

David M. Stewart

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Professional Summary

I work on thin film energy storage systems and basic materials science, making micro-batteries for microelectronics applications and fundamental battery science. Recently, I have been pursuing questions of electrochemical interface formation and kinetics, and stress-electrochemistry coupling through combined modeling and experimental techniques. I enjoy teaching physics and nanofabrication skills, mentoring and supporting early career development, and creating physics outreach programs for elementary and middle school students to enhance critical thinking skills and STEM inclusion.

Appointments & Education

University of Maryland, College Park, MD	Assistant Research Scientist	2019 – present
	Post-doctoral Research Assistant	2016 – 2019
University of Maine, Orono ME	Ph.D. Physics	2016
	Graduate Research Assistant	2013 – 2016
University of Florida, Gainesville, FL	B.S. Physics	2011

Research

U. of Maryland
DOE BES
Co-PI
2019 – present

Thin Film Platforms for Solid-State Ionic Devices. Directing several projects with collaborators and advisees, all in the vein of using thin film structures to study fundamental phenomena in solid-state batteries. My three primary thrusts are:

1. *Electrochemo-mechanical coupling:* by combining multiphysics modeling and novel experimental approaches, we are seeing new couplings between stress and electrochemical fields and the effects on bulk ion transport. Experiments using Raman-strain microscopy uncovered diffusion lengths 100x longer in stressed Si anodes and explained canonical results with new modeling techniques confirmed by experiment. Models of discharge dynamics in 3D structures similarly revealed much longer diffusion lengths than imagined, but which are restricted by stress from nanoconfinement. Upcoming experiments will study cathode materials and investigate the predicted nanoconfinement effects.
2. *Solid-state ionic interfaces:* by taking a systematic, surface science approach to interface formation, we investigate the buried boundary between electrode and electrolyte, which controls most aspects of battery performance. We use patterning techniques to form an array of film stacks together, each exposing different interfaces of the battery for characterization. Cathodoluminescence studies of band bending at battery heterojunctions revealed the coupling between electron and Li⁺ ion equilibria and transport and physical connections to the electrochemical

concept of charge transfer impedance. These studies further inform modeling of advanced architectures in thrust 1.

3. *Artificial grain boundaries*: the propagation of Li dendrites through grain boundaries plagues solid-state batteries, while controlling the plating and stripping process is essential to cycle efficiency in advanced cells. By fabricating interlayers with well-defined properties between solid electrolytes, we study deposition and transport of Li along homo- and heterogenous boundaries. Under applied stress, plating/stripping and the propagation of Li dendrites can be dynamically altered, giving insight into new mechanical modeling efforts. When confined to nanopores, overlapping space-charge regions could lead to new transport processes.

U. of Maryland
DOE EFRC
2017 – 2019

Nanostructures for Electrical Energy Storage. Developed and characterized ALD thin film electrodes based on SnO_2 as anodes for 3D micro-batteries. Found a process to mingle SnO_2 and Sn_3N_4 depositions to produce SnO_xN_y films of varying composition. Thin films had greater reversibility as Li^+ electrodes than bulk examples (80% retention over 500 cycles as opposed to 40%), and the cycle stability was found to smoothly improve with increasing N:O ratio, while most other electrochemical properties were unchanged. This provides a high-performance, conformal anode for 3D batteries, as demonstrated in our published papers, and in ongoing work to this day.

Also used multiphysics modeling to study different micro-battery architectures, and projected performance of various design optimizations for both experiments and manufacturability. Models showed competitive performance with conventional cells and unveiled new avenues of research into stress-electrochemistry coupling and confinement effects on transport. These models are helping a spin-off company begin commercializing 3D battery technology developed in this group.

U. of Maine
NSF DMR
2012 – 2016

ZrB₂ and h-BN Thin Films for Harsh, High Temperature Environment Sensors.

For my Ph.D. work, I deposited thin film ZrB_2 samples by e-beam co-evaporation, and the electrical, chemical, crystal phase, and morphological stability was studied under air, vacuum, and inert atmosphere annealing up to 1200 °C. We also analyzed the performance of environmental barriers at these temperatures, including amorphous Al_2O_3 by ALD and high crystallinity h-BN coatings by reactive sputtering with substrate biasing.

With collaborators in electrical engineering, Candidate thin film stacks were fabricated piezoelectric sensors on YSZ substrates for high temperature sensors. Rapid oxidation of the bare ZrB_2 led to quick failure in air, but in vacuum or inert atmosphere the films survived thermal cycling between 23-850 °C for a total of 45 hours at 850 °C. ALD Al_2O_3 was found to be a better oxidation barrier, but thermal expansion mismatch induced too large a stress for the films to remain intact. Devices using ZrB_2 may hold the most promise in sensors for spacecraft, especially due to the radiation hardness.

U. of Maine
NSF DMR
2012 – 2013

Hard X-ray Absorption Spectroscopy. Using XPS and PES to gauge depth distribution of composition in thin film Pt-Si and ZrO_2 - ZrB_2 composite samples with different processing conditions. XANES of ionic liquids for flow batteries (group visit to NSLS at Brookhaven National Lab) and thin film ZrB_2 samples (a

solo user proposal I submitted to ALS at Argonne National Lab) led to two publications.

U. of Florida
NSF CHE
2010 – 2012

Predictions of exciton lifetimes in quantum dot solar cells. Performed density functional theory calculations on several Si nanoparticle structures with and without Ag adsorbate clusters and dopants. Photo-absorption strength and exciton lifetimes were compared for different structures, and improved solar cell efficiency (2x improvement in lifetime) was predicted for a combination of larger Ag adsorbate clusters on doped, amorphous QDs.

Advising & Mentoring

Graduate

Osma Gomez	2023 – 2027	Ph.D. Chemistry. Sputter deposition and electrochemical characterization of $A_xV_2O_5$ thin films (A=Li, Mg, Na) (working title)
Stefan Theodoru	2023 – 2026	Ph.D. Materials Science. Thin-film neuromorphic devices based on material property changes induced by ion insertion (working title)
Victoria Ferrari	2019 – 2024	Ph.D. Materials Science. Interfaces in thin-film solid-state batteries (working title)
Haotian Wang	2019 – 2022	Ph.D. Materials Science. Electrochemo-mechanics characterization of Si electrode/Si based solid-state battery
Sam Klueter	2017 – 2020	M.S. Materials Science. Investigating Aluminum Nitride as a Protection Layer for Lithium Germanium Thiophosphate Solid Electrolytes

Undergraduate

Stephanie Yang	2023 –	B.S. Mechanical Engineering. Thin film deposition and patterning of micro-batteries
Matthew Jarvis	2023 – 2024	B.S. Chemical Engineering. Bulk vs boundary transport of ions in solid electrolytes confined to nanopores, and computational modeling for experiment design.
Lukas Karapin-Springroum	2023 – 2024	NSF REU Student. Electrochemical characterization of lithium dendrite growth in artificial grain boundaries of solid-state electrolytes.
Saleh Kemal	2022	NSF REU Student. Electrochemical characterization of anode-free, thin film solid-state batteries for understanding kinetics of Li plating.
Paolo Lami	2020 – 2022	B.S. Mechanical Engineering. Multiphysics finite element analysis of mechanical confinement effects in solid-state batteries and related experiments.

- Timothy Blier 2016 **B.S. Physics.** Polishing and heat treatment of lattice matched substrates for epitaxial h-BN growth.
- Analise Roti-roti 2015 **NSF REU Student.** Processing and characterization of nanolaminate metal films for high temperature sensors.

Teaching

Microprocessing Materials

UMD Dept. of Materials Science & Engineering

Guest Lecturer. Prepared and presented lectures on thin film deposition techniques and processing for microelectronics fabrication, and prepared homework assignments.

Modern Physics

UMe Dept. of Physics & Astronomy

Guest Lecturer. Prepared and presented lectures on modern physics topics such as nuclear radiation, Plank's law, and the discovery of quantum mechanics.

Introductory Physics with Calculus

UMe Dept. of Physics & Astronomy

Teaching Assistant. Led recitation sections using inquiry-based learning and group discussion, facilitated labs, volunteered tutoring and exam prep after hours.

Service

Public Outreach

Physics is Fun and Discovery Days. Developed and led public shows and interactive demos for local K-12 students and families. Helped develop and present the "Quantum for Kids" program, a four-hour event for elementary and middle school students. Recorded demos on super conductivity for remote classes and outreach videos. U. of Maryland
2018 – 2021

Society of Physics Students. Volunteered to tutor undergrad students in all introductory course sections weekly and at special exam review sessions. U. of Maine
2014 – 2016

Maine Engineering Week Expo. Performed table demos on crystal structures for K-12 students and families. Gave public tours of surface science labs. U. of Maine
2015

4-H Science Saturday. Prepared an opening talk on nanoscale science and helped with hands on science demos with middle school girls using ACS PCSA Materials Science Kits. U. of Maine
2014

Early Career Development Programs

MRS Career Advancement Committee Member. Leading organization of the "Meet the New Research Hires" poster session for connecting early career scientists with jobs in national labs and companies. Hosted a panel webinar on the faculty application process. 2020 – present

DOE Early Career Network Representative. Led discussion groups on mentoring and public outreach. Supported organization of webinars on tenure, proposal writing, and research at national labs. 2018 – 2020

Publications

(accepted) B. Hoang, V.C. Ferrari, H. Wang, **D.M. Stewart**, R. Damircheli, C.F. Lin. "From Amorphous to Crystalline Thin-Film FeF₃ Conversion Electrodes by Sputtering Deposition." *ACS Applied Materials & Interfaces*, **X**, XX, XXXX (2023).

H. Wang, Y. Song, V.C. Ferrari, N.S. Kim, S.B. Lee, P. Albertus, G.W. Rubloff, **D.M. Stewart**. "In Situ Raman Mapping of Si Island Electrodes and Stress Modeling as a Function of Lithiation and Size." *ACS Applied Materials & Interfaces*, **15**, 34, 40409-18 (2023).
doi.org/10.1021/acsami.3c06287

Y. Song, B. Bhargava, **D.M. Stewart**, A.A. Talin, G.W. Rubloff, P. Albertus. "Status of and opportunities in electrochemical-mechanical coupling measurements." *Joule* **7**, 1-23 (2023).
doi.org/10.1016/j.joule.2023.03.001

Z. Levy, V.C. Ferrari, P. Rosas, M. Walker, K. Duddella, H. Kalpak, M. Haseman, **D.M. Stewart**, G.W. Rubloff, L.J. Brillson. "Lithium Spatial Distribution and Split-off Electronic Bands at Nanoscale V₂O₅/LiPON Interfaces." *ACS Applied Energy Materials*, **6**, 9, 4538-48 (2023).
doi.org/10.1021/acsaem.2c03683

H. Wang, N.S. Kim, Y. Song, P. Albertus, S.B. Lee, G.W. Rubloff, **D.M. Stewart**. "Micro-Raman Stress Characterization of Crystalline Si as a Function of the Lithiation State." *ACS Applied Materials & Interfaces*, **15**, 8, 10752-60 (2023). doi.org/10.1021/acsami.2c22530

D. Fontecha, R.B. Nuwayhid, A.C. Kozen, **D.M. Stewart**, G.W. Rubloff, K.E. Gregorczyk. "Low temperature plasma-enhanced atomic layer deposition of sodium phosphorus oxynitride with tunable nitrogen content." *Journal of Vacuum Science & Technology A*, **40**, 3, 032403 (2022).
doi.org/10.1116/6.0001752

V.C. Ferrari, N.S. Kim, S.B. Lee, G.W. Rubloff, **D.M. Stewart**. "Co-sputtering of lithium vanadium oxide thin films with variable lithium content to enable advanced solid-state batteries." *Journal of Materials Chemistry A*, **10**, 23, 12518-31 (2022). doi.org/10.1039/D2TA01021F

A. Jarry, S. Ricote, A. Geller, C. Pellegrinelli, X. Zhang, **D.M. Stewart**, I. Takeuchi, E. Wachsman, E.J. Crumlin, B. Eichhorn. "Assessing Substitution Effects on Surface Chemistry by in Situ Ambient Pressure X-ray Photoelectron Spectroscopy on Perovskite Thin Films, BaCe_xZr_{0.9-x}Y_{0.1}O_{2.95} (x = 0; 0.2; 0.9)." *ACS Applied Materials & Interfaces*, **10**, 43, 37661-70 (2018).
doi.org/10.1021/acsami.8b12546

D.M. Stewart, A.J. Pearse, N.H. Kim, E.J. Fuller, A.A. Talin, K.E. Gregorczyk, S.B. Lee, G.W. Rubloff. "Tin Oxynitride Anodes by Atomic Layer Deposition for Solid State Batteries." *Chemistry of Materials*, **30**, 8, 2526-34 (2018). doi.org/10.1021/acs.chemmater.7b04666

A.J. Pearse, T.E. Schmitt, E. Sahadeo, **D.M. Stewart**, A.C. Kozen, K. Gerasopoulos, A.A. Talin, S.B. Lee, G. Rubloff, K.E. Gregorczyk. "Three-Dimensional Solid-State Lithium-Ion Batteries Fabricated Via Conformal Vapor-Phase Chemistry." *ACS Nano*, **12**, 5, 4286-94 (2018).
doi.org/10.1021/acsnano.7b08751

D.M. Stewart, and R.J. Lad. "Enhanced Crystallinity of h-BN Films Induced by Substrate Bias During Magnetron Sputtering." *Phys. Stat. Sol. B: Basic Solid State Physics*, **255**, 1700458 (2017).
doi.org/10.1002/pssb.201700458

D.M. Stewart, G.P. Bernhardt, R.J. Lad. "Zirconium Diboride Thin Films for Use in High Temperature Sensors and MEMS Devices." *Proc. SPIE Microtech*, **10246** © SPIE (2016). doi.org/10.1117/12.2266561

D.M. Stewart, R.W. Meulenberg, and R.J. Lad. "Nanostructure and bonding in zirconium diboride thin films studied by X-ray spectroscopy." *Thin Solid Films*, **596**, 155–159 (2015). doi.org/10.1016/j.tsf.2015.06.063

C.A. Apblett, **D.M. Stewart**, R.T. Fryer, J.C. Sell, H.D. III Pratt, T.M. Anderson, and R.W. Meulenberg. "In situ XANES and EXAFS analysis of redox active Fe center ionic liquids." *Electrochimica Acta*, **185**, 156–61 (2015). doi.org/10.1016/j.electacta.2015.09.093

R.J. Lad, **D.M. Stewart**, R.T. Fryer, J.C. Sell, D.J. Frankel, G.P. Bernhardt, R.W. Meulenberg. "Electrically Conductive Pt-Zr-B and Pt-Si Thin Films for Use in High Temperature Harsh Environments." *Mat. Res. Soc. Symp. Proc.* **1746** © Materials Research Society (2015).

D.M. Stewart, D.J. Frankel, and R.J. Lad. "Growth, structure, and high temperature stability of zirconium diboride thin films." *J. Vac. Sci. Tech. A*, **33**, 031505 (2015). doi.org/10.1116/1.4916565

J.C. Sell, **D.M. Stewart**, G.P. Bernhardt, D.J. Frankel, and R.J. Lad. "Electrically stable nanocomposite thin films formed by oxidation of Pt-ZrB₂ nanolaminate templates." *J. Vac. Sci. Tech. B*, **33**, 021805 (2015). doi.org/10.1116/1.4914313

D.M. Stewart, M.G. Mavros, and D.A. Micha. "Light Absorption by Crystalline and Amorphous Silicon Quantum Dots with Silver Adsorbates and Dopants." *J. Phys. Chem. C* **116**, 23107–12 (2012). doi.org/10.1021/jp3075805

Presentations

SPIE OP106 (invited)	"Platforms for characterizing thin film electrochemical energy storage devices," D.M. Stewart , V.C. Ferrari, H. Wang, G.W. Rubloff.	2023
NNFC-UMD International Workshop & Summer School (invited)	"Physical Processes in thin film batteries: from fabrication to operation," D.M. Stewart , V.C. Ferrari, H. Wang, G.W. Rubloff.	2023
242nd ECS Meeting (invited)	"Multi-Scale Electrochemo-Mechanical Experiments on Thin Film Battery Materials," <u>Y. Song</u> , B. Bhargava, Z. Warecki, D.M. Stewart , P. Albertus.	2022
MRS Spring Meeting	"Thin-Film Battery Architecture Approaches for High Power and Energy," D.M. Stewart , R.B. Nuwayhid, K.E. Gregorczyk, A.J. Jarry, G.W. Rubloff.	2019
ECS AIMES (invited)	"Conformal Energy Storage: Atomic Layer Deposition of 3D Solid State Batteries," <u>A.J. Pearse</u> , K.E. Gregorczyk, D.M. Stewart , G.W. Rubloff	2018
AVS 64th Symposium	"Synthesis and Characterization of All Solid-State SnO _x N _y /LiPON/Li Batteries," D.M. Stewart , A.J. Pearse, K.E. Gregorczyck, G.W. Rubloff.	2017
232nd ECS Meeting	"Exploring Electrochemical Energy Storage of SnO ₂ , Sn ₃ N ₄ , and SnO _x N _y through ALD," D.M. Stewart , A.J. Pearse, K.E. Gregorczyck, G.W. Rubloff.	2017

MRS Spring Meeting	“ZrB ₂ and h-BN Composite Thin Films for Use in Harsh Environments Above 1000 °C,” <u>D.M. Stewart</u> , J.C. Sell, R.W.Meulenberg, and R.J. Lad.	2016
APS March Meeting	“Synthesis and Oxidation Resistance of h-BN Thin Films,” <u>D.M. Stewart</u> , R.W. Meulenberg, and R.J Lad.	2016
ICMCTF	“Growth and Nanostructure of Zirconium Diboride Thin Films for High Temperature Electronics,” <u>D.M. Stewart</u> , R.W. Meulenberg, and R.J. Lad.	2015
AVS 61st Symposium	“Growth and Phase Stability of Zirconium Diboride Thin Films,” <u>D.M. Stewart</u> , D.J. Frankel, and R.J. Lad	2014