2.4.5 Respiratory chain

The respiratory chain of mitochondria consists of a series of membrane-bound redox centres which catalyse the transfer of electrons from NADH and FADH$_2$ to O$_2$, forming H$_2$O and translocating protons across the inner membrane (Figure 2.24). Translocation of protons is made possible by release of redox energy that accompanies electron transfer from the strong reductant NADH to the strong oxidant O$_2$, and is functionally linked to electron transfer. (This electron transfer involves a release in redox energy of 1.14 V which is equivalent to 52.7 kcal of chemical energy, enough to drive the synthesis of three ATP molecules.) In this way, a protonmotive force (D$\mu$H$^+$) is created across the inner membrane and is used to drive phosphorylation of ADP via the ATP synthase complex (Figure 2.24, right side).

Plant mitochondria have a respiratory chain which is more complicated than that of animals and contains additional NADH dehydrogenases and an alternative oxidase which catalyses cyanide-insensitive O$_2$ consumption. These additional enzymes (which are also found in most fungi) do not translocate protons and therefore are not linked to ATP synthesis; they are often referred to as the non-phosphorylating bypasses of the plant respiratory chain. The other complexes of the chain are common to all mitochondria and have been extensively studied in animals and fungi and to some extent in plants. They have been assigned Roman numerals by researchers of mammalian respiration (Figure 2.24).

According to structural arrangements that underlie electron transport in plant mitochondria, large protein-containing complexes of the respiratory chain are immersed in the inner membrane by virtue of their hydrophobic subunits, and interact with one another via two smaller molecules: ubiquinone and cytochrome c. The lipid-soluble ubiquinone is small enough to move rapidly along and across the membrane, and participates in H$^+$ transport across the membrane as well as shuttling electrons from complexes I and II to complex III. Location and oxidation–reduction status are shown in Figure 2.25. Cytochrome c is a small haem-containing protein located on the outer surface of the inner membrane, which shuttles electrons between complexes III and IV. In this respect, the respiratory chain is similar in layout to the photosynthetic electron transport chain: three large complexes which communicate by a quinone and a small mobile protein (Cyt c or plastocyanin). However, orientation of components in the membrane is inverted and the net reaction catalysed is opposite to that in chloroplasts (Figure 1.11).

(a) NADH oxidation

Complex I, NADH-ubiquinone oxido-reductase (Figure 2.24), is a large multi-subunit complex of 30–40 polypeptides, seven of which are synthesised in the mitochondrion. One of the subunits, a 50 kDa protein, contains flavinmononucleotide as a cofactor and is the dehydrogenase which oxidises NADH and passes electrons to FeS-containing proteins of the complex, and eventually to ubiquinone. The passage of electrons through the complex is accompanied by H$^+$ translocation across the membrane (mechanism poorly understood). Complex I is inhibited specifi?cally by the flavonoid rotenone and analogues. The NADH-binding site is exposed to the matrix and the complex oxidises NADH produced
by the TCA cycle and other NAD-linked enzymes.

Plant mitochondria contain another matrix-located NADH dehydrogenase which is insensitive to rotenone and does not pump protons across the membrane (called the ‘rotenone-insensitive bypass’). Plant mitochondria also oxidise NADH and NADPH by two dehydrogenases on the outside of the inner membrane. This oxidation is not inhibited by rotenone and is not linked to $H^+$ translocation. These external dehydrogenases are presumed to oxidise NAD(P)H produced in the cytosol.

(b) Succinate oxidation

Complex II (Figure 2.24) is succinate dehydrogenase, which also spans the membrane and has its active site exposed to the matrix. It consists of $\gamma$e subunits, one of which is encoded by the mitochondrial genome in plants while the rest are synthesised in the cytosol. SDH also contains FeS and haem centres which participate in electron transfer from succinate to ubiquinone. Unlike complex I, complex II does not pump $H^+$ and succinate oxidation is therefore linked to the synthesis of less ATP (see below). Malonate, an analogue of succinate, is a strong competitive inhibitor of succinate dehydrogenase.

(c) Cytochromes

![Figure 2.25 The protonmotive Q cycle mechanism of proton translocation at complex III of the respiratory chain.](image)

Figure 2.25 The protonmotive Q cycle mechanism of proton translocation at complex III of the respiratory chain. Oxidised quinone (UQ) accepts an electron from Cyt $b_{562}$ of complex III and a proton from the matrix to form the semiquinone (UQH). The semiquinone accepts another proton from the matrix and an electron from complex I (or II) to form the quinol which then diffuses across the membrane (broken arrows) to interact with Cyt $b_{566}$ and the FeS protein of complex III near the outside of the inner membrane. UQH$_2$ is oxidised to the semiquinone by Cyt $b_{566}$, losing a proton to the external medium in the process, which then reduces $b_{562}$. The semiquinone is oxidised by the FeS protein (not shown), losing another proton which then reduces Cyt $c_1$ and thence Cyt $c$. The quinone formed then diffuses back across the membrane to interact with Cyt $b_{562}$. In this way, one electron is transferred from complex I (or II) on one side of the membrane to Cyt $c$ on the other, with another electron and UQ shuttling back and forth across the membrane. Concurrently, two $H^+$ are translocated from the matrix to the external medium for each electron flowing to Cyt $c$. Broken arrows indicate diffusion of both fully oxidised and fully reduced ubiquinone; unbroken arrows indicate electron flow. (Original drawing courtesy David Day)
Complex III (Figure 2.24) is the cytochrome $b/c_1$ complex, consisting of two $b$-type cytochromes, $b_{566}$ and $b_{562}$, cytochrome $c_1$, an FeS protein named the Rieske iron–sulphur protein and several other polypeptides. The complex contains eight subunits, one of which is synthesised in the mitochondrion. Electron flow from ubiquinol to cytochrome $c$ is accompanied by the translocation of four $H^+$ per electron pair, across the membrane, via the so-called Q cycle. According to this mechanism, ubiquinone is reduced on the matrix side of the membrane by one electron from complex I or II and one from Cyt $b_{562}$. The quinol then diffuses across to the outside of the membrane to reduce Cyt $c_1$ and the Rieske FeS centre; the electron from $c_1$ is passed on to $c$ and then in turn to cytochrome oxidase, while the FeS electron is handed on to Cyt $b_{566}$, then to $b_{562}$, which reduces ubiquinone. Thus the $b$ cytochromes participate in the movement of electrons across the complex but do not participate in the reduction of Cyt $c$ (Figure 2.25). Various inhibitors of complex III have been discovered, with antimycin A and myxothiazol most widely used in research.

The final complex of the main respiratory chain (Figure 2.24) is complex IV, cytochrome $c$ oxidase. As the name implies, cytochrome $c$ oxidase accepts electrons from cytochrome $c$ on the outside of the inner membrane and transfers them to the inside of the membrane where $O_2$ is reduced to form $H_2O$. The complex contains 7–9 polypeptides (three of which are synthesised in the mitochondrion). Two cytochrome haem centres, $a$ and $a_3$, and two copper atoms make up its redox active components. Like complex I, cytochrome oxidase is a proton pump, but the mechanism is still poorly defined.

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