicity and can be easily mixed at a molecular level in deionized water without using organic solvents. Additionally, all the non-carbonaceous products can be easily removed by water washing and further recycled by heat drying. The tailored syntheses result in porous nanosheet structures and uniform heteroatom doping of the final carbons. Based on their typical porosities and chemical compositions, these two carbons have been specifically used as cathode and anode materials in Na-ion capacitors. Electrochemical characterization and first-principles calculations show that the porous nanosheet structures and heteroatom doping endow the carbon electrodes with battery-capacitive storage features, thus leading to their excellent electrochemical performance in half cells. Beneficial from the compatible kinetics of cathode and anode, the assembled Na-ion capacitor exhibits high energy density (135.3 Wh kg<sup>-1</sup>) and power density (16.1 kW kg<sup>-1</sup>) as well as ultralong lifetime (88.6% of the initial capacity after 8000 cycles).

**JU LI**

Professor of Nuclear Science and Engineering, <http://web.mit.edu/nse/people/faculty/li.html>

Professor of Materials Science and Engineering, <https://dmse.mit.edu/people/ju-li>

Lab: <http://li.mit.edu/>

Publications: <http://li.mit.edu/Archive/Papers/>

Ju Li is Professor of Nuclear Science and Engineering and Professor of Materials Science and Engineering at MIT. His group (<http://Li.mit.edu>) performs computational and experimental research on mechanical properties of materials, and energy storage and conversion. Ju obtained a PhD degree in nuclear engineering from MIT in 2000, and Bachelor's degree in Physics from University of Science and Technology of China in 1994. He is a recipient of the 2005 Presidential Early Career Award for Scientists and Engineers, 2006 MRS Outstanding Young Investigator Award, and 2007 TR35 award from Technology Review magazine. Thomson Reuters included Ju in its Highly Cited Researchers list in 2014, among 147 scientists world-wide in the Materials Science category. Ju was elected Fellow of the American Physical Society in 2014.

**Electrochemically Driven Mechanical Energy Harvesting**

Principal Investigator: Ju Li

Project Dates: July 15, 2016 – June 30, 2019

[https://www.nsf.gov/awardsearch/showAward?AWD\\_ID=1610806](https://www.nsf.gov/awardsearch/showAward?AWD_ID=1610806)

Energy harvesting, which is any technology that converts otherwise wasted energy of various forms into electricity, represents a key component in energy sustainability for modern society. In mechanical energy harvesting alone, several types of electric power generators have been demonstrated, including piezoelectric, electrokinetic and triboelectric generators. These devices have enabled a wide range of applications, from small self-powered devices to auxiliary power units for wearable electronics. However, due to the short-lived electric current, these power generators are most efficient for vibrational energy harvesting at a relatively high frequency and inherently limited in the low frequency regime where every-day human activities such as walking take place. This research project aims to develop a unique type of mechanical energy harvester that exploits the typical configuration of the electrochemical cells in batteries and specifically targets harvesting low frequency motions. Such energy harvesters may work as auxiliary generators, powering ubiquitous computing, communications and wearable electronics. The project will also offer interdisciplinary research experience in experimental design, computational materials science and mechanics to both undergraduates and graduates at MIT and Penn State, as well as enhance minority involvement and participation in science and engineering, and stimulate the interests of students in the research field of innovative energy-storage materials and energy harvesting. The objective of this project is to uncover the underlying mechanisms of electrochemically driven mechanical energy harvesting so as to control and optimize power and energy generation at targeted low frequency through an integrated experimental-modeling approach. To fulfill this goal, the team will adopt a multiscale method to model the stress-voltage coupling and to predict current and power output of mechanical energy harvesters. Guided by the modeling results, mechanical energy harvester prototypes will be fabricated, tested and diagnosed. The integrated experimental-modeling approach enables a fundamental understanding of the key design parameters that govern the performance of mechanical energy harvesters in particular, and helps foster transformative progress for understanding a broad range of stress-mediated electrochemical processes in general.

**A Novel Moisture-Insensitive and Low-Corrosivity Ionic Liquid Electrolyte for Rechargeable Aluminum Batteries**

Li, C., Patra, J., Li, J., Rath, P.C., Lin, M.-H., Chang, J.-K.

Advanced Functional Materials, 2020, Article number 1909565,  
<https://doi.org/10.1002/adfm.201909565>

Rechargeable aluminum batteries (RABs) are extensively developed due to their cost-effectiveness, eco-friendliness, and low flammability and the earth abundance of their electrode materials. However, the commonly used RAB ionic liquid (IL) electrolyte is highly moisture-sensitive and corrosive. To address these problems, a 4-ethylpyridine/ $\text{AlCl}_3$  IL is proposed. The effects of the  $\text{AlCl}_3$  to 4-ethylpyridine molar ratio on the electrode charge–discharge properties are systematically examined. A maximum graphite capacity of  $95 \text{ mAh g}^{-1}$  is obtained at  $25 \text{ mA g}^{-1}$ . After 1000 charge–discharge cycles,  $\approx 85\%$  of the initial capacity can be retained. In situ synchrotron X-ray diffraction is employed to examine the electrode reaction mechanism. In addition, low corrosion rates of Al, Cu, Ni, and carbon-fiber paper electrodes are confirmed in the 4-ethylpyridine/ $\text{AlCl}_3$  IL. When opened to the ambient atmosphere, the measured capacity of the graphite cathode is only slightly lower than that found in a  $\text{N}_2$ -filled glove box; moreover, the capacity retention upon 100 cycles is as high as 75%. The results clearly indicate the great potential of this electrolyte for practical RAB applications.

#### A low-cost intermediate temperature Fe/Graphite battery for grid-scale energy storage

Dai, T., Yang, L., Ning, X., Zhang, D., Narayan, R.L., Li, J., Shan, Z.  
Energy Storage Materials, Volume 25, March 2020, Pages 801-810,  
<https://doi.org/10.1016/j.ensm.2019.09.008>

Due to their compactness, storage/supply flexibility, modularity and factory manufacturability, batteries are excellent candidates for large scale energy storage applications. However, the widespread application of most batteries hitherto developed is hindered by their high cost. Here, an intermediate temperature molten salt battery is developed that emphatically resolves this issue by using all earth-abundant and cheap elements. Operated at  $170 \text{ }^\circ\text{C}$ , the cell comprises of an Fe metal anode, NaCl saturated  $\text{NaAlCl}_4$  electrolyte and an  $\text{AlCl}_4^-$  intercalated graphite cathode in the fully charged state. It has a capacity retention of 85% after nearly 10,000 cycles. After characterizing the anode, it was determined that the high reversibility of the Fe to  $\text{FeCl}_2$  solid state transformation are responsible for the absence of dendritic growth on such a metal anode. Different electrode capacity matching strategies are discussed in the context of ensuring safe operation during overcharging. Finally, the overall material cost of the Fe/Graphite cell is estimated to be  $33.9 \text{ } \$ \text{ kWh}^{-1}$ , which can potentially meet the demands of the commercial energy storage market.

#### Li metal deposition and stripping in a solid-state battery via Coble creep

Chen, Y., Wang, Z., Li, X., Yao, X., Wang, C., Li, Y., Xue, W., Yu, D., Kim, S.Y., Yang, F., Kushima, A., Zhang, G., Huang, H., Wu, N., Mai, Y.-W., Goodenough, J.B., Li, J.  
Nature, Volume 578, Issue 7794, 13 February 2020, Pages 251-255,  
<https://doi.org/10.1038/s41586-020-1972-y>

Solid-state lithium metal batteries require accommodation of electrochemically generated mechanical stress inside the lithium: this stress can be<sup>1,2</sup> up to 1 gigapascal for an overpotential of 135 millivolts. Maintaining the mechanical and electrochemical stability of the solid structure despite physical contact with moving corrosive lithium metal is a demanding requirement. Using in situ transmission electron microscopy, we investigated the deposition and stripping of metallic lithium or sodium held within a large number of parallel hollow tubules made of a mixed ionic-electronic conductor (MIEC). Here we show that these alkali metals—as single crystals—can grow out of and retract inside the tubules via mainly diffusional Coble creep along the MIEC/metal phase



boundary. Unlike solid electrolytes, many MIECs are electrochemically stable in contact with lithium (that is, there is a direct tie-line to metallic lithium on the equilibrium phase diagram), so this Coble creep mechanism can effectively relieve stress, maintain electronic and ionic contacts, eliminate solid-electrolyte interphase debris, and allow the reversible deposition/stripping of lithium across a distance of 10 micrometres for 100 cycles. A centimetre-wide full cell—consisting of approximately 10<sup>10</sup> MIEC cylinders/solid electrolyte/LiFePO<sub>4</sub>—shows a high capacity of about 164 milliampere hours per gram of LiFePO<sub>4</sub>, and almost no degradation for over 50 cycles, starting with a 1× excess of Li. Modelling shows that the design is insensitive to MIEC material choice with channels about 100 nanometres wide and 10–100 micrometres deep. The behaviour of lithium metal within the MIEC channels suggests that the chemical and mechanical stability issues with the metal–electrolyte interface in solid-state lithium metal batteries can be overcome using this architecture.

### **Optimal annealing of Al foil anode for prelithiation and full-cell cycling in Li-ion battery: The role of grain boundaries in lithiation/delithiation ductility**

Yu, Y., Li, S., Fan, H., Xu, H., Jiang, M., Huang, Y., Li, J.  
Nano Energy, Volume 67, January 2020, Article number 104274,  
<https://doi.org/10.1016/j.nanoen.2019.104274>

While self-supporting Al foil anode has high theoretical capacity and appropriate potential for Li-ion batteries, the poor initial Coulombic efficiency (ICE) retards its wide industrial applications, making prelithiation necessary. Herein, we develop a facile and efficient mechanical prelithiation (MP) approach suitable for mass production. Even though ICE was improved from 70% to 90% after MP, the cycling performance is still deficient, which we attribute to the insufficient density of grain boundaries that leads to poor lithiation/delithiation ductility (LDD), characterized by the rapid loss in electronic percolation across the foil. As a classic strategy in metallurgy to tune the grain boundaries, thermal annealing and recrystallization is further exploited to optimize the LDD of Al foil. For standard Al foil, whose grain size is big with lots of dislocations inside, MP followed by electrochemical cycling causes cracking, electrolyte infiltration and SEI formation. Its electronic percolation (damage) is monitored in real time, and is found to decay rapidly as the insulating SEI blocked all the electron transport paths of one grain (or a cluster of grains). But if MP takes place after annealing standard Al foil at 300 °C for 15min, the dislocations recombined to achieve refined grains whose sharp GB network can slide effectively to relieve stress buildup due to phase transitions and suppress deep crack development, and the prelithiated foil achieved superior electrochemical performance, with significant life extension in the in-plane electronic conductance. However, interestingly, upon further increase in the annealing temperature, as the grain size turns bigger, the electrochemical performance of prelithiated foil deteriorates. Based on the comparison of the microstructures and electrochemical performance at different thermal annealing conditions, we found that the GB density before MP plays an essential role in the stress relief and keeping electronic percolation during cycling. Our optimized prelithiated Al foil maintains 80% capacity retention after 100 cycles in LiFePO<sub>4</sub>//LiAl<sub>y</sub> full cell with 1.8 × excess lithium. It cycles significantly better than pure LiBCC foil of equal thickness (65 μm), especially in lean-electrolyte condition, suggesting such safe, cheap and high energy density metallic foil anodes deserve comparable attention as pure lithium metal anode.

### **Gradient Li-rich oxide cathode particles immunized against oxygen release by a molten salt treatment**

Zhu, Z., Yu, D., Yang, Y., Su, C., Huang, Y., Dong, Y., Waluyo, I., Wang, B., Hunt, A., Yao, X., Lee, J., Xue, W., Li, J.

Nature Energy, Volume 4, Issue 12, 1 December 2019, Pages 1049-1058,  
<https://doi.org/10.1038/s41560-019-0508-x>

Lithium-rich transition metal oxide ( $\text{Li}_{1+X}\text{M}_{1-X}\text{O}_2$ ) cathodes have high energy density above 900 Wh  $\text{kg}^{-1}$  due to hybrid anion- and cation-redox (HACR) contributions, but critical issues such as oxygen release and voltage decay during cycling have prevented their application for years. Here we show that a molten molybdate-assisted LiO extraction at 700 °C creates lattice-coherent but depth (r)-dependent  $\text{Li}_{1+X(r)}\text{M}_{1-X(r)}\text{O}_2$  particles with a Li-rich ( $X \approx 0.2$ ) interior, a Li-poor ( $X \approx -0.05$ ) surface and a continuous gradient in between. The gradient Li-rich single crystals eliminate the oxygen release to the electrolyte and, importantly, still allow stable oxygen redox contributions within. Both the metal valence states and the crystal structure are well maintained during cycling. The gradient HACR cathode displays a specific density of 843 Wh  $\text{kg}^{-1}$  after 200 cycles at 0.2C and 808 Wh  $\text{kg}^{-1}$  after 100 cycles at 1C, with very little oxygen release and consumption of electrolyte. This high-temperature immunization treatment can be generalized to leach other elements to avoid unexpected surface reactions in batteries.

### *New electrode design may lead to more powerful batteries*

#### **An MIT team has devised a lithium metal anode that could improve the longevity and energy density of future batteries.**

David L. Chandler, MIT News Office, February 3, 2020, <http://news.mit.edu/2020/solid-batteries-lithium-metal-electrode-0203>

New research by engineers at MIT and elsewhere could lead to batteries that can pack more power per pound and last longer, based on the long-sought goal of using pure lithium metal as one of the battery's two electrodes, the anode.

The new electrode concept comes from the laboratory of Ju Li, the Battelle Energy Alliance Professor of Nuclear Science and Engineering and professor of materials science and engineering. It is described today in the journal Nature, in a paper co-authored by Yuming Chen and Ziqiang Wang at MIT, along with 11 others at MIT and in Hong Kong, Florida, and Texas.

The design is part of a concept for developing safe all-solid-state batteries, dispensing with the liquid or polymer gel usually used as the electrolyte material between the battery's two electrodes. An electrolyte allows lithium ions to travel back and forth during the charging and discharging cycles of the battery, and an all-solid version could be safer than liquid electrolytes, which have high volatility and have been the source of explosions in lithium batteries....

#### **JENNIFER L M RUPP**

Thomas Lord Associate Professor in Materials Science, <https://dmse.mit.edu/people/jennifer-l-m-rupp>

Lab: <https://ecm.mit.edu/>

Publications: <https://ecm.mit.edu/pubs/articles/>

Prof. Jennifer Rupp is the Thomas Lord Associate Professor of Electrochemical Materials in the Department of Materials Science and Engineering, and Associate Professor in the Department of Electrical Engineering and Computer Science at MIT. Previously, she was a non-tenure track assistant professor at ETH Zurich Switzerland where she held two prestigious externally funded career grants, namely an ERC Starting Grant (SNSF) and Swiss National Science Foundation (SNF) professorship.

She previously held positions as visiting and senior scientist at MIT (2012–2011) and the National Institute of Materials Science (NIMS) in Tsukuba Japan (2011), and was a postdoc at ETH Zurich (2010–2006). The Rupp team's current research interests are on solid-state material design and tuning of structure–property relations for novel energy and information devices and operation schemes. This ranges from alternative energy storage via solid state batteries, solar-to-synthetic fuel conversion or novel types of neuromorphic memories, and computing logic entities for data storage and transfer beyond transistors and new sensing functions to track chemicals in the environment. Here, her team goes the whole way from material design, novel processing techniques to make ceramics, cermets or glassy-type ceramic structures, up to novel device prototypes, their operation and characteristics.

### **Electrochemical Materials Lab**

<https://ecm.mit.edu/>

Research: <https://ecm.mit.edu/research/expertise/>

Publications: <https://ecm.mit.edu/pubs/articles/>

The Electrochemical Materials Laboratory is part of MIT's Materials Science and Engineering and Electrical Engineering and Computer Science departments. The lab is led by Prof. Dr. Jennifer L.M. Rupp.

### **Solid State Li-Ion Batteries**

<https://ecm.mit.edu/research/batteries/>

Li-ion batteries dominate the portable electronics market. However, the current electrode materials are still far away from satisfying the large energy density required for various applications (e.g. electric vehicles). Solid inorganic electrolytes become quite important at this point that can enable the use of high capacity electrode materials, which are otherwise not very stable and safe to be used in liquid electrolytes.  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  and doped variants are especially interesting solid electrolyte candidates with high Li-ion conductivities in the range of  $\sim 10^{-4}$  S/cm at RT and with possible large thermal operation windows, up to 1000 °C.

### **Solid Oxide Fuel Cells**

<https://ecm.mit.edu/research/sofcs/>

Solid Oxide Fuel Cells are electrochemical devices that can directly convert chemical into electrical energy and also operate in reverse mode as electrolyzers, e.g. to store chemical fuels. We focus in particular on micro-Solid Oxide Fuel Cells on chip which are miniaturized thin film-based cells where all active compounds, electrodes and electrolyte, form a free-standing membrane on a Si-chip separating the fuel from the air supply. Despite short history of this new device class first commercial cells are on the market to replace batteries for portable electronics or as grid-independent chargers. We target in particular to a fundamental understanding of the electro-chemomechanics in these cells, namely the interaction of ionic charge transport "electro", oxygen non-stoichiometry "chemical" and membrane strain "mechanics" interaction. Besides innovative routes to gain high surface reactive site electrodes and micro-fuel cell making and testing in hydro-carbon fuels is studied to suggest most efficient and direct operation on the latter fuels.

### **All-Solid-State Glucose Fuel Cell for Energy Harvesting in the Human Body**

[http://ilp.mit.edu/expertise\\_project\\_detail.jsp?project\\_id=32836](http://ilp.mit.edu/expertise_project_detail.jsp?project_id=32836)

...Here, we innovate a miniaturized glucose fuel cell that is fully composed of solid-state materials based on thin film processing. This all-solid-state glucose fuel cell can be scaled down to the sub-micrometer range for unprecedented miniaturization and is built on a Si chip using semiconductor fabrication methods suitable for integrated and direct powering of bio-electronic implants. Through the use of abiotic catalysts instead of conventional biological catalysts such as enzymes and microbes, long-term stability and increased power density are in perspective. Freestanding fuel cell membranes based on a proton conducting oxide on Si chips were assembled using a microfabrication route with standard semiconductor processing techniques. Oxide thin films were prepared via pulsed laser deposition. The anode is in contact with glucose in phosphate-buffered saline solution to mimic blood, whereas the cathode is in contact with oxygen. Performance characterizations were carried out via electrochemical impedance spectroscopy and galvanostatic polarization curve measurements. We report that the proposed cell is electrochemically active and shows promise in functioning as the first all-solidstate glucose fuel cell with a roughly 100-fold lowered thickness of the device (only 250 nm) compared to polymer-based glucose fuel cells.

#### **A low ride on processing temperature for fast lithium conduction in garnet solid-state battery films**

Pfenninger, R., Struzik, M., Garbayo, I., Stilp, E., Rupp, J.L.M.

Nature Energy, Volume 4, Issue 6, 1 June 2019, Pages 475-483, <https://doi.org/10.1038/s41560-019-0384-4>

A critical parameter for the large-scale integration of solid-state batteries is to establish processing strategies to assemble battery materials at the lowest processing temperature possible while keeping lithium conduction up. Despite extensive research efforts, integrating ceramic film electrolytes while keeping a high lithium concentration and conduction at a low processing temperature remains challenging. Here, we report an alternative ceramic processing strategy through the evolution of multilayers establishing lithium reservoirs directly in lithium–garnet films that allow for lithiated and fast-conducting cubic solid-state battery electrolytes at unusually low processing temperatures. A lithium–garnet film processed via the multilayer processing approach exhibited the fastest ionic conductivity of  $2.9 \pm 0.05 \times 10^{-5} \text{ S cm}^{-1}$  (at room temperature) and the desired cubic phase, but was stabilized at a processing temperature lowered by 400 °C. This method enables future solid-state battery architectures with more room for cathode volumes by design, and reduces the processing temperature.

#### **Building better all-solid-state batteries with Li-garnet solid electrolytes and metalloid anodes**

Afyon, S., Kravchyk, K.V., Wang, S., Broek, J.V.D., Hänsel, C., Kovalenko, M.V., Rupp, J.L.M.

Journal of Materials Chemistry A, Volume 7, Issue 37, 2019, Pages 21299-21308, <https://doi.org/10.1039/c9ta04999a>

All-solid-state batteries provide new opportunities to realize safe, non-flammable, and temperature-tolerant energy storage and display a huge potential to be the core of future energy storage devices, especially in applications where energy density is key to the technology. Garnet-type solid-state electrolytes based on cubic  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  possess one of the highest  $\text{Li}^+$  conductivities, a wider electrochemical stability window compared to liquid electrolytes, and exceptional chemical and thermal stabilities among various solid electrolytes. Most of the first reports, however, employ lithium metal as the anode with unavoidable Li-dendrite formation through polycrystalline Li-garnet electrolytes at current densities above  $0.5 \text{ mA cm}^{-2}$ . Accordingly, alternative materials and processing strategies for anodes or interlayers are inherently needed for

high currents and fast charging for Li-garnet-type battery integration. Here, we demonstrate, through the use of a composite anode based on antimony nanocrystals, that metalloids offer high and stable storage capacities of up to 330 mA h g<sup>-1</sup> for Li-garnet all-solid-state batteries at reasonably high current densities (e.g. 240 mA g<sup>-1</sup>) at 95 °C. The results are also compared towards standard liquid type electrolytes and reveal high coulombic efficiencies and improved cycle stability for the solid-state cell design. Guidelines and aspects to process alternative materials and impact the interface design towards fast lithium charge transfer between the metalloid and the Li-garnet electrolyte are formulated. The architecture and scalable processing of metalloid-based batteries are obvious advantages of this work, opening a promising avenue to avoid Li-dendrite formation at high current loads in garnet-type all-solid-state rechargeable batteries.

### **DONALD R SADOWAY**

John F Elliott Professor of Materials Science and Engineering,  
<https://dmse.mit.edu/people/donald-r-sadoway>

Professor Sadoway's research seeks to establish the scientific underpinnings for technologies that make efficient use of energy and natural resources in an environmentally sound manner. This spans engineering applications and the supportive fundamental science. The overarching theme of his work is electrochemistry in nonaqueous media.

Specific topics in applied research are the following: environmentally sound electrochemical extraction and recycling of metals, lithium solid-polymer-electrolyte batteries, advanced materials for use as electrodes, separators, and walls in fused-salt electrolysis cells and batteries, electrochemical sensors, electrochemical synthesis of thin films of compound semiconductors in fused-salt and cryogenic media, and electrochemically controlled superconducting devices.

### **Modeling discontinuous potential distributions using the finite volume method, and application to liquid metal batteries**

Weber, N., Landgraf, S., Mushtaq, K., Nitz, M., Personnettaz, P., Weier, T., Zhao, J., Sadoway, D.  
Electrochimica Acta, Volume 318, 20 September 2019, Pages 857-864,  
<https://doi.org/10.1016/j.electacta.2019.06.085>

The electrical potential in a battery jumps at each electrode-electrolyte interface. We present a model for computing three-dimensional current and potential distributions, which accounts for such internal voltage jumps. Within the framework of the finite volume method we discretize the Laplace and gradient operators such that they account for internal jump boundary conditions. After implementing a simple battery model in OpenFOAM we validate it using an analytical test case, and show its capabilities by simulating the current distribution and discharge curve of a Li|Bi liquid metal battery.

### **A borate decorated anion-immobilized solid polymer electrolyte for dendrite-free, long-life Li metal batteries**

Ma, C., Feng, Y., Xing, F., Zhou, L., Yang, Y., Xia, Q., Zhou, L., Zhang, L., Chen, L., Ivey, D.G., Sadoway, D.R., Wei, W.  
Journal of Materials Chemistry A, Volume 7, Issue 34, 2019, Pages 19970-19976,  
<https://doi.org/10.1039/c9ta07551h>

Abrupt Li dendrite growth and the safety hazards caused by liquid electrolytes are generally acknowledged as major technical barriers for the practical application of Li metal batteries. Solid polymer electrolytes (SPEs) are promising to overcome these obstacles, but suffer from rigidity-conductivity inconsistency, ununiform ion distribution and inferior interfacial compatibility. Herein, an anion-immobilized SPE using vinylene carbonate as the rigid polymer backbone and flexible ether oxygen chains containing anion-trapping boron moieties is proposed, which facilitates the Li<sup>+</sup> transport and adjusts the ion distribution. This ingenious design along with facile in situ preparation effectively integrates a favorable Young's modulus (2.41 GPa), high ionic conductivity ( $9.11 \times 10^{-4}$  S cm<sup>-1</sup> at 25 °C) and a high Li<sup>+</sup> transference number (0.68), as well as achieving a stable solid electrolyte interface layer. As a result, these integrative properties enable dendrite-free LiFePO<sub>4</sub>/Li batteries with excellent rate capacity (8C, 98.3 mA h g<sup>-1</sup>) and superior long-term cyclability over 600 cycles at 30 °C, providing a new strategy for safe and high-energy all-solid-state energy storage systems.

### YANG SHAO-HORN

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Yang Shao-Horn studies materials for electrochemical and photoelectrochemical energy storage and conversion, which is centered on examining the influence of surface chemistry and electronic structures of thin films and nanomaterials on lithium storage and catalytic activity of small molecules of energy consequence, and applying fundamental understanding in reaction mechanisms to design new materials for lithium storage and electrocatalysis of oxygen reduction, water splitting, methanol oxidation and CO<sub>2</sub> reduction.

### Electrochemical Energy Lab

<http://web.mit.edu/eel/index.html>

Research: <http://web.mit.edu/eel/research.html>

Publications: <http://web.mit.edu/eel/publications.html>

Our research programs are centered on understanding the electronic structures of surfaces, with emphasis on metal oxides, searching for descriptors of catalytic activity, surface/interface reactivity and ion transport, and applying fundamental understanding to design materials for oxygen electrocatalysis, CO<sub>2</sub> reduction, ion intercalation and ion conductors, in electrochemical/photoelectrochemical energy conversion and storage, including lithium-ion, flow and metal-air batteries, proton exchange membrane and solid oxide fuel cells.

Our programs include extensive experimental components including synthesis of well-defined surfaces and nanostructured materials, and investigation of processes at the surfaces/interfaces using electrochemical methods coupled with ex situ and in situ X-ray-based and electron-based spectroscopy. These experimental components are used in conjunction with Density Functional Theory computation efforts to develop new, physically based reaction mechanisms and design principles of materials.

**FSI-inspired solvent and "full fluorosulfonyl" electrolyte for 4 v class lithium-metal batteries**

Xue, W., Shi, Z., Huang, M., Feng, S., Wang, C., Wang, F., Lopez, J., Qiao, B., Xu, G., Zhang, W., Dong, Y., Gao, R., Shao-Horn, Y., Johnson, J.A., Li, J.

Energy and Environmental Science, Volume 13, Issue 1, January 2020, Pages 212-220,

<https://doi.org/10.1039/c9ee02538c>

High-voltage rechargeable lithium-metal batteries (LMBs) require electrolytes that are compatible with both the Li metal anode (LMA) and the metal-oxide cathode. Herein, by imitating the fluorosulfonyl imide group from a well-known LMA-compatible salt, lithium bis(fluorosulfonyl) imide (LiFSI), we come up with an organic solvent dimethylsulfamoyl fluoride (FSO<sub>2</sub>NC<sub>2</sub>H<sub>6</sub>), a fluorosulfonamide (FSA) with two methyl substituents, to develop a new "full fluorosulfonyl" (FFS) electrolyte. Remarkably, it enables a highly reversible LMA with an excellent initial coulombic efficiency (CE) ~91%, and rapidly approaching 99% within only 10 cycles, with average CE outperforming the well-known LMA-compatible fluoroethylene carbonate (FEC)-based electrolyte. Furthermore, benefitting from its high anodic stability against the oxidative LiNi<sub>0.6</sub>Mn<sub>0.2</sub>Co<sub>0.2</sub>O<sub>2</sub> (NMC622) and LiMn<sub>2</sub>O<sub>4</sub> (LMO) surfaces, the LiNMC622 cell retains 89% of its original capacity after 200 cycles using a limited Li excess anode. This electrolyte design strategy opens a new avenue for exploring new medium-concentration organic electrolytes for 4 V class lithium-metal batteries (LMBs).

**Solvent- And Anion-Dependent Li<sup>+</sup>-O<sub>2</sub> - Coupling Strength and Implications on the Thermodynamics and Kinetics of Li-O<sub>2</sub> Batteries**

Leverick, G., Tataru, R., Feng, S., Crabb, E., France-Lanord, A., Tułodziecki, M., Lopez, J., Stephens, R.M., Grossman, J.C., Shao-Horn, Y.

Journal of Physical Chemistry C, Volume 124, Issue 9, 5 March 2020, Pages 4953-4967,

<https://doi.org/10.1021/acs.jpcc.9b09968>

Lithium-oxygen (Li-O<sub>2</sub>) batteries offer considerably higher gravimetric energy density than commercial Li-ion batteries (up to three times) but suffer from poor power, cycle life, and round-trip efficiency. Tuning the thermodynamics and pathway of the oxygen reduction reaction (ORR) in aprotic electrolytes can be used to enhance the Li-O<sub>2</sub> battery rate and discharge capacity. In this work, we present a systematic study on the role of the solvent and anion on the thermodynamics and kinetics of Li<sup>+</sup>-ORR, from which we propose a unified descriptor for its pathway and kinetics. First, by thoroughly characterizing the solvation environment of Li<sup>+</sup> ions using Raman spectroscopy, <sup>7</sup>Li NMR, ionic conductivity, and viscosity measurements, we observe increasing Li<sup>+</sup>-anion interactions with increasing anion DN in low DN solvents such as 1,2-dimethoxyethane and acetonitrile but minimal Li<sup>+</sup>-anion interactions in the higher DN dimethyl sulfoxide. Next, by determining the electrolyte-dependent Li<sup>+</sup>/Li, TBA<sup>+</sup>, O<sub>2</sub>/TBA<sup>+</sup>-O<sub>2</sub><sup>-</sup>, and Li<sup>+</sup>, O<sub>2</sub>/Li<sup>+</sup>-O<sub>2</sub><sup>-</sup> redox potentials versus the solvent-invariant Me<sub>10</sub>Fc reference potential, we show that stronger combined solvation of Li<sup>+</sup> and O<sub>2</sub><sup>-</sup> ions leads to weaker Li<sup>+</sup>-O<sub>2</sub><sup>-</sup> coupling. Finally, using rotating ring disk electrode measurements, we show that weaker Li<sup>+</sup>-O<sub>2</sub><sup>-</sup> coupling in electrolytes with strong combined solvation leads to an increased generation of soluble Li<sup>+</sup>-O<sub>2</sub><sup>-</sup> type species and faster overall kinetics during Li<sup>+</sup>-ORR.

**Revealing electrolyte oxidation: Via carbonate dehydrogenation on Ni-based oxides in Li-ion batteries by in situ Fourier transform infrared spectroscopy**

Zhang, Y., Katayama, Y., Tataru, R., Giordano, L., Yu, Y., Fraggadakis, D., Sun, J.G., Maglia, F., Jung, R., Bazant, M.Z., Shao-Horn, Y.

Energy and Environmental Science, Volume 13, Issue 1, January 2020, Pages 183-199,  
<https://doi.org/10.1039/c9ee02543j>

Understanding (electro-)chemical reactions at the electrode-electrolyte interface (EEI) is crucial to promote the cycle life of lithium-ion batteries. In this study, we developed an in-situ Fourier-transform infrared spectroscopy (FT-IR) method, which provided unprecedented information on the oxidation of carbonate solvents via dehydrogenation on  $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$  (NMC). While ethylene carbonate (EC) was stable against oxidation on Pt up to 4.8 VLi, unique evidence for dehydrogenation of EC on  $\text{LiNi}_0.8\text{Co}_0.1\text{Mn}_0.1\text{O}_2$  (NMC811) at voltages as low as 3.8 VLi was revealed by in situ FT-IR measurements, which was supported by density functional theory (DFT) results. Unique dehydrogenated species from EC were observed on NMC811 surface, including dehydrogenated EC anchored on oxides, vinylene carbonate (VC) and dehydrogenated oligomers which could diffuse away from the surface. Similar dehydrogenation on NMC811 was noted for EMC-based and LP57 (1 M LiPF<sub>6</sub> in 3:7 EC/EMC) electrolytes. In contrast, no dehydrogenation was found for NMC111 or surface-modified NMC by coatings such as Al<sub>2</sub>O<sub>3</sub>. In addition, while the dehydrogenation of solvents was observed in 1 M electrolytes with different anions, they were not observed on NMC811 in the concentrated electrolyte (EC/EMC with 3.1 M LiPF<sub>6</sub>), indicating lithium coordination could suppress dehydrogenation. Dehydrogenation of carbonates on NMC811 accompanied with rapid growth of interfacial impedance with increasing voltage revealed by electrochemical impedance spectroscopy (EIS), while the electrode-electrolyte combinations without dehydrogenation did not show significant impedance growth. Therefore, minimizing carbonate dehydrogenation on the NMC surface by tuning electrode reactivity and electrolyte reactivity is critical to develop high-energy Li-ion batteries with long cycle life.

#### **Molecular Design of Stable Sulfamide- and Sulfonamide-Based Electrolytes for Aprotic Li-O<sub>2</sub> Batteries**

Feng, S., Huang, M., Lamb, J.R., Zhang, W., Tatara, R., Zhang, Y., Guang Zhu, Y., Perkinson, C.F., Johnson, J.A., Shao-Horn, Y.

Chem, Volume 5, Issue 10, 10 October 2019, Pages 2630-2641,

<https://doi.org/10.1016/j.chempr.2019.07.003>

Electrolyte instability is one of the most challenging impediments to enabling lithium-oxygen (Li-O<sub>2</sub>) batteries for practical use. The use of physical organic chemistry principles to rationally design new molecular components may enable the discovery of electrolytes with stability profiles that cannot be achieved with existing formulations. Here, we report on the development of sulfamide- and sulfonamide-based small molecules that are liquids at room temperature, capable of dissolving reasonably high concentration of Li salts (e.g., lithium bis(trifluoromethane)sulfonimide [LiTFSI]), and exceptionally stable under the harsh chemical and electrochemical conditions of aprotic Li-O<sub>2</sub> batteries. In particular, N, N-dimethyl-trifluoromethanesulfonamide was found to be highly resistant to chemical degradation by peroxide and superoxide, stable against electrochemical oxidation up to 4.5 V Li, and stable for >90 cycles in a Li-O<sub>2</sub> cell when cycled at <4.2 V Li. This study provides guiding principles for the development of next-generation electrolyte components based on sulfamides and sulfonamides.

#### **Revealing Electronic Signatures of Lattice Oxygen Redox in Lithium Ruthenates and Implications for High-Energy Li-Ion Battery Material Designs**

Yu, Y., Karayalali, P., Nowak, S.H., Giordano, L., Gauthier, M., Hong, W., Kou, R., Li, Q., Vinson, J., Kroll, T., Sokaras, D., Sun, C.-J., Charles, N., Maglia, F., Jung, R., Shao-Horn, Y.

Chemistry of Materials, Volume 31, Issue 19, 8 October 2019, Pages 7864-7876,

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Anion redox in lithium transition-metal oxides such as  $\text{Li}_2\text{RuO}_3$  and  $\text{Li}_2\text{MnO}_3$  has catalyzed intensive research efforts to find transition-metal oxides with anion redox that may boost the energy density of lithium-ion batteries. The physical origin of the observed anion redox remains debatable, and more direct experimental evidence is needed. In this work, we have shown electronic signatures of oxygen-oxygen coupling, direct evidence central to lattice oxygen redox ( $\text{O}_2^-/(\text{O}_2)^{n-}$ ), in charged  $\text{Li}_{2-x}\text{RuO}_3$  after Ru oxidation ( $\text{Ru}^{4+}/\text{Ru}^{5+}$ ) upon first electron removal with lithium deintercalation. Experimental Ru L<sub>3</sub>-edge high-energy-resolution fluorescence-detected X-ray absorption spectra (HERFD-XAS), supported by ab initio simulations, revealed that the increased intensity in the high-energy shoulder upon lithium deintercalation resulted from increased O-O coupling, inducing (O-O)  $\sigma^*$ -like states with  $\pi$  overlap with Ru d-manifolds, in agreement with O K-edge XAS spectra. Experimental and simulated O K-edge X-ray emission spectra further supported this observation with the broadening of the oxygen nonbonding feature upon charging, also originated from (O-O)  $\sigma^*$  states. This lattice oxygen redox of  $\text{Li}_{2-x}\text{RuO}_3$  was accompanied by a small amount of  $\text{O}_2$  evolution in the first charge from differential electrochemistry mass spectrometry but diminished in the subsequent cycles, in agreement with the more reduced states of Ru in later cycles from Ru L<sub>3</sub>-edge HERFD-XAS. These observations indicated that Ru redox contributed more to discharge capacities after the first cycle. This study has pinpointed the key spectral fingerprints related to lattice oxygen redox from a molecular level and constructed a transferrable framework to rationally interpret the spectroscopic features by combining advanced experiments and theoretical calculations to design materials for Li-ion batteries and electrocatalysis applications.

#### Enhanced Cycling Performance of Ni-Rich Positive Electrodes (NMC) in Li-Ion Batteries by Reducing Electrolyte Free-Solvent Activity

Tatara, R., Yu, Y., Karayaylali, P., Chan, A.K., Zhang, Y., Jung, R., Maglia, F., Giordano, L., Shao-Horn, Y.

ACS Applied Materials and Interfaces, Volume 11, Issue 38, 25 September 2019, Pages 34973-34988, <https://doi.org/10.1021/acsami.9b11942>

The interfacial (electro)chemical reactions between electrode and electrolyte dictate the cycling stability of Li-ion batteries. Previous experimental and computational results have shown that replacing Mn and Co with Ni in layered  $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$  (NMC) positive electrodes promotes the dehydrogenation of carbonate-based electrolytes on the oxide surface, which generates protic species to decompose LiPF<sub>6</sub> in the electrolyte. In this study, we utilized this understanding to stabilize  $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$  (NMC811) by decreasing free-solvent activity in the electrolyte through controlling salt concentration and salt dissociativity. Infrared spectroscopy revealed that highly concentrated electrolytes with low free-solvent activity had no dehydrogenation of ethylene carbonate, which could be attributed to slow kinetics of dissociative adsorption of Li<sup>+</sup>-coordinated solvents on oxide surfaces. The increased stability of the concentrated electrolyte against solvent dehydrogenation gave rise to high capacity retention of NMC811 with capacities greater than 150 mA h g<sup>-1</sup> (77% retention) after 500 cycles without oxide-coating and Ni-concentration gradients or electrolyte additives.

#### CARL V THOMPSON

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Professor Thompson and his students carry out research on thin films and nanostructures for use in micro- and nano-systems, especially electronic, electromechanical and electrochemical systems. His group carries out basic research on structure evolution during deposition and post-deposition processing of thin films. The latter includes research on templated solid-state dewetting of thin films and nanostructures, for development of new patterning methods and for basic studies of capillary-driven morphological evolution. Prof. Thompson's group also carries out research on the mechanisms of carbon nanotube growth and metal-catalyzed etching for creation of semiconductor nanowire arrays. Carbon nanotubes are also used in research on metal-air batteries and capacitive desalination devices, and nanowires are used in research on solid state supercapacitors. Thin film Li-ion microbatteries and thermogalvanic energy harvesting devices for applications in autonomous microsystems are also under investigation.

### **Modeling the Effect of Lithium Superoxide Solvation and Surface Reduction Kinetics on Discharge Capacity in Lithium-Oxygen Batteries**

Batcho, T.P., Leverick, G., Shao-Horn, Y., Thompson, C.V.

Journal of Physical Chemistry C, Volume 123, Issue 23, 13 June 2019, Pages 14272-14282,

<https://doi.org/10.1021/acs.jpcc.9b03493>

Li-O<sub>2</sub> batteries could potentially yield significantly higher capacities than Li-ion batteries. Achieving high capacity requires efficient void-filling of the cathode by the insoluble insulating discharge product Li<sub>2</sub>O<sub>2</sub>, which forms by two competing mechanistic pathways. One is a surface-mediated pathway that leads to formation of thin films of Li<sub>2</sub>O<sub>2</sub> on the electrode. The other is a solvent-mediated pathway, involving the solvation of a Li<sup>+</sup>-O<sub>2</sub><sup>-</sup> intermediate that disproportionates and leads to the formation of large toroidal particles. As the solvent pathway produces large particles that are more efficient for void-filling than thin films produced by the surface pathway, there has been an active search for modifications that can promote the solvent pathway. We construct a model that demonstrates how discharge parameters influence each pathway and can be optimized to yield high capacity. We test the model with rotating ring-disk electrode experiments, which allow for the direct measurement of the relative contributions of solution and solvent pathways as a function of rotation rate, water content, voltage, and choice of solvent. We show that favorability of solvation of Li<sup>+</sup>-O<sub>2</sub><sup>-</sup> has a weak effect on the solvation rate and a large effect on the surface pathway rate. This insight can help guide strategies to optimize capacity in Li-O<sub>2</sub> batteries.

### **Multi-cell thermogalvanic systems for harvesting energy from cyclic temperature changes**

Linford, P.A., Xu, L., Huang, B., Shao-Horn, Y., Thompson, C.V.

Journal of Power Sources, Volume 399, 30 September 2018, Pages 429-435,

<https://doi.org/10.1016/j.jpowsour.2018.07.080>

Two types of electrochemical systems for harvesting energy from cyclic changes in environmental temperature using the thermogalvanic effect are demonstrated. Both systems are based on two battery stacks which function in either a dual-temperature or single-temperature configuration. In the dual-temperature configuration, two LiCoO<sub>2</sub>/Li cells were separately cycled between two temperatures to achieve an energy conversion with an efficiency of 0.22%, free of heat recuperation, and a peak output power of 0.4 μW when cycled between 20 °C and 50 °C. This energy conversion efficiency is comparable to other proposed systems for thermal energy harvesting such as charge-free thermally regenerative electrochemical cycle (TREC) devices, thermocapacitive devices and

ionic thermoelectric supercapacitors. However, this system can function with a broader range of materials, which will likely allow further increases in efficiency and power. A single-temperature configuration in which two stacks of cells were cycled together between two temperatures was also demonstrated. Both systems are attractive for harvesting thermal energy for self-powered sensor networks, especially in remote areas.

### **BRIAN L WARDLE**

Professor of Aeronautics and Astronautics, <https://aeroastro.mit.edu/brian-wardle>  
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Professor Wardle is Director of MIT's Nano-Engineered Composite aerospace Structures (NECST) Consortium, and necstlab. He is active in the Materials Processing Center (MPC) ISN, CMSE, and MEMS@MIT (part of the Microsystems Technology Laboratory) communities.

### **necstlab**

<http://necstlab.mit.edu/>  
Research: <http://necstlab.mit.edu/research>  
Publications: <http://necstlab.mit.edu/publications>

The necstlab (pronounced next lab) research group explores new concepts in engineered materials and structures, and is directed by Prof. Wardle in the Dept. of Aeronautics & Astronautics at MIT. The group's mission is to lead the advancement and application of new knowledge at the forefront of materials and structures understanding, with research contributions in both science and engineering. Applications of interest include enhanced (aerospace) advanced composites, multifunctional attributes of structures such as damage sensing, and also microfabricated (MEMS) topics. A significant effort over the past decade has been to use nanoscale materials to enhance performance of advanced aerospace materials and their structures through the industry supported NECST Consortium.

### **Multifunctional nanocomposite structural separators for energy storage**

Acauan, L.H., Zhou, Y., Kalfon-Cohen, E., Fritz, N.K., Wardle, B.L.  
Nanoscale, Volume 11, Issue 45, 7 December 2019, Pages 21964-21973,  
<https://doi.org/10.1039/c9nr06954b>

Separators in energy storage devices such as batteries and supercapacitors are critical elements between the much-researched anodes and cathodes. Here we present a new "structural separator" comprised of electrically-insulating aligned alumina nanotubes, which realizes a structural, or mechanically robust, function in addition to allowing charge transfer. The polymer nanocomposite structural separator is demonstrated in a supercapacitor cell and also as an interface reinforcement in an aerospace-grade structural carbon fiber composite. Relative to a polymeric commercial separator, the structural separator shows advantages both electrically and structurally: ionic conductivity in the supercapacitor cell is doubled due to the nanotubes disrupting the semi-crystallinity in the polymer electrolyte, and the structural separator creates an interface that is 50% stronger in the advanced composite. In addition to providing direct benefits to existing energy storage devices, the structural separator is best suited to multifunctional structural energy storage applications.

## ECONOMICS OF ENERGY STORAGE

### **WILLIAM H GREEN, JR**

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William Green is the Hoyt C. Hottel Professor of Chemical Engineering. He is a world leader in computer-aided chemical kinetic modeling, and leads a team of 20 researchers focusing on reaction kinetics, quantum chemistry, numerical methods, and fuel chemistry. In addition to his extensive work on kinetic modeling and combustion, oxidation, and pyrolysis chemistry, he has performed techno-economic assessments of proposed fuel changes and biofuel production options, he has written several papers on spectroscopy, and he has addressed a variety of industrial engineering problems involving fuels, catalysis, and emissions. His work has been presented in more than 220 articles, which have cumulatively been cited more than 8,800 times. His research has been honored with several national awards; most recently he was named a Fellow of the American Association for the Advancement of Science in 2016. Prof. Green received his BA in Chemistry (with Highest Honors) from Swarthmore College in 1983, and his PhD in Physical Chemistry from the University of California, Berkeley in 1988. After postdoctoral research at Cambridge University and the University of Pennsylvania, he was a principal investigator at Exxon's Corporate Research Laboratory for six years before joining the MIT faculty in 1997. He chaired the sessions on Combustion at the AIChE National Meetings for a decade, and played a leadership role in the DOE's Combustion Energy Frontier Research Center. He convened the 7th International Conference on Chemical Kinetics at MIT in 2011. He served as Executive Officer of the MIT Department of Chemical Engineering from 2012-2015, and was the Editor of the International Journal of Chemical Kinetics from 2008-2013.

### **Green Research Group**

<http://greengroup.mit.edu/>

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Publications: <http://greengroup.mit.edu/publications>

The Green research group focuses on the central problem of reactive chemical engineering: quantitatively predicting the time evolution of chemical mixtures. Accurate chemical kinetic models are extremely powerful and valuable, since they allow predictions about the impact of modifying a system; already many significant public policy and business decisions are made on the basis of kinetic model predictions. For example, the Montreal Protocol, which imposed a worldwide ban on certain halocarbons, was based on a kinetic model of the ozone layer. We are developing this simulation technology to solve practical problems related to the atmospheric chemistry of organic pollutants, the conversion of natural gas to liquid fuels, the oxidation of organics in the gas and liquid phase, the removal of sulfur contaminants from gasoline, and the formation of carcinogenic pollutants in combustion.

### **Recharging systems and business operations to improve the economics of electrified taxi fleets**

Hsieh, I.-Y.L., Nunes, A., Pan, M.S., Green, W.H.

Sustainable Cities and Society, Volume 57, June 2020, Article number 102119,

<https://doi.org/10.1016/j.scs.2020.102119>

While vehicle electrification offers great benefits to society, mass-market adoption of battery electric vehicles remains a challenge owing to the long recharging times and limited recharging infrastructure. High opportunity costs tied to long recharging times are particularly problematic for commercial fleet operators. With an aim to improve the economics of electrified taxi fleets, we present a framework for techno-economic analysis, examining the cost competitiveness of various recharging business models (i.e., combined ecosystems of recharging systems and taxi operations). When considering the achievable throughput of the recharging systems, we find that—on a per-kilometer basis—1) battery swapping emerges as a cost-effective option although it requires higher upfront investments for the battery inventory requirement; 2) increasing vehicle fleet size enhances the economic viability of double-shift taxi electrification. We expect that an electrified taxi fleet relying on the right recharging systems/operations could achieve cost parity with a gasoline-powered taxis system by 2022. Between now and then, the electrification of high-use vehicles requires government support; policies discussed include purchase subsidies and revenue-neutral gas tax imposition. By using real-world financial data taken from an operating electrified taxi fleet in Beijing, this paper provides a theoretical and practical reference for cities moving toward electric taxi ecosystems and sustainability.

### Learning only buys you so much: Practical limits on battery price reduction

Hsieh, I.-Y.L., Pan, M.S., Chiang, Y.-M., Green, W.H.  
Applied Energy, Volume 239, 1 April 2019, Pages 218-224,  
<https://doi.org/10.1016/j.apenergy.2019.01.138>

Wide deployment of electric vehicles (EVs) would greatly facilitate global de-carbonization, but achieving the emission targets depends on future battery prices. Conventional learning curves for manufacturing costs, used in many battery projections, unrealistically predict battery prices will fall below \$100/kWh by 2030, pushing EVs to hit price parity with internal combustion engine vehicles (ICEVs) in the absence of incentives. However, in reality, essential materials costs set practical lower bounds on battery prices. Our 2-stage learning curve model projects the active material costs and NMC-based Lithium-ion battery pack price with mineral and material costs as the respective price floors. The improved model predicts nickel-manganese-cobalt (NMC) battery prices will fall only to about \$124/kWh by 2030 – much cheaper than today, but still too expensive to truly compete with ICEVs, due primarily to the high prices of cobalt, nickel, and lithium. Our results suggest that stabilizing raw materials prices and/or stimulating R&D activities on alternative battery chemistries will be important to achieve environmentally sustainable EV-based ground transportation at an attractive price.

### OMER KARADUMAN

PhD Candidate, Department of Economics, <https://economics.mit.edu/grad/omerk>

Omer Karaduman is a PhD candidate at MIT Economics Department. He is interested in Electricity Markets and Market Design.

### Economics Grid-Scale Energy Storage

Omër Karaduman

Job Market Paper, January 1, 2020, <https://economics.mit.edu/files/18357>

The transition to a low-carbon electricity system is likely to require grid-scale energy storage to smooth the variability and intermittency of renewable energy. I investigate whether private incentives for operating and investing in grid-scale energy storage are optimal and the need for

policies that complement investments in renewables with encouraging energy storage. In a wholesale electricity market, energy storage systems generate profit by arbitraging inter-temporal electricity price differences. In addition, storage induces non-pecuniary externalities due to production efficiency and carbon emissions. I build a new dynamic equilibrium framework to quantify the effects of grid-scale energy storage and apply it to study the South Australian Electricity Market. This equilibrium framework computes a supply function equilibrium using estimated best responses from conventional sources to observed variation in the residual demand volatility. Accounting for storage's effect on equilibrium prices is quantitatively important: previous methods that ignore this channel overestimate the profitability of operating a storage unit. The first set of results shows that although entering the electricity market is not profitable for privately operated storage, such entry would increase consumer surplus and total welfare and reduce emissions. A storage operator that minimizes the cost of acquiring electricity could further improve consumer surplus by twice as much. Importantly, a competitive storage market cannot achieve this outcome because other power plants distort prices. These results argue for a capacity market to compensate for a private firm for investing in storage. The second set of results shows that at moderate levels of renewable power, introducing grid-scale storage to the system reduces renewable generators' revenue by decreasing average prices. For high levels of renewable generation capacity, storage increases the return to renewable production and decreases CO<sub>2</sub> emissions by preventing curtailment during low-demand periods.

#### APURBA SAKTI

Research Scientist, <http://energy.mit.edu/profile/apurba-sakti/>

Apurba Sakti joined the Department of Chemical Engineering at MIT in April 2014 as a postdoctoral associate and was promoted to a Research Scientist at the Energy Initiative in January 2016. Prior to MIT, Sakti was a graduate research assistant in the Vehicle Electrification Group at Carnegie Mellon University while completing his Ph.D. in Engineering and Public Policy. For his doctoral dissertation, Sakti worked on the design and cost of batteries and the associated public policy implications for personal vehicle electrification. His work has since been mentioned in the New York Times, and the methods applied by a start-up to improve battery manufacturing. Sakti has experience working with the United Nations Development Programme in Zagreb and the American Council for an Energy Efficient Economy in Washington, D.C. At MIT, Sakti is focusing on different techno-economic aspects of energy storage systems.

#### Review of wholesale markets and regulations for advanced energy storage services in the United States: Current status and path forward

Sakti, A., Botterud, A., O'Sullivan, F.

Energy Policy, Volume 120, September 2018, Pages 569-579,  
<https://doi.org/10.1016/j.enpol.2018.06.001>

Today, advanced energy storage technologies, particularly electrochemical batteries, represent an increasingly economic option for supporting the integration of renewable energy resources and providing the grid with greater operational flexibility. Crucially though, the large-scale deployment of these assets, and the development of successful business models to support them is heavily reliant on policy, regulation and market design. In this paper, we present a comprehensive review of the array of federal, ISO/RTO and state-level rules and regulations shaping today's energy storage deployment across the United States. We highlight the fragmented and heterogeneous nature of existing market participation models available for advanced energy storage across restructured power markets and emphasize the need for design changes to power markets at all

timescales to allow for the more efficient integration of energy storage. We also reflect on how well FERC's recent Order 841 does in terms of providing a framework for the establishment of more fit-for-purpose market participation models for storage, something that will be key for today's evolving power sector as it becomes more dependent on intermittent renewable resources.

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Jessika Trancik is an Associate Professor of Energy Studies at the Massachusetts Institute of Technology. She is also an external professor at the Santa Fe Institute. She received her BS in materials science and engineering from Cornell University and her PhD in materials science from the University of Oxford as a Rhodes Scholar. Before MIT, she spent several years at the Santa Fe Institute as an Omidyar Fellow, and at Columbia University as an Earth Institute Fellow, where her research focused on energy systems modeling. Her research group studies the dynamic costs and environmental impacts of energy technologies to inform technology design and policy.

Prof. Trancik's research centers on evaluating the environmental impacts and costs of energy technologies, and setting design targets to help accelerate the development of these technologies in the laboratory. This work involves assembling and analyzing expansive datasets, and developing new quantitative models and theory. Projects focus on electricity and transportation, with an emphasis on solar energy conversion and storage technologies.

### Trancik Lab

<http://trancik.mit.edu/>

Projects: <http://trancik.mit.edu/projects/>

Publications: <http://trancik.mit.edu/publications/>

Our projects focus on evaluating the costs and environmental impacts of energy technologies to accelerate their improvement. Through data analysis and modeling, we study expected changes to technology performance over time, due to innovation and evolving operational contexts. By relating performance to design and manufacturing decisions, our research informs technology development in the laboratory and technology policy. We work on a variety of energy conversion and storage technologies for electricity and transportation.

### *Value of storage technologies*

<http://trancik.mit.edu/storage-technology-optimization/>

Stationary and mobile energy storage technologies can synchronize energy demand and supply, but need to be evaluated against energy consumption patterns. Here we analyze energy consumption patterns against an intermittent energy supply — from wind and solar energy or vehicle charging stations — to evaluate diverse storage technologies and their development trends.

### Storage Requirements and Costs of Shaping Renewable Energy Toward Grid Decarbonization

Ziegler, M.S., Mueller, J.M., Pereira, G.D., Song, J., Ferrara, M., Chiang, Y.-M., Trancik, J.E.

Joule, Volume 3, Issue 9, 18 September 2019, Pages 2134-2153,

<https://doi.org/10.1016/j.joule.2019.06.012>

Deeply decarbonizing electricity production will likely require that low-carbon sources meet energy demand throughout days, years, and decades. Wind and solar energy are possible low-carbon options, but resource variability can limit their reliability. Storage can help address this challenge by shaping intermittent resources into desired output profiles. But can solar and wind energy with storage cost-competitively fulfill this role? How do diverse storage technologies compare? We address these questions by analyzing systems that combine wind and solar energy with storage to meet various demand profiles. We estimate that energy storage capacity costs below a roughly \$20/kWh target would allow a wind-solar mix to provide cost-competitive baseload electricity in resource-abundant locations such as Texas and Arizona. Relaxing reliability constraints by allowing for a few percent of downtime hours raises storage cost targets considerably, but would require supplemental technologies. Finally, we discuss storage technologies that could reach the estimated cost targets. Wind and solar energy can produce decarbonized electricity, but to reliably meet demand these intermittent resources require other technologies such as energy storage, supplemental generation, demand management, and transmission expansion. Many studies estimate the costs of supplying electricity with renewables for particular storage cost assumptions. Here we study which characteristics most impact renewable electricity costs, including cost features of proposed storage technologies. Considering 20 years of resource fluctuations, we capture large, infrequent events affecting storage requirements. We estimate that cost-competitively meeting baseload demand 100% of the time requires storage energy capacity costs below \$20/kWh. If other sources meet demand 5% of the time, electricity costs fall and the energy capacity cost target rises to \$150/kWh. The results can inform policy and investments in technology research, development, and deployment. Solar and wind energy can help to decarbonize electricity production but require other technologies, such as energy storage, to reliably meet demand. We study systems combining intermittent renewables with storage and other technologies and compare their electricity costs to alternatives. We estimate that in high-resource regions, with optimal resource mixes, low storage energy capacity costs (<\$20/kWh) are necessary for cost-competitive, reliable baseload electricity generation. However, when other technologies meet 5% of demand, costs can be halved, even with significantly more expensive storage.

## ENERGY CONVERSION AND FUEL CELLS

### YOGESH SURENDRANATH

Paul M Cook Career Development Associate Professor of Chemistry,

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Lab: <http://www.interphases.org/home/>

Publications: <http://www.interphases.org/publications/>

The Surendranath Lab is focused on addressing global challenges in the areas of chemical catalysis, energy storage and utilization, and environmental stewardship. Fundamental and technological advances in each of these areas require new methods for controlling the selectivity and efficiency of inner-sphere reactions at solid-liquid interfaces. Our strategy emphasizes the bottom-up, molecular-level, engineering of functional inorganic interfaces with a current focus on electrochemical energy conversion.

### Surendranath Group

<http://www.interphases.org/home/>

Research: <http://www.interphases.org/research/>

Publications: <http://www.interphases.org/publications/>



Global challenges in the areas of chemical catalysis, energy storage and utilization, and environmental stewardship require new methods for controlling the selectivity and efficiency of inner-sphere reactions at solid-liquid interfaces. Our group works to solve these problems via bottom-up, molecular-level engineering of functional inorganic interfaces with a focus on electro-chemical energy conversion.

### Oxygen Reduction Catalysis at Tunable Metal Sulfide Nanofilms

Principal Investigator: Yogesh Surendranath

Project Dates: March 1, 2015 – February 29, 2020

[https://www.nsf.gov/awardsearch/showAward?AWD\\_ID=1454060](https://www.nsf.gov/awardsearch/showAward?AWD_ID=1454060)

Renewable energy sources such as solar and wind will play an increasing role in meeting the growing energy demands of the future. However, these sources are intermittent, having reliable energy when the sun doesn't shine or wind doesn't blow requires storage in an energy dense form such as a chemical fuel. The fuel energy can then be released to produce electricity on demand in a fuel cell. Currently, fuel cells are expensive and unsustainable due to the high cost and scarcity of the platinum-based catalysts needed to convert fuel to electricity. This project aims to develop low-cost, non-toxic, earth-abundant catalysts to replace platinum in future fuel cells. The work will allow graduate and undergraduate students and postdoctoral fellows to learn the modern techniques in chemistry for renewable energy science and to collaborate to discover new catalysts. The research work will also be integrated with a broad-based outreach effort, The Catalyst Genome Project, which will allow amateur researchers of all ages to discover, evaluate, and collaborate in the search for new catalysts for renewable energy storage.

With this award, the Chemical Catalysis Program of the Chemistry Division is funding Dr. Yogesh Surendranath of the Massachusetts Institute of Technology to systematically investigate the oxygen reduction reaction (ORR) mediated by late transition metal sulfide (MS<sub>x</sub> where M = Ni, Co, Fe) nanofilm electrocatalysts. Late transition metal sulfides (LTMSs) represent an attractive class of low-cost, earth-abundant ORR catalysts for low-temperature fuel cell cathodes but their development and optimization have been hampered by a lack of mechanistic understanding and an absence of fundamental design principles. The project will utilize a recently developed layer-by-layer chemical electrodeposition method for preparing nanometer-thick crystalline LTMS films to probe the active site structure and mechanism of ORR on these materials. From these studies, the work aims to extract broad periodic trends and overarching design principles that will be used to synthesize high-performance nanoparticulate LTMS ORR catalysts primed for integration into advanced fuel cell cathodes.

### Graphite Conjugation Eliminates Redox Intermediates in Molecular Electrocatalysis

Jackson, M.N., Kaminsky, C.J., Oh, S., Melville, J.F., Surendranath, Y.

Journal of the American Chemical Society, Volume 141, Issue 36, 11 September 2019, Pages 14160-14167, <https://doi.org/10.1021/jacs.9b04981>

The efficient interconversion of electrical and chemical energy requires the intimate coupling of electrons and small-molecule substrates at catalyst active sites. In molecular electrocatalysis, the molecule acts as a redox mediator which typically undergoes oxidation or reduction in a separate step from substrate activation. These mediated pathways introduce a high-energy intermediate, cap the driving force for substrate activation at the reduction potential of the molecule, and impede access to high rates at low overpotentials. Here we show that electronically coupling a molecular

hydrogen evolution catalyst to a graphitic electrode eliminates stepwise pathways and forces concerted electron transfer and proton binding. Electrochemical and X-ray absorption spectroscopy data establish that hydrogen evolution catalysis at the graphite-conjugated Rh molecule proceeds without first reducing the metal center. These results have broad implications for the molecular-level design of energy conversion catalysts.

### Mixed Electron-Proton Conductors Enable Spatial Separation of Bond Activation and Charge Transfer in Electrocatalysis

Yan, B., Bisbey, R.P., Alabugin, A., Surendranath, Y.

Journal of the American Chemical Society, Volume 141, Issue 28, 2 June 2019, Pages 11115-11122, <https://doi.org/10.1021/jacs.9b03327>

Electrochemical energy conversion requires electrodes that can simultaneously facilitate substrate bond activation and electron-proton charge transfer. Traditional electrodes co-localize both functions to a single solid|liquid interface even though each process is typically favored in a disparate reaction environment. Herein, we establish a strategy for spatially separating bond activation and charge transfer by exploiting mixed electron-proton conduction (MEPC) in an oxide membrane. Specifically, we interpose a MEPC WO<sub>x</sub> membrane between a Pt catalyst and aqueous electrolyte and show that this composite electrode is active for the hydrogen oxidation reaction (HOR). Consistent with H<sub>2</sub> activation occurring at the gas|solid interface, the composite electrode displays HOR current densities over 8-fold larger than the diffusion-limited rate of HOR catalysis at a singular Pt|solution interface. The segregation of bond activation and charge separation steps also confers excellent tolerance to poisons and impurities introduced to the electrolyte. Mechanistic studies establish that H<sub>2</sub> activation at the Pt|gas interface is coupled to the electron-proton charge separation at the WO<sub>x</sub>|solution interface via rapid H-diffusion in the bulk of the WO<sub>x</sub>. Consequently, the rate of HOR is principally controlled by the rate of H-spillover at the Pt|WO<sub>x</sub> boundary. Our results establish MEPC membrane electrodes as a platform for spatially separating the critical bond activation and charge transfer steps of electrocatalysis.

### HARRY L. TULLER

R.P. Simmons Professor of Ceramics and Electronic Materials,

<https://dmse.mit.edu/people/harry-l-tuller>

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Dr. Tuller's research focuses on defects, transport and electronic structure of metal oxides and their integration into sensors; fuel cells; solar cells, and MEMS devices.

### Crystal Physics and Electroceramics Laboratory

<http://electroceramics.mit.edu/>

Our research is devoted to the modeling, processing, characterization and optimization of energy related devices (sensors, batteries, fuel cells, solar/photolysis cells) and the integration of sensor, actuator and photonic materials into microelectromechanical (MEMS) systems.

### Chemomechanics of Fuel Cell Related Materials

Authors: Sean R. Bishop, WooChul Jung, Jae-Jin Kim, and Harry L. Tuller (in collaboration with groups of Professors Krystyn Van Vliet, Sidney Yip, Bilge Yildiz and Yang Shao-Horn)

Sponsor: Department of Energy

[http://electroceramics.mit.edu/index.php?option=com\\_content&view=article&id=62&Itemid=77](http://electroceramics.mit.edu/index.php?option=com_content&view=article&id=62&Itemid=77)

Solid oxide fuel cells (SOFCs) directly convert chemical to electrical energy with high efficiency and can operate using a wide variety of fuels from hydrogen, kerosene, to gasified coal. Many of the more advanced materials in SOFCs experience significant changes in oxygen content, or oxygen stoichiometry, during operation, resulting in changes in volume and elastic properties termed chemomechanics. This chemical expansion, analogous to temperature induced thermal expansion, is oxygen nonstoichiometry induced and can have a negative impact on SOFC performance. In this project, we are studying the chemical expansion coefficient, elastic properties, and oxygen stoichiometry of thin film and bulk SOFC materials. Thin films are of particular interest since they allow for control of strain and increase the surface to volume ratio, particularly important for electrode performance. The chemomechanical properties are being investigated using high temperature, atmosphere controlled nanoindentation, high resolution x-ray diffraction, dilatometry, impedance spectroscopy, and thermo-gravimetry techniques.

### Tailoring Nonstoichiometry and Mixed Ionic Electronic Conductivity in $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}/\text{SrTiO}_3$ Heterostructures

Harrington, G.F., Kalaev, D., Yildiz, B., Sasaki, K., Perry, N.H., Tuller, H.L.  
ACS Applied Materials and Interfaces, Volume 11, Issue 38, 25 September 2019, Pages 34841-34853, <https://doi.org/10.1021/acsami.9b08864>

The oxygen deficiency or excess, as reflected in the nonstoichiometry of oxide films, plays a crucial role in their functional properties for applications such as micro solid oxide fuel cells, catalysis, sensors, ferroelectrics, and memristors. High concentrations of oxygen vacancies may be beneficial or detrimental according to the application, and hence there is interest in controlling the oxygen content of films without resorting to compositional changes. Here, we demonstrate that substantial changes in the nonstoichiometry of  $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  (PCO), a model mixed ionic electronic conductor, can be achieved by fabricating multilayers with an inert material,  $\text{SrTiO}_3$  (STO). We fabricated heterostructures using pulsed laser deposition, keeping the total thickness of PCO and STO constant while varying the number of layers and thickness of each individual layer, to probe the effects of the PCO/STO interfaces. Conductivity measurements as a function of oxygen partial pressure ( $\text{PO}_2$ ) and temperature showed a significant weakening of the  $\text{PO}_2$  dependence compared to bulk PCO, which scaled with the density of interfaces. We confirmed that this change was due to variations in nonstoichiometry, by optical transmission measurements, and show that the lower oxygen content is consistent with a decrease in the effective oxygen reduction enthalpy of PCO. These results exemplify the dramatic differences in properties between films and their bulk counterparts, achievable by interface engineering, and provide generalized insight into tailoring the properties of mixed ionic electronic conductors at the nanoscale.

### BILGE YILDIZ

Professor of Nuclear Science and Engineering, <http://web.mit.edu/nse/people/faculty/yildiz.html>

Professor of Materials Science and Engineering, <https://dmse.mit.edu/people/bilge-yildiz>

Lab: <http://web.mit.edu/yildizgroup/LEI/index.html>

Publications: <http://web.mit.edu/yildizgroup/LEI/publications.html>

Bilge Yildiz is a professor in the Nuclear Science and Engineering and the Materials Science and Engineering Departments at MIT MIT, where she leads the Laboratory for Electrochemical Interfaces. She received her Ph.D. degree at MIT in 2003 and her B.Sc. degree from Hacettepe University in Turkey in 1999. After working at Argonne National Laboratory as research staff, she returned to MIT as an assistant professor in 2007. Her leadership responsibilities at MIT include

the Low Carbon Energy Center on Materials in Energy and Extreme Environments, and one of the Integrated Research Groups of MIT's NSF sponsored Materials Research Science and Engineering Center.

Her research focuses on laying the scientific groundwork and proof-of-principle material systems for the next generation of high-efficiency devices for energy conversion and information processing, based on solid state mixed ionic-electronic conducting (MIEC) material, by combining in situ surface sensitive experiments with first-principles calculations and novel atomistic simulations. Her work has made significant contributions to advancing the molecular-level understanding of oxygen reduction and oxidation kinetics on MIEC solid surfaces, and of ion and electron transport, under electro-chemo-mechanical conditions. The scientific insights derived from her research guide the design of novel surface chemistries for efficient and durable solid oxide fuel cells, thermo-/electro-chemical splitting of H<sub>2</sub>O and CO<sub>2</sub>, corrosion resistant films, high energy density solid state batteries, and red-ox based memristive information storage.

#### Laboratory for Electrochemical Interfaces

<http://web.mit.edu/yildizgroup/LEI/index.html>

Research: <http://web.mit.edu/yildizgroup/LEI/research.html>

Publications: <http://web.mit.edu/yildizgroup/LEI/publications.html>

The Laboratory for Electrochemical Interfaces focuses on laying the scientific groundwork and proof-of-principle material systems for the next generation of high-efficiency devices for energy conversion and information processing, based on solid state mixed ionic-electronic conducting (MIEC) materials. We have thus far made significant contributions to advancing the molecular-level understanding of oxygen reduction and oxidation kinetics on MIEC solid surfaces, and of ion and electron transport, under electro-chemo-mechanical conditions. The scientific insights derived from our research guide the design of novel surface chemistries for efficient and durable solid oxide fuel cells, thermo-/electro-chemical splitting of H<sub>2</sub>O and CO<sub>2</sub>, for corrosion resistant films in a wide range of extreme environments as in nuclear energy and oil exploration, for high energy density solid state batteries, and for red-ox based memristive information storage.

#### *Solid oxide fuel and electrolysis cells*

<http://web.mit.edu/yildizgroup/LEI/research.html>

Solid oxide fuel and electrolysis cells (SOFC, SOEC) offer promising routes for clean and sustainable energy and fuels conversion routes. We investigate how cathode and anode materials (perovskite oxides) evolve at their surface, in response to electrochemical, temperature and gas stimuli in solid oxide fuel and electrolysis cells. This is important to resolve the degradation mechanisms, and design better surface chemistries with enhanced durability and efficiency. We use state-of-the-art synchrotron X-ray spectroscopy techniques, and first-principles and thermodynamic calculations, to resolve and predict the surface chemistry of perovskite oxides under realistic conditions.

#### *Solid state Li-ion batteries*

<http://web.mit.edu/yildizgroup/LEI/research.html>

Solid state batteries with solid electrolytes offer superior energy density and safety compared to the present Li-ion batteries with liquid electrolytes. To realize their full potential in applications, we resolve the interfacial degradation in all-solid-state batteries and come up with physically-based

strategies to improve their durability and charging rates. Our approach uses model systems comprising thin film cathodes on dense solid electrolyte. The design allows us to characterize cation-interdiffusion and detrimental phase formation at the buried interface, and correlate those phenomena with interfacial resistance.

### **Polar or not polar? the interplay between reconstruction, Sr enrichment, and reduction at the La<sub>0.75</sub>Sr<sub>0.25</sub>MnO<sub>3</sub> (001) surface**

Hess, F., Yildiz, B.

Physical Review Materials, Volume 4, Issue 1, 31 January 2020, Article number 015801, <https://doi.org/10.1103/PhysRevMaterials.4.015801>

Perovskite oxides used in heterogeneous catalysis and electrocatalysis are tuned by substitutional doping. Sr-doped LaMnO<sub>3</sub> is a popular choice of electrode material for electrochemical energy conversion. At elevated temperatures, relevant to solid oxide fuel or electrolysis cells, Sr enriches at the surface, which leads to fast degradation of the oxygen exchange activity at the surface. In this work, we investigate the effect of oxygen partial pressure  $p(\text{O}_2)$  and temperature on Sr segregation at the La<sub>0.75</sub>Sr<sub>0.25</sub>MnO<sub>3</sub>(001) (LSM25) surface by ab initio thermodynamics calculations, taking into account different terminations and point defects SrLa, VO $\cdot$ , VMn, VLa, Oad, as well as associated defects of the type [VO $\cdot$ -Vcation]. This model of the LSM25(001) surface addresses the connection between point defects and surface stability and makes quantitative predictions about the surface termination and Sr enrichment. Our results indicate that the MnO<sub>2</sub> termination is stable under oxidizing conditions, while a partially covering SrO termination on MnO<sub>2</sub> is stable for reaction conditions between 1000 and 1400 K and effective oxygen partial pressures between 10<sup>-11</sup>bar and 0.1 bar relevant to solid oxide fuel cell (SOFC) cathodes. Under more reducing conditions, we find that Sr is enriched at the surface regardless of surface termination. This trend is a direct consequence of the increased formation of positively charged oxygen vacancies at the surface, and this conclusion holds regardless of which surface termination is assumed. The partial SrO termination is exceptionally stable under SOFC cathode conditions because it minimizes the surface dipole density, while all the defect-free terminations of LSM25(001) are unstable due to surface polarity. This newly proposed termination leaves both Sr, as well as Mn and O sites of the MnO<sub>2</sub> layer exposed at the surface and available for interaction with the gas phase. We propose that the LSM25(001) surface may consist of coexisting (La,Sr)O and MnO<sub>2</sub> domains under SOFC cathode conditions, and we propose to include such a micropatterned surface in the future discussion of the active site in the oxygen reduction reaction.

## **ENERGY HARVESTING**

### **ANANTHA P CHANDRAKASAN**

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Anantha P. Chandrakasan is the dean of engineering at MIT and the Vannevar Bush Professor of Electrical Engineering and Computer Science (EECS). At MIT since 1994, he has previously served as the department head of EECS (2011–2017) and as director of the MIT Microsystems Technology Laboratories (2006–2011).

His research interests include ultra-low-power circuit and system design, energy harvesting, energy efficient RF circuits, and security hardware. He is a co-author of *Low Power Digital CMOS Design* (Kluwer Academic Publishers, 1995), *Digital Integrated Circuits* (Pearson Prentice-Hall, 2003, 2nd edition), and *Sub-threshold Design for Ultra-Low Power Systems* (Springer 2006).

#### **A Silicon MEMS em vibration energy harvester**

Yang, Y., Radhakrishna, U., Ward, D., Chandrakasan, A.P., Lang, J.H.  
Journal of Physics: Conference Series, Volume 1407, Issue 1, 4 December 2019, Article number 012022, <https://doi.org/10.1088/1742-6596/1407/1/012022>

This paper presents an optimized silicon-MEMS electromagnetic vibration energy harvester suitable for applications such as machine health monitoring. The harvester comprises a DRIE-etched silicon suspension, and pick-and-place N42 NdBF<sub>e</sub> magnets and copper coils, housed in a 3D-printed package. The harvester is designed to operate near 50 Hz with 0.5-1 g vibrations using a long-stroke suspension. Multi-domain harvester optimization results in an open-circuit voltage of 1.7 V, a matched-load power output of 2.2 mW, and a matched-load power-output density of 1.23 mW/cm<sup>3</sup> at 1.1 g with a resonance frequency of 76.3 Hz.

#### **A MEMS Magnetic-Based Vibration Energy Harvester**

Shin, A., Radhakrishna, U., Yang, Y., Zhang, Q., Gu, L., Riehl, P., Chandrakasan, A.P., Lang, J.H.  
Journal of Physics: Conference Series, Volume 1052, Issue 1, 26 July 2018, Article number 012082, <https://doi.org/10.1088/1742-6596/1052/1/012082>

This paper presents the design, analysis and integrated fabrication of a MEMS magnetic-based vibration energy harvester targeted for machine health monitoring. The design consists of Si-springs, permanent magnets as mass, and coils wound on the top and bottom side of the harvester package for mechanical-to-electrical energy conversion based on the Lorentz-force principle. The harvester is optimized to have its translational resonant-mode match external vibrations while separating higher-order modes. Mechanical and magnetic optimization of the harvester is carried out together with optimization of its power and control electronics in order to provide maximum output power from a vibration input that can vary its frequency by  $\pm 5\%$ . The harvester achieves an open-circuit voltage amplitude of 145 mV and delivers 165  $\mu$ W to a matched load at the resonance frequency of 45.7 Hz.

#### **SANG-GOOK KIM**

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Sang-Gook Kim is a professor in the Department of Mechanical Engineering. He received his B.S. degree from Seoul National University (1978), M.S. from KAIST (1980), and Ph.D. from MIT (1985). He held positions at Axiomatics Co., Cambridge, MA (1986) and Korea Institute of Science and Technology (1986-1991). Then he became a corporate executive director at Daewoo Corporation, Korea, and directed the Central Research Institute of Daewoo Electronics Co. until 2000 when he joined MIT. He is currently the Micro/Nano Area Head of the Department of Mechanical Engineering at MIT. Prof. Kim's research has been in the field of product realization throughout his career at both the industry and academia. His recent research includes piezoelectric MEMS energy harvesting, micro ultrasonic transducers and nano-engineered energy conversion

for carbon neutrality and solar water splitting systems. He is a fellow of CIRP (International Academy for Production Engineering), fellow of ASME, and overseas member of Korean National Academy of Engineering.

#### **Park Center for Complex Systems: Micro Nano Systems Laboratory**

<https://micronanosystems.mit.edu/>

Research: <https://micronanosystems.mit.edu/current-research/mems-energy-harvesting>

Publications: <https://micronanosystems.mit.edu/publications-0>

The design and manufacturing across scales with newly developed materials such as piezoelectric thin films, photonic crystals or carbon nanotubes (CNTs) has become increasingly complex. Our research has aimed to establish a fundamental product-design-development framework to mitigate the complexity by developing adequate design and manufacturing processes for new materials and by creating new functionalities at the systems level.

#### **Buckled MEMS beams for energy harvesting from low frequency vibrations**

Xu, R., Akay, H., Kim, S.-G.

Research, Volume 2019, 2019, Article number 1087946, <https://doi.org/10.34133/2019/1087946>

Vibration energy harvesters based on the resonance of the beam structure work effectively only when the operating frequency window of the beam resonance matches with the available vibration source. None of the resonating MEMS structures can operate with low frequency, low amplitude, and unpredictable ambient vibrations since the resonant frequency goes up very high as the structure gets smaller. Bistable buckled beam energy harvester is therefore developed for lowering the operating frequency window below 100Hz for the first time at the MEMS scale. This design does not rely on the resonance of the MEMS structure but operates with the large snapping motion of the beam at very low frequencies when input energy overcomes an energy threshold. A fully functional piezoelectric MEMS energy harvester is designed, monolithically fabricated, and tested. An electromechanical lumped parameter model is developed to analyze the nonlinear dynamics and to guide the design of the nonlinear oscillator based energy harvester. Multilayer beam structure with residual stress induced buckling is achieved through the progressive residual stress control of the deposition processes along the fabrication steps. Surface profile of the released device shows bistable buckling of 200 $\mu$ m which matches well with the amount of buckling designed. Dynamic testing demonstrates the energy harvester operates with 50% bandwidth under 70Hz at 0.5g input, operating conditions that have not been demonstrated by MEMS vibration energy harvesters before.

#### **JEFFREY H LANG**

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Associate Director of Microsystems Technology Laboratories (MTL), <https://www.mtl.mit.edu/>

Lab: <https://www.rle.mit.edu/lees/>

Upon completion of three Course 6 degrees at MIT (SB '75, SM '77 and PhD '80 with a doctoral thesis on electrostatically-shaped reflecting antennas co-supervised by former professors David Staelin and James Melcher), Jeffrey Lang joined the MIT faculty in 1980, becoming full professor in 1992. He is a member of the Research Laboratory of Electronics and the Microsystems Technology Laboratories.

### A Robust Electromagnetic MEMS Vibration Energy Harvester

[http://ilp.mit.edu/expertise\\_project\\_detail.jsp?project\\_id=32834](http://ilp.mit.edu/expertise_project_detail.jsp?project_id=32834)

Modern production plants lack an effective way to autonomously monitor equipment health. It is uneconomical to engage personnel solely to monitor machines that function normally most of the time and impractical to wire plant-wide arrays of sensors for power and communication. As an alternative, vibration energy harvesters could power autonomous sensor networks that communicate wirelessly. Further, vibration-based machine health monitoring could be an effective method of assessing real-time machine performance. Such monitoring could become preventive by prompting maintenance prior to unrecoverable plant failures. To this end, this project seeks to advance the state of vibration energy harvesting.

Previous work yielded silicon-micro-electromechanical systems (MEMS) electromagnetic vibration energy harvesters suitable for powering machine health sensors. To further improve robustness and increase electrical power output, a new harvester is designed, fabricated, and demonstrated using the MP35N alloy. Its design and optimization follow that developed for earlier silicon harvesters. The new material has a mechanical modulus close to that of the silicon while not being brittle. Thus, with similar material thickness, we maintain the harvester footprint while improving robustness. The MP35N alloy allows for less stressful full stroke operation, enabling improved output power while being much more tolerant of external shock.

Fabrication of the new harvester combines electric discharge machining and water-jet cutting for prototype production. The Lorentz-force harvester, with its folded-spring-suspended magnets, is packaged between two coupling coils using 3D-printed plastic package parts. The new harvester can survive large transient accelerations, common in an industrial setting; such accelerations are unsustainable by a comparable silicon harvester. This added durability brings the harvester much closer to practical application. The improved robustness enables the installation of back-irons, further improving the output power. The power output and power density (1.47 mW/cm<sup>3</sup>) are comparable to that of the previous record-setting silicon device.

### Contactless Current and Voltage Detection Using Signal Processing and Machine Learning

[http://ilp.mit.edu/expertise\\_project\\_detail.jsp?project\\_id=32813](http://ilp.mit.edu/expertise_project_detail.jsp?project_id=32813)

Measuring current and voltage in electrical systems is a critical task in industrial environments and can be used to monitor power quality and machine and process performance. Easily retrofitted contactless measurements are preferred, but they can require difficult installations and bulky hardware. In contrast, we are developing a contactless clip-on sensor that will estimate voltage and current in three-phase power cables. Our goal is to create a measurement system that uses less hardware than present state-of-the-art solutions while maintaining a high level of accuracy.

Current is estimated using an array of magnetic field sensors embedded in a yoke that fits around the cables. The measurements are filtered to remove magnetic fields from external sources, such as adjacent cables or eddy currents. This filtering employs a Best Linear Unbiased Estimate of cable currents that is based on a covariance matrix calculated from a probabilistic model of external magnetic fields detected by the sensor array. Additionally, we are using collected data to train neural networks and explore whether machine learning can generate a better estimate. To estimate voltage, we employ guarded electrodes in the yoke that fit snugly against the cables. We then sense



cable voltage capacitively coupled to the electrodes and use a physical model of the electrode system to estimate the voltage differences between cables.

At present, the system can estimate voltage with an error of less than 1% and current with an error of less than 2%, even in the presence of electric and magnetic field interference. This performance is comparable to currently used contactless detection systems but uses significantly less hardware and should thus be less costly to manufacture. Furthermore, since our estimates produce full current and voltage waveforms, we can calculate quantities such as instantaneous power and power quality.

### **Simulation and Modelling of a Spatially-Efficient 3D Wireless Power Transfer System for Multi-User Charging**

Wang, H.-W., Wang, N.X., Lang, J.H.

Journal of Physics: Conference Series, Volume 1407, Issue 1, 4 December 2019, Article number 012104, <https://doi.org/10.1088/1742-6596/1407/1/012104>

This paper presents the design, modelling and simulation of a wireless power transfer system with improved 3D spatial efficiency. It is shown that a rotational field driven by balanced magnetic coils carrying phase-shifted currents can achieve almost uniform efficiency in 3-D space. Both 2-coil and 3-coil transmitting systems are designed and studied. Effective mutual inductance is proposed to visualize the magnetic fields from a multiple transmitter system, and efficiency distributions are simulated. Different excitation modes including phase-shifted and non-phase-shifted currents are analysed and compared. The results provide an approach to the design and excitation of the 3D multiple-transmitting-coil system.

### **Co-optimization of a piezoelectric energy harvesting system for broadband operation**

Zhao, S., Radhakrishna, U., Hanly, S., Ma, J., Lang, J.H., Buss, D.

Journal of Physics: Conference Series, Volume 1407, Issue 1, 4 December 2019, Article number 012010, <https://doi.org/10.1088/1742-6596/1407/1/012010>

The goal of this research is to increase the bandwidth (BW) over which substantial energy can be harvested using a piezoelectric energy harvester (PEH). The key innovation is the use of bias-flip (BF) electronics at the output of a PEH having a large electromechanical coupling coefficient  $k_{e2}$ . For a PEH with large  $k_{e2}$ , the open-circuit resonance frequency  $f_{oc}$  is substantially larger than the short-circuit resonance frequency  $f_{sc}$ . Over the intervening range, the reactive part of the conjugate matched load impedance is small, and can be approximated using BF electronics in which the BF voltage is sufficiently small and the BF losses are small. This results in a large BW over which substantial energy can be harvested. Experimental results using a commercially available PEH are presented to demonstrate this concept. Design guidelines are provided for achieving PEHs having increased  $k_{e2}$ .

## **THERMAL ENERGY HARVESTING AND STORAGE**

### **GANG CHEN**

Carl Richard Soderberg Professor of Power Engineering,

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Director, Solid-State Solar-Thermal Energy Conversion Center (S3TEC Center),

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Lab: <http://web.mit.edu/nanoengineering/>

Publications: <http://web.mit.edu/nanoengineering/publications/>

Gang Chen is the Carl Richard Soderberg Professor of Power Engineering and the director of the MIT Pappalardo Micro/Nano Engineering Laboratory. His research interests center on nanoscale thermal transport and energy conversion phenomena and their applications in energy storage and conversion, thermal management, and water treatment and desalination. He has made important contributions to the understanding of heat transfer in nanostructures and exploited them to develop energy conversion, storage, and water technologies. Chen is fellows of the US National Academy of Engineering and the American Academy of Arts and Sciences.

### NanoEngineering Group

<http://web.mit.edu/nanoengineering/>

Publications: <http://web.mit.edu/nanoengineering/publications/>

The Nanoengineering Group is part of the Mechanical Engineering Department at MIT. Our research is focused on nanoscale energy transport, conversion, and storage. There are fundamental differences between transport processes at the nanoscale and the macroscale due to quantum and classical size effects; for example, both classical diffusion laws and Planck's law for blackbody radiation break down in nanostructures. We explore these effects for improving energy conversion efficiency and storage density, and thermal energy transport. Examples include development of nanostructured thermoelectric materials for direct conversion between thermal and electric energy, use of nanotechnology to advance solar thermal and solar photovoltaic devices, fundamental investigation of phonon transport. Our work is interdisciplinary and combines mechanical engineering, electrical engineering, physics, and materials science.

### Thermal Storage

<http://web.mit.edu/nanoengineering/research/storage.shtml>

Our recent ARPA-E award is on heat storage materials. The second law of thermodynamics allows us to collect heat for free, or almost. Heat can be used to generate electricity using either steam engines or thermoelectric devices. Storing it is important and very useful for power plants where a constant supply of electricity can be sustained even during the peak hours. Furthermore, solar energy is an infinite and free source of light (for photovoltaics) and heat (thermophotovoltaics and thermoelectrics) which can be used and stored for our energy needs. A large amount of heat can be stored in the form of latent heat. Our goal is therefore to design novel materials with a large latent heat, able to store up to 1 MJ/kg or more. Furthermore to be able to quickly extract this stored heat, the material needs to have a large thermal conductivity as well. Other considerations are safety, stability, abundance and low fabrication cost. For these reasons, we are considering metallic alloys instead of traditionally used salts, as the phase change material.

### Thermal energy storage radiatively coupled to a supercritical Rankine cycle for electric grid support

Meroueh, L., Chen, G.

Renewable Energy, Volume 145, January 2020, Pages 604-621,

<https://doi.org/10.1016/j.renene.2019.06.036>

Frequent variation in electricity demand strains power plants, thereby increasing CO<sub>2</sub> emissions. Grid integration of intermittent renewables exacerbates this problem. Energy storage can mitigate demand fluctuations. Yet, common grid-scale storage technologies are geographically limited or

prohibitively expensive. Storing electricity as heat, although thermodynamically counter-intuitive, can be cheaper and nonrestrictive. To do so, high temperatures are desired according to the second law of thermodynamics. Here, we analyze electricity storage through the phase change of solid to molten silicon and discharge the stored heat radiatively to a working fluid, allowing system flexibility. We use heat transfer analyses to determine whether radiative discharge of a thermal energy storage system to supercritical water is a viable method. Our analysis shows a system cost of  $\$45 \pm 10$  per kWh and 12-hr round-trip efficiency of  $\sim 38\%$ – $43\%$ . Rather than constructing additional gas-fired peaker plants to address peak loads, the proposed system can be implemented and use existing infrastructure from retired coal power plants. This approach is compatible with current power plants as well as renewable energy, providing a segue from fossil fuels to renewable energy dependent power plants.

#### **Video: Advanced Materials and Systems at the Energy and Water Nexus**

ILP Video, January 7, 2020, <http://ilp.mit.edu/videodetail.jsp?confid=null&ilp-videos=Y&id=3020#>

This talk will present some of our recent work on advanced materials and systems at the energy and water nexus, including thermoelectric and thermogalvanic materials and systems for direct conversion of heat into electricity, high thermal conductivity semiconductors and polymers, optically opaque and infrared transparent fabrics, clean water technologies, and grid level energy storage systems. Thermoelectric materials have seen significant improvements over last two decades, but innovations are needed to develop their applications since their heat-to-electricity conversion efficiencies are still limited. In addition, electrochemical systems such as batteries can also be used to convert heat into electricity, which could be especially attractive for low temperature waste heat recovery. Although thermoelectric energy conversion calls for low thermal conductivity materials, many other applications require high thermal conductivity materials. We are developing materials with high thermal conductivity ranging from semiconductors to polymers, including BAs which has second highest thermal conductivity behind diamond. As another example, we show that polymers can be made as thermally conductive as metals by aligning molecular orientations despite that they start with low thermal conductivity. After these examples, we turn attention to energy and water technologies based on engineering thermal radiation. With properly chosen polymer fiber diameters, we design fabrics so that they are opaque to visible light and yet allow thermal radiation from human body to escape to environment for passively cooling of human body. We also demonstrate the ability of boiling water and even creating super-heated steam under unconcentrated sunlight. The talk will conclude with a discussion of a novel approach to grid level energy storage.

#### **JEFFREY C GROSSMAN**

Morton (1924) and Claire Goulder and Family Professor in Environmental Systems,  
<https://dmse.mit.edu/people/jeffrey-c-grossman>, <https://www.rle.mit.edu/people/directory/jeffrey-grossman/>  
Department Head / Materials Science and Engineering  
Margaret MacVicar Faculty Fellow  
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Publications: <https://www.rle.mit.edu/gg/publications/>

Jeffrey C. Grossman is the Department Head of Materials Science and Engineering at the Massachusetts Institute of Technology and the Morton and Claire Goulder and Family Professor in Environmental Systems. He received his PhD in theoretical physics from the University of Illinois and performed postdoctoral work at the University of California at Berkeley. He was a Lawrence

Fellow at the Lawrence Livermore National Laboratory and returned to Berkeley as director of a Nanoscience Center and head of the Computational Nanoscience research group, with a focus on energy applications. In fall 2009, he joined MIT, where he has developed a research program known for its contributions to energy conversion, energy storage, membranes, and clean-water technologies. In recognition of his contributions to engineering education, Grossman was named an MIT MacVicar Faculty Fellow and received the Bose Award for Excellence in Teaching, in addition to being named a fellow of the American Physical Society. He has published more than 200 scientific papers, holds 17 current or pending U.S. patents, and recently co-founded a company to commercialize graphene-oxide membranes.

### The Grossman Group

<https://www.rle.mit.edu/gg/>

Research: <https://www.rle.mit.edu/gg/research/>

Publications: <https://www.rle.mit.edu/gg/publications/>

Our research spans nanomaterials, electronic and optoelectronic devices, water desalination, and renewable energy, where our team members have broad expertise and are able to work laterally across these topics. We foster a strong culture of collaboration where a constant feedback loop between theory and experiment facilitates novel discoveries and efficiency/performance breakthroughs. We engage with several government agencies and industrial partners to maximize the impact of our work and harvest the benefits of our discoveries for society. We maintain a strong relationship with our alumni and foster long term relationships between our members as they go on to further pursue academic or industry positions.

### Thermal Harvesting and Storage

<https://www.rle.mit.edu/gg/research/thermal-transport/>

Understanding thermal transport at the nano and mesoscale is crucial to designing efficient thermoelectric devices. Our group focuses on designing novel thermoelectric architectures and understanding their thermal and electronic behavior at various scales using a combination of atomistic and continuum scale calculations. Currently, we are designing functionalized forms of graphene and nanoporous silicon that exhibit low thermal conductivity, and at the same time show high electronic conductivity – a useful characteristic for applications in thermoelectric devices.

### Solvent- And Anion-Dependent Li<sup>+</sup>-O<sub>2</sub> - Coupling Strength and Implications on the Thermodynamics and Kinetics of Li-O<sub>2</sub> Batteries

Leverick, G., Tatara, R., Feng, S., Crabb, E., France-Lanord, A., Tułodziecki, M., Lopez, J., Stephens, R.M., Grossman, J.C., Shao-Horn, Y.

Journal of Physical Chemistry C, 2020, <https://doi.org/10.1021/acs.jpcc.9b09968>

Lithium-oxygen (Li-O<sub>2</sub>) batteries offer considerably higher gravimetric energy density than commercial Li-ion batteries (up to three times) but suffer from poor power, cycle life, and round-trip efficiency. Tuning the thermodynamics and pathway of the oxygen reduction reaction (ORR) in aprotic electrolytes can be used to enhance the Li-O<sub>2</sub> battery rate and discharge capacity. In this work, we present a systematic study on the role of the solvent and anion on the thermodynamics and kinetics of Li<sup>+</sup>-ORR, from which we propose a unified descriptor for its pathway and kinetics. First, by thoroughly characterizing the solvation environment of Li<sup>+</sup> ions using Raman spectroscopy, <sup>7</sup>Li NMR, ionic conductivity, and viscosity measurements, we observe increasing Li<sup>+</sup>-anion interactions with increasing anion DN in low DN solvents such as 1,2-dimethoxyethane

and acetonitrile but minimal Li<sup>+</sup>-anion interactions in the higher DN dimethyl sulfoxide. Next, by determining the electrolyte-dependent Li<sup>+</sup>/Li, TBA<sup>+</sup>,O<sub>2</sub>/TBA<sup>+</sup>-O<sub>2</sub><sup>-</sup>, and Li<sup>+</sup>,O<sub>2</sub>/Li<sup>+</sup>-O<sub>2</sub><sup>-</sup> redox potentials versus the solvent-invariant Me<sub>10</sub>Fc reference potential, we show that stronger combined solvation of Li<sup>+</sup> and O<sub>2</sub><sup>-</sup> ions leads to weaker Li<sup>+</sup>-O<sub>2</sub><sup>-</sup> coupling. Finally, using rotating ring disk electrode measurements, we show that weaker Li<sup>+</sup>-O<sub>2</sub><sup>-</sup> coupling in electrolytes with strong combined solvation leads to an increased generation of soluble Li<sup>+</sup>-O<sub>2</sub><sup>-</sup>-type species and faster overall kinetics during Li<sup>+</sup>-ORR.

### Laser-sculptured ultrathin transition metal carbide layers for energy storage and energy harvesting applications

Zang, X., Jian, C., Zhu, T., Fan, Z., Wang, W., Wei, M., Li, B., Follmar Diaz, M., Ashby, P., Lu, Z., Chu, Y., Wang, Z., Ding, X., Xie, Y., Chen, J., Hohman, J.N., Sanghadasa, M., Grossman, J.C., Lin, L.

Nature Communications, Volume 10, Issue 1, 1 December 2019, Article number 3112,  
<https://doi.org/10.1038/s41467-019-10999-z>

Ultrathin transition metal carbides with high capacity, high surface area, and high conductivity are a promising family of materials for applications from energy storage to catalysis. However, large-scale, cost-effective, and precursor-free methods to prepare ultrathin carbides are lacking. Here, we demonstrate a direct pattern method to manufacture ultrathin carbides (MoC<sub>x</sub>, WC<sub>x</sub>, and CoC<sub>x</sub>) on versatile substrates using a CO<sub>2</sub> laser. The laser-sculptured polycrystalline carbides (macroporous, ~10–20 nm wall thickness, ~10 nm crystallinity) show high energy storage capability, hierarchical porous structure, and higher thermal resilience than MXenes and other laser-ablated carbon materials. A flexible supercapacitor made of MoC<sub>x</sub> demonstrates a wide temperature range (–50 to 300 °C). Furthermore, the sculptured microstructures endow the carbide network with enhanced visible light absorption, providing high solar energy harvesting efficiency (~72 %) for steam generation. The laser-based, scalable, resilient, and low-cost manufacturing process presents an approach for construction of carbides and their subsequent applications.

### Optically-regulated thermal energy storage in diverse organic phase-change materials

Han, G.G.D., Deru, J.H., Cho, E.N., Grossman, J.C.

Chemical Communications, Volume 54, Issue 76, 2018, Pages 10722-10725,  
<https://doi.org/10.1039/C8CC05919E>

Thermal energy storage and release in aliphatic phase-change materials are actively controlled by adding azobenzene-based photo-switches. UV activation of the additives induces supercooling of the composites, allowing for longer thermal storage at lower temperatures. The mechanism of this process is studied by comparing phase change behavior across diverse materials.

### *Saving heat until you need it*

**A new concept for thermal energy storage involves a material that absorbs heat as it melts and releases it as it resolidifies — but only when triggered by light.**

Nancy W. Stauffer, MIT Energy Initiative, December 19, 2018, <http://news.mit.edu/2018/thermal-energy-storage-material-saves-heat-1219>

More than half of all the energy used to power mechanical, chemical, and other processes is expelled into the environment as heat. Power plants, car engines, and industrial processes, for example, produce vast amounts of heat but use a relatively small fraction of it to actually do work. And while

sunlight delivers abundant radiant energy, today's photovoltaic devices convert only a fraction of it into electricity. The rest is either reflected or absorbed and converted into heat that goes unused.

The challenge is finding a way to store all that thermal energy until we want to use it. Jeffrey Grossman, the Morton and Claire Goulder and Family Professor in Environmental Systems and professor of materials science and engineering, has been working on that problem for more than a decade.

A good way to store thermal energy is by using a phase-change material (PCM) such as wax. Heat up a solid piece of wax, and it'll gradually get warmer — until it begins to melt. As it transitions from the solid to the liquid phase, it will continue to absorb heat, but its temperature will remain essentially constant. Once it's fully melted, its temperature will again start to rise as more heat is added. Then comes the benefit. As the liquid wax cools, it will solidify, and as it does, it will release all that stored phase-change heat — also called latent heat.

PCMs are now used in applications such as solar concentrators, building heating systems, and solar cookers for remote regions. But while PCMs can give off abundant heat, there's no way to control exactly when they do it. The timing depends on the temperature of the air around them....

### **ASEGUN S HENRY**

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Dr. Asegun Henry started as an Associate Professor in the Department of Mechanical Engineering at MIT in 2018, where he directs the Atomistic Simulation & Energy (ASE) Research Group. Prior to MIT, he was an Assistant professor in the Woodruff school of Mechanical Engineering at Georgia Tech from 2012 to 2018. He holds a B.S. degree in Mechanical Engineering from Florida A & M University as well as a M.S. and Ph.D. in Mechanical Engineering from MIT. Professor Henry's primary research is in heat transfer, with an emphasis on understanding the science of energy transport, storage and conversion at the atomic level, along with the development of new industrial scale energy technologies to mitigate climate change. After finishing his Ph.D. he worked as a postdoc in the Materials Theory group at Oak Ridge National Laboratory (ORNL) and then as postdoc in the Materials Science Department at Northwestern University. After Northwestern, he worked as a fellow in the Advanced Research Projects Agency – Energy (ARPA-E), where he focused on identifying new program areas, such as higher efficiency and lower cost energy capture, conversion and storage.

### **Atomistic Simulation & Energy Research Group**

<https://ase.mit.edu/>  
Research: <https://ase.mit.edu/latest-research-initiatives/>  
Publications: <https://ase.mit.edu/publications>

We are an academic research group within the Department of Mechanical Engineering at MIT. We study heat transfer at the atomic level and also work on developing technologies that can help to mitigate climate change. This website provides an overview of our work and is also intended to serve as an educational resource for those interested in learning about energy and the thermal sciences.

### *Thermal Energy Grid Storage (TEGS) Concept*

<https://ase.mit.edu/projects/thermal-energy-grid-storage-tegs/>

Thermal Energy Grid Storage (TEGS) involves storing excess electricity as heat until it is needed back on the grid. TEGS serves a purpose similar to electrochemical batteries, but at a lower cost that can enable higher penetration of renewable energy to mitigate climate change. The projected cost is also similar to pumped hydroelectric storage, which is the cheapest storage technology, but without geographic constraints.

### **Thermal energy grid storage using multi-junction photovoltaics**

Amy, C., Seyf, H.R., Steiner, M.A., Friedman, D.J., Henry, A.

Energy and Environmental Science, Volume 12, Issue 1, January 2019, Pages 334-343,

<https://doi.org/10.1039/c8ee02341g>

As the cost of renewable energy falls below fossil fuels, the key barrier to widespread sustainable electricity has become availability on demand. Energy storage can enable renewables to provide this availability, but there is no clear technology that can meet the low cost needed. Thus, we introduce a concept termed thermal energy grid storage, which in this embodiment uses multi-junction photovoltaics as a heat engine. We report promising initial experimental results that suggest it is feasible and could meet the low cost required to reach full penetration of renewables. The approach exploits an important tradeoff between the realization of an extremely low cost per unit energy stored, by storing heat instead of electricity directly, and paying the penalty of a lower round trip efficiency. To understand why this tradeoff is advantageous, we first introduce a general framework for evaluating storage technologies that treats round trip efficiency, as well as cost per unit energy and power, as variables.

### *“Sun in a box” would store renewable energy for the grid*

**Design for system that provides solar- or wind-generated power on demand should be cheaper than other leading options.**

Jennifer Chu, MIT News Office, December 5, 2018, <http://news.mit.edu/2018/liquid-silicon-store-renewable-energy-1206>

MIT engineers have come up with a conceptual design for a system to store renewable energy, such as solar and wind power, and deliver that energy back into an electric grid on demand. The system may be designed to power a small city not just when the sun is up or the wind is high, but around the clock.

The new design stores heat generated by excess electricity from solar or wind power in large tanks of white-hot molten silicon, and then converts the light from the glowing metal back into electricity when it's needed. The researchers estimate that such a system would be vastly more affordable than lithium-ion batteries, which have been proposed as a viable, though expensive, method to store renewable energy. They also estimate that the system would cost about half as much as pumped hydroelectric storage — the cheapest form of grid-scale energy storage to date.

“Even if we wanted to run the grid on renewables right now we couldn't, because you'd need fossil-fueled turbines to make up for the fact that the renewable supply cannot be dispatched on demand,” says Asegun Henry, the Robert N. Noyce Career Development Associate Professor in the Department of Mechanical Engineering. “We're developing a new technology that, if successful,

would solve this most important and critical problem in energy and climate change, namely, the storage problem.”

Henry and his colleagues have published their design today in the journal Energy and Environmental Science....

### ALEXIE KOLPAK

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Lab: <http://kolpak.mit.edu/index.html>

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Alexie Kolpak joined the MIT faculty in July 2012 as an Assistant Professor. She graduated from the University of Pennsylvania, where she earned a B.A. in Biochemistry and an M.S. in Chemistry in 2002, then a Ph.D. in Physical Chemistry in 2007. Following postdoctoral research in the Department of Applied Physics at Yale and the Department of Materials Science and Engineering at MIT, she joined the MIT faculty in Mechanical Engineering in the summer of 2012. Professor Kolpak's research employs atomic and electronic structure modeling techniques such as density functional theory (DFT) to elucidate fundamental chemical and physical principles of surface and interfacial phenomena. Her research is highly interdisciplinary in nature and has included strong collaborations with experimental colleagues aimed at the engineering of novel materials systems for a variety of important applications in renewable energy and electronics technologies.

### Kolpak Group

<http://kolpak.mit.edu/index.html>

Publications: <http://kolpak.mit.edu/Publications.html>

Our research is focused on using first-principles computations and atomistic simulations to understand and design multifunctional materials and heterostructures, with a focus on sustainable energy applications such as photovoltaics, photo- and electrochemical water splitting, CO<sub>2</sub> capture and conversion, thermoelectrics, and ultra-low power electronics. Trends in system complexity and component scale in each of these areas have made understanding the role of interfaces — the boundaries between different materials or phases — increasingly important for designing and optimizing performance of practical devices. The underlying objectives of our work are thus to develop fundamental synthesis-structure-function-performance relationships for solid-solid and solid-solvent interfaces. Additionally, we are interested in investigating the possibilities of novel physics and chemistry at interfaces, which can lead to creative new tools for tailoring materials behavior from the nanoscale to the macroscale.

### Parameter-free model to estimate thermal conductivity in nanostructured materials

Romano, G., Kolpak, A.M., Carrete, J., Broido, D.

Physical Review B, Volume 100, Issue 4, 29 July 2019, Article number 045310,

<https://doi.org/10.1103/PhysRevB.100.045310>

Achieving low thermal conductivity and good electrical properties is a crucial condition for thermal energy harvesting materials. Nanostructuring offers a very powerful tool to address both requirements: in nanostructured materials, boundaries preferentially scatter phonons compared to electrons. The computational screening for low-thermal-conductivity nanostructures is typically limited to materials with simple crystal structures, such as silicon, because of the complexity arising



from modeling branch- and wave-vector-dependent nanoscale heat transport. The phonon mean-free-path (MFP) dependent Boltzmann transport equation (MFP-BTE) approach is a model that overcomes this limitation. To illustrate this, we analyze thermal transport in 75 nanoporous half-Heusler compounds for different pore sizes. Our calculations demonstrate that, in most cases, the optimization of thermal transport in nanostructures should take into account both bulk thermal properties and geometry-dependent size effects, two aspects that are typically engineered separately. To enable efficient calculations within this paradigm we derive a model, based on the "gray" formulation of the BTE, that can decouple the influence of the geometry and the material on the effective thermal conductivity with relatively little loss in accuracy compared to the MFP-BTE. Our study motivates the need for a holistic approach to engineering thermal transport and provides a method for high-throughput low-thermal conductivity materials discovery.

### EVELYN N WANG

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Evelyn N. Wang is the Gail E. Kendall Professor and the Associate Department Head in the Mechanical Engineering Department at MIT. She is the Associate Director of the Solid State Solar Thermal Energy Conversion (S<sub>3</sub>TEC) Center, a DOE Energy Frontiers Research Center. She received her BS from MIT, and MS and PhD from Stanford University in mechanical engineering. From 2006 to 2007, she was a postdoctoral researcher at Bell Laboratories.

Her research interests include fundamental studies of micro/nanoscale heat and mass transport and the development of efficient thermal management; solar thermal energy conversion; and water harvesting systems. Her work on solar thermophotovoltaic energy conversion was selected as one of 10 breakthrough technologies in 2017 by the MIT Technology Review, and her work on water harvesting from air was selected as one of 10 emerging technologies in 2017 by Scientific American and the World Economic Forum.

### Device Research Laboratory

<http://drl.mit.edu/>  
Research: <http://drl.mit.edu/research.cgi>  
Publications: <http://drl.mit.edu/publications.cgi>

The DRL combines fundamental studies of micro and nanoscale heat and mass transport processes with the development of novel nanostructured materials to create innovative solutions in thermal management, thermal energy storage, solar thermal energy conversion, and water desalination. We leverage state-of-the-art micro/nanofabrication, unique measurement, and model prediction capabilities to enable mechanistic insights into complex fluid, interfacial, and thermal transport processes. This approach has led to new and important functionalities to enhance heat and mass transfer for various applications.

### Advanced Thermal Storage

<http://drl.mit.edu/research.cgi?p=storage>

Despite recent advances in electric batteries for sustained power delivery, weight and overall capacity, their energy storage densities remain much lower than gasoline and other liquid fuels. As a result, there is currently a substantial disadvantage to electric vehicles (EVs) compared to their internal combustion engine counterparts, particularly in terms of driving range. In this project an advanced thermo-adsorptive battery (ATB) will be developed to provide both cooling and heating in an electric vehicle with minimal use of the electric battery. This will potentially result in a 30% increase in the driving range versus the use of conventional climate control technology in EVs.

This technology relies on the development of novel, highly porous nanostructured materials which include zeolites and metal organic frameworks (MOF) to enable high water adsorption capacities. Incorporating the nanostructured materials within a carefully designed thermal system will significantly promote both heat and mass transfer, resulting in a compact (30 L) and lightweight (< 35 kg) thermo-adsorptive battery with heating and cooling capacities greater than 2.5 kWh for climate control in EVs. A successful implementation of this technology can also be broadly applicable to residential and commercial buildings including datacenters and telecom facilities, whereby heating and cooling via the proposed technique can significantly decrease electricity consumption during peak demand. Furthermore, with the use of an environmentally benign refrigerant, the global warming potential is also minimized.

#### **Solar Energy: Solar Thermophotovoltaic**

<http://drl.mit.edu/research.cgi?p=solar>

Solar radiation is one of Earth's most abundant renewable resources and the conversion of this solar energy into electricity can be accomplished by a number of methods. Among the most promising is solar thermal power generation, an approach that uses mirrors to concentrate sunlight on an absorbing surface, either a tower or a pipe, which in turn transfers heat to a fluid. The heat transfer fluid collects the thermal solar energy and is pumped to a heat exchanger that creates steam to power the turbine of an electric generator. While effective at generating electricity, a number of inefficiencies arise when running the equipment at extremely high temperatures and when operation is limited to periods of sufficient sunlight.

At the Device Research Laboratory, we are working to minimize these inefficiencies by studying micro-nano structures for enhanced thermal fluid properties. Micro/nano-particles can improve the fluid's ability to absorb solar radiation by decreasing emissive losses at high temperatures [1]. Further, thermal storage and heat transfer can be increased through the heat of fusion of phase-change micro/nano-particles [2], ultimately boosting the capacity factor of a concentrated solar power plant.

In addition, we research direct conversion of solar irradiation to electrical energy through the use of thermophotovoltaics (TPVs). We are investigating the overall performance and complex energy conversion mechanisms of solar TPVs through experiments [3-6] and a high-fidelity thermal electrical system-level model [7]. Since the efficiency of a TPV system is highly dependent on the optical properties of the thermal emitter and the PV cell, we work on incorporating advanced materials and designs to our prototype in order to demonstrate relatively high converter efficiencies.

#### **High temperature stability of transparent silica aerogels for solar thermal applications**

Strobach, E., Bhatia, B., Yang, S., Zhao, L., Wang, E.N.

APL Materials, Volume 7, Issue 8, 1 August 2019, Article number 081104,  
<https://doi.org/10.1063/1.5109433>

Solar thermal energy systems combined with low-cost thermal storage provide a sustainable, dispatchable source of renewable energy. One approach to increase the attractiveness of these systems is to use high-performing solar transparent, thermally insulating silica aerogel to significantly increase efficiency. Several past works have proposed using these ultra-nanoporous materials to reduce thermal losses in the receiver, but only recently have aerogels reached the high solar transparency necessary to be considered for concentrated solar applications (>97%). However, the durability and stability of optically transparent silica aerogels at the operating conditions of solar-thermal receivers has not been examined. Here, we investigate the high temperature stability of transparent silica aerogel for use in concentrated solar thermal energy applications. Transparent samples (visible transmission >95% at 4 mm thickness) were annealed for several months at 400, 600, and 800 °C to investigate the relative change in nanostructure, solar transparency, and effective thermal conductivity. Results showed that at 400 and 600 °C, the temperature-dependent changes reach a plateau within 30 days of continuous annealing, but at 800 °C, samples are structurally unstable. A simple receiver efficiency model was used to show stable performance at 400 and 600 °C temperatures, even after months of exposure. This work validates that transparent silica aerogels can be used in solar thermal receivers below 800 °C, yielding appreciable increases in efficiency for solar energy harvesting operation.

#### **Harnessing Heat beyond 200 °C from Unconcentrated Sunlight with Nonevacuated Transparent Aerogels**

ACS Nano, 2019, <https://doi.org/10.1021/acsnano.9b02976>

Heat at intermediate temperatures (120-220 °C) is in significant demand in both industrial and domestic sectors for applications such as water and space heating, steam generation, sterilization, and other industrial processes. Harnessing heat from solar energy at these temperatures, however, requires costly optical and mechanical components to concentrate the dilute solar flux and suppress heat losses. Thus, achieving high temperatures under unconcentrated sunlight remains a technological challenge as well as an opportunity for utilizing solar thermal energy. In this work, we demonstrate a solar receiver capable of reaching over 265 °C under ambient conditions without optical concentration. The high temperatures are achieved by leveraging an artificial greenhouse effect within an optimized monolithic silica aerogel to reduce heat losses while maintaining high solar transparency. This study demonstrates a viable path to promote cost-effective solar thermal energy at intermediate temperatures.

## **PROGRAMS, LABS, CENTERS**

### **MIT CLIMATE**

<https://climate.mit.edu/>

MIT Climate is MIT's central portal to all the work happening across MIT on climate change, and a place for worldwide discussion and learning.

For the MIT community, this site brings together and showcases the education, research, and innovation by MIT's administration, departments, labs, centers, and student and alumni groups.

For the world, this portal is a window into the cutting-edge climate science and action emerging from MIT and beyond, as well as a place to ask questions of experts, dig into emerging climate research, and engage in a global dialogue with people around the world.

Climate change demands society's urgent attention, though the science and impacts can sometimes be unclear. MIT Climate aims to connect questions to answers, research to solutions, and knowledge to action.

MIT Climate is a partnership of the MIT Environmental Solutions Initiative and MIT Open Learning, with support from the MIT Office of the Vice President for Research.

### Decarbonizing the Electricity Sector

December 4, 2019, <https://climate.mit.edu/posts/decarbonizing-electricity-sector-december-4-2019>

The third of MIT's six Climate Action Symposia, Decarbonizing the Electricity Sector, was held on Wednesday, December 4, 2019. Topics included:

- developments in solar energy, energy storage, and nuclear energy;
- electrification in the building and transportation sectors; and
- innovation opportunities for zero-carbon electricity technologies in the coming decades.

The Climate Action Symposia series aims to advance our community's understanding and expand our capacity to generate solutions for the urgent global challenge of climate change. Over the 2019-2020 academic year, the six symposia examine the current state of climate science and policy, as well as pathways for decarbonization of the global economy. We will also look at how universities can and should contribute solutions, including MIT's efforts under our Plan for Action on Climate Change.

### *Getting the carbon out of the electricity sector*

**MIT symposium looks at the role of advances in storage, solar, nuclear, EVs and more in cutting greenhouse gas emissions.**

David L. Chandler, MIT News Office, December 9, 2019, <http://news.mit.edu/2019/decarbonizing-electricity-sector-1209>

The generation of electricity is a huge contributor to the world's emissions of climate-altering greenhouse gases, producing some 25 percent globally. That's because more than two-thirds of the world's electricity is still being produced by burning fossil fuels. But progress in a variety of areas could allow for drastic reductions in those emissions, as several specialists in engineering and economics outlined last week at the third of six climate change symposia being held this academic year at MIT.

Titled "Decarbonizing the Electricity Sector," the symposium centered on four areas: improvements in solar energy and storage systems, advances in nuclear power and fusion, electric vehicles, and expanding access to electricity in the developing world while curbing emissions.

"Globally, we are in the midst of a major decarbonization strategy to create clean electricity," said Paul Joskow, a professor of economics at MIT's Sloan School of Management and co-moderator of

the symposium. But, he said, it will also be essential to cut emissions from the other major sectors, especially in transportation and in building operations.

Jessika Trancik, an associate professor of energy studies at MIT's Institute for Data, Systems, and Society and the event's other moderator, said that "solar represents one of the biggest successes," given that solar module prices have dropped by 90 percent since 2000. But there is still great potential for significant further progress in the next few years.

Moungi Bawendi, the Lester Wolfe Professor of Chemistry, described some promising research on solar technology, including the use of perovskite-based solar cells with potential for much greater output for a given weight. This technology may open up possibilities for solar panels that could be integrated into building exteriors, including transparent ones incorporated in windows....

### MIT ENERGY INITIATIVE

<http://energy.mit.edu/>

Director: Robert Armstrong, <http://energy.mit.edu/profile/robert-armstrong/>

Research: <http://energy.mit.edu/energy-research/>

Relevant Research: <http://energy.mit.edu/area/power-distribution-energy-storage/>

The MIT Energy Initiative is MIT's hub for energy research, education, and outreach—connecting faculty, students, and staff to develop the technologies and solutions that will deliver clean, affordable, and plentiful sources of energy. Our mission is to develop low- and no-carbon solutions that will efficiently and sustainably meet global energy needs while minimizing environmental impacts, dramatically reducing greenhouse gas emissions, and mitigating climate change. Within MIT, we strive to foster a sense of community among those interested in energy.

### Saving heat until you need it

<http://energy.mit.edu/research/thermal-energy-storage/>

MIT researchers have demonstrated a new way to store unused heat from car engines, industrial machinery, and even sunshine until it's needed. Central to their system is a "phase-change" material that absorbs lots of heat as it melts and releases it as it resolidifies. Once melted and activated by ultraviolet light, the material stores the absorbed heat until a beam of visible light triggers solidification and heat release. Key to that control are added molecules that respond to light by changing shape—from one that impedes solidification to a different one that permits it. In a proof-of-concept experiment, the researchers kept a sample mixture in liquid form down to room temperature—fully 10°C below where it should have solidified—and then, after 10 hours, used a light beam to trigger solidification and release the stored thermal energy.

### Energy Storage Center

<http://energystoragecenter.mit.edu/>

The Energy Storage Research Center promotes collaboration between MIT researchers and industry members to advance vital energy storage technologies and move these new technologies swiftly from lab to market.

### *Review of wholesale markets and regulations for advanced energy storage services in the United States: Current status and path forward*

Apurba Sakti, Audun Botterud, Francis O'Sullivan

Energy Policy, Volume 120, September 2018, Pages 569-579,  
<https://doi.org/10.1016/j.enpol.2018.06.001>

Today, advanced energy storage technologies, particularly electrochemical batteries, represent an increasingly economic option for supporting the integration of renewable energy resources and providing the grid with greater operational flexibility. Crucially though, the large-scale deployment of these assets, and the development of successful business models to support them is heavily reliant on policy, regulation and market design. In this paper, we present a comprehensive review of the array of federal, ISO/RTO and state-level rules and regulations shaping today's energy storage deployment across the United States. We highlight the fragmented and heterogeneous nature of existing market participation models available for advanced energy storage across restructured power markets and emphasize the need for design changes to power markets at all timescales to allow for the more efficient integration of energy storage. We also reflect on how well FERC's recent Order 841 does in terms of providing a framework for the establishment of more fit-for-purpose market participation models for storage, something that will be key for today's evolving power sector as it becomes more dependent on intermittent renewable resources.

### ***Energy Storage for the Grid: Policy Options for Sustaining Innovation***

David M. Hart, William B. Bonvillian, Nathaniel Austin  
MIT Energy Initiative Working Paper, April 2018, <http://energy.mit.edu/wp-content/uploads/2018/04/MITEI-WP-2018-04.pdf>

The electric power sector must be transformed in the twenty-first century. The threat of climate change, and the difficulty of reducing carbon emissions from other sources, means that power sector emissions must fall to near zero. Grid-scale energy storage has the potential to make this challenging transformation easier, quicker, and cheaper than it would be otherwise.

A wide array of possibilities that could realize this potential have been put forward by the science and technology community. Grid-scale storage has become a major focus for public research and development (R&D) investment around the world. The public sector has also played a crucial role in moving some of these ideas from the laboratory into practice. In the United States, federal investments pushed storage technologies forward in the early 2010s, and state and regional initiatives provided a pull as the federal push slackened in the last few years.

The shift from federal push policies to regional and state pull policies coincided with the consolidation of the grid-scale energy storage market around lithium-ion (Li-ion) batteries. This technology now accounts for more than 90% of the global and domestic markets. It is relatively mature, compared to the battery alternatives, and benefits from large-scale use in electronics and, more recently, electric vehicles (EVs). These qualities have enabled rapid price-cutting for grid-scale applications. Most projections suggest that Li-ion batteries will dominate the grid-scale market as that market grows rapidly in the coming years....

### **MATERIALS RESEARCH LABORATORY**

<https://mrl.mit.edu/index.php>

Director, Carl Thompson: [https://dmse.mit.edu/people/carl-v-thompson?page=8&qt-\\_none\\_=1](https://dmse.mit.edu/people/carl-v-thompson?page=8&qt-_none_=1)

Research: <https://mrl.mit.edu/index.php/about-mrl/research-areas>

The Materials Research Laboratory (MRL) will provide a unified nexus for support of interdisciplinary interactions among materials researchers within MIT. It will serve as a portal and

mediator for external interactions with industry, government and other academic institutions. It will also partner with MIT.nano and other organizations to provide the tools and research environments that promote research breakthroughs, and will build on a rich history of innovation and entrepreneurship in the MIT materials research community to help translate breakthroughs to technologies that impact society. The creation of the MRL will also better enable MIT to communicate to the public the profound role that materials research plays in creating and advancing all of the technologies that affect our daily lives.

The MRL encompasses research on energy conversion and storage, quantum materials, spintronics, photonics, metals, integrated microsystems, materials sustainability, solid-state ionics, complex oxide electronic properties, biogels, and functional fibers. These are all interdisciplinary topics in materials. Each plays a critical role with the focus on scientific discovery, and how to design and make materials that lead to systems that have improved performance or that enable new approaches to existing problems.

### MICROSYSTEMS TECHNOLOGY LABORATORIES

<https://www.mtl.mit.edu/>

Director, Hae-Seung (Harry) Lee: <https://www.mtl.mit.edu/node/123>

Research: <https://www.mtl.mit.edu/research-overview>

2019 Annual Research Review: <https://www.mtl.mit.edu/mtl-annual-research-report-2019>

The research activities of MTL are extraordinarily broad. The common thread is the interest of MTL faculty in microsystems. These are systems that exploit the unique attributes of micro-scale and nanoscale devices and circuits to address areas of pressing human concern. MTL faculty pursue a number of technologies that explore new materials and structures, new nanofabrication techniques, new devices, new circuit concepts, new system architectures and new algorithms to synthesize complex systems that advance the state of the art. MTL's activities encompass integrated circuits and systems, electronic and photonic devices, MEMS, bio-MEMS, molecular devices, nanotechnology, sensors, actuators, to name just a few. The range of materials reaches well beyond Si and Ge to include III-V compound semiconductors, nitride semiconductors, graphene and other 2D materials, polymers, glass, organics, and many others.

The Energy section of the 2019 MTL Annual Research Report ([https://www.mtl.mit.edu/sites/default/files/attachments/section\\_03\\_0.pdf](https://www.mtl.mit.edu/sites/default/files/attachments/section_03_0.pdf)) highlights several storage related research, including:

#### High Capacity CMOS-compatible Thin Film Batteries on Flexible Substrates

M. J. Chon, A. Weathers, M. Polking, J. Kedzierski, D. Nezich, H. Chea, L. Racz, C. V. Thompson  
Sponsorship: Lincoln Laboratories

The miniaturization of sensors through advancements in low-powered MEMS devices in integrated circuits has opened up new opportunities for thin film microbatteries. However, many of the available thin film battery materials require high-temperature processes that necessitate additional packaging materials, which reduce the overall energy density of these batteries. Previous research with collaborators in Singapore demonstrated an all-solid-state materials system with high volumetric capacity that exclusively utilizes CMOS-compatible (i.e., room temperature) processes. This process allows integration of these batteries with CMOS circuits as distributed power supplies or for integrated autonomous microsystems. Additionally, the ability to deposit all components of the battery at room temperature makes it possible to fabricate these batteries on thin, flexible

substrates that can be densely stacked to achieve energy densities comparable to bulk batteries, which has been the focus of this project. We have successfully demonstrated a full thin film microbattery using germanium (Ge) and ruthenium dioxide (RuO<sub>2</sub>) as anode and cathode materials, respectively, with lithium phosphorous oxynitride (LiPON) as the solid-state electrolyte (Figure 1b). Although RuO<sub>2</sub> has traditionally been used as an anode material, it has significantly higher volumetric capacity than typical cathode materials and sufficiently high electrochemical potential versus Ge to provide an output voltage of about 0.5V at a capacity of about 40 Ah/cm<sup>3</sup> (Figure 1a). These materials are deposited onto a thin (~5 μm), flexible polyimide substrate with integrated interconnects and peeled off the handle substrate (Figure 2). These battery films can be stacked for higher power and energy densities and folded to fit any volume.

### Crystal Engineering of Mixed Cation Perovskite for Fabrication of Highly Efficient Solar Cells

M. M. Tavakoli, J. Kong  
Sponsorship: ENI S.p.A

Inorganic-organic perovskite solar cells (PSCs) have caught tremendous interest from many research groups in the field of photovoltaic devices due to their low cost, ease of fabrication, and excellent optical and electrical properties, which resulted in a record certified personal consumption expenditure (PCE) of 23.3%. The presence of surface and grain boundary defects in organic-inorganic halide perovskite films is detrimental to both the performance and operational stability of PSCs. Here, we study the effect of chloride (Cl) additives on the bulk and surface defects of mixed-cation and halide PSCs. We found that using an anti-solvent technique divides the perovskite film into two separate layers, i.e., a bottom layer with large grains and a thin capping layer with small grains. Moreover, we demonstrate that the addition of formamidinium chloride (FACl) into the precursor solution removes the small grain perovskite capping layer and suppresses the formation of bulk and surface defects (Figure 1). This modification by FACl provides the perovskite film with remarkably improved orientation, crystallinity, and large grain size up to over 1 μm (Figure 2a). Time-resolved photoluminescence measurements show longer lifetimes for perovskite films modified by FACl and subsequently passivated by 1-adamantylamine hydrochloride (ADAHCl) than for the reference sample. Based on these treatments, we improve the quality of perovskite film and increase the power conversion efficiency (PCE) from 19.43% for a reference sample to 21.2% for the modified device by Cl additives. This efficiency is among the highest reported values for a planar perovskite solar cell. This PCE enhancement is mostly due to the improvement of open circuit voltage (V<sub>oc</sub>) from 1110 mV to 1152 mV (Figure 2b). Moreover, the device modified by Cl additives shows a lower hysteresis effect than the reference sample. Importantly, the molecular engineering created by applying Cl additives greatly enhances the stability of the PSCs, which show only 5% degradation after aging for 90 days, which is higher than the 16% PCE loss of the reference device (Figure 2c). Additionally, we found that the modified device with Cl additives shows a smaller ideality factor of 1.8 than 2.1 for the reference device, due to the lower recombination. Our proposed approach opens up a new direction for the commercialization of efficient and stable solar cell devices.

### Buckled MEMS Beams for Energy Harvesting from Low-frequency Vibrations

R. Xu, H. Akay, S-G. Kim  
Sponsorship: MIT-SUTD International Design Center

Vibration energy harvesters based on the resonance of the beam structure work effectively only when the operating frequency window of the beam resonance matches that of the available vibration source. None of the resonating micro-electro-mechanical system (MEMS) structures can



operate with low-frequency, low-amplitude, and unpredictable ambient vibrations since the resonant frequency rises as the structure gets smaller. A bi-stable buckled beam energy harvester has been developed to lower the operating frequency window below 100Hz for the first time at the MEMS scale. This design does not rely on the resonance of the MEMS structure but operates with the large snapping motion of the beam at very low frequencies when input energy overcomes an energy threshold. A fully functional piezoelectric MEMS energy harvester was designed, monolithically fabricated, and tested. An electromechanical lumped parameter model was developed to analyze the nonlinear dynamics and to guide the design of the nonlinear oscillator-based energy harvester. Multi-layer beam structure with residual stress-induced buckling was achieved through the progressive residual stress control of the deposition processes along with fabrication steps. The surface profile of the released device shows bistable buckling of  $200\mu\text{m}$ , which matches well with the amount of buckling designed. Dynamic testing demonstrates that the energy harvester operates with 50% bandwidth under 70Hz at 0.5g input, operating conditions that have not been demonstrated by MEMS vibration energy harvesters before.

### **A Robust Electromagnetic MEMS Vibration Energy Harvester**

Y. Yang, U. Radhakrishna, J. F. Hunter, J. H. Lang

Sponsorship: Analog Devices, Inc.

Modern production plants lack an effective way to autonomously monitor equipment health. It is uneconomical to engage personnel solely to monitor machines that function normally most of the time and impractical to wire plant-wide arrays of sensors for power and communication. As an alternative, vibration energy harvesters could power autonomous sensor networks that communicate wirelessly. Further, vibration-based machine health monitoring could be an effective method of assessing real-time machine performance. Such monitoring could become preventive by prompting maintenance prior to unrecoverable plant failures. To this end, this project seeks to advance the state of vibration energy harvesting. Our previous work yielded silicon-micro-electromechanical systems (MEMS) electromagnetic vibration energy harvesters suitable for powering machine health sensors. To further improve robustness and increase electrical power output, a new harvester is designed, fabricated, and demonstrated using the MP35N alloy. Its design and optimization follow that developed for earlier silicon harvesters. The new material has a mechanical modulus close to that of the silicon while not being brittle. Thus, with similar material thickness, we maintain the harvester footprint while improving robustness. The MP35N alloy allows for less stressful full stroke operation, enabling improved output power while being much more tolerant of external shock. Fabrication of the new harvester combines electric discharge machining and water-jet cutting for prototype production. The Lorentz-force harvester, with its folded-spring-suspended magnets, is packaged between two coupling coils using 3D-printed plastic package parts. The new harvester can survive large transient accelerations, common in an industrial setting; such accelerations are unsustainable by a comparable silicon harvester. This added durability brings the harvester much closer to practical application. The improved robustness enables the installation of back-irons, further improving the output power. The power output and power density ( $1.47\text{ mW/cm}^3$ ) are comparable to that of the previous record-setting silicon device.

### **All-solid-state Glucose Fuel Cell for Energy Harvesting in the Human Body**

P. Simons, M. A. Gysel, J. L. M. Rupp

Efficiently powering sensors, pacemakers, and bio-electronic devices for the human body defines a new era of medicine to track, support, and operate bodily functions. Glucose fuel cells have seen a

renaissance in recent years as an implantable power source harvesting energy from readily available fuels in the human body. Compared to existing implantable batteries, glucose fuel cells require much less frequent replacement surgery. However, state-of-the-art glucose fuel cells are based primarily on relatively bulky polymer electrolytes, suffer from long-term stability issues, and exhibit low power densities. Here, we innovate a miniaturized glucose fuel cell that is fully composed of solid-state materials based on thin film processing. This all-solid-state glucose fuel cell can be scaled down to the sub-micrometer range for unprecedented miniaturization and is built on a Si chip using semiconductor fabrication methods suitable for integrated and direct powering of bio-electronic implants. Through the use of abiotic catalysts instead of conventional biological catalysts such as enzymes and microbes, long-term stability and increased power density are in perspective. Freestanding fuel cell membranes based on a proton conducting oxide on Si chips were assembled using a microfabrication route with standard semiconductor processing techniques. Oxide thin films were prepared via pulsed laser deposition. The anode is in contact with glucose in phosphate-buffered saline solution to mimic blood, whereas the cathode is in contact with oxygen. Performance characterizations were carried out via electrochemical impedance spectroscopy and galvanostatic polarization curve measurements. We report that the proposed cell is electrochemically active and shows promise in functioning as the first all-solidstate glucose fuel cell with a roughly 100-fold lowered thickness of the device (only 250 nm) compared to polymer-based glucose fuel cells.

#### **SOLID-STATE SOLAR-THERMAL ENERGY CONVERSION CENTER (S3TEC)**

<https://s3tec.mit.edu/>

Principal Investigator: Gang Chen, <https://s3tec.mit.edu/node/8>

Research: <https://s3tec.mit.edu/research-overview>

Publications: <https://s3tec.mit.edu/publications>

The S3TEC Center aims at advancing fundamental science and developing materials to harness heat from the sun and convert this heat into electricity via thermoelectric, thermogalvanic and thermophotovoltaic technologies.

#### **TATA CENTER FOR TECHNOLOGY AND DESIGN**

<https://tatacenter.mit.edu/>

Director: Robert Stoner, <https://tatacenter.mit.edu/team/robert-stoner/>

Focus Areas: <https://tatacenter.mit.edu/services/>

The Tata Center for Technology and Design trains and supports MIT researchers working to solve challenges facing communities in India and the developing world. Our work spans six overlapping areas: agriculture, energy, environment, health, housing, and water.

Tata Center projects go beyond the lab and seek real-world impact, guided by the core principles of relevance, practicality, and sensitivity to context.

Working with collaborators throughout India, and with our sister-centre at the Indian Institute of Technology, Bombay, the Tata Center creates solutions designed to serve human needs.

#### **Energy**

<https://tatacenter.mit.edu/service/energy/>

A disparity in energy demand and availability affects both urban and rural areas in India. A significant surge of population movement into cities, with a concordant need for energy, particularly in transportation, electricity, and household fuels, results in intermittent power outages and surges. Meanwhile, one third of the country's rural population lacks electricity.

This presents enormous opportunities to develop innovative ways to develop and distribute energy. Among those being researched by Tata Center are the production of biofuels, the conversion of waste products into energy, and the development of autonomous micro-powergrids. Solutions developed by the Tata Center for India will have long-ranging implications throughout the developing world.

### ***On-Demand High-Throughput Synthesis of Zeolites and MOFs For Energy, Storage, Separation and Catalysis***

<https://tatacenter.mit.edu/portfolio/on-demand-high-throughput-synthesis-of-zeolites-and-mofs-for-energy-storage-separation-and-catalysis/>

This Tata Center-funded study focuses on developing low-cost, high-throughput and energy-efficient synthesis routes for a wide variety of zeolites and MOFs that can be available on-demand for numerous applications. Zeolites are a class of aluminosilicate material that is crystalline and microporous in nature. They have a three-dimensional framework with repeating 'TO<sub>4</sub>' units, with T being Si or Al atoms that are connected by sharing O atoms resulting in uniform-sized channels and cavities with molecular dimensions. While MOF (Metal-Organic Frameworks) are microporous materials consisting of metal ions (or clusters) that are coordinated by organic ligands forming 3D frameworks. There are thousands of known zeolite structures, however, only around 200 have been successfully synthesized in the laboratory, of which only around 40 frameworks are available in nature and around 10-15 frameworks are commercially available. Existing synthesis routes have shortfalls with regards to the production efficiency, lead times, infrastructure (or lab space, instrumentation).

The proposed solution is to build a high throughput flow-microreactor that synthesizes zeolite and MOF crystals in-flow. We also propose using machine learning algorithms that are capable of extracting material synthesis parameters from thousands of published literature, databases, and patents, in order to map out synthesis space. The primary advantages offered by this route would be access to a large number of frameworks via predictive algorithms, and the capability of synthesizing a variety of porous materials within a few minutes. The microreactor setup can be scaled up relatively easily for large-scale industrial production. This represents a potent combination which would be beneficial for academic research and industrial consumption likewise. Zeolites and MOFs have extensive applications in energy, separation, catalysis, storage water, food, and health sciences. Most of the applications originate from their ion-exchange, open coordination sites, adsorbent capabilities, and microporosity....

### ***Solar Energy Storage for Solar Cooking: Research, Development & Market Testing***

<https://tatacenter.mit.edu/portfolio/solar-energy-storage-for-solar-cooking-research-development-market-testing/>

More than half the world still cooks their food and heats their home and water using rudimentary stoves. The UN estimates that smoke from primitive stoves kills 1.9 million people annually, more than malaria and AIDS combined. In addition, cooking fuel is becoming increasingly scarce, expensive, and time-intensive to find.

A solution to these problems is to use clean, renewable, and free sunlight, to meet these energy needs. However, current solar stoves do not supply on-demand heating, are not robust, and are often heavy and cumbersome. These challenges inhibit their widespread implementation.

This project is designing low-cost thermal batteries that utilize a novel micro-encapsulated fuel media to provide on-demand energy release for cooking and heating applications.

### *Capturing Biogas as a Sustainable Energy Source to Power Rural Communities*

<https://tatacenter.mit.edu/portfolio/capturing-biogas-as-a-sustainable-energy-source-to-power-rural-communities/>

Access to clean, sustainable energy is of critical importance to the industrialization of rural India. A major source of largely untapped energy comes in the form of biogas, which is produced from the anaerobic digestion of farm and landfill waste. This energy source is a renewable alternative to natural gas, but unfortunately, it is not produced in high enough purity to be used directly as a fuel.

This research seeks to design small-scale membrane-based separation devices for upgrading biogas on site in rural areas, thereby providing access to reliable, renewable energy in communities not readily connected to “grid” power.

## MIT-RELATED STARTUPS

### MIT STARTUP EXCHANGE

<https://startupexchange.mit.edu/>

MIT Startup Exchange actively promotes collaboration and partnerships between MIT-connected startups and industry, principally members of MIT’s Industrial Liaison Program (ILP). MIT Startup Exchange and the ILP are integrated programs of MIT Corporate Relations.

“MIT-connected” startups are based on licensed MIT technology, or are founded by MIT faculty, staff, or alumni. Currently, over 1,700+ startups are registered with MIT Startup Exchange and monthly additions are helping to shape and define an innovative and entrepreneurial community.

The industry side of the exchange is represented primarily by 260+ ILP member companies. Meetings between MIT Startup Exchange startups and industry are facilitated by program directors at MIT’s Industrial Liaison Program. Each program director manages a portfolio of ILP member companies, and their primary role is to match company research interests with relevant MIT faculty and researchers. Increasingly, on-campus agendas include MIT Startup Exchange startups, based on their potential to rapidly explore and assess new technologies.

### 24M TECHNOLOGIES INC.

MIT Relationships: Yet-Ming Chiang (Co-Founder, Chief Scientist, MIT Faculty)  
Cambridge, MA, <http://24-m.com/>

24M solves the grand challenge of lithium-ion batteries with the invention of the SemiSolid lithium-ion battery, a revolutionary technology for the architects of our energy future. By upending the design of the battery cell, as well as the manufacturing process, the company solves the critical,

decades-old challenge associated with the world's preferred form of energy storage: reducing its high cost while maintaining its strengths. Founded and led by some of the battery industry's foremost inventors, scientists and entrepreneurs, 24M is headquartered in Cambridge, Massachusetts, just blocks away from MIT in the heart of a dynamic innovation ecosystem.

The simple truth is that lithium-ion batteries are made the wrong way. The process is cumbersome. It's wasteful. It's woefully inefficient. 24M's novel manufacturing process strips out the waste, speeds production and reduces the overall footprint to cuts capital costs requirements by more than 50% and accelerate its adoption. We call it SemiSolid lithium-ion. A better process. A better battery. A better energy future.

#### **AMBRI, INC.**

MIT Relationships: Donald Sadoway (Co-Founder, Chief Scientific Advisor, MIT Faculty), David Bradwell (Co-Founder, CTO, MIT Alumnus)  
Marlborough, MA, <https://ambri.com/>

Ambri (formerly Liquid Metal Battery Corporation) is commercializing an innovative grid-scale energy storage technology -- the Liquid Metal Battery (LMB) -- that was developed at MIT in the lab of Professor Donald Sadoway. The LMB technology was inspired by the concept of reversing large-scale electrometallurgical processes that consume huge quantities of electricity (i.e., aluminum smelting). Applying the principles of large-scale electrometallurgy has enabled Ambri to create a low-cost, long-lifespan and safe storage solution. Research at MIT was funded by grants from the Department of Energy's ARPA-E program, Total and other sources. To date, Ambri has raised more than \$50 million in equity financing; Ambri's investors include Khosla Ventures, Bill Gates, Total, KLP Enterprises and the Swiss insurance company, GVB. Ambri's storage technology is unlike anything that exists in today's market.

#### **ANTORA ENERGY**

MIT Relationship: David Bierman (Co-Founder, MIT Alumnus)  
Berkeley, CA, <https://www.cyclotronroad.org/antora>

Antora Energy is building a low-cost thermal battery for grid-scale energy storage. By combining inexpensive thermal storage media at high temperatures with high-efficiency thermophotovoltaic energy conversion, we will support the widespread integration of renewable resources on the electricity grid.

#### **CADENZA INNOVATION**

MIT Relationships: Dr. Christina Lampe-Onnerud (Founder, CEO, MIT Alum), Per Onnerud (CTO, MIT Alum)  
Wilton, CT, <https://cadenzainnovation.com/>

Our company's mission is to deploy our intellectual property, field-proven operational and mass production expertise, along with our key technology partners to build Cadenza Innovation into a global technology leader in energy density, lowest cost, and safety. Cadenza Innovation is licensing its technology to allow immediate access to its highly simplified design for large lithium-ion energy storage systems.

### A novel way to advance a better battery design

**Led by “Queen of Batteries” Christina Lampe-Onnerud, Cadenza Innovation is licensing its lithium ion battery cell architecture to manufacturers around the world.**

Zach Winn, MIT News Office, November 7, 2018, <http://news.mit.edu/2018/cadenza-innovation-supercell-battery-1107>

Cadenza Innovation has developed a new design that improves the performance, cost, and safety of large lithium ion batteries. Now, with an unusual strategy for disseminating that technology, the company is poised to have an impact in industries including energy grid storage, industrial machines, and electric vehicles.

Rather than produce the batteries itself, Cadenza licenses its technology to manufacturers producing batteries for diverse applications. The company also works with licensees to both optimize their manufacturing processes and sell the new batteries to end users. The strategy ensures that the four-year old company’s technology is deployed more quickly and widely than would otherwise be possible....

### FORM ENERGY

MIT Relationships: Yet-Ming Chiang (Founder, MIT Faculty), Marco Ferrara (Founder, MIT Alumnus), Billy Woodford (Founder, MIT Alumnus)  
Somerville, MA, <https://www.formenergy.com/>

Form Energy is a small team of passionate people committed to helping the world transition to renewable energy with technology. We are developing a new class of ultra-low-cost, long-duration energy storage systems to make renewable energy available even when the sun sets, or the wind stops blowing.

Form’s technology has the potential to transform the electric grid by making renewable energy dispatchable year-round. The company’s core technology was invented at MIT and is supported by category leading investors including Breakthrough Energy Ventures, MIT’s The Engine, and Prelude Ventures. Our team members are active learners who like working on tough technology problems that can only be solved with a combination of scientific innovation and hard work.

### HEILA TECHNOLOGIES

MIT Relationships: Francisco Morocz (Co-Founder, CEO, MIT Alum), Jorge Elizondo (Sr. Engineer, MIT Alum)  
Somerville, MA, <https://heilatech.com/>

Heila Technologies is an MIT startup focused on creating a novel distributed microgrid controller that creates a seamless experience for microgrid installation. By utilizing patent-pending hardware and advanced software, the Heila IQ distributed control platform integrates and coordinates disparate energy sources and loads based on local sensors, removing the need for expensive overhead and delays associated with integration and reconfiguration that other microgrid controllers require.

### HELIX POWER

MIT Relationships: Matthew Lazarewicz (Founder, President, MIT Alum), Donald Bender (Co-Founder, MIT Alum)

Somerville, MA, <https://www.helixpower.com/>

Helix Power is introducing an advance energy storage technology using high power short duration flywheels as an “extreme energy management” tool for applications such as metro trains, capable of charging or discharging 1WM for 90 seconds.

Implementation has the potential to manage and reduce greenhouse gases at an accelerated rate.

The initial application can reduce metro train propulsion energy requirements by 30-50%.

Our interest is to adapt this technology to improve wind and solar integration, microgrid effectiveness, and industrial applications.

### **NANORAMIC LABORATORIES**

MIT Relationships: John Cooley (Co-Founder, President, COO, MIT Alumnus)

Boston, MA, <https://www.nanoramic.com/>

Established 2009 in Boston, MA, Nanoramic® Laboratories was founded by MIT graduates and experts in the use of nanocarbons in energy storage devices. Our culture of transparency, empowerment, disciplined thinking, and experimentation is what drives us to build world-class technology. In addition to Nanoramic's® groundbreaking Neocarbonix™ Electrode technology, the Nanoramic® product family includes Thermexit™ and FastCAP® Ultracapacitors. Thermexit™ is a line of high-end thermal interface gap filler pads. Thermexit™ gap fillers are a non-reactive, non-silicon, no cure system featuring high thermal conductivity and high thermal stability. FastCAP® Ultracapacitors is an industry leader in harsh environment energy storage, producing the only ultracapacitors capable of operating in temperatures up to 150C and under conditions of high shock and vibration. FastCAP® products also include wide temperature range lithium-ion capacitors, structural ultracapacitors, and the only reflowable, low ESR, slim profile ultracapacitor on the market.

### **POLYJOULE**

MIT Relationships: Eli Paster (Co-Founder, CEO, MIT Alum), Zhengguo Zhu (Chief Chemist, MIT Alum), Ian Hunter (Co-Founder, Scientific Advisor, MIT Faculty), Timothy Swager (Co-Founder, Scientific Advisor, MIT Faculty)

Billerica, MA, <http://www.polyjoule.com/>

PolyJoule has developed a non-lithium form of energy storage that is built purposely for the electricity grid. Safety is molecularly designed into our battery chemistry, streamlining permitting and usability. PolyJoule cells can respond to both base loads and peak loads in microseconds, allowing the same battery system to participate in multiple power markets and deployment use cases. Upfront system costs are low. Lifetime cell reliability is high.

### **SOLIDENERGY SYSTEMS**

MIT Relationships: Qichao Hu (Founder, CEO, MIT Alumnus)

Woburn, MA, <http://www.solidenergysystems.com/>

SolidEnergy today manufactures the world's lightest rechargeable cells at pilot scale for prototype demonstration and specialized aerospace markets. But our real future lies in the materials we

supply—anodes and electrolyte—for mainstream markets such as consumer electronics and electric vehicles. We supply these to large Li-ion cell manufacturers to be integrated with a separator and cathode into full cells which can be customized for different applications including drones, consumer electronics and electric vehicles.

Because our anode and electrolyte materials are compatible with existing Li-ion cell manufacturing processes, we can achieve scalability by using existing infrastructure. This eliminates the need for costly infrastructure investment. It's all part of our open ecosystem. It means a more seamless end-user experience, faster prototyping and no limits to growth.