

MSE 522 – Solid State Ionics Fall 2023

Instructor: Prof. Nicola H. Perry
Class Time: Tu & Th 2:00-3:20PM
Class Location: 137 Loomis Laboratory
4 credit hours

Email:	nhperry@illinois.edu (“MSE 522” as subject line); <i>Canvas discussion preferred</i>
Office Hours:	TBD ~ will poll class to determine best times
Course Website:	Canvas (https://canvas.illinois.edu/courses/39081) : hosts reading links, lecture slides, videos, class recordings, calendar, links to Zoom and Gradescope, grades for quizzes, discussion board, announcements, etc.
Homework:	Posted and turned in on Gradescope

Primary Text:

1. *Physical Chemistry of Ionic Materials: Ions and Electrons in Solids* by Joachim Maier – free e-book available online (need to be on campus, or on VPN, or using library proxy bookmarklet on browser)

Note: An improved 2nd edition of this text came out this year but is not yet available for free. I have asked the library to stock a hard copy of it at the Grainger engineering library reference desk.

Supplemental Texts:

1. *Defects in Solids* by Richard Tilley – free e-book available through the library
2. *The Defect Chemistry of Metal Oxides* by D.M. Smyth, Oxford University Press: New York (2000) – at Grainger Engineering Library
3. *Solid State Electrochemistry I* and *Solid State Electrochemistry II* edited by V.V. Kharton – free e-books available through the library
4. *Solid State Electrochemistry* by Peter Bruce – free e-book available through the library
5. *Defects and Transport in Crystalline Solids* by Per Kofstad and Truls Norby – free e-book available online through on-campus internet or VPN
6. Additional readings from recent literature – will be listed on Canvas and accessible online through the on-campus internet or VPN

Prerequisites:

Some familiarity with thermodynamics and ionic materials (e.g., oxides) through research or coursework will be helpful (e.g., as would be attained in one or more of: MSE 401, 403, 420, or 422)

Class Description and Objectives:

General Objective:

My goal as the instructor is to serve students through clear teaching and accessible and engaging discussions so that students can explore, understand, apply, and hopefully enjoy Solid State Ionics.

Specific Objectives:

Students will be able to:

- 1) calculate point defect concentrations using formation energies, develop Brouwer diagrams, describe several means of tailoring point defect concentrations through independent variables, and apply equilibrium thermodynamics to the case of defective solids
- 2) write point defect reactions in Kroger-Vink notation to describe defect processes, and apply a non-equilibrium thermodynamics and chemical kinetics framework to describe defect reactions and kinetic behavior
- 3) describe operation of various solid state ionics applications (including open circuit cells, cells using current, and cells generating current)

- 4) select measurement techniques appropriate for investigating solid state electrochemical material/device behavior and select materials appropriate for different functions within the devices
- 5) use appropriate resources for finding up-to-date information on solid state ionics for continued learning
- 6) critically analyze, synthesize, and communicate approaches and findings in relevant technical literature and propose original ideas building on it, using both oral and written formats

Course readings, videos, discussions, quizzes, and assignments are designed to help students make progress toward these objectives. Assessment (grading) will be based on demonstrated student learning gains towards these objectives.

Course catalog description of content:

Solid state ionic materials applied in energy conversion, energy storage, catalysis, sensing, responsive coatings, neuromorphic computing, and memory. Underlying point defect behavior, i.e., transport and reactions, through equilibrium thermodynamics, chemical kinetics, and irreversible thermodynamics. Practical solid state electrochemistry techniques and case studies.

Class Outline & Topics:

Notes: Instructor reserves option to remove or add topics as necessitated by time constraints, travel, and/or student interest. Additional readings/ resources to those noted may be provided through Canvas.

<i>Slides Title (Approx. # Lectures)</i>	<i>Topics</i>	<i>Readings</i>
MODULE A: Introduction		
Syllabus and Intro (2 classes)	Meet classmates & instructor Course content & format Defining solid state ionics History of solid state ionics Applications & science Recent developments	Knauth & Tuller review article
MODULE B: Review		
Review (2 classes)	Bonding Coordination environments Crystalline & amorphous structure (inorganic)	Kofstad & Norby pp. 1-26 Maier ch. 2 Yanagida et al. "The Chemistry of Ceramics" 2 nd ed. (1996) (as a reference)
MODULE C: Equilibrium Thermodynamics Applied to Defective Solids a.k.a. "Defects"		
Defects 1 (1 class)	Point defect formation frameworks (electronic, ionic)	Maier ch. 5 Smyth ch. 3 Tilley ch. 1-2
Defects 2 (1 class)	Defect reaction rules Intrinsic reactions (Frenkel, Schottky, anti-Frenkel, anti-Schottky, anti-site, association/dissociation, ionization/trapping, electronic disorder) Extrinsic reactions (substitution, acceptor/donor doping, exchange with gas / redox, compensating defects)	Smyth ch. 4-11 (as a reference) Selected articles on Canvas (reference re: space charge, etc.)
Defects 3 (2 classes)	Brouwer diagrams	

	Electroneutrality conditions Mass-action expressions pO ₂ dependence of concentrations	
Defects 4 (3 classes)	Higher-dimensional defects Interfacial defect chemistry True vs. trivial size effects Nano-ionics	
Defects 5 (2 classes)	Chemo-mechanical coupling Photo-ionics	
MODULE D: Chemical Kinetics & Irreversible Thermodynamics a.k.a. "Transport & Reactions"		
Transport & Reactions 1 (1 class)	<i>Irreversible thermodynamics framework for transport & reactions</i> (pure reaction, pure transport: conduction vs. diffusion) Linear regime (flux-force relationships) Driving forces Fick's 1 st law, Ohm's law Nernst-Einstein eq.	Maier ch. 6
Transport & Reactions 2 (1 class)	<i>Chemical kinetics framework for transport & reactions</i> (pure reaction, pure transport: conduction vs. diffusion) Non-linear reaction rates with large driving forces Fluxes in chemical kinetics Nernst-Einstein eq. through a different lens Applicability ranges	
Transport & Reactions 3 (2-3 classes)	<i>Mobility, diffusivity, conductivity</i> Atomistic diffusion/ ion conduction mechanisms Temperature dependence Phenomenological diffusion coefficients Correlation & Haven ratio	
Transport & Reactions 4 (2 classes)	<i>Diffusion-limited kinetics</i> Fick's 2 nd law Spatially resolved concentration profiles Time resolved integrated concentration profiles (short vs. long times) Boundary conditions & initial conditions	

	Critical length for D- vs. k-limited kinetics	
Transport & Reactions 5 (1 class)	<i>Interfacial reaction-limited kinetics</i> Spatially resolved concentration profiles Time resolved integrated profiles Mixed k- & D-limited regime Phenomenological k values Factors impacting k (effective interfacial rate constant)	
MODULE E: Solid State Electrochemistry a.k.a. "Measurement & Applications"		
Measurement & Applications 1 (3 classes)	<i>Solid-state electrochemistry</i> Electrochemical cells: current & voltage expressions Electrochemical cells: components & materials <i>Open-circuit cells</i> Governing equations Equilibrium stationary state (potentiometric gas sensors, formation energy measurements) Non-equilibrium stationary state (transference number measurements, minority carrier conductivity, chemical pumps) Non-equilibrium transient state (D, k by chemical depolarization measurements)	Maier ch. 7 Selected articles on Canvas
Measurement & Applications 2 (2-3 classes)	<i>Cells with applied current</i> Conductivity gas sensors (bulk & surface types) Electrolysis cells (incl. efficiency, thermodynamics) Memristors Types of electrodes (reversible, selectively blocking; materials selection) Stoichiometry polarization Coulometric titration Impedance spectroscopy	
Measurement & Applications 3 (2 classes)	<i>Cells generating current</i> Fuel cells (operation, types, applications, materials selection, degradation)	

	Primary & secondary batteries (operation, types, materials, metrics, degradation)	
--	---	--

Grading Policies:

Learning gains will be promoted and assessed with the following assignments:

- Quizzes (52.5% of total grade)
 - There will be quizzes approximately every 2 weeks throughout the semester.
 - Quizzes will cover materials presented in class, in readings, and on homework.
 - Study guides will be provided for each quiz.
- Homework (15% of total grade)
 - There will be approximately 3±1 assignments throughout the semester.
- Term paper (15% of total grade)
 - Students will write a proposal-style report describing a potential new opportunity for development/understanding of solid-state-ionic materials, measurement or simulation approaches, or applications. This must be different than students' existing research.
 - Papers will be turned in electronically, and portions of the written assignments will be due at different times through the semester, to enable feedback.
- Presentations (10% of total grade)
 - Students will present short summaries and analysis of recent key journal articles in the field of solid state ionics, using Powerpoint (or equivalent) slides.
 - Papers should be shared with the class a week in advance of the presentation.
- Participation (7.5% of total grade)
 - Classes such as this are greatly improved by active discussion and participation.
 - You could participate by, for example: 1) asking questions after student presentations, 2) asking or answering questions during class, 3) summarizing small-group discussions in class, 4) sharing research articles/ news during class that are relevant to the content, etc.
 - You can miss up to 3 in-person classes without losing participation credit if you are participating actively when attending in-person.

Late Homework Assignment Policy:

- *20% of total available score lost per day late* (unless for a valid, documented reason)
- If you have a valid, documented reason for a late assignment, I can discuss this on a case-by-case basis

Late Quizzes/ Papers/ Presentations Policy:

- *Lowest quiz grade automatically dropped*
- No credit for late submission
 - Reasons: fairness of the quiz process; I need enough time to grade
- If you anticipate needing to re-schedule a quiz for a documented, valid reason, please let me know as far in advance as possible.
- Documented, valid emergencies causing you to miss a deadline for one of these can be discussed on a case-by-case basis.

Academic Integrity:

The University of Illinois at Urbana-Champaign Student Code should also be considered as a part of this syllabus. Students should pay particular attention to Article 1, Part 4: Academic Integrity. Read the Code at the following URL: <http://studentcode.illinois.edu/>.

Academic dishonesty *may result in a failing grade*.

Every student is expected to review and abide by the Academic Integrity Policy: <https://studentcode.illinois.edu/article1/part4/1-401/>. Ignorance is not an excuse for any academic

dishonesty. It is your responsibility to read this policy to avoid any misunderstanding. *Do not hesitate to ask the instructor* if you are ever in doubt about what constitutes plagiarism, cheating, or any other breach of academic integrity.

Use of Artificial Intelligence (AI):

You might be considering use of AI-derived large-language models (LLMs) and other AI tools, such as ChatGPT, to see if they may contribute to aspects of your learning, work, and research. Their use is by no means expected nor required in this course, but for initial policy guidance, see the points below:

- If you use LLMs or other AI tools, consider carefully the terms of the agreement that you signed to access them, and in particular pay attention to issues of privacy/confidentiality/proprietary nature in anything you submit and their data collection/use policies.
- Please be aware that AI tools are limited when it comes to complex analysis/tasks in some scenarios and can output flawed/incorrect, over-simplified, out-of-date, inadequate, harmful, biased, or even made-up results; therefore, it's important to be aware of their limitations and critically evaluate any output from them that you may wish to use.
- Class assignments are carefully chosen and structured with particular learning objectives targeted. I have refined these assignments in MSE 522 over the years with the goal of helping your learning and professional development in skills such as compelling written communication, clear verbal communication, resourcefulness, and quantitative problem-solving. Over-reliance on LLMs on assignments will hinder your skill development and to some extent squander this opportunity during your education to try new things, grow, and improve. On the other hand, exploring how LLMs may augment your learning as an adjunct, peripheral tool could be valuable as long as you are not relying on them for the core of your work or thought.
- Ultimately you are responsible for the accuracy, originality, organization, analysis, and critical thought in any work that you submit in a class. Work submitted needs to reflect your own understanding, knowledge, and creativity. Submitting text, homework solutions, presentation slides, presentation script, etc. directly taken from LLMs' and AI tools' output as your own work is plagiarism, which is a very serious violation of academic integrity. AI and LLMs should be seen just as tools to help specific steps (e.g., brainstorming), which should be cited, and work submitted/presented must always be synthesized yourself, in your own words and format.
- All references and sources must be acknowledged. Directly quoted text/figures/material has particular rules for referencing, whereas use of concepts and ideas is cited differently. Similarly, any use of LLMs and AI output must also be acknowledged in work you turn in. If you use AI / LLMs in any way at any stage of submitted coursework, cite and precisely explain how you use them. Also, if requested on an assignment, append to your submission any AI tool / LLM input prompts used and the output that the LLM/ AI tool provided.
- Further details may be included with relevant assignments, if needed, and if anything is unclear about policy or if you have questions related to AI use, please contact the instructor in advance. Given that AI capability is rapidly evolving, the instructor reserves the right to adjust/append this policy as needed.

Mental Health

Significant stress, mood changes, excessive worry, substance/alcohol misuse or interferences in eating or sleep can have an impact on academic performance, social development, and emotional wellbeing. The University of Illinois offers a variety of confidential services including individual and group counseling, crisis intervention, psychiatric services, and specialized screenings which are covered through the Student Health Fee. If you or someone you know experiences any of the above mental health concerns, it is strongly encouraged to contact or visit any of the University's resources provided below. Getting help is a smart and courageous thing to do for yourself and for those who care about you.

- Counseling Center (217) 333-3704
- McKinley Health Center (217) 333-2700
- National Suicide Prevention Lifeline (800) 273-8255
- Rosecrance Crisis Line (217) 359-4141 (available 24/7, 365 days a year)

If you are in immediate danger, call 911.

Community of Care

As members of the Illinois community, we each have a responsibility to express care and concern for one another. If you come across a classmate whose behavior concerns you, whether in regards to their well-being or yours, we encourage you to refer this behavior to the Student Assistance Center (217-333-0050 or <http://odos.illinois.edu/community-of-care/referral/>). Based on your report, the staff in the Student Assistance Center reaches out to students to make sure they have the support they need to be healthy and safe. Further, as a Community of Care, we want to support you in your overall wellness. We know that students sometimes face challenges that can impact academic performance (examples include mental health concerns, food insecurity, homelessness, personal emergencies). Should you find that you are managing such a challenge and that it is interfering with your coursework, you are encouraged to contact the Student Assistance Center (SAC) in the Office of the Dean of Students for support and referrals to campus and/or community resources.

Disability-Related Accommodations:

To obtain disability-related academic adjustments and/or auxiliary aids, students with disabilities must contact the course instructor as soon as possible and provide the instructor with a Letter of Academic Accommodations from Disability Resources and Educational Services (DRES). To ensure that disability-related concerns are properly addressed from the beginning, students with disabilities who require assistance to participate in this class should apply for services with DRES and see the instructor as soon as possible. If you need accommodations for any sort of disability, please speak to me after class, or make an appointment to see me or see me during my office hours. DRES provides students with academic accommodations, access, and support services. To contact DRES, you may visit 1207 S. Oak St., Champaign, call 217-333-1970, e-mail disability@illinois.edu or visit the DRES website at <http://www.disability.illinois.edu/>. Here is the direct link to apply for services at DRES, <https://www.disability.illinois.edu/applying-services>.

Diversity:

I greatly value the diversity that students bring to the classroom, particularly in a discussion/presentation-heavy class such as MSE 522. I learn a lot from your questions, ideas, interests, and comments. Together as a class, our perspective on the science and applications is greatly broadened when everyone participates. More generally, it's clear that diverse participation in engineering is needed to ensure that technology is designed to serve and be accessible to the whole population rather than a narrow subset. In science, diverse perspectives and lenses benefit the whole community through increasing creativity and innovation. Further, in the context of increasing globalization, students need to be well prepared for teamwork and communication in a multicultural and international setting to address challenges where Solid State Ionics knowledge can assist (e.g., climate change, disease epidemics, water accessibility, sustainable energy, etc.). My goal is to create an inclusive classroom environment where all students can take risks to fully participate and thereby grow and learn. If you have suggestions for the instructor on improving the course environment and culture from a diversity perspective, please do reach out.

Excerpts from College's Inclusivity Statement:

The Grainger College of Engineering is committed to the creation of an anti-racist, inclusive community that welcomes diversity... The College recognizes... that Black, Hispanic, and Indigenous voices and contributions have largely either been excluded from, or not recognized in, science and engineering, and that both overt racism and micro-aggressions threaten the well-being of our students and our university community. The effectiveness of this course is dependent upon each of us to create a safe and encouraging learning environment that allows for the open exchange of ideas while also ensuring equitable opportunities and respect for all of us. Everyone is expected to help establish and maintain an environment where students, staff, and faculty can contribute without fear of personal ridicule, or intolerant or offensive language. If you witness or experience racism, discrimination, micro-aggressions, or other offensive behavior, you are encouraged to bring this to the attention of the course director if you feel comfortable. You can also report these behaviors to the Bias Assessment and Response Team (BART) (<https://bart.illinois.edu/>). Based on your report, BART members will follow up and reach out to students to make sure they have the support they need to be healthy and safe. If the reported behavior also violates

university policy, staff in the Office for Student Conflict Resolution may respond as well and will take appropriate action.

Sexual Misconduct Reporting Obligation:

The University of Illinois is committed to combating sexual misconduct. Faculty and staff members are required to report any instances of sexual misconduct to the University's Title IX Office. In turn, an individual with the Title IX Office will provide information about rights and options, including accommodations, support services, the campus disciplinary process, and law enforcement options.

A list of the designated University employees who, as counselors, confidential advisors, and medical professionals, do not have this reporting responsibility and can maintain confidentiality, can be found here: wecare.illinois.edu/resources/students/#confidential.

Other information about resources and reporting is available here: wecare.illinois.edu.

Religious Observances:

Illinois law requires the University to reasonably accommodate its students' religious beliefs, observances, and practices in regard to admissions, class attendance, and the scheduling of examinations and work requirements. You should examine this syllabus at the beginning of the semester for potential conflicts between course deadlines and any of your religious observances. If a conflict exists, you should notify your instructor of the conflict and follow the procedure at <https://odos.illinois.edu/community-of-care/resources/students/religious-observances/> to request appropriate accommodations. This should be done in the first two weeks of classes.

Family Educational Rights and Privacy Act (FERPA):

Any student who has suppressed their directory information pursuant to Family Educational Rights and Privacy Act (FERPA) should self-identify to the instructor to ensure protection of the privacy of their attendance in this course. See <https://registrar.illinois.edu/academic-records/ferpa/> for more information on FERPA.

Emergency Preparedness:

Emergency response recommendations and campus building floor plans can be found at the following website: <https://police.illinois.edu/em/run-hide-fight/>. Further guidance from campus police is given below:

Run > Hide > Fight

Emergencies can happen anywhere and at any time. It is important that we take a minute to prepare for a situation in which our safety or even our lives could depend on our ability to react quickly. When we're faced with almost any kind of emergency – like severe weather or if someone is trying to hurt you – we have three options: Run, hide or fight.



Run

Leaving the area quickly is the best option if it is safe to do so.

- ▶ Take time now to learn the different ways to leave your building.
- ▶ Leave personal items behind.
- ▶ Assist those who need help, but consider whether doing so puts yourself at risk.
- ▶ Alert authorities of the emergency when it is safe to do so.



Hide

When you can't or don't want to run, take shelter indoors.

- ▶ Take time now to learn different ways to seek shelter in your building.
- ▶ If severe weather is imminent, go to the nearest indoor storm refuge area.
- ▶ If someone is trying to hurt you and you can't evacuate, get to a place where you can't be seen, lock or barricade your area if possible, silence your phone, don't make any noise and don't come out until you receive an Illini-Alert indicating it is safe to do so.



Fight

As a last resort, you may need to fight to increase your chances of survival.

- ▶ Think about what kind of common items are in your area which you can use to defend yourself.
- ▶ Team up with others to fight if the situation allows.
- ▶ Mentally prepare yourself – you may be in a fight for your life.

Please be aware of people with disabilities who may need additional assistance in emergency situations.

Other resources

- ▶ police.illinois.edu/safe for more information on how to prepare for emergencies, including how to run, hide or fight and building floor plans that can show you safe areas.
- ▶ emergency.illinois.edu to sign up for Illini-Alert text messages.
- ▶ **Follow the University of Illinois Police Department** on Twitter and Facebook to get regular updates about campus safety.