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플루오르화 폴리비닐리덴 바인더의 분자량이 유기계 전기이중층 커패시터의 전기화학적 특성에 미치는 영향

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Effects of Molecular Weight of Polyvinylidene Fluoride Binder on Electrochemical Performances of Organic Electric Double-Layer Capacitors

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초록: 본 논문에서는 바인더가 유기계 전기이중층 커패시터(EDLCs)의 전기화학적 성질에 미치는 영향을 조사하기 위하여 플루오르화 폴리비닐리덴(polyvinylidene fluoride, PVDF) 바인더의 분자량을 다르게 하여 EDLC를 조립한 후 다양한 전기화학적 특성 분석을 실시하였다. 특성 분석 결과, 낮은 분자량의 PVDF를 사용하여 조립된 EDLC는 높은 분자량의 PVDF를 사용하여 조립된 EDLC보다 낮은 저항 및 높은 용량 특성을 나타냈으나 충-방전이 진행되는 동안 활물질과 도전재 사이의 구조가 높은 분자량의 PVDF를 사용하여 조립된 EDLC에 비해 느슨해져 결과적으로 낮은 수명을 나타내었다. 따라서 높은 성능을 갖는 EDLC를 제조하기 위해서는 적절한 바인더 분자량이 요구된다.

Abstract: Herein, we assembled electric double-layer capacitor (EDLCs) electrodes with polyvinylidene fluoride (PVDF) as the binder. The effect of the molecular weight of PVDF on the electrochemical properties of the EDLCs were investigated by various characterization tools. The EDLCs assembled using PVDF with low molecular weight showed relatively good capacitance compared to those assembled using PVDF with high molecular weight owing to their low resistance. However, in long-term durability experiments, EDLCs assembled using PVDF with high molecular weights showed higher durability than EDLCs assembled using PVDF with low molecular weights. To investigate the underlying reasons, field emission-scanning electron microscopy (FE-SEM) was applied. Although all prepared EDLC electrodes showed tightly packed morphologies before charge–discharge process was conducted, morphologies of electrodes using low molecular weight PVDF were gradually loosed as charge–discharge process was conducted. As a result, an appropriate binder molecular weight is required to prepare EDLC with high performances.

Keywords: electric double-layer capacitor, binder, molecular weight, rate capability, cycle stability.

Introduction

Electric double-layer capacitors (EDLCs), a type of supercapacitor, have been actively studied as electrical energy storage devices.[1-6] EDLCs use charge separation in a Helmholtz double-layer at the interface between the electrode surface and electrolyte.[1-4] Accordingly, EDLCs have many advantages including fast charge–discharge rate, durable life cycle, and high power density compared to secondary batteries using various chemical reactions for charge-discharge processes. Thus, EDLCs have great potential for important applications in many fields, and significant attempts to develop EDLCs with better electrochemical performance have been made.[7,8] Particularly, many studies on electrode materials, including active materials, conductive additives, and binders have been conducted to enhance the electrochemical performances of EDLCs.[9-11]

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Table 1. Physical Properties of the Commercially Available Activated Carbons[20]

	Activation method	Raw material	S_{BET}[a] ($\mathrm{m^2\,g^{-1}}$)	$D_{\mathrm{avg.}}$[b] (nm)	V_{total}[c] ($\mathrm{cm^3g^{-1}}$)
YP50F	Gas activation by steam	Coconut shell (hard carbon)	1590	1.8	0.8
MSP20	Chemical activation by KOH	Phenolic resin (hard carbon)	2279	1.8	1.0
CEP21KS	Chemical activation by KOH	Cokes (soft carbon)	2030	1.9	1.0

[a]Specific surface area: calculated by the Brunauer–Emmett–Teller (BET) plot. [b]Average pore diameter: determined by the Barret–Joyner–Hallender (BJH) method with the desorption branch. [c]Total pore volume.

Electrode materials for EDLCs are generally classified as active materials, conductive additives, or binders.[12-16] Porous carbon materials are widely used as active materials as they can store electrical energy to form a Helmholtz double-layer. Commercially, activated carbons such as YP series (Kuraray Co.), MSP20 (Kansai Coke & Chemicals Co.), and CEP series (Power Carbon Technology Co.) are used as active materials (Table 1).[17-19]

In addition, nanocarbon materials with high specific surface area[21-31] and carbon aerogels or carbon xerogels[32-38] have been recently used as active materials for studies on EDLCs and have shown high performances. As conductive additives, carbon blacks are generally used due to their high conductivity arising from their well-connected structure. Binders can be classified as organic or aqueous binders. Polyvinylidene fluoride (PVDF) is a representative organic binder, while polytetrafluorethylene (PTFE) is a representative aqueous binder. In EDLCs, binders are important for combining active materials and conductive additives, and to attach electrode materials to the current collector. Polymers are often used as binders, but overuse of binders leads to high resistance of the assembled EDLCs. Accordingly, binders are well-known to have a strong effect on electrode resistance. Thus, binders are important electrode materials and highly influence the electrochemical performances of the EDLCs. Nevertheless, studies regarding binders for EDLCs are quite rare compared to those on active materials and conductive additives. Therefore, we investigated the effects of binders on the electrochemical performances of EDLCs using three different molecular weights. Herein, YP50F and Super-P were applied as an active material and conductive additive, respectively. To thoroughly investigate the effects of molecular weight of binder on EDLCs, various characterization tools including cyclic voltammetry, galvanostatic charge–discharge, four-point probe, electrochemical impedance spectroscopy, and field emission-scanning electron microscopy (FE-SEM) were used.

Experimental

Preparation of EDLCs. All chemicals were used without further purification after purchase. As an active material, YP50F (Kuraray Co.), a representative active material in commercial EDLCs, was applied and Super-P (MMM Carbon Co.) was used as a conductive additive. In addition, PVDF (Sigma-Aldrich) with three different molecular weights were dissolved in 1-methyl-2-pyrrolidon (NMP, Daejung) and mixed as binders. Herein, three different molecular weights of PVDF are 180000, 275000, and 534000.

First, the active material and conductive additive were mixed for 30 min using a ball-mill to obtain a homogeneous powder-type mixture. Afterwards, the prepared PVDF binder was added to the powdered mixture of the active material and conductive additive to prepare the electrode materials in the form of a slurry-type mixture. Subsequently, the slurry composed of the electrode materials was vigorously stirred for 1 h. The mass ratio of active material, conductive additive, and binder was fixed at 8:1:1. A homogeneous slurry-type mixture was coated on the current collector with a gap of 23 μm using a blade apparatus. Following the coating, the coated electrode was dried at 70 ℃ *in vacuo* for 24 h, and pressed using a double-roll press at 80 ℃. After drying, the circular electrodes (18 mm in diameter) were obtained using a punching apparatus to assemble coin-type EDLCs (CR2030-battery-size). Finally, coin-type EDLCs were assembled using the prepared electrodes, separator, and spacer. The electrodes were soaked in an organic electrolyte (1 M tetraethylammonium tetrafluoroborate in acetonitrile; $\mathrm{TEABF_4}$/ACN) for 12 h in a glovebox filled with nitrogen gas. The soaked electrodes were placed opposite of each other and a separator was loaded between the electrodes. The EDLCs was sealed using a coin-cell crimper (Wellcos Co.). Thus, we finally obtained EDLCs using binders with different molecular weights, which were named according to the applied molecular weight of the binder (PVDF_X, X = molecular weight of binder * 10^{-3} = 180, 275, and 534).

Electrochemical Characterization of EDLCs. To confirm the electrochemical properties of the prepared EDLCs, we performed cyclic voltammetry (CV, CS310, CorrTest), galvanostatic charge–discharge analysis (C–D, CS310, CorrTest), four-point probe measurement (FPP, CMT-SR1000N, Advanced Instrument Technology), and EIS (CS310, CorrTest).

We recorded CV curves at various scan rates ranging from 5 to 100 mVs^{-1} in voltage range of 0–2.7 V. We also obtained C–D results at constant current loads from 0.1 to 7 Ag^{-1} at a fixed voltage range. The specific capacitances (gravimetric capacitance (C_g) and volumetric capacitance (C_v)) of the EDLCs were calculated using the discharge curve from the C–D measurements. The C_v values of the EDLCs were obtained by multiplying C_g and the electrode density ($\rho_{electrode}$). The $\rho_{electrode}$ value was determined from the ratio of the loading mass of active materials to the total electrode volume. To confirm the resistance properties of the prepared EDLCs, FPP and EIS measurements were performed. Through the FPP measurements, we directly confirmed the sheet resistances of the EDLCs. Through the EIS analysis we confirmed the charge-transfer resistance (R_{ct}) and were used to show results of the EIS analysis over a frequency range of 100 kHz to 0.01 Hz. To investigate the long-term durability of the EDLCs, the C–D of 2000 cycles was measured. The durability test was conducted at constant current loads of 1 Ag^{-1} at a voltage range of 0 to 2.7 V. In addition, field emission–scanning electron microscopy (FE-SEM, SU-70, Hitach) was used to confirm the morphological changes of the EDLC electrodes during the C–D of 2000 cycles.

Results and Discussion

Capacitance Properties of the EDLCs. First, we will describe some differences between two- and three-electrode (2_E and 3_E) systems for understanding the capacitance properties of EDLCs before discussing these properties of the prepared EDLCs. Although the majority of researchers use the 3_E system, a 2_E system was used in this study to measure the

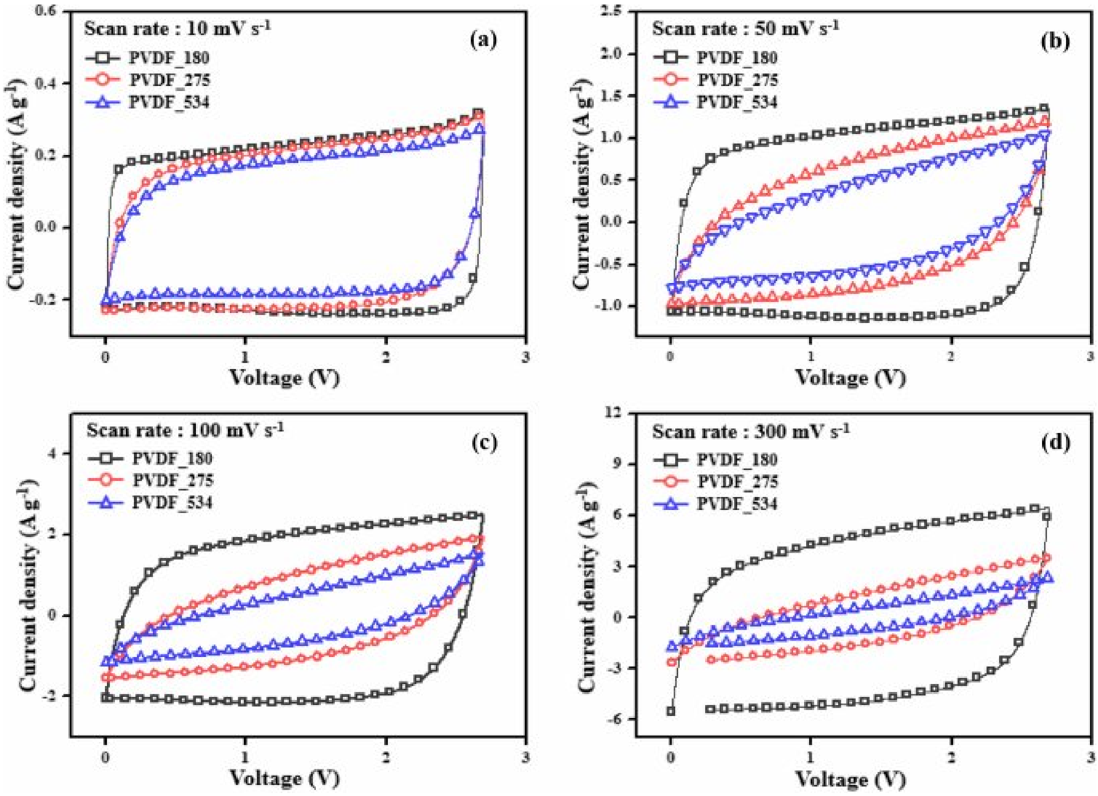

Figure 1. Cyclic voltammograms of the electric double-layer capacitors at a fixed scan rate: (a) 10 mVs^{-1}; (b) 50 mVs^{-1}; (c) 100 mVs^{-1}; (d) 300 mVs^{-1}.

capacitances of the EDLC cells. This is because using the 2_E system would have more industrial worth compared with using the 3_E system. Assuming that each EDLC electrode has the same weight, the following equation relates the specific capacitances determined using a 3_E system and 2_E system.[39]

$$C_{3E} = 4 \times C_{2E} \tag{1}$$

Where C is the specific capacitance. Therefore, eq. (1) can be used to analyze the capacitance properties determined using a 3_E system. Herein, we successfully configured a 2_E system to measure the electrochemical properties.

The CV results at various scan rates (10, 50, 100, and 300 mVs^{-1}) are shown in Figure 1.

At scan rate of 10 mV s^{-1}, which was the lowest scan rate used in this study, all prepared EDLCs showed CVs with a rectangular shape. However, with increasing scan rate, the CV areas of PVDF_275 and PVDF_534 rapidly decreased, whereas that of PVDF_180 showed a fairly well-maintained rectangular shape even at the highest scan rate. To summarize the CV results, all prepared EDLCs exhibited good capacitance properties at 10 mVs^{-1}, but the capacitance properties of PVDF_275 and PVDF_534 rapidly decreased with increasing scan rate. From this trend, we inferred that the molecular weight of binder highly influenced the capacitance properties of the EDLCs at high-rate of C–D. To confirm this trend, we conducted C–D tests and the obtained results are shown in Figure 2. Moreover, the specific capacitances calculated from C–D results are presented in Figure 3 and Table 2.

The formulas for the specific capacitance calculated from the C–D results are as follows.

$$C_g = \frac{I \cdot \Delta t}{m \cdot \Delta V} \tag{2}$$

$$C_v = C_g \times \rho_{\text{electrode}} \tag{3}$$

where C_g is the gravimetric capacitance, C_v is the volumetric capacitance, I is the discharge current, Δt is the time required

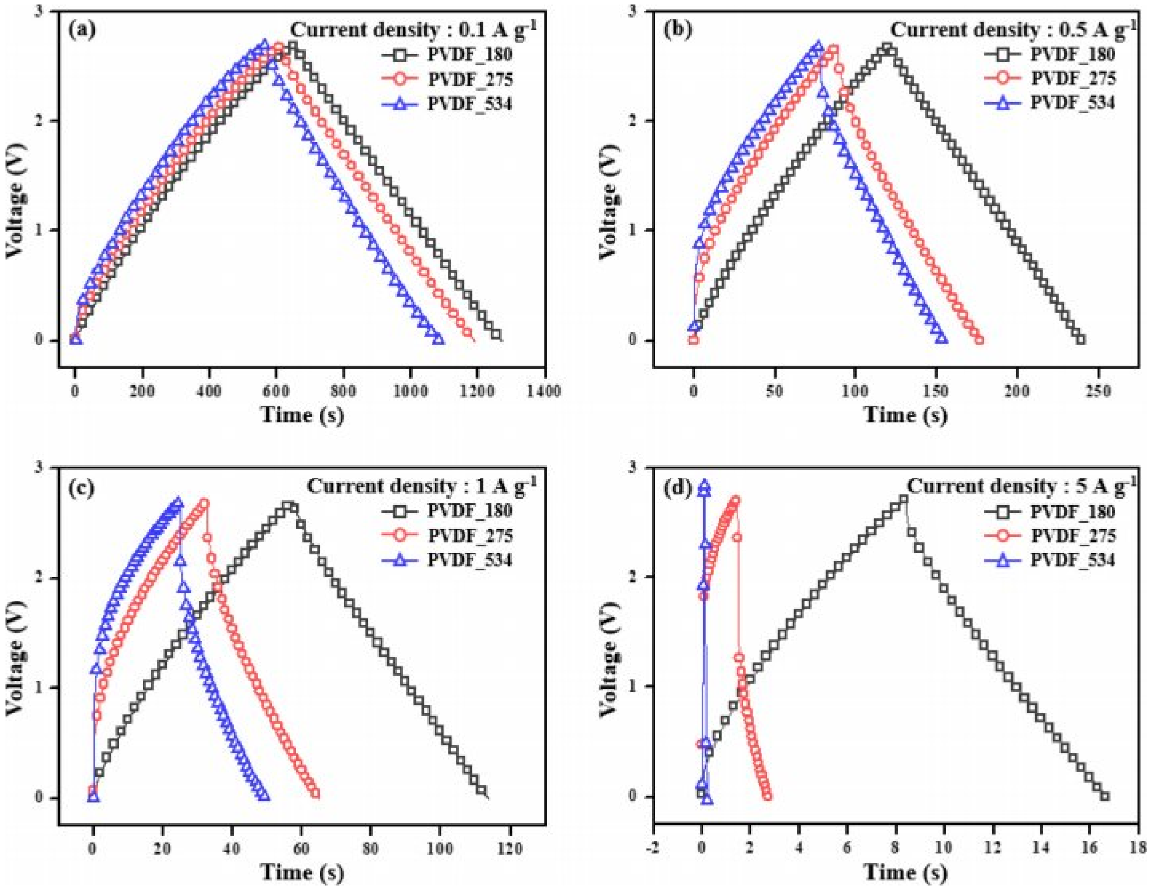

Figure 2. Galvanostatic charge–discharge profiles of the electric double-layer capacitors at a constant current density of (a) 0.1 Ag^{-1}; (b) 0.5 Ag^{-1}; (c) 1 Ag^{-1}; (d) 5 Ag^{-1}.

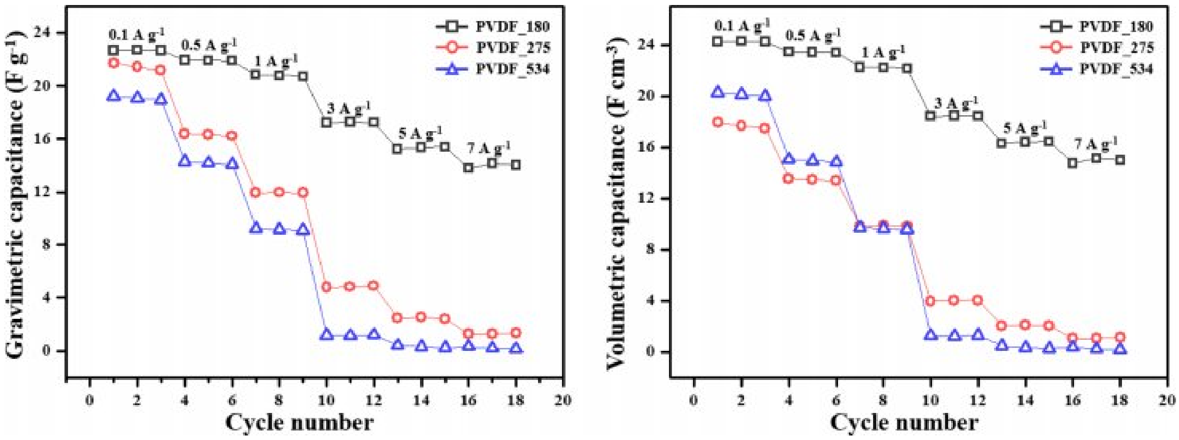

Figure 3. Specific capacitances of the electric double-layer capacitors.

Table 2. Specific Capacitances and Retention Ratios of the Prepared Electric Double-Layer Capacitors

Current density (A g^{-1})	Gravimetric capacitance (Fg^{-1})						Volumetric capacitance (Fcm^{-3})						$R_{\text{ret}}{}^{a}$
	0.1	0.5	1	3	5	7	0.1	0.5	1	3	5	7	
PVDF_180	22.7	21.9	20.7	17.2	15.4	14.0	24.2	23.4	22.1	18.4	16.4	15.0	0.62
PVDF_275	21.2	16.2	11.9	4.9	2.4	1.4	17.5	13.4	9.8	4.0	2.0	1.1	0.07
PVDF_534	19.0	14.1	9.1	1.2	0.2	0.2	20.0	14.8	9.6	1.3	0.2	0.2	0.01

[a] Retention ratio with increasing charge–discharge rate: calculated from the ratio of gravimetric capacitances at 0.1 and 7 Ag^{-1}.

for discharge, m is the weight of the two electrode materials, ΔV is the change in voltage during discharge, and $\rho_{\text{electrode}}$ is the density of the active materials on the electrodes determined from the ratio of loading mass to volume of the electrode materials. We obtained the same trend as observed for the CV results. Although all prepared EDLCs showed good capacitance properties at a low C–D rate (1 Ag^{-1}), the capacitance properties of EDLCs using binders with high molecular weight rapidly decreased with increasing rate of C–D. In other words, the EDLCs prepared with binders of low molecular weight showed good rate capability. To compare the rate capability of the prepared EDLCs, retention ratios of gravimetric capacitance were calculated, and the obtained results are presented in Table 2. The retention ratios were determined from the ratios of gravimetric capacitance at 0.1 and 7 Ag^{-1}. The EDLC prepared with low molecular weight binder showed a high retention ratio, while the EDLC with high molecular weight binder showed a lower retention ratio.

To summarize, we investigated effects of molecular weight of the PVDF binder on the capacitance properties of the EDLCs. The prepared EDLCs showed relatively high capacitances at low C–D rates, where capacitances were gradually reduced with increasing rates. The EDLCs showed different rate capabilities, where the EDLCs prepared using binders with high molecular weight showed poor rate capability. Thus, we concluded that the capacitance properties of EDLCs are highly influenced by the molecular weight of binders at a high C–D rate compared to the low-rate range. Moreover, based on our previous studies, the electrical conductivity of the electrode materials is a crucial factor at high C–D rates.[40] Therefore, we predicted that the difference of EDLC rate capabilities originated from differences in the resistance properties of the EDLCs prepared with different molecular weights of PVDF binder.

Resistance Properties of the EDLCs. To confirm the resistance properties of the EDLCs prepared using binder with three different molecular weights, we conducted FPP measurements and EIS analysis (Table 3 and Figure 4).

In the FPP results, PVDF_180 showed the lowest resistance, as predicted from its corresponding capacitance properties. Furthermore, the sheet resistance increased with increasing molecular weight of the binder. To clearly confirm the resistance properties, EIS analysis was performed and the results were represented by Nyquist plots, which is representative plot to present the EIS results. Prior to discussing the resistance performances of the prepared EDLCs, we will first explain the

Table 3. Sheet Resistances of the Electric Double-Layer Capacitors

	PVDF_180	PVDF_275	PVDF_534
R_{sheet}[a] (ohm sq.$^{-1}$)	480.7	690.0	1050.5

[a] Sheet resistance: confirmed by four-point probe measurement.

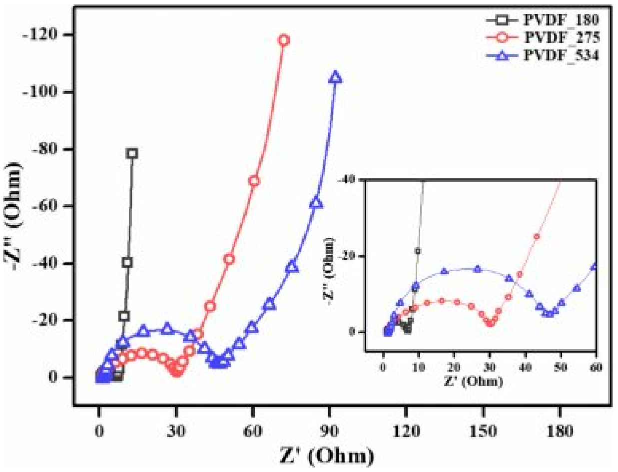

Figure 4. Electrochemical impedance spectra of the electric double-layer capacitors.

generation of Nyquist plots from EIS measurements. The Nyquist plots can be divided into three regions. The first is the region from which the bulk solution resistance (R_s) can be deduced from the x-intercept where the initial graph begins in the high-frequency range. R_s appears differently depending on the electrolyte and solvent used and is related to migration of the electrolyte ions far from the electrode. The semi-circular region, which appears in the intermediate frequency range, is a region that can be used as an index representing the charge transfer resistance (R_{ct}). They can be divided into electron transfer and ion transfer resistance. The ion transfer resistance is related to charge transfer through the movement of the electrolyte ion into the structural pores between the relatively large active material particles, and can be interpreted as resistance to the movement of electrons in the electrode and the movement of electrons between the electrode and current collector. Finally, the Warburg response region is related to migration of the electrolyte ions in the micropores of the electrode material in the low-frequency range. When all pores are saturated with electrolyte ions, the Warburg response region ends and a linear region with a sharp increase close to parallel to the y-intercept is displayed.[41-43] As shown in Figure 4, the results of EIS were in good agreement with those of FPP. Particularly, the R_{ct} trends determined by the radius of the semi-circle decreased in the order of: PVDF_534, PVDF_273, and PVDF_180. As a result, the R_{ct} of the EDLCs decreased with increasing molecular weight of PVDF binder. One cause of this phenomenon is that the distance between the active material and conductive additive in the electrode gradually decreases as the molecular weight of the binders decreased. In other words, the low molecular weight of the binder brings the electrode materials in the EDLCs relatively closer together compared to the high molecular weight binders. This results in low resistance properties and good rate capability of the resulting EDLCs. Considering our previous studies regarding the relationship between the capacitance properties and resistance properties of EDLCs,[40] the resistance results presented herein are good agreement with capacitance properties.

Long-term Durability of the EDLCs. To confirm the long-term durability of the prepared EDLCs, 2000 C–D cycles were performed. For confirmation, we used a current density of 1 A g^{-1} because all prepared EDLCs showed good and similar capacitance results at this current density. The obtained results are shown in Figure 5.

Interestingly, contrasting results to the capacitance and resistance results were obtained. From the results of capacitance and resistance, the EDLC prepared using PVDF binder with the lowest molecular weight showed the best performances among the prepared EDLCs. However, the durability of PVDF_180 rapidly decreased as the number of C–D cycles increased. In contrast, PVDF_275 and PVDF_534, which showed relatively poor rate capabilities due to their high resis-

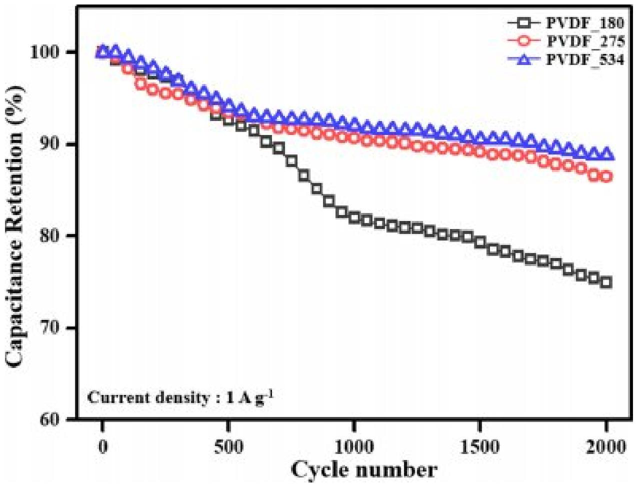

Figure 5. Long-term durability of the electric double-layer capacitors.

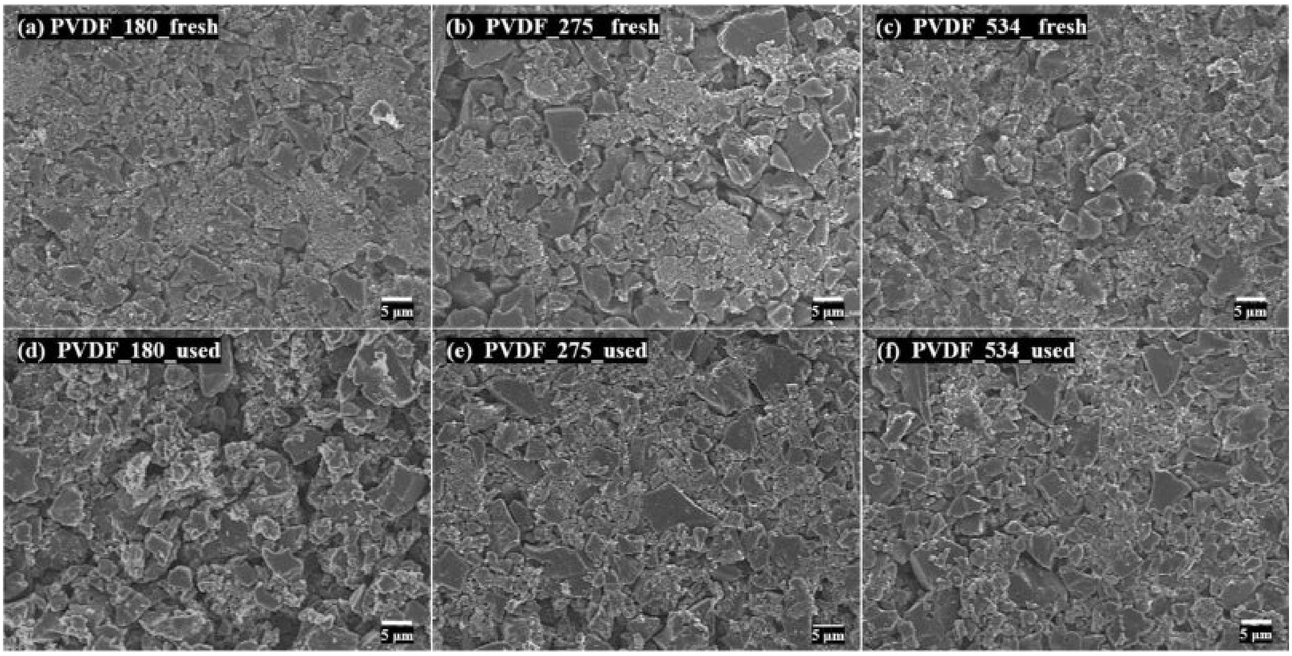

Figure 6. FE-SEM images of electrodes of the electric double-layer capacitors. (a), (b), (c): fresh; (d), (e), (f): used.

tances, showed well-maintained capacitance properties during the 2000 C–D cycles. To investigate the causes of the obtained durability results, we directly confirmed the morphological changes of the electrode surface during the 2000 C–D cycles through FE-SEM images (Figure 6). Initially, it was observed that the active material and conductive additives of all prepared EDLC electrodes were tightly packed. As the 2000 C–D cycles progressed, these tightly packed morphologies were separated. Herein, PVDF_275 and PVDF_534 showed small gaps between the electrode materials compared to PVDF_180. As a result, we concluded that differences in the spacing change during C–D cycling governs the durability of the prepared EDLCs, and the binders with high molecular weight formed EDLCs with good long-term durability.

Binders play an important role connecting active materials and conductive additives in EDLC electrodes. However, when the molecular weight of binder is too low, the binder cannot maintain the connection of the active material and conductive additive during long-term C–D cycling, resulting in poor capacitance properties of the EDLCs. Through our previous studies, we confirmed that connection of the active material and conductive additive in EDLC electrodes highly influenced the electrochemical performances of EDLCs.[44] Furthermore, we concluded that an appropriate molecular weight of the binder is required for optimal EDLC performance with high cycle stability and good electrochemical performance.

Conclusions

Herein, we thoroughly investigated the effects of the molecular weight of the binder on the electrochemical performances of EDLCs. For this investigation, we prepared EDLCs using PVDF binders with three different molecular weights. As an active material and conductive additive, we used a commercial activated carbon and carbon black, respectively. Through electrochemical characterization, we confirmed that the binder molecular weight strongly affected the electrochemical performances of EDLCs. All prepared EDLCs showed considerable capacitance at low C–D rates, but differences in electrochemical performances at high C–D rates were observed. EDLCs prepared using a PVDF binder with low molecular weight showed good rate capability and low resistance properties compared to those prepared using PVDF binders with high molecular weights. In other words, EDLCs prepared using PVDF binders with high molecular weight showed poor electrochemical performance at high C–D rates. However, in the long-term durability test, contrasting results were obtained. The capacitance properties of the EDLCs prepared using PVDF binders with low molecular weights rapidly decreased with increasing number of C–D cycles. In contrast, EDLCs prepared using PVDF binders with high molecular weights exhibited relatively well-maintained capacitances during the long-term durability test. The FE-SEM images confirmed that the differences in durability originated from the spacing of electrode materials as C–D analysis was conducted. It was concluded that the molecular weight of the binder strongly affected the electrochemical performances of the prepared EDLCs, and that an appropriate molecular weight of binder is required for realizing EDLCs with high cycle stability and good electrochemical performance.

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