

Titanium-Manganese Electrolyte for Redox Flow Battery

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Large-scale batteries play an important role in the effective use of renewable energy like wind and solar power. Among various battery technologies, redox flow batteries (RFBs) offer high-speed response, independent design of power and energy, high safety, and thus have attracted more attention than ever. All-vanadium RFBs are the most mature technology and have been used in practical applications. As the prices of renewable energy power generation continue to decline, cost reduction of the battery system has become the major issue. In order to reduce the cost, many efforts have been made to develop a low cost electrolyte. We focused on a low cost manganese material, and developed a Ti (IV) and Mn (II) mixed aqueous electrolyte, and applied it to a Ti-Mn RFB. This paper briefly introduces development of electrolyte research and the characteristics of the Ti-Mn electrolyte.

Keywords: renewable energy, large-scale battery, redox flow battery, manganese, titanium

1. Introduction

With the aim of realizing a low-carbon society, the use of renewable energy sources including wind and solar has been growing rapidly around the world. However, the mass introduction of such power sources with outputs fluctuating depending on weather conditions requires grid stabilization measures. The use of large-scale batteries is one solution.⁽¹⁾ As shown in Fig. 1, a redox flow battery consists of a cell stack for converting electric energy to chemical energy and vice versa, pipe, pumps and tanks of electrolyte for accumulating chemical energy. This battery has some features such as easy upsizing because of the independent design of power and energy, fast response, a long cycle life, safety (non-combustible), and being able to always precisely monitor and control the charge state of the battery. Redox flow batteries are expected to serve as large-scale batteries for power grids.⁽²⁾ However, since the energy density is about one tenth of other types including lithium-ion batteries, they are not suitable for small mobile equipment such as electric vehicles.

Since 1985, we have been refining this redox flow battery technology through many demonstration experi-

ments.⁽³⁾ Now, our immediate task is to reduce costs before full-scale implementation. In Japan, aiming at the realization of stationary large-scale batteries, a goal has been set to reduce the battery cost to a level similar to pumped-storage hydroelectricity by 2020.⁽⁴⁾ In the United States, under the leadership of the Department of Energy, the Joint Center for Energy Storage Research (JCESR) co-established by industry, academia, and the government in 2012, has been conducting research and development on the next-generation low-cost and high-performance batteries including redox flow batteries.⁽⁵⁾ Against this backdrop, we are working on improving the performance and reducing the cost of the entire system including electrolyte, which is one of the key components of a battery, as well as the cell stack and the circulation system. For the electrolyte, we focused attention on a low-cost manganese material, for which the application to flow batteries had been abandoned because of the precipitation of manganese dioxide in principle, and conducted development with the intention of applying this material to redox flow batteries. This paper describes the trend of electrolyte research for redox flow batteries and the characteristics of the titanium-manganese electrolyte.

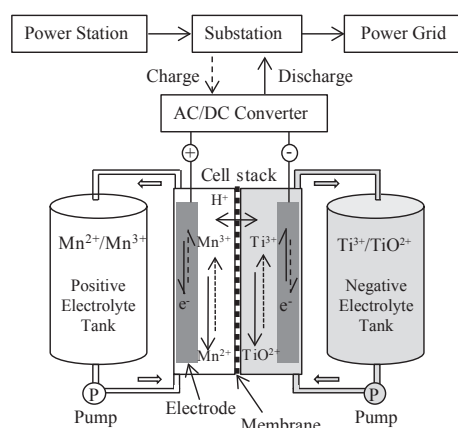


Fig. 1. Principle and configuration of a redox flow battery

2. Electrolyte for Redox Flow Batteries

An electrolyte is a solution of an ionic active material, which causes oxidation-reduction reaction, in an electrically conductive solvent. When the positive and negative electrodes are made of ionic active materials with different oxidation-reduction potentials, a voltage, or an electromotive force is generated between the two electrodes. A variety of combinations of ions are available in principle. However, many requirements must be satisfied by an electrolyte in terms of availability, performance, reliability and safety. (1) Availability: The raw materials must be inexpensive and supplied stably; (2) Performance: The electrolyte must generate a high electromotive force and contain a high concentration of active materials; (3) Reliability: The electrolyte must be chemically stable, non-toxic, and eco-

friendly; and (4) Safety: The electrolyte must be noncombustible. In actual applications, the active materials at the positive and negative electrodes pass through a membrane and are mixed with each other, which results in another problem, the reduction in battery capacity.

Since the publication of the principle of redox flow batteries in the 1970s, research and development has been conducted actively around the world. All-vanadium redox flow batteries have already been commercialized as a representative of redox flow batteries. However, to respond to the worldwide demand, it is necessary to develop an electrolyte that can be produced and supplied stably at lower cost and battery systems with higher electromotive force. In recent years, efforts have been made to develop redox flow batteries that use organic materials, instead of metal ion active materials.^{(6),(7)} Figure 2 is a summary of electrolyte organized by solvent and active material. Aqueous electrolyte based on inorganic solvents, such as sulfuric acid and hydrochloric acid, has advantages including high conductivity and high reactivity of active materials. However, since they involve electrolysis of water, electromotive force is approximately 1.5 V or lower. In contrast, non-aqueous electrolytes with organic solvents are free from electrolysis and high electromotive force can be obtained. However, they have a disadvantage of high internal resistances due to the low conductivity of the organic solvents.

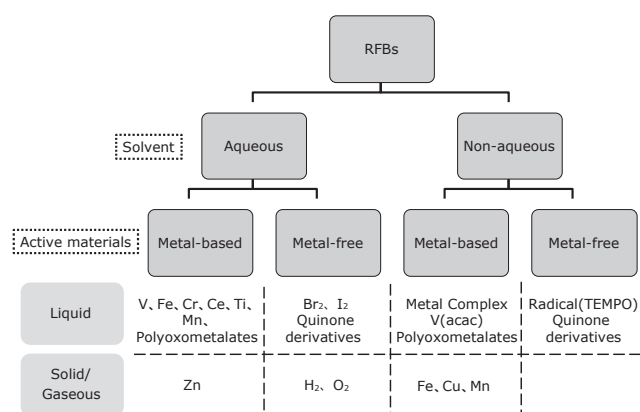


Fig. 2. Classification of electrolytes and typical active materials

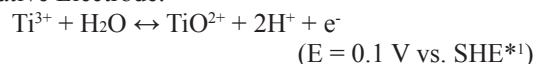
3. Titanium-Manganese Electrolyte

3-1 Operation principle and issues of titanium-manganese redox systems

A titanium-manganese electrolyte is a promising low-cost candidate. Both titanium and manganese are inexpensive materials and exist abundantly as natural resources. As the following equations of the cell reaction indicate, the electromotive force is 1.41 V in a sulfuric acid solution, which is high among aqueous electrolytes. However, since the Mn³⁺ ion is chemically unstable in an aqueous solution, the precipitation of manganese dioxides (MnO₂) occurs in principle due to the disproportionation reaction during charging. If the manganese dioxides settle in the tank, the battery capacity can be reduced and clogging of the cell

stack can take place. When applying this material to redox flow batteries, some measures must be taken to stabilize the Mn³⁺ ion and suppress MnO₂ precipitation.

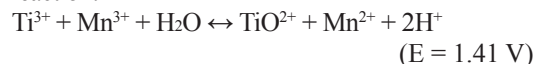
Negative Electrode:



Positive Electrode:



Cell Reaction:



Disproportionation Reaction:



The disproportionation reaction equation indicates that the Mn³⁺ ion can be stabilized by increasing acidity and raising the concentration of Mn²⁺ ions. There are some methods for forming metal complexes by changing the coordinate structure of the Mn³⁺ ions. However, even with these methods, it is basically difficult to stabilize Mn³⁺ ions at high concentration, and therefore the energy density of the battery is limited. In addition, the stabilization of the Mn³⁺ ions by forming strong metal complexes can lead to the loss of electrochemical activity. We discovered that the precipitation of MnO₂ can be suppressed by applying a Ti-Mn electrolyte. We examined the precipitation of MnO₂ and evaluated the cell performance of the Ti-Mn electrolyte.^{(8),(9)}

3-2 Basic characteristics of a Ti-Mn electrolyte

Table 1 shows the concentrations of the electrolytes used in this research. The Mn and Ti electrolytes were prepared by dissolving 1M (mol/dm³) of MnSO₄ and TiOSO₄ in 3M of sulfuric acid solution. The Ti+Mn and 1.5Ti+Mn electrolytes were prepared by dissolving 1M and 1.5M of TiOSO₄ in the Mn electrolyte respectively.

Table 1. Concentrations of electrolytes

Electrolyte	TiOSO ₄ [mol/dm ³]	MnSO ₄ [mol/dm ³]	H ₂ SO ₄ [mol/dm ³]
Ti	1	0	3
Mn	0	1	3
Ti+Mn	1	1	3
1.5Ti+Mn	1.5	1	3

(1) Electrochemical characteristics

First of all, to investigate the electrochemical reactivity of the Ti and Mn ions, we conducted electrochemical measurement using a small flow cell with an electrode area of 0.785 cm². We used a carbon felt material for both the working electrode and counter electrode, and kept the electrolyte at the working electrode still and the electrolyte at the counter electrode flowed during the measurement. The voltammetry curve*² of the oxidation-reduction reaction corresponding to the entire active material (Mn) at the positive electrode is shown in Fig. 3 (a). The Mn electrolyte indicated a single oxidation peak and two reduction peaks at 1.3 V and 0.97 V. It is assumed that these peaks

originated from the reduction reactions of $\text{Mn}^{3+}/\text{Mn}^{2+}$ and $\text{MnO}_2/\text{Mn}^{2+}$. In the case of the Ti+Mn electrolyte, the oxidation peak shrinks, which means the oxidation reaction of Mn is suppressed. The reduction peak of $\text{MnO}_2/\text{Mn}^{2+}$ is shifted from 0.97 V to 1.1 V, indicating that the reduction reaction rate of $\text{MnO}_2/\text{Mn}^{2+}$ is increased. Based on the total electric charge of the oxidation-reduction reaction, we found that the number of reactive electrons of Mn is 1.5 or more. The voltammetry curve of the negative electrode (Ti) is indicated in Fig. 3 (b). The oxidation peak of $\text{Ti}^{3+}/\text{TiO}^{2+}$ was shifted a little from -9 mV to -35 mV, but there seems to be almost no effects of the mixing of Mn^{2+} ions.

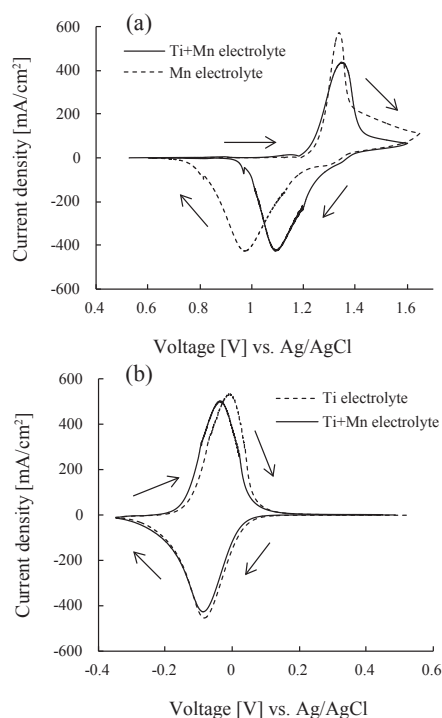


Fig. 3. Voltammetric measurements for (a) positive and (b) negative half-cell

Figure 4 is the result of the investigation of the relationship between the state of charge (SOC) and electrolyte potential. Here, each Mn ion at the positive electrode can go through reactions equivalent to those with 1.5 or more electrons. The SOC of Mn was calculated from the charged electrical quantities based on a one-electron reaction for each Mn ion. Generally, the electrolyte potential at the positive electrode rises with the increase in the SOC. However, in this Ti-Mn system, it started to decrease in the middle. The reason for the drop in the electrolyte potential may be the reduction in the concentration of Mn^{3+} ions due to the precipitation of MnO_2 . The potential of the Mn electrolyte peaked near an SOC of 40%. In the case of the Ti+Mn electrolyte, the electrolyte potential continued to rise up to an SOC of 90%. These results suggest that the coexisting Ti suppressed the disproportionation reaction of the Mn^{3+} ions. In the low SOC area, the Ti+Mn electrolyte has low potential. This phenomenon suggests the formation of some kind of complex of the Ti and Mn ions. In the high

SOC area with an SOC of 100% or higher, the Mn electrolyte was not able to be charged due to a high overpotential. In the case of the Ti+Mn electrolyte, it was possible to continue charging up to an SOC of 150%.

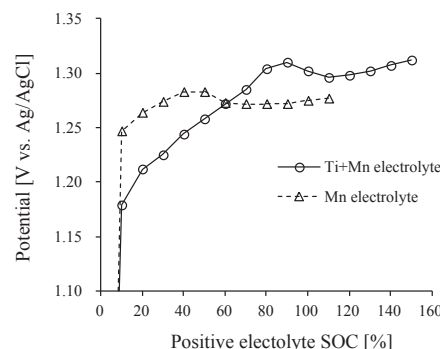


Fig. 4. Relationship between the positive electrolyte potential and SOC

(2) Morphology of MnO_2

The precipitation of MnO_2 was observed using an FE-SEM.*3 Figure 5 are the FE-SEM images of the MnO_2 derived from an electrolyte with an SOC of 90% by allowing it stand at 35°C for two weeks. It was found that with the existence of Ti in the Mn electrolyte, the MnO_2 changed from cactus-shaped clusters with sizes around 2,000 nm to fine particles of 5 nm. It is considered that the morphology change of the MnO_2 particle enabled charging up to 150%.

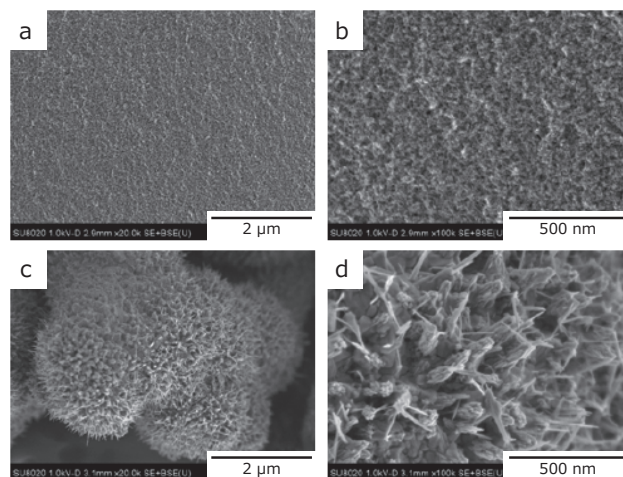


Fig. 5. FE-SEM images of MnO_2 precipitates derived from (a,b) Ti+Mn electrolyte and (c,d) Mn electrolyte

(3) Battery characteristics

With the aim of utilizing the 1.5-electron reaction of Mn, we conducted constant-current charge/discharge test

with a current density of 50 mA/cm² using the 1.5Ti+Mn electrolyte in a flow cell with an electrode area of 9 cm². As Fig. 6 illustrates, a high energy density of 23.5 kWh/m³ was achieved. This is equivalent to a number of reactive electrons of 1.35 per each Mn ion. The coulombic efficiency,*⁴ voltage efficiency,*⁵ and energy efficiency*⁶ were 99.5%, 89.2%, and 88.7% respectively.

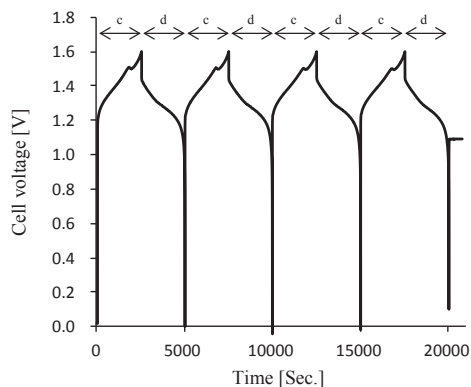


Fig. 6. Charge/discharge test: (c) charge; (d) discharge

We discovered that with the existence of Ti (TiO²⁺), MnO₂ particles become so small that they can be dispersed in the electrolyte, and they can be used for a flow battery. On the other hand, the current density was not sufficiently high for practical use. It is necessary to improve the battery performance by reducing the cell resistances. In addition, carbon corrosion was observed on the positive electrode, which made it clear that the durability of the electrode needs to be enhanced.

4. Improving Battery Performance

4-1 Resistance components

The keys to improving the performance of a redox flow battery are to improve the supply of active materials and reactivity. The internal resistance of a battery can be separated into Ohmic resistance, charge transfer resistance, and mass transport resistance components by using the electrochemical impedance method. An electrode made of a porous material such as felt has paths for supplying active materials. Since it is also a site in which battery reactions take place, it has substantial effects on the charge transfer and mass transport resistance components. Carbon is an ideal electrode material from the viewpoints of chemical stability, electrical conductivity, surface area, and cost. However, since the carbon surface has low electrochemical activity, it is important to improve the electrochemical properties by modifying the surface through thermal, chemical, or electrochemical treatment.

4-2 Surface treatment of electrodes

In this research, commercially available high-temperature oxidation resistant carbon paper was selected as the means for improving the durability of the positive elec-

trode. For surface treatment, the electrodes were heat-treated in air at 700°C for 0.5 to 2 hours. To evaluate battery performance, the Ti+Mn electrolyte was used and electrochemical impedance was measured using a symmetrical cell with an electrode area of 3 cm² to separate the resistances of the positive and negative electrodes.

Figure 7 (a) shows the impedance spectra of a battery using a positive electrolyte with an SOC of 50%. Two arcs were observed on all samples. The larger high-frequency arc and the smaller low-frequency arc were attributed to charge transfer and mass transport process, respectively. With the heat-treated electrode, the high-frequency arc was significantly shrunken and the rate of the oxidation-reduction reaction of Mn³⁺/Mn²⁺ on the surface of the electrode increased considerably. Since extending the time of heat-treatment had limited effects on the reduction of charge transfer resistance, the improvement in the wettability of the carbon surface was more likely to be helpful in enhancing kinetics of the electrode than the increase in the surface area. The impedance spectra of a battery using a negative electrolyte with an SOC of 50% are indicated in Fig. 7 (b). Similar to the positive electrode, the rate of oxidation-reduction reaction of the Ti³⁺/TiO²⁺ at the negative electrode is greatly enhanced by heat-treatment. However, the charge transfer resistance of the negative electrode was twice as high as that of the positive electrode. It is assumed that the insufficiency of electrochemically active surface area was the cause of high charge transfer resistance.

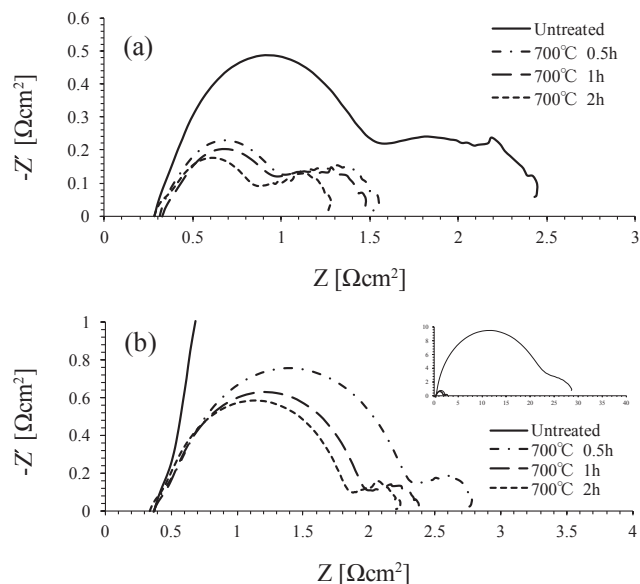


Fig. 7. The impedance spectra: (a) positive electrode; (b) negative electrode

4-3 Current-voltage and output characteristics

We examined the relationship between the cell voltage and current density during discharging, using carbon paper electrodes heat-treated for two hours in air at 700°C for both positive and negative electrodes. The result is shown

in Fig. 8. The polarization curve indicates a voltage loss due to charge transfer and mass transport, with the Ohmic resistance removed. The cell voltage dropped abruptly in the high current density area, which was because of the rapid increase in mass transport resistance. In addition, raising SOC significantly increased voltage loss. It is suggested that under high SOC, the precipitation of MnO_2 at the positive electrode reduced the concentration of Mn^{3+} ions, which are active materials, and disturbed the reactant transport. As Fig. 9 illustrates, the battery output reached a peak of 357 mW/cm^2 at an SOC of 50%.

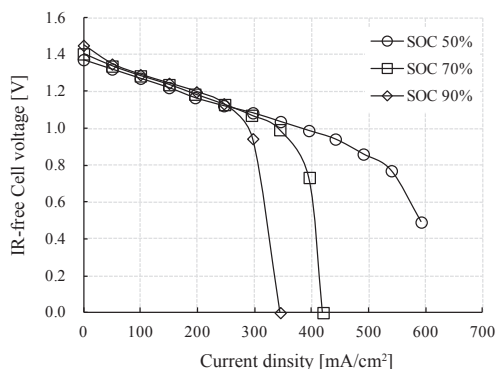


Fig. 8. Polarization curves with varying SOC

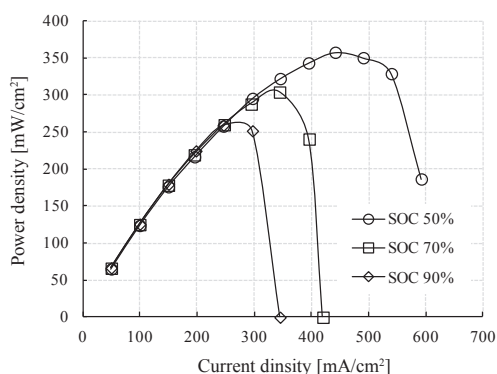


Fig. 9. Power density curves with varying SOC

Next, we investigated the relationship between battery output and current density using carbon felt with a capacitance 50 times larger than that of carbon paper, which is supposed to have a larger electrochemically active surface area. The result is indicated in Fig. 10. The maximum output of the battery increased to 478 mW/cm^2 at an SOC of 50%. This demonstrated the improvement of battery performance by increasing the surface area of the negative electrode. When carbon felt with the same capacitance was used for the positive electrode as well, the maximum output of the battery rose to 640 mW/cm^2 . However, because of significant oxidation and corrosion of the electrode, stable performance could not be obtained. The result suggested the possibility of further enhancement of battery perfor-

mance by developing a positive electrode that is highly resistant to oxidation with a large surface area.

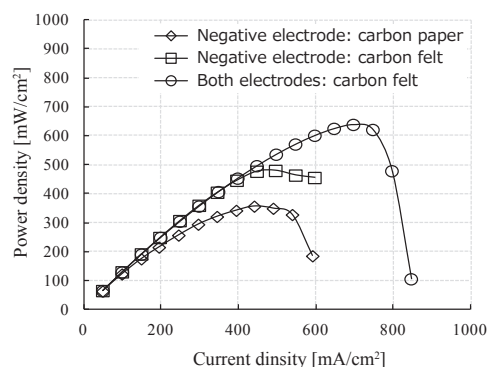


Fig. 10. Power density curves with varying electrodes

4-4 Result of testing small batteries

Table 2 lists the result of a constant-current charge/discharge test using negative electrodes made of carbon paper and high-capacitance carbon felt. Using a negative electrode with high capacitance led to improving voltage efficiency and energy efficiency. For battery performance, high energy efficiency of 83.2% under a current density of 100 mA/cm^2 was obtained.

Table 2. Single cell charge/discharge test result

Positive electrode	Negative electrode	Current density [mA cm^{-2}]	Coulombic efficiency [%]	Voltage efficiency [%]	Energy efficiency [%]
Carbon paper	Carbon paper	100	99.6	73.8	73.5
		200	99.7	52.8	52.6
	Carbon felt	100	99.8	83.4	83.2
		200	99.0	76.8	76.0

5. Conclusion

This research focused on an inexpensive manganese material as the electrolyte for a redox flow battery. It was discovered that the principle issue of the precipitation of solid MnO_2 due to a disproportionation reaction could be alleviated by mixing Ti with the Mn electrolyte to stabilize Mn^{3+} ions and suppressing the particles growth of MnO_2 . In the evaluation of a small flow cell using this Ti-Mn electrolyte, energy density as high as 23.5 kWh/m^3 could be achieved, which is expected to significantly reduce the cost of the electrolyte. We also found that the electrochemical reactivity was considerably improved by enhancing the surface wettability of the carbon electrodes and increasing the surface areas. With the aim of further improving the performance of a Ti-Mn redox flow battery, we will continue research and development for reducing the resistance and enhancing the durability of the positive electrode.

6. Acknowledgements

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Technical Terms

- *1 SHE: Abbreviation for standard hydrogen electrode.
- *2 Voltammetry curve: A voltage-current curve obtained by changing the electric potential applied to the electrodes, and measuring the response current.
- *3 FE-SEM: Abbreviation for field emission-scanning electron microscope.
- *4 Coulombic efficiency: The percentage of electrical quantity (Ah) used for battery reaction to the quantity used for charging and discharging.
- *5 Voltage efficiency: The percentage of voltage (V) loss due to an overpotential in the current used for charging and discharging.
- *6 Energy efficiency: The percentage of the loss of energy (Wh) to the total energy calculated by multiplying the coulombic efficiency and voltage efficiency.

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