

**Massachusetts Institute of Technology
Department of Mechanical Engineering
Cambridge, Massachusetts 02139**

**2.625 Electrochemical Systems: Fundamentals, Materials and Applications
Fall 2007**

Instructor: Prof. Yang Shao-Horn, Room 3-158; 3-2259; shaohorn@mit.edu
TAs: Ethan Crumlin, Room 31-066; 3-0536; ecrumlin@mit.edu

Lectures: Tuesdays and Thursdays 2:30pm-4:00pm
Lectures will be held in Room 1-132

Recitations: Wednesdays 4:00-5:00pm
Recitations will be held in Room 5-233

Office Hours: By Appointment

Supporting Materials:

Text (recommended; not required)

Fundamentals of Electrochemical Science and Engineering

Bard, A. J., and L. R. Faulkner. *Electrochemical Methods*. 2nd ed. New York: Wiley, 2001. ISBN: 0471043729.

Newman, J., Thomas-Alyea, K.E. *Electrochemical Systems*, 3rd ed. New York: Wiley, 2004, ISBN: 0-471-47756-7.

Modern Electrochemistry 2A, 2nd edition, J.O.M. Bockris, A.K.N. Reddy and M. Gamboa-Aldeco

Class website: <http://stellar.mit.edu/S/course/2/fa07/2.625/index.html>

All lecture notes, homework problems and solutions, exams and exam solutions will be posted on this website. Please make sure that you register so that you can have access to the course materials.

All Lab demos of electrochemical measurements will be in 31-054/31-056.

Prerequisites: 3.53, 2.005, 3.046 or permission of instructor

Grading policy

2 exams 50% (25% each)

Homework 20%

Recitation/Lab Demo 10%

Project 20% (10% oral + 10% written report)

There is no final exam

Lecture and Recitation Schedule

1. Thermodynamics and Kinetics of electrochemical processes

Lec1 - 9/6R Introduction and goal of the course. Global energy needs and challenges, and overview of different energy technologies. Unique characteristics of electrochemical processes.

Handouts for electrochemistry fundamentals: Chapters 1 and 2 of Newman and Thomas-Alyea. Chapters 1 and 2 of Bard and Faulkner.

Handouts for chemical equilibrium: chapter 15-17 of Heat and Thermodynamics by Mark W. Zemansky and Richard H. Dittman

Handouts for classic thermodynamics: Tester and Modell, Thermodynamics and Its Applications, Chapters 3, 4 and 5, particularly sections 3.2, 5.1 and 5.8, describing adiabatic work interactions, the Fundamental Equation of thermodynamics and how it is modified for non P - V work.

Lec2 – 9/11T Thermodynamics and Chemical Thermodynamics
Thermodynamic functions of mixing, Ideal solutions.
Conditions for chemical Equilibrium, chemical potential.
Taught by Visiting Professor R. Savinell from Chemical Engineering at Case Western Reserve University

Rec1 – 9/12W *Example problems*

Lec3 – 9/13R Ideal-gas reactions: Law of Mass Action and Equilibrium constants, Electrochemical potentials, Nernst equation, efficiency. Applications of Nernst equations to concentration cells and Nernstian half-cell potential.
Taught by Visiting Professor R. Savinell from Chemical Engineering at Case Western Reserve University

1st Homework out

Lec4 – 9/18T Standard electrode potentials, Electrode processes (Faradaic and nonfaradaic), Faraday's Law and Description of electrochemical cells. Applications to proton exchange membrane fuel cells.

Rec2 – 9/19W *Example problems and lab demo of thermodynamic or interfacial potential measurements.*

Lec5 – 9/20R The electrified interface, Introduction of the electrical double layer concept. Electron Work function and interfacial potential.

*1st Homework In
2nd Homework out*

Lec6 – 9/25T Motivation for chemical kinetics and electrode kinetics. Chemical kinetic rates - overview. Concepts of surface thermodynamics and kinetics – adsorbate-surface interactions such as physisorption and chemisorption.

Rec 3 – 9/26W Electrical capacitance of the interface and potential of zero charge. Example problems.

Lec7 – 9/27R Langmuir Isotherm (kinetic and thermodynamic standpoints) and Sabatier principle of catalysis

*2nd Homework in
3rd homework out*

Lec8 – 10/02T Surface reactivity and electronic structure – the d band center theory of Hammer and Norskov 1996. Reactivity of O₂ and CO on Pt and PtM alloy surfaces.

Rec4 – 10/03W Potential energy profiles for different modes of adsorption – nonactivated and activated adsorption, and activated dissociative adsorption.

Lec9 – 10/04R Review of Chemical and Electrochemical Thermodynamics concepts and examples

3rd homework in

10/9T Student holidays and no class

Rec5 – 10/10W Example problems (Ethan Crumlin)

Exam1–10/11R Open book exam – Exam I – Electrochemical Thermodynamics
Covers lectures to 9/20, recitations 1-3 and homework 1-3.

Lec10 – 10/16T Macroscopic Butler-Volmer Model for one-step and one electron transfer process. Exchange current density and transfer coefficient.

4th homework out

Rec6 – 10/17W Application in hydrogen electro-oxidation on Pt surfaces. Cyclic voltammetry measurements of adsorption. Hydrogen and OH adsorption. Exchange current densities of different electrocatalysts for oxidation of hydrogen and hydrogen evolution.

Lec11 – 10/18R Microscopic theories of charge transfer. Application of the Butler-Volmer models in oxygen electrode. Activity of different metals for oxygen reduction.

Lec12 – 10/23T Theory of rotating disk and ring-disk measurements of electrode kinetics. Applications to oxygen reduction and hydrogen oxidation

*4th homework in
5th homework out*

Rec7 – 10/24W Example problems and lab demo of rotating disk and ring-disk measurements of electrode kinetics

Lec13 – 10/25R Modes of Transport (diffusion, migration and transport). Transport laws. Concepts of mobility, conductance, transference number and diffusivity. Review of Fick's 1st and 2nd Law.
Taught by Professor R. Savinell

Lec14 – 10/30T Review of Surface and Electrochemical reactions kinetics concepts and examples.

5th homework in

Rec8 – 10/31W Example problems

Lec15 – 11/1/06R Take home exam (no lecture) – Chemical kinetics, surface kinetics and thermodynamics and electrode kinetics
Lectures from 9/25 to 10/23, Homework 4-5 and Recitations 4-7.

Lec16 – 11/6T

- Rec9 – 11/7W Discussion of take home exam
- Lec17 – 11/8R Limiting current densities and ion concentration profiles in infinitely dilute solutions
- Project topics out
- Lec18 – 11/13T Concepts of diffusion coefficients, transference number and mobility. Survey of different liquid, polymer and ceramic materials as electrolytes for ion conduction and different measurement techniques.
- Rec10 – 11/14W Examples and lab demo of conductivity and diffusivity measurements. Lab demo of EIS experiments of Nafion membrane conductivity and micro-SOFCs.
- Lec 19– 11/15R Preparation and properties of nanoparticles by Paul Alivisatos's seminar at MIT.
- Lec20 – 11/20T Electrochemical model and application of porous electrodes Application to Lithium battery technologies. Concepts of intercalation, intercalation thermodynamics, structures and compounds. The state-of-the-art battery technologies for hybrid, plug-in and electrical vehicles.
- Project topics selected
- Rec11 – 11/21W Controlled current methods and potential step methods. Application to conductivity and diffusivity measurements.
- 11/22R Thanksgiving holidays and no class
- Lec22 – 11/27T Basics of Electrochemical impedance spectroscopy (EIS). Application of EIS to conductivity measurements. In-plane and cross-plane conductivity.
- Rec12 – 11/28W Application of EIS to electrode kinetics studies for oxygen electrode. Application of EIS to lithium batteries and electrochemical capacitors.

Lec23–11/29R	Lithium battery technologies. Concepts of intercalation, intercalation thermodynamics, structures and compounds. The state-of-the-art battery technologies for hybrid, plug-in and electrical vehicles.
Lec24 – 12/4T	Proton exchange membrane (PEM) and Solid oxide (SO) fuel cell technologies for transportation. Current performance and current challenges. Overview of Synthesis and processing of catalysts for fuel cells
Rec13 – 12/5W	Lab demo of PEM and SOFC fuel cells
Lec25 – 12/6R	Towards first-principles Electrochemistry Guest lecture by Professor Nicola Mazari from DMSE (to be confirmed)
Lec26 – 12/11T	Photoelectrochemical devices – Graetzel cells, principles, performance and challenges.
12/12W	Project written report due
12/13-12/14	Oral presentations

Other recommended references:

1. **Fuel Cell Systems Explained** by James Larminie and Andrew Dicks, John Wiley & Sons
2. **Fuel Cells: From Fundamentals to Applications (Hardcover)** by Supramaniam Srinivasan, Springer; 1 edition (May 5, 2006)
3. **Fuel Cell Fundamentals (Hardcover)** by Ryan O'Hayre (Author), Suk-Won Cha (Author), Whitney Colella (Author), Fritz B. Prinz, Wiley; Har/Cdr edition (December 2, 2005)
4. **Fundamentals of Electrochemistry (The ECS Series of Texts and Monographs) (Hardcover)** Vladimir S. Bagotsky (Editor)