ETS CYCLE

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- In eukaryotes => Electron transport and oxidative phosphorylation => inner **mitochondrial** membrane.

- These processes => re-oxidize NADH and FADH2 <= from the citric acid cycle (mitochondrial matrix), glycolysis (cytoplasm) and fatty acid oxidation (mitochondrial matrix) and => trap the energy released as ATP.

- **Oxidative phosphorylation** => major source of ATP in the cell.

- In prokaryotes => electron transport and oxidative phosphorylation components => in the plasma membrane.

Redox Potential

- Oxidation => loss of electrons.
- Reduction => gain of electrons.
- In chemical reaction :
- if one molecule is oxidized => another must be reduced
- i.e. oxidation-reduction reaction => transfer of electrons.

- when NADH => oxidized to NAD+ => it loses electrons.

- When molecular oxygen => reduced to water => it gains electrons :

$$NADH + H^+ + \frac{1}{2} O_2 \rightleftharpoons NAD^+ + H_2O$$

- Oxidation-reduction potential, E, (redox potential)
- a measure of affinity of a substance for electrons and
- is measured relative to hydrogen.

- **Positive** redox potential
- substance => higher affinity => electrons than hydrogen

- so would accept electrons from hydrogen,

- e.g., Oxygen , a strong oxidizing agent

- **Negative** redox potential
- substance has a lower affinity for electrons than does hydrogen
- would donate electrons to H^+, forming hydrogen,
- e.g., NADH , a strong reducing agent

For biological systems,

- **standard redox potential** for a substance (**E0'**)

- measured at pH 7 & expressed in volts.

- In oxidation-reduction reaction

- electron transfer is occurring

- total voltage change of the reaction (change in electric potential, ΔE) => is the sum of voltage changes of individual oxidation-reduction steps.

- **Standard free energy change** of a reaction at pH 7 => $\Delta G0'$ => calculated from the change in redox potential $\Delta E0'$ of substrates and products:

$$\Delta G0' = -n\, F\, \Delta E0'$$

Where, n -- number of electrons transferred,

$\Delta E0'$ -- in volts (V),

$\Delta G0'$ -- in kilocalories per mole (kcal mol-1) and

F -- constant called Faraday (23.06 kcal V-1 mol-1).

- A reaction with a positive ΔE0’ has a negative ΔG0’ (i.e., is **exergonic**).
- Thus for the reaction:

$$NADH + H^{+} + \tfrac{1}{2}\,O_2 \rightleftharpoons NAD^{+} + H_2O$$

$$\Delta E_0{}' = +\ 1.14\ V$$

$$\Delta G^{0\prime} = -\ 52.6\ kcal\ mol^{-1}.$$

Electron Transport from NADH

Comparing the energetic of the oxidation of NADH:

$$NADH + H^+ + ½\,O_2 \rightleftharpoons NAD^+ + H_2O \qquad \Delta G^{0'} = -\,52.6\ kcal\ mol^-$$

and the synthesis of ATP:

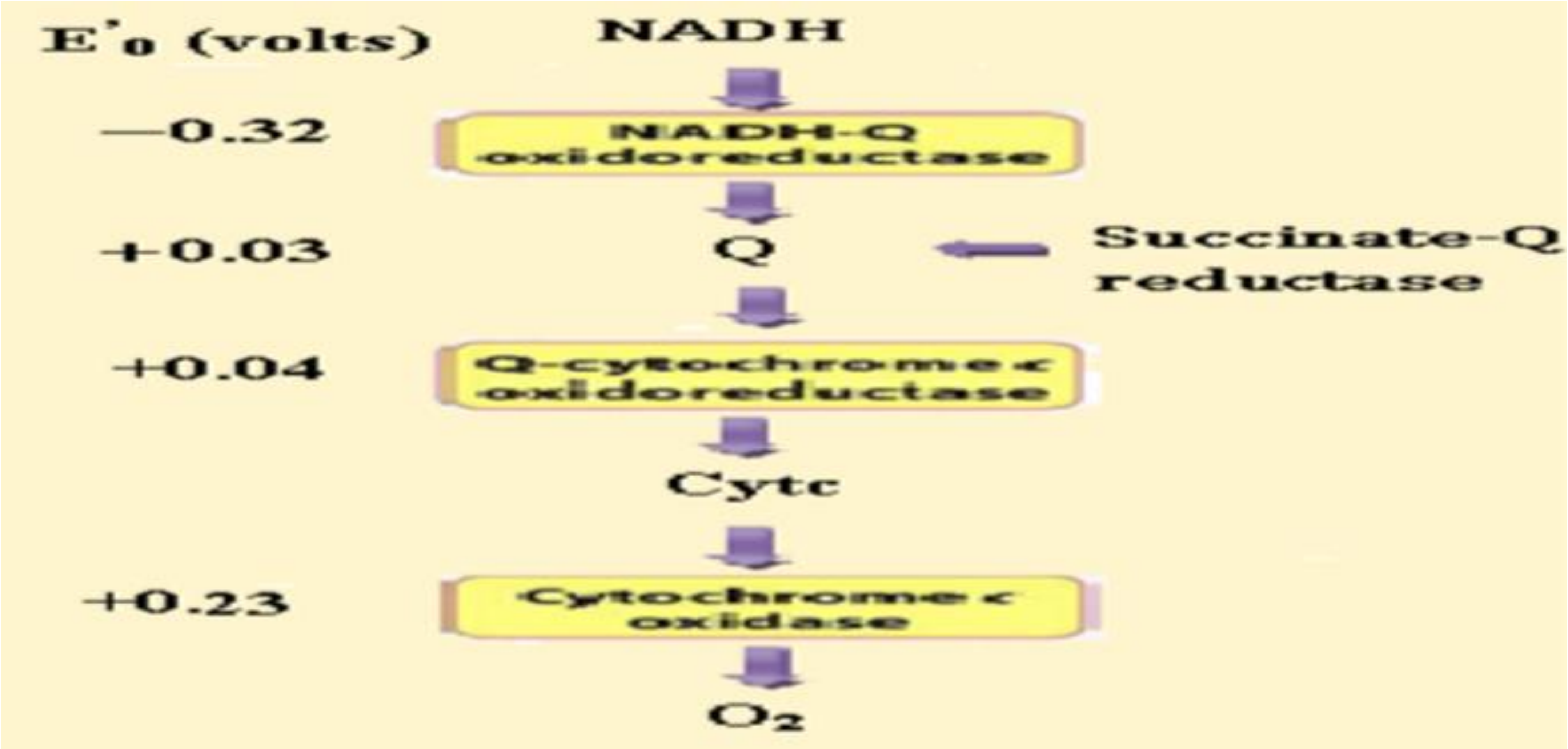
$$ADP + P_i + H^+ \rightleftharpoons ATP + H_2O \qquad \Delta G^{0'} = +\,7.3\ kcal\ mol^-$$

Thus, the oxidation of NADH releases sufficient energy to drive the synthesis of several molecules of ATP.

- NADH oxidation and ATP synthesis → not occur in a single step.

- Electrons → not transferred from NADH → oxygen directly.

- Electrons are transferred from NADH → oxygen → along a chain of electron carriers → called **electron transport chain** (**respiratory chain**).



Organisation of Electron Transport Chain complexes

Electron Transport Chain

Consists of 3 large protein complexes embedded in **inner mitochondrial membrane :**

- NADH dehydrogenase complex (Complex I)
- Succinate Q reductase
- The cytochrome bc1 complex (Complex II)
- cytochrome oxidase (Complex III)

- Electrons flow from NADH to oxygen through these three complexes
- Each complex contains → several electron carriers → work sequentially → carry electrons down the chain.

- 2 free electron carriers are also needed to link these large complexes:
  - Ubiquinone {coenzyme Q (CoQ)}
  - cytochrome c

ATP Synthesis (Oxidative Phosphorylation)

- NADH and FADH2 are **oxidized** by electron transport through → respiratory chain → Synthesis of ATP.

- Energy liberated by electron transport => used to create a proton gradient across the mitochondrial inner membrane => that is used to drive ATP synthesis (chemiosmotic hypothesis)→ in presence of ATP synthase .

- Thus the **proton gradient couples electron transport and ATP synthesis** .

(not a chemical intermediate as in substrate level phosphorylation.)

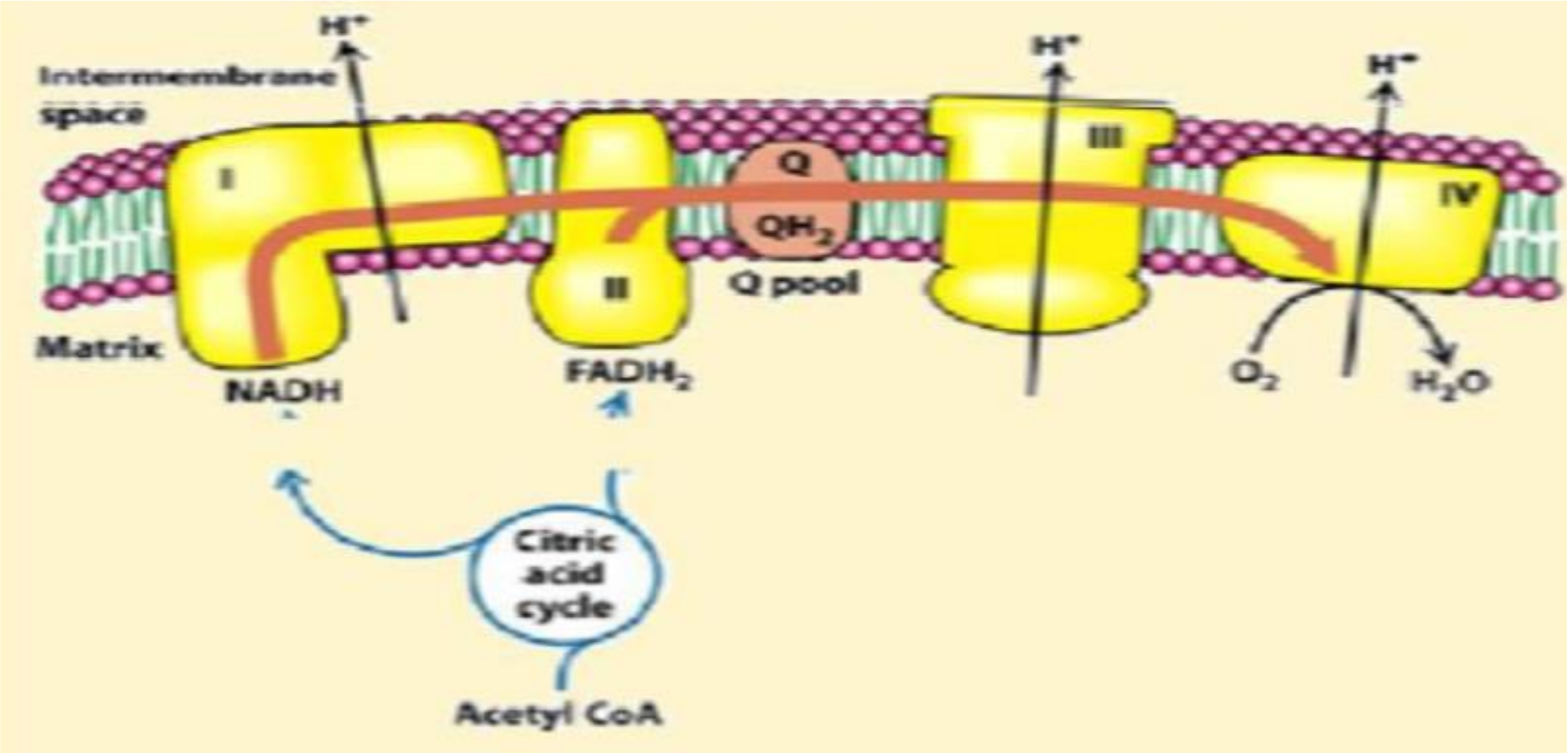
(enzyme → originally → **ATPase** because → without input of energy from electron transport → the reaction can reverse and actually **hydrolyzes ATP**.)

Summary

- Electron transport down the respiratory chain → from **NADH oxidation** => causes **H+ ions** to be pumped out → into the inter membrane space by **three H+ pumps** → **NADH dehydrogenase**, **cytochrome bc1 complex** and **cytochrome oxidase**.
- Free energy change => in transporting an electrically charged ion => across a membrane => leads to formation of **electrochemical proton gradient**.

- The pumping out of H+ ions → generates a higher concentration of H+ ions → in inter membrane space and an electrical potential →the side of the inner mitochondrial membrane facing the inter membrane space → positive.
- Protons flow back → mitochondrial matrix according to electrochemical gradient through ATP synthase → drives ATP synthesis.
- The ATP synthase is driven by proton-motive force → which is the sum of pH gradient (the chemical gradient of H+ ions) and membrane potential (electrical charge potential across the inner mitochondrial membrane).

- **FADH2** is re oxidized → via ubiquinone → its oxidation causes H+ ions to be pumped out only by the **cytochrome bc1 complex** and **cytochrome oxidase** → so the amount of ATP made from FADH2 is **less** than from NADH.
- Measurements → show that 2.5 ATP molecules are synthesized per NADH oxidized whereas 1.5 ATPs are synthesized per FADH2 oxidized.



Summary of Electron Flow

THANK YOU