Energy Storage in Batteries and Fuel Cells

Tetsuya Kajita and Takashi Itoh

Abstract Batteries and fuel cells (FCs) are the two major types of solar energy storage devices currently in use. Secondary batteries reversibly convert stored chemical energy (e.g., from solar power devices) into electrical energy. FCs generally convert chemical energy from fuel into electricity via chemical reactions with oxygen. Hydrogen is the most common fuel, but hydrocarbons such as natural gas and methanol are sometimes used. FCs are distinct from batteries in that the former require a constant source of fuel and oxygen (e.g., through solar electrolysis of water) to sustain their chemical reactions, and can continuously produce electricity for as long as these inputs are supplied. A system consisting of stored hydrogen in a cylinder tank and an FC system functions as a battery. In this chapter, we discuss batteries and FCs for use with solar power devices, in terms of current practice and future perspectives.

1 Secondary Batteries

Many current applications (e.g., cellular phones, bicycles, mobile computers, vehicles, and large-scale storage) use secondary batteries because they are rechargeable, low in total cost, and flexible, and also because they have a light environmental impact. Batteries can be roughly classified as either physical or chemical. Chemical batteries are further divided into primary (nonrechargeable) and secondary (rechargeable) batteries; we discuss secondary chemical batteries in this section. The electrochemical reactions in secondary batteries are reversible, and such batteries use different combinations of battery elements, such as sodium-sulfur, redox flow, lead-acid, nickel-cadmium, nickel metal hydride, and lithium ion.

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A charge-discharge reaction is a fundamental operating mechanism of secondary batteries, which make use of an oxidation-reduction potential based on differential ionization tendencies. A secondary battery consists of cathode and anode active materials, and an electrolyte. The active materials of the cathode (reduction) and anode (oxidation) undergo a redox reaction during battery discharge. The sum of these potentials is the standard battery voltage. Figure 1 shows the electrochemical reaction in a secondary battery.

During charging, the cathode active material (C in Fig. 1) is oxidized, thus producing electrons, and the anode active material (A in Fig. 1) is reduced, thus consuming electrons. In contrast, during discharge the cathode active material is reduced and the anode material is oxidized. These electron flows constitute the current in the external circuit. An electrolyte enables internal ion flow between the anode and cathode, facilitating electrochemical reaction on the surface of the electrodes.

In general, the performance requirements for a secondary battery are high potential (high voltage), high capacity, long charge-discharge cycle life, high output, low cost, and high safety. However, there is no secondary battery that satisfies all of these requirements. The criteria for high-efficacy performance differ by secondary battery type. Figure 2 shows energy density calculations (capacity multiplied by average voltage) for several types of secondary batteries. It is clear that Li ion batteries are the most useful but also the most expensive. In contrast, lead-acid batteries have a lower cost.

We next describe several types of secondary batteries.
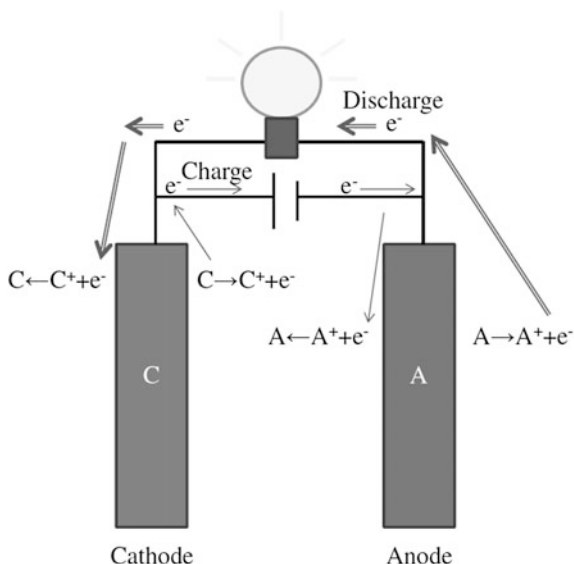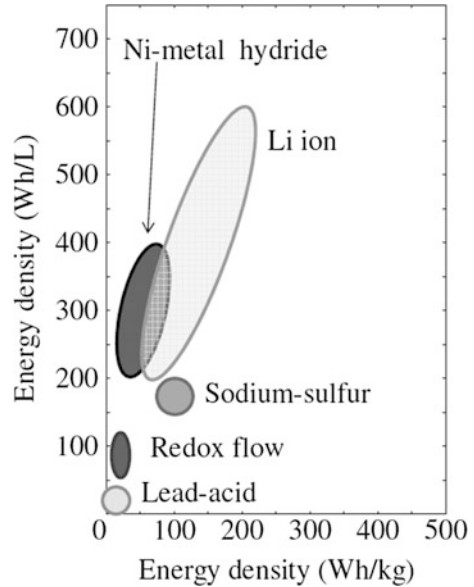
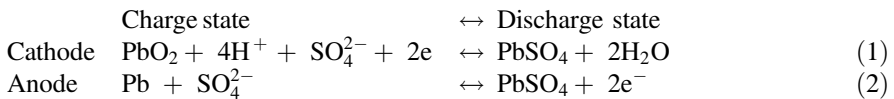**Fig. 1** Schematic of a secondary battery

Fig. 2 Energy density in several types of secondary batteries

1.1 Lead-Acid Batteries

Most old types of secondary batteries are lead-acid batteries, which were invented by Gaston Plante (1834–1889) 150 years ago. Lead oxide, lead, and sulfuric acid are the cathode active material, anode active material, and electrolyte, respectively. The electrochemical reactions on each electrode are as follows (Fig. 3).

$$
\begin{array}{lll}
 & \text{Charge state} & \leftrightarrow \text{Discharge state} \\
\text{Cathode} & PbO_2 + 4H^+ + SO_4^{2-} + 2e & \leftrightarrow PbSO_4 + 2H_2O & (1) \\
\text{Anode} & Pb + SO_4^{2-} & \leftrightarrow PbSO_4 + 2e^- & (2)
\end{array}
$$

During discharge, both the cathode and anode active materials are converted to lead sulfate ($PbSO_4$). The electrolyte loses its dissolved sulphuric acid and becomes mostly water. The reverse reaction occurs during charging. The battery voltage is 2 V, which is larger than the theoretical potential of water electrolysis.

Lead-acid batteries deteriorate over the course of the charge-discharge cycle. The lead sulfate generated during discharge on the anode readily crystallizes (termed sulfation) and is largely insoluble in the electrolyte, thereby deteriorating battery performance. Additionally, repeated charge-discharge cycles exfoliate lead oxide from the cathode, a situation that can be minimized by optimizing electrode shape. Hydrogen and oxygen generation on the anode and cathode due to water electrolysis via overcharging is a safety problem. However, lead-acid batteries are designed such that the gas is absorbed. This type is called a valve-regulated lead acid battery [1].
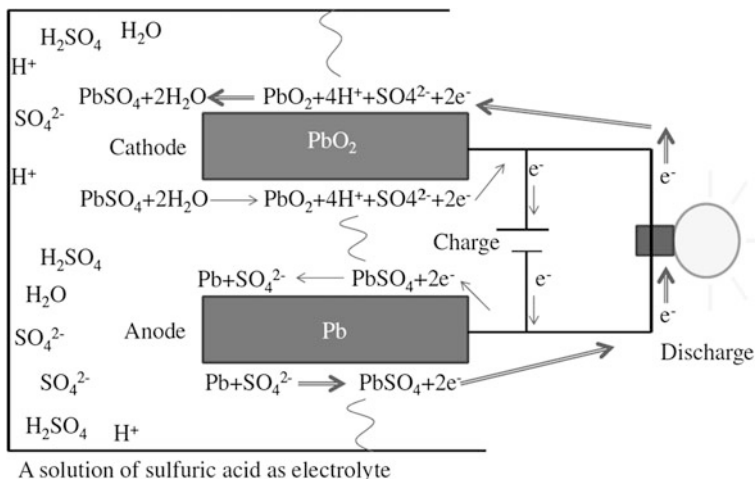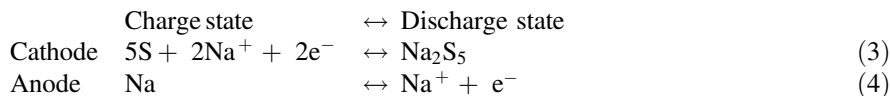
Fig. 3 Schematic of a lead-acid battery

In many applications, lead-acid batteries are used due to their low cost, long cycle life, and high safety, despite having a very low capacity (energy density) compared with other secondary batteries. Lead-acid batteries have recently come into use in large-scale energy storage and in power variation control for large-scale power generation, such as wind and solar.

We next discuss batteries that improve upon the capacity and cycle life of lead-acid batteries.
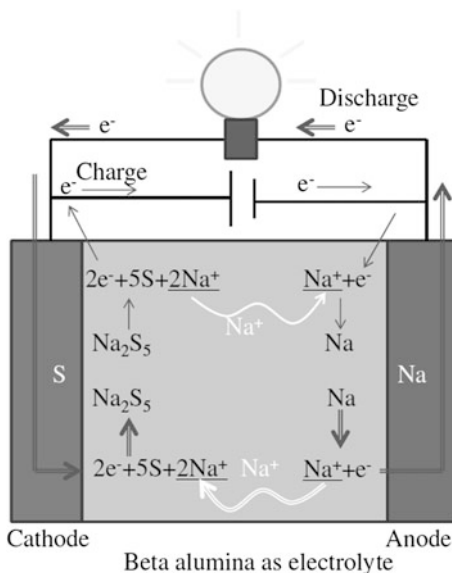
1.2 Sodium-Sulfur Batteries

Thirty years ago, Ford Motor Company developed sodium-sulfur batteries for electric vehicles. Sulfur and sodium are the cathode and anode active materials, respectively, and a beta alumina is the solid electrolyte. These batteries require a high operating temperature (300–350 °C) because of ionic conductivity in the solid electrolyte and the necessity of keeping the active materials in a molten state [2]. The reactions on the electrodes are as follows (Fig. 4).

$$
\begin{array}{llll}
& \text{Charge state} & \leftrightarrow \text{Discharge state} & \\
\text{Cathode} & 5S + 2Na^+ + 2e^- & \leftrightarrow Na_2S_5 & (3) \\
\text{Anode} & Na & \leftrightarrow Na^+ + e^- & (4)
\end{array}
$$

During discharge, sulfur is reduced and becomes Na_2S_5 at the cathode; sodium is oxidized and becomes sodium ion at the anode. The sodium ions migrate toward the cathode through the electrolyte. Although further discharge is possible, solid-state

Fig. 4 Schematic of a
sodium-sulfur battery

Na_2S_2 forms, which is indicative of poor discharge performance. During charging the reverse electrochemical reaction occurs at the electrodes. The battery voltage is 2 V.

Sodium-sulfur batteries must be handled with care because the active materials are combustible. If the battery burns, extinguishing the fire is difficult because water reacts with sodium. However, the battery can be manufactured at low cost because the component materials are common.
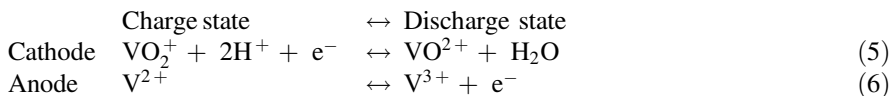
Sodium-sulfur batteries are used in large-scale energy storage due to their low cost, long cycle life, and high capacity, despite the necessity of a very high temperature. Their use is especially common in large urban areas because high energy density enables miniaturization. The high energy density and long cycle life of sodium-sulfur batteries have prompted their use in practical applications such as power load-leveling and power variation control in large-scale power generation. The practical application of sodium-sulfur batteries is expected to advance through the effective use of their high energy density, long cycle life, and low cost.

1.3 Redox-Flow Batteries

The National Aeronautics and Space Administration developed the redox-flow battery in the 1970s [3]. The active materials are in a liquid state and cause an oxidation-reduction reaction at the surface of electrochemically inactive electrodes in the battery. Elements that have multiple ionization states [such as iron (Fe^{3+}/Fe^{2+}), chromium (Cr^{3+}/Cr^{2+}), and vanadium (V^{5+} to V^{2+})] serve as active materials. A proton-exchange membrane separates the active materials. Storage tanks and

pumps are needed in order to store and circulate the two liquid active materials from the tanks to the battery. The following discussion focuses on vanadium redox-flow batteries because of their current use in practical applications [4].

Vanadium oxide and vanadium are the cathode and anode active materials, respectively, dissolved in sulfuric acid. The reactions on the electrodes are as follows (Fig. 5).

$$\text{Charge state} \quad\quad \leftrightarrow \text{Discharge state}$$

Cathode $\quad VO_2^+ + 2H^+ + e^- \quad \leftrightarrow VO^{2+} + H_2O \quad\quad\quad\quad\quad\quad (5)$

Anode $\quad V^{2+} \quad\quad\quad\quad\quad\quad \leftrightarrow V^{3+} + e^- \quad\quad\quad\quad\quad\quad\quad (6)$

During discharge, the cathode reduces pentavalent vanadium (VO_2^+) to tetravalent vanadium (VO^{2+}), and the anode oxidizes divalent vanadium to trivalent vanadium. The resulting hydrogen ion (H^+) produced at the cathode migrates to the anode through the proton-exchange membrane and maintains the electrical neutrality of the liquid active materials. During charging, the reverse electrochemical reaction occurs. The battery voltage is 1.4 V. Water electrolysis is problematic
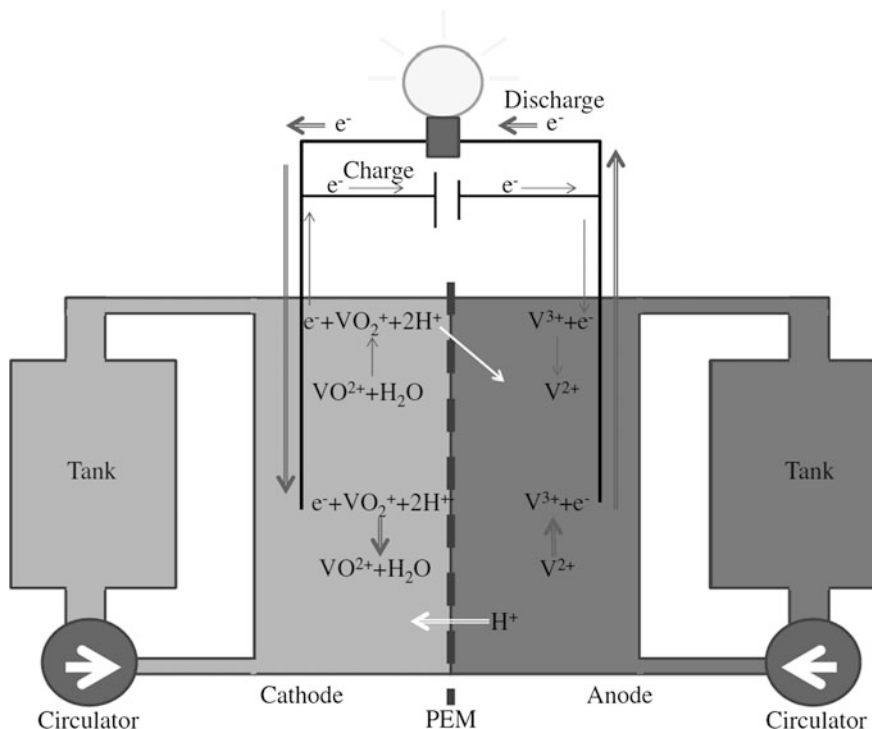

Fig. 5 Schematic of a redox-flow battery

during charging because the active materials are dissolved in acidic water. However, this problem can be addressed by making use of an overvoltage in the inactive electrode materials. For instance, carbon decreases the hydrogen production potential and increases the oxygen production potential. Additional problems such as the battery's low energy density and limitations in large-scale energy storage are due to the battery requiring a tank and circulator.

On the other hand, redox-flow batteries have a longer cycle life and lower cost. Furthermore, the battery has a flexible layout, in which the power-generating section (electrodes and proton-exchange membrane) and power-storing section (tank) are separate. This advantage is particularly effective for large-scale energy storage, which facilitates the use of redox-flow batteries in power-leveling and power variation control. Large-scale demonstrations will be necessary for realizing future applications of redox-flow batteries on a larger scale.

1.4 Ni-Metal Hydride Batteries

Battelle-Geneva Research Center invented the Ni-metal hydride battery in 1967. It uses a hydrogen-absorbing alloy and NiO(OH) as the anode and cathode active materials, respectively. The electrolyte is aqueous potassium hydroxide. The reaction on the electrode is as follows (Fig. 6). M indicates an intermetallic hydrogen-absorbing alloy. In most cases the compounds have the formula AB_5; A is a rare-earth mixture of lanthanum, cerium, neodymium, and praseodymium termed a mischmetal, and B is nickel, cobalt, manganese, and/or aluminum [5, 6].
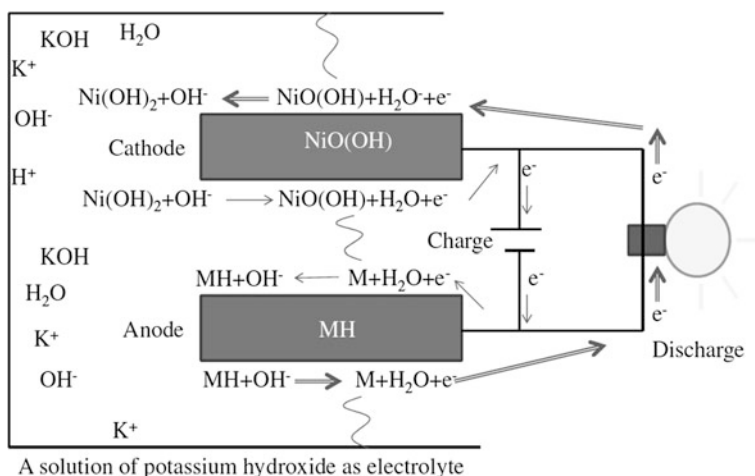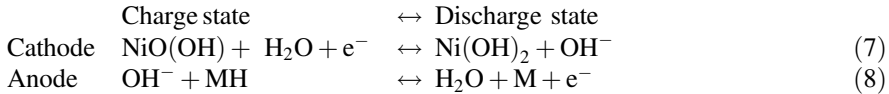

Fig. 6   Schematic of a Ni-metal hydride battery

	Charge state	$\leftrightarrow$ Discharge state	
Cathode	$NiO(OH) + H_2O + e^-$	$\leftrightarrow Ni(OH)_2 + OH^-$	(7)
Anode	$OH^- + MH$	$\leftrightarrow H_2O + M + e^-$	(8)

During discharge, the cathode reduces $NiO(OH)$ to $Ni(OH)_2$, and the anode oxidizes the hydrogen-absorbing alloy to hydrogen ion. During charging, the reverse electrochemical reaction occurs. The battery voltage is 1.2 V. The battery suppresses gas production during overcharge or overdischarge. The cathode produces oxygen under such conditions. Gas diffuses to the anode, where it reacts to form water, or the anode absorbs the hydrogen. However, hydrogen absorption is not sufficiently fast to prevent excessive hydrogen buildup if the discharge current is too large.

Ni-metal hydride batteries exhibit a well-known memory effect, which decreases their capacity. If the battery is repeatedly recharged after being only partially discharged, the maximum usable capacity in the battery decreases. Repeating the complete charge-discharge cycle several times negates the memory effect.

Ni-metal hydride batteries are used in many applications such as digital cameras, electric razors, and hybrid electric vehicles (HEVs) due to a long cycle life, light environmental load, low internal resistance, and high safety. More than 6 million HEVs equipped with a Ni-metal hydride battery are running worldwide. A demonstration test of a large-scale Ni-metal hydride battery was recently started, with applications in large-scale energy storage, power load-leveling, and power variation control.

1.5 Li Ion Batteries

In the 1970s, M. S. Whittingam proposed a Li ion battery that uses titanium sulfide and lithium metal as the cathode and anode, respectively. A layered transition metal oxide as the cathode active material [7], graphite as the anode active material [8], an ethylene carbonate as the electrolyte solvent [9], and aluminum foil as an electric collector in the cathode [10] are several subsequent innovations. Sony and Asahi Kasei released the first commercial Li ion battery in the 1990s.

In general, Li ion batteries use an organic solvent that has $LiPF_6$ dissolved in it. An organic solvent containing a chain carbonate and cyclic carbonate is almost always used in Li ion batteries, and some additive is included. The reactions at the electrode are as follows. Figure 7 shows the electrochemical reaction that uses the maximum amount of Li (x = 1).
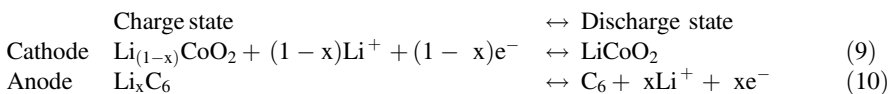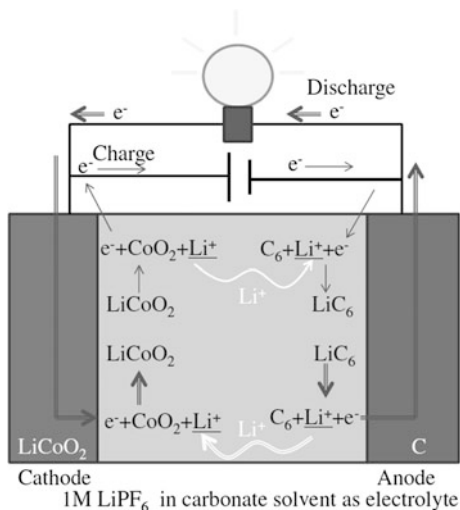
	Charge state	$\leftrightarrow$ Discharge state	
Cathode	$Li_{(1-x)}CoO_2 + (1-x)Li^+ + (1-x)e^-$	$\leftrightarrow LiCoO_2$	(9)
Anode	Li_xC_6	$\leftrightarrow C_6 + xLi^+ + xe^-$	(10)

During discharge, the cathode reduces $Li_{(1-x)}CoO_2$, by using intercalating Li ion, to $LiCoO_2$, and the anode oxidizes the Li-intercalated graphite and deintercalates the Li ion. During charging, the reverse electrochemical reaction occurs. The battery voltage ranges from approximately 3–4 V.

During overcharge, the cathode heats up and the electrolyte decomposes, transforming the crystal structure of the cathode active material. This may cause a fire or explosion because the electrolyte is an organic solvent. During overcharge, gas production and Cu foil elusion at the anode destroys the battery's function. As a countermeasure, an electrical circuit in modern batteries prevents overcharge and overdischarge.

Li ion batteries are used in many applications, such as cellular phones, bicycles, mobile computers, HEVs, and electric vehicles, since such batteries have a high capacity (energy density) and long cycle life. The energy density is 2× that of Ni-metal hydride batteries. Improvements in safety and cycle life are needed for large-scale applications.

1.5.1 Future Perspectives for Batteries

Efforts to improve the energy density, safety, cycle life, and cost of secondary batteries are now in progress. An all-solid-state battery is attractive in terms of safety and cycle life. However, low ionic conductivity of the solid electrolyte and of the interface between the electrolyte and active material is a considerable obstacle for practical applications. Metal air secondary batteries that use metal and air (oxygen) as the anode and cathode, respectively, have five times the theoretical energy density of Li ion batteries. However, the basic composition of such an improved battery has been not established yet. Using Na, Mg, and Ca as charge

carriers in secondary batteries is drawing attention because of the low material cost. The composition of batteries using these charge carriers is almost the same as that of a Li ion battery, and practical use in the near future is expected.

2   Fuel Cells

Around the world, energy consumption has grown during the last century and continues to increase rapidly to meet growing needs. A possible solution to this problem is water electrolysis. Figure 8 shows a schematic of water electrolysis pertinent to FCs. Upon application of a direct current voltage to the aqueous electrolyte, current flows between the electrodes, and hydrogen and oxygen evolve at the anode and cathode, respectively. The reaction in a FC is the reverse reaction. Supplying hydrogen and oxygen to the anode and cathode, respectively, results in current flow along with the production of water, the only product of an FC. This indicates that FCs are environmentally friendly power-generation systems.

Sir William Robert Grove (1811–1896) invented FCs. They are fundamentally different alternatives to combustion-driven energy-conversion systems in that they directly convert the chemical energy of fuel into electricity [11–15]. Figure 9 shows the principle of the anode and cathode reactions in FCs, which consist of an anode and cathode to which the fuel (hydrogen gas) and oxidant (oxygen gas) flow, respectively. There is an electrolyte between the anode and cathode. Electrochemical reactions occur at both electrodes. The overall reaction in an FC can be obtained by summing both electrode reactions.
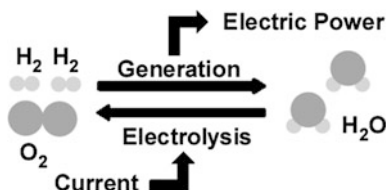

Fig. 8 Schematic for the relationships between water electrolysis and FC reactions
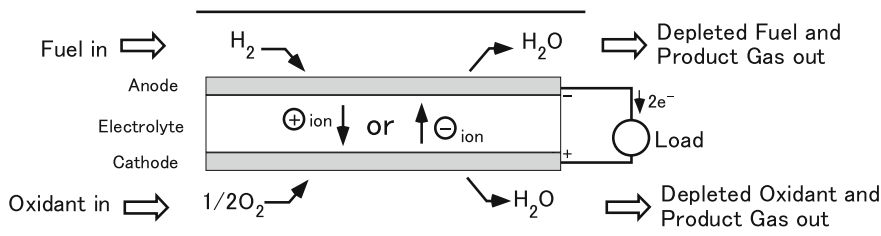

Fig. 9 Principles of the anode and cathode reactions in FCs

$$H_2 + 0.5O_2 \leftrightarrow H_2O \tag{11}$$

There are several types of FCs, which are usually classified by electrolyte and operating temperature (Table 1), as follows.

(a) Polymer electrolyte fuel cell (PEFC)
(b) Alkaline fuel cell (AFC)
(c) Phosphoric acid fuel cell (PAFC)
(d) Molten carbonate fuel cell (MCFC)
(e) Solid oxide fuel cell (SOFC)
(f) Direct methanol fuel cell (DMFC)

MCFCs and SOFCs are high-temperature FCs. PEFCs, AFCs, PAFCs, and DMFCs are low-temperature FCs. In general, low-temperature FCs (except DMFCs) use only H_2 as fuel. MCFCs and SOFCs can also use CO and CH_4 as fuel through internal conversion (12) and reforming (13) reactions, respectively.

$$CO + H_2O \rightarrow H_2 + CO_2 \tag{12}$$

$$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2 \tag{13}$$
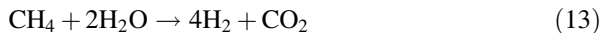
Low-temperature FCs are suitable for small-scale applications up to 100 kW (e.g., portable and mobile electric devices, automotive, and house electric power-generation systems). High-temperature FCs are most suitable for mid- and large-scale power-generation systems. The next section introduces various types of FCs in detail.

2.1 Polymer Electrolyte Fuel Cells

PEFCs use thin films of a polymer electrolyte membrane (PEM) as the electrolyte. PEFCs are sometimes also termed proton-exchange membrane fuel cells. Figure 10 shows the principle of the anode and cathode reactions in a PEFC. Hydrogen and oxygen are the anode fuel and cathode oxidant, respectively, and the cell's operating temperature is around 80 °C. PEFCs primarily consist of three elements, which are the PEM, bipolar plates, and catalyst. The future of PEFCs depends on development of these three elements.

The thickness of a PEM is approximately 0.05–0.1 mm. Since a PEM consists of a perfluorosulfonic acid polymer, PEFCs should operate at temperatures less than 80 °C. The PEM is sandwiched between the anode and cathode electrodes. Both the electrodes contain a platinum or platinum alloy catalyst on carbon, and both the catalyst and the carbon have a high specific surface area. The membrane electrode assembly comprises the electrodes and the PEM, and dictates cell performance. The theoretical output voltage is 1.23 V; however, the actual output voltage is

Table 1 Characteristics of various types of FCs

	(a) PEMFC	(b) AFC	(c) PAFC	(d) MCFC	(e) SOFC	(f) DMFC
Fuel	Hydrogen	Hydrogen	Hydrogen	Hydrogen Carbon monoxide (CO) Methane (CH_4)	Hydrogen CO CH_4	Methanol
Oxidant	Oxygen (air)	Oxygen	Oxygen (air)	Oxygen (air)	Oxygen (air)	Oxygen (air)
Electrolyte	Proton-exchange membrane	Potassium hydroxide (KOH)	Phosphoric acid (H_3PO_4)	Molten carbonate [$(Li/Na/K)_2CO_3$]	Zirconia (ZrO_2) doped with Y_2O_3	Proton-exchange membrane
Charge carrier	Proton (H^+)	Hydroxide ion (OH^-)	H^+	Carbonate ion (CO_3^{2-})	Oxide ion (O^{2-})	H^+
Catalyst	Platinum-related metal	Platinum-related metal	Platinum-related metal	None	None	Platinum-related metal
Anode reaction	$H_2 \rightarrow 2H^+ + 2e^-$	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	$H_2 \rightarrow 2H^+ + 2e^-$	$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$	$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$
Cathode reaction	$0.5O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$0.5O_2 + 2H_2O + 2e^- \rightarrow 2OH^-$	$0.5O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$0.5O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$	$0.5O_2 + 2e^- \rightarrow O^{2-}$	$1.5O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$
Approx. operating temperature (°C)	30–100	50–260	150–220	600–700	500–1000	20–90
Waste heat utilization	Warm water	Warm water, steam	Warm water, steam	Steam turbine, gas turbine	Steam turbine, gas turbine	Warm water
Approx. efficiency (%)	30–40	45–50	40–45	50–65	55–70	30–40

Fig. 10 Principles of the anode and cathode reactions in PEFCs
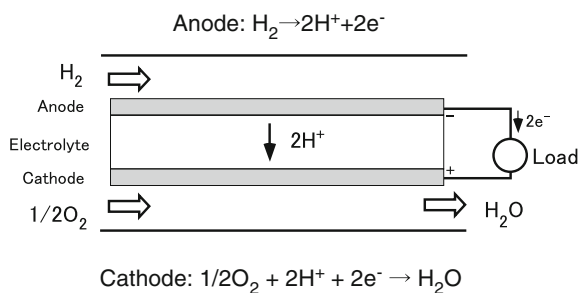
approximately 0.65–0.75 V because of the anode and cathode overvoltage, and the voltage loss of the cell elements.
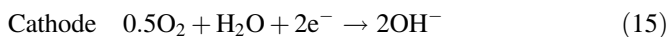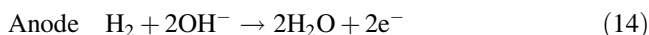
Bipolar plates distribute the fuel and oxidant within the cell, separate the individual cells in the stack, carry current and water away from each cell, and keep the cells cool. Nonporous graphite, a variety of coated metals, and a number of composite materials have been suggested for use as bipolar plate materials. The most widely used bipolar plate material is composite materials that contain graphite, which has low corrosion resistance and high conductivity. However, graphite is brittle and lacks mechanical strength, and therefore it is difficult to reduce plate thickness.

Catalysts for PEFCs are also important because PEFCs operate at temperatures less than 100 °C. Since hydrogen does not react with oxygen at such temperatures, PEFCs require a catalyst to lower the activation energy. The catalyst is typically platinum (particles that are several nanometers in diameter with a large specific surface area) or a related metal. Hydrogen and oxygen molecules adsorb on the platinum surface, and dissociate into hydrogen and oxygen atoms at the adsorption site on each electrode.

PEFCs require high-purity hydrogen. At present, steam reforming is the most common industrial hydrogen production method. Ideally, hydrogen production would be solar powered, making it environmentally friendly.

2.2 Alkaline Fuel Cells

AFCs use an aqueous solution of potassium hydroxide as the electrolyte. Figure 11 shows the principle of the anode and cathode reactions in an AFC. The reactions at the anode and cathode are as follows.
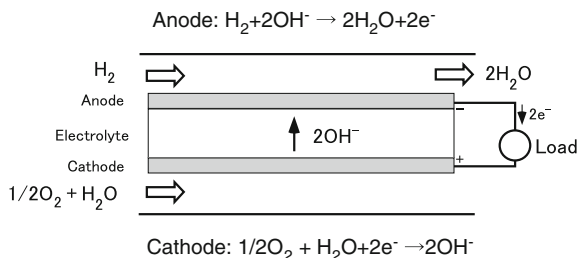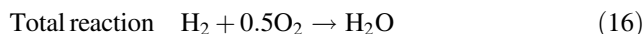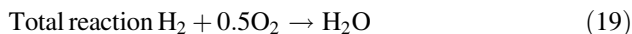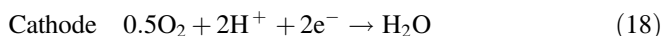
$$\text{Anode} \quad H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \tag{14}$$

$$\text{Cathode} \quad 0.5O_2 + H_2O + 2e^- \rightarrow 2OH^- \tag{15}$$

Anode: $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$

Cathode: $1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$

Fig. 11 Principle of the anode and cathode reactions in AFCs

$$\text{Total reaction} \quad H_2 + 0.5O_2 \rightarrow H_2O \tag{16}$$

AFCs can use nickel-related metal as electrodes. The operating temperature is approximately 50–260 °C. Regarding electrolyte durability, only pure hydrogen and oxygen can be used in AFCs because dissolved carbon dioxide impurities decrease cell performance, though development in this area is progressing. AFCs currently have only specialized applications in spacecraft, but use in hydrogen supply infrastructure has been proposed. Technological development may improve the prospects of AFCs.
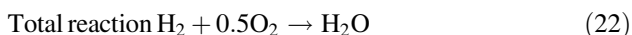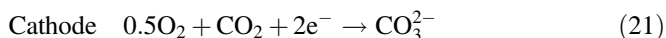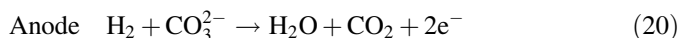
2.3 Phosphoric Acid Fuel Cells

PAFCs include a phosphoric acid solution impregnated in a separator as the electrolyte. The anode and cathode reactions, as well as the total reactions, of PAFCs are as same as the reactions of PEFCs (Fig. 10), as follows.

$$\text{Anode} \quad H_2 \rightarrow 2H^+ + 2e^- \tag{17}$$

$$\text{Cathode} \quad 0.5O_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{18}$$

$$\text{Total reaction} \, H_2 + 0.5O_2 \rightarrow H_2O \tag{19}$$
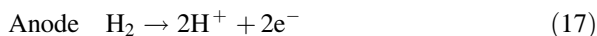
The operating temperature and power-generation efficiency are approximately 200 °C and 40 %, respectively. Analogously to PEFCs, the platinum catalyst may deteriorate if there is carbon monoxide in the fuel. Commercialization is progressing and PAFC power-generation plants for onsite 50–200 kW energy production are in development. Many PAFC plants continuously generate electric power for more than 40,000 h, which is the PAFC development lifetime target.

2.4 Molten Carbonate Fuel Cells

MCFCs use a mixture of alkali carbonate (Li_2CO_3, Na_2CO_3, and K_2CO_3) melts as electrolytes at high temperature. Figure 12 shows the principles of the anode and cathode reactions in MCFCs. The anode and cathode reactions are as follows.

$$\text{Anode} \quad H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^- \tag{20}$$

$$\text{Cathode} \quad 0.5O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-} \tag{21}$$

$$\text{Total reaction} \, H_2 + 0.5O_2 \rightarrow H_2O \tag{22}$$

MCFCs operate at 600—700 °C. The carbonate mixture forms highly CO_3^{2-} conductive molten salt. The cathode reduces oxygen molecules in the presence of CO_2 to CO_3^{2-}. The carbonate ions modulate electrical conductance inside the cell to the anode. The anode oxidizes hydrogen gas and carbonate ions, producing CO_2 and H_2O as exhaust gas. CO_2 gas can be reused at the cathode. Summing both the anode and cathode reactions gives the overall reaction for MCFCs. Water is the only final product. Although FCs generally use hydrogen fuel, MCFCs can also use CO and CH_4 through internal conversion and internal reforming reactions, respectively.

At MCFC operating temperatures, an anode consisting of nickel alloy and aluminum (and/or chromate) as well as a nickel oxide cathode are sufficient for the necessary electrochemical reactions. The nickel alloy is a catalyst, and reactions (12) and (13) produce CO and CO_2. For this reason, MCFCs can use hydrogen fuel, even if the fuel contains CO from coal gasification gas. Within the cell, it is also possible to reform methane, which is the main component of natural gas. Methane reforming can also be done outside the cell; this is called external reforming and is suitable for large-scale plants. Compared with internal-reforming MCFCs, external-reforming MCFCs are simpler and lighter.

Fig. 12 Principle of the anode and cathode reactions in MCFCs
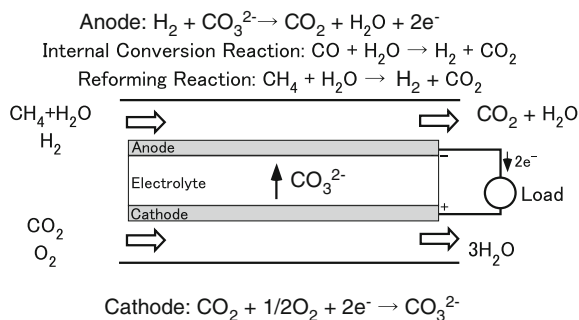
MCFC melt composition is a key issue pertinent to cell performance and lifetime. Molten carbonate melts upon electrolyte impregnation of the porous $LiAlO_2$, and melt composition of Li–Na-K carbonates depends on melting point, conductivity, and Ni solubility.

2.5 Solid-Oxide Fuel Cell

Like MCFCs, SOFCs do not require a platinum catalyst or reformer for internally producing hydrogen fuel. SOFCs also exhibit good power-generation efficiency. The anode and cathode reactions in SOFCs are as follows.

$$Anode \quad H_2 + O^{2-} \rightarrow H_2O + 2e^- \tag{23}$$

$$Cathode \quad 0.5O_2 + 2e^- \rightarrow O^{2-} \tag{24}$$

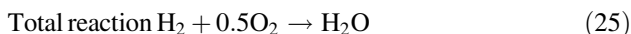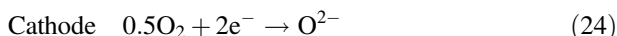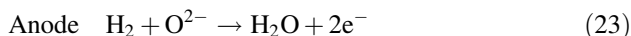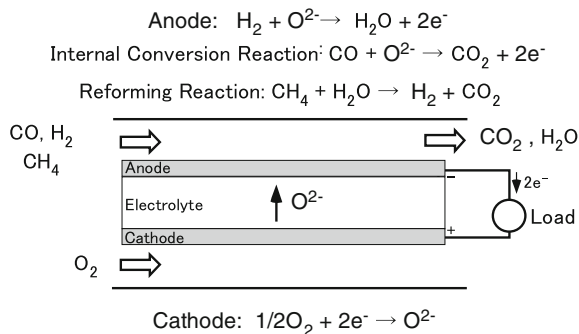$$Total\ reaction\ H_2 + 0.5O_2 \rightarrow H_2O \tag{25}$$

Figure 13 shows the principle of the anode and cathode reactions in SOFCs. They typically operate at approximately 500–1000 °C. O^{2-} is the electrolytic charge carrier, and ZrO_2 (zilconia), doped with 8–10 mol% Y_2O_3 (yttria), is the electrolyte, termed yttria-stabilized zirconia (YSZ). A porous gas-diffusion structure (metallic YSZ and related materials) is the anode. The high porosity and large surface area of the electrodes facilitate rapid mass transport of the reactant and product gases. The cathode is also porous and can be made of a strontium-doped lanthanum manganite $(La_{0.84}Sr_{0.16})MnO_3$ and related materials, as well as lanthanum strontium ferrite and lanthanum strontium cobalite.

SOFCs can attain at least 96 % of their theoretical open-circuit voltage. In the absence of a major internal resistance drop they can operate at high current densities $(1000\ mA/cm^2)$, and they have a high fuel-conversion efficiency. Like MCFCs,
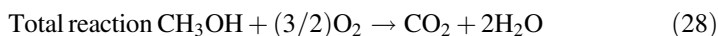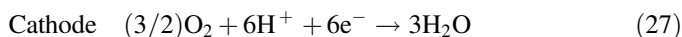

Fig. 13 Principle of the anode and cathode reactions in SOFCs

Anode: $H_2 + O^{2-} \rightarrow H_2O + 2e^-$

Internal Conversion Reaction: $CO + O^{2-} \rightarrow CO_2 + 2e^-$

Reforming Reaction: $CH_4 + H_2O \rightarrow H_2 + CO_2$

Cathode: $1/2O_2 + 2e^- \rightarrow O^{2-}$

SOFCs require no CO_2 recycling, leading to further simplification. Their use at alternative thermal power stations, such as thermal electric power plants, is expected.

2.6 Direct Methanol Fuel Cell

DMFCs are similar to PEFCs. Instead of hydrogen gas (as in PEFC), DMFC uses liquid methanol directly. Figure 14 shows the principle of the anode and cathode reactions in DMFCs. The chemical reactions at the anode and cathode are as follows.

$$\text{Anode} \quad CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \tag{26}$$

$$\text{Cathode} \quad (3/2)O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \tag{27}$$

$$\text{Total reaction} \; CH_3OH + (3/2)O_2 \rightarrow CO_2 + 2H_2O \tag{28}$$
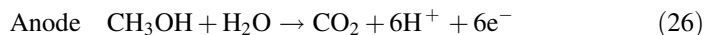
At the anode, methanol is converted to water, carbon dioxide, protons, and electrons. Oxygen reacts with the proton, and the final products are water and carbon dioxide. The actual reactions in DMFCs are complex. First, methanol adsorbs on the platinum catalyst, is oxidized, and releases a proton.

$$CH_3OH \rightarrow CH_2OH \rightarrow HCHO \rightarrow CHO \rightarrow CO \tag{29}$$
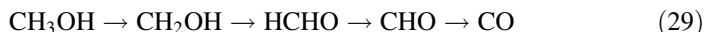
Each oxidation step on the platinum catalyst yields one proton (reaction 29). The final product is carbon monoxide, which poisons the platinum catalyst. Solving this issue will require development of a catalyst that is unaffected by CO (e.g., a platinum-related alloy).

DMFCs have a more serious problem. Methanol molecules permeate the PEM, which is called crossover. The membrane electrode assembly of DMFCs is generally permeable to water and methanol. Unreacted methanol migrates to the cathode and reacts with oxygen, yielding carbon dioxide and water. This process

Fig. 14 Principle of the anode and cathode reactions in DMFCs
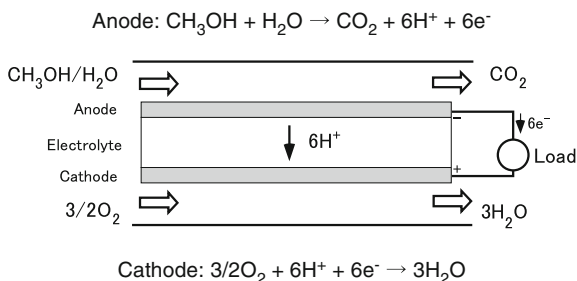
produces thermal energy not electrical power. One solution may be to decrease the methanol concentration, but doing so decreases the electrical power output. Another solution may be to use a different PEM to decrease methanol permeability.

DMFCs should be useful for mobile electronic devices, laptop computers, and cell phones. These devices require an easy method for methanol refill via a small cartridge. Investigations on using DMFCs in power-assisted bicycles and cars are also progressing.

2.6.1   Future Perspectives for Fuel Cells

Researchers are currently working to improve fuel cells in terms of their energy density, cycle life, and cost. Moreover, many governments are promoting the commercialization of stationary FCs and FC-based electric vehicles. The development of electrolytes, bipolar plates, and catalysts is important for the spread of FCs in the future; also important is new technology for hydrogen generation, transport, and supply. Further development of FCs will be required in order to get a clearer picture of their promise for solving today's energy challenges.

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