The electron transport chain

In the electron transport chain, electrons flow downward in energy from coenzyme NADH and flavoprotein FADH2 to the terminal electron acceptor, molecular oxygen, O2. Electrons move spontaneously from carriers of lower reduction potential (E'o) to carriers of higher reduction potential. Molecules involved in the ETC have reduction potentials between the values for NAD+/NADH couples and oxygen/H2O couples. Energy extracted from the transfer of electrons is most efficiently conserved when it is released in a step wise fashion, and is accomplished with four distinct protein complexes in the mitochondrial membrane:

Complex I = NADH-coenzyme Q reductase (NADH dedhydrogenase)

Complex II = succinate-conenzyme Q reductase (succinate dehydrogenase)

Complex III = coenzyme Q-cytochrome c reductase

Complex IV = cytochrome c oxidase

Complex I oxidizes NADH and reduces coenzyme Q (UQ), transferring a pair of electrons from NADH to UQ. The oxidation of one NADH and reduction of UQ results in a net transport of protons from the matrix side to the intermembrane space. Complex II oxidizes succinate and reduces UQ, yielding a net reduction potential of +0. 029 V, which does not contribute to the transport of protons across the inner mitochondrial membrane. Complex III facilitates the transfer of electrons from UQ to cytochrome c (cyto c) via the Q cycle, which oxidizes UQH2 and reduces cyto c, releasing four protons into the intermembrane space for every two electrons that pass through the Q cycle. Complex IV accepts electrons from cyto c and reduces oxygen to form H2O, driving proton transport across the inner mitochondrial membrane into the intermembrance space. For every four electrons used to reduce oxygen, four protons are released into the intermembrance space.

Components of the ETC are arranged in line with the flow of electrons from donors with lower affinity for electrons toward acceptors with higher affinity for electrons. Affinity for electrons is measured by the reduction potential. The transfer of electrons does not occur in a simple linear sequence. Electrons can enter the ETC at different entry points, either through Complex I or Complex II, and then the pathways converge at Complex III. As Fig. 1 shows, electrons move from more negative to more positive reduction potentials on the energy scale.

Table 13-7 presents the following reduction potentials for reactions that occur in the ETC:

NAD+ + 2H+ 2e- ƒ NADH + H+ ΔE’o = -0. 320 V

FAD + 2H+ +2e- ƒ FADH2 ΔE’o = -0. 219 V

Fumarate + 2H+ + 2e- ƒ Succinate ΔE’o = +0. 031 V

Q + 2H+ + 2e- ƒ QH2 ΔE’o = +0. 045 V

cyt c1(Fe3+) + e- ƒ cyt c1(Fe2+) ΔE’o = +0. 220 V

cyt c(Fe3+) + e- ƒ cyt c(Fe2+) ΔE’o = +0. 254 V

½ O2 + 2H+ + 2e- ƒ H2O ΔE’o = +0. 816 V

As mentioned, molecules involved in the ETC have reduction potentials between the values for NAD+/NADH couples and oxygen/H2O couples. Electrons move from more negative to more positive reductions potentials in the following order:

NADH ƒ Q ƒ cytochrome c1 ƒ cytochrome c ƒ O2

Reactions that have positive reduction potentials have negative free energy and are energetically favorable. Complex III has a more positive reduction potential than Complex I and II, and Complex IV has a more positive reduction potential than Complex III. The reduction potential for each complex can be estimated with the half reactions and reduction potentials provided in Table 13-7. Below are the net equations for each complex:

Complex I NADH + 5H+N + Q ↔ NAD+ + QH2 + 4H+P

Complex II Succinate + Q ↔ fumarate + QH2

Complex III QH2 + 2 cyt c1 + 2H+N ↔ Q + 2 cyt c1 + 4 H+P

Complex IV 4 cyt c + 8 H+N + O2 ↔ 4 cyt c + 4 H+P + 2 H2O

For example:

Complex I NADH + 5H+N + Q ↔ NAD+ + QH2 + 4H+P

NAD+ + 2H+ 2e- ƒ NADH + H+ ΔE’o = -0. 320 V

Q + 2H+ + 2e- ƒ QH2 ΔE’o = +0. 045 V

ΔE’o = E’oacceptor – E’odonor

ΔE’o = 0. 045 – (-0. 320) = +0. 365 V

Complex III QH2 + 2 cyt c1 + 2H+N ↔ Q + 2 cyt c1 + 4 H+P

Q + 2H+ + 2e- ƒ QH2 ΔE’o = +0. 045 V

cyt c1(Fe3+) + e- ƒ cyt c1(Fe2+) ΔE’o = +0. 220 V

ΔE’o = [2 x 0. 220] – 0. 045 = +0. 395 V

The reduction potential for Complex III is greater than that of Complex I, correlating to flow of electrons in the ETC. Electrons move from more negative to more positive reductions potentials.

In addition, both overall reactions for NADH/FADH2 to O2 are positive values, another indication that electrons moving from Complex I/II to Complex IV is energetically favorable. The calculations are provided below.

This is the overall reaction for electrons that travel from NADH to O2

NADH + H+ + ½ O2 ƒ NAD+ + H2O

NAD+ + 2H+ 2e- ƒ NADH + H+ ΔE’o = -0. 320 V

½ O2 + 2H+ + 2e- ƒ H2O ΔE’o = + 0. 816 V

ΔE’o = 0. 816 – (-0. 320) = +1. 136 V

This is the overall reaction for electrons that travel from FADH2 to O2

FADH2 + ½ O2 ƒ FAD + H2O

FAD + 2H+ +2e- ƒ FADH2 ΔE’o = – 0. 219 V

½ $O_2 + 2H^+ + 2e^-$ ƒ H_2O ΔE’o = + 0. 816 V

ΔE’o = 0. 816 – (-0. 219) = +1. 035 V

As a result of the ETC, the net reaction for the transfer of two electrons from NADH through the respiratory chain to molecular oxygen is highly exergonic (positive reduction potentials and negative free energy). For each pair of electrons transferred to O_2, four protons are pumped out of the matrix into the intermembrane space by Complex I, four by Complex III and two by Complex IV, producing a proton gradient that drives ATP synthesis (Fig. 2).