Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (Third Year)

Subject: Chemistry

Course Code: CHC-105

Course Title : Physical Chemistry

Unit: Section A- Electrochemistry

Module Name: Oxygen Overvoltage and metal overvoltage.

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Notes:

<u>Overvoltage / Over potential:</u>

- It is the difference between the theoretical cell voltage and the actual voltage that is necessary to cause electrolysis.

Or

- The additional potential, over and above the standard electrode potential, which is needed to secure the evolution of the gas.

Over potential = E – E°

- It is mainly observed with hydrogen evolution at cathode and oxygen evolution at anode.
- An over potential exists for any gas at any electrode.

How Overvoltage Occurs ?

- The over potentials arise on account of the energy required for the adsorption of gas to occur on metal surface.
- The reactions taking place at the electrodes are as follows:

- At Cathode : $2H^+ + 2e^- \rightarrow H_{2(g)}$

- At Anode : $2OH^- \rightarrow ½\ O_{2(g)} + H_2O + 2e^-$

Net reaction: $2H^+ + 2OH^- \rightarrow H_{2(g)} + ½\ O_{2(g)} + H_2O_{(l)}$

- For the above electrolytic cell the potential at which continued evolution of H_2 and O_2 gas takes place is measured to be 1.7 Volts.

- Thus we find that theoretical reversible potential is greater than the actual decomposition potential by 1.7 – 1.23 = **0.47 Volts.**
- This excess potential is termed as over voltage.
- It is given by the formula

$$\eta = E_d - E_r$$

where E_d = Decomposition potential of the electrolyte

E_r. = Theoretical reversible potential of the cell

Oxygen overvoltage:

- The difference between the theoretical oxygen reduction potential (+1.23 V) and experimentally observed electrode potential.
- The reactions taking place at the electrodes are as follows:

- Oxidation: $H_2O_{(l)} \rightarrow ½\ O_{2(g)} + 2H^+ + 2e^-$

- Reduction: $½\ O_{2(g)} + 2H^+ + 2e^- \rightarrow H_2O_{(l)}$

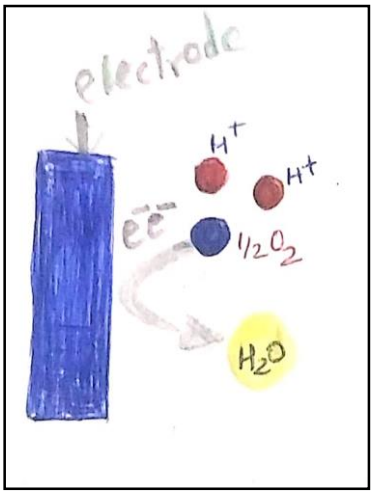

Fig: Mechanism for O_2 overvoltage

Metal overvoltage:

- The potential at which metal ions start depositing at a appreciable rate on cathode is generally close to reversible electrode potential of the same metal.
- It is evident that the value varies largely with the nature of the metal.
- **Example: (1)** The reversible electrode potential of Zn- metal in contact with its own ion solution is – 0.76 V. i.e. the potential at which Zn^{+2} ions deposit on Zn – rod used as cathode is very close or slightly higher than is – 0.76 V.

- **Example : (2)** The reversible electrode potential of hydrogen is – 0.41 V for Cd - salt solution at neutral pH. While E^{o} for Cd is -0.40V.
- Given below is the table of Hydrogen and Oxygen overvoltages for different metals at very low current density.

Electrode	Hydrogen overvoltage (V)	Oxygen overvoltage (V)
Platinum	0.00	0.25
Iron	0.08	0.24
Nickel	0.22	0.06
Cadmium	0.48	0.43
Lead	0.64	0.32
Zinc	0.70	--
Mercury	0.80	--

- The variation of hydrogen over voltage with current density at constant temperature is given by Tafel's equation:

$$\eta = a + b \log I_d$$

where a and b are constant and I_d is current density.

METHODS FOR DETERMINING OXYGEN OVERVOLTAGE:

- The determination of oxygen overvoltage is complicated as oxygen electrode does not exhibit a thermodynamically reversible behavior.
- The other complication for η determinations is based on the high current densities used in the industrial alkaline water electrolysis.

Factors affecting Oxygen Overvoltage:

- **Current density :** if H_2 is not removed then over voltage increases with current density.
- **Temperature:** is inversely proportional to over voltage (2 mv / degree)

- **pH:** in strongly acidic or alkaline solutions deviations will occur due to accumulation of ions near the cathode.
- **The gas (oxygen) shielding anode**
- **The electrolyte filling near the gas-shielded anode**
- **Concentrating polarization**

Applications of overvoltage:

- Electro-deposition of metals in aqueous solutions.

Electrodes with high over voltages are used in electrolytic reduction process that increases activity of hydrogen thereby enhancing the reducing power of electrode.

- Corrosion of metals.
- Industrial synthesis of Cl_2 and sodium hydroxide by electrolysis of aqueous NaCl is also the reason of over voltage.