

Biological oxidation

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Definition:

- Biological oxidation is the enzyme-catalyzed process in which electrons are removed from organic molecules (like carbohydrates, fats, or proteins) and transferred to an electron acceptor, typically oxygen.
- This process releases energy, which is used to form ATP.

Purpose:

- To produce energy for cellular functions by converting nutrients into ATP (adenosine triphosphate).

Location in the Cell:

- Primarily occurs in the mitochondria of eukaryotic cells.

Main Processes Involved:

1. Glycolysis

- Occurs in the cytoplasm.
- Glucose is partially oxidized to form pyruvate.
- Produces a small amount of ATP and NADH.

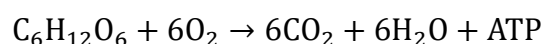
2. Citric Acid Cycle (Krebs Cycle)

- Takes place in the mitochondrial matrix.
- Pyruvate is further oxidized to carbon dioxide.
- Generates NADH and FADH₂ for the electron transport chain.

3. Electron Transport Chain (ETC)

- Located in the inner mitochondrial membrane.
- Electrons from NADH and FADH₂ pass through a series of proteins.
- Oxygen acts as the final electron acceptor and combines with protons and electrons to form water.
- The movement of electrons drives ATP synthesis via oxidative phosphorylation.

Simplified Overall Reaction for Glucose Oxidation:



Key Enzymes and Coenzymes:

- **Dehydrogenases** – catalyze removal of hydrogen (electrons).

- **NAD⁺ (Nicotinamide adenine dinucleotide)** – electron carrier.
- **FAD (Flavin adenine dinucleotide)** – electron carrier.
- **Cytochromes** – proteins involved in the electron transport chain.

Coenzyme Systems Involved in Biological Oxidation

- These are **non-protein** molecules that assist enzymes in transferring electrons (and sometimes hydrogen atoms).

Let's discuss the most important ones:

A. Nicotinamide Coenzymes (NAD⁺ / NADH)

- **Full name:** Nicotinamide Adenine Dinucleotide
- **Derived from:** Niacin (Vitamin B3)
- **Oxidized form:** NAD⁺
- **Reduced form:** NADH + H⁺
- **Function:**
 - NAD⁺ accepts **2 electrons** and **1 proton** during oxidation of substrates.
 - Transports electrons to the **electron transport chain (Complex I)**.
- **Common in:** Catabolic reactions (glycolysis, TCA cycle, β-oxidation)
- **Example:**
 - In TCA cycle:
 - Isocitrate → α-ketoglutarate (produces NADH)

B. Nicotinamide Coenzymes (NADP⁺ / NADPH)

- **Full name:** Nicotinamide Adenine Dinucleotide Phosphate
- **Oxidized form:** NADP⁺
- **Reduced form:** NADPH
- **Function:**
 - NADPH is used in **reductive biosynthesis** (e.g., fatty acid synthesis).
 - Also plays a role in maintaining **glutathione** in reduced form (antioxidant system).
- **Common in:** Anabolic reactions (fatty acid and cholesterol synthesis)

C. Flavin Coenzymes (FAD / FADH₂ and FMN / FMNH₂)

- **Derived from:** Riboflavin (Vitamin B2)
- **Forms:**
 - **FAD (Flavin Adenine Dinucleotide)**

- **FMN (Flavin Mononucleotide)**

- **Function:**

- Accepts **2 electrons** and **2 protons**
- FAD is tightly bound to enzymes (as prosthetic group)
- Electrons from FADH_2 enter **ETC at Complex II**

- **Common in:** Succinate dehydrogenase (TCA cycle), Acyl-CoA dehydrogenase (β -oxidation)

D. Coenzyme Q (Ubiquinone / Ubiquinol)

- **Lipid-soluble electron carrier** in the inner mitochondrial membrane.
- **Oxidized form:** Ubiquinone (Q)
- **Reduced form:** Ubiquinol (QH_2)
- **Function:**
 - Transfers electrons from Complex I and II to Complex III in ETC.
 - Can accept **electrons** and **protons**.
- Important in maintaining mitochondrial electron flow.

E. Cytochromes

- Proteins with **heme prosthetic groups** that carry **one electron** at a time.
- Iron atom in heme cycles between **Fe^{2+} (reduced)** and **Fe^{3+} (oxidized)**.
- Types: **Cytochrome b, c_1 , c, a, a_3**
- Located in **Complex III and IV** of ETC.
- **Cytochrome c** is a mobile carrier between Complex III and IV.

F. Iron-Sulfur (Fe-S) Proteins

- Contain **$\text{Fe}^{2+}/\text{Fe}^{3+}$** centers coordinated by sulfur atoms and cysteine residues.
- Participate in **single-electron transfers**.
- Found in **Complex I, II, and III** of ETC.

Electron transport chain (ETC) and its mechanism

Introduction

- The **Electron Transport Chain (ETC)** is a series of protein complexes and mobile electron carriers embedded in the inner mitochondrial membrane. Its main role is to:
 - Transfer **electrons** from **NADH** and **FADH_2** to **oxygen**
 - Pump **protons (H^+)** from the **matrix** into the **intermembrane space**
 - Create a **proton gradient** used to generate ATP

- This process is the final stage of aerobic respiration and is tightly coupled to oxidative phosphorylation.

Location

- **ETC** is located in the inner mitochondrial membrane
- Proton pumping occurs across the inner membrane, creating a gradient between the matrix and intermembrane space

Components of the ETC

Membrane-bound complexes:

Complex	Name	Electron Donor	Cofactors	Main Function
I	NADH: Ubiquinone oxidoreductase (NADH dehydrogenase)	NADH	FMN, Fe-S	Pumps H ⁺
II	Succinate: Ubiquinone oxidoreductase (Succinate dehydrogenase)	FADH ₂	FAD, Fe-S	No H ⁺ pumping
III	Ubiquinol: Cytochrome c oxidoreductase	CoQH ₂	Cyt b, Cyt c ₁ , Fe-S	Pumps H ⁺
IV	Cytochrome c oxidase	Cyt c	Cyt a, Cyt a ₃ , Cu	Pumps H ⁺ , reduces O ₂ to H ₂ O
V	ATP synthase	Uses H ⁺ gradient	-	Makes ATP

Mobile carriers:

- **Coenzyme Q (Ubiquinone)** – lipid-soluble, carries electrons from Complex I/II to III
- **Cytochrome c** – water-soluble protein, carries electrons from Complex III to IV

Net Proton Pumping (per NADH)

Complex	Protons Pumped
I	4
III	4
IV	2
Total	10 H⁺ per NADH

- For **FADH₂**, Complex I is bypassed → only **6 H⁺** pumped per FADH₂

Mechanism of Energy Capture



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