I. Equivalent Circuit Models

Lecture 2: Electrochemical Energy Conversion

MIT Student

Galvanic cells convert different forms of energy (chemical fuel, sunlight, mechanical pressure, etc.) into electrical energy and heat. In this lecture, we are interested in some examples of galvanic cells.
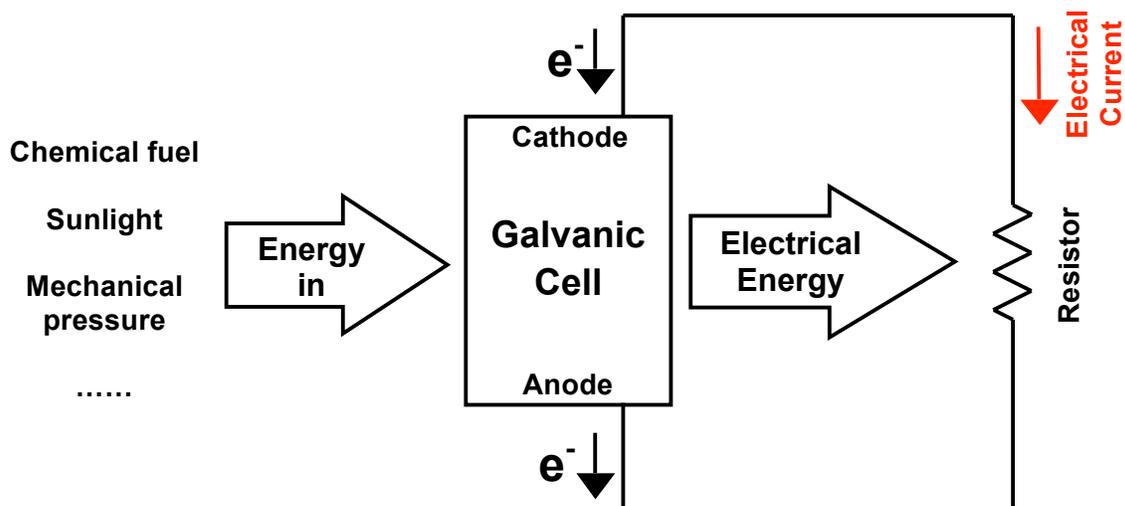
Figure 1: Energy Conversion of Galvanic Cell

1. Voltage Sources

1.1 Polymer Electrolyte Membrane (PEM) Fuel Cell

PEM fuel cells employ a polymer membrane to move ions from anode to cathode. Figure 2 shows the structure of Hydrogen-oxygen PEM fuel cell. Hydrogen molecules are oxidized to protons at the anode. Electrons travel through an external load resistance. Protons diffuse through the PEM under an electrochemical gradient to the cathode. Oxygen molecules adsorb at the cathode, are reduced and react with the protons to produce water. The product water is absorbed into the PEM, or evaporates into the gas streams at the anode and cathode. The detailed reactions are

Anode (oxidation reaction, produces electrons):

$$H_{2(g)} \rightarrow 2H^+ + 2e^-$$

Cathode (reduction reaction, consumes electrons):

$$\frac{1}{2}O_{2(g)} + 2H^+ + 2e^- \rightarrow H_2O_{(l)}$$

Net reaction:

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$$
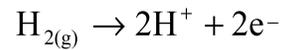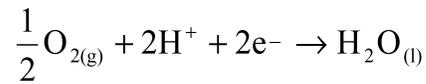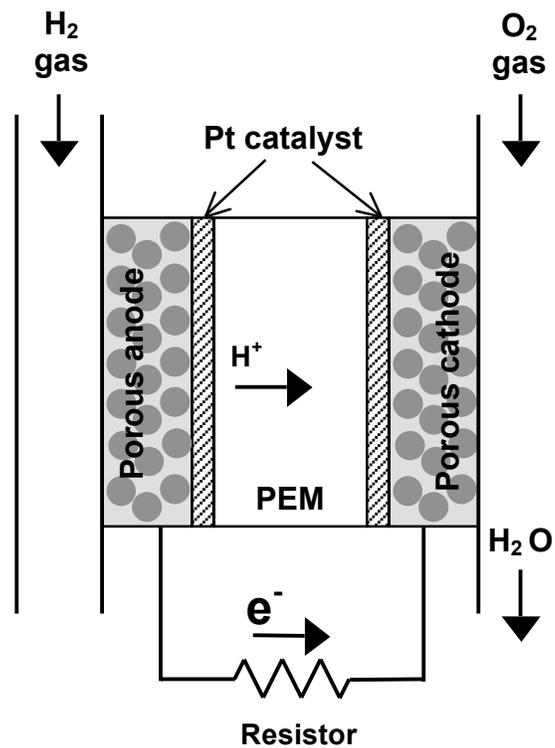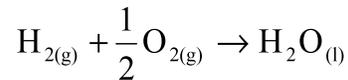
Figure 2: Hydrogen-oxygen PEM fuel cell

The equivalent circuit of PEM fuel cell is shown in Figure 3. The resistors and capacitors are related to different effects:

R_D^a: gas diffusion at anode
R_D^c: gas diffusion at cathode
R_i^a: interfacial charge transfer at anode
R_i^c: interfacial charge transfer at cathode
R_M: ion transfer in membrane
C_i^a: interfacial charge storage at anode
C_i^c: interfacial charge storage at cathode
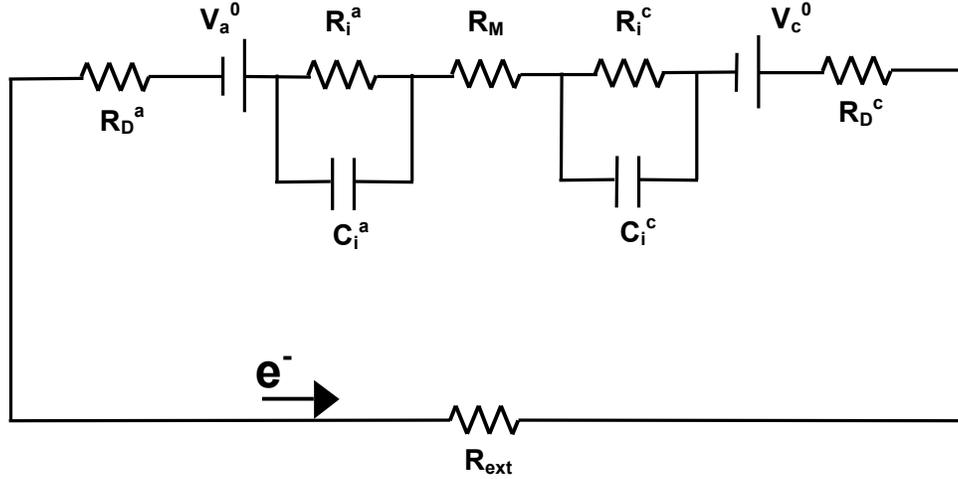
Figure 3: Equivalent circuit of PEM fuel cell

1.2 Solid Oxide Fuel Cell (SOFC)

Solid oxide fuel cells are a class of fuel cell characterized by the use of a solid oxide material as the electrolyte. In contrast to PEM fuel cells, which conduct positive hydrogen ions (protons) through a polymer electrolyte from the anode to the cathode, the SOFCs use a solid oxide electrolyte to conduct anions, e.g. negative oxygen ions, from the cathode to the anode, as shown in Figure 2. The electrochemical oxidation of the oxygen ions thus occurs on the anode side. The detailed reactions are

Anode (oxidation reaction, produces electrons):
$$H_{2(g)} + O^{2-} \rightarrow H_2O_{(l)} + 2e^-$$
Cathode (reduction reaction, consumes electrons):
$$\frac{1}{2}O_{2(g)} + 2e^- \rightarrow O^{2-}$$

Net reaction:
$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$$

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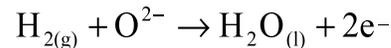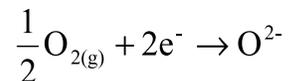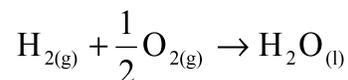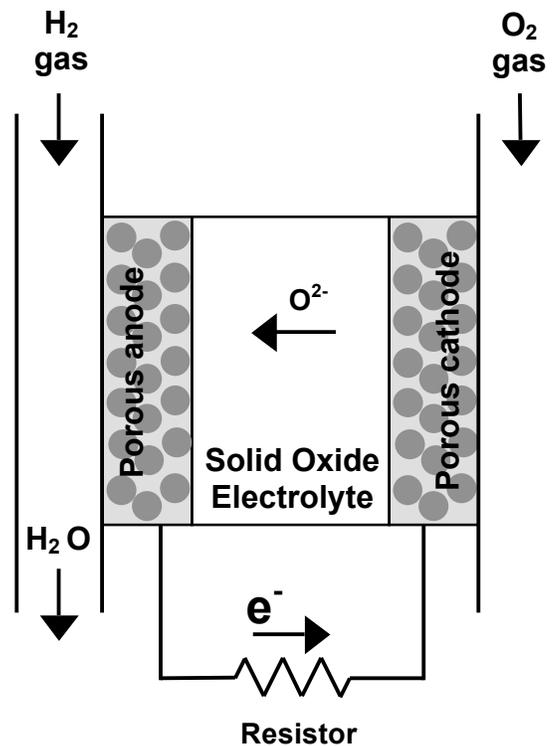
Figure 4: Solid oxide fuel cell

2. Current Sources

2.1 Silicon p-n Junction Solar Cell

Before we learn silicon solar cell, we need to understand some basic concepts of semiconductor physics.

A fundamental result of solid-state physics states that in semiconductor electrons with specific energies are allowed to stay in sharply define bands leaving bandgaps of forbidden energies in between. As shown in Figure 5, the two key bands around the fundamental bandgap are given special names. The band immediately below is called the valence band while the band immediately above is called the conduction band. In pure silicon, all states in valence band are occupied by electrons while all states in conduction band are empty at temperature of 0 K. At high temperatures a few states of the conduction band may actually be occupied by electrons. The electrons in the partially filled conduction band can move around in response to an applied voltage. In addition, there are empty states, called holes, in valence band which now allow electrons to move about.

The band structures of silicon can be changed by doping. Doping brings foreign atoms which do not change the silicon lattice very much but can donate or accept electrons. The atom from Column V of the periodic table can "donate" one of its electrons to the conduction band and become positively charged, which is called donor. The semiconductor with doped donors is call n-type semiconductor. The atom from Column III of the periodic table can "accept" a bonding electron and become negatively charged, which is called acceptor. The semiconductor

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with doped acceptors is call p-type semiconductor. Electron states associated with donor and acceptor atoms can be represented in the energy band diagram as shown in Figure 6. Donor states are inside the forbidden gap slightly below the conduction band edge at E_D. The reason is that it only takes a small amount of energy to release the electron the conduction band. Similarly, acceptor states are represented slightly above the valence band at E_A, as a little energy will result in the release of a hole to the valence band.
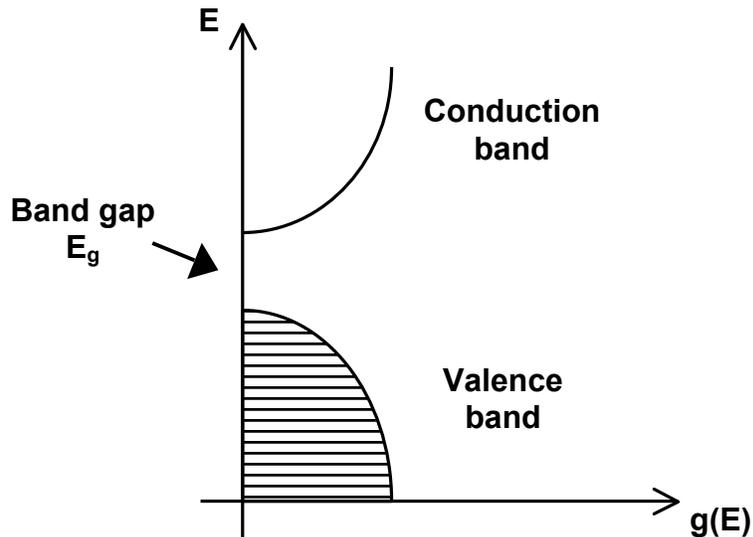
Figure 5: Band structure of Intrinsic Si at 0K
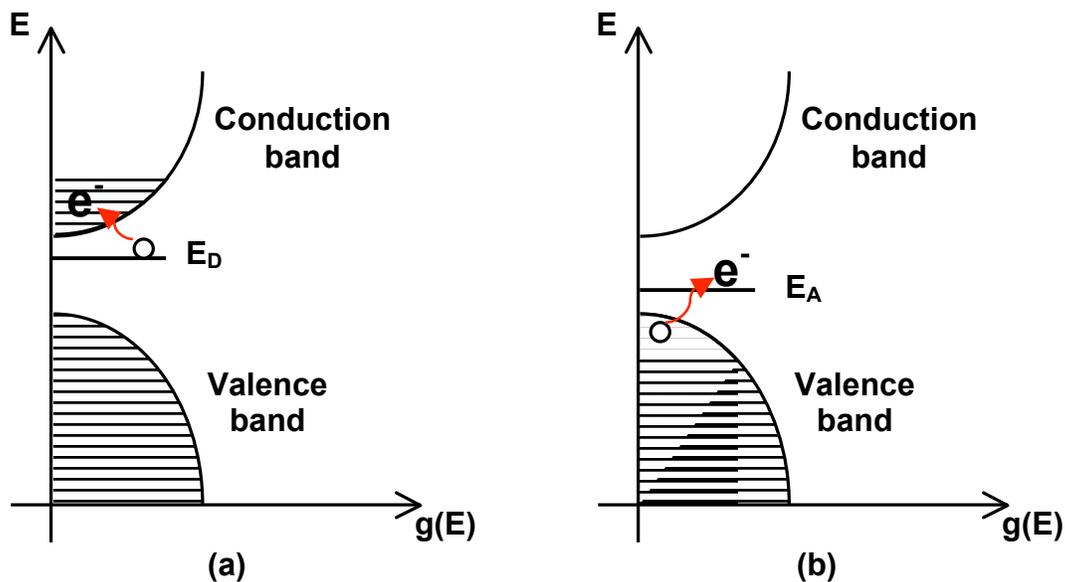
Figure 6: Band structure of doped Si. (a) n type. (b) p type.

An ideal p-n junction is a semiconductor structure where the doping level abruptly changes from n-type with a uniform donor concentration to p-type with a uniform acceptor concentration,

shown in Figure 7. Electrons on the n-side will tend to flow towards the p-side since they are presented with empty states at the same energy. At the same time, holes on the p-side will flow towards the n-side where there are lots of available states at the same energy. Once thermal equilibrium has been established and charge redistribution has stopped, a charge dipole has developed across the junction. This results in net positive charge on the n-side and net negation charge on the p-side. So there is a build-in electric field at the junction.

When the p-n junction absorb a photon with $hv > E_g$, a new electron-hole pair is produced. The build-in electric field drives the electron to the n-side and the hole to the p-side. If we connect the p-n junction to the external circuit, we will "harvest" the electron-hole pair current at electrodes.
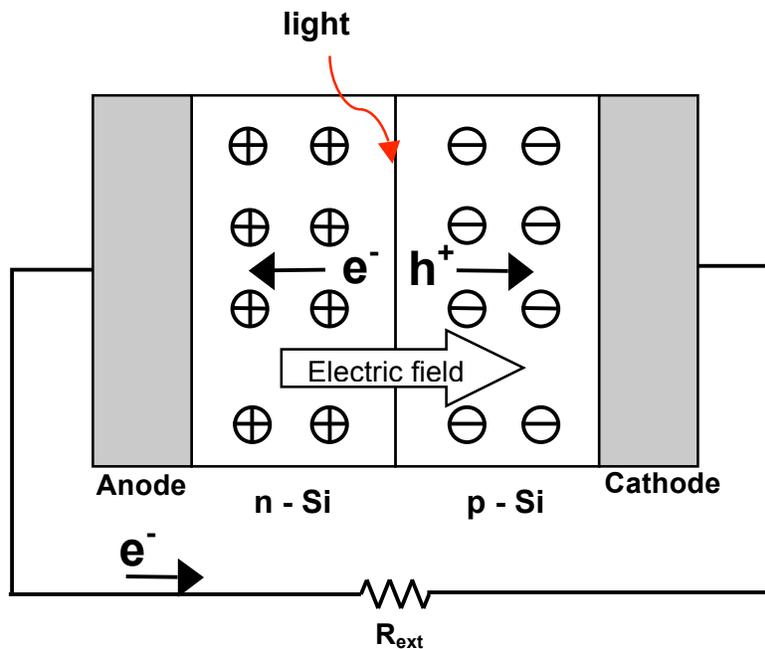
Figure 7: p-n junction solar cell

The equivalent circuit of p-n junction solar cell is shown in Figure 8(a). A p-n junction diode is in parallel with a current source where I_p is the photocurrent. Figure 8(b) shows the I-V curve of the diode. In forward bias, large current is easy to pass. But in reverse bias, only a small saturation current I_s is allowed. The I-V relation of diode can be calculate as

$$I_d = I_s \left(e^{\frac{eV_d}{kT}} - 1 \right)$$

(a)   **(b)**
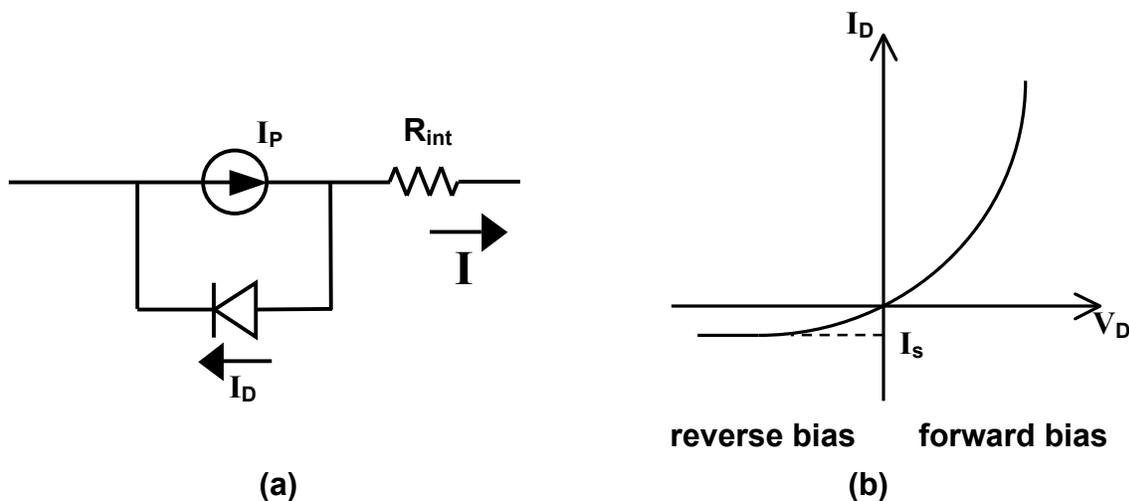
Figure 8: Equivalent circuit of p-n junction solar cell

Assuming $R_{int}=0$, the I-V relation is

$$I = I_p - I_d = I_p - I_s\left(e^{\frac{eV_d}{kT}} - 1 \right)$$

Figure 9 shows the V-I curve of p-n junction solar cell. When $I_p=0$ (dark environment), the solar cell performs as a diode. When $I_p>0$ (light environment), the open circuit voltage is

$$V_o = \frac{kT}{e}\ln\left(1 + \frac{I_p}{I_s} \right)$$
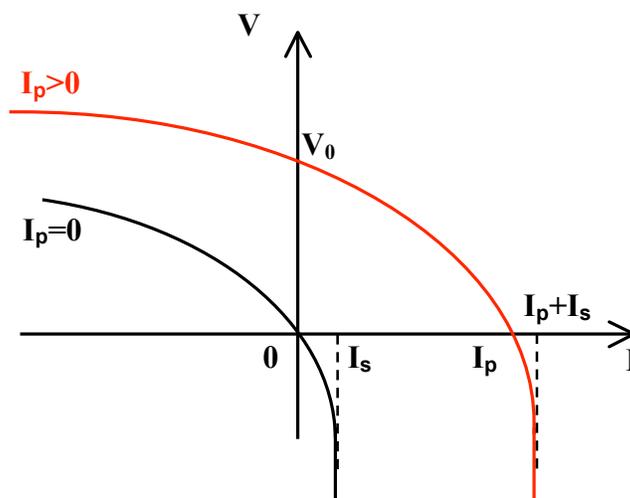
Figure 9: Current-voltage relation of p-n junction solar cell

2.2 Graetzel Cell (dye-sensitized solar cell)

A dye-sensitized solar cell is based on a semiconductor formed between a photo-sensitized anode and an electrolyte, as shown in Figure 10. The cell has three primary parts. On the top is a transparent anode made of fluorine-doped tin dioxide (S_nO_2:F) deposited on the back of a (typically glass) plate. On the back of the conductive plate is a thin layer of titanium dioxide (T_iO_2), which forms into a highly porous structure with an extremely high surface area. T_iO_2 only absorbs a small fraction of the solar photons. The plate is then immersed in a mixture of a photosensitive ruthenium-polypyridine dye and a solvent. After soaking the film in the dye solution, a thin layer of the dye is left covalently bonded to the surface of the T_iO_2. A separate backing is made with a thin layer of the iodide electrolyte spread over a conductive sheet, typically platinum metal.

Sunlight enters the cell through the transparent S_nO_2:F top contact, striking the dye on the surface of the T_iO_2. Photons striking the dye with enough energy to be absorbed will create an excited state of the dye, from which an electron can be "injected" directly into the conduction band of the T_iO_2, and from there it moves by diffusion (as a result of an electron concentration gradient) to the clear anode on top. Meanwhile, the dye molecule has lost an electron and the molecule will decompose if another electron is not provided. The dye strips one from iodide in electrolyte below the T_iO_2, oxidizing it into triiodide. This reaction occurs quite quickly compared to the time that it takes for the injected electron to recombine with the oxidized dye molecule, preventing this recombination reaction that would effectively short-circuit the solar cell. The triiodide then recovers its missing electron by mechanically diffusing to the bottom of the cell, where the counter electrode re-introduces the electrons after flowing through the external circuit.
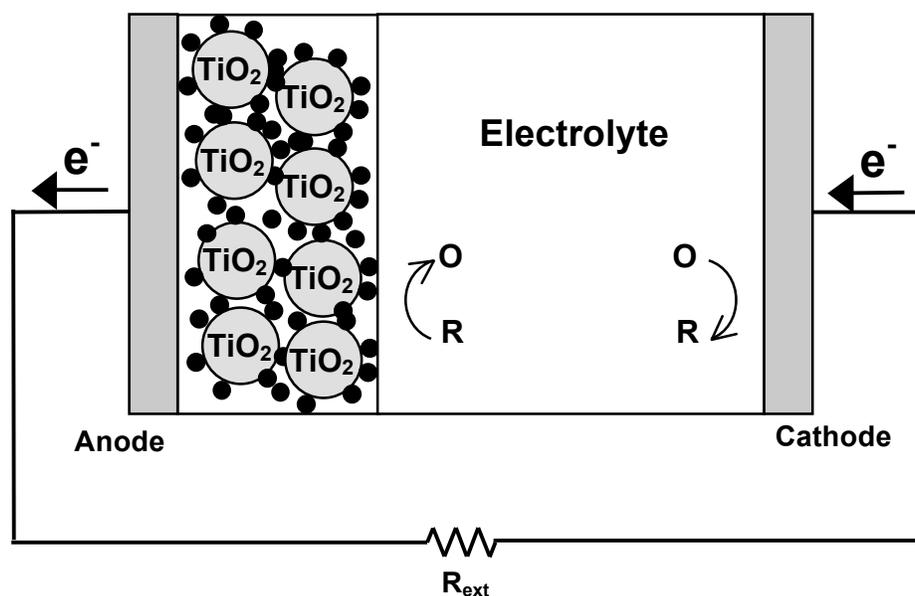
Figure 10: Dye-sensitized solar cell

Figure 11 shows the equivalent circuit of dye-sensitized solar cell. The basic idea is still the same: "harvest" the electron-hole pairs from the absorbed photons.
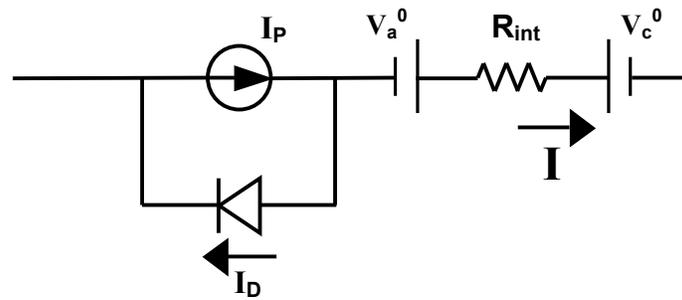
Figure 11: Equivalent circuit of dye-sensitized solar cell

2.3 Electro Kinetic Energy Conversion

A pressure-driven fluid flow through micro channels carries a net electrical charge with it, inducing both a current and a potential when the charge accumulates at the channel ends. These so-called streaming currents and streaming potentials can drive an external load and therefore represent a means of converting hydrostatic energy into electrical power, as shown in Figure 12. The notion of employing such electro kinetic effects in an energy conversion device is called electro kinetic energy conversion. Physical modeling of electro kinetic energy conversion is needed to guide the optimization of these properties. The relations of electro kinetic phenomena can be described by the following equations:

$$\begin{pmatrix} Q \\ I \end{pmatrix} = \begin{pmatrix} K_H & S \\ S & K_E \end{pmatrix} \begin{pmatrix} P \\ V \end{pmatrix}$$

where P is pressure, Q is flow rate, V is voltage and I is current. K_H is hydrodynamic conductivity of the porous material, K_E is electric conductivity and S is electro kinetic coupling. The detailed model of electro kinetic energy conversion will be discussed in Lecture 33.
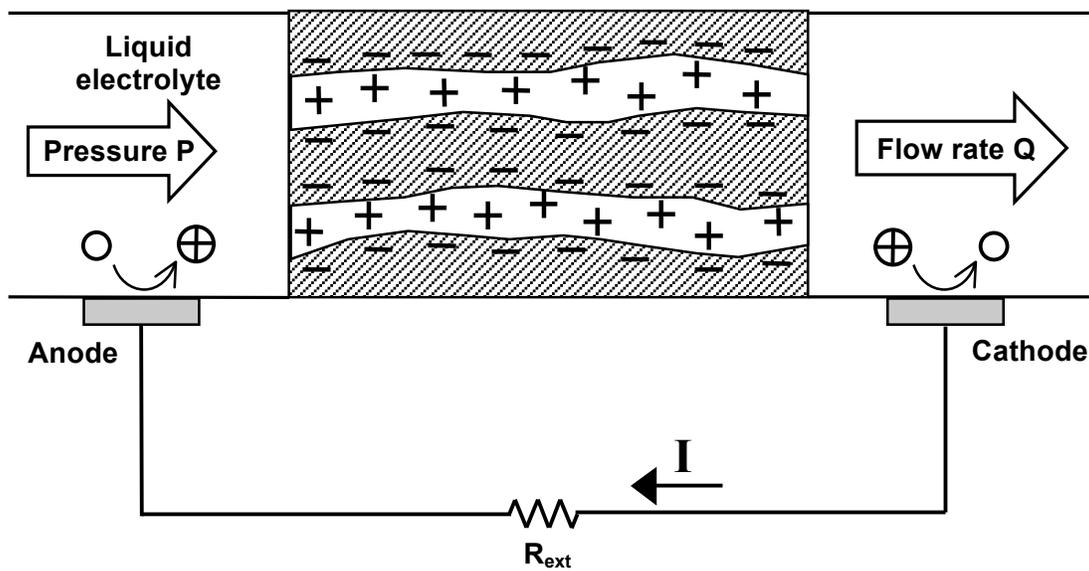
Figure 12: Electro Kinetic Energy Conversion

10.626 Electrochemical Energy Systems
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