Recent Development Trends of Redox Flow Batteries

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Along with the progress of global warming, the introduction of renewable energy sources such as solar and wind power has been promoted, and large-capacity energy storage batteries have become important as a measure to stabilize electric power systems. A redox flow battery (RFB) is one of such batteries. It is charged and discharged by redox reactions of ions in an aqueous solution containing active materials. The RFB is suitable for large capacity storage and has excellent features such as long life and high safety. We began developing RFBs in 1985 and have delivered approximately 30 units. As a global trend, research and development have been actively promoted particularly in the United States, Europe, and China since around 2010, and recently, there have been many reports on new electrolytes using organic compounds. This paper introduces the development history of RFBs, the demonstration status of large capacity systems, and the recent development trends.

Keywords: renewable energy, stabilization of an electric power system, energy storage, energy storage battery, redox flow battery

1. Introduction

Recently, global efforts have been made to promote introduction of renewable energy sources. Against this backdrop, it has been increasingly important to introduce large capacity energy storage batteries to stabilize electric power systems. Among some energy storage batteries, redox flow batteries (RFBs) are noted to offer excellent features, such as suitability for large capacity, long service life, and high levels of safety, and an RFB using vanadium (V) electrolyte has already been used for demonstration and practical operation around the world. One example is the RFB system operated by Hokkaido Electric Power Co., Inc. (HEPCO), one of the largest in the world, with a capacity of 15 MW × 4 h.

Meanwhile, cost reduction is an important issue that must be addressed in order to launch full-scale introduction of RFBs from the viewpoint of economic rationality. R&D on RFBs has been very active globally, including in the U.S. This paper presents the status of demonstration of large capacity RFB systems and the recent development trends.

2. Principle and Features of an RFB

Figure 1 shows the principle of an RFB using V electrolyte. The electrolytes are stored in external positive and negative tanks. During charging and discharging, the electrolytes are circulated to the cell by pumps to induce the redox reactions, as shown below. The measured electromotive force is about 1.4 V.

\[
\begin{align*}
\text{[Negative electrode]} & \quad \text{VO}_2^+ + \text{H}_2\text{O} \rightarrow \text{VO}_2^+ + 2 \text{H}^+ + e^- \\
\text{[Positive electrode]} & \quad \text{V}^3+ + e^- \rightarrow \text{V}^{2+}
\end{align*}
\]

Since the battery capacity (kWh) is determined by the amount of V in the tank, and the battery output (kW) is determined by the cell size (area × number of cells), an optimal design can be ensured for each application because the output and capacity can be designed independently. In terms of operation, an RFB offers the convenience of accurately monitoring the state of charge by measuring the electrolyte potential even during charging and discharging. Moreover, in principle, there are no restrictions in the number of charge and discharge cycles because the battery reaction only consists of ionic valence changes. As such, the electrolytes can be used almost permanently, and the life cycle cost is low. The cost per kWh decreases for a longer storage duration.

In terms of safety, the risks of ignition and other hazards are low because the electrolytes are aqueous solutions used at normal temperature. There are few restrictions in terms of installation. One disadvantage is that the energy density is relatively small compared to other types of batteries due to the restrictions in solubility of aqueous solutions.

As discussed above, RFBs have unique features compared to other types of batteries. They can be optimally designed to meet various requirements of energy storage batteries. When designing RFB systems, it is important to understand these features and characteristics.
3. History of Development

A battery that is designed to generate electricity by supplying substances used as energy sources from outside the battery is referred to as a fuel cell. A chemically or electrically chargeable fuel cell is referred to as a regenerative fuel cell.

RFBs are a type of regenerative fuel cell and their research history is very long. The principle of RFB systems was first proposed in 1974 by L. H. Thaller of the National Aeronautics and Space Administration (NASA), U.S.(1) Almost at the same time, Nozaki et al. of the National Institute of Advanced Industrial Science and Technology (AIST) launched basic research on a Fe/Cr RFB and other RFBs in Japan.(2) Later, in around 1985, a V/V RFB(3) was invented by Professor Skyllas-Kazacos of the University of New South Wales (UNSW) in Australia. The performance of RFBs was dramatically improved, leading to practical use.

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
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<tbody>
<tr>
<td>1949</td>
<td>Kangro (a patent in Germany): Ti/Fe and the others</td>
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<tr>
<td>1980</td>
<td>AIST (ETL at that time) started R&amp;D (Ken Nozaki et al.)</td>
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<tr>
<td>1985</td>
<td>Sumitomo Electric and KEPCO: Fe/Cr RFB 60 kW × 8 h (1989), V RFB 450 kW × 2 h (1996)</td>
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<td>1989</td>
<td>UNSW in Australia: V RFB basic patent (1986) (Prof. Maria Skyllas-Kazacos)</td>
</tr>
<tr>
<td>1998</td>
<td>AIST: In-vehicle tests on a 10 kW redox super capacitor (non flow type)</td>
</tr>
<tr>
<td>2001</td>
<td>Sumitomo Electric commercialized V RFBs.</td>
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<tr>
<td>2005</td>
<td>NEDO: 170 kW × 6h (2000), 6 MW × 1.5h (2005) for wind power generation</td>
</tr>
<tr>
<td>2009</td>
<td>The enactment of the American Recovery and Reinvestment Act (ARRA) DOE started to fund for the development of RFBs in the U.S.</td>
</tr>
<tr>
<td>2010</td>
<td>IFBF, a society that specializes in RFBs, was organized in June 2010. Now, its annual meeting is held with much fanfare. Due to these vigorous activities, the annual number of papers presented about RFBs exceeded 400 in 2014 (refer to Table 1).</td>
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In around 1980, the difference in demand for electricity between day and night started to emerge as an issue in Japan. To level the power load, national projects started to develop large capacity energy storage batteries to supplement a pumped hydro energy storage system. The development of four types of energy storage batteries, i.e., three types of RFBs (Fe/Cr, Zn/Br, and Zn/Cl) and a NaS battery, was promoted. Concurrently, joint developments were also promoted between electric power companies and battery manufacturers. Sumitomo Electric Industries, Ltd. commercialized a V/V RFB in 2001, but the circumstances surrounding the electric power industry in Japan have changed since then. Energy storage batteries came to be installed at customer locations (distributed installation) instead of electric power companies. Customers stored inexpensive electricity during nighttime and discharged electricity in the daytime (peak period). They had an advantage in terms of electricity rate, while the electric power companies had an advantage in terms of load leveling.

Subsequently, introduction of renewable energy sources was promoted around the world as a measure to cope with global warming. It became important to introduce large capacity energy storage batteries to stabilize the electric power systems. In around 2010, such research activities gained momentum rapidly, mainly in the U.S. and China.

In the U.S., investment in renewable energy and other energy sources was promoted by the enactment of the American Recovery and Reinvestment Act (ARRA) in 2009. The Department of Energy (DOE) extended a large amount of financial support for the development of energy storage technologies, including RFBs. In 2010, a mandate AB 2514 was enacted in California, U.S. It set a target for electric power companies to introduce energy storage solutions equivalent to 1.3 GW by 2020. Procurement has been promoted every two years. In Europe, the International Flow Battery Forum (IFBF), a society that specializes in RFBs, was organized in June 2010. Now, its annual meeting is held with much fanfare. Due to these vigorous activities, the annual number of papers presented about RFBs exceeded 400 in 2014 (refer to Table 1).

4. Track Record in RFB Systems

Sumitomo Electric has installed about 30 systems in total, including equipment for practical use at plants and electric power companies, demonstration equipment, and testing equipment for national projects (refer to Table 2).

Regarding large capacity equipment operated in an electric power system, a 15 MW × 4 h RFB system was installed at HEPCO for a demonstration project by funding of the Ministry of Economy, Trade and Industry (METI).(4) Also, at an electric power company in California, a 2 MW × 4 h system is in operation for a project under the auspices of the New Energy and Industrial Technology Development Organization (NEDO).(5)

In an electric power system, both short-term output fluctuations in the order of seconds to minutes and long-term output fluctuations in the order of hours must be controlled to regulate the frequency and voltage. RFBs are able to regulate both short-term and long-term fluctuations
because they are suitable for a longer storage duration.

(1) An RFB system \([15 \text{ MW} \times 4 \text{ h}]\) operated in Hokkaido

Photo 1 shows the appearance of the system. The rated output is 15 MW, but 30 MW operation (double the rated output) is possible to cope with short-term fluctuations. A demonstration test was conducted for three years from the commencement of operation in December 2015. It aimed to develop the control and operation technologies for the RFB system and evaluate the performance, maintainability, and other features. Control techniques include control for suppressing short-term or long-term fluctuations, hybrid control that combines both control, and an operation to absorb an oversupply power.

![Photo 1. The 15 MW × 4 h RFB system](image)

An example of control test results to suppress short-term fluctuations is shown in Fig. 2. The effectiveness of reducing the frequency deviation was confirmed. After the three-year demonstration test was completed, practical operation of this system was commenced. It has been operated almost continuously to date. Figure 3 shows the trends in performance change. There has been no significant change in battery discharge capacity or system efficiency. We assume that the results are additional evidence of the 20-year durability of the system (design service life).

![Fig. 2. Demonstration test results of the governor-free equivalent control function with the 15 MW × 4 h RFB system](image)

(2) An RFB system operated in California \([2 \text{ MW} \times 4 \text{ h}]\)

In California, photovoltaic (PV) power generation has been increasingly introduced. The load drops in the daytime as power generation is sufficient, and this power load curve is called a duck curve due to its shape. There are three issues from the viewpoint of system operation: (a) rapid demand fluctuations for a few hours in the morning and evening, (b) shift in oversupply power in the daytime to the peak period at night, and (c) measures to ensure the short-term quality of electric power on the power distribution grid (voltage regulation).

This NEDO project aims to demonstrate the operation of multipurpose and composite applications, including: operations in the power distribution system, trading in the wholesale power market in the power transmission system, and evaluation of economic efficiency. Operation started in March 2017. Figure 4 shows the appearance of the system, and Fig. 5 shows a conceptual diagram of the demonstration operation.

![Fig. 3. Performance change of the 15 MW × 4 h RFB for 3 years](image)

In the first stage (from March 2017), the basic characteristics and reliability of the RFB system were evaluated based on composite operation modes, including voltage regulation and oversupply power adaptation in the power distribution grid. In the second stage (from December 2018), electric power trading started in the wholesale power market operated by the California Independent System Operator (CAISO). The most profitable operation
techniques in specific hours and seasons will be verified by flexibly combining multiple trading schemes in the ancillary service market (e.g., frequency regulation) and energy trading market.

5. Recent Development Trends

An RFB system consists mainly of electrolytes, cell stacks, and circulation systems. This section introduces the development trends of electrolytes and cell stacks.

5-1 Electrolytes (redox couples)

The electrolytes should be characterized by a high electromotive force and solubility. They should also be safe and inexpensive. For aqueous solution systems, side reactions, such as generation of hydrogen and oxygen due to water electrolysis, should be minimal. For active materials, metal and organic compounds are considered as candidates. Aqueous solution and non-aqueous solution are considered as candidates for solvents.

In the 1970s, basic research on metal ions including Fe/Cr systems started at NASA and AIST. In Japan, three types of RFBs (Fe/Cr, Zn/Br, and Zn/Cl) were developed in the 1980s. Zn/Ce and Zn/Fe are two other examples of systems that use zinc for the negative electrode. Systems that use the same active materials for the positive and negative electrolytes include an Fe/Fe system. In the U.K., the Na/Br system called Regenesys was developed on the large scale as a unique RFB.

Currently, the V/V system is the mainstream in the world. The V/V RFB uses the same active materials for the positive and negative electrolytes. This offers advantages such as prevention of battery capacity decrease (due to mixing through the membrane). There are also few side reactions in V/V system.

Recently, research on redox couples that use organic compounds is particularly active. Papers released by a group led by Professor Aziz of Harvard University in 2014 in Nature and in 2015 in Science attracted much public attention. In the research, anthraquinones (organic compounds) were used in place of conventional metal ions as active materials for the negative electrolyte. The charge and discharge reactions are shown in Fig. 6. The redox reaction of anthraquinones is reversible and stable, and electron transfer is fast. According to the report, a safe electrolyte derived from plants can be manufactured at low cost. Examples of research in which quinones were applied have been also reported by other researchers in the U.S. (University of Southern California), Spain, and other countries.

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There have been other examples in which TEMPO and methyl viologen (both are organic compounds) were used as active materials as in the case of quinones. They were reported as aqueous system RFBs using organic compounds for both the positive and negative electrolytes. This RFB uses sodium chloride (which is neutral) as an electrolyte, and are reported to be highly safe.

A study has been conducted to disperse active materials in the form of organic polymer particles instead of dissolving such materials in an electrolyte. If polymer particles of high molecular weight can be dispersed in high density, the energy density may be increased at low viscosity. This would also suppress mixing of active materials for the positive and negative electrolyte through the membrane, and an inexpensive porous membrane could be applied. In a different report, a composite of activated carbon and quinones was used instead of polymer particles.

In recent trends, these reports about organic redox systems have aroused the interest of researchers in fields other than conventional batteries. Organic redox systems offer high
flexibility in terms of molecular design, such as potential control by selecting and introducing functional groups. They have a future potential for significant development.

5-2 Cell stacks

With an electrolyte selected, efficient reactions should be achieved by cell stacks. As shown in Fig. 7, the general structure consists of electrodes, ion exchange membranes, and bipolar plates. These flat plate components are laminated. To design the cell stack structure, the materials for electrodes and ion exchange membranes are developed by taking into account the characteristics of the electrolyte such as density, viscosity, reactivity, and other features. To reduce the cost, it is important to achieve high power output. The internal resistance should be lower, and the pressure loss when circulate the electrolytes should be smaller.

In general, carbon materials are used as electrode materials. They are used in various forms and structures depending on the characteristics of electrolyte. The surface is usually modified in some way to increase reactivity. A membrane requires functionality to allow the charge carrier to penetrate while isolating active materials of positive and negative electrolytes. In general, an ion exchange membrane that has ion selectivity is used. When different active materials are applied for the positive and negative electrolytes, crossover of active materials through a membrane becomes an issue, thus premixed electrolyte composition for positive and negative electrolytes has also been developed.

In addition to the development of these materials, the design of channels to efficiently supply electrolytes to electrodes also plays a key role. Various structures have been proposed for channels depending on the characteristics of the electrolytes (see Fig. 8). For electrolytes whose reactivity is low (e.g., Fe/Cr RFB), a flow-through method for forcibly sending the solution into electrodes is effective. For highly active materials (e.g., Br, Cl), a flow-by method is also used to feed the solution with low pressure loss by taking full advantage of diffusivity.

Recently, new cell structures have been proposed, including a structure in which highly active thin electrodes are applied by providing a channel on the bipolar plate using fuel cell technology to supply electrolyte with low pressure loss. The output of cell stacks has been shown to increase further.

6. Further Developments

Based on the new development trends discussed above, Sumitomo Electric has been working on improvement and development focused on cost reduction. The basic policy is to achieve high output of the cells, apply inexpensive electrolytes, and simplify and downsize the systems.

6-1 Downsizing of the systems

Regarding cell stacks, we have been working to improve the electrode materials and ion exchange membrane materials and to develop cell structures that reduce the pressure loss during electrolyte circulation. Thus, the internal resistance has been reduced and the high power output has been achieved.

RFBs are characterized by high flexibility in system design. The layout can be changed flexibly depending on the application and installation location. Recently, a commonly used design is to store all the equipment in a container, reduce the transport cost, and simplify the on-site construction, as in the case of other energy storage batteries.

Photo 2 shows an example of a container-type 250 kW × 3 h system that we developed. High power output cells were applied, circulation equipment was downsized, and components were integrated and stored in the container.
6-2 Development of new electrolytes

Regarding electrolytes, active materials derived from more inexpensive materials should be applied. We have developed a Ti/Mn electrolyte by applying titanium (Ti) to the negative electrode and manganese (Mn) to the positive electrode. The basic battery reaction is as shown in the equation below. The electromotive force is about 1.4 V, which is equivalent to that of a V RFB.

\[
\begin{align*}
\text{[Positive electrode]} & : \text{Mn}^{2+} \rightleftharpoons \text{Mn}^{3+} + e^- \\
\text{[Negative electrode]} & : \text{TiO}^{2+} + 2\text{H}^+ + e^- \rightleftharpoons \text{Ti}^{3+} + \text{H}_2\text{O}
\end{align*}
\]

Regarding the development issue, some of the Mn (trivalent) ions change to solid particles of manganese dioxide (MnO₂) in the positive electrolyte during charging (disproportionation reaction* shown in the equation below), and the particles aggregate with each other, causing the battery performance to decrease. MnO₂ is an active material for batteries, and it is widely used for dry batteries. When MnO₂ is used in an RFB, it must be dispersed in an electrolyte to flow. MnO₂ is a solid, and it is also necessary to improve reactivity.

\[
2\text{Mn}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Mn}^{2+} + \text{MnO}_2 + 4\text{H}^+
\]

As an improvement measure, it was found that the disproportionation reaction can be suppressed to some extent by mixing Ti ions into the Mn ions of the positive electrolyte. Photo 3 shows the form of MnO₂ particles in electrolytes. It was found that the particle size decreased when Ti ions were mixed.

![Photo 3. Form of MnO₂ particles in electrolytes (a, b) with Ti, (c, d) without Ti](image)

(1) Evaluation tests on small RFBs with a Ti/Mn electrolyte

The basic characteristics of an electrolyte (TiOSO₄: 1.5 M, MnSO₄: 1 M, H₂SO₄: 3 M) were measured for a small cell with an electrode area of 9 cm². An energy density (23.5 kWh/m³) equivalent to that of a V/V RFB was confirmed under the condition of current density of 50 mA/cm² and flow rate of 0.6 cc/min./cm². The functionality of MnO₂ as an active material was also confirmed in an RFB.

Charge and discharge cycle tests were also conducted on two cell stacks with an electrode area of 500 cm². Under the same test conditions, stable performance was confirmed after 40 cycles or more.

(2) Evaluation tests on a practical size cell stack with a Ti/Mn electrolyte

While making improvements, including to the electrode materials, a prototype test was conducted on a 10 kW-class cell stack that consists of 30 cells with an electrode area of 1,800 cm². An example of the test results is shown in Fig. 9; long-term stable operation (140 cycles or more) was confirmed.

![Fig. 9. Example of the test results on a 10 kW-class cell stack with Ti/Mn electrolyte](image)

7. Future Prospects

The power generation cost of renewable energy has been decreasing year after year; renewable energy is expected to be increasingly introduced. In these electric power systems, the need for energy storage batteries is expected to increase further to regulate short-term and long-period output fluctuations. The applications have been diverse, including installation at electric power companies on a large scale, installation at the sites of power generation operators, and installation at the locations of general customers (independent or shared). New trial tests also have been conducted to achieve integrated control of these energy storage batteries.

In terms of performance, the technology of RFBs has already reached a level for commercial operation in electric power systems. RFBs can offer high design flexibility in principle, and they are expected to offer flexible solutions for various needs in the future. R&D has been actively promoted from various aspects around the world. I expect that these development efforts will further improve the performance and reduce the cost of RFBs and lead to widespread use of RFBs in various applications.
8. Acknowledgements

A part of this research was funded by the Ministry of Economy, Trade and Industry (METI). The results of the large scale demonstration projects described in Chapters 4(1) and 4(2) of this article are based on the results of the project of METI, and the project of the New Energy and Industrial Technology Development Organization (NEDO), respectively.

Technical Terms

*1 Redox reaction: Reaction in which electrons are transferred between ions or compounds in a chemical reaction (as used in this paper).

*2 Active material: A substance that reacts chemically (electrode reaction) at the positive electrode and the negative electrode in a battery.

*3 Disproportionation reaction: Chemical reaction in which two molecules or more of the same substance react to generate two or more different types of substances.

References

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