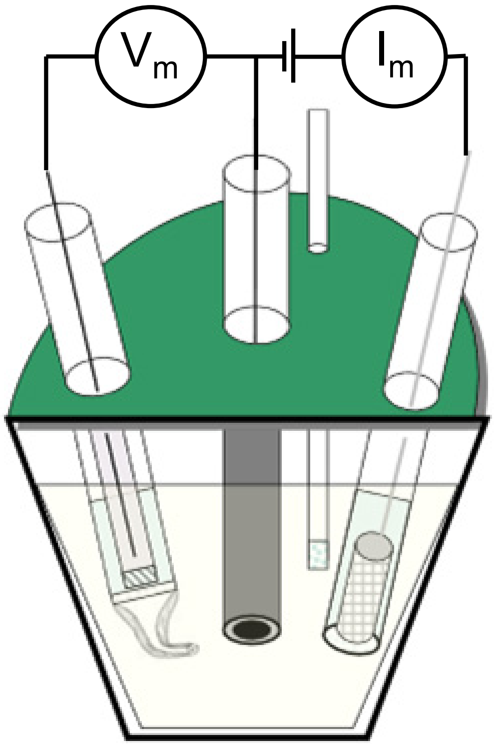
Practical Electrochemistry

Advanced Electrochemistry

Review Potentiostat

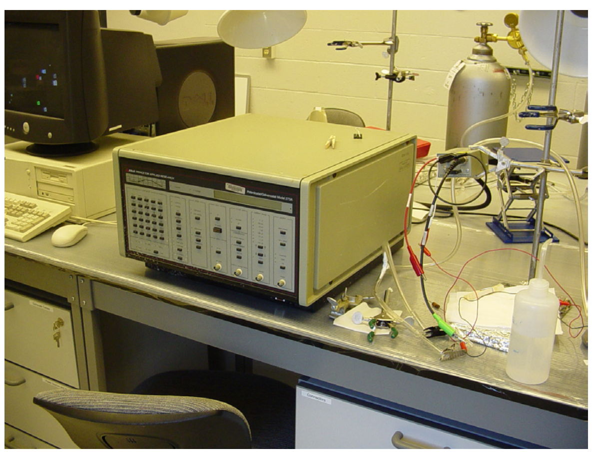
Basic idea: control E_{WE} relative to E_{RE} using a feedback loop

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

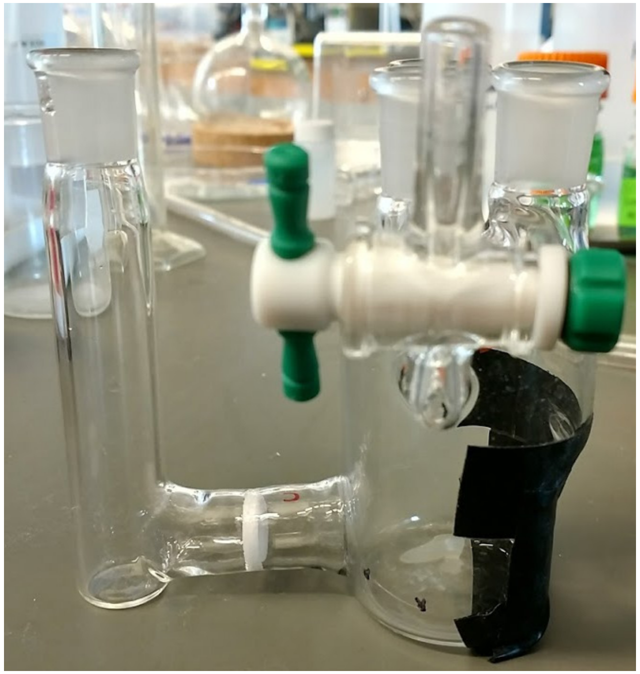
Analytical Cell

- 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

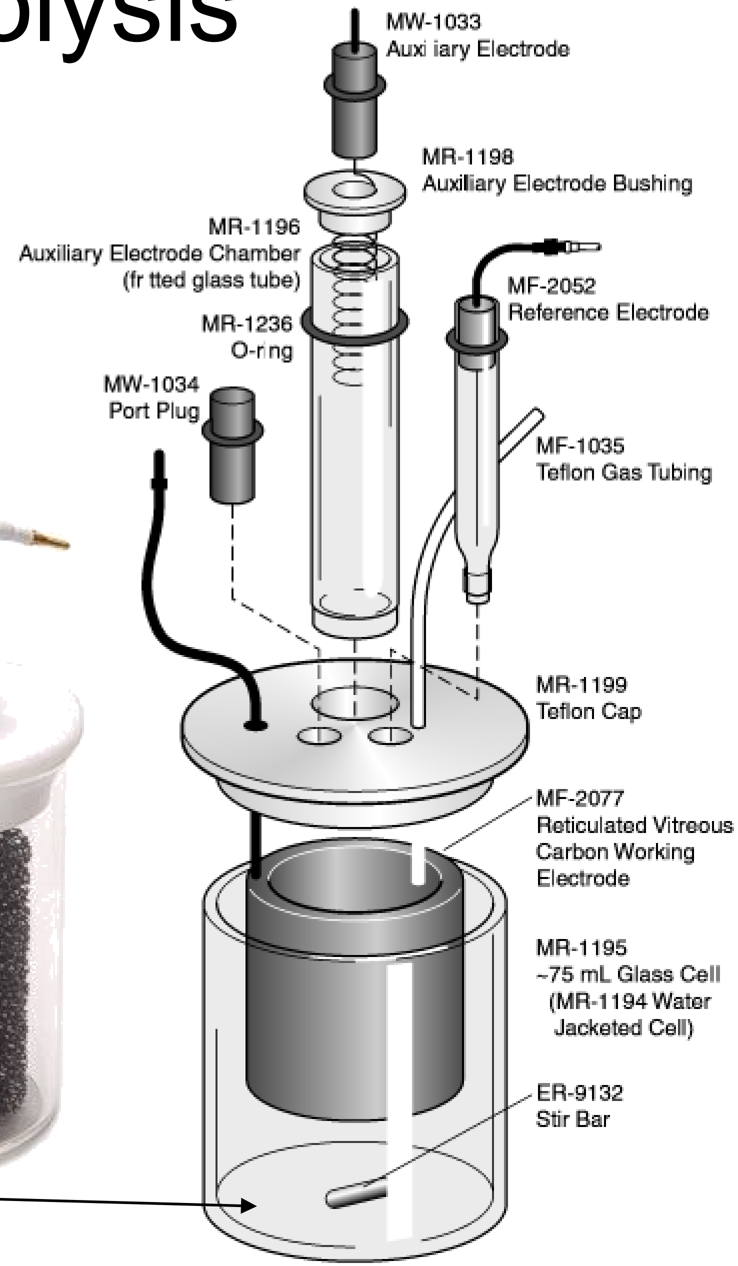
- Keeps CE product away from WE



Imagine that you want to study O + e- -> 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

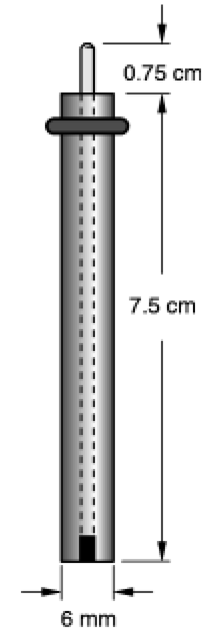
http://www.basinc.com/products/ec/bulk.php

Simple Cells Work Too

Angled

Working Electrodes

Typical disc working electrodes

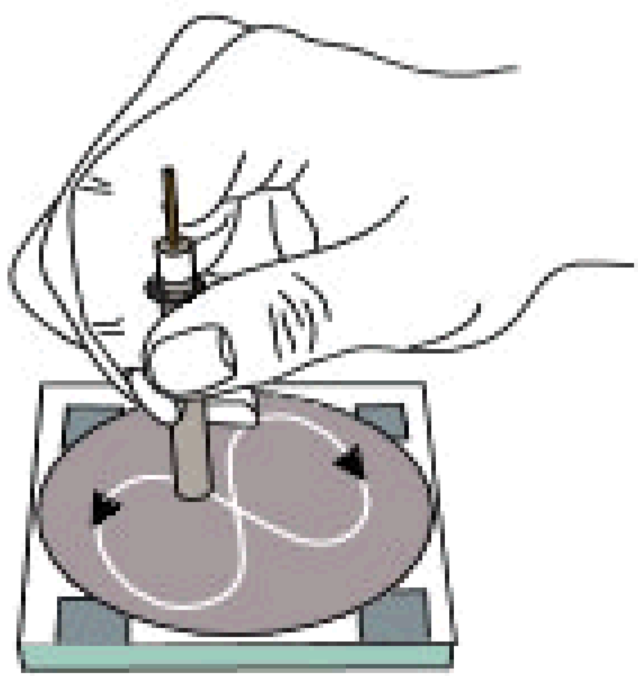


Common materials are Pt, Au, and GC.
Can make your own WE by embedding wire into epoxy/glass tube and sanding/polishing tip

http://www.basinc.com/products/ec/sve.php

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 um, 3 um, 1 um, .3 um, 0.1 um, 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 make your Own using inert epoxy (Hysol 1C) glass tubing, and Pt wire.

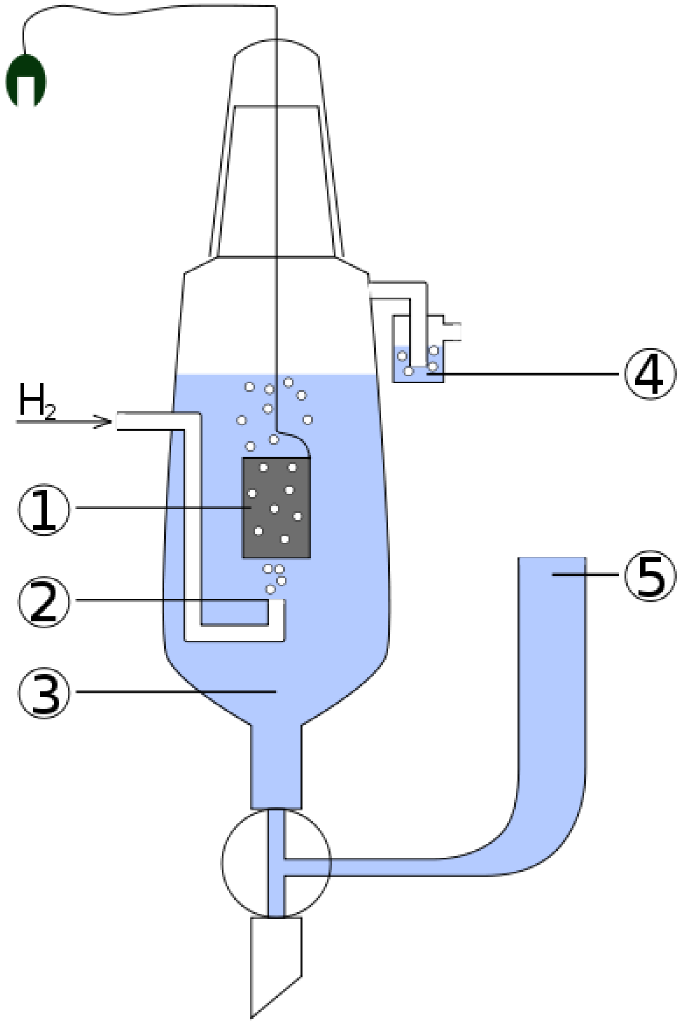
Typically Pt used as the CE material – it is very inert and easy to clean (via Piranha solution or via a flame)

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

http://www.basinc.com/products/ec/auxele.php

Reference Electrodes

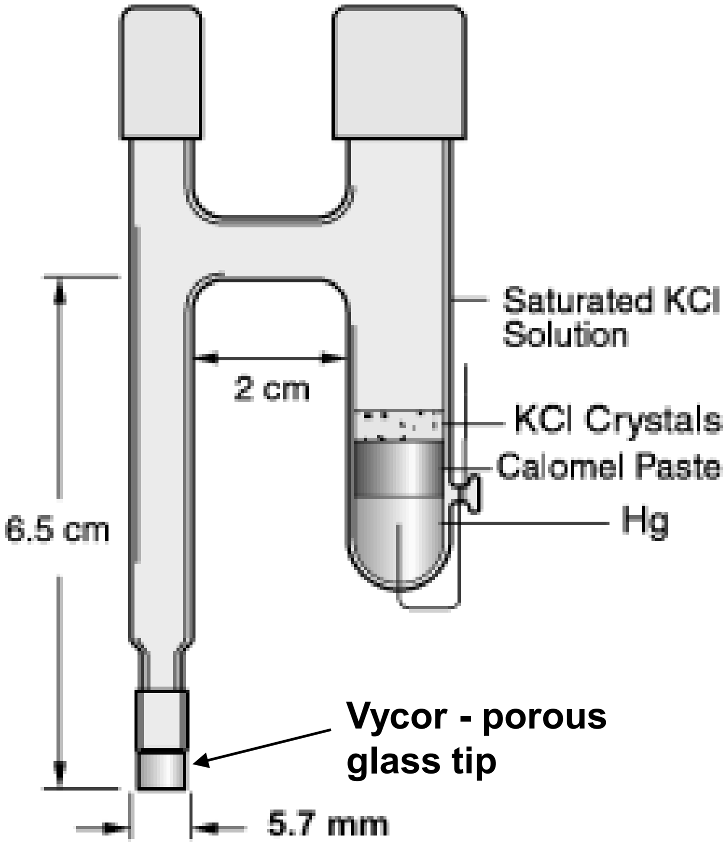
Aq. NHE or SHE



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

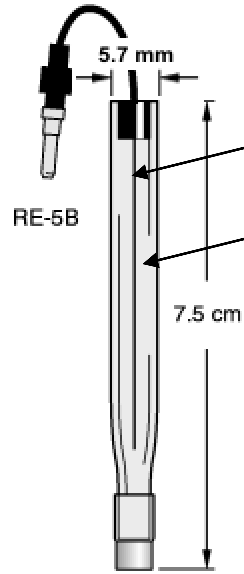
Challenges, need H_2 source, Pt must be very clean! Rarely used.

Other Aqueous Reference Electrodes



SCE saturated calomel electrode

$$AgCl(s) + e^- \leftrightharpoons Ag(s) + Cl^-$$



Ag|AgCl Reference electrode –

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

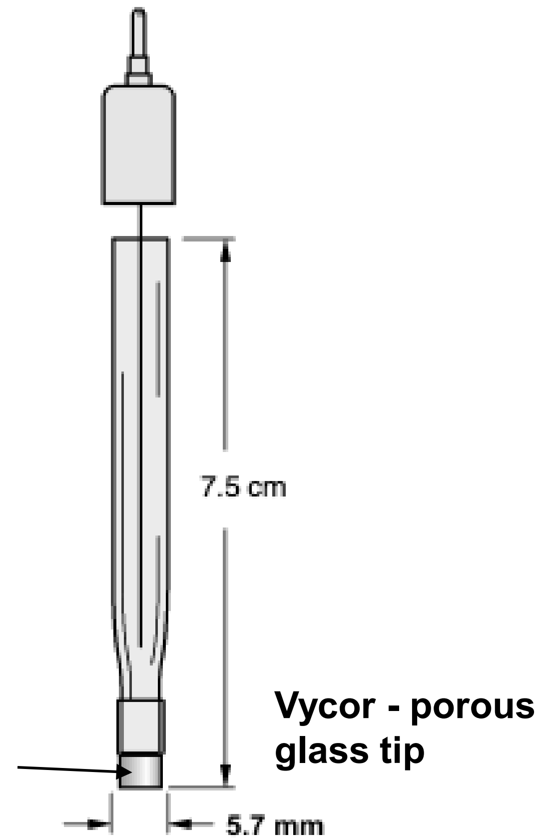
Hg|HgO ref. electrode
Often used in basic solutions

HgO(s) + 2H+ + 2e- → Hg(l) + H2O

http://www.basinc.com/products/ec/ref.php

Non-Aqueous Reference Electrodes

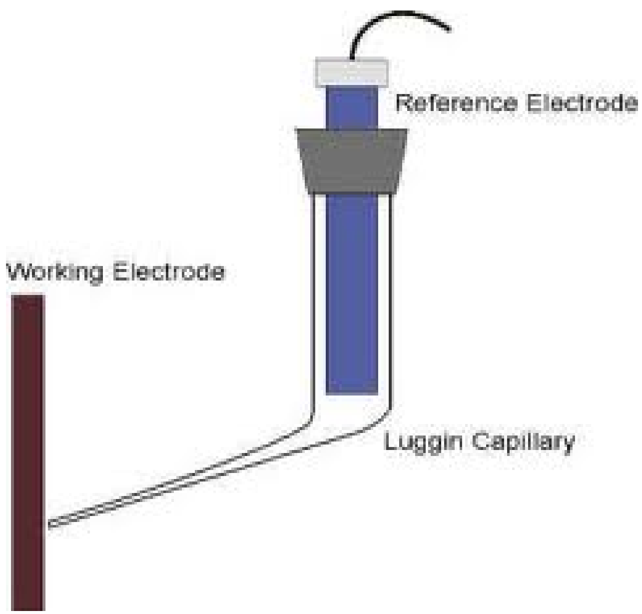
Non-aqueous Silver/Silver Ion (Ag/Ag^+) Reference Electrode

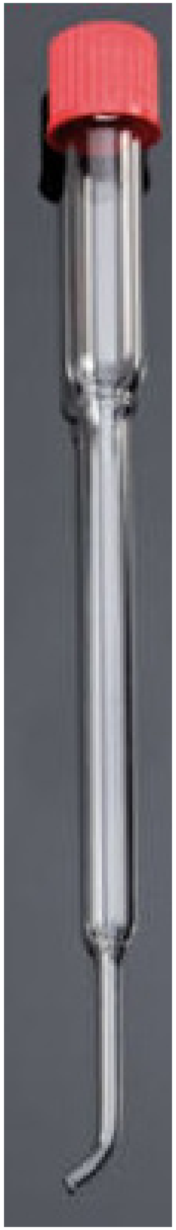


Ag wire in ~ 1 mM $AgNO_3$ in electrolyte of choice

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 ootential in that solution (e.g. $Fc|Fc^+$)

Luggin Capillary for RE





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 MOhm water (i.e. no trace metal ion content)
- Often sparge with inert gas to remove dissolved O_2.
- 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

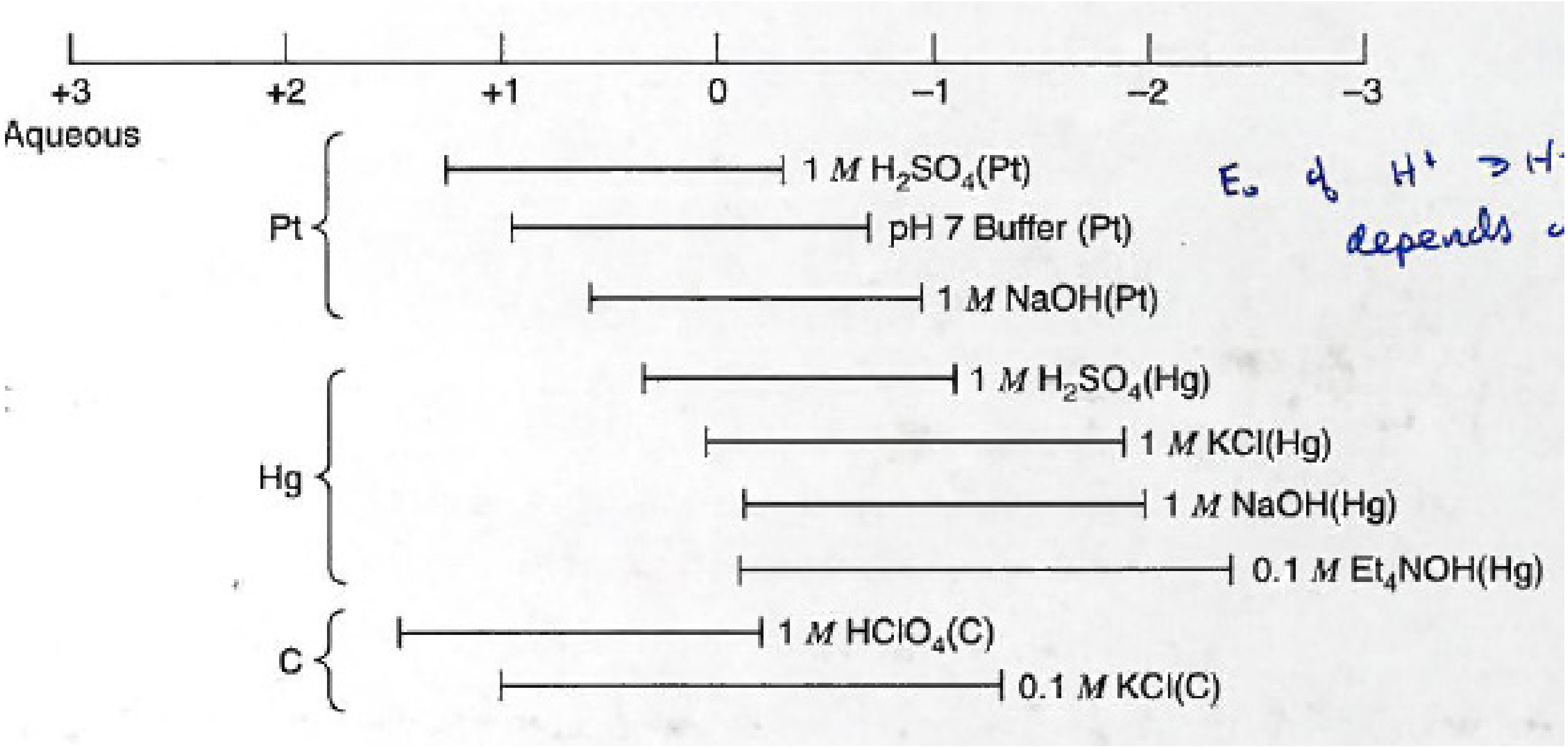
- 1.0 M KCl (will form Cl_2 under oxidizing conditions)
- 0.5 M K_2SO_4
- 1 N H_2SO_4 or $HClO_4$ (acid electrolytes, can purchase with 6N purity)
- 0.1 M – 1 M KOH (basis electrolyte)
- If electrochemical reaction being studied consumes or generates protons, must use buffer (e.g. phosphate etc) near 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



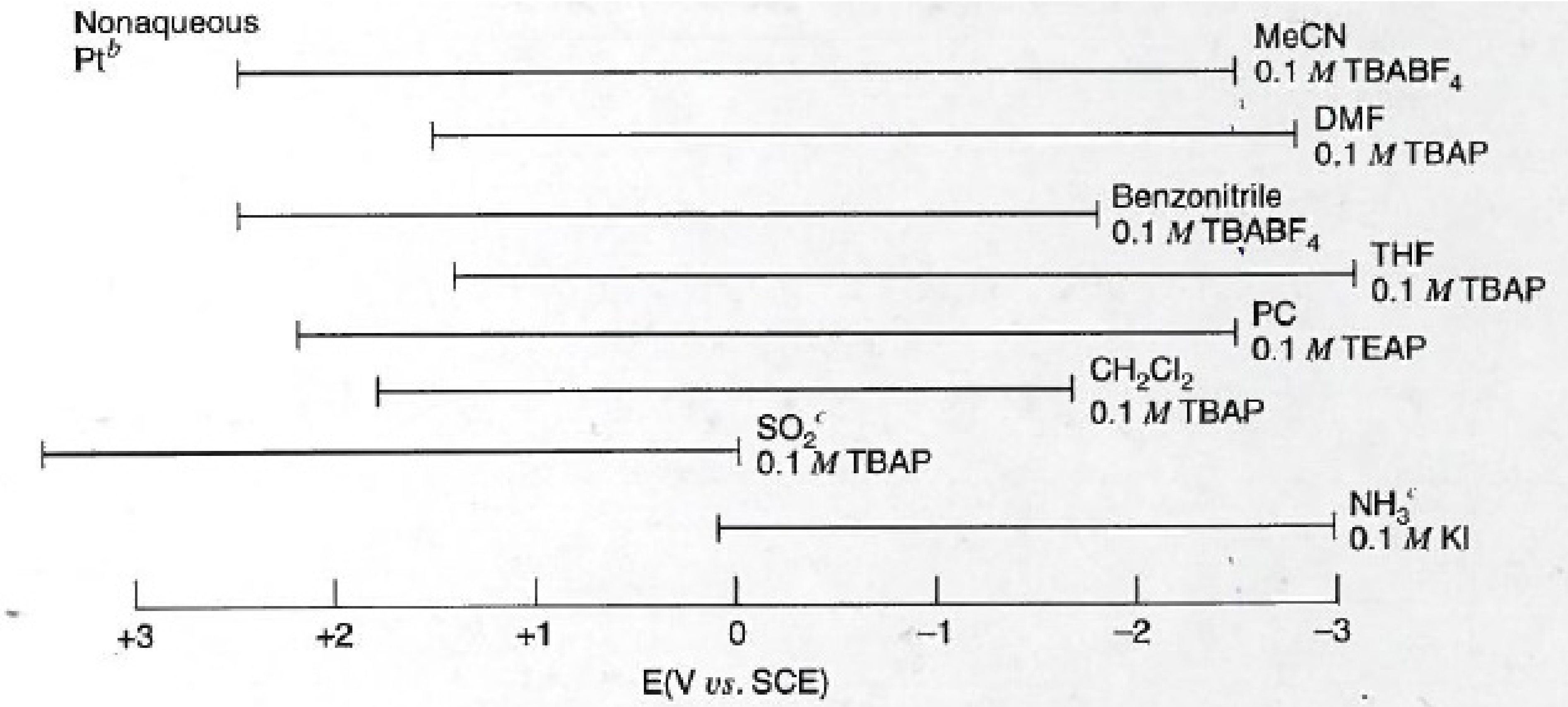
Non-aqueous Electrochemistry

- Usually use highly purified, dry organic solvents
  - acetonitrile
  - dichloromethane
- Old days – distill under 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