Chemiosmosis

In chemiosmosis, the free energy from the series of redox reactions just described is used to pump hydrogen ions (protons) across the membrane. The uneven distribution of H^+ ions across the membrane establishes both concentration and electrical gradients (thus, 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 the hydrogen ions, the ions would tend to diffuse back across into the matrix, driven by their electrochemical gradient. Recall that 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 an integral membrane protein called ATP synthase (Figure 2). This complex protein acts as a tiny generator, turned by the force of the hydrogen ions diffusing through it, down their electrochemical gradient. The 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 (Figure 3) 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 harness the energy of sunlight in the process of photophosphorylation. Recall that the production of ATP using the process of chemiosmosis in mitochondria is called oxidative phosphorylation. 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, the electrons are used to reduce an oxygen molecule to oxygen ions. The extra electrons on the oxygen attract hydrogen ions (protons) from the surrounding medium, and water is formed.

ATP Yield

The number of ATP molecules generated from the catabolism of glucose varies. For example, the number of hydrogen ions that the electron transport chain complexes can pump through the membrane varies between species. Another source of variance stems from the shuttle of electrons across the membranes of the mitochondria. (The NADH generated from glycolysis cannot easily enter mitochondria.) Thus, electrons are picked up on the inside of mitochondria by either NAD^+ or FAD^+. As you have learned earlier, these FAD^+ molecules can transport fewer ions; consequently, fewer ATP molecules are generated when FAD^+ acts as a carrier. NAD^+ is used as the electron transporter in the liver and FAD^+ acts in the brain.

Another factor that affects the yield of ATP molecules generated from glucose is the fact that intermediate compounds in these pathways are used for other purposes. Glucose catabolism connects with the pathways that build or break down all other biochemical compounds in cells, and the result is somewhat messier than the ideal situations described thus far. For example, sugars other than glucose are fed into the glycolytic pathway for energy extraction. Moreover, the five-carbon sugars that form nucleic acids are made from intermediates in glycolysis. Certain

nonessential amino acids can be made from intermediates of both glycolysis and the citric acid cycle. Lipids, such as cholesterol and triglycerides, are also made from intermediates in these pathways, and both amino acids and triglycerides are broken down for energy through these pathways. Overall, in living systems, these pathways of glucose catabolism extract about 34 percent of the energy contained in glucose.

Dr. Seema Margret Singh
Associate Professor
Department of Botany
P.G College, Datia (M.P)

Synthesis of ATP through Electron Transport Chain

Introduction

We know that there are two pathways in cellular respiration –Glycolysis and Citric Acid Cycle that generate ATP. However most of the ATP generated during the aerobic catabolism of glucose is not generated directly from these pathways. Rather, it is derived from a process that begins with moving electrons through a series of Electron Transporters that undergoes redox reactions: The 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, which phosphorylate ADP, producing ATP.

Mechanism:

The electron transport chain is the last component of aerobic respiration and is the only part of glucose metabolism that uses atmospheric oxygen. Oxygen continuously diffuses into plants, in animals; it enters the body through the respiratory system. Electron transport is a series of redox reactions that resemble a relay race in that electrons are passed rapidly from one component to the next, to the end point of the chain where the electrons reduces molecular oxygen, producing water. There are four complexes composed of proteins, labelled I to IV 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. In electron transport chain of prokaryotes may not require oxygen as some live in anaerobic conditions. The common feature of all electron transport chain is the presence of a proton pump create a proton gradient across a membrane.

Complex I:

To start, two electrons are carried to the first complex aboard NADH. This complex I is composed of Flavin Mononucleotide (FMN) and an Iron Sulfur (Fe-S) containing proteins. FMN which is derived from vitamin B_2, also called riboflavin is one of the several prosthetic groups or co-factors in the electron transport chain. The enzyme in complex I is NADH dehydrogenase and is avery large protein, containing 45 amino acid chains. Complex I can pump four 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.

Q and complex II:

Complex II directly receives $FADH_2$, which does not pass through complex I. the compound which connects the first and second complexes to the third is Ubiquinone (Q). The Q molecule is lipid soluble and freely moves through the hydrophobic ore 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 ETC, 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. The number of ATP molecules ultimately obtained is directly proportional to the number of proton pumped across the inner mitochondrial membrane.

Complex III:

The third complex is composed of cytochrome b, another Fe-S protein, Rieske centre (2Fe-2S), and cytochrome c protein, this complex is also called cytochrome oxidoreductase. Cytochrome proteins have a prosthetic group of heme. The heme molecule is similar to the heme in haemoglobin, but it carries electrons, not oxygen. As a result the iron ion at its coreis reduced and oxidized as it passes the electrons, fluctuating between different oxidation states; Fe++ (reduced) and Fe^{+++} (oxidized). The heme molecule in cytochrome have slightly different characteristic due to the effect of different proteins binding them, complex III pumps proton through the membrane and pass it's electron to cytochrome c for transport to the IV^{th} complex of proteins and enzymes (cytochrome c is the acceptor of electrons from Q; whereas Q carries pairs of electrons, cytochrome c accept only one at a time).

Complex IV:

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. The cytochromes hold an oxygen molecule very tightly between the iron and copper ion until the oxygen is completely reduced. The reduced oxygen then picks up to hydrogen ions from the surrounding medium to make water (H_2O). The removal of the hydrogen ions from the system contributes to the ion gradient used in the process of chemiosmosis.

Chemiosmotic Regeneration of ATP:

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