

# Ethylene carbonate-based organic electrolytes for high performance aluminium electrolytic capacitors

Masayuki Morita \*, Yoshiharu Matsuda

Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Yamaguchi University, 2557 Tokiwadai, Ube 755, Japan

Received 4 January 1995

## Abstract

The utilization of ethylene carbonate (EC)-based solutions has been examined as the electrolyte of aluminium electrolytic capacitors. The electrolytic conductivities of alkylammonium salts in the solutions containing propylene carbonate (PC),  $\gamma$ -butyrolactone (BL) or sulfolane (S) as a co-solvent varied with both the solvent composition and the ion size of the salt. The maximum conductivity of 0.5 M tetraethylammonium hydrogen maleate (TEAM),  $9.8 \times 10^{-3} \text{ S cm}^{-1}$ , was obtained in a 20 mol% EC + 80 mol% BL composition. The thermal stability of the electrolyte solution varied also with the electrolyte composition; the solutions containing higher mol% EC tended to be unstable towards thermal stimulation. The anodic behaviour of the formation of aluminium oxide was briefly examined in the EC-based electrolytes containing small amounts of water. The oxide films formed in the TEAM solutions were highly resistant to corrosion, suggesting that the present electrolyte system has a high ability for the oxide film restoration in the capacitor.

**Keywords:** Aluminium; Electrolytic capacitors; Organic electrolytes; Electrolytic conductivity

## 1. Introduction

The extensive progress in the electronics technologies demands advanced capacitors with high performance. The conventional aluminium electrolytic capacitors used ethylene glycol-containing ammonium borate (high-voltage type) [1,2] and  $\gamma$ -butyrolactone (BL)-containing alkylammonium salts (low-voltage type) [2–5] as the electrolyte solutions. Recently, new types of aluminium electrolytic capacitors with solid conductors have been developed [6,7]. However, organic electrolyte solutions have still been important for large size capacitors with high electric capacities [2,8,9]. In this respect, it is necessary to search improved electrolyte solution systems consisting of organic solvents. Among the physicochemical properties, the following [2] are of special importance for the electrolyte solutions of high performance capacitors: (i) high ionic conductivity; (ii) wide operation temperature range (including high thermal stability), and (iii) high ability towards the self-restoration (healing) of the aluminium oxide film. We proposed a new electrolyte system based on ethylene carbonate (EC) as the main solvent for aluminium electrolytic capacitors [10,11]. The EC-based solutions containing lithium salts have also been investigated as stable electrolyte solutions for rechargeable lithium bat-

teries [12]. As EC is solid below room temperature (melting point: 36.2 °C), a co-solvent with a lower melting point is needed. In the present paper, we attempted to use BL, propylene carbonate (PC), and sulfolane (S) as the co-solvents. The basic properties were investigated for the solutions containing tetraethylammonium salts. That is, the electrolytic conductivity and thermal stability of the solution, and the anodic formation of aluminium oxide in the solution were investigated as a function of the electrolyte composition.

## 2. Experimental

The solvent EC was extra pure grade (Mitsubishi Chemical, battery grade) and used as received. The co-solvents PC, BL and S were of commercial grade and used after purification by usual methods described in Refs. [13–15]. The electrolytic salts were tetraethylammonium ( $\text{Et}_4\text{N}^+ = \text{TEA}^+$ ) salts of hydrogen maleate (*cis*- $\text{HOOC} = \text{CHCOO}^- = \text{M}^-$ ) and of hydrogen phthalate (*o*- $\text{HOOC}_6\text{H}_4\text{COO}^- = \text{P}^-$ ). These were synthesized from  $\text{Et}_4\text{NOH}$  and the corresponding organic acids, purified by re-crystallization and dried under a vacuum below 100 °C [11]. The electrolytic salts were dissolved in pure or mixed solvents under a dry argon atmosphere. The salt concentration was usually 0.5 M. Hereinafter, the electrolytic solutions are expressed as TEAM/EC + PC,

\* Corresponding author.

Table 1  
Selected physical properties of the solvents

Solvent	Melting point (°C, 1 atm)	Relative permittivity, $\epsilon$	Viscosity, $\eta \times 10^{-2}$ (P)	Donicity, $DN$
Ethylene carbonate (EC)	39–40	89.6 <sup>a</sup>	1.86 <sup>a</sup>	16.4
Propylene carbonate (PC)	–49.2	64.4 <sup>b</sup>	2.530 <sup>b</sup>	15.1
$\gamma$ -Butyrolactone (BL)	–42	39.1 <sup>b</sup>	1.751 <sup>b</sup>	15.9
Sulfolane (S)	28.86	42.5 <sup>c</sup>	9.87 <sup>c</sup>	14.8

<sup>a</sup> at 40 °C.

<sup>b</sup> at 25 °C.

<sup>c</sup> at 30 °C.

TEAP/EC + S, etc. The water content in the solution was less than 200 ppm, unless otherwise noted.

The electrolytic conductivity was measured with a conventional a.c. impedance bridge (ANDO: DRZ-2M, 10 kHz) at 25 °C. The thermal stability of the electrolytic solution was estimated by an accelerated method [16]. The solution was enclosed in a glass tube under a dry argon atmosphere and then heated at 85 °C for 500 h. The conductivity and the absorption spectrum were measured.

The anodic formation of the aluminium oxide film was examined in the EC-based electrolytes using a conventional beaker cell. A glassy carbon plate and a silver wire were used as the counter electrode and the pseudo-reference electrode, respectively [10].

### 3. Results and discussion

The selected physical properties of the solvents, EC, PC, BL and S, are listed in Table 1. These are aprotic polar solvents which have sufficiently high permittivity (dielectric constant) to dissociate the electrolytic salts in the solutions. However, high viscosities of the solvents, especially in PC and S, may be a disadvantage for the conduction of resulting dissociated ions. The melting points of EC and S are rather high, but mixtures of EC + S were liquid over wide mixing ratios, even below room temperature. The concentration of the EC compositions, where the mixed solvents containing 0.5 M salts remain liquid at room temperature, were generally 0–80 mol%.

Figs. 1 and 2 show, respectively, the conductivities ( $\kappa$ ) of TEAM and TEAP (0.5 M) as a function of the solvent composition. In the EC + PC and EC + S systems, the conductivities of both maleate and phthalate increased with the EC content in the solvent, while the conductivities in the EC + BL system showed a maximum at the solvent compositions of about 20 mol% EC. Since the co-solvent S has the highest viscosity of all examined ones, the ionic conduction in the solutions containing S are mostly governed by the viscosity of the system. Thus, the conductivities in EC + S increased with EC content in the solvent. In this case, some solvent–solvent and solvent–ion interactions possibly affect the curvature in the relation (i.e. negative deviation from a straight

line) [16]. As PC has a molecular structure similar to that of EC and its viscosity is only a little higher than that of EC, the conductivities in EC + PC show almost linear increases with the EC contents but their extents are rather small. Similarly, the difference in the viscosity between EC and BL is quite small, which leads to little change in the conductivity with the solvent composition in the EC + BL system. However, possible solvent–solvent interaction in this system might be

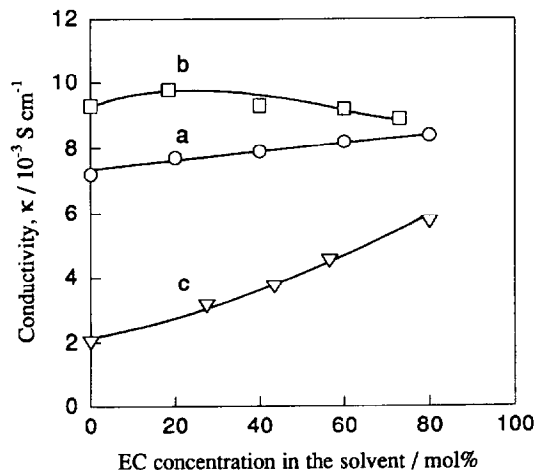


Fig. 1. Conductivity of 0.5 M TEAM in mixed EC + co-solvent at 25 °C: (a) EC + PC; (b) EC + BL, and (c) EC + S.

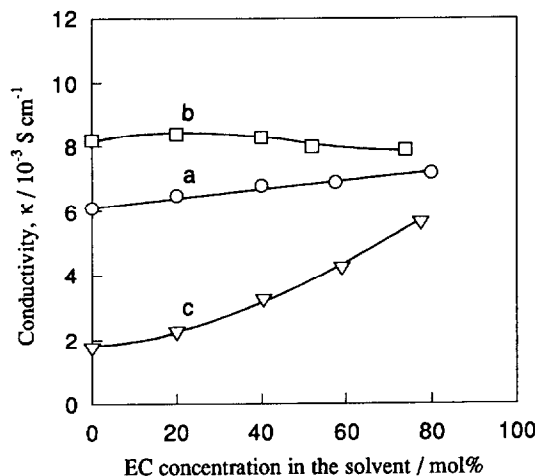


Fig. 2. Conductivity of 0.5 M TEAP in mixed EC + co-solvent at 25 °C: (a) EC + PC; (b) EC + BL, and (c) EC + S.

responsible for the appearance of the conductivity maxima in the mixed solvents of about 20 mol% EC [17].

With respect to the salts, the conductivity of maleate (TEAM) was generally higher than that of phthalate (TEAP). This is mainly due to a difference in the anion size ( $M^- < P^-$ ) [5,10,16]. The maximum conductivity of  $9.8 \times 10^{-3} \text{ S cm}^{-1}$  for TEAM/EC + BL (20 mol% EC) was about 10 times higher than that for ammonium borate (0.5 M) in ethylene glycol, an electrolyte solution for high voltage-type aluminium capacitors, but somewhat lower than those of alkylammonium perchlorates in EC + BL [17].

Figs. 3–6 show the results of the accelerated thermal stability tests for the electrolytic solutions. Changes in the electrolytic conductivity after the thermal treatment (85 °C, 500 h) are summarized in Fig. 3. The electrolytic solutions containing PC showed reduced conductivities after heating. This is probably due to the thermal decomposition of PC, which might cause a decrease in the amount of the effective solvent component in the solution. Solutions based on mixed EC + BL and EC + S also gave lowered conductivity after the thermal treatment, while solutions consisting the neat BL or S solvent showed little change in conductivity after heating. These suggest that the EC component in the mixed solvent systems is not so stable towards such a thermal treatment. Slight increases in conductivity after the heat treatment observed for the solutions consisting of neat BL or S might be based on the generation of some conducting species and/or the decrease in the viscosity of the solvent [17], but we can

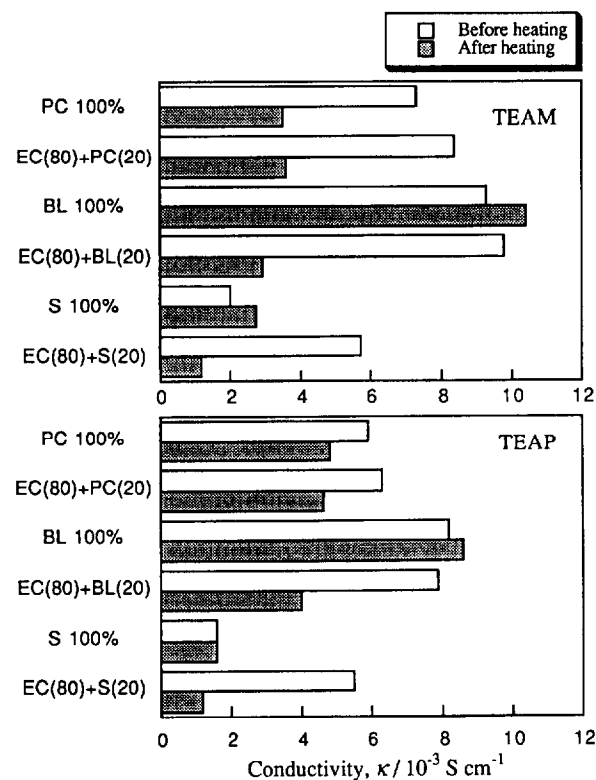


Fig. 3. Variation in conductivity at 25 °C after thermal treatment, at 85 °C and 500 h: (a) TEAM, and (b) TEAP.

regard the conductivity of those single solvent systems as essentially unchanged. This indicates that BL and S are thermally more stable than EC, and that the salts TEAM and TEAP are stable themselves under this thermal condition [2,18].

UV–VIS spectra of the electrolytic solutions were measured to monitor changes in the chemical structure of the electrolytic solution after the thermal treatment. Typical results are shown in Figs. 4–6, where the differences in the absorbance before and after the thermal treatment were recorded (the reference was the same solution before heating). In Fig. 4, the positive absorbance in the differential spectrum ( $\Delta$  absorbance) of TEAM/EC + S means generation of some UV–VIS-active species by heating the solution, and the small negative  $\Delta$  absorbance (about 350 nm) for TEAM/S suggests that a UV-active group contained in the original solution disappeared slightly after the thermal treatment. This might correspond to the small change in conductance after the thermal treatment, as shown in Fig. 3. The TEAP solution based on S or EC + S gave similar results (Fig. 5). However, the  $\Delta$  absorbance intensity, especially at

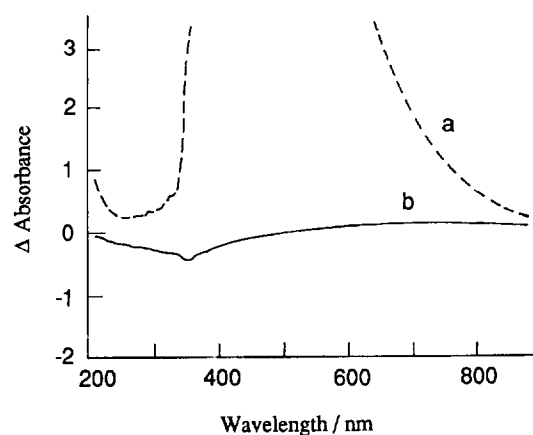


Fig. 4. Differential UV–VIS spectra of EC + S containing 0.5 M TEAM: (a) EC + S (80 mol% EC), and (b) S (0 mol% EC). Reference solution: each solution before thermal treatment.

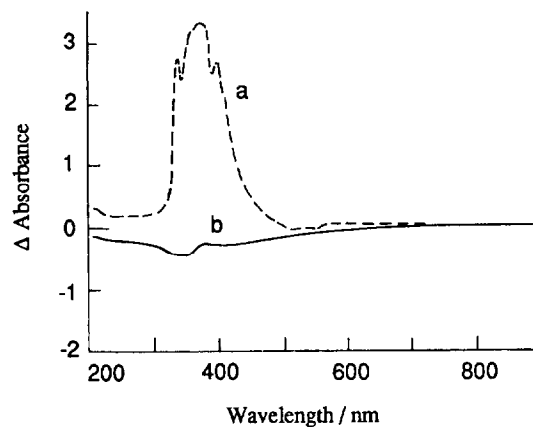


Fig. 5. Differential UV–VIS spectra of EC + S containing 0.5 M TEAP: (a) EC + S (80 mol% EC), and (b) S (0 mol% EC). Reference solution: each solution before thermal treatment.

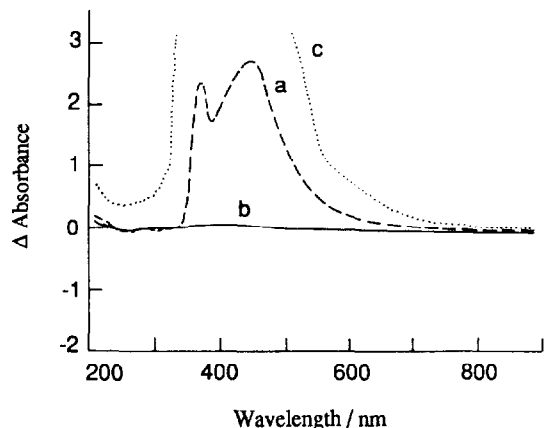


Fig. 6. Differential UV-VIS spectra of EC + BL containing 0.5 M TEAM and TEAP: (a) TEAM/EC + BL (80 mol% EC); (b) TEAMA/S (0 mol% EC), and (c) TEAP/EC + BL (80 mol% EC). Reference solution: each solution before thermal treatment.

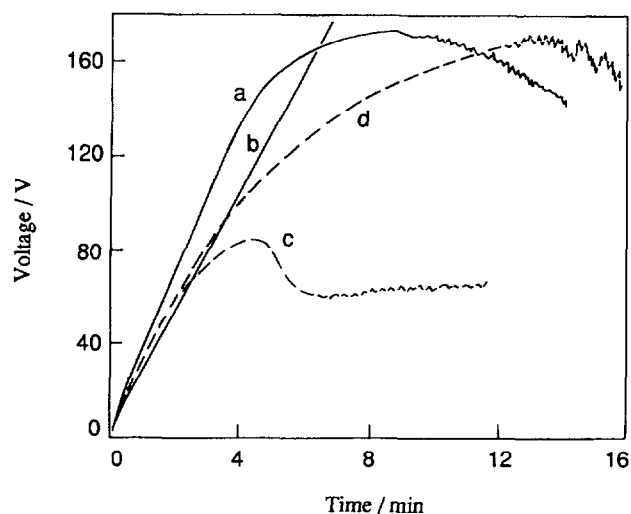


Fig. 7. Voltage-time curves for aluminium electrode in EC + S (50 mol%) containing 0.1 M TEA salts, current density:  $1.0 \text{ mA cm}^{-2}$ : (a) TEAM/EC + S with 600 ppm  $\text{H}_2\text{O}$ ; (b) TEAM/EC + S with 2700 ppm  $\text{H}_2\text{O}$ ; (c) TEAP/EC + S with 1300 ppm  $\text{H}_2\text{O}$ , and (d) TEAP/EC + S with 2500 ppm  $\text{H}_2\text{O}$ .

the longer wavelength region, was less for TEAP/EC + S than for TEAM/EC + S. The BL-based solutions without EC gave no spectrum change after the heat treatment (Fig. 6(b)), but the solutions consisting of mixed EC + BL showed significant absorbance change, suggesting the thermal decomposition of EC (Fig. 6(a)). Solutions containing PC showed marked spectrum changes, proving that PC was thermally decomposed during the heat treatment. Consequently, the results obtained in UV-VIS spectra are generally consistent with the discussion deduced from the conductivity measurements (Fig. 3). That is, the carbonate solvents (EC and PC) are thermally less stable than BL and S, and that the electrolyte salts (TEAM and TEAP) are intrinsically stable under this thermal condition.

The anodic oxidation behavior of aluminium was examined briefly in the EC-based electrolytes. Fig. 7 shows typical

voltage-time relations during constant-current polarization in EC + S containing TEAM and TEAP (0.1 M). Generally the voltage (potential of the aluminium anode versus the silver reference electrode) increases almost linearly with the polarization time because of the growth of an insulating oxide film on the aluminium surface. The anodic dissolution of the aluminium substrate and/or the oxide film causes the saturation of the voltage. The anodic decomposition of the electrolyte has also been reported for the TEAP/BL system [3,18]. The break-down of the protective film leads to the oscillation of the voltage. It is apparent from Fig. 7 that certain levels of water concentration in the solution are needed for the growth of thick protective films. That is, the anodic polarization in TEAM/EC + S (50 mol% EC) containing 2700 ppm water kept the oxidation voltage of 170 V or higher, whereas the voltage saturation and/or the film break-down occurred at about 160 V in the TEAM solution containing 600 ppm water. The same trend was observed in other electrolytic solutions. These results proved that the present electrolyte system has more or less the ability to restore the protective oxide film during the operation of the capacitor. The use of TEAP salt as the electrolyte, however, tended to decrease the maximum oxidation voltage (Fig. 7, curves (c) and (d)). Thus, the film restoration ability is lower in the solution containing TEAP than in TEAM solutions [3,11].

#### 4. Conclusions

A new electrolyte system consisting of mixed organic solvents has been proposed for aluminium electrolytic capacitors. Fundamental properties obtained in the present work are summarized as follows:

1. High electrolytic conductivities were observed for the solutions containing tetraethylammonium salts. The maximum conductivities were  $8.4 \times 10^{-3} \text{ S cm}^{-1}$  for TEAM/EC + PC,  $9.8 \times 10^{-3} \text{ S cm}^{-1}$  for TEAM/EC + BL and  $5.7 \times 10^{-3} \text{ S cm}^{-1}$  for TEAM/EC + S.
2. The carbonate solvents EC and PC were thermally less stable than BL and S, and the electrolyte salts (TEAM and TEAP) themselves were stable during the heat treatment at  $85^\circ\text{C}$  for 500 h.
3. The anodic oxidation voltage of aluminium electrode kept 170 V or above in the solutions of TEAM/EC + BL containing 2700 ppm water, suggesting that good restoration properties for the aluminium oxide film are expected in this electrolyte system.

#### Acknowledgements

The authors are very grateful to Matsushita Electronic Components Co. Ltd., and Yamaguchi Matsushita Electric Co. Ltd., for the co-operation during the present work. We also thank Yukinori Nitta, Takashi Kinoshita and Motoko Okada for their technical supports.

## References

- [1] W.J. Bernard, *J. Electrochem. Soc.*, *124* (1977) 403C.
- [2] M. Ue, K. Ida and S. Mori, *Chemitopia*, *12* (1993) 2.
- [3] M. Ue, T. Sato, H. Asahina, K. Ida and S. Mori, *Denki Kagaku*, *60* (1992) 480.
- [4] K. Matsuki, A. Sawaguchi and M. Sugawara, *Denki Kagaku*, *60* (1992) 488.
- [5] M. Ue, T. Sato and M. Takeda, *Denki Kagaku*, *61* (1993) 1080.
- [6] M. Fukuda, H. Yamamoto, I. Isa, K. Sakamoto and H. Shimada, *Ext. Abstr.*, '89th Fall Meet. The Electrochemical Society of Japan, Tokyo, Oct. 1989, p. 29, Abstr. No. 1B04.
- [7] H. Inoue, K. Kakuma, K. Mizutomi, S. Niwa and T. Ezaki, *Ext. Abstr.*, '93th Fall Meet. The Electrochemical Society of Japan, Tokyo, Oct. 1993, p.96, Abstr. No. 2D09.
- [8] T. Kudo, S. Ando and M. Nagayama, *Ext. Abstr.*, '93 Fall Meet. The Electrochemical Society of Japan, Tokyo, Oct. 1993, p. 93, Abstr. No. S2D03.
- [9] M. Takeda, M. Ue, Y. Suzuki and S. Yamazaki, *Ext. Abstr.* '93rd Fall Meet. The Electrochemical Society of Japan, Fukuoka, Oct. 1993, p. 95, Abstr. No. 2D08.
- [10] O.Y. Matsuda, Y. Nitta and M. Morita, *Denki Kagaku*, *56* (1988) 439.
- [11] Y. Nitta, M. Morita and Y. Matsuda, *Denki Kagaku*, *58* (1990) 74.
- [12] S.-I. Tobishima, J.-I. Yamaki and T. Okada, *Electrochim. Acta*, *29* (1984) 1471.
- [13] Y. Matsuda, M. Morita and K. Kosaka, *J. Electrochem. Soc.*, *130* (1983) 101.
- [14] Y. Matsuda, T. Yamamoto and M. Morita, *Denki Kagaku*, *49* (1981) 653.
- [15] Y. Matsuda, M. Morita, K. Yamada and K. Hirai, *J. Electrochem. Soc.*, *132* (1985) 2583.
- [16] Y. Matsuda, M. Morita and F. Tachihara, *Bull. Chem. Soc. Jpn.*, *59* (1986) 1967.
- [17] M. Morita, M. Goto and Y. Matsuda, *J. Appl. Electrochem.*, *22* (1992) 901.
- [18] M. Ue and S. Mori, *Electrolytic Condenser Rev.*, *45* (1994) 1.