ELECTROCHEMISTRY OF FUEL CELL

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Summary

Fuel cells are devices that utilize electrochemical reactions to generate electric power. They are believed to give a significant impact on the future energy system. In particular, when hydrogen can be generated from renewable energy resources, it is certain that the fuel cell should play a significant role.

Even today, some types of fuel cells have been already used in practical applications such as combined heat and power generation applications and space vehicle applications. Though research and development activities are still required, the fuel cell technology is one of the most important technologies that allow us to draw the environment friendly society in the twenty-first century. This section describes the general introduction of fuel cell technology with a brief overview of the principle of fuel cells and their historical background.

1. Introduction

A fuel cell is a system of electric power generation, which utilizes electrochemical reactions. It can produce electric power by inducing both a reaction to oxidize hydrogen obtained by reforming natural gas or other fuels, and a reaction to reduce oxygen in the air, each occurring at separate electrodes connected to an external circuit. The principal reaction is often described as the opposite of the electrolysis of water.

This is because hydrogen and oxygen undergo an electrochemical reaction to produce electric power and water. In fact, in the case of the fuel cells used in space vehicles, water produced in electricity generation is used for routine daily activities within the space vehicle.

2. Principle of Electricity Generation by Fuel Cells

The principle of electric power generation in fuel cells is entirely the same as the one for ordinary batteries. In batteries, however, the reactants are stored within the battery itself, and electric power generation ceases once these reactants are consumed. The most familiar example is a dry battery that is classified in the primary battery.

Also, there are storage type batteries—or the secondary batteries—that can regenerate the chemical reactants by applying electric energy from outside. In contrast, the reactants of a fuel cell are supplied from outside, and reaction products are continually discharged outside the fuel cell. Thus it can continuously supply electric power as long as an external supply of reactants is maintained.

Fuel cells and batteries use electrochemical reactions to convert the chemical energy of the fuel into electrical energy. Figure 1 shows the principle of operation of fuel cells. A fuel cell consists of two types of electron-conducting electrodes, the anode and the cathode, and an ion-conducting electrolyte.

At the interfaces between the electrodes and the electrolyte, electrochemical reaction causes charge carriers, such as electrons and ions. At the anode, an oxidation reaction occurs which generates electrons; at the cathode, a reduction reaction occurs which consumes electrons.

Ordinary oxidation and reduction reactions occur at the same place, as can be seen in combustion flames that usually release the chemical energy of fuel as heat. But in electrochemical reactions, the oxidation and reduction reactions occur at the different electrodes, separated by the electrolyte, and electric current can be drawn when these electrodes are connected via external circuit.

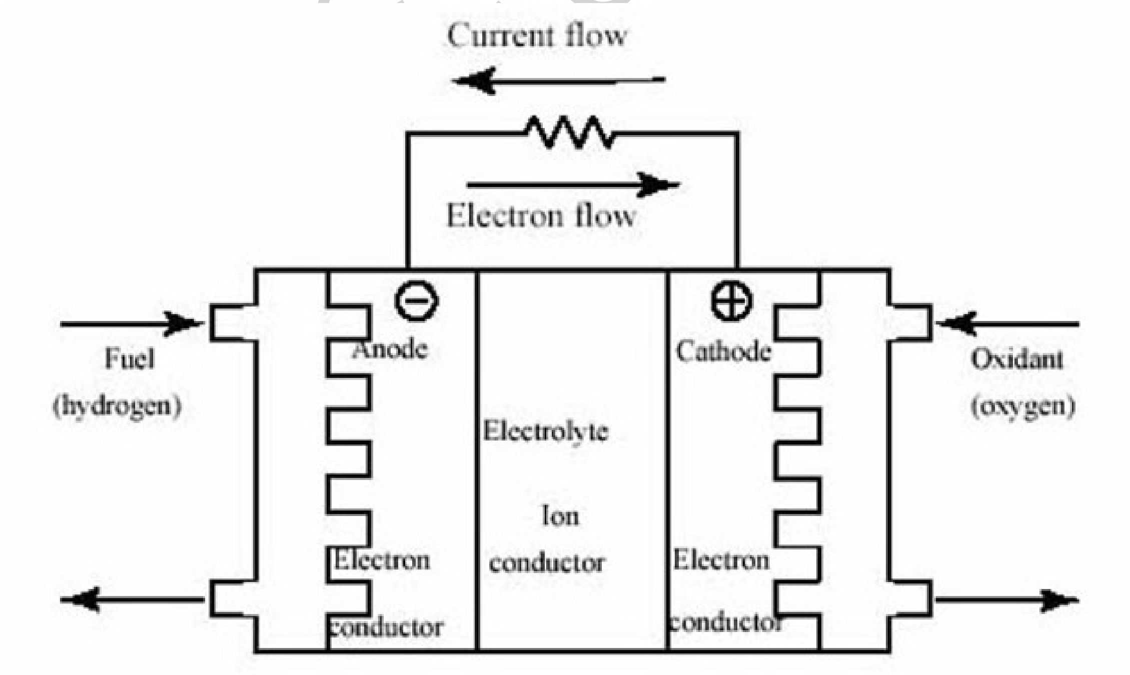

Figure 1. Schematic Diagram of the Principle of Operation of Fuel Cells

In general, in an equilibrium state in which no apparent current flows at the interface between an electrode and the electrolyte, the oxidation-reduction (redox) reaction occurring at the electrodes is written as follows:

$$aA + ne = bB$$

where e is electron, and A and B denote chemical substances involved in the reaction, with a, b and n being constants.

Also, the equilibrium electrode potential E is given by the Nernst equation:

$$E = E^\circ - (RT/nF)\ln(a_B{}^b/a_A{}^a)$$

where R is the gas constant, T is the absolute temperature, F is the Faraday constant, a_A is the activity of A, a_B is the activity of B, and E° is the standard electrode potential when the activity is equal to unity. E° is a potential intrinsic to the redox reaction; it is a measure of the ease of ionization of a metal, and of the oxidizing or reducing power of a reaction.

The activity a_i (i = A, B) is defined as follows. For gases, partial pressure p (atm ; standard condition is 1 atm) can be used as the activity. In liquid phase substances, molar concentration (in units M = mol/L; standard condition is 1 M) can be used for solutes, while $a_i = 1$ for the solvent of a dilute solution. Also, $a_i = 1$ for a pure solid and electrons in a metal.

It is possible to describe the relation between the equilibrium potential and the concentration of hydrogen ions in the electrolyte for the example of a hydrogen-oxygen fuel cell in an acidic solution as follows.

Hydrogen electrode (anode): $2H^+ + 2e = H_2$

Oxygen electrode (cathode): $(1/2)O_2 + 2H^+ + 2e = H_2O$

By applying the Nernst equation to these reactions, respectively, the electrode potentials can be calculated for anode and cathode as:

$$E_{H2} = E^\circ_{H2} - (RT/2F)\ln(a_{H+}{}^2/a_{H2})$$

$$E_{O2} = E^\circ_{O2} - (RT/2F)\ln(a_{H2O}/a_{O2}{}^{0.5}/a_{H+}{}^2)$$

Here E°_{H2} and E°_{O2} denote the standard electrode potentials of the hydrogen and oxygen electrodes; at 25 °C(298K) and one atmosphere, these are 0 V and 1.23 V respectively.

The theoretical electromotive force (emf) E of a hydrogen-oxygen fuel cell is the difference of these two electrode potentials, written as follows.

$$E = E_{O2} - E_{H2} = E^\circ_{O2} - E^\circ_{H2} - (RT/2F)\ln(a_{H2O}/a_{O2}{}^{0.5}/a_{H2})$$

where E° is the standard electromotive force for this cell, and is expressed as $E° = E°_{O2} - E°_{H2}$; at 25 °C (298K) and atmospheric pressure, it is equal to 1.23 V. In an ideal case, the standard electromotive force can be measured as the open circuit voltage.

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Biographical Sketch

Kouichi Takizawa was born 8 January 1964, in Japan. He is a researcher in fuel cell technology, Master of Engineering in electrochemistry from Tohoku University. He joined TEPCO in 1988.