

Preparation and electrochemical performance of activated carbon thin films with polyethylene oxide-salt addition for electrochemical capacitor applications

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Abstract The effect of polymer-salt addition in the activated carbon electrode for electric double-layer capacitor (EDLC) has been investigated. A series of composite thin film electrode consisting of activated carbon, carbon black, polytetrafluoroethylene and polymer-salt complex (polyethyleneoxide-LiClO₄) with an appropriate weight ratio were prepared and examined their performance for EDLCs using 1 mol L⁻¹ LiClO₄ in ethylene carbonate: diethylcarbonate electrolyte solution. The electrochemical capacitance performances of these electrodes with different compositions were characterized by cyclic voltammetry, galvanostatic charge-discharge cycling, and AC impedance measurements. By comparison, the best results were obtained with a composite electrode rich in polymer-salt additive (132 F g⁻¹ at 100 mA g⁻¹ of galvanostatic experiment). In general, the polymer-salt-containing electrode had shown improved performance over activated carbon electrodes without polymer-salt at high current density.

Keywords Electric double-layer capacitor · Activated carbon electrode · Polymer-salt complex · Rate performance

Introduction

Electric double-layer capacitors (EDLCs) have received a great deal of attention in energy storage devices with high-power applications. Activated carbons (AC) are technically

important materials, which have been used in various industrial applications for more than a century. Recent applications using AC as an electrode material for EDLCs or supercapacitors (Faradic capacitors) have ignited significant worldwide investigation into their physical and electrochemical behavior [1, 2]. ACs have been widely used as materials in EDLCs and prominent among the carbonaceous materials due to their high specific surface area, environmental safety, and relatively low cost; however, the electrical conductivity of activated carbons is low, usually 0.1–1.0 S cm⁻¹ which results in a low specific capacitance at high current density [3]. The crucial activated carbon electrodes have a specific part in the EDLC applications in terms of surface area and physical nature; the usual obtained specific capacitance ranges from 50 to 150 F g⁻¹ [1, 4] and 100 to 250 F g⁻¹ [5] in the case of organic electrolytes and aqueous electrolytes, respectively. In general, the average value is around 120 F g⁻¹; but in some cases, higher specific capacitance had been achieved with special features and conditions of the capacitor [6] such as surface area electrode, pore dimension, modification of electrode and selective electrolyte, etc.

Even though various carbonaceous materials have been examined for the capacitor electrode, their application is still limited in terms of specific energy. In order to improve the specific energy and power of supercapacitors based on carbon materials, many researchers have put a great deal of effort into their development and modification, such as the control of pore size distribution [7–9], introducing oxide materials [10, 11] or electrically conducting polymer additives/conducting polymer electrolytes [12–15], and novel type of carbon materials [16]. In a way, different forms of carbonaceous materials such as powder, fiber, paper (fabric or web), nanotubes, nanorods, and related nano-composites [17, 18] have also been introduced and analyzed for the improvement of capacitor electrochemical

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performance. In addition, the preparation of electrode for EDLC requires the additive materials; for instance, carbon black as conducting agent and PTFE as binder. These additives also have a significant effect for the EDLC performance [19, 20].

Polymer–salt (PS) such as polyethyleneoxide (PEO)–LiClO₄ complex is known as the solid electrolyte for batteries because of its high conductivity and the suitable mechanical properties and flexibility [21]. These properties of PS seemed to be suitable for the additive materials in the fabrication of EDLC electrode, because PS is expected to have a role of the binder and conducting agent at the same time.

In this study, we have prepared a series of composite thin film electrode composed of activated carbon with PS additive and examined the effect of these compositions for EDLC performance, more specifically, the specific capacitance at different charge–discharge conditions.

Experimental

Electrodes

Activated carbon (AC) powder (YP-17, Kuraray Chemical Co. Ltd., specific surface area 1,644 m²g⁻¹) was used as the active material. The polytetrafluoroethylene (PTFE), carbon black (CB; Denka Co. Ltd., specific surface area 49.8 m²g⁻¹) and polyethyleneoxide (MW≈5×10⁵, Aldrich)–LiClO₄ complex (PS) were used as binder, conducting material and additive agent, respectively. The ratio of LiClO₄/PEO in PS was kept at 2/8 and 1/1.

The prescribed amount of PS was added into the AC:CB:PTFE pre-mixed powder and then the mixture was dispersed in acetone and stirred at 400–500 rpm for 30 min using an automatic mechanical stirrer (AR100 conditioning mixer, THINKY Co. Ltd.). The slurry mixture was roll-pressed using a heating roller to form homogeneous thin films (typically, a thickness≈0.04–0.05 mm). Finally, the films were dried under vacuum (0.5 mmHg at 160 °C for 10 h) to remove moisture within the electrode materials. The composite electrode samples with different composition were prepared and listed as follows:

Notations:

- (a) AC:CB: PTFE (8:1:1)
- (b) AC:CB: PTFE (8.5:1:0.5)
- (c) AC:CB: PTFE (9:0.5:0.5)
- (d) AC:CB: PTFE:PEO₈:Li₂ (8:1:0.5:0.5)
- (e) AC: PTFE:PEO₈:Li₂ (8.5:0.5:1)
- (f) AC: PTFE:PEO₈:Li₂(8.5:0.25:1.25)
- (g) AC:CB: PTFE:PEO₈:Li₂ (8.5:0.75:0.25:0.5)
- (h) AC:CB: PTFE:PEO₈:Li₂ (8.5:0.5:0.5:0.5)

- (i) AC:CB: PTFE:PEO₈:Li₂ (8.5:0.25:0.25:1)
- (j) AC:CB: PTFE:PEO₁:Li₁ (8.5:0.25:0.25:1)
- (k) AC:CB: PTFE: Li₁ (8.5:0.25:0.25:1)

Electrochemical measurements

Test cells were fabricated in an argon atmosphere using the thin film electrode. The cells were constructed with a pair of the electrodes placed on the platinum foil current collectors (thickness 0.075 mm) and a piece of glass filter paper was inserted between them as a separator. All electrochemical measurements were carried out at 25 °C using 1 mol L⁻¹ LiClO₄ in ethylene carbonate:diethylcarbonate (EC:DEC, 1:1 volume ratio) as the electrolyte. Ag/Ag⁺ (AgNO₃ in acetonitrile) reference electrode was used for cyclic voltammetry and galvanostatic charge–discharge measurement.

Cyclic voltammetry (VMP—Multi-potentiostat, Perkin Elmer), between 0 and 1 V of potential window, was performed with a scan rate from 10 to 100 mV s⁻¹. The capacitance was calculated from the measured capacitive current from the cyclic voltammogram by applying the formula $C=i/mv$, where i is the average current, m is the weight of the electrode, and v is the scan rate. The galvanostatic charge–discharge cycling was performed between 0 and 1 V with 100 to 3,000 mA g⁻¹ of current densities. For galvanostatic cycling measurements, the formula $C=itdU^{-1}$ was applied, where t is the discharge time in the range of voltage dU , and i is the applied constant current as well as, in our calculations, the capacitance values are expressed per active material of one electrode. AC impedance on the capacitor was performed using a Solartron electrochemical unit model 1280B with frequency ranging from 10 to 20 kHz by the two-electrode set up. During the AC impedance measurement, a sinusoidal source with amplitude of 10 mV was supplied to the capacitor.

Results and discussions

Cyclic voltammetry

Figure 1 represents the typical observed cyclic voltammograms at a scan rate of 10, 50, and 100 mVs⁻¹. In all cases, a nearly rectangular shape of the voltammogram was obtained which is associated with the capacitive behavior—ideal polarized electrodes and no distinct peaks were observed over the particular scanned potential region. The voltammogram shows that the initial box shape of the curves was retained during the cycles, whereas the capacitive current varied with the composition of electrode materials, i.e., the

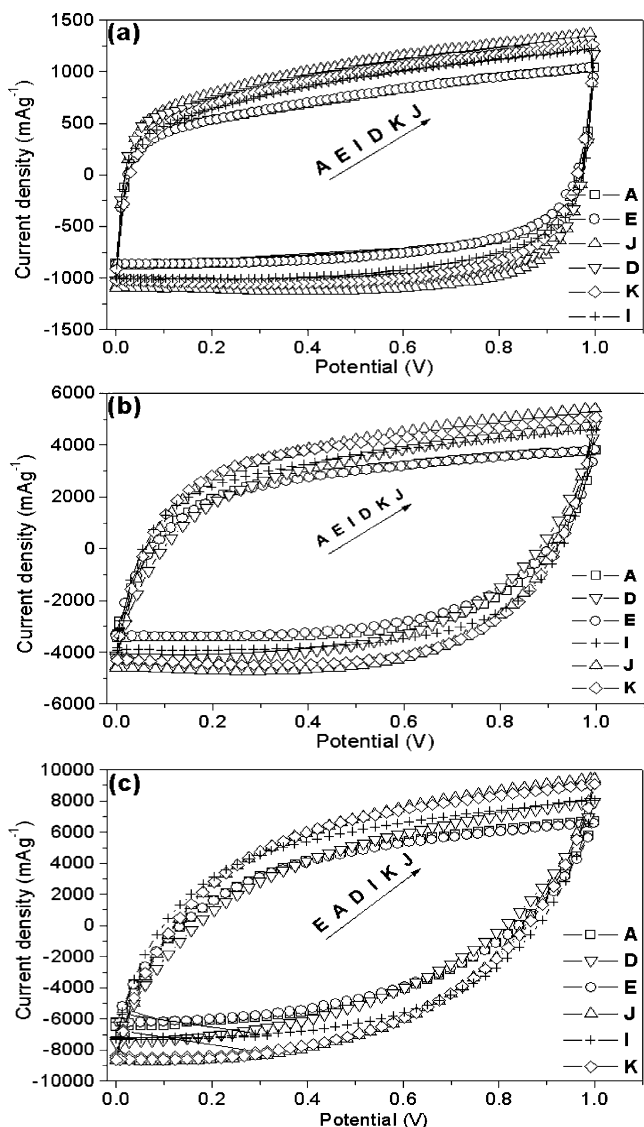


Fig 1 Cyclic voltammograms of the composite thin film electrodes in 1 mol L⁻¹ LiClO₄ EC:DEC (1:1) electrolyte solution, (a) 10 mVs⁻¹, (b) 50 mVs⁻¹ and (c) 100 mVs⁻¹ of scan rate

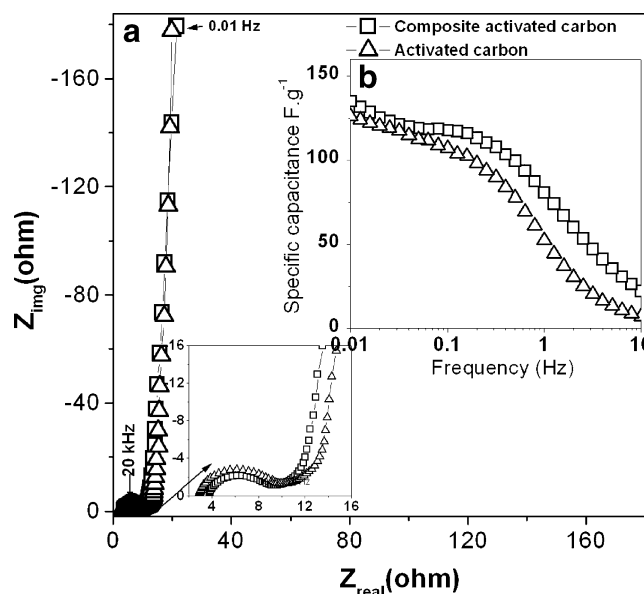


Fig 2 Complex impedance—Nyquist plot for the activated carbon composite electrode with and without PS additives; (a) complex impedance plot, (b) frequency-dependent capacitances at lower-frequency limit (AC signal level=10 mV; frequency range 10 mHz to 20 kHz)

curves were almost identical except in current density variations. This result indicates that the carbon electrodes used here are ideally polarizable in the conditions studied and obey an ideal capacitance curve of a purely electrostatic nature. At a high scan rate (50 and 100 mV s⁻¹), the curves deviate from a regular shape, which indicates imperfect reversibility at the separator–electrode interface due to ohmic drop which is the usual characteristic of EDLC, i.e., the limitation of accessible pore structure of high surface area carbons with respect to the ionic diffusivity [16, 22]. Generally, porous carbon material involved this kind of distorted current density with respect to potential. Usually, the distortion effect has been magnified at a higher scan rate

Table 1 Measured specific capacitance (F g⁻¹) from the cyclic voltammograms and galvanostatic discharge studies

Scan (mV s ⁻¹) and charge (mA g ⁻¹) rates	A	B	C	D	E	F	G	H	I	J	K
Capacitance (F g⁻¹) from cyclic voltammetry											
10 mV s ⁻¹	77.5	75.6	81.2	101.1	78.5	76.7	90.1	103.6	94.8	110.1	98.8
50 mV s ⁻¹	63.1	60.4	59.5	72.5	60.9	62.7	68.9	76.1	72.8	86.9	84.7
100 mV s ⁻¹	49.1	50.6	45.6	51.7	47.4	49.6	60.0	65.3	61.9	70.0	69.5
Capacitance (Fg⁻¹) from galvanostatic charge–discharge studies											
100 mA g ⁻¹	111.3	116.9	116.2	121.3	116.0	114.0	125.2	131.0	123.5	132.0	132.1
500 mA g ⁻¹	81.3	79.7	88.5	104.8	85.8	76.3	99.6	112.5	101.7	114.5	106.2
1,000 mA g ⁻¹	68.6	65.7	73.0	90.8	72.0	66.2	83.6	95.5	86.5	102.3	91.9
2,000 mA g ⁻¹	57.4	56.2	58.2	76.0	58.8	57.4	69.8	78.5	71.4	88.0	81.0
3,000 mA g ⁻¹	53.7	51.4	52.2	66.6	51.0	52.6	63.6	70.3	65.6	80.7	75.0

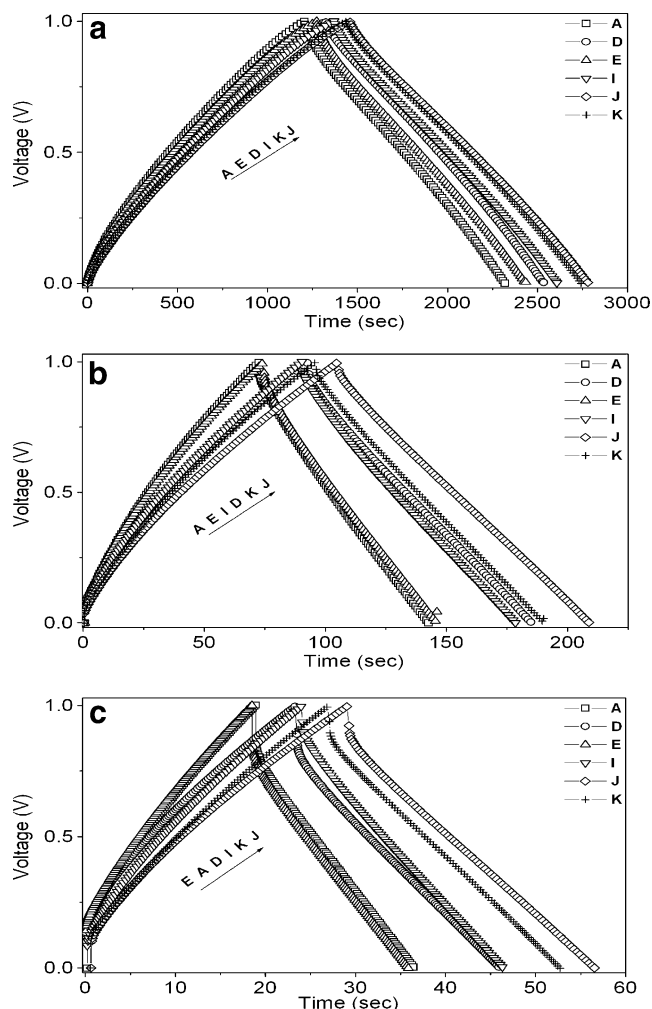


Fig 3 Galvanostatic charge–discharge curves of the thin film composite electrodes in 1 mol L⁻¹ LiClO₄ EC:DEC (1:1) electrolyte solution, (a) 100 mA g⁻¹, (b) 1,000 mA g⁻¹ and (c) 3,000 mA g⁻¹ of applied current density

in which the internal mode of activity between pores and electrolyte ions is disturbed as well as by the role of lower electrolyte conductivity and higher viscosity medium. This effect might be minimized by the right choice of electrode material and electrolyte solution. The ideal capacitor behavior is magnified at lower scan rates less than 5 mV s⁻¹ in which the adsorption/absorption equilibrium can be obtained or well resolved. The higher scan rate distortion is generally called “Electrolyte starvation effect” [7, 23–27].

The specific capacitances per weight (F g⁻¹) were calculated from the average redox current at 0.5 V of cyclic voltammograms and listed in Table 1. From the list, the PS containing electrodes (samples D, G, H and I) showed the higher specific capacitance value than that of the PS-free one (sample A, B and C). Even in the case of the lowest PS addition (sample G), the capacitance obtained was higher than the samples without PS. The sample, K, which contains only LiClO₄ salt (without PEO), showed better

capacitance than PS-free ones, but slightly lower than the samples with PS. Therefore, the addition of solely LiClO₄ could enhance the specific capacitance, though the PEO–LiClO₄ (polymer–salt) addition is more effective for the improvement of electrode characteristics. The highest capacitance was obtained by sample J which contains PS with the ratio of LiClO₄/PEO=1/1 whereas the composition of PS in electrode is the same with sample I. The specific capacitance of sample J reached ca. 1.4 times larger than that of the samples without PS.

Although one of the expected effects of PS addition is the improvement on the electrical conductivity of composite electrode materials, the addition of carbon black may still be necessary as one component of the electrode. Samples E and F did not contain CB, but PS was used, showing lower capacitance than the samples with CB and PS, especially at high scan rate. This suggests that both PS and CB may have a role to maintain enough electrical conductivity or ion diffusivity at severe conditions.

From the comparison of samples with different composition of CB and PS (samples D, G, H and I), it seems that there is a suitable composition of additive content. This means that the addition of PS could result in the reduction of CB content and could be advantageous from the view point of the mechanical strength of the thin film electrode.

The partial substitution of PS for PTFE binder (the same content of CB) has increased the capacitance values, as seen in the samples, A with D. This effect is considered to be due to the high electrical conductivity of PS. Although the addition of PTFE as a binder is necessary to form the electrode from carbon powder, this component decreases drastically the electrical conductivity of composite electrode because of its electrical insulating property [22]. Therefore, the substitution of PTFE by conducting PS even partly is quite effective for the improvement of specific capacitance without the sacrifice of mechanical strength of the electrode.

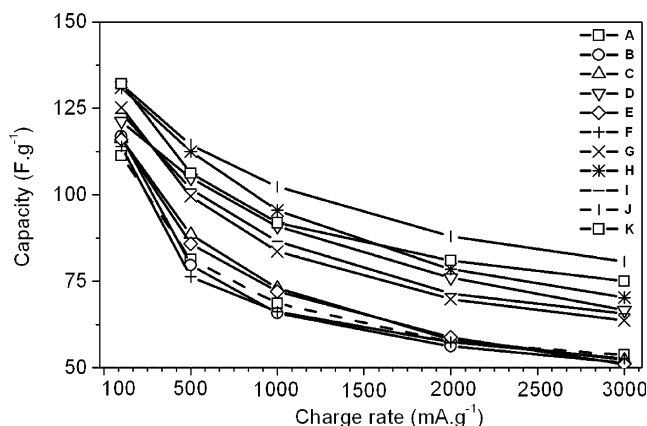


Fig 4 Specific capacitance obtained from the galvanostatic charge–discharge experiment at different current density

Table 2 IR drop estimated from galvanostatic charge–discharge curves

Charge rate (mA g ⁻¹)	IR drop (mV)										
	A	B	C	D	E	F	G	H	I	J	K
100	4.5	3.3	4.7	4.0	4.2	4.2	3.1	2.8	2.3	2.8	2.25
500	21.1	15.8	23.2	19.2	22.0	20.4	15.2	12.8	10.8	13.0	11.0
1,000	42.1	30.1	45.6	37.4	43.3	40.3	30.5	25.0	21.3	25.8	21.2
2,000	83.7	58.7	89.0	72.3	85.2	78.3	60.0	47.8	41.6	50.7	41.5
3,000	127.2	86.3	132.0	107.0	126.0	116.0	90.0	71.2	61.8	75.6	61.1

Impedance measurements

Complex impedance plots were measured for the activated carbon electrode without PS (sample B) and the one with PS additive (sample F) using the two-electrode cell configuration. The corresponding Nyquist plots of both samples were depicted in Fig. 2.

From the complex impedance spectra, an intercept from the higher frequency arc into the real axis (Z') represents the series resistance (R_s) of the capacitor. This value should be lesser for a better capacitor performance; but the PS-based capacitor slightly deviated from this section due to the thickness of the electrode or a small accumulation of charge carriers at the interface due to the presence of PEO–salt in the electrode [28]. Both samples resulted in a semi-circle at the high-frequency region followed by a nearly straight line ($\approx 90^\circ$, Warburg tail) at the lower-frequency region, i.e., ideal double-layer spike was absent. The emergence of a deviated Warburg capacitive behavior may be due to the surface roughness and internal pore resistance of electrode materials [29] (Fig 2a). These curves show a similar diffusion process, i.e., semi-circle at similar frequency region and capacitive behavior at low-frequency region. A slight difference in the internal resistance was observed such as 9.0Ω and 10.3Ω for the electrode with PS and without one at semi-circle region, respectively. This indicates that PS containing AC electrode have a lower charge transfer resistance (R_{ct}) than AC electrode without PS. The specific capacitance of the EDLCs from impedance spectra was determined by using the following relationship $C\text{-cell} = -2/(2\pi f Z'') \times 1/m$, where Z'' is the imaginary part of the total complex impedance (Ω), m is the weight of the positive electrode material excludes binder weight and f is the frequency (Hz). The high-frequency circle related the electrical connection between the active particles and the

current collector and electrolyte resistance at the pores. The specific capacitances for the electrode with PS and that of without PS are around 70 and 65 F g^{-1} , respectively, based on the single electrode capacitance calculation. The capacitance results from the ac impedance measurement are consistent with those obtained from the cyclic voltammogram.

Galvanostatic charge–discharge cycling

The dependence of specific capacitance on the applied current density (rate performance) and corresponding IR drop were examined by means of the galvanostatic charge–discharge cycling between 0 to 1 V. Figure 3 represent the typical charge–discharge curves for selected samples (A, D, E, I, J and K) at current density of 100, 1,000 and 3,000 mA g⁻¹. The calculated specific capacitances are plotted in Fig. 4 and their corresponding data and respective IR drop values which reflects the internal resistance of the test cells, were given in Tables 1 and 2, respectively.

As seen from Fig. 3, all the samples showed triangular charge–discharge curves at all given current densities. This suggests that the electrodes tested have no faradic reaction compared to the cyclic voltammetry experiment. Therefore, the PS in composite electrodes is stable and does not cause any of its electrochemical reaction at the electrode–electrolyte (solution) interface. This is also supported from the fact that the first coulombic efficiencies were of a similar level ranging from 70 to 78% for all samples, except the small increments compared with the AC electrode without PS.

From the assessment of rate performance which is indicated by the dependence of capacitance on the applied current (Fig. 4), the materials without PS (samples A, B and C) exhibited the larger decrease of the specific capacitance at

Table 3 Specific capacitance and IR drop during charge–discharge up to 1,000 cycles at 1,000 mA g⁻¹ of current density

Cycle no./sample	1 and 2 (IR drop in mV)	250	500	750	1,000
A	65.7(42.8)/69.0(42.9)	70.6(42.7)	70.4(43.0)	70(43.0)	69.9(42.6)
J	102.2(26.6)/104(26.8)	105.6(25.9)	106.4(25.0)	107.0(24.8)	107.7(24.6)
K	91.8(20.8)/ 94.1(20.7)	94(20.6)	96.5(19.1)	98.4(18.3)	97.8(18.7)

high current densities, implying poor rate performance. The specific capacitance of these samples at $3,000 \text{ mA g}^{-1}$ of current density reached only 42 to 47% of the one at 100 mA g^{-1} . On the contrary, the samples containing PS preserve well the capacitance against the application of higher charge–discharge current, suggesting superior rate performance. The sample J showed 81 F g^{-1} at $3,000 \text{ mA g}^{-1}$ of current density corresponding to 62% of the one at 100 mA g^{-1} . The unfavorable rate performance was also observed for the electrodes without CB (sample E and F) because less conductivity caused the highest IR drop at $3,000 \text{ mA g}^{-1}$. This situation is the same as the case in cyclic voltammetry as mentioned previously.

Figure 4 also indicates that the tendency of rate performance (the decay of capacitance caused by increased current density) could be divided roughly into two groups; the superior group gradually decreases the capacitance by increasing the current density while in the other group, the capacitance decreases rapidly. The latter group comprises of the composite electrodes without PS or CB and decreases the capacitance rapidly between 100 and 500 mA g^{-1} of current density. Therefore, both PS and CB are to be used at the same time. In the superior group, the sample J, which contains PS with the composition of $\text{LiClO}_4/\text{PEO}=1/1$ instead of $\text{LiClO}_4/\text{PEO}=2/8$ for other samples, showed the highest capacitance at any current density and also the most gradual decrease of capacitance against the current density increase. On the other hand, the sample K, which contains only LiClO_4 (without PEO) in the composite electrode, gave slightly lower results than the sample J, though the IR drop of sample K remained in quite a low level up to the highest current density. These results suggest that LiClO_4 itself, in the composite electrode, could enhance the conductivity, but it can act better in a polymer–salt complex because of the ionic conduction of Li^+ ion in the polymer matrix [30].

The most distinctive merit of PS addition is the suppression of IR drop at all current densities, which is nearly half of the IR drop for the samples without PS (Table 2). The smaller IR drop is observed for the PS-rich sample. A lower IR drop value indicates the low resistivity nature of the electrode; even in the higher charge rate, the ohmic drop has a lower value than the AC electrode without PS which gives the information about the lower equivalent series resistance (ESR). This one shows the good electroconductivity of the electrode as well as higher charge rate pore–electrolyte interaction reversibility [31, 32]. This indicates that the PS provides good electrical contact and it is favorable to increase its amount. The limit of PS addition from the view point of mechanical property needs to be determined by further investigation.

The sample A showed the smallest capacitance value at higher charge–discharge current, which seems to be a result

of the low capacitive value of activated carbon at a high current density [33]. The lower capacitance values are associated with larger IR drop (ohmic loss) during the cycling process, and at high charge rate, it is doubled for the case of samples without PS additives (samples A, B and C) [34]. A reduction of insulating binder (e.g., PTFE) content is important for the reduction of IR drop.

In order to estimate long-term stability, some samples were tested for 1,000 cycles at the charge rate of $1,000 \text{ mA g}^{-1}$, which is depicted in Table 3. Since the samples were fabricated as the thin film electrode, all the test cells showed good stability. From the calculated values, except initial cycles, the capacitance was almost the same or nearly the same throughout the cycling with constant IR drop. Based on this cycle performance, we can use this kind of the cell for long-term application

Conclusion

The effect of the polymer–salt (PEO-LiClO_4) addition on the activated carbon electrode for EDLC application has been investigated. It was revealed that PS could play a role of both binder and conducting agent and enhance the specific capacitance and the rate performance, as a result of decreased IR drop. This was realized by the partial replacement of low capacity carbon black and highly resistive binder PTFE. The polymer–salt complex is a well-known material as a battery electrolyte for many years now and is inexpensive with lightweight property, so that such a capacitor, which is using PS as one component, would be economically viable.

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