Electron Transport Chain

Most of the ATP generated during aerobic catabolism of glucose is not generated directly from glycolysis and citric acid cycle. It is derived from a process that begins with moving electrons through a series of electron transporters that undergo redox reactions: electron transport chain. This 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. Current of hydrogen ions powers catalytic action of ATP synthase which phosphorylates ADP to produce ATP.

Electron transport chain is the last component of aerobic respiration and is the only part of glucose metabolism that uses atmospheric oxygen. Electron transport is a series of redox reactions where electrons are passed rapidly from one component to the next, to the endpoint of the chain where the electrons reduce molecular oxygen to produce water. There are four complexes composed of proteins, labeled I to IV and the aggregation of these four complexes, together with associated mobile accessory electron carriers, is called the electron transport chain. Electron transport chain is present in multiple copies in inner mitochondrial membrane of eukaryotes and plasma membrane of prokaryotes. Common feature of all electron transport chains is the presence of proton pump to create a proton gradient across a membrane.

Complex I

To start, two electrons are carried to the first complex receives 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. Enzyme in complex I is NADH dehydrogenase and is a very large protein, containing 45 amino acid chains. Complex I can pump four hydrogen ions across the membrane from the matrix into the inter-membrane 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.

Q and Complex II

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). This 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. The Q receives electrons derived from NADH from complex I and electrons derived from $FADH_2$ from complex II. 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 proton pump in the first complex, fewer ATP molecules are made from $FADH_2$ electrons. Number of ATP molecules ultimately obtained is directly proportional to the number of protons pumped across the inner mitochondrial membrane.

Complex III

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 which is similar to the heme in hemoglobin, but carries electrons, not oxygen. 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). The heme molecules in the cytochromes have slightly different characteristics due to the effects of the different proteins binding them, giving slightly different characteristics to each complex. Complex III pumps protons through the membrane and passes its electrons to cytochrome c 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.

Complex IV

The fourth complex is composed of cytochrome proteins c, a, and a_3. It 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). 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). Removal of hydrogen ions from the system contributes to the ion gradient used in the process of chemiosmosis.

Chemiosmosis

In chemiosmosis, the free energy from the series of redox reactions just described is used to pump hydrogen ions (protons) across the membrane. Uneven distribution of H^+ ions across membrane establishes both concentration and electrical gradients (an electrochemical gradient), owing to the hydrogen ions' positive charge and their aggregation on one side of the membrane.

If the membrane were open to diffusion by hydrogen ions, they would tend to diffuse back across into the matrix, driven by their electrochemical gradient. As many ions cannot diffuse through the nonpolar regions of phospholipid membranes without the aid of ion channels. Similarly, hydrogen ions in the matrix space can only pass through the inner mitochondrial membrane through integral membrane protein called ATP synthase. It acts as a tiny generator, turned by the force of hydrogen ions diffusing through it, down their electrochemical gradient. Turning of parts of this molecular machine facilitates the addition of a phosphate to ADP, forming ATP, using the potential energy of the hydrogen ion gradient.

Chemiosmosis is used to generate 90 percent of the ATP made during aerobic glucose catabolism; it is also the method used in the light reactions of photosynthesis to utilize the energy of sunlight in the process of photophosphorylation. The overall result of these reactions is the production of ATP from the energy of the electrons removed from hydrogen atoms. These atoms were originally part of a glucose molecule. At the end of the pathway, electrons are used to reduce an oxygen molecule to oxygen ions. Extra electrons on the oxygen attract hydrogen ions (protons) from the surrounding medium, and water is formed.

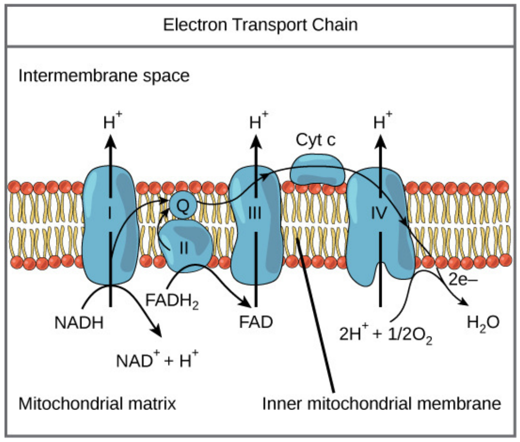

Figure: Electron transport chain is a series of electron transporters embedded in the inner mitochondrial membrane that shuttles electrons from NADH and $FADH_2$ to molecular oxygen. In the process, protons are pumped from the mitochondrial matrix to inter-membrane space and oxygen is reduced to form water.

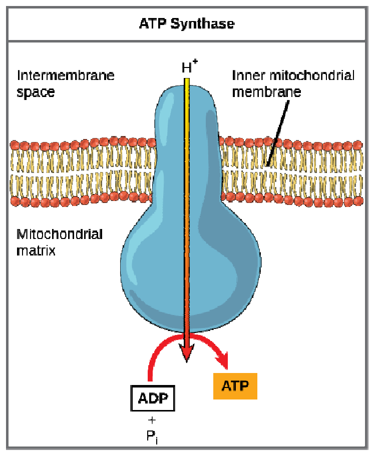

Figure: ATP synthase is a complex, molecular machine that uses a proton (H+) gradient to form ATP from ADP and inorganic phosphate (Pi). (Credit: modification of work by Klaus Hoffmeier)

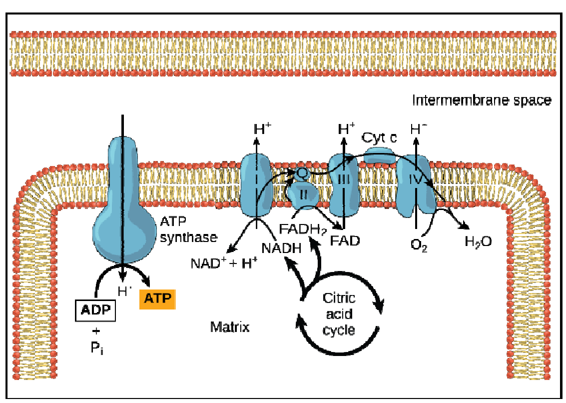

Figure: In oxidative phosphorylation, the pH gradient formed by the electron transport chain is used by ATP synthase to form ATP.

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