Practical Electrochemistry

Advanced Electrochemistry
Review Potentiostat

**Basic idea:** control $E_{WE}$ relative to $E_{RE}$ using a feedback loop

a. You tell the potentiostat what $E_{WE}$ vs $E_{RE}$ should be

b. Potentiostat measures (using high impedance voltmeter) what $E_{WE}$ vs $E_{RE}$ actually is.

c. Potentiostat applies a voltage between the WE and the CE and measures the resulting current

d. Potentiostat uses to feedback to apply whatever voltage (and current) between WE and CE so that $E_{WE}$ vs $E_{RE}$ is what you set.

Danger: what happens if RE is damaged or RE cable not hooked up?
Typical Potentiostats
Electrochemical Cells
Analytical Cell

- Currents typically small. Precise conditions (T, purge gas, etc. important)

http://www.bio-logic.info/potentiostat/glassware_cells.html#SVC-2_Voltammetry_cell_
Cell with separate CE compartment

- Keeps CE product away from WE

Imagine that you want to study $O + e^- \rightarrow R$
You start only with $O$
You reduce $O$ at the WE.
What happens at the CE?
Bulk Electrolysis

• Goal to convert O to R, for example as fast as possible.
• Used for electrosynthesis, etc.

Typically stir rapidly

Simple Cells Work Too

![Image of a simple cell with "1 M KOH" label and an angled three-neck flask.](image-url)
Working Electrodes
Typical disc working electrodes

Common materials are Pt, Au, and GC. Can make your own WE by embedding wire into epoxy/glass tube and sanding/polishing tip.

Working Electrode Polishing

Important to get mirror polish smooth, clean electrode surface

Typically using 50 nm diamond or alumina paste for gentle polish of already smooth electrode.

To remove large scratches, start with 1200 grit wet-dry sand paper and polish

Through grits: 10 μm, 3 μm, 1 μm, .3 μm, 0.1 μm, 50 nm

Rinse/sonicate with DI water between different grits.

http://www.bio-logic.info/potentiostat/glassware_cells.html#SVC-2_Voltammetry_cell
Counter (auxiliary) electrodes

Typically Pt used as the CE material – it is very inert and easy to clean (via Piranha solution or via a flame)

Other materials, such as Carbon are used when very large surface areas are needed.

Reference Electrodes
Aq. NHE or SHE

Standard hydrogen electrode scheme:
(1) platinized platinum electrode
(2) hydrogen gas
(3) Acid solution with an activity of $\text{H}^+=1 \text{ mol/l}$
(4) hydroseal for prevention of oxygen interference
(5) reservoir via which the second half-element of the galvanic cell should be attached

Challenges, need $\text{H}_2$ source, Pt must be very clean! Rarely used.
Other Aqueous Reference Electrodes

- **Vycor - porous glass tip**
- SCE saturated calomel electrode
- **AgCl coated Ag wire**
- Sat. KCl filling solution
- **HgO(s) + 2H⁺ + 2e⁻ → Hg(II) + H₂O**
- **Hg|HgO ref. electrode**
- Often used in basic solutions

**AgCl(s) + e⁻ ⇌ Ag(s) + Cl⁻**

Make your own by anodizing (~ 5 mA) Ag wire and placing in sat. KCl sol.

Non-Aqueous Reference Electrodes

Ag wire quasi-reference electrode (forms stable potential (Ag|Ag⁺) in most non-aqueous electrolytes). But, must calibrate versus a known redox couple to determine potential in that solution (e.g. Fc|Fc⁺)

Non-aqueous Silver/Silver Ion (Ag/Ag⁺) Reference Electrode

Ag wire in ~ 1 mM AgNO₃ in electrolyte of choice
The reference electrode is placed inside the Luggin. The tip of the glass capillary is placed directly next to the working electrode surface. This minimizes uncompensated resistance.
Solvents and Electrolytes
Aqueous Electrochemistry

• Use 18.2 MΩhm water (i.e. no trace metal ion content)
• Often sparge with inert gas to remove dissolved O₂.
• Typically have supporting electrolyte from 0.1 M to 1 M
  – The electrolyte increases the conductivity of the electrolyte so that the ionic current can flow without significant voltage drop
Aqueous Supporting Electrolytes

• 1.0 M KCl (will form Cl\textsubscript{2} under oxidizing conditions)
• 0.5 M K\textsubscript{2}SO\textsubscript{4}
• 1 N H\textsubscript{2}SO\textsubscript{4} or HClO\textsubscript{4} (acid electrolytes, can purchase with 6N purity)
• 0.1 M – 1 M KOH (basis electrolyte)
• If electrochemical reaction being studied consumes or generates protons, must use buffer (e.g. phosphate etc) near n
Buffers

• If electrochemical reaction being studied consumes or generates protons or (hydroxide), must use buffer @ ~ 0.1 M (e.g. phosphate etc.) if in a pH range ~ 2-11.

• Without buffer pH gradients develop at the electrode surface, change reaction conditions.
Stability Limits

V vs. SCE

- Aqueous
  - Pt
    - $1 \text{ M } H_2SO_4(Pt)$
    - pH 7 Buffer (Pt)
    - $1 \text{ M } NaOH(Pt)$
  - Hg
    - $1 \text{ M } H_2SO_4(Hg)$
    - $1 \text{ M } KCl(Hg)$
    - $1 \text{ M } NaOH(Hg)$
    - $0.1 \text{ M } Et_4NOH(Hg)$
  - C
    - $1 \text{ M } HClO_4(C)$
    - $0.1 \text{ M } KCl(C)$

The figure shows a series of redox potentials for various solutions, with the standard potential $E_0$ for $H^+ \rightarrow H$ depending on the pH.
Non-aqueous Electrochemistry

- Usually use highly purified, dry organic solvents
  - acetonitrile
  - dichloromethane
- Old days – distill under $\text{N}_2$ from drying agent (e.g. sodium) onto activated molecular sieves
- These days – get from solvent purification system, store over activated sieves; or buy in Sure-Seal bottle.
Non-Aqueous Supporting Electrolyte Salts

• Typically have bulky organic cations to solubilize in organic solvent
  – TBABF$_4$, TBAPF$_6$, are commonly used
• Li salts also highly soluble, e.g. LiClO$_4$
• Purification: recrystallized 2-3 times from appropriate solvent
• Drying: typically difficult to remove trace water. Drying > 24 hrs. at 100-150 C under vacuum (<50 mtorr) recommended.
• Can also by some salts “dry, electrochemical grade” from Sigma-Aldrich directly.
Non-Aqueous stability limits

Much larger range than aqueous conditions!
Useful Practical References

• Laboratory Techniques in Electroanalytical Chemistry, Second Edition, Peter Kissinger, William R. Heineman

• Handbook of Electrochemistry Cynthia G. Zoski