



# Electrochemistry

CHEM 5390

# Introduction

## Conduction in a cell

Charge is conducted by:

- The electrodes and leads – involves electrons
- The solution – involves migration of cations and anions
- The interface – involves oxidation and reduction

# Introduction

## Conduction in a cell

Charge is conducted by:

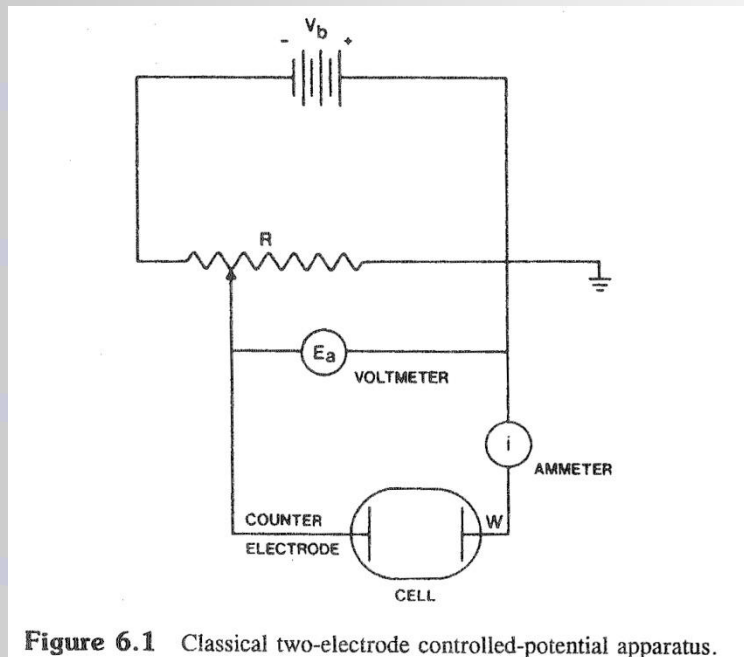
- The electrodes and leads – involves **electrons**
- The solution – involves migration of cations and anions
- The interface – involves oxidation and reduction

# Electrochemical Cell

For two electrodes in solution (a cell) – there is a working electrode (WE) and a counter electrode (CE).

These two electrodes are connected to a circuit which applies a potential difference to the cell.

# Electrochemical Cell



**Figure 6.1** Classical two-electrode controlled-potential apparatus.

The applied potential,  $E_a$  is measured between the WE and CE and the resulting current is measured in the WE lead and WE is tied to ground potential.

# Electrochemical Cell

The counter electrode in the two electrode system serves two functions:

- completes the circuit, allowing charge to flow through the cell
- maintains a constant interfacial potential difference regardless of the current

It is better if these 2 functions are separated to two electrodes.

Thus we can replace the CE with an auxiliary electrode (AUX) and a reference electrode (REF)

# Electrochemical Cell

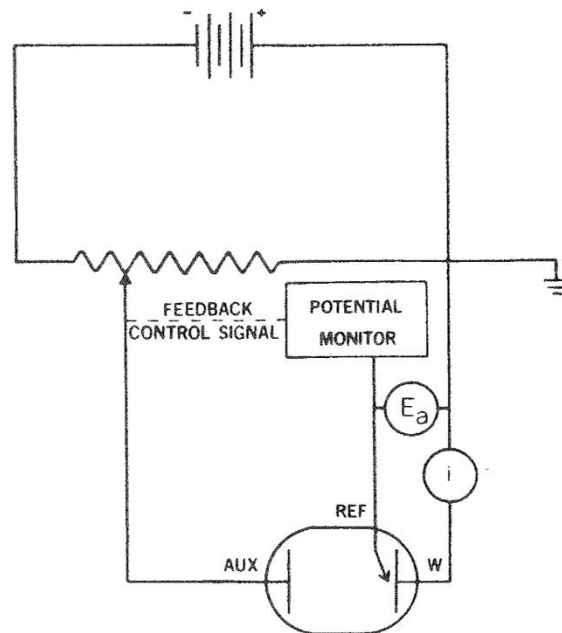
## The auxiliary electrode (AUX)

- completes the circuit, allowing charge to flow through the cell

## The reference electrode (REF)

- maintains a constant interfacial potential difference regardless of the current

# Electrochemical Cell

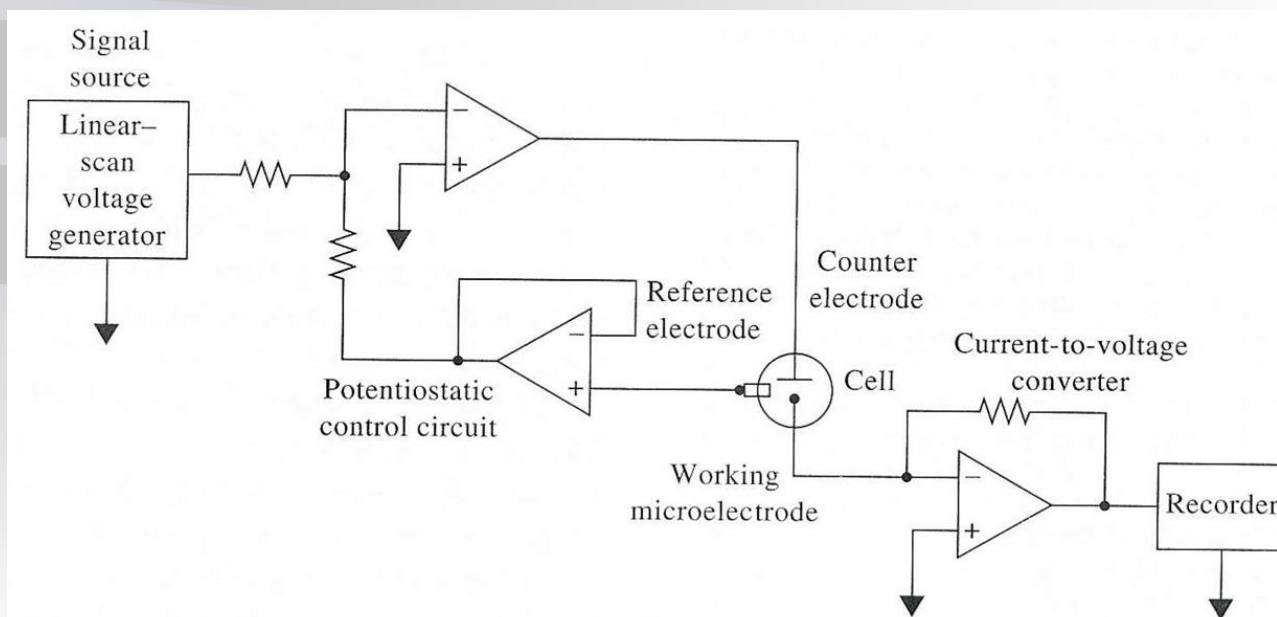


**Figure 6.4** Schematic representation of a primitive three-electrode controlled-potential apparatus.

# Electrodes

## Requirements for the electrodes:

- Working
- Counter (auxiliary)
- Reference



**Figure 25-2** A system for potentiostatic three-electrode linear-scan voltammetry.

# Electrodes

## Working

- The potential is controlled with respect to the reference.
- The potentials at which oxidation and reduction occur are the standard potentials,  $E^\circ$ .

# Electrodes

## Working

Working electrode material:

Metals: Ag, Au, Pt, Ni, SS, etc...

Carbon

Mercury

# Electrodes

## Working

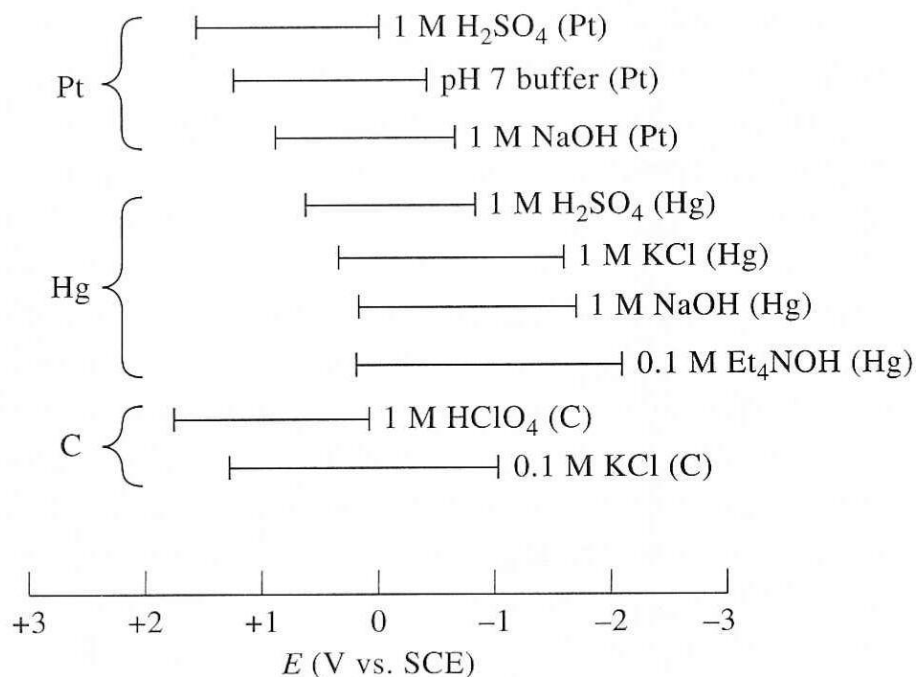
Working electrodes have a potential window.

This window determines the range of potentials the working electrode can be used.

The window is limited on the positive side by the oxidation of water to  $O_2(g)$  and on the negative side by the reduction of water to  $H_2(g)$ .

# Electrodes

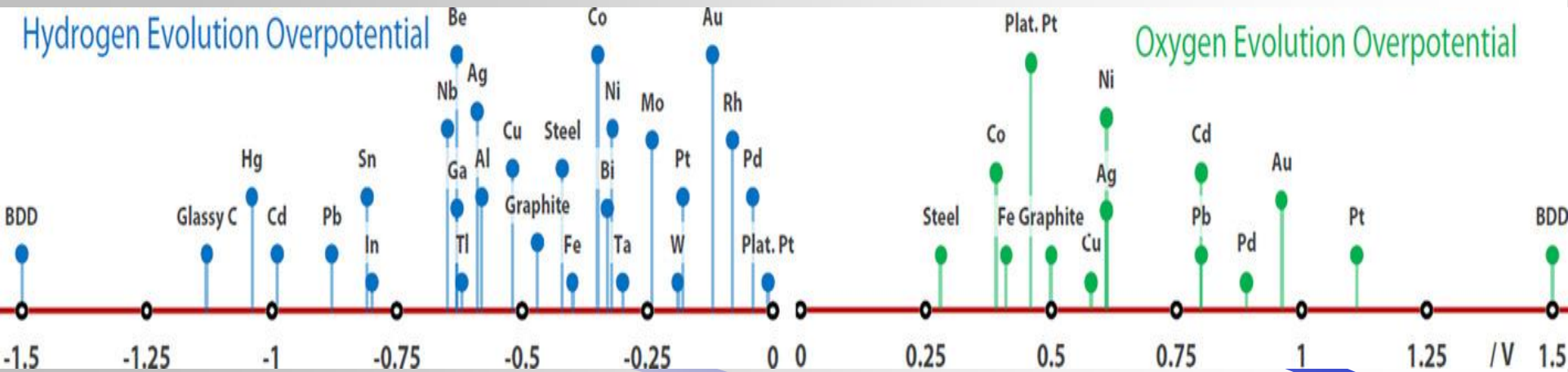
## Working



**Figure 25-4** Potential ranges for three types of electrodes in various supporting electrolytes. (Adapted from A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, back cover. New York: Wiley, 1980. Reprinted by permission of John Wiley & Sons, Inc.)

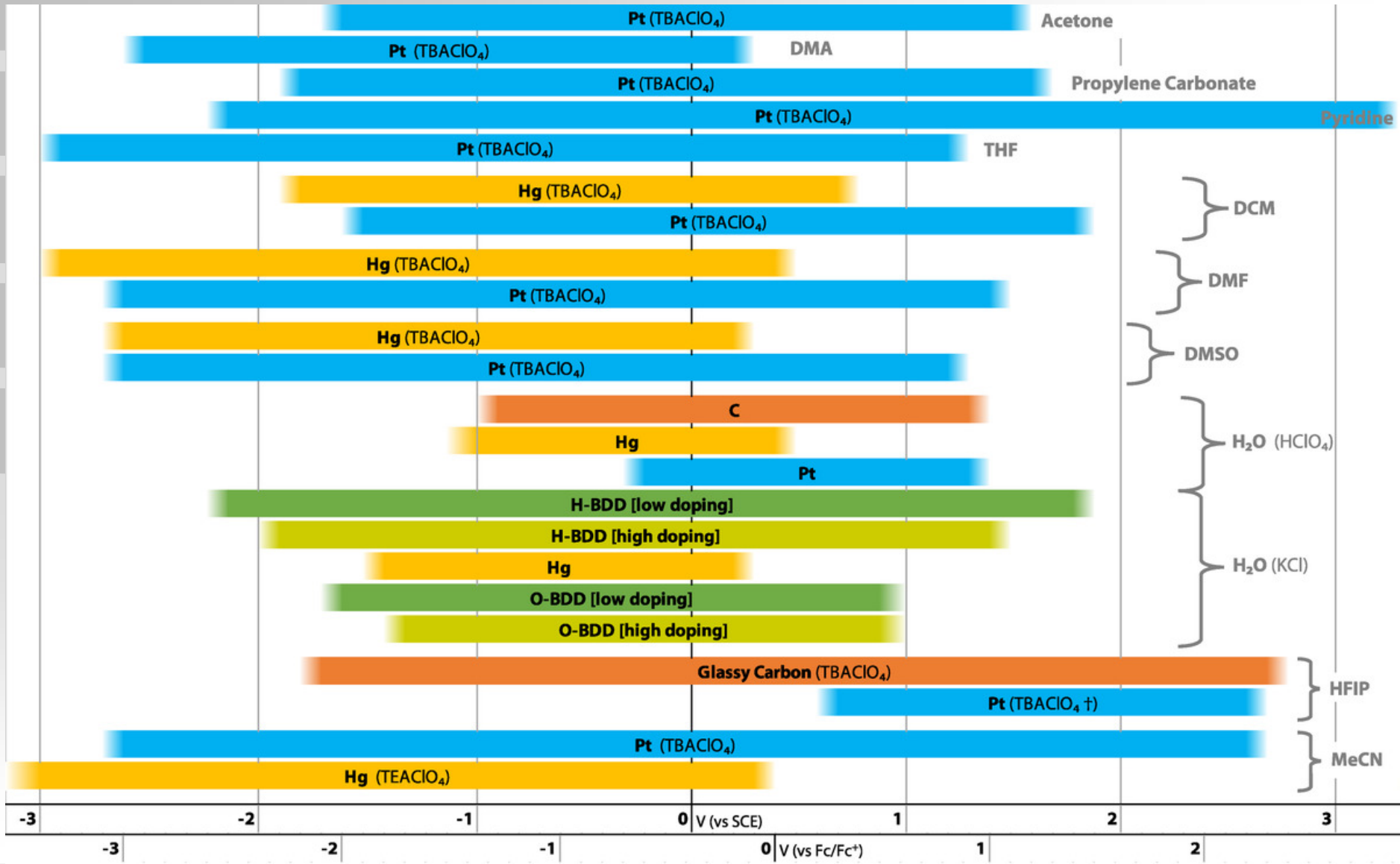
# Electrodes

## Working



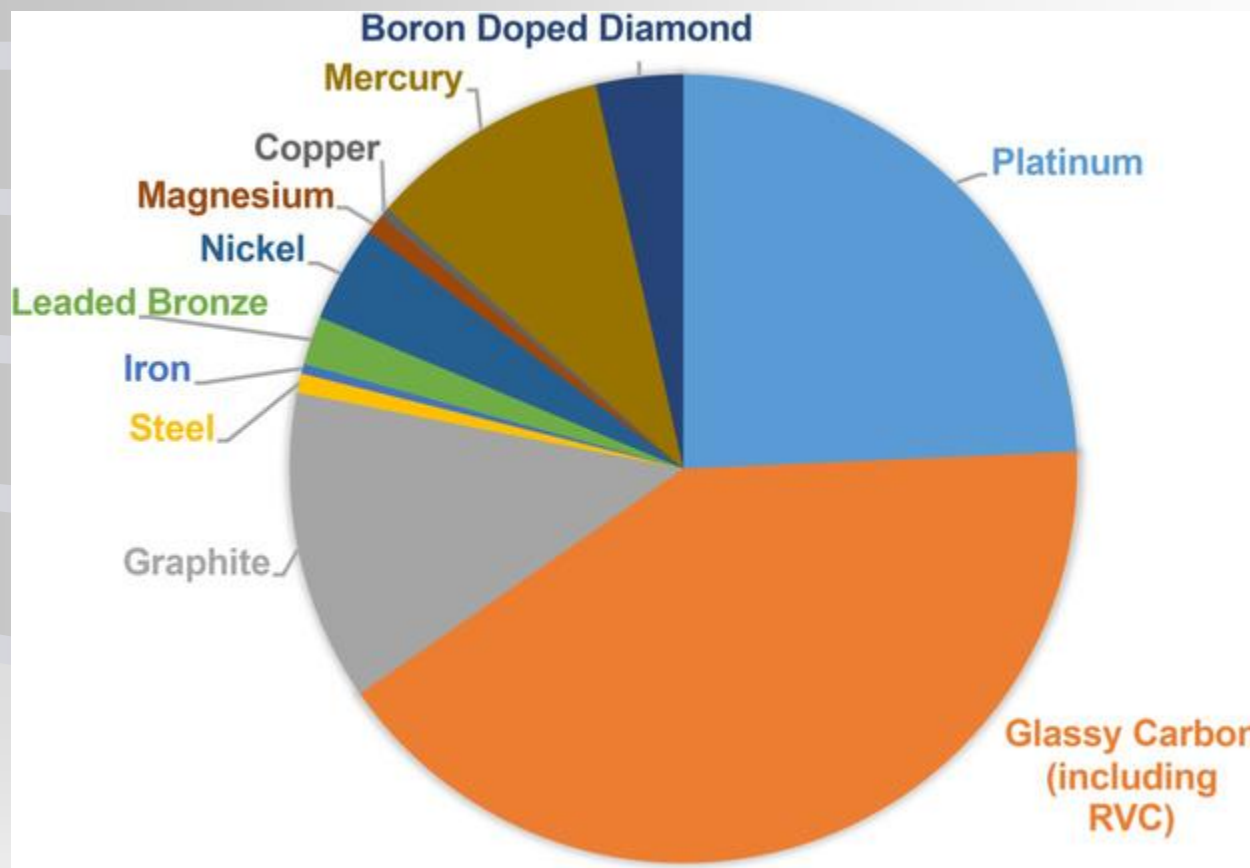
# Electrodes

## Working



# Electrodes

## Working

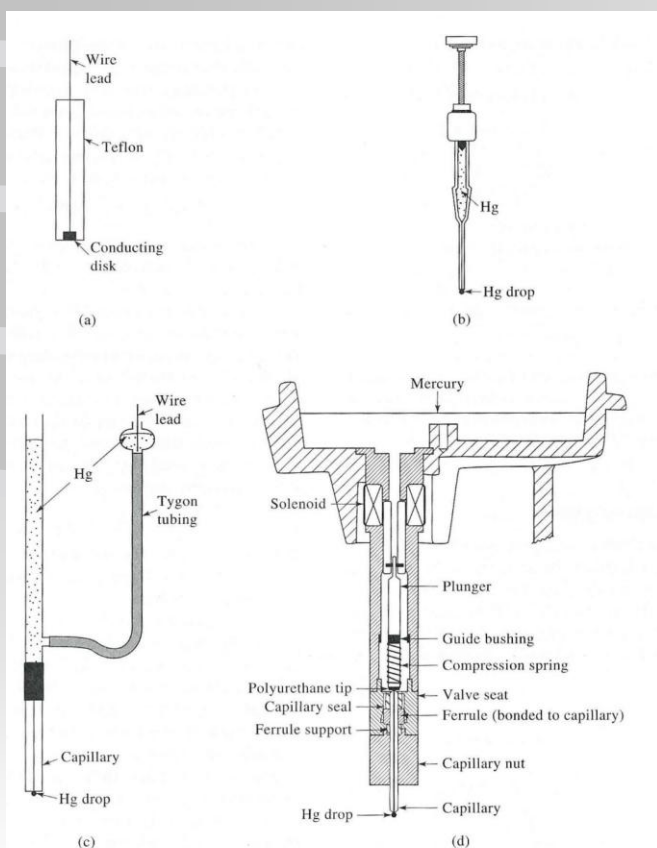


Occurrence of electrode materials used (cathode or anode) in a survey of 915 synthetic electrochemical protocols published between 2000–2017.

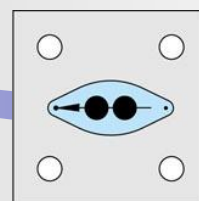
# Electrodes

## Working

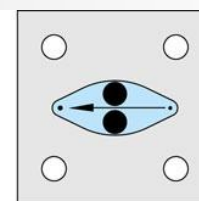
Come in a variety of shapes, compositions, and sizes.



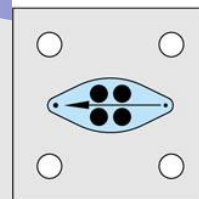
**Figure 25-3** Some common types of microelectrodes: (a) a disk electrode, (b) a hanging mercury drop electrode, (c) a dropping mercury electrode, (d) a static mercury drop electrode.



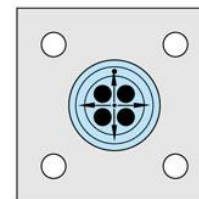
Dual, series crossflow



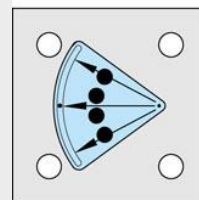
Dual, parallel crossflow



Quad square crossflow



Quad square radialflow



Quad arc crossflow

(c)

# Electrodes

## Working

Metal electrodes used are redox (inert) electrodes for studying electron transfer kinetics and mechanism.

Most common are Pt, Au, and Ag, as well as SS.

Advantages: high conductivity with low background currents, easily modified, ease of construction, polishable.

Disadvantages: can undergo corrosion or passivation.

# Electrodes

## Working

Carbon electrodes have various conducting forms with high surface activity.

# Electrodes

## Working

### Carbon

More complex than the metal electrodes.

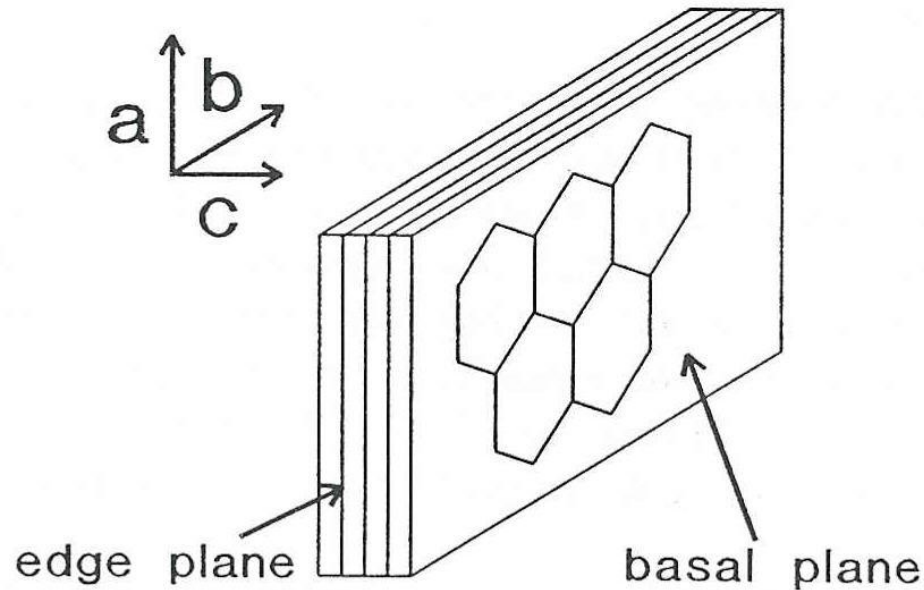
The  $sp^2$  carbon varies in conductivity, stability, hardness and porosity.

# Electrodes

## Working

### Carbon Microstructure

Single-crystal graphite is inherently anisotropic.



**Figure 10.3** Structure of highly ordered pyrolytic graphite.

# Electrodes

## Working

### Carbon Microstructure

Electrochemical properties for the two planes vary greatly.

**Table 10.1** Anisotropic Electrochemical Properties of HOPG

	Basal Plane	Edge Plane
Capacitance, $\mu\text{F}/\text{cm}^2$	$< 1.0$	$\sim 50-70$
Adsorption of anthraquinone disulfonate, $\text{pMol}/\text{cm}^2$	$< 1$	$> 150$
$k^\circ$ for $\text{Fe}(\text{CN})_6^{3-/4-}$ , $\text{cm}/\text{sec}$	$< 10^{-6}$	$0.06-0.10$

Source: Data from References 2, 9, and 10.

# Electrodes

## Working

### Carbon

Common carbon electrodes:

#### 1) HOPG-highly ordered pyrolytic graphite

Made by pyrolysis of light hydrocarbons at  $\sim 800^{\circ}\text{C}$  then treated at high temperature and pressure annealed at  $3000^{\circ}\text{C}$ .

HOPG has weak interplanar bonding so can be renewed with adhesive tape.

# Electrodes

## Working

### Carbon

Common carbon electrodes:

2) Polycrystalline graphite electrodes

a. Carbon paste electrodes (CPE)

Control porosity of graphite material by filling pores with inert liquid carbon paste is graphite mixed with Nujol (heavy hydrocarbon) or hexadecane.

Paste is then packed into shallow well.

CPE's are easily modified (i.e., steric acids, zeolites, complexing agents).

# Electrodes

## Working

### Carbon

Common carbon electrodes:

2) Polycrystalline graphite electrodes

b. Spectroscopic Graphite Electrodes

Rods with low metal impurity used in emission spectroscopy. Can immerse in molten wax (ceresin or paraffin) then place in a vacuum, polish end of rod.

# Electrodes

## Working

### Carbon

Common carbon electrodes:

2) Polycrystalline graphite electrodes

c. Graphite Composite Electrodes

Mix graphite powder with suitable filler that hardens.

# Electrodes

## Working

### Carbon

Common carbon electrodes:

2) Polycrystalline graphite electrodes

d. Glassy Carbon

High MW carbanaceous polymer (polyacrylonitrile, phenol/formaldehyde resin). Polymer is heated to 400-800°C then heated under pressure at 1000-3000°C. Hard and highly disordered.

# Electrodes

## Working

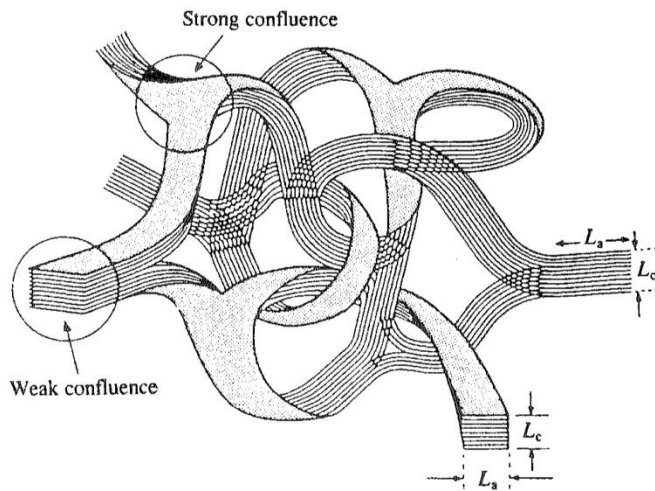


Fig. 7.1. Representation of the structure of glassy carbon, showing  $L_a$  and  $L_c$  (from Ref. 9 with permission).

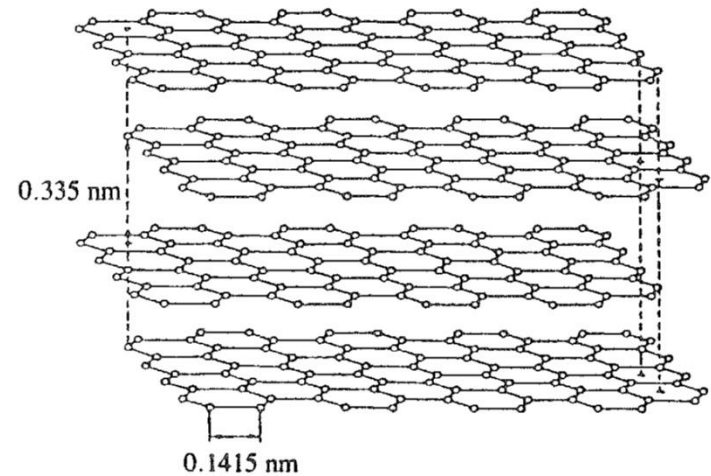


Fig. 7.2. The structure of graphite.

$L_a$  – length of microcrystallites in the graphite lattice plane (a-axis)

$L_c$  – thickness of microcrystallites perpendicular to the graphite planes (c-axis)

# Electrodes

## Working

## Carbon

**Table 10.3** Potential Limits for Carbon Electrodes

Electrode	Electrolyte	Potential Limit vs. SCE, V <sup>a</sup>	
		Positive	Negative
PG (basal)	0.1 M HCl	1.0	-0.8
Spectroscopic graphic	0.1 M HCl	1.19	-0.46
	0.1 M HCl	1.85	-0.39
WIGE	0.1 M HCl	1.0	-1.3
	Phosphate, pH 7.02	1.35	-1.38
CPE (Nujol)	1 M HCl	> 1.0	-0.9
CPE (ceresin wax paraffin oil)	0.1 M H <sub>2</sub> SO <sub>4</sub>	1.7	-1.2
Glassy carbon <sup>b</sup>	0.1 M HCl	1.05	-0.80
	0.05 M H <sub>2</sub> SO <sub>4</sub>	1.32	-0.80

<sup>a</sup>Recall that these limits depend on scan rate and electrode area.

<sup>b</sup>Background is very dependent on condition and preparation.

Source: Adapted from Reference 1.

# Electrodes

## Working Carbon

**Table 10.4**  $k^\circ$  for  $\text{Fe}(\text{CN})_6^{3-/4-}$

Electrode	Pretreatment	Electrolyte	$k^\circ$ , cm/s	Reference
HOPG, basal	Cleaved	1 M KCl	$10^{-6}$	2
HOPG, edge	Polished	1 M KCl	$\sim 0.08$	2
PG, basal	Cleaved	0.5 M KCl	0.002	2
PG, basal	Ground	0.5 M KCl	0.007	2
CPE (Nujol)		1 M KCl	$1 \times 10^{-4}$	2
CPE (hexane)		1 M KCl	0.003	2
GC-20	Polished	1 M KCl	0.002–0.06	2
GC-20	Ultraclean polish	1 M KCl	0.14	31
GC-10	High-speed polish	1 M KCl	0.007	32
GC (LeCarbone)	High-speed polish	1 M KCl	0.098	33
GC-20	Fractured	1 M KCl	0.50–0.55	34
GC-20	Polished, laser-activated <sup>a</sup>	1 M KCl	$> 0.50$	34
GC-30	Fractured	1 M KCl	$> 0.50$	8
GC-30	Polished, laser-activated <sup>a</sup>	1 M KCl	$> 0.50$	8

<sup>a</sup>25 MW/cm<sup>2</sup>.

Source: Adapted from Reference 2.

# Electrodes

## Working

### Carbon

Common carbon electrodes:

2) Polycrystalline graphite electrodes

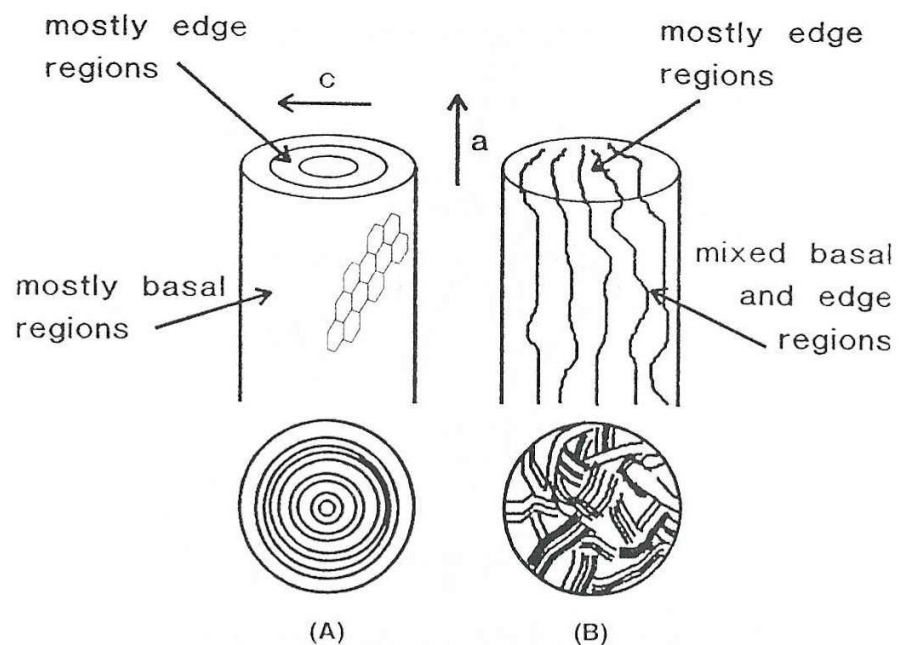
e. Carbon Fibers

Made from polyacrylonitrile (PAN) drawn into filaments during curing.

# Electrodes

## Working

## Carbon Fibers



**Figure 10.14** Illustration of carbon fibers, side and end views: (A) ordered "onion" fiber; (B) disordered "random" fiber.

# Electrodes

## Working

**Table 10.5** Features of Common Carbon Electrode Materials

Carbon material	Pretreatment	Advantages	Problems	Comments	Availability <sup>a</sup>
HOPG, basal	Cleaved	Low background, well defined, very weak adsorption	Slow kinetics	Strong dependence on defects	2
HOPG, or PG, edge	Polished Laser-activated or "roughened"	Easily renewed, strong adsorption Strong adsorption fast kinetics	Variable impurities Moderately high background		2
Carbon paste	Lightly polished	Very low background, easily renewable, reproducible	Slow kinetics for some systems, limited solvent compatibility	Widely used for aqueous oxidations, easy to modify	1
Graphite composites	Polished	Wide solvent compatibility, increased signal/background current, easy chemical modification	Binder can coat carbon	Selectivity can be varied with chemical modification	3
Glassy carbon	Polished	Wide solvent compatibility, easily prepared	Variable kinetics, background current	Probably the most common carbon electrode material	1,2
	Heat-treated	Wide solvent compatibility, easily prepared, fast kinetics	Tedious renewal		
	Laser-activated	Wide solvent compatibility easily prepared, rapid in situ renewal	Expensive, optical window required in cell	Yields fast kinetics	1,2
Carbon fibers	ECP	Sensitive, selective for cations, fast kinetics	High background current		1,2
	Polished	Small size, possibly very small volume	Variable carbon microstructure	Important for in vivo use	1 <sup>b</sup> ,2
	ECP	Selectivity, preconcentration of cations	Slow response time	Important for in vivo use	1 <sup>b</sup> ,2

<sup>a</sup>1 = Commercially available as assembled electrode, 2 = materials commercially available, must be encapsulated or mounted before use, 3 = materials commercially available, some chemical or physical steps required before mounting.

<sup>b</sup>Encapsulated fibers are commercially available with large overall dimensions (ca. 5  $\mu\text{m}$ ), but fiber electrodes with small dimensions (<20 nm) must be custom made.

# Electrodes

## **Working**

Carbon – Diamond-Liked Carbon (DLC)

Carbon - Boron Doped Diamond (BDD)

# Electrodes

## Working

### Mercury

Historically, the common working electrode used for dropping, hanging drop, and static polarography.

Has a very high negative overpotential for hydrogen evolution – used to study reduction processes – must be triply distilled.

# Electrodes

## Counter or Auxillary

The auxillary electrode is made of material that does not produce substances by electrolysis that will reach the WE surface and cause interfering reactions.

# Electrodes

## Counter

Typically inert metals such as Platinum (for acid solutions) or Chromel (Ni 80-60 Cr 20-40) (for base solutions).

# Electrodes

## Reference

An electrode with a known constant half-potential and insensitive to composition of the solution.

Ideal reference

Reversible and obeys Nernst Law

Exhibits stable potential over time

Returns to original potential in presence of small currents

Not sensitive to temperature changes

# Electrodes

## Reference

To generate the relative half-cell potentials use a standard.

i.e. Standard hydrogen reference electrode (SHE or NHE).

This is the standard reference half-cell to measure all other half-reactions against.

# Electrodes

## Standard Hydrogen Reference Electrode

SHE is a Gas electrode, made up of:

- Metal piece - Pt coated with platinum black (large surface area). Pt is in aqueous acid solution (HCl = 1M). Solution is saturated with H<sub>2</sub> (bubble) P=1atm. Metal is site of e<sup>-</sup> transfer only.

Half reaction for SHE is :  $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$

# Electrodes

## Standard Hydrogen Reference Electrode

Half reaction for SHE is :  $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$

Shorthand:  $\text{Pt}, \text{H}_2(\text{p}=1.00\text{atm}) \mid ([\text{H}^+] = 1.00\text{M}) \parallel$   
(25°C)

can be the anode or cathode.

This half-reaction is assigned 0.00V.

Half-wave potential are always written as reduction reactions.

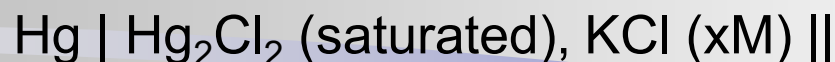
i.e. SHE is the anode, other is the cathode.

# Electrodes

## Reference

### Calomel Electrodes (SCE)

Consist of Hg in contact with solution of calomel and KCl.



KCl usually 0.1, 1 M, and 4.6 ← saturated SCE

SCE used to be most commonly used reference electrode until ~2018.

Advantage -- easy to prepare

Disadvantage -- sensitive to temperature changes

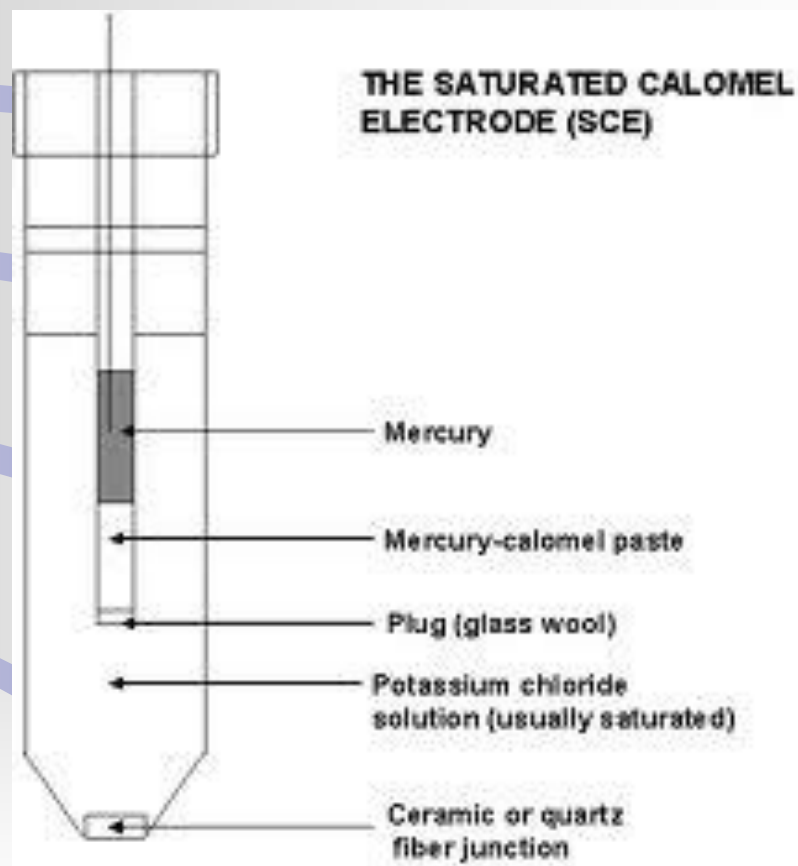
$$E^0_{\text{SCE}} = 0.244\text{V at } 25^\circ\text{C}$$



# Electrodes

## Reference

### Calomel Electrode



# Electrodes

## Reference

### Ag/AgCl Electrodes

Ag wire in solution of KCl and AgCl

Ag | AgCl (saturated), KCl (saturated) ||

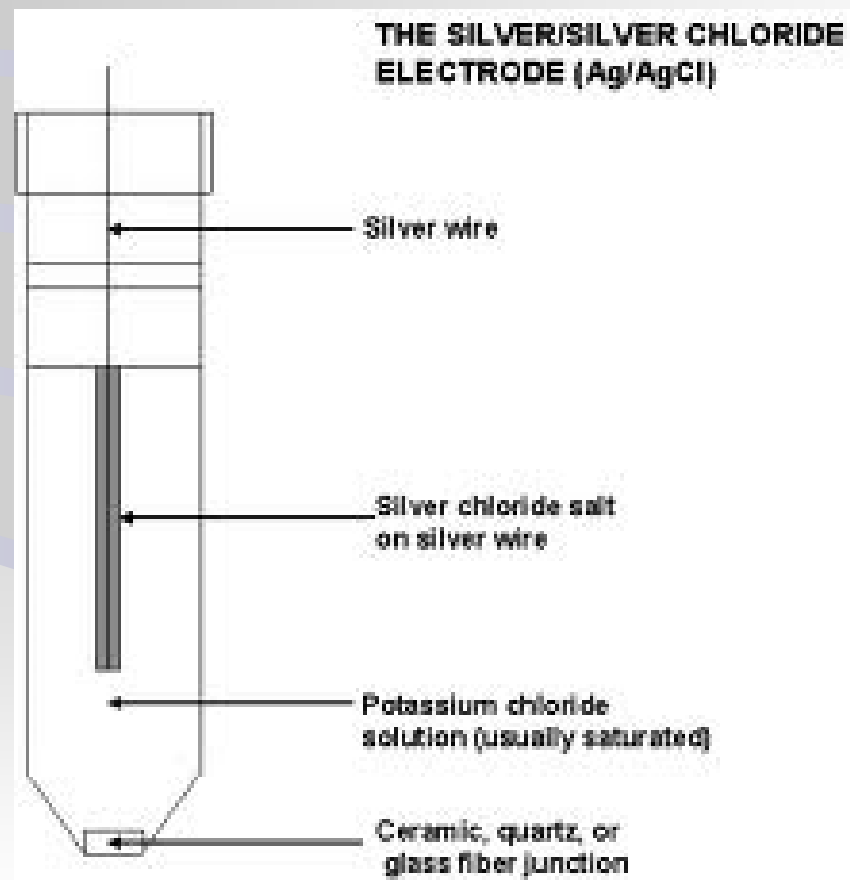


$$E^0_{\text{Ag/AgCl}} = 0.199\text{V at } 25^\circ\text{C}$$

# Electrodes

## References

### Ag/AgCl Electrode



# Electrodes

## Reference

- Ag/AgCl better for uncontrolled temperature (lower T coefficient)
- However, Ag reacts with more ions

# Electrodes

## Reference

**TABLE 23-1** Potentials of Reference Electrodes in Aqueous Solutions

Temperature, °C	Electrode Potential (V), vs. SHE				
	0.1 M <sup>c</sup> Calomel <sup>a</sup>	3.5 M <sup>c</sup> Calomel <sup>b</sup>	Saturated <sup>c</sup> Calomel <sup>a</sup>	3.5 M <sup>b,c</sup> Ag/AgCl	Saturated <sup>b,c</sup> Ag/AgCl
10		0.256		0.215	0.214
12	0.3362		0.2528		
15	0.3362	0.254	0.2511	0.212	0.209
20	0.3359	0.252	0.2479	0.208	0.204
25	0.3356	0.250	0.2444	0.205	0.199
30	0.3351	0.248	0.2411	0.201	0.194
35	0.3344	0.246	0.2376	0.197	0.189
38	0.3338		0.2355		
40		0.244		0.193	0.184

<sup>a</sup>Data from: R. G. Bates in *Treatise on Analytical Chemistry*, 2d ed., I. M. Kolthoff and P. J. Elving, Eds., Part I, Vol. 1, p. 793, Wiley: New York, 1978.

<sup>b</sup>Data from: D. T. Sawyer and J. L. Roberts Jr., *Experimental Electrochemistry for Chemists*, p. 42, Wiley: New York, 1974.

<sup>c</sup>"M" and "saturated" refer to the concentration of KCl and not Hg<sub>2</sub>Cl<sub>2</sub>.

# Class Assignment

- Research paper Topic
- Read Chapter 1, 4, and 13

“Electrochemical Methods” Bard

