

The electron transport chain



**ASSIGN
BUSTER**

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°) 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 dehydrogenase)

Complex II = succinate-coenzyme 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

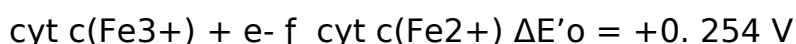
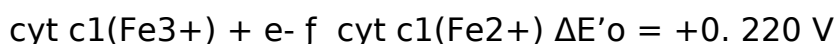
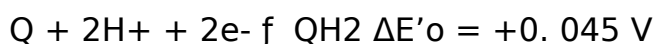
form H₂O, driving proton transport across the inner mitochondrial membrane into the intermembrane space. For every four electrons used to reduce oxygen, four protons are released into the intermembrane space.

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:



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 → Q → cytochrome c₁ → cytochrome c → 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 $\text{NADH} + 5\text{H}^+ + \text{Q} \leftrightarrow \text{NAD}^+ + \text{QH}_2 + 4\text{H}^+$

Complex II $\text{Succinate} + \text{Q} \leftrightarrow \text{fumarate} + \text{QH}_2$

Complex III $\text{QH}_2 + 2 \text{cyt } c_1 + 2\text{H}^+ \leftrightarrow \text{Q} + 2 \text{cyt } c_1 + 4 \text{H}^+$

Complex IV $4 \text{cyt } c + 8 \text{H}^+ + \text{O}_2 \leftrightarrow 4 \text{cyt } c + 4 \text{H}^+ + 2 \text{H}_2\text{O}$

For example:

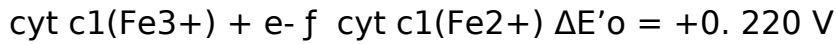
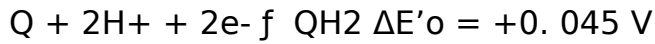
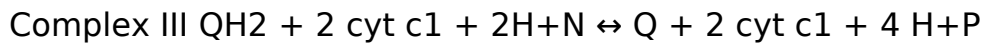
Complex I $\text{NADH} + 5\text{H}^+ + \text{Q} \leftrightarrow \text{NAD}^+ + \text{QH}_2 + 4\text{H}^+$

$\text{NAD}^+ + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{NADH} + \text{H}^+ \quad \Delta E'^{\circ} = -0.320 \text{ V}$

$\text{Q} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{QH}_2 \quad \Delta E'^{\circ} = +0.045 \text{ V}$

$\Delta E'^{\circ} = E'^{\circ}_{\text{acceptor}} - E'^{\circ}_{\text{donor}}$

$$\Delta E'_{o} = 0.045 - (-0.320) = +0.365 \text{ V}$$

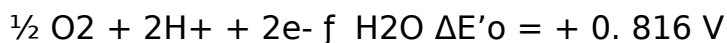
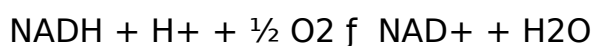


$$\Delta E'_{o} = [2 \times 0.220] - 0.045 = +0.395 \text{ V}$$

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.

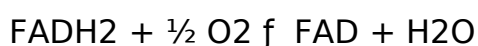
In addition, both overall reactions for NADH/FADH₂ to O₂ are positive values, another indication that electrons moving from Complex I/II to Complex IV is energetically favorable. The calculations are provided below.

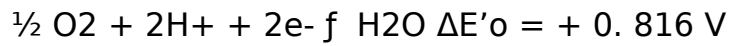
This is the overall reaction for electrons that travel from NADH to O₂



$$\Delta E'_{o} = 0.816 - (-0.320) = +1.136 \text{ V}$$

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





$$\Delta E'_{\text{o}} = 0.816 - (-0.219) = +1.035 \text{ V}$$

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 O₂, 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).