

## Chapter 14

### Oxidative Phosphorylation

**Prokaryotes** are bacteria containing a single chromosome and no membrane-bound organelles or nuclear envelope. Gram negative bacteria have two membranes – an inner and an outer.

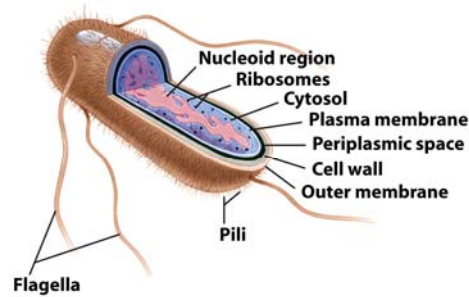


Figure 1-14 Principles of Biochemistry, 4/e  
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**Eukaryotes** contain multiple chromosomes surrounded by a membrane (nucleus) and membrane-bound organelles. Some organelles such as the nucleus and mitochondrion have two membranes.

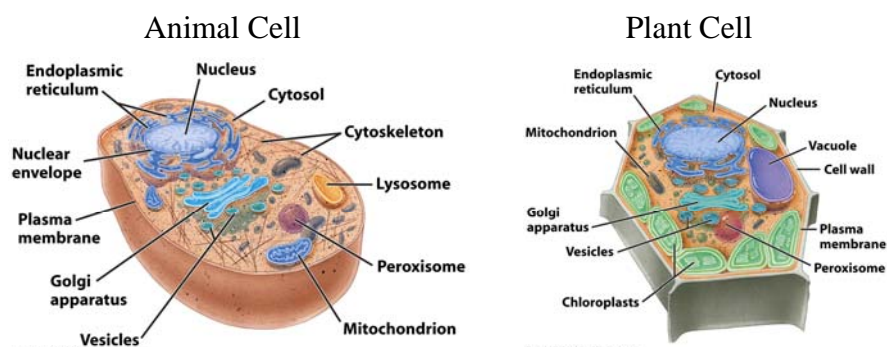


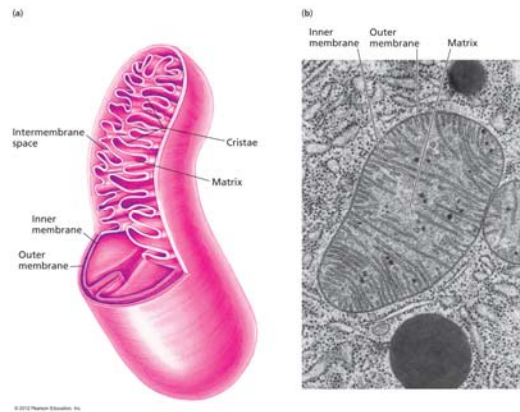
Figure 1-15a Principles of Biochemistry, 4/e  
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Figure 1-15b Principles of Biochemistry, 4/e  
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The **mitochondrion** is thought to be an ancient prokaryotic, gram-negative, aerobic bacterium that took up **symbiotic** residence in a primitive, eukaryotic, anaerobic host.

Mitochondria have their own DNA, ribosomes, and transfer RNAs.

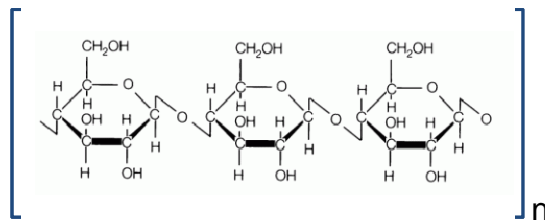
They contain an outer, highly permeable membrane and an inner impermeable membrane.



The interior **matrix** contains pyruvate deH<sub>2</sub>ase, TCA cycle enzymes, and enzymes for oxidation of amino acids and fatty acids.

It is the **“furnace”** of the cell.

(The **burning** of paper:  $(C_6H_{10}O_5)_n + 6nO_2 \rightarrow + 6nCO_2 + 5nH_2O$ )



### Part 1: Electron Flow

High  $G$  electrons from glycolysis, TCA cycle, AA, and fatty acid oxidation are funneled into universal electron carriers:

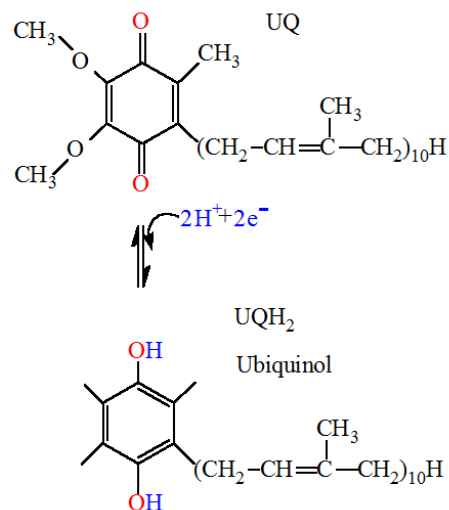
NADH / NADPH / FADH<sub>2</sub> The e<sup>-</sup> are then transferred to a chain of e<sup>-</sup> carriers in the inner membrane of the mitochondrion.

This is called the *respiratory chain*.

The electron carriers are 4 protein complexes and their coenzymes.

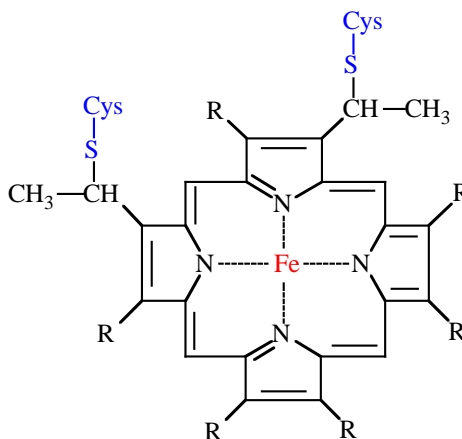
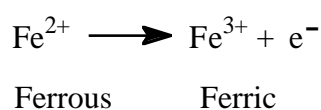
#### 1. Coenzyme Q = Ubiquinone

It is lipid soluble and can diffuse through the membrane accepting and donating e<sup>-</sup>.



2. A family of cytochromes – all cytochromes except cyt c are integral membrane proteins. They have different amino acid sequences and bind slightly different *iron-containing hemes*.

*Part of cytochrome c*



Cyt c is a peripheral membrane protein that binds Heme C covalently through Cys residues.

The standard reduction potential, a measure of the  $G$  of the  $\text{e}^{-}$ , is different in each protein.

Tables 10-4 & 14-1.

Table 14.1 Standard reduction potentials of mitochondrial oxidation-reduction components

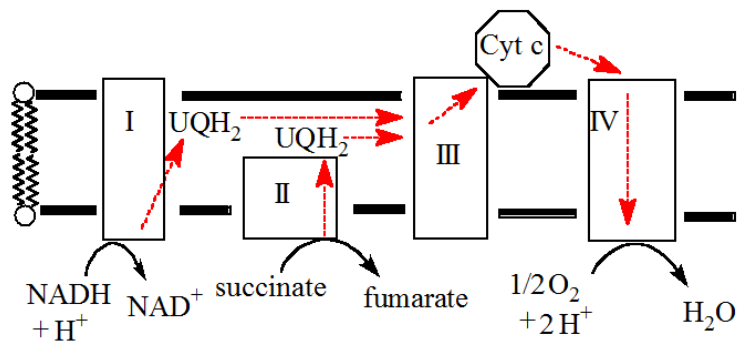
Substrate of Complex	$E^{\circ}$ (V)
NADH	-0.32
Complex I	
FMN	-0.30
Fe-S clusters	-0.25 to -0.05
Succinate	+0.03
Complex II	
FAD	0.0
Fe-S clusters	-0.26 to 0.00
$\text{QH}_2/\text{Q}$	+0.04
$(\cdot\text{Q}^{\ominus})/\text{Q}$	-0.16
$(\text{QH}_2)/\text{Q}^{\ominus}$	+0.28
Complex III	
Cytochrome $b_1$	-0.01
Cytochrome $b_H$	+0.03
Fe-S cluster	+0.28
Cytochrome $c_1$	+0.22
Cytochrome c	+0.22
Complex IV	
Cytochrome a	+0.21
$\text{Cu}_A$	+0.24
Cytochrome $a_3$	+0.39
$\text{Cu}_B$	+0.34
$\text{O}_2$	+0.82

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### 3. Fe-S Proteins



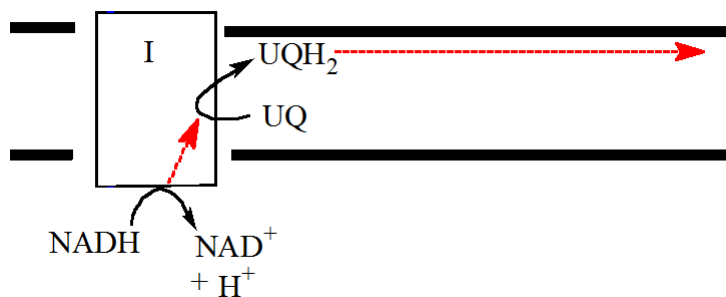
The  $G$  of the bound and released  $e^-$  is different in different proteins. Here is a summary of the passage of  $e^-$  and  $H^+$  through the respiratory chain.



(see Figure 14.6: Textbook uses  $Q$  instead of  $UQ$ )

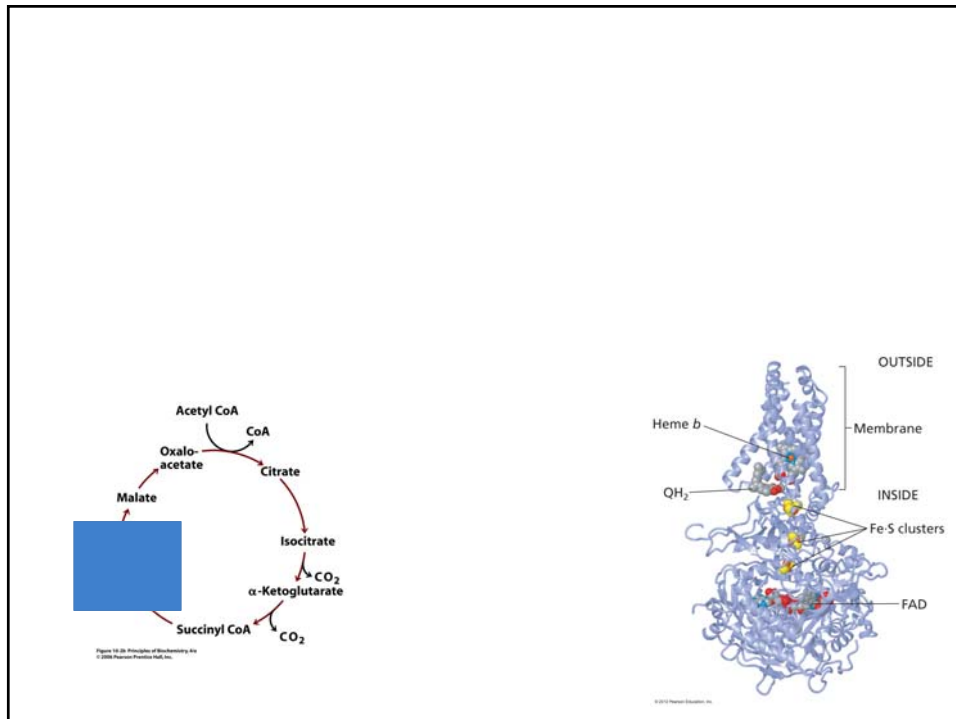
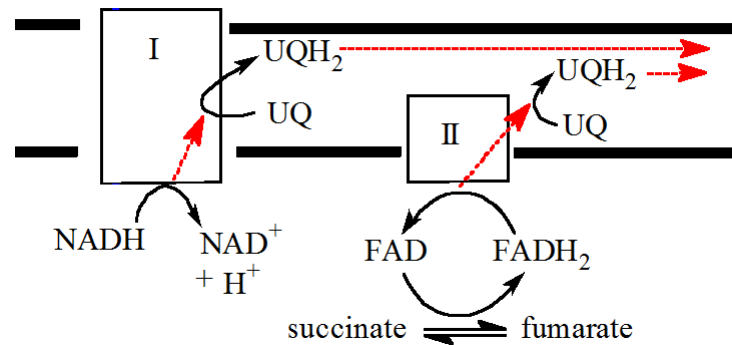
### Complex I - NADH deH<sub>2</sub>ase

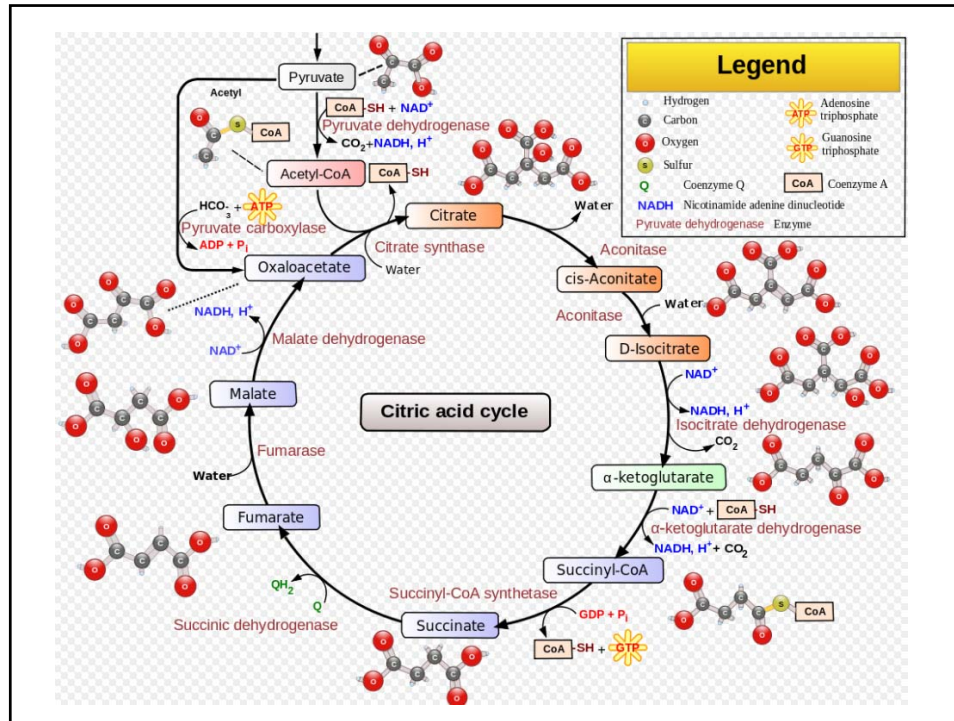
Consists of more than 25 proteins, 7 Fe-S centres, and FMN (FMN = Flavin mononucleotide)



### Complex II – Succinate deH<sub>2</sub>ase

Consists of 4 proteins including Fe-S proteins, and covalently-bound FAD. It is the only membrane-bound enzyme of the TCA Cycle.



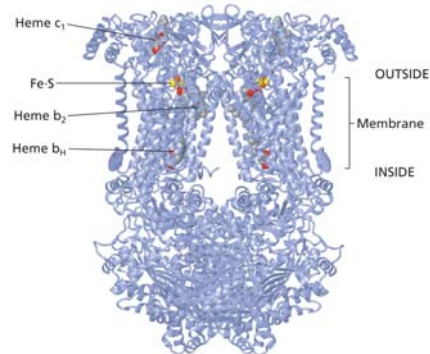


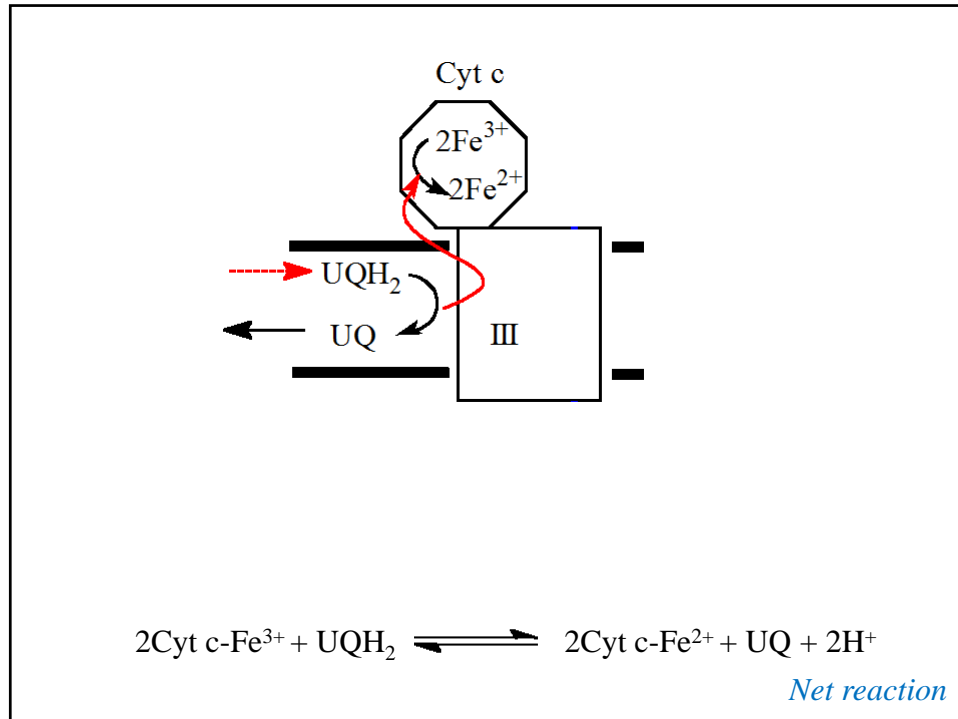
### Complex III - UQ-Cyt c oxidoreductase

Consists of 10 proteins including Cyt  $b_{562}$ , Cyt  $b_{566}$ , Cyt  $c_1$ , Fe-S protein.

The last  $e^-$  acceptor is Cyt  $c$  which dissociates from Complex III and carries one  $e^-$  to Complex IV.

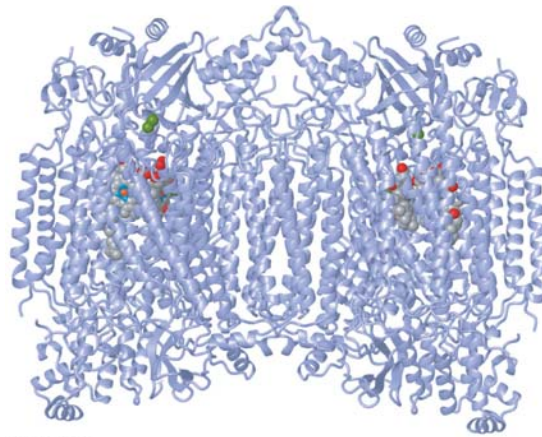
This is an ancient protein with homologs in chloroplasts and bacteria.



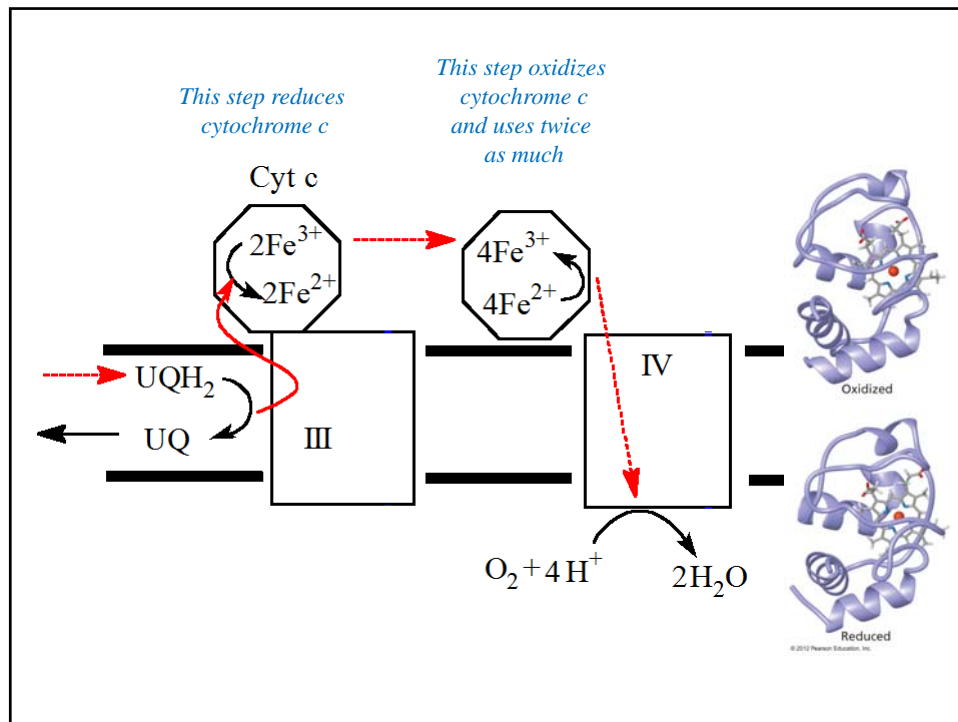


### Complex IV - Cytochrome Oxidase

Consists of about 10 proteins including cytochromes a and a<sub>3</sub>.







### Energetics:

e<sup>-1</sup> in NADH and FADH<sub>2</sub> have high *G*;  
 From Complex I to Complex IV e<sup>-</sup> flow is down the *G* hill,  
 i.e. reactions favoured.