CHAPTER 13

**Redox Rxns** (OIL RIG)

*Reduction* – RED CAT(hode)

* Gains electrons (generation)
* Occurs at Cathode
  + Attracts cations
* Less likely to corrode

*Oxidation* – AN(ode) OX

* Losses electrons (consumption)
* Occurs at Anode
  + Attracts anions
* More likely to corrode

EX. Zn2+ + 2e- 🡪 Zn Eº = -.763 (Anode)

Cu2+ + 2e- 🡪 Cu Eº = +.337 (Cathode)

**Galvanic Cells**

*Nernst Equation*:

Eº - standard Emf at 25ºC, N - # of electrons transferred

Cion – molar conc. of ions

Things to Note:

if electrolyte conc surrounding anode < 1 M,

🡪 more negative half-cell rxn

🡪 higher driving force for corrosion

If single electrode in one electrolyte, macroscopic cathodes/anodes form from structural irregularities

If two electrodes in same ion w/ different concs 🡪 low conc. is anode

* Same for oxygen conc. cells

|  |  |
| --- | --- |
| Electrolyte Type | Cathodic Reaction |
| Acidic | 2H++ 2e- 🡪 H2 |
| Basic or neutral | O2 + 2H2O + 4e- 🡪 4OH- |
| oxidizing agent | O2 + 4H+ + 4e- 🡪 2H2O |

*Grain Boundary Eº cells*

* At higher energy
* Impurities migrate to grain boundaries
* Solute segregation 🡪 more cathodic

*Multi-Phase Cells*

* One phase more anodic than another

🡪 inc. corrosion rates

* IMPURITIES 🡪 precipitation of intermetallic phases 🡪 new an/cat regions 🡪 corrosion

**Corrosion**

*Faraday’s Equation*:

I = current, I = current density, M = molar mass

W = weight, F = constant (96500 C/mol)

*Definitions*

Polarization – displacement of electrode potential from equilibrium values, creating a net current flow

|  |  |
| --- | --- |
| Activation Polar | Concentration Polar |
| Rxn controlled | Diffusion controlled |
| Must surmount AE |

Passivation – conditional loss of reactivity

EX. Surface layer

Oxide Film Theory – passive film always a diffusion layer of rxn products

Adsorption Theory – passive metals always covered by chemisorbed films of oxygen

**Polarization Curve** (metal potential vs curr. Density)

As Electrode potential made more +

🡪 metal behaves more actively

When potential reaches Epp (primary passive pot)

🡪 current dens inc 🡪 corrosion rate inc.

Further potential inc. makes metal active again

**Corrosion Types**

|  |  |
| --- | --- |
| Type | Details |
| Uniform/General | Controlled by coatings, inhibitors, cathodic protection |
| Galvanic | Electrochemical rxn leads to corrosion of one metal  -avoid large Acat/Aanode |
| Pitting | Localized attacks, create holes  -initiation, grows w/ gravity  🡪 high acidity at bottom (anode)  🡪 cathode rxn at surface |
| Crevice | Localized corrosion under shielded surface  -stagnant sol 🡪 O2 used up, not replaced 🡪 high metal conc.  🡪 anions come to balance  🡪 free acid 🡪 corrosion |
| Intergranular | Localized corrosion along highly reactive grain boundary  EX. SS heated to sensitizing temp (500-800C)  🡪 chromium precipitate 🡪 region becomes anodic 🡪 COR |
| Stress | Cracking due to tensile stress, can be residual  Forms at pit, perpendicular to stress, can stop from s.removal |
| Erosion | Accelerates corrosion due to motion btwn fluid, surface  -in direction of flow, bc of film removal, abrasive action |
| Cavitation | Caused by air bubble collapse in liquid near metal surface  Collapse 🡪 very high P (60k psi) 🡪 damaged surface  -likely from high velo flow |
| Fretting | at interface btwn materials subjected to vibration, slip  🡪 metal fragments oxidize 🡪 act as abrasive btwn surfaces |
| Selective Leach | Intentional corrosive removal of undesired element  -resultant alloy is weakened |
| H2 Damage | Carrying capacity reduced from interaction w/ hydrogen  -H2 diffused into metal  -can remove via bakeout |

**Protective Films**

*Oxidation*

-Starts by lateral expansion of discrete oxide nuclei

🡪 metal diffuses as cations or electrons across film

*Rate*

Linear – W = KLt

If ion diffusion is controlling step – W2 = Kpt + C (para)

Logarithmic – W = Kelog(Ct + A)

|  |  |
| --- | --- |
| Dependency | Optimization |
| Voxide/Vmetal | good |
| Adherence | good |
| Film Melting Point | high |
| Vapor Pressure | low |
| Coeff of expansion | = to metal |
| Temp plasticity | high |
| Conductivity | low |
| Diffusion coeff of metal, oxygen | Low, low |

**Corrosion Control**

*Material Selection*

Metallic: Reducing 🡪 nickel, copper, Oxidizing 🡪 chro.

Non-metallic: limit polymers w/ strong acids, ceramics are good but break easily

*Coatings*

Metal Coatings: applied via electroplating, roll bonding, can have many layers

Organic: paints, varnishes. Apply carefully

Inorganic: lined w/ steel, coated w/ glass

*Design*

Provide allowance for corrosion in thickness

Weld, don’t rivet 🡪 avoids crevice corrosion

No dissimilar metals 🡪 avoids galvanic corrosion

No sharp pipe bends 🡪 avoids erosion

Easy draining 🡪 avoids concentration cells

Avoid hot spots

*Environment Control*

Low temp 🡪 lower rxn rate

Dec. fluid velocity 🡪 lower erosion corrosion

Removing oxygen from liquids 🡪 reduces corrosion

Reducing corrosive ion conc. 🡪 dec. corrosion rate

Adding inhibitors 🡪 retarding catalysts, dec. corrosion

*Cathodic/Anodic Protection*

Cathodic – electrons supplied to metal to be protected

🡪 done via external DC source or galvanic coupling

Anodic – externally impressed anodic currents form protective passive films on metal & alloy surfaces.

🡪 Applied via potentiostat

Current 🡪 more passive 🡪 dec. corrosion rate

Misc:

CHAPTER 14

**Conduction**

Metallic bonds make valence e- mvmt possible

Outer valence e- are free to move btwn ion cores

Positive ion cores vibrate w/ greater amplitude, increasing temperature

Motion is random, & restricted in absence of e field

With e-field, electrons attain drift velocity

*Ohm’s Law*:

I = current (A), R(Ω), V = potential difference (V)

J = curr. Density (A/m2), E = electric field (V/m)

*,*

A = conductor area, l = conductor length

|  |  |  |
| --- | --- | --- |
| Conductors | Insulators | Semi-Conductors |
| Copper  Silver  Gold  σ ≈ 107 | Polyethylene  Polystyrene  σ ≈ 10-14 | Silicon  Geranium |

Energy Band Gaps – determine materials electronegativity

Valence band - outermost e- orbital of a material that electrons actually occupy

Conduction band – the lowest e- orbital that electrons can jump into from valence band

Drift velocity Vd = μE (μ = electron mobility m2/(V\*s))

Graph (Vd/time) Accelerate, collide, accelerate, …

🡪 saw tooth graph

Current flow is OPPOSITE electron flow

Electrical Resistivity ρtotal = ρT + ρr

ρr = residual comp: structural imperfections (lesser)

ρT = ρ0C(1 + αΤΤ)

αT = coeff of resistivity

ΡΤ is the thermal comp: elastic waves(phonons) generated due to vibration of core scatter electrons

🡪 resistivity increases with temp

🡪 alloying increases resistivity

μp, μn = hole, electron mobilities, q = 1.6e-19 (C), ni = intrinsic carrier concentration, Eg = bandgap energy

|  |  |  |
| --- | --- | --- |
| Difference | P-type | N-type |
| Doping Element | Group III | Group V |
| Doping Nature | Creates holes (acceptor) | Provides extra electrons(donor) |
| Impurity | Al, Ga, In, etc. | P, As, Sb, Bi |
| ΔE | Ea - Ev | Ec - Ed |
| Majority/min  carriers | Holes / Electrons | Electrons / Holes |

**pn Junction**

|  |  |
| --- | --- |
| Reverse Biased | Forward Biased |
| n-type to positive terminal, p-type to neg  -majority carrier electrons and hole move away from junction  -current doesn’t flow  -leakage flow to min. carriers | n-type: negative term, p-type to positive  -majority carriers repelled to junction and recombine  -current flows (no depletion zone) |

**PN Junction Applications**

*Rectifier Diodes*: convert AV to DV (direct voltage)

🡪 when AC signal applied to diode, current flows only when p-region is positive 🡪 halfway recognition is achieved

*Bipolar Junction Transistor* (BJT): 2 pn junctions

Emitter: n-type, emits electrons. Forward Biased

Base: p-type, controls flow of charge, 0.01mm thick

Collector: n-type, collect charge carrier. Reverse Biased

*Microelectronic planar bipolar transistors*: large island of n-type silicon first formed in silicon substrate

🡪 smaller island of n and p types formed on the above

*MOSFET*: metal oxide semiconductor field effect transistor

🡪 two islands of n-type in substrate of p-type Si

🡪 btwn n-type Si source and drain, is a p-type region

🡪 surface layer of SiO2 formed on p region, another layer of polysilicon on SiO2 layer

🡪 electrons flow btwn source and drain if positive voltage difference (also can amplify current)

*Photolithography*

Coat wafer w/ photoresist 🡪 expose to UV light 🡪 pattern left where mask is transparent 🡪 remove remaining photoresist with hydrofluoric acid

*Silicon Diffusion*

Thin SiO2 patterns serve as masks to prevent dopant atoms from penetrating into silicon

🡪 high conc. of dopant deposited near surface

🡪 wafers places in high temp furnace 🡪 necessary conc. of dopant atom at particular depth attained

*Ion Implantation* (at room temp)

Dopant atoms ionized to high energies through a high potential different of 50-100 KV

🡪 On striking, ions embed in Si

🡪 photoresist or SiO2 mask is used to mask desired regions

🡪 damage to Si lattice is caused, can be healed by annealing

*MOS Integrated Circuit Fabrication*

SiN4 deposited by CVD 🡪 boron ions implanted to suppress unwanted conduction 🡪 SiO2 layer is grown in inactive regions 🡪 SiN4 removed by etchants 🡪 insulating layer deposited on wafer by CVD 🡪 Al deposited on wafer 🡪 protective layer deposited on entire surface

*Complimentary Metal Oxide Semiconductor (MOS)*

Circuits containing both MOSFET types (NMOS, PMOS)

🡪 made by isolating NMOS devices w/ p-type material islands

🡪 used in LSI circuits in microprocessors, cpu memories

*Compound Semiconductors*

MX semiconductors are major semiconducting compounds

🡪 as molecular mass inc., energy bond gap dec., electron mobility inc.

🡪 inc. ionic bonding character 🡪 energy bond gap increases 🡪 electron mobility decreases

EX. Gallium Arsenide (GaAs)

* Higher mobility
* GaAS devices have better radiation resistance

*Misc*:

Movement of electrons is opposite the electric field

As impurities conc. inc 🡪 carrier mobility dec.

Conductivity inc w/ temperature as more impurities are ionized

Exhaustion Range: temp at which donor is fully ionized

Saturation Range: Acceptor atoms fully ionized

🡪 beyond, further temp inc becomes intrinsic conduction dominant 🡪 “Intrinsic Range”

CHAPTER 10

**Polymers** – large molecules formed by polymerization processes to connect small monomer molecules

why? – Wide range of properties, light weight 🡪 low density, easy fabrication, low conductivity 🡪 high e resistivity

**Polymer Classification**

*Natural Polymer EX. 1:* *Proteins – “Polyamides”*

Amino Acids

* Amino Group (-NH2)
* Carboxyl Group (-COOH)
* R group (20 side chains)

2 AA’s 🡪 Amino group 1 + carboxyl group 2 🡪 peptide bond

Peptide bond 🡪 O=C-N-H where C,N link back to original amino acid 🡪 called an “Amide”

This happens over and over with AA’s until you have a polypeptide (“polyamide”) w/ an N terminus, C terminus, X R groups, & X – 1 peptide bonds

*Natural Polymer* *EX. 2: Polysaccharides*

Carbohydrate polymers contain a number of sugar molecules bonded together

* Consist of carbon, hydrogen, and oxygen, usually with H:O = 2:1 (think water) ≈ Cm(H2O)n
* Starch, cellulose are examples

*Most Common Synthetic Polymers:* *Polyethylene (PE)*

• 80 million tons produced annually, no branches 🡪 high crystallinity

*Polypropylene*

• 2nd most used 🡪 packaging and labeling

• 2013 market was 55 million tons

• big pendant group 🡪 low crystallinity

*Poly(Vinyl Chloride) [PVC]*

3rd most used 🡪 pipes, electric cables, furniture, construction

*Nanocrystalline Linear Polymer Structure*

• Zig-Zag configuration in ethylene due to 109º angle btwn carbon covalent bonds

• Chains randomly entangled

🡪 more entanglement 🡪 increased tensile strength

🡪 more branching 🡪 decreased tensile strength

Semi-Crystalline Polymers

Amorphous – chains are in irregular manner

Crystalline lamellae – chains are folded to make lamellae structure arranged in regular mannor

• Crystallinity of polymer affects optical, thermal, & mechanical properties of the polymer

• polymers are rarely 100% crystalline due to the difficulty for all regions of all chains to become aligned

*Architecture*:

Linear Network (“hydrogel”)

Branched Dendrimer

Star Shaped

*Propertie*s:

Thermoplastics – heat 🡪 softening, become moldable

• PE, PVC, PP . Easy to process

Thermosets – stiffening, x link 🡨 heat

• Polyurethane, more stability at high temp

*Compositon*:

Monomer 🡪 A

Homopolymer 🡪 AAAAAAA

Copolymer 🡪 ABCABC

**Polymer Processing**

*Injection Molding -* Uses reciprocating screw mechanism

* More uniform delivery of melt for injection
* High quality, low labor cost, but high initial cost

*Extrusion -* Melted plastic forced by a rotating screw though an opening and used to produce pipes, rods, etc.

*Blow Molding* – Compressed air is blown into a heated cylinder or pipe of plastic to press it against the wall of mold

*Thermoforming –* Heated plastic sheet is forced into contours of a mold by pressure

*Compression Molding (Thermosetting)* – Pressure is applied on heated plastic by upper mold, molten plastic fills the cavities

* Low initial cost, simple
* Less wear and abrasion than other molds
* Difficult to mold complex parts, Creates (spills)

**Material Structure-Property Relationship**

What determines main properties of polymers? MW & composition

MW0 = monomer molar mass, n = degree of polymerization

• It’s impossible to have identical molecular weight in a batch synthetic polymer synthesis

Average “molecular weight” Mº

* Number average Mºn
* Weight average Mºw

Wi = weight fraction

The longer the chain 🡪 the greater the weight contribution

PDI: Polydispersity Index = Mºw/Mºn

• if PDI value is close to 1, “monodisperse”

**Polymer Microscopic Structure**

• dependent on MW & chemical properties

c: crystalline region, a: amorphous region, s: total sample

**Polymer Crystallization Process**

MW inc. 🡪 entanglement inc.

Crystallinity inc 🡪 stiffness inc.

**Bio-Inspired Materials**

*Hierarchical Structure of Bone & Nacre* (smallest to largest)

Collagen molecule 🡪 Tropocollagen triple helix 🡪 HA nanocrystal 🡪 Collagen fibril 🡪 Osteons and Haversian canals 🡪 Compact bone

Proteins + Chitin & 30nm grains 🡪 breaking of mineral bridges 🡪 inelastic shearing resisted by nano-asperities 🡪 organic layer acting as viscoelastic glue 🡪 tablet interlocking during sliding 🡪 nacre

Engineered Nanocomposites

|  |  |  |
| --- | --- | --- |
| Materials | Processing | Applications |
| Polymer +  Clay Platelets | Blending 🡪 nanocomposite | Transportation, packaging, sport, medic, etc. |

Burdock Plant 🡪 Velcro

Mussels 🡪 Water Adhesion

Lotus Leaf 🡪 Self-Cleaning

* superhydrophobic

Gecko’s Feet 🡪 Advanced Adhesives

• Physical structure of feet allow them to stick to walls

• 6.5 million foot hairs, could hold weight of 260lb man if all are stuck at the same time

• Van der Waals force 🡪 one pad is weak, but a billion is strong (large surface area)

How it works:

- Upon stepping, gecko spreads toes. Foot is placed on surface in a rolling fashion

- Pads at the tip of the hair contact surface, slide slightly back

- Motion brings gecko molecules closer to surface molecules

- if (g) positive side is away from (s) as it approaches, electrons in (s) will reposition so positive side will be towards (g)

- The molecules stay together bc electron move in unison, constantly maintaining an opposite polarity

- To release, (g) moves foot slightly, changing angle of each hair

CHAPTER 6 TERMS

Hardness – measure of the resistance of a metal to permanent (plastic) deformation

Ductility – measure of the ability of a material to change shape without rupturing

Elastic Modulus – the ratio shear stress of shear strain

Shear stress – ratio of shear force over area applied

Shear Strain – shear displacement / distance it acts