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 $FADH_2$ for the electron transport chain.
3. **Electron Transport Chain (ETC)**
   - Located in the inner mitochondrial membrane.
   - Electrons from NADH and $FADH_2$ 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:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + ATP$$

Key Enzymes and Coenzymes:

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

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- **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 / $FADH_2$ and FMN / $FMNH_2$)

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

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- **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 **Fe^{2+}/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

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- 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_2O
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 **$FADH_2$**, Complex I is bypassed → only **6 H^+** pumped per $FADH_2$

Mechanism of Energy Capture

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