

Lecture 2: Basic Physics of Galvanic Cells & Electrochemical Energy Conversion

Notes by MIT Student (and MZB)

In this lecture, we talk about the basic science of the galvanic cells and give several commonly-seen examples in real application.

1: Electrochemical cells and its operating parts

The galvanic cell, or called voltaic cell, is an electrochemical cell that converts the chemical energy to electrical energy from the spontaneous redox reactions taking place in the cell. The redox reaction is Faradic reaction, which is defined as reaction involved with electron transfer from/to electrode to/from ions. In an electrochemical cell, there are two half reactions that are giving and receiving electrons to electrode respectively, leading to a neutral overall reaction.

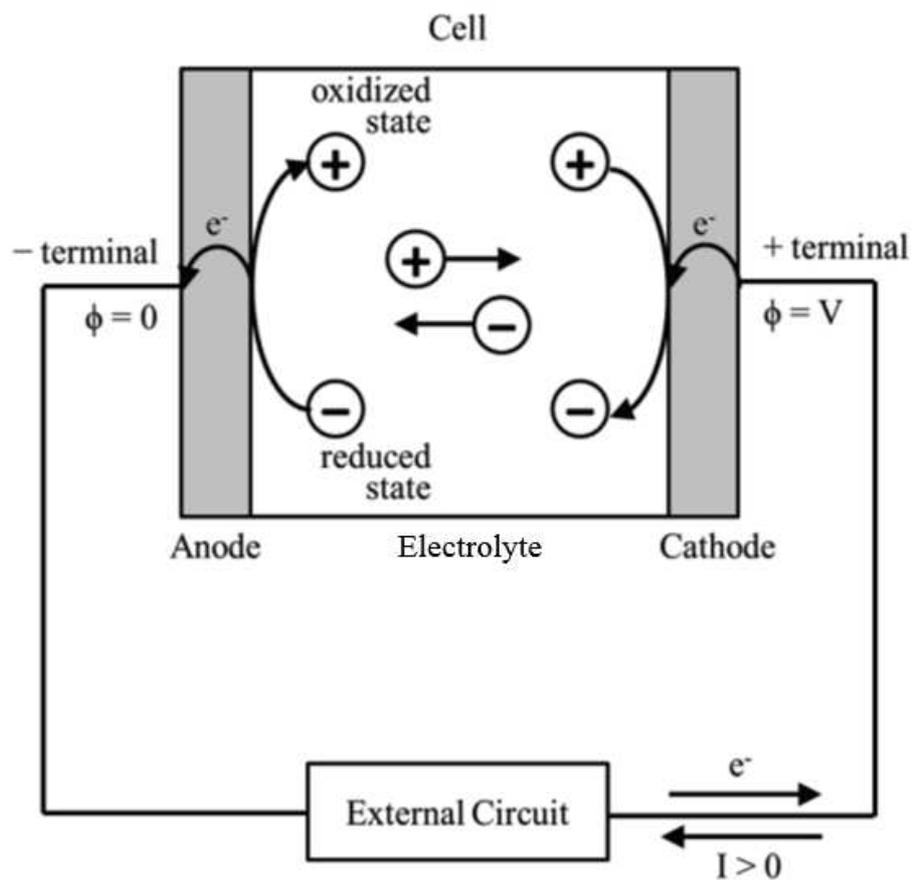


Figure 1 Galvanic Operation of an Electrochemical Cell^[1]

Consisting parts of electrochemical cell (shown in Figure 1):

Anode: An anode is defined as an electrode through which positive/negative electric charge flows into/out of a polarized electrical device.

In the case of electrochemical cell, an oxidation reaction occurs at the anode, producing the electron (negative charge) that flows out of the cell through the external circuit.

Cathode: A cathode is defined as an electrode through which positive/negative electric charge flows out of/into a polarized electrical device.

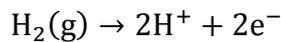
In the case of electrochemical cell, a reduction reaction occurs at the cathode surface to consume the electrons coming from the external circuit.

Electrolyte: Electrolyte is an insulator for electrons, but a conductor for the oxidized/reduced species migrating from anode/cathode to cathode/anode, which keeps the charge neutrality in the cell.

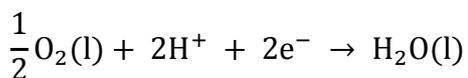
Here are 4 examples of electrochemical cells:

Example 1: PEM fuel cell

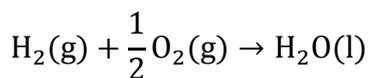
Anode half reaction:



Cathode half reaction:



Net reaction:



Electrolyte: Proton Exchange Membrane, made of polymer

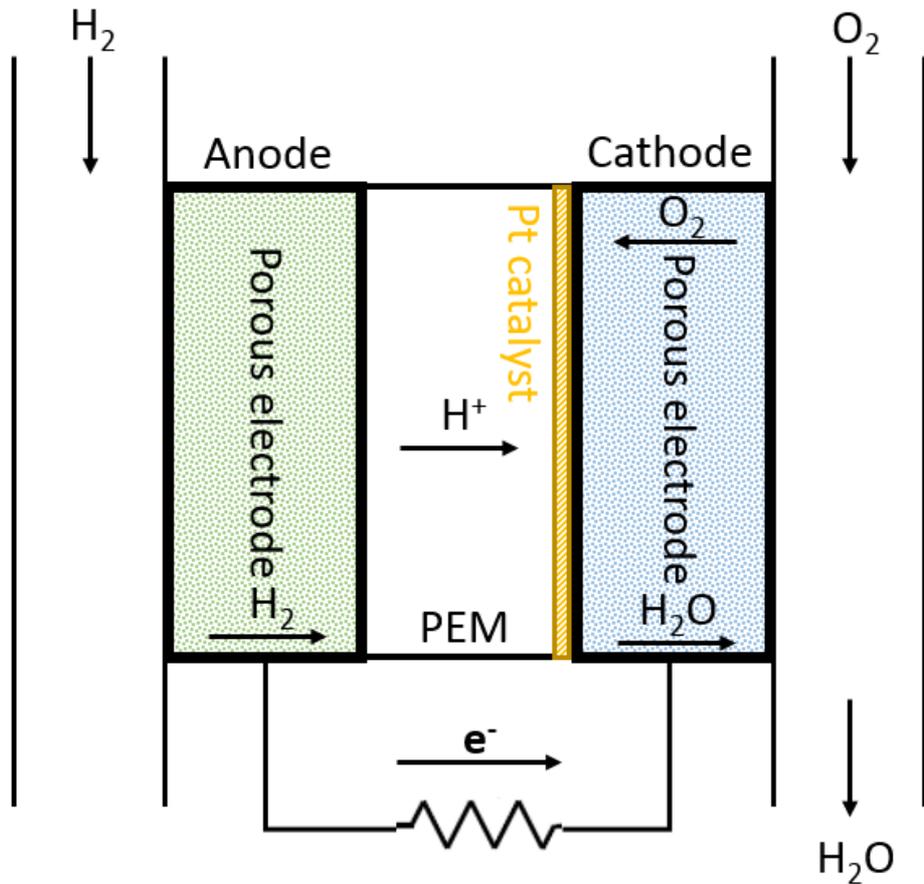


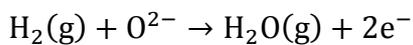
Figure 2 Schematics of PEM fuel cell

Advantages: The PEM cell can operate at room temperature.

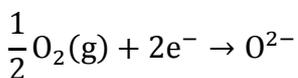
Shortcomings: The Oxygen Reduction Reaction (ORR) at the cathode surface has a slow reaction kinetics. In real PEM fuel cell, there shall be Pt catalyst at the cathode to increase reaction kinetics, which increase the expense.

Example 2: SOFC fuel cell

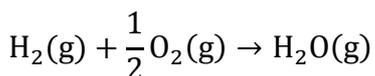
Anode half reaction:



Cathode half reaction:



Net reaction:



Electrolyte: Solid electrolyte, such as Ytria-stabilized zirconia

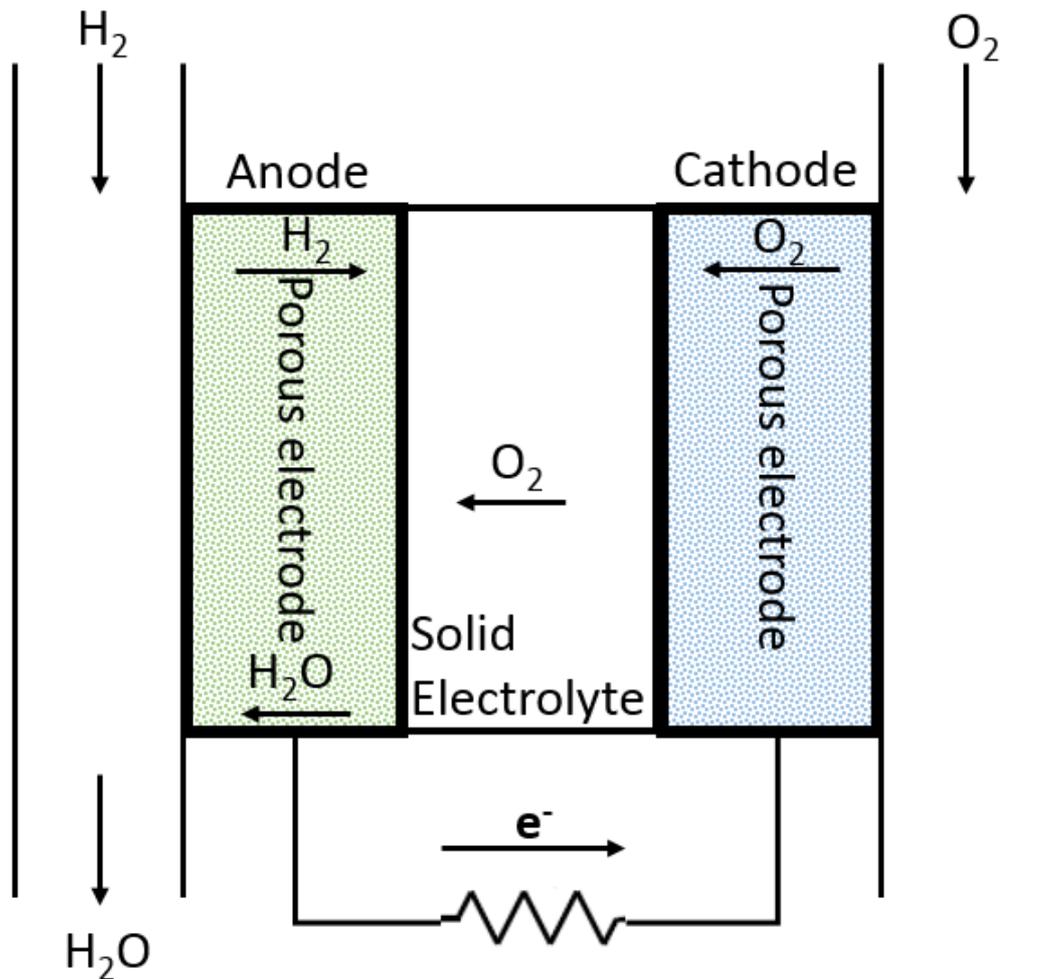


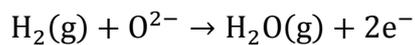
Figure 3 Schematics of SOFC Cell with H₂ fuel

Advantages: SOFC cell has much higher reaction kinetics so no catalyst needed.

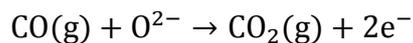
Shortcomings: Solid electrolyte does not have good conductivity, so this cell must operate at high temperature like 850 Celsius degree to ensure enough diffusivity of oxygen.

CH₄ can also be introduced as the fuel for anode. Because SOFC cell operates at high temperature, so CH₄ gas will decompose into H₂ and CO. In that case, the reactions within the cell will be much more complicated as:

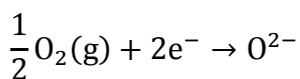
Anode half reactions:



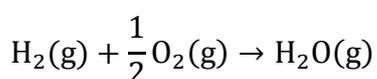
or



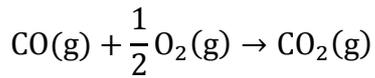
Cathode half reaction:



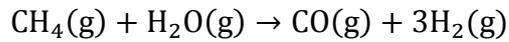
Net reaction:



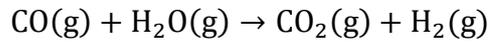
or



In the anode fuel flow, there might be steam reforming reaction such as:



In the porous anode electrode, the gas shift reactions may happen, such as:



Electrolyte: Solid electrolyte, such as Ytria-stabilized zirconia

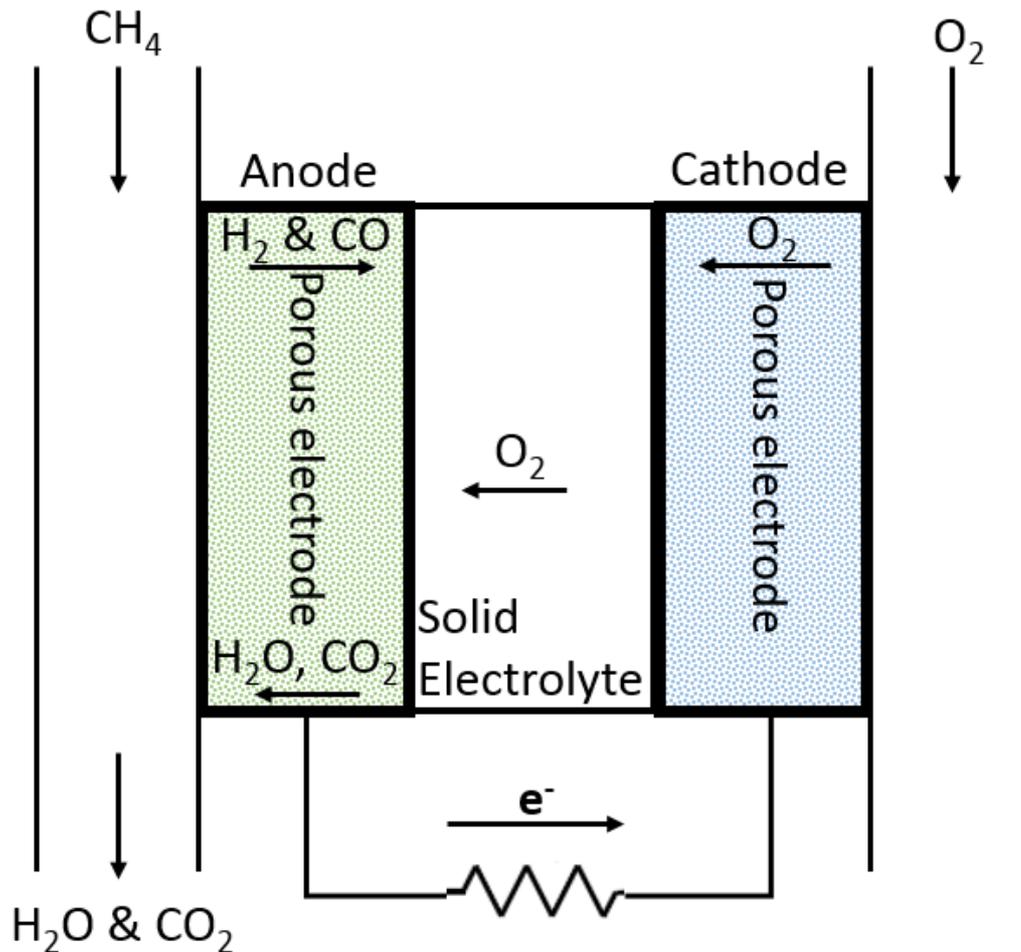
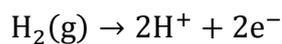


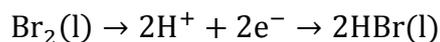
Figure 4 Schematics of SOFC Cell with CH₄ fuel

Example 3: HBr flow battery

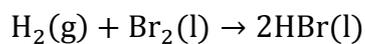
Anode half reaction:



Cathode half reaction:



Net reaction:



Electrolyte: Proton Exchange Membrane

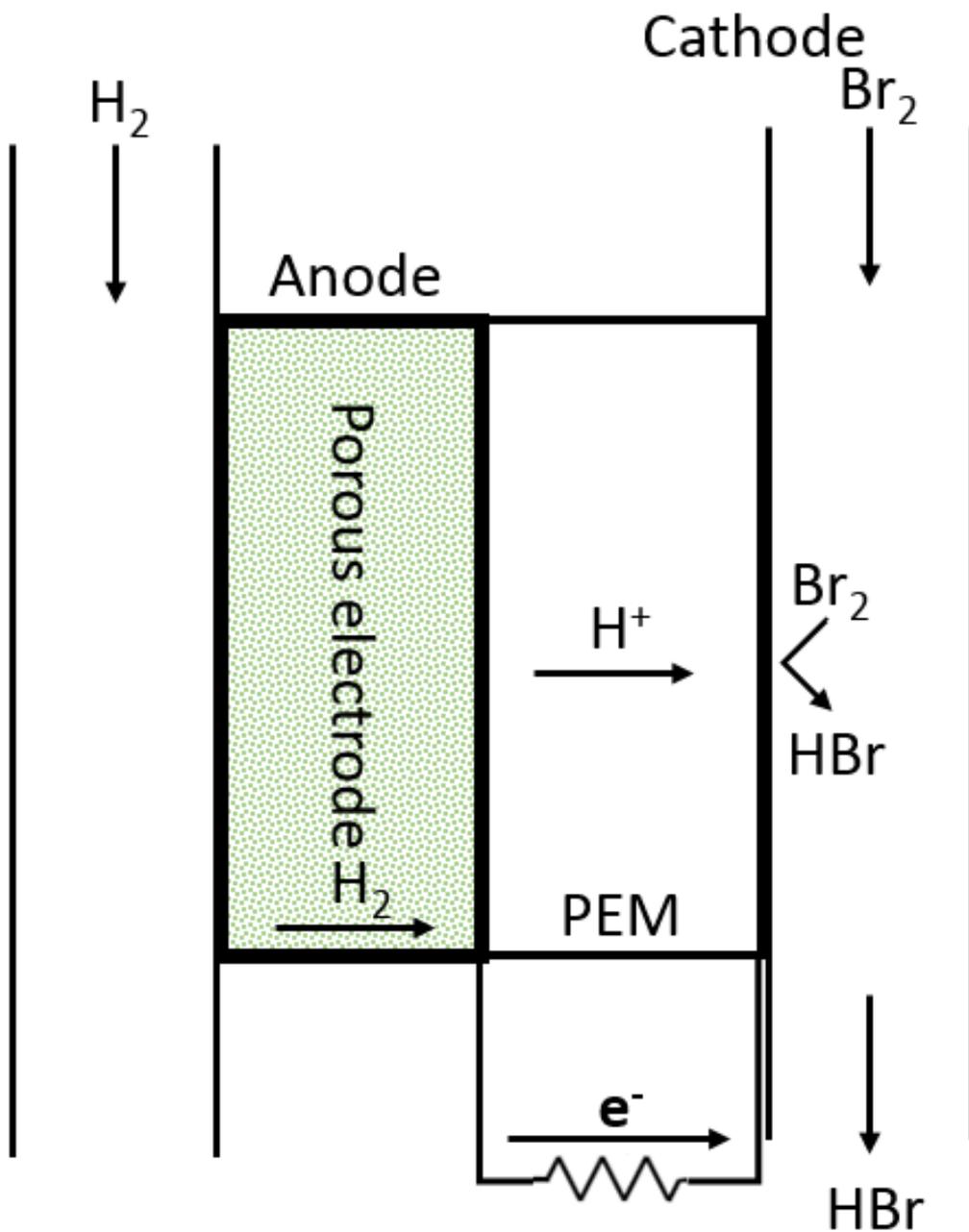


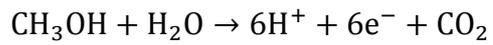
Figure 5 Schematics of HBr flow Battery

Advantages: The half reactions of this cell have fast kinetics; Br_2 dissolves quite well, which is good for high concentration of reaction species. The construction of this cell is very cheap.

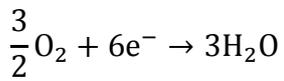
Shortcomings: HBr and Br_2 can corrode the PEM film. One solution is to make the cell “membraneless”, that is use the flow of the reaction species instead of introducing the membrane to separate anode and cathode reactions. However, this might lead to “cross-over” problem, which means the reaction species at anode/cathode can reach the cathode/anode, and degrades the cell performance.

Example 4: Direct methanol fuel cell

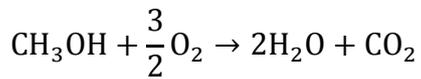
Anode half reaction:



Cathode half reaction:



Net reaction:



Electrolyte: Proton Exchange Membrane, made of polymer

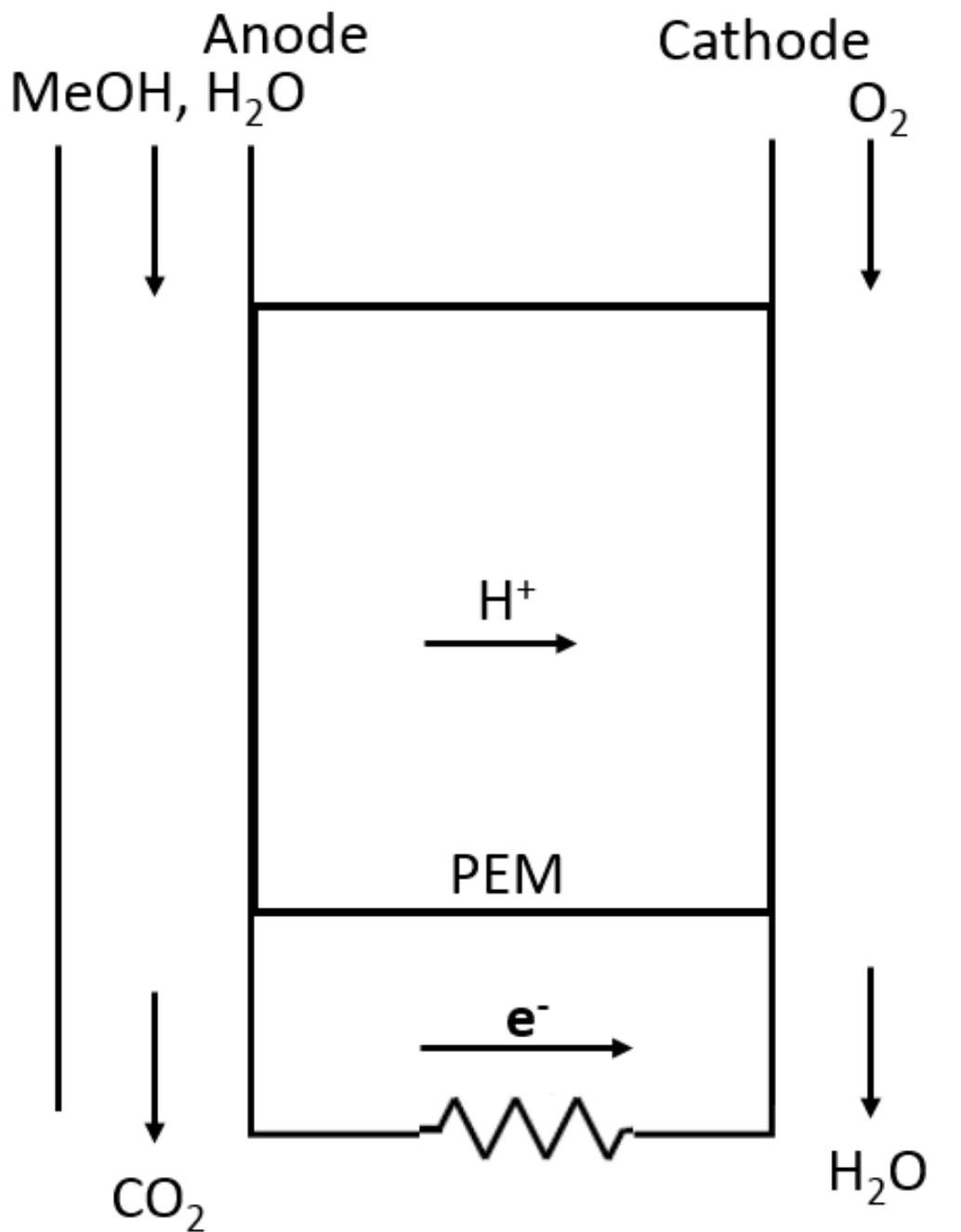


Figure 6 Schematics of the Direct Methanol Fuel Cell

Advantage: The methanol fuel cell has high energy density because of the fuel it uses.
 Shortcomings: The power density of this cell is quite low. One of the reason is that water is produced at the cathode and consumed at the anode, which lead to a “water drag” issue. The other reason there is methanol crossing the PEM film to cathode. This “cross-over” issue lead to degradation of this cell.

2: Equivalent circuit

To investigate the cell performance with different applied current condition, we can use an equivalent circuit as a simple model. More physical models that including effects of the reaction kinetics and the transport issues will be talked about in later lecture.

The simplest model is as shown in Figure 7 below:

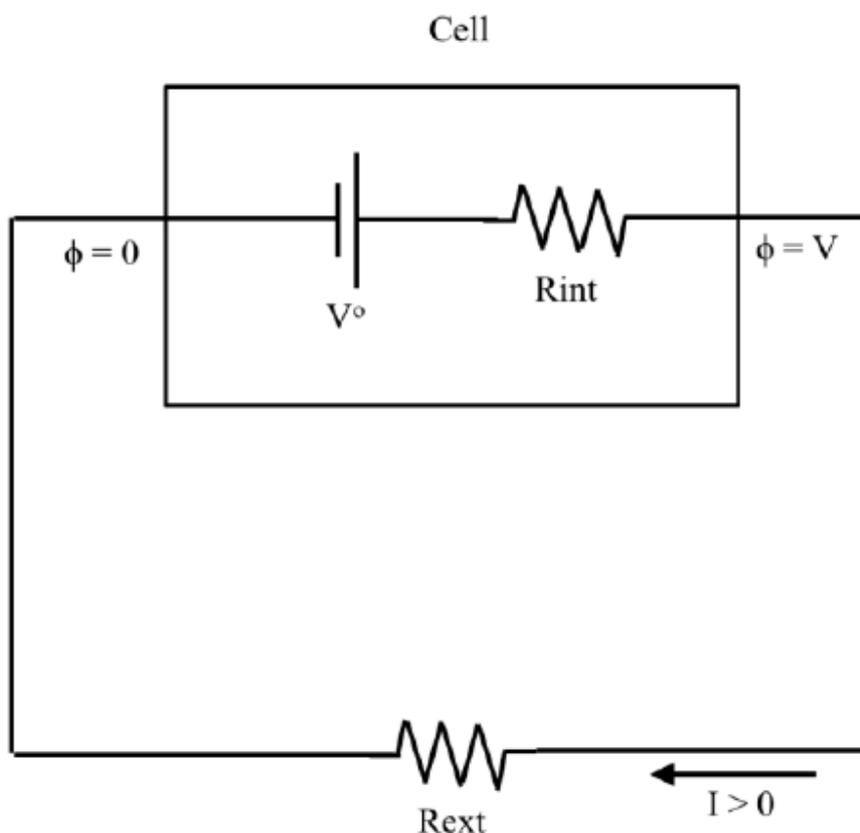


Figure 7 Equivalent Circuit of a Galvanic Cell^[1]

Where:

V^0 : the Open Circuit Voltage (OCV) of the cell. It can be calculated as $V_c^0 - V_a^0$, in which V_c^0 and V_a^0 are the standard equilibrium potential of cathode and anode.

R_{int} : the internal resistance, which can be estimated as the sum of interface resistance of cathode, interface resistance of anode and the resistance through electrolyte.

R_{ext} : the resistance of external circuit.

Assuming constant internal resistance, according to Kirchoff's law:

$$V = IR_{ext} = V_0 - IR_{int}$$

V is the output cell voltage. It's a linear function of applied current I .

When R_{ext} equals zero, the cell gets short. We can define the short circuit current I_s as: $I_s = V_0/R_{int}$

The cell power P is defined as the electrical work done by the cell per unit time:
 $P = IV$

To calculate the maximum power that can be derived from the cell, we need to take the derivation of P to I :

$$\frac{dP}{dI} = \frac{d(IV)}{dI} = \frac{d(I(V_0 - IR_{int}))}{dI} = V_0 - 2IR_{int}$$

When P is maximum as P_{max} , we have:

$$\frac{dP}{dI}(I = I_{max}) = V_0 - 2I_{max}R_{int} = 0$$

$$I_{max} = V_0/2R_{int} = \frac{I_s}{2}$$

$$P_{max} = \frac{I_s}{2} \left(V_0 - \frac{I_s R_{int}}{2} \right) = \frac{V_0 I_s}{4}$$

The dependence of cell voltage and the cell power to the current can be plotted as bellow:

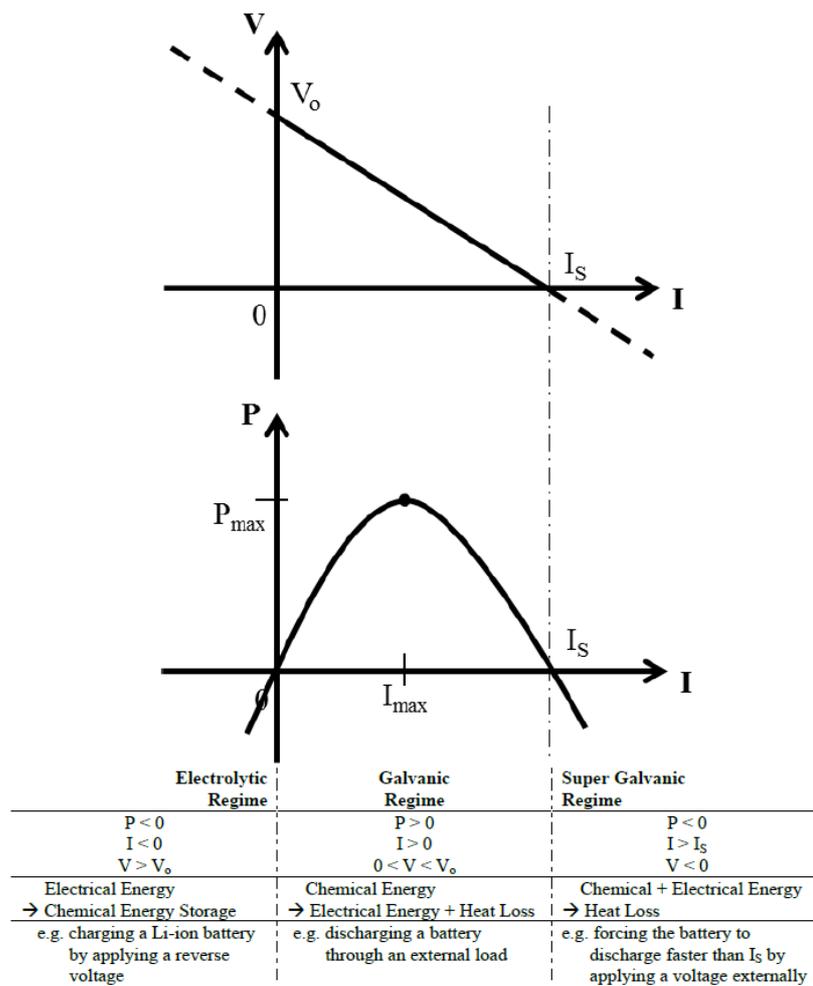


Figure 8 Cell Voltage and Power Behaviors as a Function of Current^[1]
in different regimes of Cell Operation

However, the case is much more complicated in reality. A general cell voltage and applied current relation is described in the Figure 9 below. The overpotential refers to the potential difference between the thermodynamically determined reduction potential and experimentally observed value of a redox reaction.

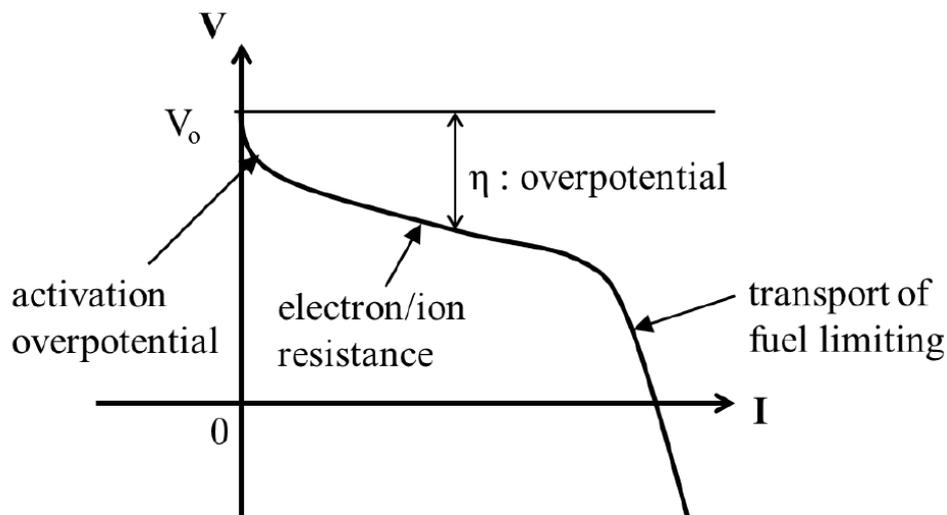


Figure 9 Cell Voltage of Typical cell as a Function of Current^[1]

Basically this curve can be divided into 3 regions.

The first region with small overpotential is reaction kinetics limited. The current has an exponential relation with the overpotential that can be described with Butler-Volmer equation which will be talked about in later lectures.

In the second region, the current and the overpotential has a linear relation. The limiting factor is the resistance, which can be from the electron or ion transport. In this region, the simple equivalent circuit model described in this lecture is applicable.

One way to estimate the overpotential at the transition from region 1 to region 2 is as: $\Delta V \sim k_B T / e$, k_B is the Boltzmann coefficient, T is the temperature and e is the charge of electron. The reason is the charge transfer is typically a thermally activated process, so the reaction rate scales as $e^{\eta / k_B T}$ where η is the activation "overpotential," or extra voltage (energy per charge), required to sustain the current. At room temperature, only a small overpotential ($\eta \sim k_B T / e = 26 \text{ mV}$) is required to overcome the thermal voltage, and region 1 is small, unless the kinetic prefactor is small (e.g. without a good catalyst). At typical SOFC operating temperatures, the activation overpotential is larger ($\eta \sim k_B T / e = 74 \text{ mV}$ at $800 \text{ }^\circ\text{C}$), although still much less than the cell voltage, which is set by bond breaking energies of the half cell reactions ($\sim 1 \text{ eV}$).

In the last region, the transport of reaction species cannot sustain the current, leading to a huge drop of cell voltage. This will be described with Nernst equation and diffusion equations in later lectures.

Reference: [1] Lecture 1: Basic Physics of Galvanic Cells By Juhyun Song (and MZB);

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