

Lecture 7 “Chemical Energy Sources – Galvanic Cells and Fuel Cells”

Goal of the lecture: To understand the principles of electrochemical energy conversion, the construction and operation of galvanic cells and fuel cells, and their applications as efficient chemical energy sources.

Brief lecture notes: Chemical energy sources are systems that convert chemical energy directly into electrical energy through redox (oxidation–reduction) reactions. These include **galvanic cells** (also known as voltaic cells) and **fuel cells**, which are both based on the same electrochemical principle but differ in design, operation, and application.

1. Galvanic Cells

A **galvanic cell** is an electrochemical device that generates electricity from spontaneous chemical reactions. It consists of two half-cells connected by a **salt bridge** or porous membrane that allows ionic movement while preventing direct mixing of the solutions. Each half-cell contains an electrode immersed in an electrolyte, where oxidation occurs at the **anode** and reduction at the **cathode**. The flow of electrons through the external circuit provides usable electrical energy.

The cell potential (electromotive force, E°_{cell}) is the difference between the reduction potentials of the two electrodes and can be calculated using:

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

The relationship between cell potential and Gibbs free energy is:

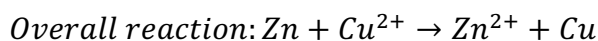
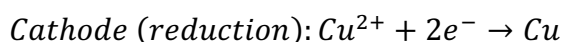
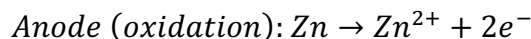
$$\Delta G = -nFE^\circ$$

where

- ΔG° is the Gibbs free energy change (J/mol),
- n is the number of electrons transferred,
- F is the Faraday constant (96,45 C/mol).

Example – Daniell Cell (Zn–Cu Cell):

This classical galvanic cell consists of a zinc electrode in ZnSO_4 solution and a copper electrode in CuSO_4 solution connected by a salt bridge.



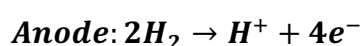
The cell produces an EMF of approximately **1.10 V** at standard conditions (25°C, 1 M, 1 atm).

Galvanic cells are widely used in batteries such as the **lead–acid battery**, **nickel–cadmium (Ni–Cd)**, and **lithium-ion cells**, which store and supply electrical energy for portable devices and vehicles.

2. Fuel Cells

A **fuel cell** is an electrochemical cell that continuously converts the chemical energy of a fuel and an oxidizing agent into electrical energy, as long as reactants are supplied. Unlike galvanic cells, fuel cells **do not require recharging**; instead, they operate like a flow system where fuel and oxidant are fed continuously to electrodes.

The most common example is the **hydrogen–oxygen fuel cell**, which generates electricity and water with high efficiency and no harmful emissions.



The standard EMF of the hydrogen–oxygen fuel cell is **1.23 V at 25°C**, but practical voltages are slightly lower due to internal resistance and losses.

Fuel cells use electrolytes such as **proton exchange membranes (PEM)** or **alkaline solutions (KOH)**, depending on the type. The efficiency of fuel cells (60–80%) is significantly higher than that of conventional combustion engines because no intermediate heat conversion step is involved.

Table 1 – Comparison between Galvanic Cells and Fuel Cells

Feature	Galvanic Cell	Fuel Cell
Energy source	Stored chemicals	Continuous fuel supply
Reactants	Contained within cell	Fed continuously
Duration	Limited (requires recharging)	Long as fuel is supplied
Example	Daniell cell, lithium-ion battery	H ₂ –O ₂ fuel cell, methanol fuel cell
Efficiency	40–60%	60–80%
Pollution	May produce waste	Environmentally clean (main product: water)

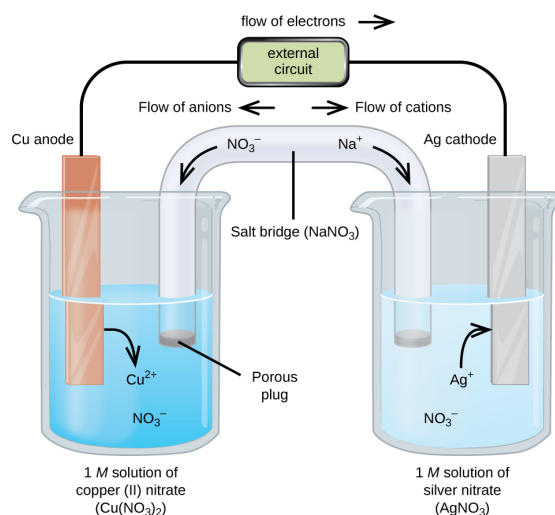
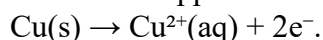


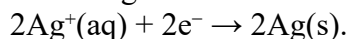
Figure 1 – Schematic Representation of a Galvanic Cell

The electrochemical setup (Fig. 1) represents a **Cu–Ag galvanic cell**, which converts chemical energy into electrical energy through spontaneous redox reactions. The cell consists of two half-cells connected by an external wire and a salt bridge. The copper electrode (Cu) is placed in a 1 M solution of copper(II) nitrate ($\text{Cu}(\text{NO}_3)_2$), while the silver electrode (Ag) is placed in a 1 M solution of silver nitrate (AgNO_3).

In this cell, **copper acts as the anode**, where oxidation occurs. Copper metal loses electrons and forms copper ions according to the reaction:

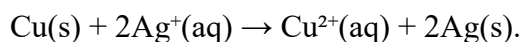


At the same time, **silver acts as the cathode**, where reduction takes place. Silver ions in the solution gain electrons and deposit as metallic silver:



Electrons flow through the external circuit from the copper anode to the silver cathode, generating an electric current. The **salt bridge**, which contains sodium nitrate (NaNO_3), allows ions to move between the two solutions to maintain electrical neutrality. Nitrate ions (NO_3^-) migrate toward the copper side, while sodium ions (Na^+) move toward the silver side.

The overall cell reaction is:



This reaction is spontaneous and produces an electromotive force (EMF) of about **0.46 volts**, calculated from the standard electrode potentials of the two half-cells. The copper electrode gradually dissolves, while silver metal is deposited on the silver electrode.

Questions for self-control

1. What is the main difference between galvanic cells and fuel cells?
2. Write the half-cell reactions and overall reaction for the Daniell cell.
3. How is cell potential related to Gibbs free energy?
4. Describe the working principle of a hydrogen–oxygen fuel cell.
5. Compare the advantages and disadvantages of galvanic and fuel cells.

Literature:

1. Atkins, P., de Paula, J. *Atkins' Physical Chemistry*, 11th Edition, Oxford University Press, 2018.
2. Moran, M.J. *Fundamentals of Engineering Thermodynamics*, 9th Edition, Wiley, p.156.
3. House, J.E. *Fundamentals of Quantum Chemistry*, 2nd Edition, Academic Press, 2004.
4. Hammes-Schiffer, S. et al. *Physical Chemistry for the Biological Sciences*, University Science Books, 2009.
5. Zhdanov, V.P. *Elementary Physicochemical Processes on Solid Surfaces*, Springer, 1991.