ELECTRON TRANSPORT CHAIN AND OXIDATIVE PHOSPHORYLATION

(RESPIRATORY CHAIN)

IMPORTANCE AND LOCATION

- Importance: these are the mechanism by which NADH plus H^+ and $FADH^2$ are used to generate ATP
- Location: inner mitochondrial membrane.

REVIEW OF MITOCHONDRIAL STRUCTURE

- Porous (~5 kDa) outer mitochondrial membrane
- Intra mitochondrial space not just space but filled with enzymes, e.g.
- Tight (and highly convoluted) intra mitochondrial membrane forming *cristae*
- Matrix .

In summary, the respiratory chain can be characterized as the process during which NADH + H^+ and $FADH_2$ are oxidized under consumption of oxygen and water and ATP are generated.

The generation of water (oxyhydrogen reaction) is strongly exergonic:

$2\ H_2 + O_2 > 2\ H_2O$.

In the respiratory chain, this energy is gradually set free in a number of intermediate steps (an electron transport chain) and can thus be used for the generation of energy-rich compounds.

1. NADH + H^+ is oxidized resulting in NAD^+. The hydrogen is passed on to a further hydrogen-acceptor, the FAD.

2. $FADH_2$ is oxidized by cytochromes. Cytochromes (cytochrome b, cytochrome c, cytochrome a , etc.) are proteins with haeme-groups (porphyrin rings) as cofactors. Located in the centre of this ring is an iron ion of changing valency:

$Fe^{III} <> Fe^{II}$

While FAD accepts both electrons and protons, cytochromes transport only electrons. The protons are given off into solution. In the respiratory chain, the Fe^{III} of cytochrome b is at first changed into Fe^{II}. In plant cells, at least three different cytochrome b-types are in series. The iron ion of cytochrome b achieves its original Fe^{III} state again by transferring one electron to cytochrome c which transfers it in a further step onto cytochrome a. A quinone/hydroquinone system may be inserted between the flavoprotein and the cytochromes.

3. The reduced cytochrome a transfers the electrons onto oxygen that reacts immediately with free protons to form water.

REDUCING POTENTIAL

Theoretically ~ 7 ATP could be produced ($NADH \rightarrow O^2$ 1.12 V (table of standard reduction potentials)

Since $\Delta G'^\circ$ for ATP *synthesis* is +30.5 kJ/mol, 7.1 ATP (One step, one ATP)

(3 steps, 3 ATP) Some energy “lost” as heat in order to drive the reaction

The end result of glucose degradation: the oxidation is coupled to a decrease of the free energy; 686 kcal/mol (= 2881 kJ/mol) are obtained by the complete oxidation of glucose. How much of this energy can the cell use?

1. Six mol ATP per mol glucose are generated (substrate chain phosphorylation). This is because all steps after the breaking down of fructose-1,6-phosphate have to be counted twice (once for each of the two resulting C_3 molecules), so it is 3 x 2 ATPs. Of these six ATPs, two are needed to start glycolysis. That leaves four.
2. During the course of glycolysis up to acetyl-CoA, 2 x 2 $NADH + H^+$ are generated. An additional 3 x 2 $NADH + H^+$ and 1 x 2 $FADH_2$ are produced in the citric acid cycle. One $NADH + H^+$ gives three, one $FADH_2$ two ATPs when fed into the respiratory chain. This

sums up to 34 ATPs plus the 4 ATPs of glycolysis. A total of 38 mol ATP are thus gained by the cell's degradation of one mol glucose. Since each energy-rich bond of ATP contains 7.3 kcal/mol (= -30.6 kJ/mol), the 38 ATP equal 277 kcal/mol (ca 1163 kJ/mol).