

— **Headline** —

Chemical Capacitors and Quaternary Ammonium Salts

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A capacitor is an electrical device that can store energy in an electric field between a pair of closely spaced conductors. Its application as an energy storage device—an alternative to rechargeable batteries—has been receiving considerable attention. There are chemical capacitors using liquid electrolytes such as aluminum electrolytic capacitors and double-layer capacitors, and they utilize quaternary ammonium salts in their nonaqueous electrolytes. After a brief explanation of the working principles of these chemical capacitors and their requirements for electrolytes, the practical applications of quaternary ammonium salts for aluminum electrolytic capacitors and double-layer capacitors are reviewed from the historical and technological viewpoints based on research conducted in our laboratory.

Key Words : Aluminum Electrolytic Capacitor, Double-Layer Capacitor, Liquid Electrolyte, Quaternary Ammonium Salt

1 Introduction

A capacitor is an electrical device that can store energy in an electric field between a pair of closely spaced conductors. Capacitors are one of the passive components (LCR) of the electrical circuits used in many electronic appliances. Besides application as an impedance device that differentiates between high-frequency and low-frequency signals (filtering, signal processing), their application as an energy storage device (an alternative to rechargeable batteries) has been receiving considerable attention.¹⁾

As far as the capacitor shown in Fig. 1 is concerned, there is no electrochemistry where reactions between an electrode (electronic conductor) and an electrolyte (ionic conductor) are studied. However, there are chemical capacitors that utilize liquid electrolytes, *i.e.*, aluminum electrolytic capacitors and double-layer capacitors. It is interesting to note that the first capacitor, the Leyden jar, which was invented in 1745 and 1746 independently

by German scientist Ewald Georg von Kleist and Dutch physicist Pieter van Musschenbroek at the University of Leyden, also utilized a liquid electrolyte. The earliest form of the device consisted of a glass jar, partly filled with water, having a metallic nail inserted through a cork to touch the water, which happened to be impure and thus acted as a conductor.

Nonaqueous electrochemistry, on the other hand, developed from rapid scientific and technological advances in electrochemistry including, for example, the inventions of conducting polymers and lithium-ion batteries.^{2,3)} Although quaternary ammonium salts such as R_4NY ($R = C_2H_5, C_4H_9, Y = ClO_4, BF_4, \text{ and } PF_6$) have long been used as supporting salts for electrochemical measurements in nonaqueous media,^{4,5)} they now have industrial application as supporting salts for nonaqueous electrolytes in chemical capacitors. Here, the author reviews the historical and technological aspects of quaternary ammonium salts in practical application based on research conducted over the past twenty years in our laboratory.

2 The Physics of Capacitors

When a voltage V is applied to a capacitor, electric charges of equal magnitude Q , but opposite polarity, build up on each plate, as shown in Fig. 1. The capacitance C is a measure of the amount of electric charges and is defined by:

$$C = Q/V. \quad (1)$$

The capacitance is given by:

$$C = \epsilon A/d, \quad (2)$$

where ϵ , A , and d are the permittivity of the dielectric, the surface area of the conducting plates (electrodes),

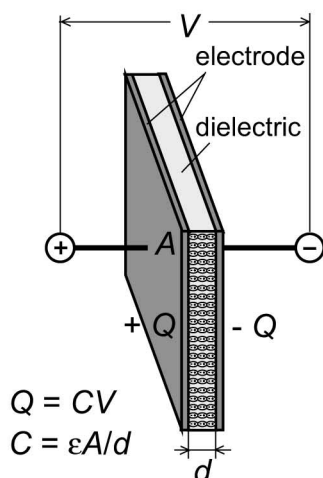


Fig. 1 Basic concept of capacitors.

Table 1 Classification and characteristics of main capacitors.

Type	dielectric	C/F	ϵ_r	d/nm	R_f	V_b/Vnm^{-1}
ceramic	metal oxides (BaTiO ₃ , etc)	$10^{-12} \sim 10^{-5}$	$10^2 \sim 10^4$	$10^2 \sim 10^5$	1	$10^{-3} \sim 0.2$
aluminum electrolytic	Al ₂ O ₃	$10^{-7} \sim 10^0$	8 ~ 10	$10 \sim 10^3$	~ 180	0.7
tantalum electrolytic	Ta ₂ O ₅	$10^{-7} \sim 10^{-4}$	23 ~ 27	10 ~ 500	~ 400	0.6
film	plastic (PET, etc)	$10^{-9} \sim 10^{-5}$	2 ~ 4	$500 \sim 10^4$	1	0.02
double-layer	electrolyte	$10^{-2} \sim 10^4$	3 ~ 7	~ 0.5	~ 10^7	3

R_f : roughness factor

and the distance between them, respectively. The energy stored is given by:

$$E = 1/2 QV = 1/2 CV^2. \quad (3)$$

The maximum energy that can be stored in a capacitor is limited by the maximum electric field that the dielectric can withstand before it breaks down. Practical capacitors are often classified according to the material used as the dielectric listed in Table 1, where the relative permittivity is defined by:

$$\epsilon_r = \epsilon/\epsilon_0, \quad (4)$$

where ϵ_0 is the permittivity of a vacuum ($8.854 \times 10^{-12} \text{ Fm}^{-1}$).

3 Aluminum Electrolytic Capacitors

3.1 Outline

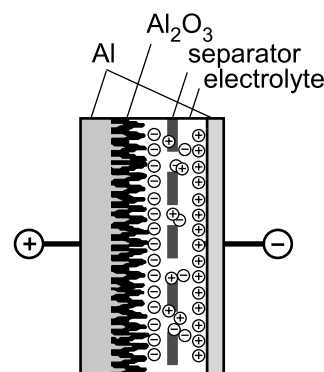
The aluminum electrolytic capacitor was invented by Julius Edgar Lilienfeld in 1928,⁶ and was successfully manufactured by Toshio Satoh (the founder of Nippon Chemi-Con Corp.) in Japan in 1931. It is constructed from two aluminium foils, one of which is coated with an insulating aluminum oxide layer, and a paper separator soaked in a liquid electrolyte, as shown in Fig. 2. The layer of insulating aluminum oxide on the surface of the etched aluminum foil is the dielectric, the foil insulated by the oxide layer is the anode, and the liquid electrolyte and the second foil act as cathode. It is the thinness of this layer and the enlarged surface area that provide high capacitance (see Table 1). The aluminum oxide layer can withstand an electric field strength of the order of 10^9 Vm^{-1} . The combination of high capacitance and high voltage results in high energy density. Aluminum electrolytic capacitors used to be referred to as chemical condensers (capacitors), however, they are not now classified as electrochemical capacitors.

3.2 Requirements for electrolytes

Since it is extremely difficult to prepare the electrode facing the etched anode foil surface, the opposing electrode is created by filling the structure with an electrolyte, which essentially functions as a true cathode. The basic functional requirements for the electrolyte are as follows.

(1) High electrolytic conductivity

Since the presence of the electrolyte and separator increase the equivalent series resistance (ESR) of the

**Fig. 2** Principle of aluminum electrolytic capacitors.

capacitor, a highly conductive electrolyte is indispensable. (2) Good film-forming ability

The electrolyte must repair the defects in the dielectric to maintain its integrity by the anodization of Al, when a direct current is applied (self-healing effect).

(3) High chemical stability

The electrolyte must be stable in contact with the materials used in the capacitor.

(4) Wide operational temperature range

Since the capacitors must operate in the temperature range of at least -25 to 85°C , and preferably at -55 to 125°C , an electrolyte material satisfying the above requirements 1 ~ 3 over a wide temperature range is desired.

3.3 Components of electrolyte materials

The electrolytes for aluminum electrolytic capacitors consist of solvent, acid, and base components. The acid should be a weak acid, and preferably a polybasic acid, because strong acids and monobasic acids have poor film-forming ability and tend to dissolve Al electrodes rather than passivate them.

It is reported that an ammonium borate/glycerine system was used in 1932, and the glycerine was replaced with ethylene glycol (EG) several years later.⁷ Although this ammonium borate/EG system is still in use for high voltage application ($> 300 \text{ V}$), the presence of water produced by the esterification reaction between the two principal components has restricted its operation to within a temperature range of -25 to 85°C . Different solvents started to be introduced in 1956, when the operational temperature range was widened to extend from -55 to 125°C by the introduction of N,N-dimethylformamide (DMF).⁸ In addition to these new solvents, various

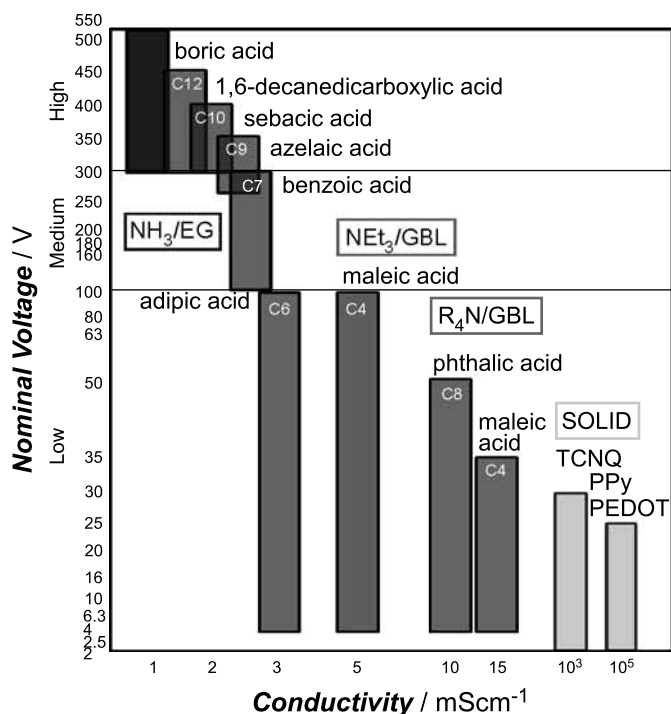


Fig. 3 Electrolyte materials for aluminum electrolytic capacitors.

carboxylic acids were also introduced, and the ammonium adipate/EG system became the most common electrolyte for low voltage application (< 100 V). γ -Butyrolactone (GBL) was introduced in 1978 in Japan to replace DMF due to its good compatibility with rubber seals, its low corrosion behavior, and its low toxicity. In these aprotic solvents, alkylamines were used as a base instead of ammonia to dissolve the carboxylic acid components. It was not until we patented quaternary ammonium salts of carboxylic acids in 1987 that GBL became the second major solvent after EG for use in aluminum electrolytic capacitors.⁹⁾

The sustaining voltage of aluminium electrolytic capacitors is essentially limited by their aluminum oxide dielectrics, electrolytes, and separators. The electrolyte, in particular, is a major controlling factor that determines the maximum operating voltage of aluminium electrolytic capacitors, and various kinds of electrolytes are employed depending on their nominal voltages, as shown in Fig. 3.

3. 4 Properties of quaternary ammonium carboxylates

Quaternary ammonium salts of carboxylic acids are not special compounds and their application to aluminium electrolytic capacitors has been reported in the literature.¹⁰⁾ However, their advantages were not recognized until we started investigating them in 1985.¹¹⁾

The first advantage of quaternary ammonium bases over alkylamines and ammonia is to afford a high dissociation ability, particularly in aprotic solvents, which results in high electrolytic conductivity. Quaternary ammonium salts of hydrogen maleate and phthalate showed electrolytic conductivity in GBL more than 3 fold that shown by their trialkyl ammonium counterparts due

Table 2 Conductometric analysis of quaternary and trialkyl ammonium carboxylate salts in GBL.

Salt	κ/Scm^{-1}	$\Lambda_0/\text{Scm}^2\text{mol}^{-1}$	K_d/M
Et_3NH <chem>OC(=O)C1=CC=CC=C1C(=O)O</chem>	4.1	46.7	0.44×10^{-2}
$\text{Me}_2\text{Et}_2\text{N}$ <chem>OC(=O)C1=CC=CC=C1C(=O)O</chem>	13.7	46.4	0.10
Et_3NH <chem>OC(=O)C1=CC=CC=C1C(=O)O</chem>	3.2	42.7	0.44×10^{-2}
$\text{Me}_2\text{Et}_2\text{N}$ <chem>OC(=O)C1=CC=CC=C1C(=O)O</chem>	10.8	42.5	0.10

1 M in GBL, 25 °C.

to their high dissociation constant (K_d), as shown in Table 2.¹²⁾ These $\text{Me}_n\text{Et}_{4-n}\text{N}$ salts ($n = 1 \sim 4$) were prepared by the quaternization of the corresponding tertiary amines with dimethyl carbonate¹³⁾ and their conductometric analysis was carried out in GBL.^{12,14)} The concentration (C) dependence of electrolytic conductivity (κ) of triethylmethylammonium hydrogen maleate (TEMAM) and tetramethylammonium hydrogen phthalate (TMAP) in GBL at 25 °C is shown in Fig. 4 (a) in comparison with earlier systems, *i.e.*, a mixture of maleic acid and triethylamine in GBL ($\text{NEt}_3 \cdot \text{MA}/\text{GBL}$) and a mixture of adipic acid and ammonia in EG ($\text{NH}_3 \cdot \text{AA}/\text{EG}$).^{11,14)} The $\text{R}_4\text{N}/\text{GBL}$ systems showed higher solubility and electrolytic conductivity. The temperature (T) dependence of their electrolytic conductivity is given in Fig. 4 (b). The $\text{R}_4\text{N}/\text{GBL}$ systems showed some electrolytic conductivity even at -60 °C.

The second advantage of quaternary ammonium salts is their high thermal stability. Since there is no vaporization of the amine or ammonia base components and little reaction between carboxylic acids and GBL, deterioration at an elevated temperature (115 °C) was seen to be small, as shown in Fig. 4 (c).^{11,18)} The phthalate solution showed excellent thermal stability, although the maleate solution showed gradual deterioration due to its degradation.

The film-forming ability of these quaternary ammonium salts was thoroughly examined, and was found to be dependent entirely on the kind and concentration of carboxylate anion and the amount of contaminated water.¹⁵⁾ The maleate solution showed fast and efficient film formation resulting in a barrier-type oxide layer while the phthalate solution afforded a porous-type layer at low water concentration, which is not appropriate for this application.¹⁵⁻¹⁷⁾ The breakdown voltage (V_b) of anodic aluminum oxide films in quaternary ammonium systems was lower than that of their trialkyl ammonium counterparts according to the following empirical equation:

$$V_b = a - b \log \kappa, \quad (5)$$

where a and b are constants for a given electrolyte composition.

A conventional quality control technique of EG-based electrolytes has been pH measurement, because aluminum

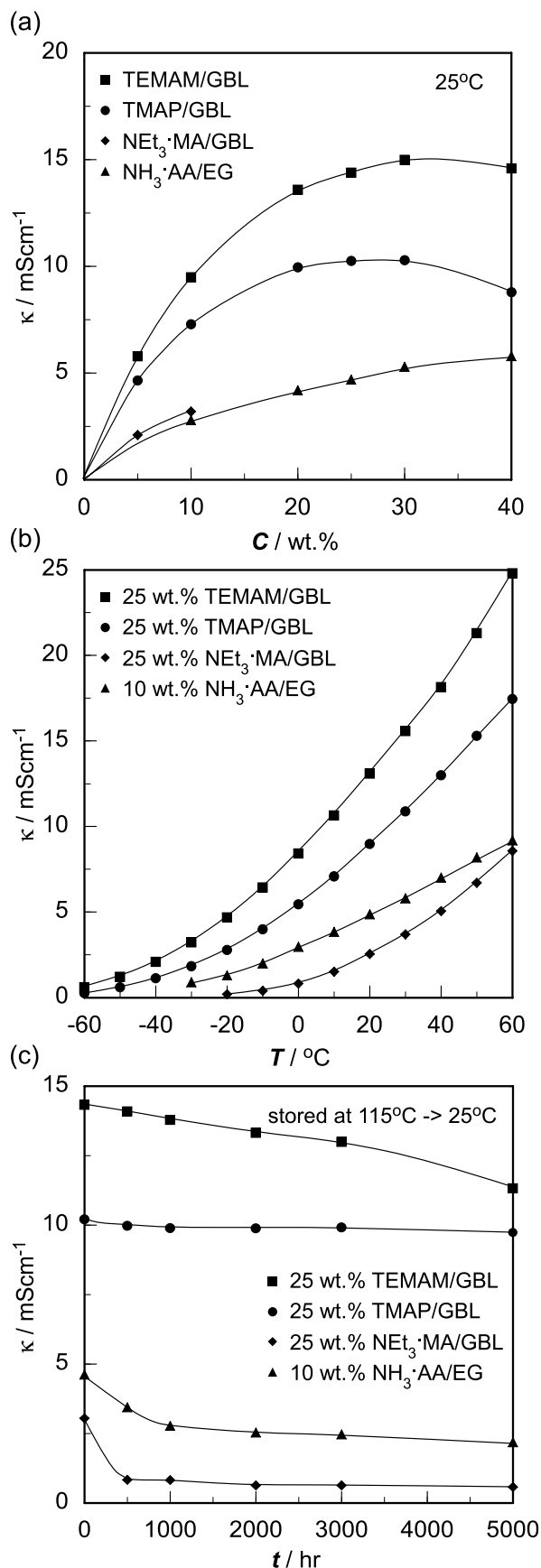
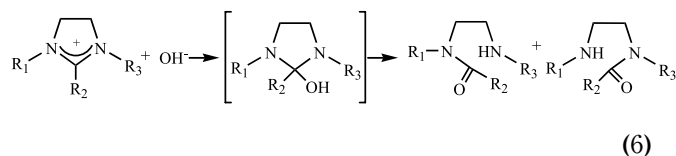


Fig. 4 Properties of quaternary ammonium/GBL system in comparison with trialkyl ammonium/GBL system and ammonium/EG system. (a) Concentration dependence of electrolytic conductivity, (b) temperature dependence of electrolytic conductivity, and (c) deterioration in electrolytic conductivity during storage at 115°C.

oxide dielectrics are most compatible with electrolytes having a weakly acidic pH (6~7). However, since GBL has a much wider acidity potential range (pH scale; *ca.* 30) than EG (*ca.* 16), ordinary pH measurement systems for aqueous solutions (pH scale; 14) created misunderstanding, and a suitable system using a nonaqueous reference electrode was therefore developed.¹⁹⁾ The high basicity of the $\text{R}_4\text{N/GBL}$ system caused a serious corrosion problem that resulted in liquid leakage through the rubber seal. This leakage was caused by the cathodic reaction generating a concentrated alkaline substance around the cathode tab, which has a nobler potential than the cathode foil.²⁰⁾ This liquid leakage was prevented by the adoption of a TiN-coated cathode to reverse the potential relationship between foil and tab,²¹⁾ however, this accident forced replacement of the tetraalkylammonium salts with corresponding imidazolidinium salts (a so-called amidine system).²²⁾ Since the imidazolidinium cations work as a magic acid, which neutralizes the generated OH^- according to the following reaction,²³⁾ they were very useful for suppressing the liquid leakage.



3.5 Further progress

An intrinsic disadvantage of quaternary ammonium systems is a lower sustaining voltage, which limits the nominal voltage up to 50 V. However, the demands of the automotive industry for 100 V class high performance aluminum electrolytic capacitors are increasing. The sustaining voltage was enhanced by the addition of silica organo-sols dispersed in EG while maintaining the high electrolytic conductivity and thermal stability of the quaternary ammonium/GBL systems including amidines,²⁴⁾ and this new system has been successfully introduced into the market.²⁵⁾ We expect the commercial launch of another entirely new system using AlF_4^- anion, which also overcomes the limitation of sustaining voltage while increasing electrolytic conductivity, in the near future.²⁶⁾

4 Double-Layer Capacitors

4.1 Outline

The double-layer capacitor based on a double-layer mechanism was developed in 1954 by H. I. Becker using a porous carbon electrode.²⁷⁾ At that time it was recognized as one of electrolytic capacitors according to the patent title: "Low voltage electrolytic capacitor". In 1971, the Standard Oil Co. (SOHIO) appealed useful application of this device,²⁸⁾ and it was commercialized by Matsushita Electric Industrial Co. (Gold CapacitorTM)²⁹⁾ and Nippon Electric Co. (Super CapacitorTM)³⁰⁾ independently for the first time in Japan in 1978. The double-layer capacitor is constructed from a pair of electrodes made of activated carbon with a high surface area, and a separator soaked in a liquid electrolyte, as shown in Fig. 5. A molecule-thin

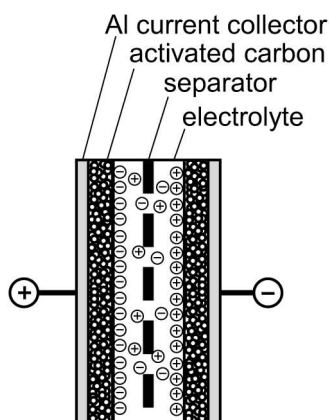


Fig. 5 Principle of double-layer capacitors.

layer of electrolyte acts as the dielectric. The double-layer capacitor is one of electrochemical capacitors, and is often called a supercapacitor or ultracapacitor in the sense that it has unusually high capacitance compared with conventional capacitors, due to the thinness of the double-layer and its very high surface area (see Table 1).

4.2 Requirements for electrolytes

In principle, any ionic conductor can be used as an electrolyte of a double-layer capacitor provided that a current due to electrochemical reactions (Faradaic current) does not flow in the desired potential region. Two types of liquid electrolytes are used in practice: nonaqueous electrolytes such as $\text{Et}_4\text{NBF}_4/\text{PC}$ (propylene carbonate) solution,²⁹⁾ and aqueous electrolytes such as H_2SO_4 solution.³⁰⁾ Because the nonaqueous electrolyte can withstand higher voltage than its aqueous counterpart (*ca.* 3 V vs. 1 V), double-layer capacitors with nonaqueous electrolytes came to dominate the market from the viewpoint of high energy density. The basic functional requirements for the electrolyte are as follows.

(1) High electrolytic conductivity

Since the internal resistance of the capacitor leads to energy loss due to voltage drop during charge-discharge cycling, an electrolyte material with a high electrolytic conductivity is desired.

(2) High electrochemical stability

Since the maximum operational voltage of a capacitor is governed by the decomposition voltage of the electrolyte material, an electrolyte material having a wide stable potential region (electrochemical window) for a given electrode is desired.

(3) High double-layer capacitance

Since the capacitance of a capacitor is proportional to the capacitance of an electrode, an electrolyte material showing a high double-layer capacitance for a given electrode is desired.

(4) Wide operational temperature range

Since the capacitors must operate in the temperature range of at least -25 to 60°C , and preferably -40 to 85°C , an electrolyte material satisfying the above requirements 1–3 over a wide temperature range is desired.

4.3 Components of electrolyte materials

Concentrated nonaqueous solutions composed of an aprotic organic solvent and a quaternary ammonium salt

of a strong acid are preferably used. Double-layer capacitors using coconut charcoal with $\text{Et}_4\text{NClO}_4/\text{PC}$ ³¹⁾ and activated carbon fiber with $\text{Et}_4\text{NBF}_4/\text{PC}$ ³²⁾ have been commercialized. Although many other organic solvents were investigated in our laboratory for this application, PC proved to be the best solvent from the viewpoint of overall performance, for example, in terms of electrolytic conductivity, electrochemical window, liquidus range, and resistance toward hydrolysis.^{33–35)} While acetonitrile (AN) is partly used in the US and EU because it is an ideal solvent in terms of high electrolytic conductivity, it is not used in Japan due to its high toxicity.

We also investigated numerous other onium salts having different cations and anions and the following results were observed in PC solvent.^{33–37)}

(1) Electrolytic conductivity

Et_4N^+ , Et_4P^+ > Me_4P^+ > Pr_4N^+ , Pr_4P^+ > Bu_4N^+ , Bu_4P^+ > Li^+ > Me_4N^+ (for ClO_4^- , BF_4^- , PF_6^-)

BF_4^- > PF_6^- , ClO_4^- , CF_3SO_3^- > AsF_6^- , SbF_6^- , $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ > $\text{C}_4\text{F}_9\text{SO}_3^-$ > BET_4^- (for Et_4N^+)

(2) Electrochemical window

Hex_4N^+ > R_4N^+ , R_4P^+ (R = Me, Et, Pr, Bu) (no remarkable difference)

SbF_6^- > AsF_6^- , PF_6^- > BF_4^- > $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, $\text{C}_4\text{F}_9\text{SO}_3^-$ > ClO_4^- , CF_3SO_3^- > BET_4^- (for glassy carbon electrode)

(3) Double-layer capacitance³⁸⁾

BF_4^- > PF_6^- > Et_4N^+ > Bu_4N^+

(for activated carbon electrode)

Despite these efforts, $\text{Et}_4\text{NBF}_4/\text{PC}$ remains the major electrolyte used for double-layer capacitors.

4.4 Properties of quaternary ammonium tetrafluoroborates

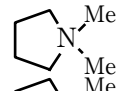
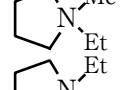
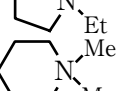
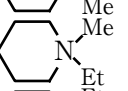
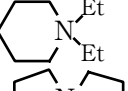
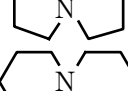
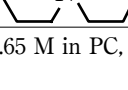
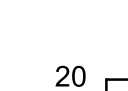
To gain a better understanding of electrolytes and to identify better electrolyte candidates, new asymmetric tetraalkylammonium and cyclic quaternary ammonium salts were synthesized and an optimization of cation structure was carried out based on a conductometric analysis in PC.^{33–35,39–41)} From the observed molar conductivity (Λ) and limiting molar conductivity (Λ_0), the degree of dissociation (γ) was calculated by:

$$\gamma = \Lambda / \Lambda_0 \quad (7)$$

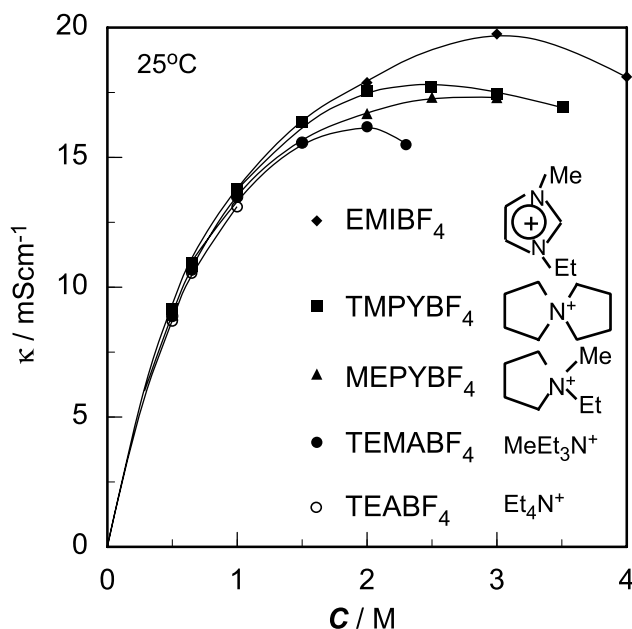
Triethylmethylammonium (TEMABF_4), 1-ethyl-1-methylpyrrolidinium (MEPYBF_4), and tetramethylene-pyrrolidinium (TMPYBF_4) salts had almost the same degree of dissociation at 0.65 M as the tetraethylammonium salt (TEABF_4), as shown in Table 3. It was concluded that the higher electrolytic conductivity of these three salts was attributable to their smaller ion sizes without loss of their high dissociation properties even at the practical concentration of 0.65 M ($\text{M} = \text{mol dm}^{-3}$). Their electrolytic conductivity extends over 2 M due to their high solubility in PC, whereas TEABF_4 can be dissolved up to only 1 M, as shown in Fig. 6.

Recent power applications require a high concentration of supporting salts due to the ion depletion in large size double-layer capacitors during charge. TEMABF_4 produced by our new process¹³⁾ has been used as an alternative to TEABF_4 for this reason.^{42,43)} MEPYBF_4 has

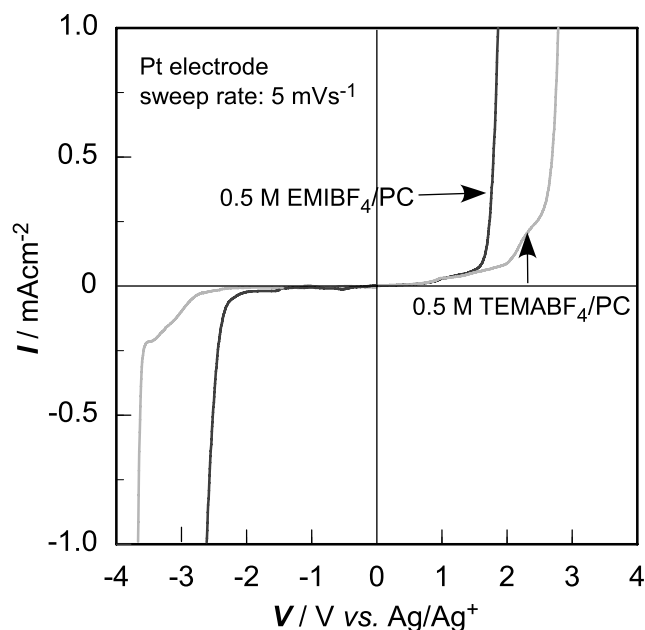
Table 3 Conductometric analysis of quaternary ammonium tetrafluoroborate salts in PC.

Salt	κ /Scm ⁻¹	Λ /Scm ² mol ⁻¹	Λ_0	γ
Me ₄ N BF ₄	insol.	—	35.0	—
Me ₃ EtN BF ₄	10.16	15.63	34.9	0.45
Me ₂ Et ₂ N BF ₄	10.34	15.91	34.6	0.46
MeEt ₃ N BF ₄	10.68	16.43	34.3	0.48
Et ₄ N BF ₄	10.55	16.23	33.8	0.48
 BF ₄	10.36	15.94	34.4	0.46
 BF ₄	10.82	16.65	34.2	0.49
 BF ₄	10.40	16.00	34.0	0.47
 BF ₄	10.20	15.69	34.2	0.46
 BF ₄	10.40	16.00	34.0	0.47
 BF ₄	10.17	15.65	33.8	0.46
 BF ₄	10.94	16.83	34.0	0.50
 BF ₄	9.67	14.88	33.6	0.44

0.65 M in PC, 25 °C.

**Fig. 6** Concentration dependence of electrolytic conductivity of quaternary ammonium tetrafluoroborate salts in PC.

also been used, but disappeared from the market due to high cost. TMPYBF₄, which has higher solubility and conductivity, was also recently introduced to the

**Fig. 7** Electrochemical window of EMIBF₄.

market.⁴⁴⁾ 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIBF₄) is the most famous ionic liquid.⁴⁵⁾ This salt also has extremely high solubility resulting in the highest electrolytic conductivity, as shown in Fig. 6, due to its higher dissociation ability.³⁴⁾ Although EMIBF₄ has a narrower electrochemical window due to the existence of π electrons, as shown in Fig. 7, it was in practical use.

4.5 Further Progress

Ionic liquids have attracted considerable attention as liquid electrolytes for electrochemical energy storage devices as their nonvolatile and nonflammable properties are considered to increase device safety. A double-layer capacitor consisting of activated carbon cloth electrodes and an ionic liquid (EMI(CF₃SO₂)₂N) was proposed for the first time by Covalent Associates, Inc.⁴⁶⁾ We have also examined the performance of a double-layer capacitor composed of a pair of activated carbon electrodes and an ionic liquid selected from EMIF·2.3HF, EMIBF₄, EMINbF₆, EMITaF₆, EMICF₃SO₃, EMI(CF₃SO₂)₂N and EMI(C₂F₅SO₂)₂N in comparison with a conventional nonaqueous electrolyte (1 M TEMABF₄/PC) and aqueous electrolyte (4.5 M H₂SO₄/H₂O).^{47,48)} EMIBF₄ afforded the highest energy density over 25 °C, but failed at -25 °C due to solidification.

To improve the intrinsic narrower electrochemical window of EMI salts, new ionic liquids having a diethylmethyl(2-methoxyethyl)ammonium (DEME) cation were prepared.⁴⁹⁾ A double-layer capacitor using DEMEBF₄ (mp = 8 °C, κ = 1.3 mScm⁻¹ at 25 °C) gave excellent thermal stability and worked at 150 °C, while those using 1 M TEABF₄/PC and EMIBF₄ failed. However, it still had poor low temperature characteristics, which is a disadvantage common among ionic liquids with fluoroanions.

We have also prepared a series of quaternary ammonium salts based on perfluoroalkyltrifluoroborate anions, C_nF_{2n+1}BF₃⁻.⁵⁰⁾ EMIC₂F₅BF₃ (mp = -1 °C, κ = 12.2 mScm⁻¹ at 25 °C)⁵¹⁾ and EMICF₃BF₃ (mp = -20 °C, κ = 14.8 mS

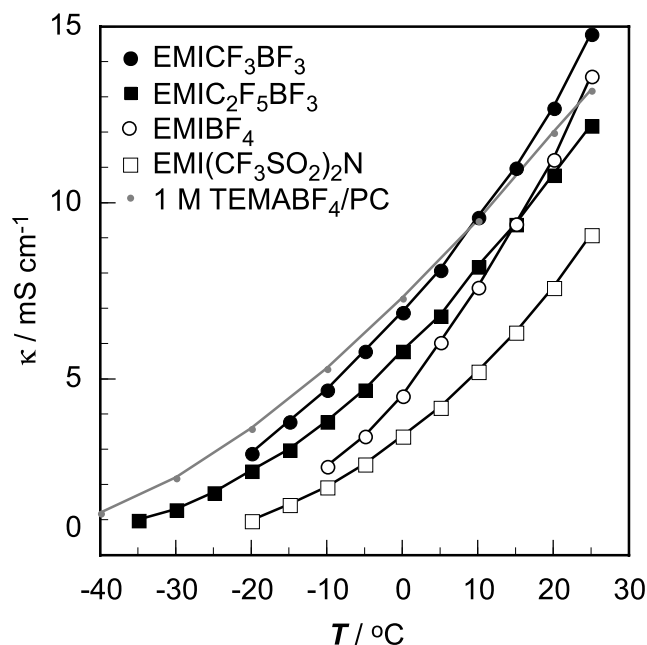


Fig. 8 Temperature dependence of electrolytic conductivity of ionic liquids.

cm^{-1} at 25°C)⁵²⁾ showed high electrolytic conductivity comparable to 1 M TEMABF₄/PC down to -35°C , as shown in Fig. 8.⁵³⁾ A double-layer capacitor using EMIC₂F₅BF₃ exhibited excellent low temperature characteristics.⁵¹⁾ This invention was a technological breakthrough that overcame the common disadvantage of most ionic liquids with fluoroanions.

5 Conclusion

Chemical capacitors with nonaqueous electrolyte solutions including quaternary ammonium salts are expected to continue to receive much attention as energy storage devices. It was shown that the inventions of new electrolyte materials have dramatically improved the performance of chemical capacitors. The author hopes that the readers of this article will be encouraged to make efforts to explore new chemical structures capable of overcoming the current limitations of chemical capacitors.

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