And we begin… 1

# Lecture #1 of 17

1

Welcome to CHEM 248! 2

Most of the organization of the following *~1000 slides* was designed by Prof. Penner and graciously shared with us. Of course, I alter – and will continue to alter – the slides and flow, but most of the initial vision was his, not mine. Thus, if you like the course, please tell him.

2

Welcome to CHEM 248! 3

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Helpful Pre-(non-)requisite Courses

Chemistry
- Thermodynamics
- Quantum Mechanics
- Kinetics

Physics
- General Physics
- Electricity & Magnetism
- Condensed Matter (Solid-State) Physics

Chemical Engineering
- Transport Phenomena

Materials Science and Engineering
- Theory of Diffusion
- Materials Physics

3

Welcome to CHEM 248! 4

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Hey look! Slide numbers.

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- Transport Phenomena

Materials Science and Engineering
- Theory of Diffusion
- Materials Physics

4

**Our Electro(analytical)chemistry syllabus**: 5

Chem 248: Electrochemistry (http://www.chem.uci.edu/~ardo/echem.html)
Department of Chemistry, UC Irvine, Fall 2023 *Version Date: 2023.09.26*

**Instructor** Professor Shane Ardo (ardo@uci.edu)
*Office Hours*: Mon. @ 8 – 9 am, *and* 5 – 6 pm *(via Zoom; no sessions on M11/13, M12/4)*

**Meeting Times**
*Lecture*: T/Th @ 8 – 9:20 am **in PSCB 240** *(no class on T11/14, Th11/23 (holiday); Zoom link should be used when feeling ill; video-recorded lectures available)*
Final Exam Period is Tues. 12/12 @ 8 – 10 am *(Presentations occur during this time)*

"*Discussion*" (8): Mon. @ 1 – 2:50 pm *or* 3 – 4:50 pm **in RH 453** *(no class on M11/13; Zoom on M12/4)*

*Presentations*: Last *three* meeting periods *(T12/5, Th12/7, T12/12)*

**Course Objectives**
- To understand and explain the theory behind fundamental electrochemical processes
- To be able to design, perform, troubleshoot, and analyze electroanalytical experiments and data
- To quantitatively and qualitatively assess problems, and empirical data from the peer-reviewed literature
- To summarize and explain seminal and recent electrochemical peer-reviewed literature and technologies

**Required Resources**
Electrochemical Methods: Fundamentals and Applications (2nd edition) by A. J. Bard and L. R. Faulkner
ISBN: 978-0-471-04372-0; Chapters Covered: **A:** 1, 15, 4, 5; **B:** 2, 13, 3, 6; ***Extra:*** 12, 9, 10, 16, 17, 18
Peer-Reviewed Journal Articles and Additional Problems (http://www.chem.uci.edu/~ardo/echem.html)
Bio-Logic Potentiostat Software for PC (https://www.biologic.net/support-software/ec-lab-software/)

5

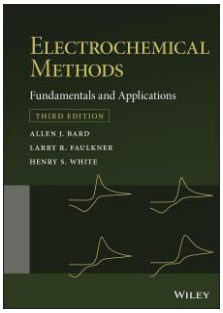
**Discussion sessions** are… actually hands-on (lab) activities! 6

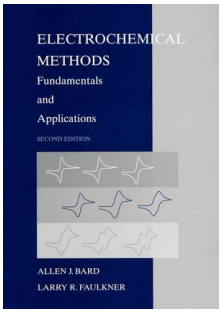
- 8 weeks of Monday "Discussion" sessions (for 15 people… thus far)
  *Audit'ers – if you'd like to participate, please let me know*
- Each section will (ideally) have 7(-ish) people in it; ***is it balanced?***
- Each discussion session has an associated lab activity; I plan to share a link to the video of each lab, as well as a type-written procedure that includes a post-lab assignment, the weekend prior to the activity
- We only have <2 hours to try each lab, so please arrive on time and ready to participate in each discussion session, meaning wearing the appropriate PPE
- Assignments are not due every week, but in general are due after two related lab activities are performed
- There is little time to "discuss" things during discussion sessions, and so please attend office hours for that
- *Discussion on 12/4 is a special opportunity for outreach by asking questions from undergraduate student presentations at Cal State LA*

6

**Our textbook**: 7

Please make sure you have access to the 2nd (on right), or 3rd (on left), edition
(Purchase it if you will perform electrochemistry; it is a top resource.)




7

Electrochemistry: **(UPDATED)** 8

***… where physics and chemistry meet; thus, we need to know our physics!***

**Textbook Resources (also Section 1.6 in B&F)**

(1) "*Electrochemical Methods*" (3rd ed.) by Allen J. Bard and Larry R. Faulkner (UT, Austin) and Henry S. White (Univ. of Utah), John Wiley & Sons, Inc., 2022.
(2) "*Modern Electrochemistry*" (3 volumes: 1, 2A, and 2B; 2nd ed.) by John O'M. Bockris (TAMU), Amulya K. N. Reddy, et al., Springer, 2001.
(3) "*Electrochemical Systems*" (3rd ed.) by John Newman (UC, Berkeley) and Karen E. Thomas-Alyea (Verdox), John Wiley & Sons, Inc., 2004.

Electrochemistry is mostly *physical analytical chemistry* and as a close second is *chemical transport engineering* and as a close third is *materials physics*. Thus, although this course is formally taught out of the UCI Department of Chemistry, you will learn fundamental and applied physics and chemical engineering in this course. Both chemists and non-chemists will be challenged. Electrochemistry requires a strong working knowledge of thermodynamics, chemical kinetics, and transport phenomena. Each of these is a course in itself, and not all in the same departments. That poses a problem. This electrochemistry course is not a required core course, but obviously will draw interest from a range of students with varying and diverse backgrounds. Therefore, topics in the course will be very easy to some and challenging to others, but together we can get through the course and the material. The way the course is structured is two lectures and one hands-on discussion session per week for ten weeks. In addition to discussion of electrochemical phenomena, you will also be directed to seminal literature publications (~50) and will perform 8 "labs" and deliver a synchronous presentation. **This is going to be so much fun!**

8

**Our syllabus** (continued): 9

**Topics Covered** *(tentative)*

| | |
|---|---|
| $A_{1,15}$ | Review+ (Nomenclature, Balancing equations, Electrodes, Potentiostats, Diagrams) |
| $A_{4,5}$ | Mass Transfer (Nernst–Planck equation (migration, diffusion, convection), Fick's laws of diffusion, Cottrell equation, Anson plot, Ultramicroelectrode (UME)) |
| $B_2$ | Thermodynamics (Electrochemical potential, Nernst equation, Underpotential deposition (UPD), Liquid-junction potential, Donnan potential, pH probe, Ion-selective electrodes (ISEs)) |
| $B_{13}$ | Charged Interfaces (Ionic activity, Diffuse double layer and models, Boundary layer) |
| $B_{3,6}$ | Electron Transfer Kinetics (Marcus–Gerischer theory, Butler–Volmer equation, Tafel equation, Catalysis and volcano plots, Cyclic voltammograms, Randles–Sevcik equation, Corrosion) |
| ***Extra*** | Methods (Potential/Current step/sweep/pulse, Hydrodynamic RDE, Impedance spectroscopy, Scanning probe electrochemistry, Spectro-/Photo-electrochemistry) |

**Grading** *(10% of lowest score will be dropped, leaving 90% for course grade determination)*

| | |
|---|---|
| 50% | *Asynchronous Assignments (8)*: "Lab activity" write-up and several related problems due one week after odd-numbered activities (**Mondays @ noon**: **10/9**, **10/23**, **11/6**, **11/27**, *and* **Tues. 12/12 @ 8 a**) |
| 20% | *Asynchronous Exam A* (*24 hours*; available **Mon. 11/6 @ 5 pm** *through* **Mon. 11/13 @ 11 am**) |
| 20% | *Asynchronous Exam B* (*24 hours*; available **Mon. 11/27 @ 5 pm** *through* **Mon. 12/4 @ 11 am**) |
| 10% | *Synchronous Presentation* (~15 min per student; occurs during the last week of classes (**Tues. 12/5** *and* **Thurs. 12/7**), *and* during the final exam period (**Tues. 12/12 @ 8 – 10 am**)) |

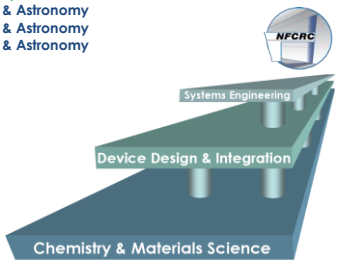
**Course Policies**

Late assignments and make-up exams are not accepted, although *I will regrade exams upon specific request.*
Add/Drop Info (use WebReg): https://www.reg.uci.edu/calendars/quarterly/2023-2024/quarterly23-24.html
UCI Chemistry Enrollment-Related Questions: https://www.chem.uci.edu/studentaffairs/, or chemistry@uci.edu
UCI Laptop Requirements for Students: https://www.oit.uci.edu/undergrads/laptop-requirements-students/
UCI Policy on Academic Integrity and Honesty: https://aisc.uci.edu/policies/academic-integrity/
UCI Human Resources Working Well Student Resources: https://hr.uci.edu/partnership/workingwell/

9

**UCI has a lot of Electrochemists…** 10

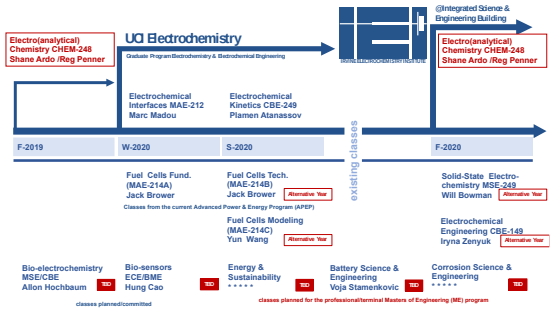
| | | |
|---|---|---|
| Jenny Yang | Chemistry | ➢ Electrochemical energy technologies |
| John Hemminger | Chemistry | ➢ Electrochemical Interfaces |
| Matthew Law | Chemistry | ➢ Electrocatalytic Systems |
| Reginald Penner | Chemistry | ➢ Bio-electrochemistry |
| Rob Corn | Chemistry | |
| Shane Ardo | Chemistry | |
| Huolin Xin | Physics & Astronomy | |
| Phil Collins | Physics & Astronomy | |
| Zuzanna Siwy | Physics & Astronomy | |
| Iryna Zenyuk | CBE | |
| Plamen Atanassov | CBE | |
| Robert Nielsen | CBE | |
| Vojislav Stamenkovic | CBE | |
| Jack Brouwer | MAE | |
| Marc Madou | MAE | |
| Yun Wang | MAE | |
| Will Bowman | MSE | |
| Allon Hochbaum | MSE | |
| Daniel Mumm | MSE | |
| Regina Ragan | MSE | |
| Xiaoqing Pan | MSE | |




… do you work in any of these, or other, groups? Which ones?

10

**… and thus, UCI has a lot of courses in Electrochemistry…** 11




**… and even M.S. and Ph.D. Degree Programs in Electrochemical Engineering!**

11

**… and Electrochemistry is VERY important!** 12

**Advances, Challenges, and Long-Term Opportunities in Electrochemistry: Addressing Societal Needs - A Workshop**

*The U.S. National Academies of Sciences, Engineering, and Medicine (2019)*

https://www.nationalacademies.org/our-work/advances-challenges-and-long-term-opportunities-of-electrochemistry-addressing-societal-needs-a-workshop

"Advances in electrochemistry are enabling new developments in energy storage, energy conversion, catalysis, synthesis, separations, and instrumentation. The workshop Advances, Challenges, and Long-Term Opportunities in Electrochemistry: Addressing Societal Needs, held in Washington, DC, on November 18-19, 2019, provided a venue for scientists in various sectors to discuss electrochemistry applications and the future of the field. Specifically, the workshop reviewed emerging applications of electrochemistry; discussed instrumentation, educational, human-resource, and other needs to enable advances in electrochemistry; and highlighted new technologies and processes that could be developed in light of breakthroughs in fundamental and applied research in electrochemistry. Ultimately, the workshop explored how electrochemistry could transform technologies related to various applications. This Proceedings of a Workshop-in Brief summarizes the presentations and discussions that took place during the workshop."

12

Let's get started…

13

# Introduction and Review of Electrochemistry

Chapter "0"

… sort of…

13

14

**Looking forward… our review of Chapter "0"**

- **Cool applications**
- *Redox half-reactions*
- *Balancing electrochemical equations*
- *History of electrochemistry and Batteries*
- *IUPAC terminology and* $E_{cell} = E_{red} - E_{ox}$
- *Thermodynamics and the Nernst equation*
- *Common reference electrodes*
- *Standard and Absolute potentials*
- *Latimer and Pourbaix diagrams*
- *Calculating* $E_{cell}$ *under non-standard-state conditions*
- *Conventions*

14

Q: What processes occur in electrochemistry?

15

A: Fall, 2023: Those that occur when the electrochemical potential of **electrons in a solid** influence, or are influenced by, **chemical reactions and/or transport**

A: Spring, 2019: Those that occur when the electrochemical potential of **electrons in a solid** influence, or are influenced by, **chemical reactions**, including…

A: Winter, 2017: Those involving the motion/transport of charge – carried by entities other than *unsolvated* electrons and holes – through phase(s), or the transfer of charge across interface(s).

15

Q: What processes occur in electrochemistry? 16

A: Winter, 2017: Those involving the motion/transport of charge – carried by entities other than *unsolvated* electrons and holes – through phase(s), or the transfer of charge across interface(s).

*Example:* Electroplating

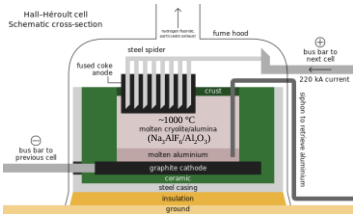
https://lmchromecorp.com/

16

Q: What processes occur in electrochemistry? 17

A: Winter, 2017: Those involving the motion/transport of charge – carried by entities other than *unsolvated* electrons and holes – through phase(s), or the transfer of charge across interface(s).

*Example:* Aluminum extraction




http://en.wikipedia.org/wiki/Hall%E2%80%93H%C3%A9roult_process

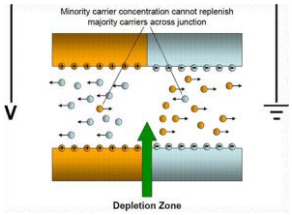
17

Q: What processes occur in electrochemistry? 18

A: Winter, 2017: Those involving the motion/transport of charge – carried by entities other than *unsolvated* electrons and holes – through phase(s), or the transfer of charge across interface(s).

*Example:* ionic circuits

Prof. Zuzanna Siwy (UCI)




http://www.physics.uci.edu/~zsiwy/

18

Q: What processes occur in electrochemistry? 19

A: Winter, 2017: Those involving the motion/transport of charge – carried by entities other than *unsolvated* electrons and holes – through phase(s), or the transfer of charge across interface(s).

*Example:* corrosion

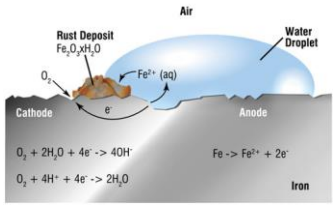
http://www.greenprophet.com/2012/11/energy-solar-rust-israel/

19

Q: What processes occur in electrochemistry? **(UPDATED)** 20

A: Winter, 2017: Those involving the motion/transport of charge – carried by entities other than *unsolvated* electrons and holes – through phase(s), or the transfer of charge across interface(s).

*Example:* corrosion




https://www.machinerylubrication.com/Read/29116/inhibiting-rust-corrosion

20

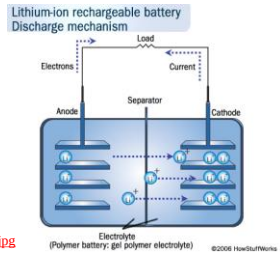
Q: What processes occur in electrochemistry? 21

A: Winter, 2017: Those involving the motion/transport of charge – carried by entities other than *unsolvated* electrons and holes – through phase(s), or the transfer of charge across interface(s).

*Example:* $Li^+$ battery

***Nobel Prize in Chemistry in 2019!***
https://www.nobelprize.org/prizes/chemistry/2019/press-release/

http://www.evworld.com/images/a123_csize.jpg



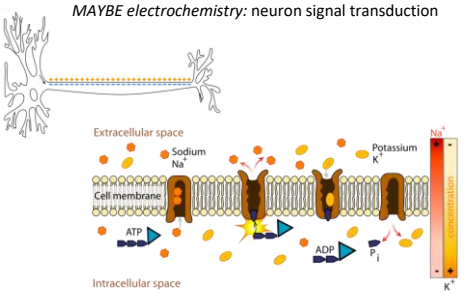

http://auto.howstuffworks.com/fuel-efficiency/vehicles/lithium-ion-battery-car1.htm

21

Q: What processes occur in electrochemistry? 22

A: Winter, 2017: Those involving the motion/transport of charge – carried by entities other than *unsolvated* electrons and holes – through phase(s), or the transfer of charge across interface(s).

*MAYBE electrochemistry:* neuron signal transduction

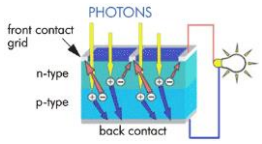



22

Q: What processes occur in electrochemistry? 23

A: Winter, 2017: Those involving the motion/transport of charge – carried by entities other than *unsolvated* electrons and holes – through phase(s), or the transfer of charge across interface(s).

***NOT electrochemistry****:* pn-junction photovoltaic cell




http://www.azom.com/article.aspx?ArticleID=3744

http://newscenter.lbl.gov/2011/09/15/tracking-the-sun-iv/

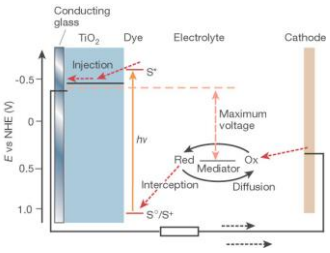
23

Q: What processes occur in electrochemistry? 24

A: Winter, 2017: Those involving the motion/transport of charge – carried by entities other than *unsolvated* electrons and holes – through phase(s), or the transfer of charge across interface(s).

*Example:* dye-sensitized solar cell

Prof. Michael Grätzel (EPFL)




Grätzel, *Nature*, 2001, *414*, 338

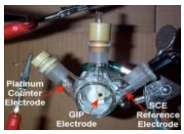
24

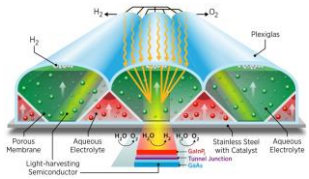
Q: What processes occur in electrochemistry? 25

A: Winter, 2017: Those involving the motion/transport of charge – carried by entities other than *unsolvated* electrons and holes – through phase(s), or the transfer of charge across interface(s).

*Example:* photoelectrochemical water electrolysis (splitting)

Dr. John Turner (NREL)



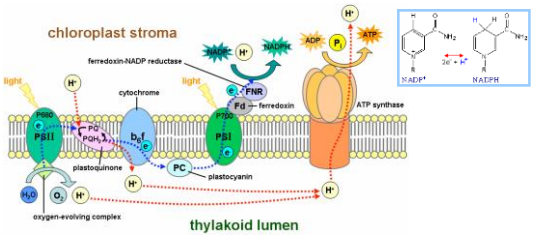

https://www.nrel.gov/hydrogen/hydrogen-production-delivery.html

25

Q: What processes occur in electrochemistry? 26

A: Winter, 2017: Those involving the motion/transport of charge – carried by entities other than *unsolvated* electrons and holes – through phase(s), or the transfer of charge across interface(s).

*PROBABLY electrochemistry:* photosynthesis in green plants



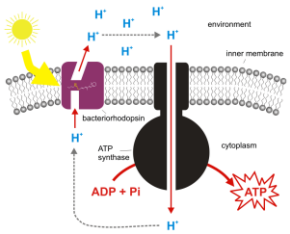

http://en.wikipedia.org/wiki/Photosystem_II

26

Q: What processes occur in electrochemistry? 27

A: Winter, 2017: Those involving the motion/transport of charge – carried by entities other than *unsolvated* electrons and holes – through phase(s), or the transfer of charge across interface(s).

*MAYBE Electrochemistry:* Archaea photosynthesis




http://en.wikipedia.org/wiki/Bacteriorhodopsin

27

28

so we can already conclude that electrochemistry is...

... super cool!

... extremely diverse.

... at the heart of some very important, and still unsolved, scientific and technological challenges.

... and consequently, an extremely active area of scientific endeavor.

28

... wow, those were some neat applications... 29

... I wish I could learn more about all of them!

29

... wow, those were some neat applications... 30

... I wish I could learn more about all of them!

... **Lucky you! ... Lucky us!**

- Synchronous presentation: 12 min max + 3 min for Q&A, as 6 – 8 slides *emailed to me the day before the presentation*
- <u>One seminal and/or review publication (~70% of the time)</u>; include background, where and when it is used, why it is useful, and the nitty gritty of how it works; **your main goal should be to bridge information presented in the course to your topic, and/or teach us something entirely new**
- <u>One recent publication (within the last 5 years) (~30% of the time)</u>; include what the paper did, the major discovery, and a critical electrochemical assessment of their data interpretation, **including at least one graph or plot of useful data**!

... this, plus the discussion assignments, equal 60% of your course grade, so take them seriously, but **HAVE FUN**!

30

**e-Presentation**… topics… include… 31

- fast electrochemistry (5.9.1)
- low conductivity electrochemistry (5.9.2)
- rotating (ring) disk electrochemistry (9.3, 9.4)
- electro-osmotic flow (9.8.1)
- electrochemical impedance spectroscopy (10.4)
- bulk (water) electrolysis (11, 11.5, 11.6)
- thin-layer electrochemistry (11.7)
- stripping analysis (11.8)
- coupled reactions / catalysis (6.6, 12, 12.3)
- modified electrodes (14, 14.5.2)
- electrochemical scanning tunneling microscopy (16.2)
- scanning electrochemical microscopy (16.4)
- spectroelectrochemistry (17.1, 17.2)
- in situ, operando spectroscopy (17.3, 17.6)
- electrochemical quartz crystal microbalance (17.5)
- electro-generated chemiluminescence (18.1)
- aluminum extraction and processing
- bipolar electrochemistry
- electrodeposition / electroless deposition
- chlor-alkali process
- polymer-electrolyte fuel cells
- solid-oxide fuel cells / electrolyzers
- batteries (acid/base; intercalation)
- redox flow batteries
- electrochemical supercapacitors
- (bio)sensors
- electrodialysis
- nanopore/nanorod ion conductors

… **or propose your own to me**… but I really do prefer topics from this list

You will get one of your top 5 choices…

… more info to come later in the quarter

31

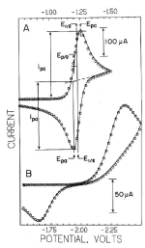
**Course goal**, i.e. the best 2-hour-long final-exam question *ever*! 32

**Q: Explain cyclic voltammetry.**

**Topics Covered**

| | |
|---|---|
| $A_{1,15}$ | Review+ (Nomenclature, Balancing equations, Electrodes, Potentiostats, Diagrams) |
| $A_{4,5}$ | Mass Transfer (Nernst–Planck equation (migration, diffusion, convection), Fick's laws of diffusion, Cottrell equation, Anson plot, Ultramicroelectrode (UME)) |
| $B_2$ | Thermodynamics (Electrochemical potential, Nernst equation, Underpotential deposition (UPD), Liquid-junction potential, Donnan potential, pH probe, Ion-selective electrodes (ISEs)) |
| $B_{13}$ | Charged Interfaces (Ionic activity, Diffuse double layer and models, Boundary layer) |
| $B_{3,6}$ | Electron Transfer Kinetics (Marcus–Gerischer theory, Butler–Volmer equation, Tafel equation, Catalysis and volcano plots, Cyclic voltammograms, Randles–Sevcik equation, Corrosion) |
| *Extra* | Methods (Potential/Current step/sweep/pulse, Hydrodynamic RDE, Impedance spectroscopy, Scanning probe electrochemistry, Spectro-/Photo-electrochemistry) |

From syllabus




Evans, …, Kelly, *J. Chem. Educ.* 1983, *60*, 290

32

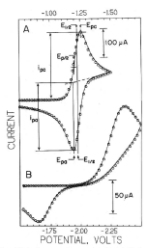
**Course goal**, i.e. the best 2-hour-long final-exam question *ever*! 33

**Q: Explain cyclic voltammetry.**

**Topics Covered**

| | |
|---|---|
| $A_{1,15}$ | Review+ (Nomenclature, Balancing equations, Electrodes, Potentiostats, Diagrams) |
| $A_{4,5}$ | Mass Transfer (Nernst–Planck equation (migration, diffusion, convection), Fick's laws of diffusion, Cottrell equation, Anson plot, Ultramicroelectrode (UME)) |
| $B_2$ | Thermodynamics (Electrochemical potential, Nernst equation, Underpotential deposition (UPD), Liquid-junction potential, Donnan potential, pH probe, Ion-selective electrodes (ISEs)) |
| $B_{13}$ | Charged Interfaces (Ionic activity, Diffuse double layer and models, Boundary layer) |
| $B_{3,6}$ | Electron Transfer Kinetics (Marcus–Gerischer theory, Butler–Volmer equation, Tafel equation, Catalysis and volcano plots, Cyclic voltammograms, Randles–Sevcik equation, Corrosion) |
| *Extra* | Methods (Potential/Current step/sweep/pulse, Hydrodynamic RDE, Impedance spectroscopy, Scanning probe electrochemistry, Spectro-/Photo-electrochemistry) |

From syllabus




**Course philosophy**

**Theory/Experiments** *versus* **Technologies (me** *vs* **you)**

I will teach the theory, history, and experimental specifics, and you will teach the technologies, and real-world and academic state-of-the-art

Evans, …, Kelly, *J. Chem. Educ.* 1983, *60*, 290

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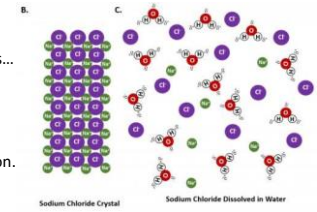
… some people think ions are more important than electrodes… **(BRIEFLY)** 34
… and I am one of them!

FYI, John O'M. Bockris's Modern Electrochemistry textbook series has the following 3 volumes…
**1: Ionics** (pp. 1 – 767)
**2A: Fundamentals of Electrodics** (pp. 771 – 1534)
**2B: Electrodics in Chemistry, Engineering, Biology and Environmental Science** (pp. 1539 – 2053)

… let's start to discuss ions…
… and how to drive their reactions…

… and let's use the board…

… and finish our discussion…
… during discussion session on Mon.




https://brainly.com/question/14682139

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