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NAAC ACCREDITED ‘A’ GRADE

Topic: RESPIRATION

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Electron Transport Chain

Most living cells produce energy from nutrients through cellular respiration that involves the taking up of oxygen to release energy. The electron transport chain or ETC is the third and final stage of this process, the other two being glycolysis and the citric acid cycle.

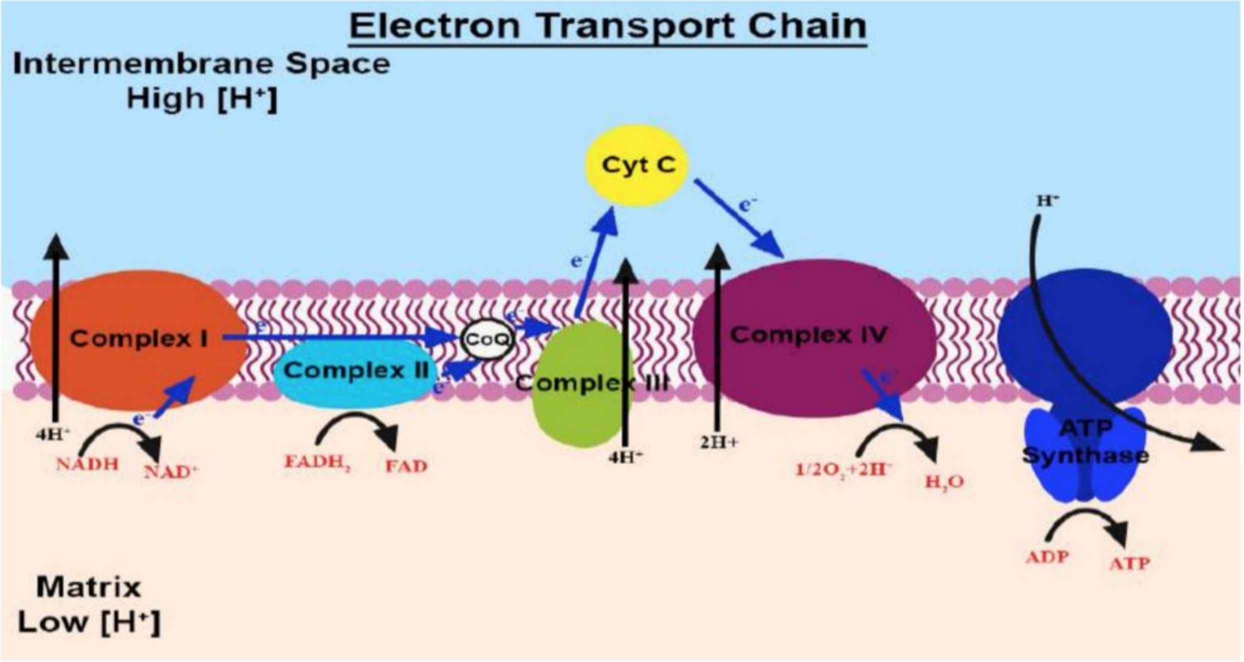
The energy produced is stored in the form of ATP or adenosine triphosphate, which

is a nucleotide found throughout living organisms.

The ATP molecules store energy in their phosphate bonds. The ETC is the most important stage of cellular respiration from an energy point of view because it produces the most ATP. In a series of redox reactions, energy is liberated and used to attach a third phosphate group to adenosine diphosphate to create ATP with three phosphate groups.

This also causes hydrogen ions to accumulate within the matrix space. Therefore, a concentration gradient forms in which hydrogen ions diffuse out of the matrix space by passing through ATP synthase. The current of hydrogen ions powers the catalytic action of ATP synthase, which phosphorylates ADP, producing ATP.

The electron transport chain is the last component of aerobic respiration and is the only part of glucose metabolism that uses atmospheric oxygen. In a series of redox reaction electrons reduce O_2, producing H_2O.



There are four complexes composed of proteins, labeled I through IV in Figure, and the aggregation of these four complexes, together with associated mobile, accessory electron carriers, is called the electron transport chain.

The electron transport chain is present in multiple copies in the **inner mitochondrial membrane of eukaryotes** and **the plasma membrane of prokaryotes**. Note, however, that the electron transport chain of prokaryotes may not require oxygen as some live in anaerobic conditions. The common feature of all electron transport chains is the presence of a proton pump to create a proton gradient across a membrane.

Complex I (NADH ubiquinone oxidoreductase)

To start, two electrons are carried to the **first complex aboard NADH**. This complex, labeled I, is composed of **flavin mononucleotide (FMN**) and **an iron-sulfur (Fe-S)-containing protein.** FMN, which is derived from vitamin B_2, also called riboflavin, is one of several **prosthetic groups** or co-factors in the electron transport chain.. The enzyme in complex I is **NADH dehydrogenase** and is a very large protein, containing 45 amino acid chains. **Complex I can pump hydrogen ions across the membrane from the matrix into the intermembrane space**, and it is in this way that the hydrogen ion gradient is established and maintained between the two compartments separated by the inner mitochondrial membrane.

$$\mathrm{NADH} + \mathrm{H}^+ + \mathrm{UQ} \rightleftharpoons \mathrm{NAD}^+ + \mathrm{UQH}_2$$

Q and Complex II (Succinate ubiquinone oxidoreductase)

Complex II directly **receives $FADH_2$**, which does not pass through complex I. The compound connecting the first and second complexes to the third is **ubiquinone (Q)**. The **Q molecule** is lipid soluble and **freely moves** through the hydrophobic core of the membrane. Once it is reduced, (QH_2), ubiquinone delivers its electrons to the next complex in the electron transport chain. **Q receives the electrons derived from NADH from complex I and the electrons derived from $FADH_2$ from complex II, including succinate dehydrogenase.** This enzyme and $FADH_2$ form a small complex that delivers electrons directly to the electron transport chain, bypassing the first complex. Since these electrons bypass and thus do not energize the proton pump in the first complex, fewer ATP molecules are made from the $FADH_2$ electrons.

$$\text{Succinate} + \text{UQ} \rightleftharpoons \text{Fumarate} + \text{UQH}_2$$

Complex III (Dihydro Ubiquinone cytochrome c oxidoreductase)

The third complex is **composed of cytochrome b, another Fe-S protein, Rieske center (2Fe-2S center), and cytochrome c proteins;** this complex is also called cytochrome oxidoreductase. Cytochrome proteins have a prosthetic group of heme. The heme molecule is similar to the heme in hemoglobin, but it carries electrons, not oxygen. As a result, the **iron ion at its core is reduced and oxidized as it passes the electrons, fluctuating between different oxidation states: Fe^{++} (reduced) and Fe^{+++} (oxidized)**. Complex III **pumps two protons** through the membrane and **passes its electrons to cytochrome c (mobile electron carrier)** for transport to the fourth complex of proteins and enzymes (cytochrome c is the acceptor of electrons from Q; however, whereas Q carries pairs of electrons, **cytochrome c can accept only one at a time).**

UQH2 +2 ferricytochrome C ⇌ UQ + 2 ferrocytochrome C + $2H^+$

Complex IV (cytochrome C oxidase)

The fourth complex is **composed of cytochrome proteins c, a, and a_3.** This complex contains **two heme groups** (one in each of the two cytochromes, a, and a_3) and **three copper ions** (a pair of Cu_A and one Cu_B in cytochrome a_3). **The cytochromes hold an oxygen molecule very tightly between the iron and copper ions until the oxygen is completely reduced.** The **reduced oxygen then picks up two hydrogen ions** from the surrounding medium **to make water (H_2O)**, known as **terminal respiration**. T**he removal of the hydrogen ions from the system contributes to the ion gradient used in the process of chemiosmosis.**

2 ferrocytochrome C + $2H^+$ +½ O2 ⇌ 2 ferricytochrome C + H_2O

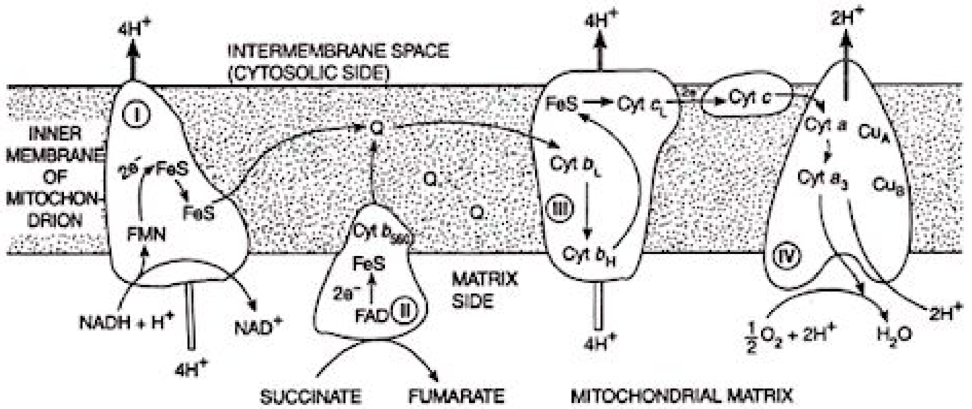
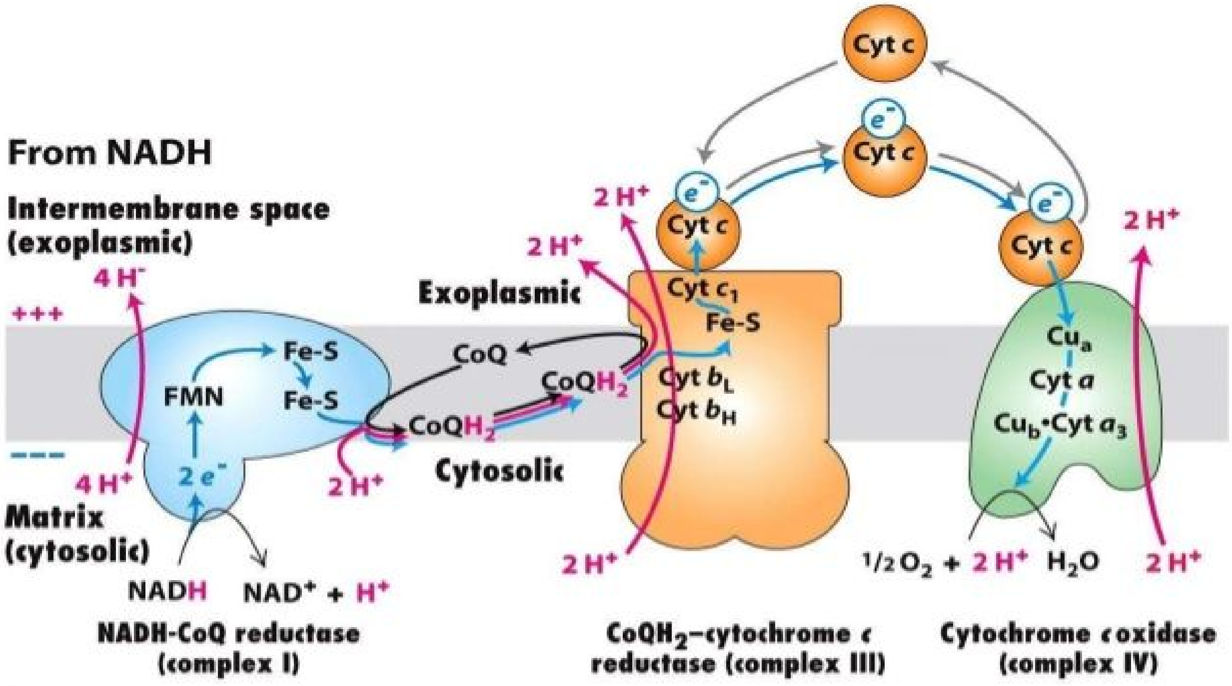
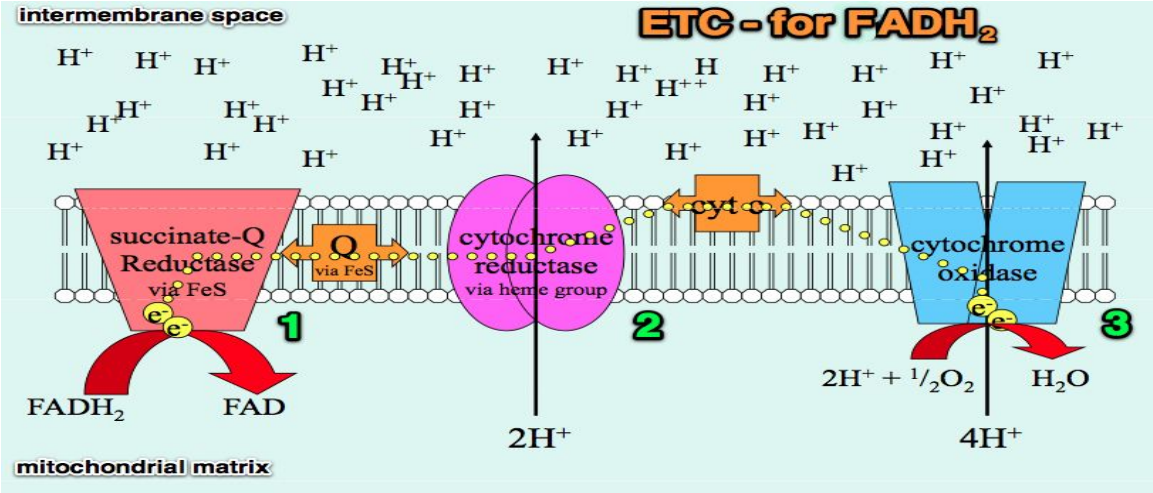


FIG. 24.6. Summary of mitochondrial electron transport chain showing the flow of electrons and protons (H^+) through the four enzyme complexes of the transport chain. Electrons reach quinone (Q) through complexs I and II. Q serves as a mobile carrier of electrons and passes them to complex III, which then passes them to cytochrome *c*, another mobile connecting link. Complex IV then transfers electrons from reduced cytochrome *c* to O_2. Electron flow through complexes I, III and IV is accompanied by proton flow from the mitochondrial matrix to the intermembrane space (cytosolic side)

Electron Transport Chain [I, III, IV] proton pomp



Electron Transport Chain [II, III,IV] proton pump



ATP Synthase

At the end of this process, the proton gradient is produced by each complex pumping protons across the membranes. The resulting proton-motive force draws the protons through the membranes via the ATP synthase molecules The flow of electrons is used by protein complexes in the mitochondrial or cell membranes to transport hydrogen ions, H+ , across the membranes. The presence of more hydrogen ions outside a membrane than inside creates a **pH imbalance** with a more acidic solution outside the membrane.

To balance the pH, the hydrogen ions flow back across the membrane through the ATP synthase protein complex, driving the **formation of ATP molecules**. The chemical energy harvested from the electrons is changed to an electrochemical form of energy stored in the hydrogen ion gradient.

When the electrochemical energy is released through the flow of the hydrogen ions or protons through the ATP synthase complex, it is changed to biochemical energy in the form of ATP. The overall chemical process is called oxidative phosphorylation..

Importance of Electron Transport Chain

- Each of the three cellular respiration phases incorporates important cell processes, but the ETC produces by far the most ATP. Since energy production is one of the key functions of cell respiration, ATP is the most important phase from that point of view.
- Where the ETC produces up to 34 molecules of ATP from the products of one glucose molecule, the citric acid cycle produces two, and glycolysis produces four ATP molecules but uses up two of them.
- The other key function of the ETC is to produce NAD and FAD from NADH and FADH in the first two chemical complexes. The products of the reactions in ETC complex I and complex II are the NAD and FAD molecules that are required in the citric acid cycle. As a result, the citric acid cycle is dependent on the ETC.
- Since the ETC can only take place in the presence of oxygen, which acts as the final electron acceptor, the cell respiration cycle can only operate fully when the organism takes in oxygen.

ETC Inhibitors:

- The ETC reactions are a highly efficient way to produce and store energy for the cell to use in its movement, reproduction and survival. When one of the series of reactions is blocked, the ETC no longer functions, and cells that rely on it die.
- Some prokaryotes have alternate ways of producing energy by using substances other than oxygen as the final electron acceptor, but eukaryotic

cells depend on oxidative phosphorylation and the electron transport chain for their energy needs.

- Substances that can inhibit ETC action can **block redox reactions**, **inhibit proton transfer or modify key enzymes**. If a redox step is blocked, **the transfer of electrons stops** and oxidation proceeds to high levels on the oxygen end while further reduction takes place at the beginning of the chain.
- When protons can't be transferred across the membranes or enzymes such as ATP synthase are degraded, the **production of ATP stops**.
- In either case, **cell functions break down** and the **cell dies**.
- Plant-based substances such as **rotenone, compounds such as cyanide and antibiotics such as antimycin A cyanide, carbon monoxide (CO), sodium azide, and oligomycin** be used to inhibit the ETC reaction and bring about targeted cell death.cin . **Rotenone inhibits complex I, carboxin inhibits complex II, antimycin A inhibits complex III, cyanide and CO inhibit complex IV, and oligomycin inhibits ATP synthase**

Uncoupling

- The synthesis of ATP by ATP synthase is linked to the proton gradient established during ETC. But it is to be noted that the ETC and the activity of ATP synthase are distinct processes that are not always coupled.
- These processes can be uncoupled by any mechanism that prevents an electrochemical gradient from being established; making the **inner membrane permeable to protons.**
- **Ionophores** act as uncouplers because they act as a channel in which protons can move into the intermembrane and back into the matrix.These molecules cause the overall pH to increase and inhibit ATP synthesis; hence are very **toxic.**

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