Application of Chitosan-based Gel Electrolytes with Ionic Liquids for High-Performance and Safe Electric Double Layer Capacitors

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ABSTRACT

Chitosan-based gel electrolytes with ionic liquids (Chi/IL) were prepared and investigated for use in electric double-layer capacitors (EDLCs). The voltage drop for the test cell with Chi/EMImBF₄ (EMImBF₄ = 1-ethyl-3-methylimidazolium tetrafluoroborate) or Chi/DEMEBF₄ (DEMEBF₄ = *N,N*-diethyl-*N*-methyl-*N*-2-methoxyethylammonium tetrafluoroborate) and activated carbon fiber cloth electrodes (ACFCs) was smaller than that with the corresponding ionic liquid electrolyte. To clarify the effect of the presence of Chi in contact with the carbon electrode, we also prepared the Chi-containing ACFC electrode (Chi+ACFC) and evaluated its charge-discharge characteristics in EMImBF₄. The results proved that the presence of Chi on the active materials reduces the internal resistances of the cell and plays an important role in the improvement of the EDLC performance. In addition, the high-voltage operation of the test cells with Chi-based gel electrolytes was investigated. These results suggest that the Chi is suitable for use in practical high-performance and safe EDLCs.

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Keywords : Gel Electrolyte, Ionic Liquid, Chitosan, Electric Double-Layer Capacitor

1. Introduction

Electric double-layer capacitors (EDLCs) are promising energy storage devices whose mechanism is based on the electric double layer formed at the electrode-electrolyte interface. EDLCs have been widely used especially as power supplies for many electric devices, owing to their high power density and long cycle life.^{1,2} Electrolytes are among the important components of EDLCs and they directly determine EDLC performance, such as charge-discharge rate property, operation voltage, and cycle life of the cell. To achieve a higher energy density, non-aqueous electrolytes are considered to be more favorable for EDLCs owing to their wide electrochemical potential windows that provide high-voltage operation, i.e., higher than 3 V.³

Room-temperature ionic liquids (ILs) have attracted considerable attention as alternative non-aqueous electrolytes for EDLCs because of their unique properties such as low volatility and low flammability, which can improve the safety of EDLCs.^{4–11} ILs, however, may not be suitable for practical use because of hazardous electrolyte leakage. Therefore, we believe that solid-state electrolytes have become the key materials in developing safe EDLCs. For example, Lewandowski and Świdorska reported that IL-containing gel-type electrolytes based on synthetic polymers, such as poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP), showed relatively high ionic conductivity and the corresponding EDLC cells exhibited long-term cycle performance.¹²

Recently, we proposed a chitosan-based gel electrolyte with IL (Chi/IL gel electrolyte) as a non-aqueous electrolyte for EDLCs.¹³ Chitosan is a heteropolymer consisting of D-glucosamine and a small fraction of *N*-acetyl-D-glucosamine residues, and is also a typical polysaccharide derived from chitin found in the cells of crustaceans, the exoskeletons of insects, and the cell walls of fungi. It is highly abundant in nature and has the advantages of being an environmental friendly and low-cost material; hence, it is widely used as a raw material for cosmetics, food additives, weight control products, water purification, and biochemical. Regarding the

application to gel electrolytes for electrochemical devices, the use of the Chi can reduce the total cost and environmental burden when compared to the use of conventional host polymers, such as poly(ethylene oxide) (PEO) and PVdF. The results of our previous study suggested that the Chi/IL gel electrolyte was believed to be a promising electrolyte material for EDLCs because of its high ionic conductivity compared with that of other IL-based gel electrolytes. We also found that the EDLC based on the Chi/IL gel electrolyte showed an excellent cycle performance (over 5,000 cycles) with a higher discharge capacity. Such high performance might originate from the effects of the high affinity of Chi toward the electrode materials and results in improvement of the electrode/gel electrolyte interface.

In this study, we further investigated the advantages of the use of Chi as the host polymer in a gel-type electrolyte including an ionic liquid, and discuss possible implications for improving EDLC performance by means of various electrochemical measurements.

2. Experimental

2.1 Syntheses

The Chi/EMImBF₄ (EMImBF₄ = 1-ethyl-3-methylimidazolium tetrafluoroborate) and (DEMEBF₄ = *N,N*-diethyl-*N*-methyl-*N*-2-methoxyethylammonium tetrafluoroborate) gel sheets were prepared by the same procedure that we previously reported.¹³ To investigate the effect of the presence of Chi on the surface of the active material, a Chi-containing activated carbon fiber cloth electrode (Chi+ACFC) was also prepared as described below. A Chi aqueous solution (2 wt%), obtained by dissolving Chi (FH-80, KIMICA Corporation) in 2% acetic acid aqueous solution, was cast into an ACFC (ACC-562-25, Nippon Kynol Inc., specific surface area: ca. 1950 m² g⁻¹). Next, the ACFC with Chi was immersed in 1.0 mol dm⁻³ KOH solution as a crosslinking agent for a few minutes at ambient temperature. After gelation, the electrode obtained was thoroughly rinsed with distilled water and immersed in ethanol overnight. Next, the electrode was punched out into a disk shape with a diameter of

Figure 1. (Color online) Schematic illustrations of the EDLC cell construction in this study. (a) ACFC|EMImBF₄|ACFC, (b) ACFC|Chi/EMImBF₄|ACFC, and (c) Chi+ACFC|EMImBF₄|Chi+ACFC.

10 mm and rinsed again with ethanol, followed by immersion in EMImBF₄ (Kanto Chemicals Co., Ltd.). The Chi+ACFC electrode was finally obtained by drying under vacuum at 10⁻² Pa at 70°C for 48 h.

2.2 Electrochemical measurements

The ionic conductivity of the Chi/EMImBF₄ gel electrolyte obtained was evaluated via an AC impedance method by using the SI-128787A connected to an impedance/gain-phase analyzer (SI-1260, Solartron Analytical) with an applied AC amplitude of 10 mV and a frequency range of 500 kHz to 10 mHz. The ionic conductivity of the gel was estimated from the measured resistance when the imaginary component at high frequency fell to zero for a test cell fabricated using a pair of platinum disk electrodes and a gel sample that was mounted in a Teflon[®] container with platinum current collectors. To evaluate the temperature dependence of the ionic conductivity, the test cell was located in a thermally controlled chamber (SU-241, ESPEC Co.).

An image of the two-electrode symmetric test cell with ACFCs and the gel electrolyte is shown in Fig. 1(b). After a pair of ACFC electrodes was immersed in EMImBF₄ for 2 h under reduced pressure prior to cell assembly, the two-electrode symmetric test cell with these electrodes and the obtained gel electrolyte was constructed for the electrochemical measurements. For comparison, we also assembled a test cell using a pair of ACFCs and liquid EMImBF₄ with a separator (GB-100R, Advantec Toyo Kaisha, Ltd.) [Fig. 1(a)]. The cell containing the Chi+ACFC composite electrode, the EMImBF₄ liquid electrolyte, and a separator were also assembled as shown in Fig. 1(c). Because the solid gel electrolyte exists on the ACFC electrode, the internal resistance is higher than the other cell configurations mentioned above. All of the components were mounted in a Teflon container, which constituted the cell exterior, with Pt current collectors. The whole assembly procedure was performed under a highly pure argon atmosphere in a glove box.

Chronoamperometric measurement was carried out with the cell voltage step applied from 2 to 2.5 V by using a computerized electrochemical interface (SI-128787A Solartron Analytical). Galvanostatic charge/discharge measurement was performed in a certain cell voltage range, with an upper cell voltage from 2.5 to 4.0 V at constant current densities of 10–100 mA cm⁻² using

Figure 2. Temperature dependence of the ionic conductivity (a) for the Chi/EMImBF₄ gel electrolyte (●) and EMImBF₄ (○) and (b) for the Chi/DEMEBF₄ gel electrolyte (■) and DEMEBF₄ (□).

a computerized battery charge/discharge analyzer (HJ-SM8, Hokuto Denko Co.). AC impedance measurements for the EDLC test cells were also performed to clarify the electrode/electrolyte interface.

3. Results and Discussion

3.1 Ionic conductivity of Chi/IL gel electrolytes

Figure 2 shows the temperature dependences of the ionic conductivity of the Chi/EMImBF₄ [Fig. 2(a)] and Chi/DEMEBF₄ [Fig. 2(b)] gel electrolytes as well as the corresponding liquids for comparison. It should be noted that both Chi-based gel electrolytes exhibited ionic conductivities in the whole range of the temperature as high as the corresponding liquid-phase electrolyte. Moreover, the gels are thermally stable, even with the use of a polysaccharide. These gels also demonstrated a comparable ionic conductivity to those of liquid-phase ionic liquids at low temperature. As shown in Fig. 2, the ionic conductivities for all electrolytes exponentially faded as the temperature fell; that is, they behaved as a non-Arrhenius system, which is generally observed for gel electrolytes containing ionic liquids.^{14–16} To evaluate the temperature dependence of their ionic conductivities, the obtained curves were fitted to the Vogel-Tamman-Fulcher (VTF) equation:¹⁷

$$\sigma = \frac{A}{T^{1/2}} \exp \left[\frac{-E_A}{R(T - T_0)} \right] \quad (1)$$

Table 1. Parameters describing fits to the VTF equation for ionic conductivities of the Chi-based gel electrolytes and the neat ionic liquids.

Sysntem	$A/S \text{ cm}^{-1} \text{ K}^{-1/2}$	$E_A/\text{kJ mol}^{-1}$	T_0/K	(R)
Chi/EMImBF ₄	20.6	4.9	167	0.999
Chi/DEMEBF ₄	27.5	6.3	193	0.999
EMImBF ₄	24.3	5.2	163	0.999
DEMEBF ₄	32.2	6.5	190	0.999

where A is a pre-exponential factor related to the number of charge carriers, E_A is the activation energy for conduction, R is the universal gas constant, and T_0 is the ideal glass transition temperature at which the conductivity reverts to zero. The estimated values of A , E_A , and T_0 are summarized in Table 1. The VTF A parameters for gel electrolytes were lower than those for the corresponding ionic liquid, presumably because of the decrease in the number of charge carriers caused by the co-existence of supporting polymers. By contrast, the activation energy for the ionic conductivity of Chi/EMImBF₄ and Chi/DEMEBF₄ were 4.9 and 6.3 kJ mol⁻¹, respectively. These values were slightly lower than those for the corresponding ionic liquids, EMImBF₄ (5.2 kJ mol⁻¹) and DEMEBF₄ (6.5 kJ mol⁻¹), indicating that the small amount of fast carrier-ion transfer is achieved even in the gel-type electrolytes, probably because of the moderately weak coulombic interaction between ionic liquids and Chi.

3.2 EDLC performance of Chi/EMImBF₄ gel electrolyte

Our previous report with regard to the Chi-based gel electrolyte described the improvement of an EDLC charge-discharge performance, particularly its rate capability, by applying the gel electrolyte.¹³ On the basis of the results of the ionic conductivity mentioned in Section 3.1, the use of Chi as a host polymer for the gel electrolyte might not be able to provide such a high-rate performance of the EDLC with the electrolyte. Therefore, we assume that the good performance of the EDLC composed of the Chi-based gel (Chi/EMImBF₄) was affected not by its ionic conductivity but by interfacial resistance. AC impedance analysis for the EDLC cell with Chi/EMImBF₄ has already been investigated, and has proved the lower electrode/electrolyte interfacial resistance compared with the cell composed of liquid EMImBF₄.¹³ Herein, to further clarify the origins of such high-rate EDLC performance, we carried out chronoamperometric tests for the cell with the Chi/EMImBF₄ gel electrolyte. The chronoamperometry must be an adequate technique for the practical evaluation for EDLCs because we can evaluate the kinetic behavior of the electrode from obtained current response. The current-time response of both cells with the Chi/EMImBF₄ gel electrolyte and with neat EMImBF₄ after the cell voltage changed from 2.0 to 2.5 V is shown in Fig. 3(a). At initial time period ~2 s, the cell with Chi/EMImBF₄ showed a higher current density than that with EMImBF₄, indicating that the charge storage kinetics is relatively fast in the presence of the Chi matrix. After that, although a rapid current decay was observed for the cell with Chi/EMImBF₄ gel electrolyte, the current for the cell with EMImBF₄ decreased much more slowly. The observed current responses were plotted as a function of the application period (especially at the initial time region) in Fig. 3(b) on a logarithmic scale. According to current

Figure 3. Chronoamperograms for EDLC cells with Chi/EMImBF₄ (●) and liquid EMImBF₄ (▽) with step cell voltage, $\Delta V = 0.5$ V (from 2.0 to 2.5 V) (a) for 100 s and (b) at the initial time region. (c) Total coulomb transition for EDLC cells with Chi/EMImBF₄ (●) and liquid EMImBF₄ (▽). (d) Equivalent circuit model for evaluation of each parameter.

Table 2. Calculated RC time constant value for EDLC cells with EMImBF₄ and Chi/EMImBF₄.

	RC time constant/s	R_{sol}/Ω	C_{dl}/F
Chi/EMImBF ₄	0.27	3.4	0.080
EMImBF ₄	0.41	5.3	0.077

decay after 0.025 s at which the cell began charging, we estimated several EDLC parameters [series resistance of an electrolyte (R_{sol}), capacitance based on the charge storage in electric double layer (C_{dl}), and their RC time constant ($R_{\text{sol}} \cdot C_{\text{dl}}$)] from the following equation:

$$\ln i = \ln \frac{\Delta V}{R_{\text{sol}}} - \frac{t}{R_{\text{sol}} \cdot C_{\text{dl}}} \quad (2)$$

where i (A) is the observed current, ΔV (V) is the cell voltage change, and t (s) is the application time. These estimated parameters are summarized in Table 2. From this, the RC time constant and the value of R_{sol} for the Chi/EMImBF₄ gel electrolyte were lower than those for EMImBF₄. The use of the Chi-based gel, however, reduced the R_{sol} value more than expected in the discussion of its ionic conductivity. This suggests that the high affinity of Chi to an activated carbon provides active sites where the charge carriers are adsorbed/desorbed, which leads to the apparent decrease of internal resistance, R_{sol} . In addition, the increase in C_{dl} for Chi/EMImBF₄ was consistent with the results of galvanostatic charge-discharge behavior as described in our previous report.¹³ Figure 3(c) shows the cumulative coulomb transition during application time for both cells. After a rapid increase at a few tens of seconds, the cumulative coulomb for both cells became constant and reached the same value of approximately 0.31 C cm^{-2} , indicating that both cells can store the same amount of electric charge with the same mechanism (i.e., electric double-layer-based storage mechanism). Comparing both curves, however, it was observed that no more than 30 s was required for the cell with Chi/EMImBF₄ to reach the constant coulomb value, whereas the cell with neat EMImBF₄ required over 50 s to finish being charged. Therefore, we conclude that the use of Chi-based gel electrolyte simply affects the charge-discharge kinetics of EDLC. Hence, it follows that the use of a Chi-based gel for EDLCs is effective for fast charge-discharge operation, which is consistent with our previous results.

3.3 Chitosan-containing electrode

To investigate the effect of the presence of Chi in the vicinity of carbon electrodes, a cell composed of a couple of Chi+ACFC composite electrodes and a glass fiber separator impregnated with the liquid EMImBF₄, as illustrated in Fig. 1(c), were evaluated by several electrochemical measurements. Figure 4 compares the charge-discharge curves of the cell assembled with the Chi+ACFC electrodes and that assembled with ACFC at current densities of 10 and 100 mA cm⁻². At a low current density of 10 mA cm⁻², the cell with Chi+ACFC exhibited a larger discharge capacity (110 F g^{-1}) than that of the cell with liquid EMImBF₄ (88 F g^{-1}) [Fig. 4(a)]. Notably, the cell with Chi+ACFC retained its discharge capacitance even if the pores inside the ACFC were filled with Chi. The cell voltage drop (ΔV_{drop}) was also reduced by the use of the Chi+ACFC electrodes (ΔV_{drop} for Chi+ACFC was 0.15 V, and that for ACFC was 0.24 V). These results prove the high-rate capability of the EDLC using the Chi-based gel electrolyte reported in our previous report, and indicate that the presence of Chi close to the electrode surface plays an important role in the improvement of the EDLC performance. For the operation at a high current density (i.e., 100 mA cm⁻²), a large cell voltage drop was observed for

Figure 4. Charge-discharge curves for EDLC cells with Chi+ACFC (—) and liquid EMImBF₄ (---). Charge-discharge current density: (a) 10, and (b) 100 mA cm⁻², cell voltage: 0–2.5 V.

the cell with Chi+ACFC owing to a certain internal resistance, probably a contact resistance between the electrode and the current collector owing to a protruded gel (discussed below), but it was comparable to that observed for the cell with ACFC despite of a large amount of Chi-gel inside the pores of the electrode [Fig. 4(b)]. Figure 5 shows the Nyquist plots estimated by electrochemical impedance spectroscopy with a frequency range of 1 MHz to 10 mHz at a cell voltage of 0 V. Comparing the imaginary component of the Nyquist plot of both cells, the cell with Alg+ACFC improved its specific capacitance compared with ACFC. This is consistent with the results of the galvanostatic charge-discharge measurements as shown in Fig. 4. Focusing the resistive component observed as high frequency, the series resistance for Chi+ACFC was higher than that for ACFC; furthermore, a semicircle was observed only for Chi+ACFC. In general, the semicircle in the high-frequency region represents the impedance of parallel resistance and capacitance at the contact interface, such as active materials/electrolyte.^{14,18} However, the observed semicircle may be due to a lack of electric conductivity at the interface between ACFC and the Pt current collector,^{15,19} the excess of Chi-gel covers the ACFC surface and leads to poor contact between the electrode and current collector. Then, the resistive component for the cell with Chi+ACFC, observed as the slope at a middle frequency (45° inclination at the frequency region of approximately 100–0.5 Hz shown in the inset of Fig. 5), was relatively small compared with that for ACFC. Because the component contributed to the limiting diffusion resistance, the

Figure 5. Nyquist plots of the EDLC cells with Chi+ACFC (—) and liquid EMImBF₄ (---) at open circuit potential and varying frequencies from 20 kHz to 10 mHz.

presence of Chi inside the electrode apparently promotes fast-moving charge carriers. However, the ionic conductivity of the Chi/EMImBF₄ gel did not exceed that of liquid EMImBF₄, as shown in Fig. 2, suggesting that the small diffusion resistance in the cell with Chi+ACFC arises from the good affinity between the activated carbon and the Chi-gel, which expands the active site where the charge carriers are stored.

3.4 Chi/DEMEBF₄ gel electrolyte

We prepared the Chi gel film containing a quaternary ammonium-based IL, DEMEBF₄ (Chi/DEMEBF₄), and constructed a two-electrode test cell composed of a pair of ACFC and Chi/DEMEBF₄, as shown in Fig. 1(b). Figure 6 shows typical charge-discharge curves for both cell with Chi/DEMEBF₄ and that with DEMEBF₄ at a current density of 2.5 and 50 mA cm⁻². The EDLC cell with the gel electrolyte could not operate at a high current density over 80 mA cm⁻², probably owing to the low conductivity of the gel electrolyte, as described in Section 3.1. At the low current density of 2.5 mA cm⁻², both cells exhibit a typical charge-discharge profile for EDLC, and the curve for Chi/DEMEBF₄ completely traces that for DEMEBF₄ [Fig. 6(a)]. On the other hand, it was found that the cell with the gel electrolyte showed a lower cell voltage drop at the current density of 50 mA cm⁻² (ΔV_{drop} for Chi/DEMEBF₄ and DEMEBF₄ were 1.61 and 1.77 V, respectively) [Fig. 6(b)], which indicates that the effect of the presence of the Chi matrix at the electrode surface also appears even if a quaternary ammonium-based IL is employed.

Finally, we investigated the withstand voltage of the cell with the Chi-based gel electrolyte. Figure 7 shows charge-discharge curves at a current density of 2.5 mA cm⁻² in the cell voltage range from 2.5 to 4.2 V for Chi/DEMEBF₄ and liquid DEMEBF₄. In addition, the coulombic efficiencies of the charge-discharge performance of the cells for each operation cell voltage are also represented. Judging from the curves and the coulombic efficiency, both cells are found to be electrochemically stable up to 4.0 V. Considering that both cells are fabricated using the same components except for an electrolyte, the distortion of typical triangular shape over 4.0 V is expected to be due to decomposition of DEMEBF₄, suggesting that the electrochemical decomposition of Chi is negligible at this high-voltage operation.

Figure 6. Charge-discharge curves for EDLC cells with Chi/DEMEBF₄ gel electrolyte (—) and liquid DEMEBF₄ (---) at a current density of (a) 2.5 and (b) 50 mA cm⁻² with operation cell voltage from 0 to 2.5 V.

4. Conclusion

In this study, we further investigated the electrochemical characteristics of the EDLC cell with Chi/IL gel electrolytes. It was found that the charge storage process for the Chi/IL gel electrolyte is faster than that for the corresponding IL owing to the presence of the Chi matrix, which has potential to improve the rate performance of EDLCs. According to the results of chronoamperometry, the use of Chi-based gel electrolyte reduced inner resistance, improved electric double-layer capacitance, and shortened RC time constant, presumably caused by the high affinity of Chi toward the activated carbon which can support penetration of charge carriers to a carbon electrode surface. The effect of the presence of the Chi matrix in contact with the carbon electrode was also studied by using Chi-containing electrode, proving that the presence of the Chi matrix on the electrode surface plays an important role in the improvement of the EDLC performance. These advantages of the use of a Chi-based gel electrolyte can exploit the full potential of ionic liquid electrolytes for EDLCs.

Acknowledgments

This work was supported by a Grant-in-Aid for Challenging Exploratory Research (No. 23655182) and the “Strategic Project to Support the Formation of Research Bases at Private Universities”: Matching Fund Subsidy from MEXT (the Ministry of Education, Culture, Sports, Science and Technology of Japan).

Figure 7. Charge-discharge curves for EDLC cells with (a) the Chi/DEMEBF₄ gel electrolyte and (c) liquid DEMEBF₄ at various cell voltages. Charge-discharge current density: 2.5 mA cm⁻². (b and d) The corresponding coulombic efficiency of the cell is also shown as an inset.

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