Q. ~~The cell SC~~

Q. The cell SCE || (0.1) HCl | $AgCl_{(s)}$, Ag gave emf of 0.24 V and 0.26 V with buffer having pH value 2.8 and unknown pH value respectively. Calculate pH.

$E_{SCE} = -0.2422$ V.

$E_{cell} = E^{\circ}_{g} - 0.0591\,pH$.

$0.24 = E^{\circ}_{g} - 0.0591 \times 2.8$

$E^{\circ}_{g} = \cancel{0.6476}\ 0.40576$

$pH = E^{\circ}_{g} - E_{cell} - E_{cal} / 0.0591$

$= \cancel{0.6476} - 0.26 - 0.2422 / 0.0591$

$= \cancel{2.46} = 1.62$

8/11

Q. A glass electrode dipped in a solution of pH = 4 offered an emf of 0.2066 V with ~~SC~~ decinormal SCE at 298 K. When dipped in a soln of unknown pH at the same temp, the recorded emf 0.1076 V. Calculate the pH of the soln.

Ans $pH = (E^{\circ}_{g} - E_{cell} - E_{cal\,(decinormal)}) / 0.0591$

$4 = (E^{\circ}_{g} - 0.2066 - 0.3335) / 0.0591$

$E^{\circ}_{g} = 0.7765$ V

$pH = (0.7765 - 0.1076 - 0.3335) / 0.0591$

$pH = \underline{\underline{5.67}}$

BATTERY TECHNOLOGY

Battery is a chemical reactor that converts chemical energy to electrical energy.
Its a device that stores chemical energy that can be used as a source of DC.

Components

- Container
- Separator - Seperates anodic & cathodic active materials
- Electrolyte
- Active materials
- Terminals.

Battery Characteristics.

- Voltage: measure of amount of electrons flowing from -ve to +ve electrode.
- Current: measure of rate of battery discharge.
- Capacity: amount of electricity that may be obtained from the battery.
- Electric Storage Density / Energy Density: electricity per unit weight of the battery (Watt hours/kg)
- Power Density: Power per unit weight of the battery
- Cycle Life: number of complete charging/discharging cycles a battery can perform.
- Shelf Life: Life time of the battery, to what extent the battery can be stored for years without self discharge
- Design Life: It is the elapsed time before a battery ~~boo~~ becomes unusable whether it is in active use or inactive.

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CLASSIFICATION & COMPARISON.

Primary Batteries.	Secondary Batteries.
1) Cell reaction is irreversible	Cell reaction is reversible.
2) Must be discarded after active elements have been consumed.	Maybe recharged multiple times from a external DC source.
3) Have a short shelf life.	Have a very long shelf life.
4) Function only as galvanic cells.	Function as galvanic cells during discharge and electrolytic cells during charging.
5) Cannot be used as energy storage devices.	Can be used as a energy storage device
6) cannot be recharged	Can be recharged.
eg: Dry Cell, Li-MnO_2 battery	eg Lead-acid battery, Ni-cd battery

BASIC REQUIREMENTS.

Primary Cell.

- Compact, light weight & fabricated easily
- High energy density & constant voltage.
- Benign environmental properties
- Longer shelf life and discharge period.
- Leak-proof containers & variety of design options.
- Economically priced.

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Secondary cell

- Long shelf life in both charged and uncharged conditions
- Longer cycle life & design life.
- High Power to weight ratio
- Short time for recharge.
- High voltage & high energy density.

SECONDARY CELLS

- Generation of electric energy, that can be restored to its original charged condition after its discharged by passing current flowing in the opposite direction'
- Large number of cycles.
- known as rechargable cells, storage cells or accumulators.
- eg lead storage cell
  Ni - Cd cell
  Li - ion batteries.

Lead storage Cell

ANODE: Spongy lead on lead grid.
CATHODE: Porous PbO_2
ELECTROLYTE: $H_2SO_{4(aq)}$ (20%) (Density 1.21-1.30g/ml)
CELL SCHEME:

$Pb/PbSO_4; H_2SO_{4(aq)}; PbSO_4 : PbO_2/Pb.$

O.C.V = 2V (Pair of plates)

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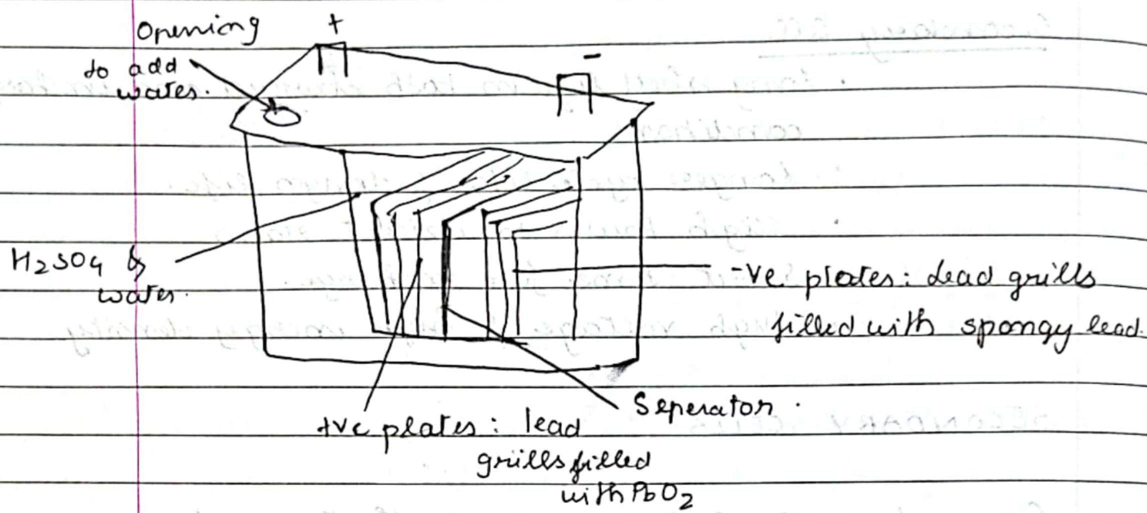

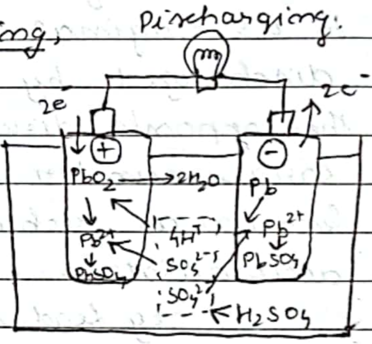

Reactions during discharging.

ANODE: $Pb_{(s)} \rightarrow Pb^{2+}_{(aq)} + 2e^-$

$Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)} \rightarrow PbSO_{4(s)}$

$\therefore Pb_{(s)} + SO^{2-}_{4(aq)} \rightarrow PbSO_{4(aq)} + 2e^-$

CATHODE: $PbO_{2(s)} + 4H^+_{(aq)} + 2e^- \rightarrow Pb^{2+}_{(aq)} + 2H_2O_{(l)}$

$Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)} \rightarrow PbSO_{4(s)}$

$PbO_{2(s)} + 4H^+_{(aq)} + SO^{2-}_{4(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$.

Overall Reaction:

$Pb_{(s)} + PbO_{2(s)} + 4H^+_{(aq)} + 2SO^{2-}_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$

Charging
Anodic pl
be conne
cathodic p
source.
Voltage
must be
Battery
stores up
energy.

Charging

ANODE: R
$PbSO_{4(s)}$

CATHODE:
$PbSO_{4(s)}$ +

NET: 2Pb

• $Pb_{(s)}$ + P

LIMITATI

• Self disch
with H_2
evolution

Pb + H_2S
PbO_2 + H

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Page No.:
Date:

Charging the discharged batteries.

Anodic plates of the discharged battery must be connected to the negative terminal and its cathodic plates to the +ve terminal of a d.c source.

Voltage slightly greater than OCV of the battery must be applied from d.c source.

Battery behaves like an electrolytic cell and stores up energy flowing into it as chemical energy.

Charging

ANODE: Reduction (Cathode of electrolytic cell)

$$PbSO_{4(s)} + 2e^- \longrightarrow Pb_{(s)} + SO_{4(aq)}^{2-}$$

CATHODE: Oxidation (Anode of electrolytic cell)

$$PbSO_{4(s)} + 2H_2O_{(l)} \longrightarrow PbO_{2(s)} + SO_{4(aq)}^{2-} + 4H^+_{(aq)} + 2e^-$$

NET: $2PbSO_{4(s)} + 2H_2O_{(aq)} \longrightarrow Pb_{(s)} + PbO_{2(s)}$

- $Pb_{(s)} + PbO_{2(s)} + 4H^+_{(aq)} + 2SO_{4(aq)}^{2-} \rightleftharpoons 2PbSO_{4(s)} + 2H_2O_{(l)}$

LIMITATIONS.

- Self discharge: They are subject to self discharge with H_2 evolution at negative plates and O_2 evolution at +ve plates.

$$Pb + H_2SO_4 \longrightarrow PbSO_4 + H_2$$

$$PbO_2 + H_2SO_4 \longrightarrow PbSO_4 + H_2O + \tfrac{1}{2}O_2$$

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- Electrolysis of water: Due to overcharging electrolysis of water takes place. Hence water content must be regularly checked and distilled water must be added.

$$2H_2O(l) + \text{electrical energy} \longrightarrow 2H_{2(g)} + O_{2(g)}$$

Consequences of overcharging

i) Reduce the acid level and damage the exposed electrode grid.

ii) Dangerous high-pressure build up that can lead to a serious risk of explosion.

- Sulfation: If left in uncharged state for a prolonged period, or operated at too high temperatures or too high acid concentration Transformation of $PbSO_4$ (porous) into dense and coarse grained form by re-crystallization.

These crystals clog the pores of the active mass and cover the plate surface so that charging becomes impossible.

This results in passivation of negative plates inhibiting acceptance while charging. The result is permanent loss of capacity.

If sulphation goes on, active mass may be pressed out and the grid will bend

Charging a sulphated battery may cause dendrites to form at the negative plate and it can short circuit.

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MODERN - MAINTENANCE FREE BATTERIES,

- without a gas release vent. Gassing controlled by using :
  1) Pb - Ca (0.1%) as the anode which inhibits the electrolysis of water.
  2) a catalyst (eg. a mixture of 98% ceria (cerium oxide) & 2% Pt that combines the H_2 & O_2 produced during discharge back into water.

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