

Ethylene carbonate-based organic electrolytes for electric double layer capacitors

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A new electrolytic solution based on a mixed solvent of ethylene carbonate (EC) with sulfolane (SL) or γ -butyrolactone (γ -BL) has been examined as an electric double layer capacitor. Fundamental properties, such as electrolytic conductivity, viscosity, and thermal stability, were measured for solutions containing quaternary alkylammonium salts as the supporting electrolyte. Maximum conductivities were obtained for the solutions with mixed solvent of 20–40 mol % EC in the EC + γ -BL system: $1.2\text{--}1.3 \times 10^{-2} \text{ S cm}^{-1}$ for EC + γ -BL dissolving 0.5 M Et_4NBF_4 ($\text{Et} = \text{C}_2\text{H}_5$). The electrochemical and the thermal stabilities of the solution were dependent on the electrolytic salt as well as the solvent composition. A stable discharge capacitance and a high coulombic efficiency were obtained in a model capacitor using carbon fibre electrodes and the organic electrolyte of EC + γ -BL/ Et_4NBF_4 (or EC + γ -BL/ Et_4NPF_6).

1. Introduction

A capacitor in which electric charge is accumulated in an electric double layer formed at an interface between a polarizable electrode and an electrolyte is called an electric double layer (EDL) capacitor. This type of capacitor has been developed for a back-up power source in various items of electronic equipment, since it has a higher electric capacitance than condensers with conventional dielectrics [1–3]. Improved properties, especially in capacitance and internal resistance, are required for the capacitor to meet expanding needs of modern microelectronics [4, 5]. The properties of EDL capacitors depend on the electrolyte as well as the polarizing electrodes [1, 5, 6].

Organic solutions are superior to the other aqueous and solid electrolytes with respect to use in practical EDL capacitors. Wide potential windows exist for organic electrolytes which allow capacitors to be made with high output voltages and high specific capacitances. For example, Matsushita Electronic Component's 'Gold Capacitor' is a commercially available EDL capacitor using an organic electrolyte, typically propylene carbonate (PC) solution containing a tetraalkylammonium salt [2, 5]. However, the conductivity of an organic electrolyte solution is generally lower than that of an aqueous electrolyte. This may be a serious disadvantage for capacitors using organic electrolytes, because the conductance of the electrolyte relates closely to the equivalent series resistance of the capacitor. Thus, the choice of an organic electrolyte solution is of technical importance in the development of high performance EDL capacitors, as well as rechargeable lithium batteries [7].

In the present work we have examined ethylene carbonate (EC)-based organic electrolytes for EDL capacitors. EC is thermally and electrochemically stable, and has a high permittivity (dielectric constant), which contributes to a higher degree of dissociation for electrolytic salts. Thus, EC has been applied to the base solvent of the electrolytes for rechargeable lithium batteries [8, 9]. In battery technology, high melting point solvents such as EC (m.p.: 39–40°C) have been mixed with proper co-solvents to achieve operation at ambient temperatures [7, 10]. We have chosen sulfolane (SL) and γ -butyrolactone (γ -BL) as the co-solvents of EC from the standpoint of their electrochemical stabilities [11, 12]. The electrolytic conductivities of quaternary alkylammonium salts were measured in solutions with different solvent compositions. The thermal and electrochemical properties of the electrolytic solutions were evaluated by an accelerated heating test and potential sweep voltammetry, respectively. A model EDL capacitor was constructed with the resulting EC-based organic electrolyte sandwiched between two electrodes made of an activated carbon fibre cloth. The performance of the capacitor was investigated by charge-discharge cycling under a controlled current density.

2. Experimental details

Extra pure EC and γ -BL (Mitsubishi Petrochemical, 'Battery Grade') were used as received. SL (Tokyo Kasei Kogyo, GR grade) was used after purification by distillation [13, 14]. The electrolytes were tetraethylammonium (Et_4N^+) and tetra-n-butylammonium

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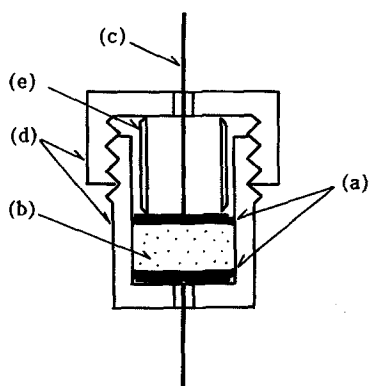


Fig. 1. Schematic illustration of the model capacitor. (a) Activated carbon fibre cloth (ACFC) electrodes, (b) electrolyte/polypropylene cloth separator, (c) lead wire, (d) Teflon case and (e) Teflon spacer.

(Bu_4N^+) salts of perchlorate (ClO_4^-), tetrafluoroborate (BF_4^-), and hexafluorophosphate (PF_6^-). These were used after drying under a vacuum at $70\text{--}100^\circ\text{C}$ for 24 h. The electrolyte solutions were prepared in a glove box filled with dry Ar. The water contents in the resulting solutions were generally below 300 p.p.m. (mg kg^{-1}).

The electrolytic conductivity was measured by an a.c. method (10 kHz). The viscosities of the solvents and the solutions were determined by using a modified Ostwald viscometer [15]. Potential sweep voltammetry was applied to determine the stable potential regions, so-called potential windows, of the electrolytes. A glassy carbon disk electrode (Yanaco, GC; 0.096 cm^2) was used as an indicator electrode. The reference and counter electrodes were an SCE and a GC plate (15 cm^2), respectively. The volume of electrolyte was about 50 cm^3 . These measurements were carried out at 25°C .

The thermal stability of the electrolytic solution was evaluated by an accelerated heating test. The solution was enclosed in a sealed Pyrex glass tube and then heated at 85°C for 500 h. Changes in the electrolytic conductivity and the absorption spectrum of the solution were measured.

A model capacitor was fabricated with a Teflon cell case (inner size: 13 mm diameter, 15 mm height). The capacitor assembly is schematically illustrated in Fig. 1. An activated carbon fibre cloth (ACFC) was used as the polarizable electrode (apparent surface area: 1.2 cm^2 , mass: about 27 mg). This ACFC was made from a phenolic resin and had a high surface area (specific surface area: $>1000\text{ m}^2\text{ g}^{-1}$). The current collector of the electrode was an Al layer coated by plasma spraying at one side of the cloth. A polypropylene non-woven cloth was used as a separator, which was impregnated with the electrolyte solution. The charge-discharge characteristics of the model capacitor were measured under a constant current cycling. The cut-off voltages of the cell were 2 V for charging and 1 V for discharging. The leakage current profile at a float voltage of 2 V and the capacitance loss from self-discharging were also examined by using the same model capacitor. These capacitor tests were carried out in

a dry argon atmosphere at room temperature ($16\text{--}22^\circ\text{C}$).

3. Results and discussion

3.1. Fundamental properties of the electrolytic solutions

Selective properties of the solvents, EC, SL and $\gamma\text{-BL}$, are listed in Table 1 and compared with those of PC, the standard organic solvent for the electrolyte in commercial EDL capacitors. These are aprotic solvents. Their permittivities (dielectric constants) are sufficiently high to dissociate the electrolytic salts almost completely in the solution. However, the relatively high viscosities of the solvents may be a disadvantage for the conduction of dissociated ions in the solution. The melting points of EC and SL are rather high, but their mixtures are liquids over wide mixing ratios even at lower temperatures ($\sim 0^\circ\text{C}$). The mixing ratios where the EC-based mixed solvents are liquid at room temperature are 10–80 mol % EC for EC + SL and 0–80 mol % EC for EC + $\gamma\text{-BL}$.

The electrolytic conductivity is one property that directly affects the resistance in the equivalent circuit of the capacitor. The higher equivalent series resistance causes a higher energy loss during charge-discharge cycling of the capacitor. Thus, a higher conductivity is required of the electrolyte solution. The conductivities (κ) of alkylammonium salts (0.5 M) in EC + $\gamma\text{-BL}$ and EC + SL as a function of the solvent composition are shown in Figs 2 and 3. In the EC + $\gamma\text{-BL}$ system, conductivity maxima were observed at EC concentration of 20–40 mol % although their dependence on the solvent composition was small. The preferred combination of the higher permittivity of EC and the lower viscosity of $\gamma\text{-BL}$ may contribute to the conductance in the mixed solvent systems [16, 17]. On the other hand, conductivities in the EC + SL system increased monotonically with increase in EC concentration in the solvent. This conductance behaviour is caused by the high viscosity of SL.

Viscosities of the mixed solvent and the solutions dissolving different salts (0.5 M) are shown in Figs 4 and 5. In both systems of EC + $\gamma\text{-BL}$ and EC + SL, the viscosity profiles showed monotonic changes with the solvent composition. The high viscosities of the EC + SL-based solutions at low EC concentration (high SL concentration) are responsible for their lower electrolytic conductivities. That is, despite the systems consisting of moderately concentrated electrolytes, Walden's rule apparently applied to the relation between the conductivity and the viscosity of the solution for both mixed solvent systems.

With respect to the electrolytic salt, solutions with higher viscosities gave lower conductivities. The order of the conductivity, $\text{Et}_4\text{NBF}_4 > \text{Et}_4\text{NClO}_4 \geq \text{Et}_4\text{NPF}_6 > \text{Bu}_4\text{NBF}_4 > \text{Bu}_4\text{NClO}_4$, seems to be associated with the order of the ion size. The ionic radius increases in the order $\text{Et}_4\text{N}^+ < \text{Bu}_4\text{N}^+$ for

Table 1. Selected properties of the organic solvents

Solvent	Melting point (m.p.)/°C (1 atm)	Relative permittivity (ϵ_r)	Viscosity (η)/10 ⁻² P	Donicity (DN)
Ethylene carbonate (EC)	39-40	89.6*	1.86*	16.4
γ -Butyrolactone (γ -BL)	-42	39.1†	1.751†	15.9
Sulfolane (SL)	28.86	42.5‡	9.87‡	14.8
Propylene carbonate (PC)	-49.2	64.4†	2.530†	15.1

*at 40°C, † at 25°C, ‡ at 30°C.

cations, and $\text{BF}_4^- \leq \text{ClO}_4^- < \text{PF}_6^-$ for anions [18]. The results shown in Figs 2 and 3 are consistent with this order. This also suggests that the alkylammonium cations and the Lewis acid anions are present at simple free ions in these organic solvent systems. That is, no ionic solvation will be taken into consideration for these electrolyte systems because of their large ionic radii [18-20].

A stable potential window, defined as a potential region where no appreciable Faradaic current flows at a polarizable electrode, is of practical importance for capacitor electrolytes, since it determines the maximum operational voltage of the capacitor. Figure 6 shows typical voltammograms measured at a GC electrode in the organic solutions containing different electrolytes. In this case, the mixing ratio of the solvent was held constant at 50/50 by mol for EC + SL and EC + γ -BL, and the electrolyte concentration was 0.5 M. It is assumed that the electrochemical decomposition of the solution substantially commences at the potential where the Faradaic current increases. In this work, the current density of 0.5 mA cm⁻² or higher was used as a diagnostic cur-

rent for the electrochemical decomposition. The decomposition potentials for the anodic and the cathodic limits (E_{da} and E_{dc} , respectively) are summarized in Table 2. It is apparent that the anodic potential limit of the solution is determined by the stability of the anion. The electrochemical stability of the anion increases in the order $\text{ClO}_4^- < \text{BF}_4^- < \text{PF}_6^-$. On the other hand, it appears that stabilities of both the cation of the electrolytic salt, and the solvent, affect the cathodic stability of the solution. The results shown in Table 2 reveal that the Bu_4N^+ salts are more stable than the Et_4N^+ salts. Also, somewhat lower E_{dc} 's of the $\text{Bu}_4\text{N}^+/\text{EC} + \text{SL}$ solutions than those of $\text{Bu}_4\text{N}^+/\text{EC} + \gamma\text{-BL}$ suggest that SL is less reducible than $\gamma\text{-BL}$. In any case, it is important that wide potential windows over 4.5 V are obtained for the EC-based solutions dissolving these alkylammonium salts.

The durability of the electrolytic solution was evaluated by an accelerated heating method. Solutions based on 50/50 (by mol) solvents were enclosed in Pyrex glass tube ampules under a vacuum and then heated at 85°C for 500 h. The electrolytic conductivity and the u.v. spectrum of the resulting solution were measured. Table 3 summarizes the conductivities of the solutions before and after the thermal treatment. The conductivities of the EC + SL solutions containing Et_4N^+ salts decreased slightly with the thermal treatment, whereas the Bu_4N^+ solutions of EC + SL

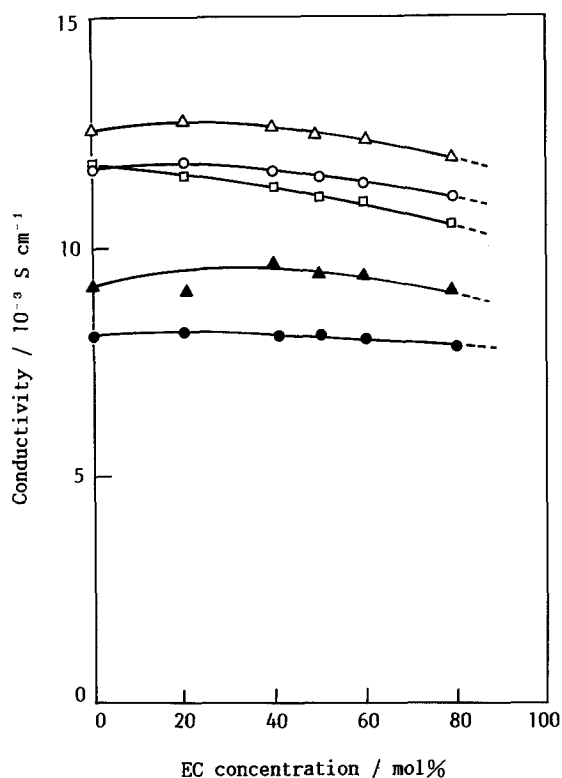


Fig. 2. Electrolytic conductivities of alkylammonium salts (0.5 M) in mixed EC + γ -BL at 25°C, (O) Et_4NClO_4 , (Δ) Et_4NBF_4 , (\square) Et_4NPF_6 , (\bullet) Bu_4NClO_4 , (\blacktriangle) Bu_4NBF_4 .

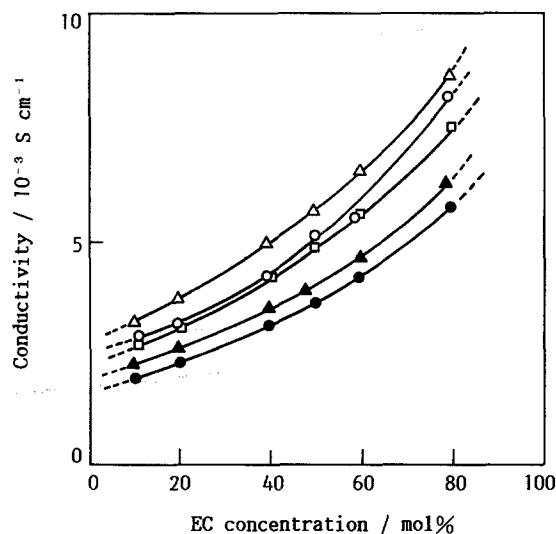


Fig. 3. Electrolytic conductivities of alkylammonium salts (0.5 M) in mixed EC + SL at 25°C, (O) Et_4NClO_4 , (Δ) Et_4NBF_4 , (\square) Et_4NPF_6 , (\bullet) Bu_4NClO_4 , (\blacktriangle) Bu_4NBF_4 .

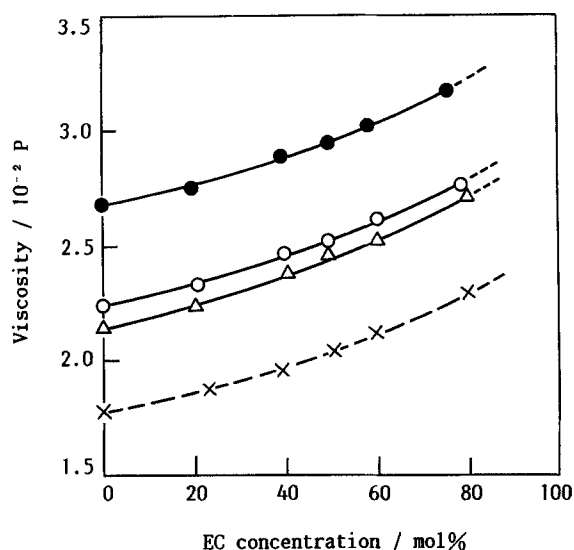


Fig. 4. Viscosities of mixed EC + γ -BL dissolving alkylammonium salts (0.5 M) at 25°C. (O) Et_4NClO_4 , (Δ) Et_4NBF_4 , (\bullet) Bu_4NClO_4 , (\times) solvent.

after heating gave insignificant increases in the conductivity. On the other hand, in the solutions based on EC + γ -BL, especially in the Et_4N^+ solutions, significant changes in the conductivity were observed after the thermal treatment. The increase in the conductivity with heating the solution was probably due to generation of some conducting species, and/or to a decrease in the viscosity of the solution by thermal decomposition of the solvent. Thus, the results shown in Table 3 suggest that the EC + γ -BL-based solutions are thermally less stable than the EC + SL-based electrolytes.

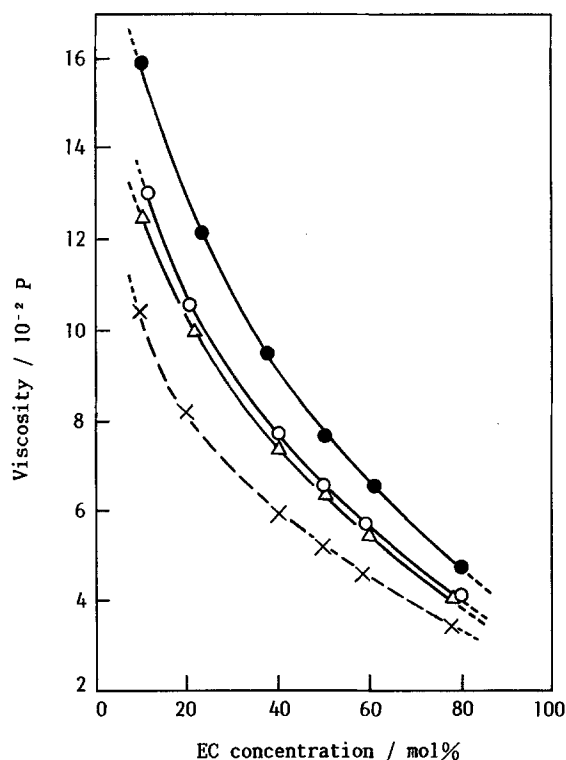


Fig. 5. Viscosities of mixed EC + SL dissolving alkylammonium salts (0.5 M) at 25°C. (O) Et_4NClO_4 , (Δ) Et_4NBF_4 , (\bullet) Bu_4NClO_4 , (\times) solvent.

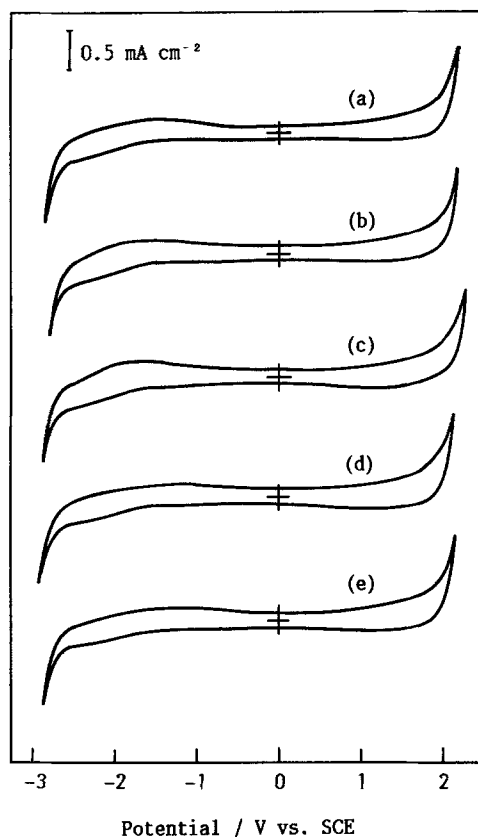


Fig. 6. Cyclic voltammograms at a GC electrode in mixed EC + γ -BL (50/50 by mol) dissolving alkylammonium salts (0.5 M) at 25°C. (a) Et_4NClO_4 , (b) Et_4NBF_4 , (c) Et_4NPF_6 , (d) Bu_4NClO_4 , (e) Bu_4NBF_4 . Scan rate: 50 mV s^{-1} .

Figure 7 shows typical u.v. spectra of the electrolytic solutions after thermal treatment. Hence, differences in the absorbances before and after the treatment (differential spectra) are recorded, for the purpose of monitoring changes in the chemical structure of the solution. In Fig. 7a, the positive absorbance in the differential spectrum (Δ absorbance) of EC + SL containing Et_4NClO_4 ($\sim 240 \text{ nm}$) means generation of some u.v.-active component by heating the solution, and the negative Δ absorbance at $\sim 280 \text{ nm}$ suggests that a u.v.-active group contained in the original solution disappeared after the thermal treatment. In contrast to this, the Bu_4NClO_4 solution after heating showed little change in the spectrum (Fig. 7b). These results are consistent with the variations in the electrolytic conductivity; the

Table 2. Stable potential window* of the organic electrolyte solution

Electrolyte	$E_{dc} - E_{da}$ (V/SCE)	
	EC + SL (50/50 by mol)	EC + γ -BL (50/50 by mol)
Et_4NClO_4	-2.6-+1.9	-2.7-+2.0
Et_4NBF_4	-2.6-+2.1	-2.7-+2.0
Et_4NPF_6	-2.8-+2.4	-2.8-+2.1
Bu_4NClO_4	-3.0-+1.9	-2.8-+1.9
Bu_4NBF_4	-2.9-+2.2	-2.8-+2.0

* Defined as a potential region where the Faradaic current does not exceed 0.5 mA cm^{-2} at a smooth glassy carbon electrode.

Table 3. Variation in the electrolytic conductivity with a thermal treatment at 85°C for 500 h

Electrolyte	Conductivity, $\kappa/10^{-3} \text{ S cm}^{-1}$			
	EC + SL (50/50 by mol)		EC + γ -BL (50/50 by mol)	
	Treatment		Treatment	
	Before	After	Before	After
Et ₄ NClO ₄	5.14	4.50	11.6	14.6
Et ₄ NBF ₄	5.70	4.81	12.5	16.1
Et ₄ NPF ₆	4.87	4.60	11.2	13.5
Bu ₄ NClO ₄	3.67	3.85	8.09	9.06
Bu ₄ NBF ₄	3.94	4.44	9.42	9.84

Bu₄N⁺ solutions with minimal conductance changes after the thermal treatment also showed insignificant changes in the u.v. spectra. The major changes in spectra (Fig. 7a) may explain the conductivity changes after heating, as shown in Table 3. However, this did not go for the γ -BL-based solutions. The u.v. spectra of EC + γ -BL dissolving Et₄N⁺ salts showed little change after the heat treatment, nevertheless rather serious changes in the conductance were observed (Table 3). Possible thermal deterioration in the EC + γ -BL-based electrolytes might not be reflected in the u.v. spectra.

3.2. Capacitor performance

Because this type of capacitor is commonly used as a power source [3], the charge-discharge properties of

the cell are the most important performance characteristic for EDL capacitors. Figures 8 and 9 show typical discharge performance for model capacitors with different organic electrolytes subjected to constant current charge-discharge cycling. The discharge capacitance, C , was determined by the following equation:

$$C = (i_D t_D) / \Delta V \quad (1)$$

where i_D is the discharge current, t_D the time required for discharging to the preset voltage, and ΔV the voltage difference (here 1 V). Discharge capacitances of 5–16 F (per 1 g carbon) were observed though the electrolyte composition influenced much on the discharge capacitance and its cycle transition. These capacitances are equivalent to the energy densities of 1.4–4.4 Ah kg⁻¹ (with respect to the carbon electrode). Higher capacitances were obtained for the cells using Et₄NBF₄ and Et₄NPF₆ salts. The use of Bu₄N⁺ salts

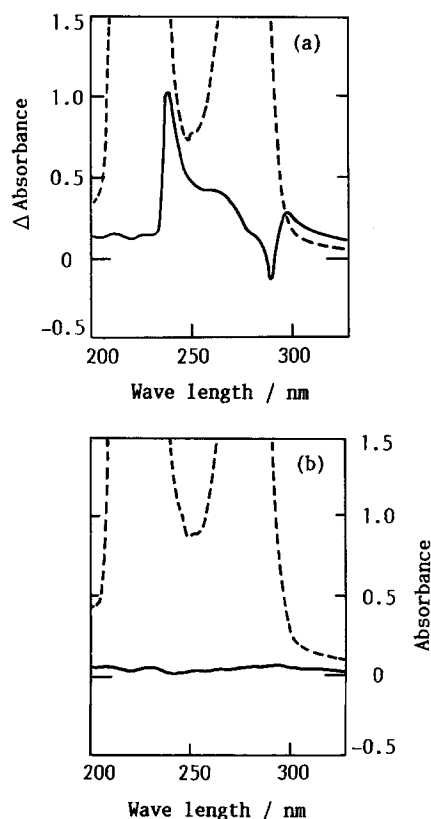


Fig. 7. Differential u.v. spectra of EC + SL (50/50 by mol) solutions dissolving (a) Et₄NClO₄ and (b) Bu₄NClO₄ (0.5 M) after heating at 85°C for 500 h. Reference solution: the same solution before heating, whose absolute spectrum is shown as a dashed line.

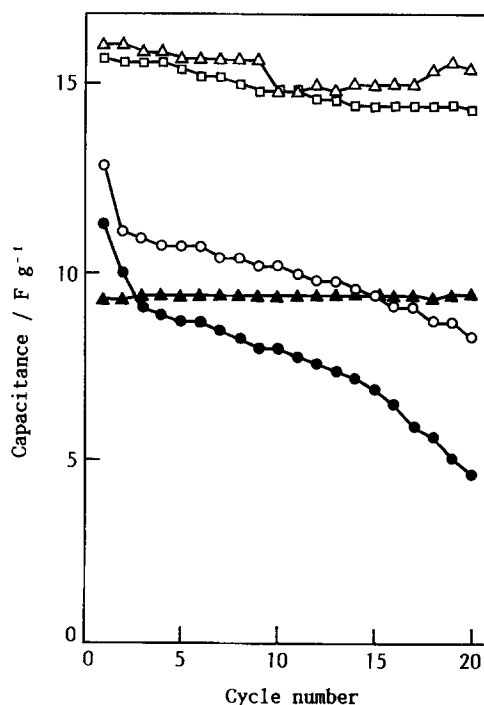


Fig. 8. Discharge capacitances of the model capacitors with EC + γ -BL (50/50 by mol) dissolving alkylammonium salts (0.5 M) as a function of the charge-discharge cycle. (O) Et₄NClO₄, (Δ) Et₄NBF₄, (□) Et₄NPF₆, (●) Bu₄NClO₄, (▲) Bu₄NBF₄.

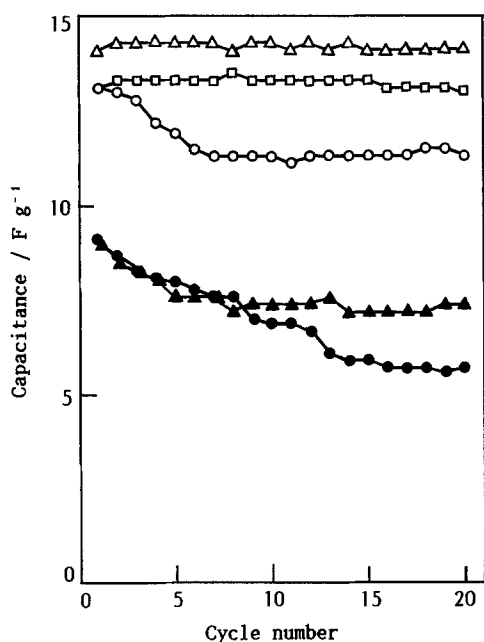


Fig. 9. Discharge capacitances of the model capacitors with EC + SL (50/50 by mol) dissolving alkylammonium salts (0.5M) as a function of the charge-discharge cycle. (○) Et_4NClO_4 , (Δ) Et_4NBF_4 , (\square) Et_4NPF_6 , (●) Bu_4NClO_4 , (\blacktriangle) Bu_4NBF_4 .

lead to rather lower discharge capacitances. This difference in the capacitance is probably caused by the difference in the amount of ion adsorbed at the carbon electrode. Since the geometric size of the Et_4N^+ cation is less than the Bu_4N^+ cation, the adsorbed amount of Et_4N^+ will be higher than that of Bu_4N^+ with respect to unit surface area of the carbon electrode.

The model capacitors using the mixed EC + γ -BL solvent generally gave higher capacitances than those using EC + SL. Relatively low capacitances in the EC + SL-based cells seem to correspond to their low conductances. The high viscosity of the EC + SL system causes low ionic mobility, and makes the solutions difficult to permeate the microporous structure of the electrode. That is, the high surface area of the carbon fibre electrode is not effectively utilized for ion adsorption from the electrolytic solution with higher viscosity.

The discharge capacitance of the cell with ClO_4^- salts decreased with repetitive cycling in both solvent systems. This suggests that solutions of ClO_4^- salts electrochemically degrade and/or cause deterioration of the surface properties of the carbon electrode through electrochemical oxidation and reduction. The percentage coulombic efficiency, η , is defined as

$$\eta = (Q_D/Q_C) \times 100 \quad (2)$$

where Q_D and Q_C are the amounts of electricity for discharging and charging, respectively. With respect to the coulombic efficiency, values of 95% or higher were obtained during the charge-discharge cycles in the capacitors with Et_4NBF_4 and Et_4NPF_6 . However, the efficiencies in the capacitors containing ClO_4^- salts were 80% or lower. The lower coulombic efficiencies in the ClO_4^- solutions mean that some irreversible

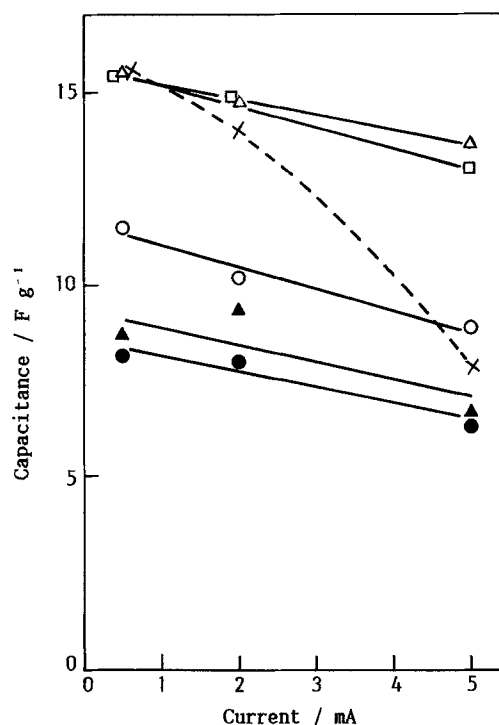


Fig. 10. Correlation between discharge capacitance and cycling current for the model capacitor with EC + γ -BL (50/50 by mol) dissolving alkylammonium salts (0.5M). (○) Et_4NClO_4 , (Δ) Et_4NBF_4 , (\square) Et_4NPF_6 , (●) Bu_4NClO_4 , (\blacktriangle) Bu_4NBF_4 , (×) Et_4NBF_4 in EC + SL (50/50).

process is occurring in these electrolyte systems during the charge-discharge cycles.

Figure 10 shows the dependence of the capacitance on the cycling current for the model capacitors with EC + γ -BL-based electrolytes. The discharge capacitance decreased with increase in the cycling current. This is probably due to a delay in the mass transport during the charge-discharge cycling under higher current densities. The different pore sizes in the active carbon electrode create an electrical double layer which can be modelled as a parallel combination of a series of electrical equivalent circuits with different impedances to describe the electrochemical processes (ion transport, adsorption/desorption) [21]. When the cycling current is sufficiently low, little polarization occurs. In this case, the electrochemical processes completely follow the electrical charging and discharging. On the other hand, under higher current densities, the electrochemical processes should not follow the current flowing in the electrical equivalent circuits with higher internal impedances. This was supported by the fact that the slopes of the capacitance-current relations in EC + SL were larger than those in EC + γ -BL, because the former electrolyte system had a higher viscosity and a lower conductance.

Self-discharge characteristics of the model capacitors with different electrolytes are shown in Fig. 11. The discharging curves were recorded under open circuit conditions after constant-current charging to a cell voltage of 2 V. For the capacitors with EC + γ -BL containing ClO_4^- salts, the cell voltage rapidly decayed on open circuit voltage after charging. The

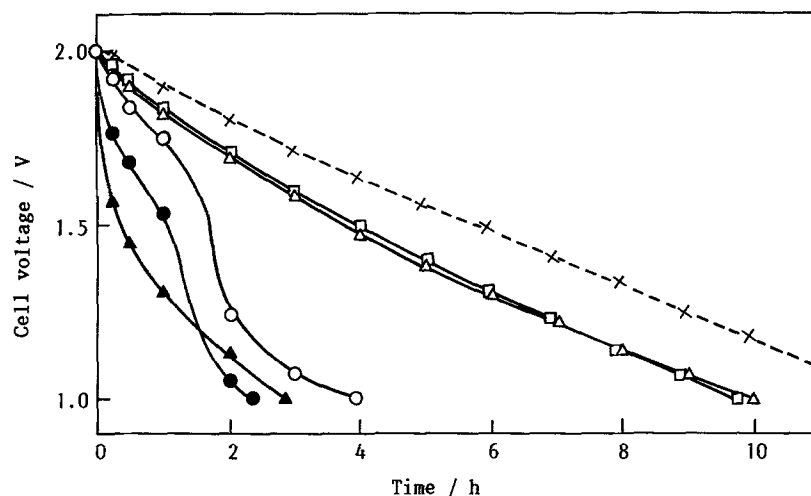


Fig. 11. Self discharge curves of the model capacitor with EC + γ -BL (50/50 by mol) dissolving alkylammonium salts (0.5M). (O) Et_4NClO_4 , (Δ) Et_4NBF_4 , (\square) Et_4NPF_6 , (\bullet) Bu_4NClO_4 , (\blacktriangle) Bu_4NBF_4 , (\times) Et_4NBF_4 in EC + SL (50/50).

Bu_4NBF_4 solutions also showed high rates of self-discharge. In contrast with these, Et_4NBF_4 and Et_4NPF_6 salts provided better voltage retention for both solvent systems. The leakage currents across the model capacitors, measured at 3 V floating, are summarized in Table 4. The results showed that the electrolyte with a higher leakage current generally leads to a higher self-discharge rate. This suggests that some common electrochemical reactions cause both phenomena of the self-discharge and the leakage current across the capacitor.

4. Conclusion

A new electrolyte system containing an EC-based mixed solvent has been proposed for an EDL capacitor. Fundamental properties obtained in this work are summarized as follows:

1. High electrolytic conductivities were observed for solutions with quaternary alkylammonium salts. The maximum conductivities were $1.3 \times 10^{-2} \text{ S cm}^{-1}$ for EC + γ -BL/ Et_4NBF_4 and $8.5 \times 10^{-3} \text{ S cm}^{-1}$ for EC + SL/ Et_4NBF_4 . The conductance profile of the solvent composition was correlated well with the solution viscosity.
2. The electrochemical stability of the solution was dependent on the anion of the electrolyte: $\text{ClO}_4^- < \text{BF}_4^- < \text{PF}_6^-$. With respect to the solvent, SL is less reducible than γ -BL. The EC + SL-based

electrolytes are thermally more stable than the EC + γ -BL-based electrolytes.

3. The model EDL capacitors consisting of active carbon electrodes and organic electrolytes gave electrical capacitances as high as $5\text{--}16 \text{ F (g carbon)}^{-1}$ ($= 1.4\text{--}4.4 \text{ Ah kg}^{-1}$). Stable charge-discharge performance and good self-discharge characteristics were obtained in the capacitors with EC + SL and EC + γ -BL containing Et_4NBF_4 or Et_4NPF_6 .

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Table 4. Leakage current in the model capacitor at a floating voltage of 2 V

Electrolyte	Leakage current*/ 10^{-4} A	
	EC + SL (50/50 by mol)	EC + γ -BL (50/50 by mol)
Et_4NClO_4	0.25	1.1
Et_4NBF_4	0.55	1.0
Et_4NPF_6	0.55	1.0
Bu_4NClO_4	0.50	1.3
Bu_4NBF_4	0.80	4.0

* Measured at 180 min after charging.

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