

Electrochemical Properties of Organic Liquid Electrolytes Based on Quaternary Onium Salts for Electrical Double-Layer Capacitors

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ABSTRACT

The electrolytic conductivities and limiting reduction and oxidation potentials for various organic liquid electrolytes based on quaternary onium salts have been measured to find better electrolytes for electrical double-layer capacitors. An electrolyte composed of tetraethylammonium cation, tetrafluoroborate anion, and propylene carbonate solvent showed well-balanced performance of high electrolytic conductivity, a wide stable potential window and resistance to hydrolysis. Among quaternary onium salts, triethylmethylammonium, ethylmethylpyrrolidinium, and tetramethylenepyrrolidinium tetrafluoroborate salts exhibited higher electrolytic conductivity than the conventional tetraethylammonium salt due to their much greater solubility.

The electrical double-layer capacitor is an electrochemical energy storage device in which electric charge is stored in the electrical double-layer formed at the interface between a polarizable electrode and an electrolyte solution when dc voltage is applied. Electrical double-layer capacitors composed of a pair of activated carbon electrodes with high surface area and an organic liquid electrolyte have been widely used as memory backup devices in many electronic appliances.¹⁻³

Recent interest in these capacitors has been stimulated by the prospective application to load levelers in electric vehicle propulsion systems, since ultracapacitors or power capacitors with large capacities have higher pulse power capability than conventional rechargeable batteries.^{1,2,4,5}

The organic liquid electrolyte for these capacitors requires a high electrolytic conductivity and a high electrochemical stability over a wide temperature range. These requirements are more stringent than those for lithium batteries. Therefore, the selection of electrolyte is restricted, for example, a popular electrolyte system comprising a lithium salt, a high permittivity solvent, and a low viscosity solvent⁶ cannot be used due to the low oxidation potential and low boiling point of the low viscosity solvent.

High permittivity solvents or their mixtures selected from propylene carbonate (PC),^{7,9,11,13-15} γ -butyrolactone

(GBL),^{7,8,10,12,16} N,N-dimethylformamide,^{7,10,12} ethylene carbonate,¹⁶ sulfolane,^{12,16,17} and 3-methylsulfolane¹⁷ have been examined by others.

In earlier research, alkali metal salts such as lithium perchlorate were examined as solutes in these liquid electrolytes,⁷⁻¹⁰ however, onium salts such as tetraalkylammonium^{11-13,16} or tetraalkylphosphonium salts^{14,15,17} have come into favor due to their better solubility and conductivity than the alkali metal salts in the high permittivity solvents.

Although tetraethylammonium tetrafluoroborate/PC electrolyte (0.5 to 1 mol dm⁻³) is the most common liquid electrolyte used in electrical double-layer capacitors,^{2,11,13} we have examined the electrochemical properties of various organic liquid electrolytes based on quaternary onium salts to gain a better understanding and find better electrolytes for electrical double-layer capacitors.

The electrolytic conductivity and stable potential window of an organic liquid electrolyte are important electrochemical properties. The electrolytic conductivity directly affects the internal resistance of a capacitor which leads to energy loss during charge-discharge cycling. The stable potential window determines the maximum operational voltage of a capacitor which manages total charge by CV product.

* Electrochemical Society Active Member.

Table I. Electrolytic conductivities of organic liquid electrolytes at 1 mol dm⁻³, 25°C.

Electrolyte	PC	GBL	DMF	AN
LiBF ₄	3.4	7.5	22	18
Me ₄ NBF ₄	2.7 ^a	2.9 ^a	7.0 ^a	10 ^a
Et ₃ NBF ₄	13	18	26 ^b	56 ^b
Pr ₂ NBF ₄	9.8	12	20 ^b	43 ^b
Bu ₄ NBF ₄	7.4	9.4	14 ^b	32 ^b
LiPF ₆	5.8	11	21	50
Me ₄ NPF ₆	2.2 ^a	3.7 ^a	11 ^a	12 ^a
Et ₃ NPF ₆	12	16	25	55
Pr ₂ NPF ₆	6.4 ^a	11	19	42
Bu ₄ NPF ₆	6.1	8.6	13	31
LiClO ₄	5.6	11	20	32
Me ₄ NClO ₄	2.9 ^a	3.9 ^a	7.8 ^a	7.7 ^a
Et ₃ NClO ₄	11	16	24 ^b	50 ^b
Pr ₂ NClO ₄	6.3 ^a	11 ^a	17 ^{a,b}	35 ^{a,b}
Bu ₄ NClO ₄	6.0	8.1	12 ^b	27 ^b
LiCF ₃ SO ₃	1.7	4.3	16	9.7
Me ₄ NCF ₃ SO ₃	9.0 ^a	14	24	46
Et ₃ NCF ₃ SO ₃	11	15	21 ^c	42 ^c
Pr ₂ NCF ₃ SO ₃	7.8	11	15 ^c	31 ^c
Bu ₄ NCF ₃ SO ₃	5.7	7.4	11 ^c	23 ^c

In mS cm⁻¹.

^a Saturated solution (<1 mol dm⁻³).

^b Ref. 20.

^c Ref. 25.

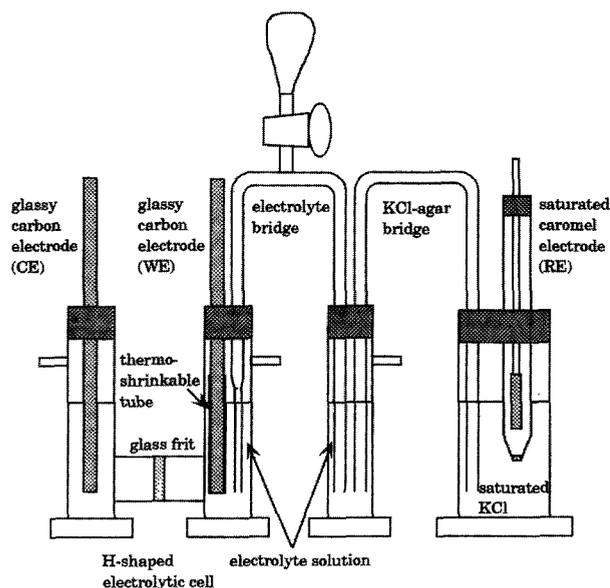


Fig. 1. Schematic diagram of cell assembly used in polarization experiments.

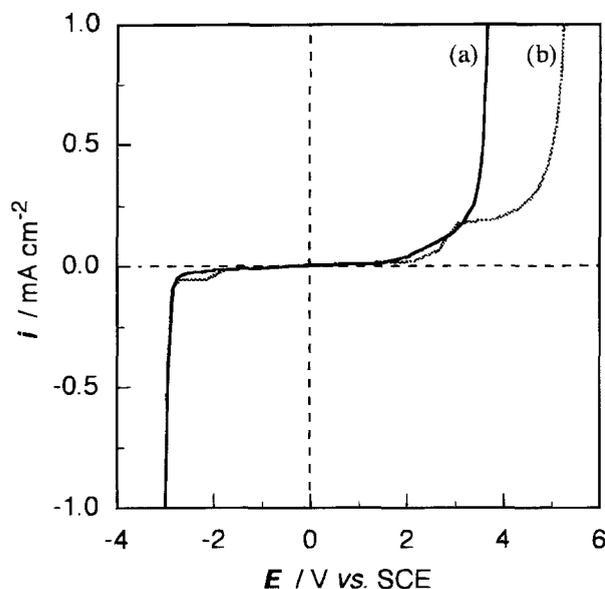


Fig. 2. Typical polarization curves of organic liquid electrolytes on a glassy carbon electrode: (a) $0.65 \text{ mol dm}^{-3} \text{ Et}_4\text{NBF}_4/\text{PC}$, (b) $0.65 \text{ mol dm}^{-3} \text{ Et}_4\text{NBF}_4/\text{GBL}$.

These electrochemical properties of organic liquid electrolytes are discussed from the chemical structures of three components: cation, anion, and solvent.

Experimental

Reagents.—Tetramethyl-, tetraethyl-, tetrapropyl- and tetrabutylammonium salts were prepared by the titration of perchloric acid (Wako Pure Chemical Industries), tetrafluoroboric acid (Morita Chemical Industries), hexafluorophosphoric acid (Morita Chemical Industries), and trifluoromethanesulfonic acid (Tokyo Chemical Industry Co.) with the corresponding tetraalkylammonium hydroxide aqueous solutions (SACHEM Inc.).

Ethyltrimethyl-, diethylmethyl- and triethylmethylammonium tetrafluoroborates were prepared by the neutralization of tetrafluoroboric acid with the corresponding quaternary ammonium bicarbonate aqueous solutions obtained from the reaction of appropriate amines with dimethyl carbonate.¹⁸

Tributylmethyl- and tetrahexylammonium tetrafluoroborates were prepared by the reaction of tributylmethylammonium iodide¹⁹ and tetrahexylammonium bromide¹⁹ with tetrafluoroboric acid.²⁰

Cyclic quaternary ammonium tetrafluoroborates were synthesized from the corresponding cyclic quaternary ammonium bromides by oxidative anion exchange in the presence of hydrogen peroxide and tetrafluoroboric acid.^{21,22} Cyclic quaternary ammonium bromides were prepared by a similar method described in the literature.^{23,24}

Tetramethyl-, tetraethyl-, tetrapropyl- and tetrabutylphosphonium tetrafluoroborates were prepared by the treatment of the corresponding tetraalkylphosphonium bromides (Tokyo Chemical Industry Co.) with tetrafluoroboric acid.

Table II. Electrolytic conductivities, limiting reduction and oxidation potentials of PC electrolytes at 0.65 mol dm^{-3} , 25°C .

Electrolyte	σ mS cm^{-1}	E vs. SCE	
		E_{red}	E_{ox}
Et_4NBF_4	10.55	-3.0	+3.6
Et_4NPF_6	9.64	-3.0	+3.6
Et_4NClO_4	9.94	-3.0	+3.1
$\text{Et}_4\text{NCF}_3\text{SO}_3$	9.38	-3.0	+3.1

Most salts were purified by repeated recrystallization from isopropanol or acetone. Salts with a larger cation than tetraethylammonium or phosphonium were purified by re-deposition into water from methanol or acetone solutions. All the salts were vacuum dried at 100°C .

Propylene carbonate, butylene carbonate, and γ -butyrolactone (Mitsubishi Petrochemical Co., Battery-grade F-PC, F-BC, and F-GBL) were used without further purification. All other solvents (Tokyo Chemical Industry Co.) were purified by careful distillation over molecular sieve 5A, which resulted in more than 99.8% purity detected by capillary gas chromatography.

Electrolyte preparation.—An electrolyte salt was dissolved in a purified solvent and the resulting electrolyte was vacuum dried at 50°C until water content dropped less than 100 ppm.

Measurements.—The relative permittivity and viscosity of solvents were measured by an LCR meter equipped with a capacitor cell (Ando Electric Co., AG-4311), and a viscosity meter (Tokyo Keiki Co., Visconic ED), respectively.

The electrolytic conductivity and water content of electrolytes were measured by a conductivity meter equipped with a standard conductivity cell (Toa Electronics, CM-60S/CGT-511B) and a moisture meter (Mitsubishi Kasei Co., CA-06), respectively.

The limiting reduction and oxidation potentials were measured by linear sweep voltammetry with an automatic polarization system (Hokuto Denko Co., HZ-1A). A pair of 3ϕ glassy carbon rods (Tokai Carbon Co., GC-10) were used as working and counterelectrodes. The sidewall of the working electrode was sealed with a thermo-shrinkable tube to limit the surface area to 7 mm^2 . The surface was polished with alumina powder before use. A saturated calomel electrode (SCE) (Toa Electronics, HC-205C) was isolated via KCl-agar and electrolyte bridge. Measurement was carried out in a nitrogen atmosphere glove box using the cell assembly depicted in Fig. 1.

Results and Discussion

Tetraalkylammonium salts have been widely used as supporting electrolyte salts in nonaqueous solvents, because of their high solubility, electrolytic conductivity, electrochemical stability, and ease of preparation and purification. However, systematic data such as the electrolytic conductivity at practical concentrations are surprisingly scarce and fragmented data are scattered in the literature.^{20,25,26}

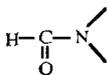
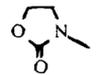
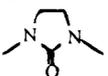
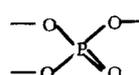
Selection of salt.—The electrolytic conductivities (σ) of lithium and symmetric tetraalkylammonium salts with popular anions²⁷ were measured in PC and GBL at 1 mol dm^{-3} , 25°C . The results are given in Table I, together with values in *N,N*-dimethylformamide (DMF) and acetonitrile (AN), which are mostly cited from the literature.^{20,25}

The conductivities generally decrease in the following order: $\text{Et}_4\text{N}^+ > \text{Pr}_4\text{N}^+ > \text{Bu}_4\text{N}^+ > \text{Me}_4\text{N}^+$, $\text{BF}_4^- > \text{PF}_6^- \geq \text{ClO}_4^- > \text{CF}_3\text{SO}_3^-$.

Tetramethylammonium salts were not useful except for trifluoromethanesulfonate due to their low solubilities. Tetraethylammonium salts are the most favorable in conductivity. The highest conductivity of tetraethylammonium tetrafluoroborate appears to come from the small anion size and moderate dissociation tendency.²⁸

The stable potential window is defined as a potential region where no appreciable faradaic current flows. Different criteria have been used for the evaluation of limiting reduction and oxidation potentials (E_{red} and E_{ox}) by different researchers. These values depend on the concentration and purity of a liquid electrolyte. Even though the same electrode and electrolyte are used, these values are also dependent on current density and potential scan rate. For example, as to the current density, 0.01,²⁹ 0.1,³⁰ 0.2,³¹ 0.5,^{16,32} 1,^{33,34} 1.5,³⁵ and 3 mA cm^{-2} ³⁶ were adopted by others. The scan rate ranged from 2 to 100 mV s^{-1} for these values.^{29,30,32,34-36}

Table III. Physical properties of dipolar aprotic solvents and electrolytic conductivities, limiting reduction and oxidation potentials of their organic liquid electrolytes containing 0.65 mol dm⁻³ tetraethylammonium tetrafluoroborate at 25°C.

Solvent	ϵ_r	η / cp	bp / °C	mp / °C	MW	σ / mS cm ⁻¹	E_{red} / V vs. SCE	E_{ox} / V vs. SCE	
propylene carbonate (PC)		65	2.5	242	-49	102	10.6	-3.0	+3.6
butylene carbonate (BC)		53 ^a	3.2 ^a	240 ^a	-53 ^a	116	7.5	-3.0	+4.2
γ -butyrolactone (GBL)		42	1.7	204	-44	86	14.3	-3.0	+5.2
γ -valerolactone (GVL)		34 ^a	2.0 ^a	208 ^b	-31 ^b	100	10.3	-3.0	+5.2
acetonitrile (AN)		36	0.3	82	-49	41	49.6	-2.8	+3.3
propionitrile (PN)		26 ^a	0.5 ^a	97	-93	55	insoluble		
glutaronitrile (GLN)		37 ^a	5.3 ^a	286 ^b	-29 ^b	94	5.7	-2.8	+5.0
adiponitrile (ADN)		30 ^a	6.0 ^a	295 ^b	2 ^b	108	4.3	-2.9	+5.2
methoxyacetonitrile (MAN)		21 ^a	0.7 ^a	120 ^b	-35 ^a	71	21.3	-2.7	+3.0
3-methoxypropionitrile (MPN)		36 ^a	1.1 ^a	165 ^b	-57 ^a	85	15.8	-2.7	+3.1
N,N-dimethylformamide (DMF)		37	0.8	153	-61	73	22.8	-3.0	+1.6
N,N-dimethylacetamide (DMA)		38	0.9	166	-20	87	15.7		
N-methylpyrrolidinone (NMP)		32	1.7	202	-24	99	8.9		
N-methyloxazolidinone (NMO)		78 ^c	2.5 ^c	270 ^b	15 ^b	101	10.7	-3.0	+1.7
N,N'-dimethylimidazolidinone (DMI)		38 ^d	1.9 ^d	226 ^d	8 ^d	114	7.0	-3.0	+1.2
nitromethane (NM)		38	0.6	101	-29	61	33.8	-1.2	+2.7
nitroethane (NE)		28 ^a	0.7 ^a	115 ^b	-90 ^b	75	22.1	-1.3	+3.2
sulfolane (TMS)		43	10.0	287	28	120	2.9	-3.1	+3.3
3-methylsulfolane (3MS)		29 ^e	11.7 ^e	276 ^b	6 ^b	134	insoluble		
dimethylsulfoxide (DMSO)		47	2.0	189	19	78	13.9	-2.9	+1.5
trimethyl phosphate (TMP)		21 ^a	2.2 ^a	197 ^b	-46 ^b	140	8.1	-2.9	+3.5

Physical properties are cited from Ref. 42 and 43 except ^a our data, ^b Ref. 45, ^c Ref. 29, ^d Ref. 46 and ^e Ref. 47.

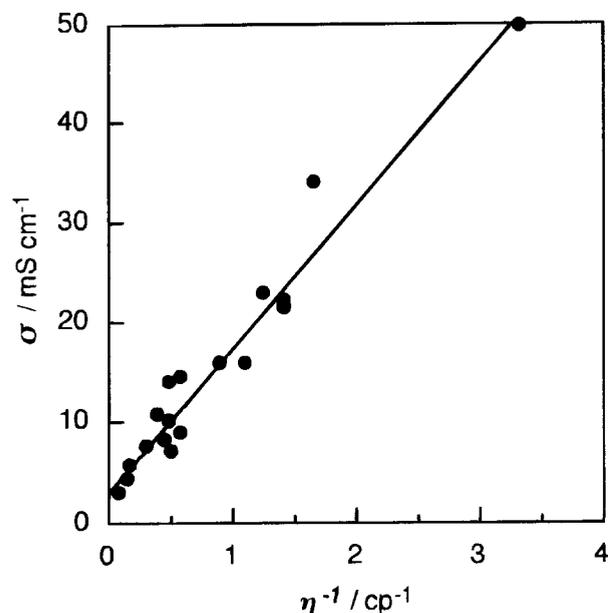


Fig. 3. Relationship between electrolytic conductivity of the electrolyte and reciprocal of viscosity of the solvent.

The limiting reduction and oxidation potentials were defined here as the potentials at which the current density exceeded 1 mA cm^{-2} when the supporting electrolyte concentration was 0.65 mol dm^{-3} ³⁷ and the scan rate was 5 mV s^{-1} . A glassy carbon electrode was used as a working electrode because it is a better substitute for the activated carbon electrode than platinum or mercury electrodes.

Typical polarization curves are shown in Fig. 2, where the cathodic and anodic polarizations were carried out separately, and potential is reported relative to the SCE.

The limiting reduction and oxidation potentials for tetraethylammonium salts in PC are summarized in Table II.

The reduction potential appeared to be limited by the decomposition of both tetraethylammonium cation and PC solvent because the reduction resulted in the formation of a polymer on the electrode and gas evolution, which contained carbon dioxide, propylene, and triethylamine.³⁸

The oxidation potentials were limited by the decomposition of ClO_4^- and CF_3SO_3^- not by BF_4^- and PF_6^- , which were more resistant to oxidation than PC. The electrochemical

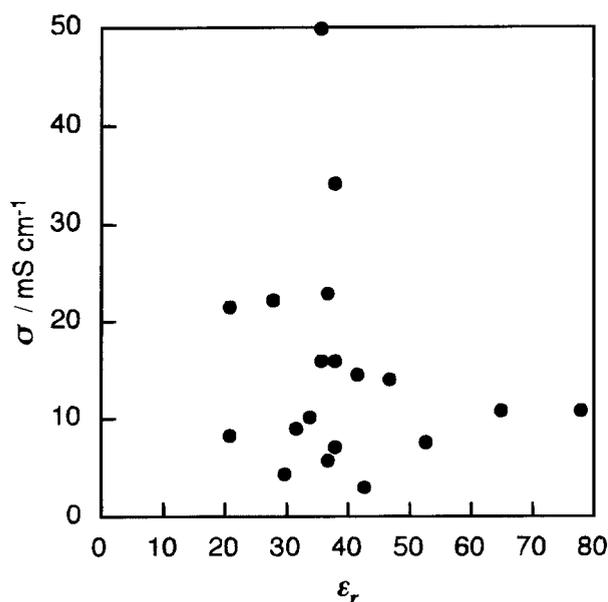


Fig. 4. Relationship between electrolytic conductivity of the electrolyte and relative permittivity of the solvent.

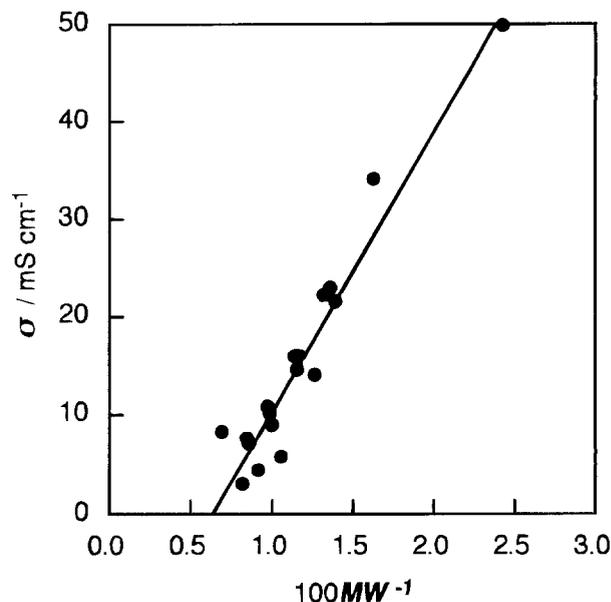


Fig. 5. Relationship between electrolytic conductivity of the electrolyte and reciprocal of molecular weight of the solvent.

stability of the anion increases in the following order:^{16,33,39} $\text{ClO}_4^- \leq \text{CF}_3\text{SO}_3^- < \text{BF}_4^- \leq \text{PF}_6^-$.

Selection of solvent.—Dipolar aprotic solvents, which exhibit no appreciable tendency to participate in the transfer of protons but are moderately good solvating and ionizing media due to their dipolar nature and their high relative permittivity more than 20,^{40,41} are essential for the liquid electrolyte of electrical double-layer capacitors to gain a large enough stable potential window. Twenty dipolar aprotic solvents have been selected, whose melting point (mp) and boiling point (bp) are below 30°C and over 100°C (except AN), respectively. These include not only popular solvents such as carbonate, lactone, nitrile, amide, nitro, sulfone, sulfoxide, and phosphate,^{42,43} but also uncommon difunctional solvents such as dinitrile and ether-nitrile. Two homologues were selected in each category, if possible, as shown in Table III, where physical properties of these solvents are listed.

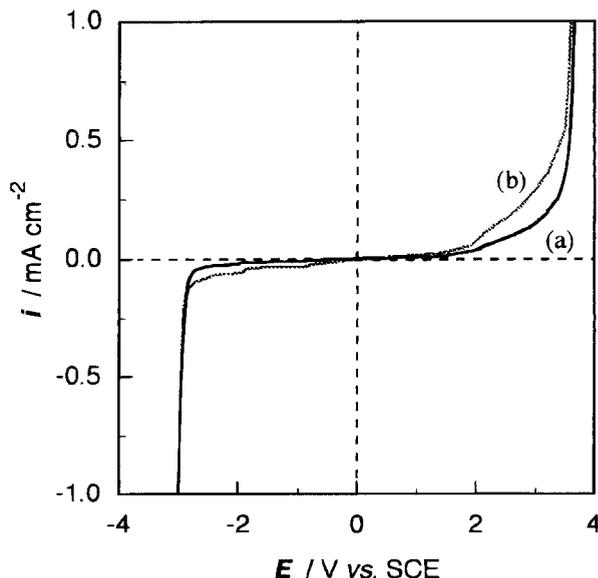


Fig. 6. Effect of contaminated water on electrochemical potential window of $0.65 \text{ mol dm}^{-3} \text{ Et}_4\text{NBF}_4/\text{PC}$ electrolyte: (a) Ag wire (H_2O ; 30 ppm), (b) SCE (H_2O ; 100 ppm).

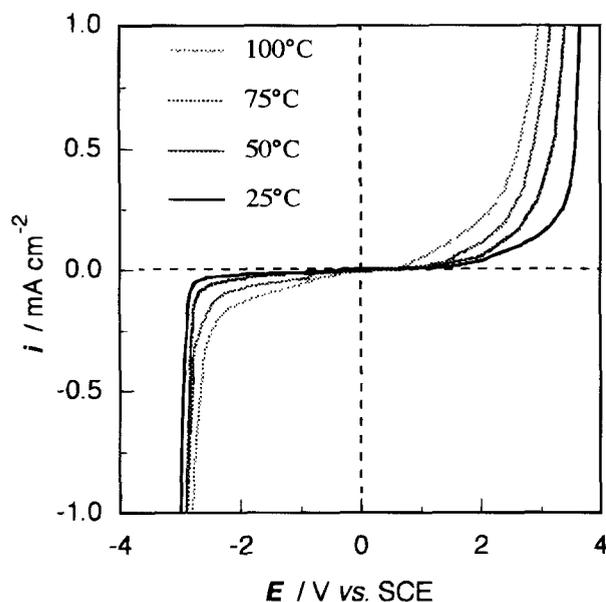


Fig. 7. Effect of temperature on electrochemical potential window of $0.65 \text{ mol dm}^{-3} \text{Et}_4\text{NBF}_4/\text{PC}$ electrolyte.

Since Et_4NBF_4 showed the highest conductivity and BF_4^- is more stable to hydrolysis than PF_6^- ,⁴⁴ we have adopted Et_4NBF_4 as the supporting electrolyte salt for examining solvents. Electrolytic conductivities and limiting reduction and oxidation potentials of the liquid electrolytes containing $0.65 \text{ mol dm}^{-3} \text{Et}_4\text{NBF}_4$ are given in Table III.

Electrolytic conductivity.—Many solvents with lower viscosities than PC showed higher conductivity of electrolytes. The observed electrolytic conductivities of the electrolytes were plotted against the reciprocals of the solvent viscosities (η). A good linear relationship was obtained as shown in Fig. 3 (correlation coefficient $r = 0.97$). No correlation between the electrolytic conductivity of the electrolyte and the relative permittivity (ϵ_r) of the solvent was observed as shown in Fig. 4. These results indicate that Et_4NBF_4 is almost equally dissociated in any higher permittivity solvent ($\epsilon_r > 20$), and conductivity is only dependent on ionic mobility. Therefore, Walden's law is realized in these concentrated solutions.

We have found a close relationship between the electrolytic conductivity of the electrolyte and the reciprocal of molecular weight (MW) of the solvent as shown in Fig. 5 ($r = 0.96$). This observation suggests the existence of some solvent-solute interaction. Because ionic mobility depends on the formula weight (FW) of the ion,²⁸ which apparently can be increased by the solvation.

Although there is no quantitative information on solvent-solute interaction, the molecular weight of the solvent can act as a good parameter to estimate the electrolytic conductivity in onium salt/dipolar aprotic solvent systems. For example, PC, γ -valerolactone, and N-methyloxazolidinone have similar cyclic structures and molecular weight. They showed almost the same electrolytic conductivity.

Stable potential window.—Direct comparison of limiting reduction and oxidation potentials is not precise. In principle, this is because the liquid junction potential between an organic liquid electrolyte and an aqueous saturated KCl solution is varied by the kind of organic liquid electrolyte. However, the values obtained are useful from a practical viewpoint because they are reproducible within *ca.* 0.1 V.

Most solvents except nitroalkanes showed a similar reduction potential (-3.0 V vs. SCE), which may be limited by the decomposition of tetraethylammonium cation. The

limiting oxidation potential was extended by the use of lactones and dinitriles. Although the more positive oxidation potential of GBL than PC has already been known,^{7,35} the oxidation potential of γ -valerolactone was reported to be lower than that of PC on a platinum electrode.³⁵ The durability of dinitriles against oxidation is first demonstrated, to our knowledge, here. The solvents with amide or sulfoxide structures showed much lower oxidation potentials due to the existence of a lone-pair on nitrogen or sulfur atom. This is the main reason why these solvents have not been used in electrical double-layer capacitors.

Effect of contaminated water.—The main factor producing ambiguity in some properties of dipolar aprotic solvents is contamination by water because a trace amount of amphiprotic solvents substantially alters the nature of the electrode process in aprotic solvent systems.

During the polarization experiments, a narrower potential window, particularly a lower oxidation potential, was observed when water contamination exceeded *ca.* 300 ppm. To avoid water contamination from an aqueous reference electrode (SCE), a silver wire was often used to get reliable values. Although the equilibrium potential of Ag/Ag^+ (dissolved anodically) shifted in some cases, almost the same stable potential window and lower residual current were observed when the SCE reference electrode was replaced with a silver wire as shown in Fig. 6. Utilization of this simple reference electrode enabled the measurements at elevated temperatures as shown in Fig. 7. The stable potential window shrank as temperature increased. Such measurement at an elevated temperature is useful for understanding the behavior of actual capacitor cells.

Current increase caused by hydrolysis of both solvent and solute was confirmed by polarization experiments, where the addition of water was correlated with hydrolysis products. For example, hydrolysis products such as propylene glycol from PC,⁴⁸ γ -hydroxybutyric acid from GBL,⁴⁹ and $\text{HF} + \text{BF}_3(\text{OH})^-$ from BF_4^- ⁵⁰ were detected.

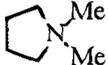
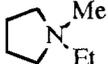
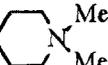
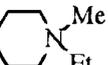
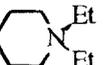
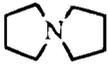
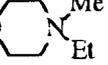
GBL is the most promising solvent from the viewpoint of electrolytic conductivity and a stable potential window as shown in Table III. However, it is more susceptible to hydrolysis than PC which hindered its intrinsic electrochemical stability.

Optimization of quaternary onium cation.—The effect of cation structure of quaternary onium tetrafluoroborate salts on the electrochemical properties of their PC electrolytes was examined. The electrolytic conductivities and limiting reduction and oxidation potentials of organic liquid electrolytes consisting of many kinds of quaternary ammonium or phosphonium tetrafluoroborate and PC are given in Table IV.

Electrolytic conductivity.—Previously, we have reported that the maximum electrolytic conductivity of organic liquid electrolytes at practical concentrations was observed for asymmetric quaternary ammonium salts with sizes between those of tetramethylammonium and tetraethylammonium salts.^{28,51} This observation was confirmed further by the introduction of cyclic quaternary ammonium salts in this work. Higher conductivities were obtained for quaternary ammonium salts with formula weights between those of tetramethylammonium and tetraethylammonium salts as shown in Fig. 8. Quaternary phosphonium salts showed a little bit lower electrolytic conductivity than corresponding ammonium salts¹⁴ except for the tetramethylphosphonium salt, which has much better solubility than the tetramethylammonium salt, presumably because of a larger atomic radius for phosphorus than nitrogen. However, quaternary phosphonium salts appear to show the same conductivity behavior as the quaternary ammonium salts.

To understand the reason why asymmetric quaternary ammonium salts such as triethylmethylammonium, ethylmethylpyrrolidinium, and tetramethylenepyrrolidinium

Table IV. Electrolytic conductivities, limiting reduction and oxidation potentials of propylene carbonate electrolytes containing 0.65 mol dm^{-3} quaternary ammonium or phosphonium tetrafluoroborate at 25°C .

Electrolyte	σ / mS cm^{-1}	E_{red} / V vs. SCE	E_{ox}	Electrolyte	σ	E_{red}	E_{ox}
$\text{Me}_4\text{N BF}_4$	2.41*	-3.10*	+3.50*	 BF_4	10.36	-3.00	+3.65
$\text{Me}_3\text{EtN BF}_4$	10.16	-3.00	+3.60	 BF_4	10.82	-3.00	+3.70
$\text{Me}_2\text{Et}_2\text{N BF}_4$	10.34	-3.00	+3.65	 BF_4	10.40	-3.00	+3.60
$\text{MeEt}_3\text{N BF}_4$	10.68	-3.00	+3.65	 BF_4	10.20	-3.05	+3.65
$\text{Et}_4\text{N BF}_4$	10.55	-3.00	+3.65	 BF_4	10.40	-3.05	+3.70
$\text{Pr}_4\text{N BF}_4$	8.72	-3.05	+3.65	 BF_4	10.17	-3.05	+3.60
$\text{MeBu}_3\text{N BF}_4$	7.80	-3.05	+3.65	 BF_4	10.94	-3.00	+3.60
$\text{Bu}_4\text{N BF}_4$	7.23	-3.05	+3.65	 BF_4	9.67	-3.00	+3.60
$\text{Hex}_4\text{N BF}_4$	5.17	-3.10	+3.85	 BF_4	8.78	-3.00	+3.60
$\text{Me}_4\text{P BF}_4$	9.21	-3.05	+3.60				
$\text{Et}_4\text{P BF}_4$	10.52	-3.00	+3.60				
$\text{Pr}_4\text{P BF}_4$	8.63	-3.05	+3.60				
$\text{Bu}_4\text{P BF}_4$	7.14	-3.05	+3.80				

* 0.1 mol dm^{-3}

tetrafluoroborates have higher conductivities than the symmetric tetraethylammonium salt, the degree of dissociation at 0.65 mol dm^{-3} was calculated by the equation, $\alpha = \Lambda/\Lambda_0$, where α , Λ , and Λ_0 are the degree of dissociation, molar conductivity, and limiting molar conductivity, respectively. The results are given in Table V, where the limiting molar conductivities of acyclic quaternary ammonium

salts are experimental values and those for cyclic quaternary ammonium salts are estimated values.²⁸

Triethylmethylammonium, ethylmethylpyrrolidinium, and tetramethylenepyrrolidinium tetrafluoroborates have almost the same degree of dissociation as the tetraethylammonium salt. We conclude that the higher conductivities of these three salts come from their smaller ion sizes without losing their high dissociation nature even at the practical concentration of 0.65 mol dm^{-3} .

These results have encouraged us to examine the electrolytic conductivity for more concentrated solutions, and we have found these three salts increase their conductivities until about 2 mol dm^{-3} due to their high solubility in PC, whereas the tetraethylammonium counterpart can be dissolved up to only 1 mol dm^{-3} , as shown in Fig. 9.

Stable potential window.—All quaternary ammonium and phosphonium tetrafluoroborates showed similar limiting reduction and oxidation potentials as shown in Table IV. No remarkable negative potential shift for limiting reduction potentials with increasing cation size was observed as was observed on mercury electrodes.^{20,31,34}

Conclusion

1. An electrolyte composed of tetraethylammonium cation, tetrafluoroborate anion, and PC solvent showed well-balanced performance of high electrolytic conductivity, a wide stable potential window, and durability against hydrolysis.

2. GBL is another promising solvent when water contamination is avoided.

3. Triethylmethylammonium, ethylmethylpyrrolidinium, and tetramethylenepyrrolidinium tetrafluoroborates are promising salts increasing electrolytic conductivity at high concentrations.

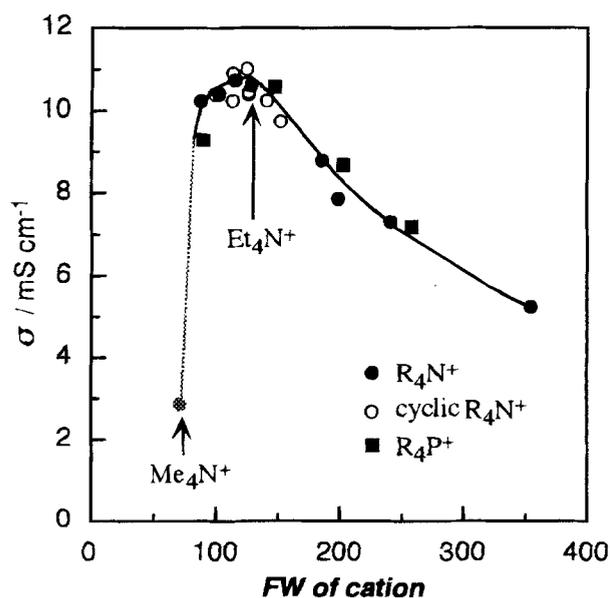
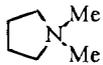
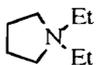
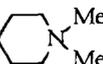
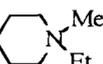
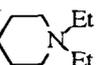
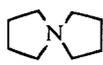
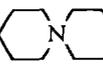


Fig. 8. Relationship between electrolytic conductivity of the electrolyte and formula weight of quaternary ammonium and phosphonium cation.

Table V. Calculated molar conductivities, limiting molar conductivities, and degree of dissociation.

Electrolyte	Λ / S cm ² mol ⁻¹	Λ_0^a	α
Me ₄ N BF ₄	24.10*	35.0	0.69*
Me ₃ EtN BF ₄	15.63	34.9	0.45
Me ₂ Et ₂ N BF ₄	15.91	34.6	0.46
MeEt ₃ N BF ₄	16.43	34.3	0.48
Et ₄ N BF ₄	16.23	33.8	0.48
 BF ₄	15.94	34.4	0.46
 BF ₄	16.65	34.2	0.49
 BF ₄	16.00	34.0	0.47
 BF ₄	15.69	34.2	0.46
 BF ₄	16.00	34.0	0.47
 BF ₄	15.65	33.8	0.46
 BF ₄	16.83	34.0	0.50
 BF ₄	14.88	33.6	0.44

* 0.1 mol dm⁻³, ^a Ref. 28.**Acknowledgment**

The authors thank Matsushita Electronic Components Company, Limited, for valuable discussion.

Manuscript submitted Feb. 14, 1994; revised manuscript received June 7, 1994.

Mitsubishi Petrochemical Company, Limited, assisted in meeting the publication costs of this article.

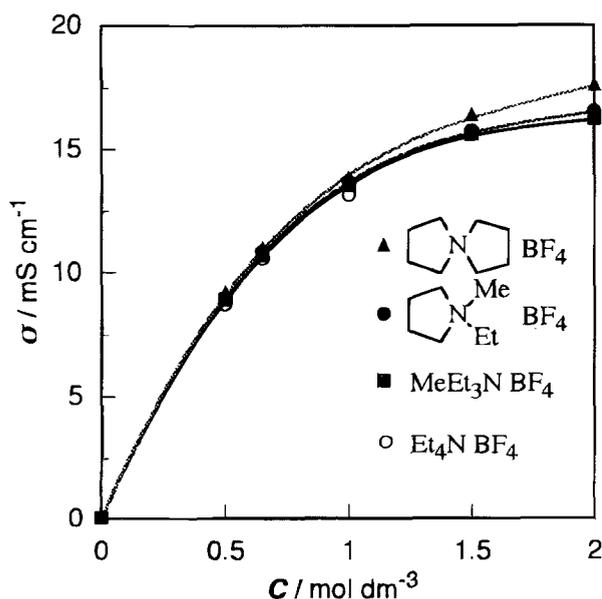


Fig. 9. Concentration dependence of electrolytic conductivities of several quaternary ammonium tetrafluoroborates in propylene carbonate at 25°C.

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Voltammetric Investigation of Hydrogen Sorption/Desorption at/within Oxide-Derived Pd Electrodes in NaOH and H₂SO₄

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ABSTRACT

Oxide-derived Pd electrodes are prepared from PdO-coated titanium electrodes (fabricated by thermal decomposition) after polarization at 0 V (*vs.* reversible hydrogen electrode, RHE) for 30 min. Hydrogen sorption/desorption at/within these electrodes as well as that at ordinary bulk Pd were compared by cyclic voltammetry. In contrast to the results for a bulk palladium electrode, both hydrogen adsorption and absorption peaks are clearly observed on the negative CV sweeps and hydrogen evolution commences after the hydrogen absorption becomes saturated for the oxide-derived Pd electrodes in NaOH and H₂SO₄ solutions. Different sources of proton supply (H⁺/H₃O⁺ in acid and H₂O in base), HSO₄⁻, SO₄²⁻ adsorption, and hydrogen damage of the Pd lattice structure account for the different responses in acidic and basic solutions. Surface morphologies of the bulk Pd and the oxide-derived Pd electrodes (where oxide is reduced in either acidic or basic solutions) were examined by scanning electron microscopy to elucidate the effect of surface roughness.

Platinum and palladium are recognized as being the best catalysts for the hydrogen evolution reaction (HER) during water electrolysis.¹ Unlike for Pt, hydrogen adsorption/desorption is practically impossible to investigate with an ordinary bulk Pd electrode since it is masked by the hydrogen absorption/desorption reaction.^{2,3} In 1975, Chevillot *et al.* studied the electrochemical behavior of hydrogen adsorption at a Pd black surface and found that two superficially adsorbed forms of hydrogen species were distinguishable.⁴ However, the behavior of both the hydrogen adsorption and absorption (together denoted hereafter as sorption) still has not been studied intensively and clearly. Recently, the influences of particle size, film thickness, and heat-treatment on hydrogen absorption have been studied^{5,6} on Pd. Moreover, Bucur and Bota,⁷⁻⁹ McBreen,¹⁰ and Szpak *et al.*¹¹ reported that sorption of hydrogen and deuterium at Pd is influenced by anion (*e.g.*, Cl⁻, S²⁻, CN⁻, and HSO₄⁻, etc.) and cation (Li⁺ and Na⁺, etc.) adsorption. These results indicate that there are complicated interactions between Pd and H.

During the past five years, the interest in the electrochemical behavior of the Pd-H and Pd-D systems has been prompted by reports that nuclear effects are induced by electrochemical compression of D within the Pd lattice.^{12,13} The compression which was reported to be responsible for this phenomenon was thought to be governed by the processes happening at the interface of the electrode and electrolyte solution; therefore, the complicated hydrogen sorption/desorption (*i.e.*, ¹H¹, ¹H², and ¹H³) at/within Pd have been widely studied recently.¹⁴⁻¹⁷ Although the cold nuclear fusion process is not presently being studied, an important finding was that the hydrogen sorption/desorption was dependent on the source of Pd.^{5,6,18,19} This may affect the activity of Pd for electrocatalytic hydrogenation of organic reactants.²⁰ Therefore, the use of modified Pd electrodes for the study of hydrogen sorption/desorption is practically important.

* Electrochemical Society Active Member.

The results in our previous paper¹⁸ revealed that two sorbed-hydrogen species are formed at such Pd electrodes prepared from PdO-coated titanium electrodes after polarization at 0 V (RHE) for 30 min. Moreover, quasi-reversible hydrogen sorption/desorption behavior was also observed in this Pd-H system. From recent results of both x-ray diffraction (XRD)¹⁸ and x-ray photoelectron spectroscopy (XPS),²¹ all the PdO on the initial PdO-coated electrodes has been reduced to Pd metal without any residual PdO. Our work clarifies the electrochemical behavior of hydrogen sorption and desorption at/within such electrodes in both NaOH and H₂SO₄ solutions to further understanding of the interactions between Pd and H which is important to both organic hydrogenation and any possible Fleischmann and Pons' effect.

Experimental

The preparation of PdO-coated titanium electrodes has been detailed in our previous paper.¹⁸ Oxide-derived Pd electrodes were obtained from a PdO-coated electrode after polarization at 0 V (RHE) for 30 min in either 1 mol dm⁻³ NaOH or 0.5 mol dm⁻³ H₂SO₄, which were always examined in their respective basic and acidic solutions. The bulk Pd electrode (99.9% pure) was provided by ELECMAT (USA). The working electrodes were painted with epoxy resin and then coated with polytetrafluoroethylene (PTFE) films with an exposed geometric area equal to 1 cm².

An electrochemical analyzer, BAS-100B (Bioanalytical System, Inc., USA) was used throughout. The electrochemical characteristics of the prepared electrodes were investigated by cyclic voltammetry. An Ag/AgCl electrode (Argenthal, 3 mol dm⁻³ KCl, 0.207 V at 298 K) was used as the reference, while a platinum wire was employed as the counterelectrode. A Luggin capillary, whose tip was set at a distance of *ca.* 2 mm from the surface of the working electrode, was used to minimize errors due to iR drop in the electrolytes. All data are reported relative to RHE. Voltammetry was carried out at various rates and in different po-