Development of Vanadium Ion Redox Capacitor

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ABSTRACT

The purpose of this study was to add the redox capacitance obtained by adding vanadium ions used in the vanadium redox flow battery to the electric double layer capacitor. CV measurement confirmed a square response characteristic of the electric double layer and a redox peak of vanadium. In EIS measurement, the characteristics as a capacitor when vanadium was added were investigated. The performance as a power storage device was measured during constant current charging and discharging, and it was found that a maximum improvement of 39% in discharge energy density was found compared to blank. However, it was confirmed that the redox capacitance addition in discharging was smaller in CV and CDC than that in charging. This irreversibility was attributed to the activated carbon fiber electrode. For comparison, ACF and CF with different internal and surface structures were compared to clarify the mechanism.

Keywords : Electric Double Layer Capacitor, Vanadium Redox Flow Battery, High Energy Density

1. Introduction

Electric double layer capacitors (EDLC) are a type of electrochemical capacitors that can be charged and discharged quickly and have high reliability. The principle is to accumulate cations and anions in the electrolyte solution in a non-Faraday process in the electric double layer formed at the interface between the positive and negative electrodes made of a material with a large specific surface area and the electrolyte solution. For this reason, when compared to secondary batteries, they had superior cycle characteristics and power density. However, the energy density of EDLC was limited by the area of the electrode-electrolyte interface, and was considerably inferior to that of secondary batteries. There are two main ways to increase the energy density of EDLCs. The first is high capacity, which is the development of new materials with large-surfaces that are structurally regulated at the nano level or add pseudo capacity. The second is to increase the operating voltage. We have been aiming for the former to increase the energy density, especially to improve it by adding redox capacitance. We have already reported the redox behavior of copper picolinate complex or hydroquinone absorbed on activated carbon already reported the redox behavior of copper picolinate complex or hydroquinone absorbed on activated carbon surface.3-5 This time, we adopted a method to obtain soluble ions from the electrolyte as redox capacitance-adding substances. This method was proposed by Sang-Eun Chun et al.6 By using heptyl viologen, high energy density is achieved while maintaining high power density and long life. This time, we adopted vanadium, which is also used in redox flow batteries, as a redox capacitance additive substance, and the redox reaction of vanadium is as follows.

\[
\begin{align*}
\text{VO}_2^+ + 2H^+ + e^- & \rightarrow \text{VO}^{2+} + H_2O \\
E^* & = 0.759 \text{ V vs. SCE, 25°C} \\
\text{VO}^{2+} + 2H^+ + e^- & \rightarrow V^{3+} + H_2O \\
E^* & = 0.096 \text{ V vs. SCE, 25°C} \\
V^{3+} + e^- & \rightarrow V^{2+} \\
E^* & = -0.499 \text{ V vs. SCE, 25°C}
\end{align*}
\]

By including this oxidation-reduction potential in the operating voltage, we tried to achieve high energy density by adding redox capacitance. In this paper, the reaction morphology was analyzed by comparing electrodes with different internal and surface structures with and without the addition of redox capacitance in a batch cell.

2. Experimental

2.1 Set up of a cell

A batch cell was used as the electrochemical cell. Figure 1 shows the drawing. Glass fiber (ADVANTEC, GB-100R) as separator, activated carbon fiber (ACF) and carbon felt (CF) as electrode, glassy carbon as collector (Nilaco, GC-20SS, 45.2 \times 10^{-4} \Omega \text{ cm}), an acrylic plate for fixing, screws and screws were used. ACF used was CH900-20 (kuraray), BW163E (toyobo), and BW554 (toyobo), and CF was one of AAF304ZS (toyobo). The glassy carbon was

![Figure 1. How to set up of a batch cell.](image-url)
insulated with masking tape to prevent contact with the electrolyte except for the places where it touched electrode and where the wires were connected. The mass of the activated carbon fiber was measured after cutting the required amount, and the mass obtained from electrode on the working electrode side was used for the subsequent calculation results. The electrode and glassy carbon were sandwiched between the separator and the center, and fixed with an acrylic plate so as not to move.

2.2 Electrode characterization
The specific surface area and pore distribution of the electrode greatly affect the capacitance of the device. Therefore, a nitrogen adsorption/desorption test at 77 K was performed using a specific surface area pore distribution measurement device Nova1200 to determine the specific surface area and pore distribution of the electrode. It was evacuated at 200°C as pretreatment. The specific surface area was analyzed by BET (Brunauer-Emmett-Teller) method, and the pore distribution was analyzed by BJH (Barrett-Joyner-Halenda) method and DFT (Density functional theory) method.

Activated carbon surface chemistry is dominated by amphoteric properties and essentially depends on heteroatom content, mainly surface functional groups, to determine surface charge, hydrophobicity, and electron density of graphene layers. There are many reports on the effect of surface functional groups on electric double layer capacitors and on the redox reaction of vanadium.7,8 Therefore, the C1s and O1s atom contents of the electrodes were measured by using X-ray photoelectron spectroscopy. The XPS measurement was performed using an X-ray photoelectron spectrometer (ULVAC-PHI PHI 5000 VersaProbe II). The atomic content was determined by measuring the wide spectrum and the narrow spectrum (C1s, O1s) using AlKa as a sample, and the binding energy was calibrated to the C1s peak at 284.6 eV.

2.3 Electrochemical measurement
The electrochemical measurement system HZ7000 (Hokuto Denko) was used for the measurement. 4.0 M H2SO4 as a blank and 0.3 M VOSO4 + 4.0 M H2SO4 as a vanadium-added solution were used as the electrolyte solution. And degassed with nitrogen for 30 minutes to remove dissolved oxygen. Before making the cell, it was immersed in electrode overnight in electrolyte. A saturated calomel electrode (SCE) was used as a reference electrode, and the electrode was inserted on the working electrode side in the electrolytic solution. The CV measurement was performed to observe the redox capacitance addition. The measurement was performed by controlling the potential of the SCE. When the working electrode was defined as the positive electrode, 0.1 to 0.9 V vs. SCE, the negative electrode was used as the measurement condition for the CV measurement. When defined, the voltage range was −0.7 to 0.1 V vs. SCE, and the scanning speed was 1 mV/s. The constant current charge/discharge measurement (CDC) was performed to evaluate the performance of the batch cell in a vanadium-added electrolyte as a power storage device. The charge and discharge voltage range was measured from 0 to 1.6 V. The electrochemical impedance measurement (EIS) was used to evaluate the capacitor characteristics of the batch cell in the electrolyte containing vanadium, and the electrochemical measurement system HZ7000 was connected to a potentialiogalvanostat and optionally a frequency response analyzer. Therefore, there is no need for external connections required for EIS measurement other than PC. The bias voltage of the AC voltage was a natural potential, and an AC voltage with an amplitude of 5 mV was superimposed from 1 mHz to 10 kHz. From the impedance value and the phase difference between AC current and AC voltage, the Nyquist diagram and the capacitance components of the real and imaginary components were obtained and analyzed.

| Table 1. Information of each electrode. |
| Electrode | Activated Carbon Fiber | Carbon Felt |
|-----------|------------------------|-----------|
| Thickness (nm) | 0.7 | 0.7 | 0.7 | 4.3 |
| Weight (g/m²) | 170 | 170 | 180 | 330 |
| Specific surface area (m²/g) | 2331.957 | 1650.140 | 1413.149 | 3.614 |
| Total volume (cc/g) | 1.126 | 0.707 | 0.680 | 0.154 |
| Mesopore volume (cc/g) | 0.156 | 0.122 | 0.091 | 0.086 |
| Micropore volume (cc/g) | 0.970 | 0.580 | 0.589 | 0.068 |

Figure 2. (a) Pore distribution of mesopores (2–50 nm) determined by BJH method (b) Pore distribution of micropores (>2 nm) determined by DFT method.

3. Results and Discussion
3.1 Electrode characterization
3.1.1 Specific surface area/pore distribution measurement
Table 1 summarizes the thickness, basis weight, and specific surface area determined by BET for each electrode. Table 1 and Fig. 2 summarize the results of the pore distribution of macropores obtained by BJH and the results of pore distribution of micropores obtained by DFT. CH900-20 showed the largest specific surface area, the BJH method showed a large peak at a pore diameter of 4.5 nm, and BW163E had a wide range of pores at 3 to 7 nm. The peak was found at around 4.5 nm, similar to that of CH900-10,
although it was a small value compared to that of CH900-10. Peaks were observed around 1.25, 1.5, and 1.75 nm. The peak sizes were CH900-20, BW163E, and BW554 in this order.

3.1.2 XPS

The XPS results are shown in Fig. 3. In the wide spectrum, a peak due to C1s was observed at 284.6 eV and a peak due to O1s was observed at 543.5 eV. The results regarding the atomic concentration and O/C ratio are shown in Table 2. BW163E showed the largest O/C value. Therefore, the amount of oxygen-containing functional groups is considered to be the largest for BW163E. The oxygen surface functional groups are considered to be ketone, phenol, carboxylic acid, etc.

3.2 Evaluation of EDLC with vanadium dissolved

3.2.1 Evaluation of redox capacitance addition in CV measurement

The presence or absence of redox capacitance addition by vanadium was observed by CV measurement, and the results of CV measurement are shown in Fig. 4. (a) The results when using 0.3 M VOSO4 + 4.0 M H2SO4 and (b) 4.0 M H2SO4 were used. On the positive electrode side, the potential sweep toward the anode was defined as charging, and the potential sweep toward the cathode was defined as discharging. On the other hand, on the negative electrode side, the potential sweep toward the anode was defined as discharge, and the potential sweep toward the cathode was defined as charge.

With respect to ACF, redox peaks centered on 0.759 V vs. SCE and 0.096 V vs. SCE on the positive electrode side and 0.499 V vs. SCE on the negative electrode side were confirmed by adding vanadium. These are considered to be V4+/V3+, V3+/V2+, and V2+/V1+, respectively.

At other potentials, a square-shaped current response is shown, similar to blank. This suggests that the electric double layer is maintained. The addition of vanadium increased the double-layer capacitance in the charging reaction. However, the discharge reduced the double-layer capacitance. From this, it was speculated that vanadium promoted the function of EDLC in charging, but could inhibit the function in discharging reaction. When comparing BW554 with CH900-20 and BW163E, BW554 showed a smaller peak of V3+/V4+. Originally, the reaction of V3+/V4+ is considered to be a slow reaction. The pore structures of CH900-20 and BW163E are considered to have some catalytic action on V3+/V4+. In CF, no square response characteristic of the electric double layer was observed. However, the peaks from V5+ to V4+ and the peaks from V2+ to V3+ related to the discharge, which were not often observed in ACF, were remarkably observed. This suggests that the electric double layer and the specific pore structure of the ACF hinder the redox reaction of the discharge in the ACF.

3.2.2 Evaluation of the effect of addition to vanadium in EIS measurement

The effect of vanadium on the electric double layer capacitor was investigated by electrochemical impedance measurement at the ACF. Figure 5 shows the Nyquist diagram. Because the electrode is porous, a transmission line model that does not include a Faraday reaction (Fig. 5b) was used for 4.0 M H2SO4, and a transmission line model that included a Faraday reaction (Fig. 5c) was used for 0.3 M VOSO4 + 4.0 M H2SO4. In both electrolytic solutions, a locus indicated by a distribution constant type circuit due to a current distribution due to a solution resistance in the pores and a dispersed resistance component in a high frequency range was drawn. However, when 0.3 M VOSO4 + 4.0 M H2SO4 was compared with 4.0 M H2SO4, the curve was slightly changed by adding vanadium. Since the impedance in the high frequency range is determined by the resistance in the pore (R pore) and the capacity (C), it is considered that the adsorption and desorption of vanadium and the oxidation-reduction affected the utilization of the porous electrode. The solution resistance (R sol) was improved by adding vanadium.

Table 2. Atomic concentration and O/C ratio determined by XPS.

|       | C [%] | O [%] | O/C |
|-------|-------|-------|-----|
| CH900-20 | 95.02 | 4.98  | 0.052 |
| BW163E  | 92.56 | 7.44  | 0.084 |
| BW554   | 94.08 | 5.92  | 0.063 |
| AAF304ZS| 93.13 | 6.87  | 0.074 |
This is thought to be due to the conductivity of vanadium. There is a difference in the position of Rsol depending on the electrode, which is considered to be a difference in ohmic resistance between the electrode and the collector. In the low-frequency region, 4.0 M H₂SO₄ exhibited a blocking electrode characteristic of a capacitor extending parallel to the imaginary axis. On the other hand, 0.3 M VOSO₄ + 4.0 M H₂SO₄ is considered to show a part of the capacitive semicircle. This was considered to be the charge transfer resistance due to the redox reaction of V³⁺/V⁴⁺ on the electrode surface. Comparing each ACF electrode, CH900-20 and BW163E showed remarkable changes due to vanadium addition. On the other hand, BW554 showed almost the same behavior as 4.0 M H₂SO₄ even when vanadium was added. In BW554, V³⁺/V⁴⁺ peaks were hardly observed in the results of CV measurement, and it is considered that the contribution of vanadium on the electrode surface and inside was small. Rct for 0.3 M VOSO₄ + 4.0 M H₂SO₄ was compared. Rct is determined from the diameter of the capacitive semicircle. It was 101 Ω for CH900-20, 65.6 Ω for BW163E, and 533 Ω for BW554. Rct is represented by the following equation, and is inversely proportional to the pore diameter and the pore depth.

\[
Rct = \frac{RC''}{XL}
\]

Rct [Ω]: charge transfer resistance over the entire area of the inner wall of the pore. Rct" [Ω·cm²]: charge transfer resistance per unit area, X [cm]: circumference of the pore, L [cm]: pore depth.

From the pore distribution, the difference between the electrodes in the pore diameter is not so clear. From this, it is considered that the influence of the element (pore structure) caused by the depth in the pore is large. EDLC profiled with vanadium was profiled by modeling the volume of frequency-related impedance data. The capacity real number component (C') and the capacity imaginary number component (C") were obtained from the following equations.

\[
Z(\omega) = \frac{1}{j\omega C(\omega)} \text{ in ohms} \tag{1}
\]
\[
C(\omega) = C'(\omega) - jC''(\omega) \text{ in farads} \tag{2}
\]
Manipulation of Eq. (1) and Eq. (2) leads to

\[
C'(\omega) = \frac{-Z''(\omega)}{\omega |Z(\omega)|^2} \tag{3}
\]
\[
C''(\omega) = \frac{Z'(\omega)}{\omega |Z(\omega)|^2} \tag{4}
\]

Where both C’ and C” have units of farads (F).

Figure 6 shows the real and imaginary components of the capacitance obtained from the electrochemical impedance measurement. C’ represents the real part of the capacitance and represents the change in available stored energy as a function of frequency. C” indicates the imaginary part of the capacitance, which corresponds...
Comparing the vanadium-added solution and the blank in the real component of capacitance, it can be seen that the redox capacitance can be added because the addition of vanadium in CH900-20 and BW163E significantly increases in the low-frequency region. However, since the imaginary capacitance component increases in the low frequency region, it can be seen that the energy loss has increased. This is thought to be due to the increase in ionic resistance in the pores caused by the addition of vanadium, as described above. In addition, the time constant was determined from the transition frequency of $C_B$ and compared. The transition frequency of 0.3 M VOSO$_4$ + 4.0 M H$_2$SO$_4$ in CH900-20 was 0.004 Hz, and that of 4.0 M H$_2$SO$_4$ was 0.02 Hz, and the time constants were 250 s and 50 s, respectively. The transition frequency of 0.3 M VOSO$_4$ + 4.0 M H$_2$SO$_4$ in BW163E was 0.0025 Hz, and that of 4.0 M H$_2$SO$_4$ was 0.012 Hz, and the time constants were 400 s and 83 s, respectively. This indicates that the addition of vanadium slowed the charge/discharge response. On the other hand, the transition frequency of 0.3 M VOSO$_4$ + 4.0 M H$_2$SO$_4$ in BW554 was 0.02 Hz or less, and that of 4.0 M H$_2$SO$_4$ was 0.016 Hz, and the time constants were 50 s and 62.5 s, respectively. This suggests that the $V^{3+}/V^{4+}$ reaction is a factor that slows the charge/discharge response.

3.2.3 Evaluation of redox capacity addition in CDC

A constant current charge/discharge measurement was performed for each ACF electrode, and the performance as a power storage device was observed, and the results are shown in Fig. 7. Regarding the charging and discharging time, negative time indicates charging and positive time indicates discharging. The energy density was improved by adding vanadium in each ACF electrode. Since the charge/discharge curves are gradual near the redox of $V^{4+}/V^{5+}$, $V^{3+}/V^{4+}$, and $V^{2+}/V^{3+}$, this is considered to be an improvement due to the addition of redox capacitance by vanadium. In CH900-20 and BW554, the IR drop of 0.3 M VOSO$_4$ + 4.0 M H$_2$SO$_4$ was smaller than that of 4.0 M H$_2$SO$_4$, and BW163E is slightly larger. The equivalent series resistance (ESR) was determined from the IR drop, which was calculated from the following equation.

$$ESR = \frac{IR_{drop}}{2I}$$

Where IR$_{drop}$ [V], I: current density [A/g]

For CH900-20, 0.3 M VOSO$_4$ + 4.0 M H$_2$SO$_4$ was 0.31 Ω/g, and 4.0 M H$_2$SO$_4$ was 0.36 Ω/g. In BW554, 0.3 M VOSO$_4$ + 4.0 M H$_2$SO$_4$ was 0.24 Ω/g, and 4.0 M H$_2$SO$_4$ was 0.30 Ω/g. It can be seen that 0.3 M VOSO$_4$ + 4.0 M H$_2$SO$_4$ shows a better value, which is attributed to the conductivity of vanadium ions and the lower solution resistance. In BW163E, 0.3 M VOSO$_4$ + 4.0 M H$_2$SO$_4$ was 0.30 Ω/g, and 4.0 M H$_2$SO$_4$ was 0.31 Ω/g. In BW163E, we thought that the contribution of ohmic resistance was large. Comparing the charge/discharge curve with the general profile in constant current charge/discharge, it is clear that charge is affected by redox capacity, but discharge is affected by the long-term relaxation process. In other words, it is clear that the redox capacitance cannot follow the electric double layer capacitance during discharge. Especially in the positive electrode, even if vanadium was added, it showed a slope similar to that of 4.0 M H$_2$SO$_4$, so it is considered that redox capacity could not be added. It is considered that the reaction of $V^{2+}/V^{3+}$ at the negative electrode accounts for the majority of the added amount in the discharge.

Figure 7. Charge/discharge curve and energy density of each electrode obtained from CDC measurement (Solid line: 0.3 M VOSO$_4$ + 4.0 M H$_2$SO$_4$, dotted line: 4.0 M H$_2$SO$_4$).
No correlation was confirmed by surface functional groups. Originally, it has been reported that oxygen-containing functional groups activate the redox reaction of vanadium. However, BW163E, which had the largest O/C in CDC, had the smallest redox capacitance addition. This suggests that in ACF, the oxygen-containing functional group may increase the hydrophilicity, promote the adsorption of water molecules, and inhibit redox capacity addition.

From the results of CV and CDC, the reason why the redox capacity during discharge was small was considered as follows.

In both cases, the product diffused into the bulk electrolyte after the charging reaction and could not be completely recovered electrochemically. In other words, in order to add redox capacitance in discharging, it is necessary to retain the product of charging. As shown in Fig. 8, the direction of adsorption due to the formation of an electric double layer and redox capacitance reaction during charging is a process in the same direction from the bulk to the inside of the pores. In contrast, in electric discharge, desorption due to electric double layer collapse is from pores to bulk, and redox reaction is from bulk to pores, which is a reverse process. Therefore, it is considered that the electric double layer capacitance reaction and the redox reaction inhibited each other in the discharge. Also, at the positive electrode, both the electrode and the vanadium ion are positively charged, so it is considered that the redox reaction did not proceed further. At this time, the electrons sent from the negative electrode were considered to have been used for the collapse of the electric double layer because the electric double layer capacity of the discharge in the CV measurement became small.

4. Conclusion

The results of CV, EIS, and CDC measurements indicate that the addition of vanadium can add redox capacitance, with a maximum improvement in energy density of 32%. However, with the improvement, the characteristics of the electric double layer capacitor deteriorated and the irreversibility of the oxidation-reduction reaction was observed. In this study, there was no correlation with the amount of oxygen-containing functional groups, and there was a difference between CF and the surface structure and internal structure that differ greatly. By analyzing each parameter of the diameter pore structure, coexistence of the electric double layer capacitance and redox capacitance is possible, and it is thought that the device can be a more effective device.

Figure 8. Behavior of electric double layer formation/disintegration and vanadium reaction.
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