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Electrical Characteristics of Super Capacitors Using KOH Gel

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Abstract: Despite aqueous electrolytes having a low cost and excellent ionic conductivity, their low withstand voltage of 1.2 V makes them problematic for battery utility because that is a very important factor in battery production. In this research, the possibility of increasing the withstand voltage while maintaining the low cost of aqueous electrolytes was investigated. In this research, the solution electrolyte was made into a viscous solid polymer electrolyte to improve the withstand voltage of the electrolyte. A solid polymer electrolyte was made from sodium polyacrylate and doped with KOH (potassium hydroxide) and pure water. The improvement of the withstand voltage was evaluated by the specific capacitance.

Key words: Electric double layer capacitor, sodium polyacrylate, potassium hydroxide.

1. Introduction

In recent years, the demand for renewable energy is increasing due to calls for energy conservation and sustainability targets, goals which require batteries that are inexpensive to install, maintenance-free, and have a long service life. EDLCs (electric double-layer capacitors) are attracting attention as long-life, high-power batteries, and among EDLCs, those using aqueous electrolytes require less specialized equipment than organic electrolytes, resulting in lower development costs and less flammability. However, applying a voltage of 1.2 V or higher causes electrolyte electrolysis, which destroys the EDLC. Consequently, the voltage must be suppressed, resulting in a low output density, which stymies its practical usage. In this study, the possibility of solving this problem by solidifying the aqueous electrolyte and improving its withstand voltage was investigated.

Therefore, in this experiment, the sodium polyacrylate a type of ion-exchange membrane, was used to make a gel-like solid electrolyte to improve the withstand voltage. Sodium polyacrylate is the sodium salt of the acrylic acid polymer $(C_3H_3NaO_2)_n$. It has strong hygroscopicity, and when water is added, it gradually expands to form a transparent gel. It has hydrophilic carboxyl groups and takes on a gel structure by incorporating water molecules into its network structure. In general, it is used in disposable diapers and refrigerants because of its high water absorbency. In this study, an attempt was made to see if the withstand voltage could be increased by making the aqueous electrolyte into a solid polymer.

2. Experiment Materials

This EDLC was a combination of an electrode, electrolytes, and a collector.

2.1 Electrode

The electrode was prepared using activated carbon made from distilled Japanese shochu waste, Ketjen black (EC-600JD; Lion Specialty Chemical Co., Ltd., Japan), styrene-butadiene rubber (TRD102A; JSR Co., Ltd., Japan), and carboxyl methylcellulose. They were prepared in a weight ratio of 8.5:1:0.15:0.35 and along with them, three times the total weight of water was

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added to the kneading machine (ARE-310; THINKY CO., Ltd., Japan). The current collector was a titanium mesh cut with an electrode crimping area of 5 cm ^{2}and a terminal area of 8 cm ^{2} The electrode was applied to the collector and pressed at 10 MPa for 10 min in a hot press machine (H300-01; Az one Co., Ltd., Japan) [1].

2.2 Electrolyte

The electrolyte consists of sodium polyacrylate (No. 110-1985; Kenith Corporation, Japan), KOH (No. 168-21815; FUJIFILM Wako Pure Chemicals Corporation, Japan), and pure water. The electrolyte was prepared by adding sodium polyacrylate to the KOH solution, wrapping it, mixing it with a stirrer and leaving it for 1 h [1]. To determine whether the capacity of the EDLC depends on the potassium ion concentration in the electrolyte, this experiment tested three different samples with two different KOH concentrations and different amounts of sodium polyacrylate. One sample, made with: sodium polyacrylate:KOH:water = 1:1:100, had a KOH concentration of 0.08 mol/L. The other had 4 mol/L KOH, which was made at a ratio of 1:12:12. It was dissolved into the same amount of sodium polyacrylate. The final sample was prepared by doubling the amount of sodium polyacrylate and mixing it with a 0.08 mol/L KOH solution. Its composition was 1:0.5:50. They were coded as S1P008, S1P4, and S2P008, respectively.

2.3 Set-up

As shown in Fig.1, a solid polymer electrolyte was inserted between the two drying electrodes which were then placed in a gas barrier bag (PB350500P; MITSUBISHI GAS CHEMICAL Co., Inc. Japan) and sealed with a sealer (V-301; Fujifilm Co., Ltd., Japan).

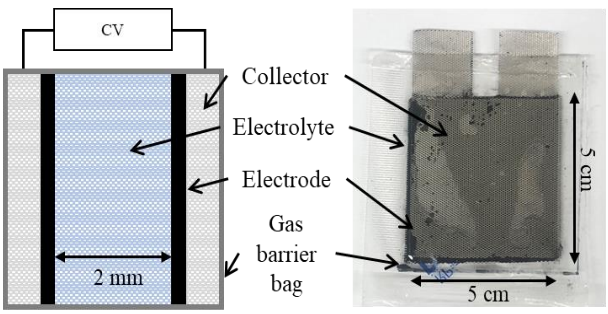

Fig. 1 Scheme of EDLC.

3. Experimented Method

3.1 Fourier Transform Infrared Spectroscopy (FT-IR)

For the sample containing only sodium polyacrylate and water, the N-H part was present as a large peak, but the reaction disappeared for the sample containing potassium. It can be assumed that this is the cause of the peak in the withstand voltage. This was probably due to the sodium polyacrylate acting as an ion exchange membrane, releasing sodium and adsorbing potassium at the same time [2].

3.2 Withstand Voltage

The withstand voltage of the electrolyte was evaluated with the CV (cyclic voltammetry). The CV was used with a scan rate of 10 mV/s, and impedance measurements were obtained in a frequency range from 20 kHz to 10 MHz Autolab potentiostat (PGSTAT204; Metrohm Japan Ltd.) [3]. Fig.2 showed the principle of impedance measurement. Cyclic voltammograms were obtained using the CV. The potential window was measured starting from 1 V and widened by 0.2 V, and the corresponding specific capacitance was recorded. When the specific capacitance decreased, that was regarded as the withstand voltage.

3.3 Cycle Measurement

For cycle measurements, S2P008 and P2K008 with withstand voltages exceeding 2.5 V were used. In the cycle test, to determine the degradation rate, the range

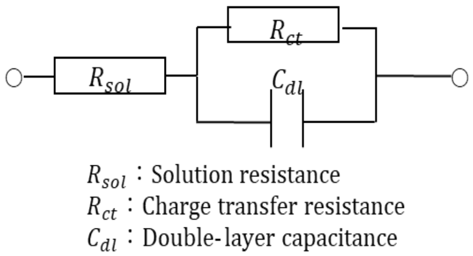

Fig. 2 Principle of impedance.

was set to 1,000 cycles, the potential window was widened to 2.5 V, and the specific capacitance was measured every 100 cycles.

4. Experiment Results

4.1 FT-IR Analysis

From the results of Fig.3, the sample containing only sodium polyacrylate and water show significant peaks in the N-H band with wavenumbers between 3,250 and 3,500 and in the C-H band with wavenumbers below 900. On the other hand, when the sample containing KOH was used as the reference material, these peaks were significantly suppressed. The results of Fig. 4 showed, it can be inferred that these differences are caused by the reduction of water absorption due to the absorption of KOH by the sodium polyacrylate. In addition, the peaks generated by the wavenumber of the KOH-containing materials seem to be the same, but the S1P4 sample, which has a large potassium component, had the most extended peak for the C-H band, which is below 900. In the area where the sample containing only sodium polyacrylate and water showed a peak and the sample containing KOH did not, there is a large N-H stretching reaction in the interval from 3,200 to 3,600 cm^{-1}. Conversely, there was an O-H stretch that reacted in the interval 2,400-2,800 cm^{-1} that was commonly peaked only in the KOH-containing samples. In addition, the C-H transformation in the 1,400-1,600 cm^{-1} region is also reactive in both cases, but the peak values are very different. The reason for the appearance of these changes is thought to be that the functional groups changed when the sodium ions of sodium polyacrylate ionized with water and the potassium ions of KOH and COO- adsorbed and bonded with the cationic potassium ions.

4.2 Withstand Voltage

In this study, the EDLC was prepared with each sample and measured using CV. When the EDLC was made using an electrolyte solution exclusively of KOH, the capacitance dropped as soon as the potential window was widened beyond 1.2 V. As the result, the capacitance of S1P008 increased even when it was expanded to 3.5 V, and that of S1P4 increased up to 2.5 V. For S2P008, it continued to increase even when it was expanded to 5 V. The S1P4 had a much larger starting specific capacitance value compared to the other samples, but it also had an earlier stage of decline. The S2P008 had a slightly lower specific capacitance than the other samples but had large withstand voltage. From these results, it was inferred that a higher concentration of KOH tends to increase the capacitance, and a higher amount of sodium polyacrylate tends to increase the withstand voltage. The reason for the difference in the peak capacitance at different voltages is related to the amount of water and the sodium polyacrylate absorbed in the water and decreased ion mobility. Table 1 and Fig. 5 show the capacitance of each sample when the potential window was widened by cyclic voltammetry.

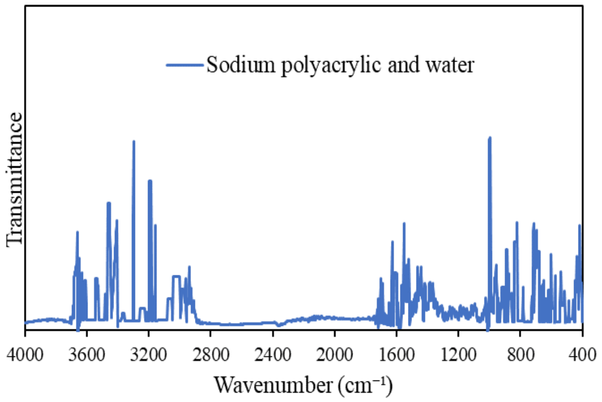

Fig. 3 Sodium polyacrylate and water.

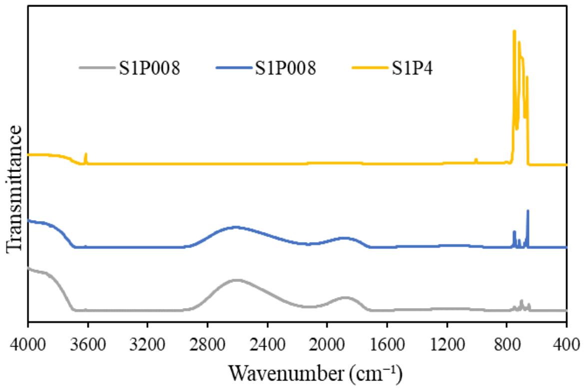

Fig. 4 Each sample's FT-IR spectrum.

Table 1 Each cyclic voltammetry.

Voltage (V)	Specific capacitance (F/g)		
	S1P008	S1P4	S2P008
1.0	26.5	71.7	16.5
2.0	36.8	94.9	32.1
2.5	43.5	98.6	39.5
3.0	46.6	43.6	49.4
3.5	49.0	-	56.9
4.0	48.9	-	72.5
4.5	46.2	-	78.3
5.0	-	-	79.7
5.5	-	-	70.2
6.0	-	-	44.7

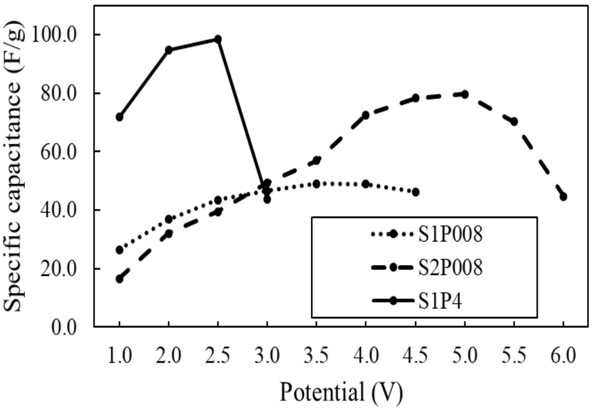

Fig. 5 Specific capacitance.

4.3 Cycle Measurement

For the cycle measurement, samples were prepared under the same conditions as for S1P008 and S2P008, and the potential difference was extended to 2.5 V for 1,000 cycles. Here, the samples that were found to have withstand voltages of 2.5 V or higher were selected. The results of specific capacitance per cycle were shown in Table 2 and Fig. 6, respectively. As the result, the specific capacitance of S2P008 decreased with each cycle, and the decrease in capacitance after 250 cycles was found to be over 21%. To determine whether the degradation in the cycle measurements was due to the electrolyte or some other factor, impedance measurements were taken to determine how the ion mobility changed. Figs. 7 and 8 showed the results of the impedance measurements for each cycle. Since the solution resistance remains the same and the charge transfer resistance increases, it can be inferred that no changes have occurred in the electrolyte, but problems have occurred in the electrode and other components. It was confirmed that the electrodes peeled off during the cycle test, which may be the reason for the degradation. If electrode delamination is prevented, the reduction in capacitance will be suppressed. On the other hand, the S2P008 sample did not show any change in specific capacitance, and the capacitance was improved. Figs. 7-10 showed the impedance results, which also show that no significant change in charge transfer resistance has occurred. This may be due to the electrolyte becoming more solid, which may have prevented the electrodes from being held down and peeled off.

Table 2 Results of cycle test.

Cycle No.	Specific capacitance (F/g)	
	S2P008	P2K008
10	11.2	52.8
100	9.8	57.9
200	9.1	57.7
300	8.3	59.0
400	7.6	59.1
500	7.4	58.7
600	7.0	59.3
700	6.9	58.0
800	6.7	62.0
900	6.7	64.3
1,000	6.6	61.6

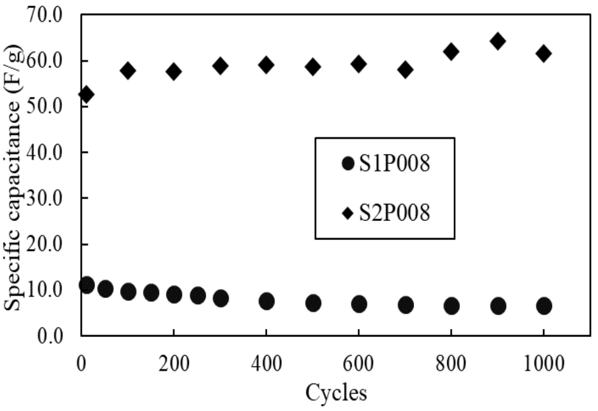

Fig. 6 Capacitance of cycle test.

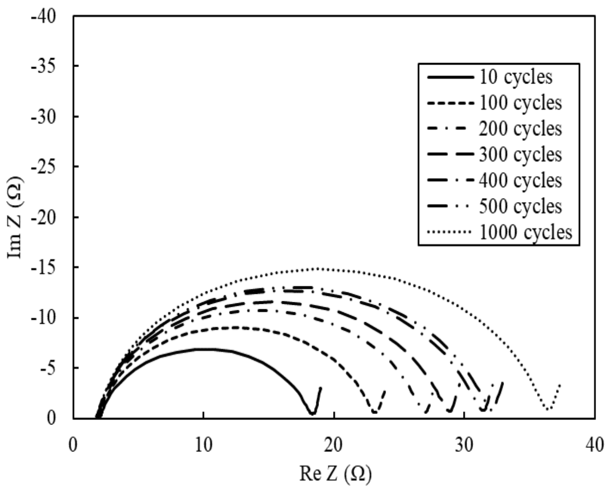

Fig. 7 Cole-Cole plot of S1P008.

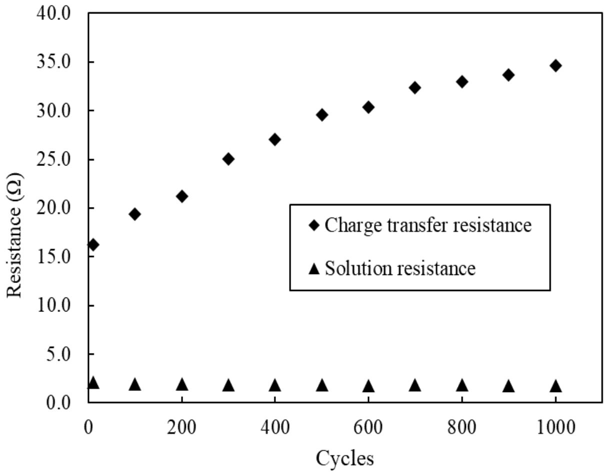

Fig. 8 Resistance of S1P008.

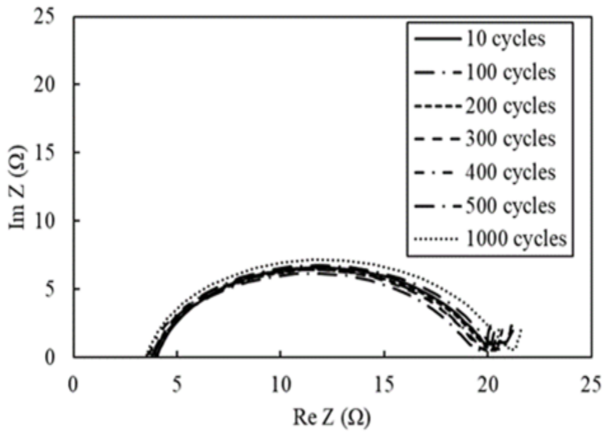

Fig. 9 Cole-Cole plot of S2P008.

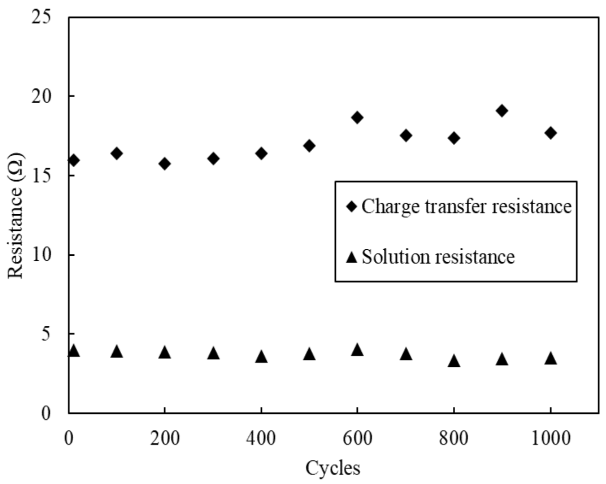

Fig. 10 Resistance of S2P008.

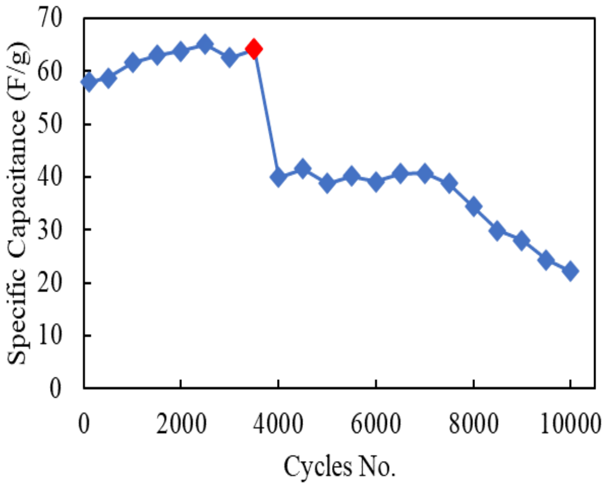

Fig. 11 Capacitance of 10,000 cycles.

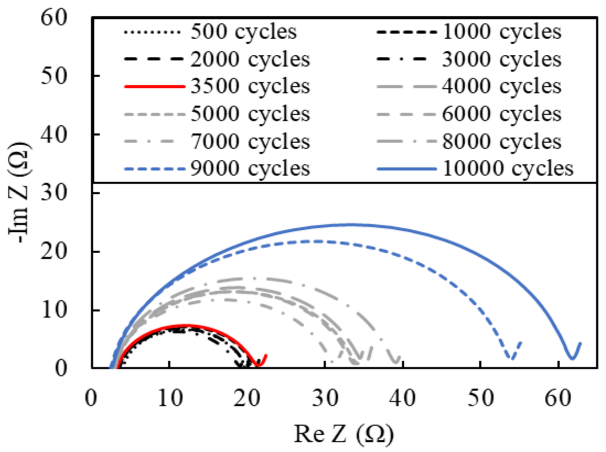

Fig. 12 Cole-Cole plot of 10,000 cycles.

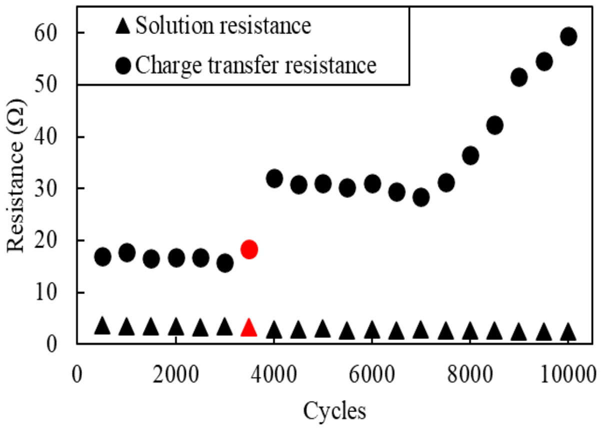

Fig. 13 Resistance of 10,000 cycles.

4.4 10,000 Cycle Measurement

Measurements were made on a sample of S2P008 for 10,000 cycles. The results are shown in Fig. 11. From there, it can be seen that the capacitance started to decrease after 3,500 cycles. The results of the internal resistance measurement are shown in Figs. 12 and 13.

5. Conclusion

It was confirmed that the withstand voltage of all samples was greater than the 1.2 V of the aqueous electrolyte alone. In particular, when a sample of S2P008 prepared by increasing the amount of sodium polyacrylate applied to the EDLC, the withstand voltage increased up to 5.0 V. The performance of the electrolyte depended on the concentration of the liquid electrolyte and the amount of sodium polyacrylate.

Even for samples exceeding 2.5 V, the S1P008 sample with less sodium polyacrylate degraded after 200 cycles, while the S2P008 sample did not degrade and averaged 59 F/g through 1,000 cycles. The results of 10,000 cycles showed no degradation up to 3,500 cycles. In the future, the optimum amount of potassium and sodium polyacrylate will be considered to balance capacity and withstand voltage in order to improve energy density.

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