Chemical stability of γ-butyrolactone-based electrolytes for aluminum electrolytic capacitors

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Abstract

γ-Butyrolactone-based electrolytes have been used as the operating electrolytes for aluminum electrolytic capacitors. The chemical stability of these electrolytes at elevated temperatures has been examined by monitoring the decrease in their electrolytic conductivities. The deteriorated electrolytes were analyzed by gas and liquid chromatography and the conductivity decrease was directly correlated with the loss of acid components. In quaternary ammonium hydrogen maleate/γ-butyrolactone electrolytes, the maleate anion decomposed by decarboxylation resulting in a complex polymer containing polyester and polyacrylate structures. Quaternary ammonium benzoate/γ-butyrolactone electrolytes decomposed by SN2 reactions giving alkyl benzoates and trialkylamines. The deterioration of the carboxylate salt/γ-butyrolactone electrolytes was accelerated by electrolysis.

Keywords: Stability; Organic electrolytes; γ-Butyrolactone; Aluminum; Capacitors

1. Introduction

The information on organic electrolytes for aluminum electrolytic capacitors is very limited [1-3], although many formulations are disclosed in patent applications.

In the early 1950s, virtually all aluminum electrolytic capacitors used, as the operating electrolyte, the reaction mixture of ammonium borate and ethylene glycol (EG). However, the increased demands for more rigorous service conditions revealed that the glycol-borate electrolyte system had serious limitations. High melting point of EG ($-13\ °C$) and the presence of water arising from the esterification reaction between two principal components restricted its operation from -25 to 85 °C. The development of entirely new electrolyte systems has been carried out and the utilization of aprotic solvents such as N,N-dimethylformamide (DMF) and γ-butyrolactone (GBL) has enlarged the operation temperature from -55 to 125 °C.

The electrolytic conductivity and the electrochemical stability of the organic electrolytes are the major controlling factors to determine the dissipation factor (internal resistance) and the shelf life of the capacitors, respectively. The deterioration of diammonium adipate/EG [4] and tertiary ammonium maleate/GBL electrolytes [5] has been examined at 105 °C for 500 h, and the reaction mechanisms were

proposed by analyzing their deteriorated products by liquid chromatography. We examined the deterioration mechanisms of quaternary ammonium carboxylate/GBL electrolytes, that are recently used as high performance electrolytes [6].

2. Experimental

2.1. Electrolytes

The organic electrolytes containing 25 wt.% of maleate, phthalate or benzoate salts were used [7]. All electrolytes were prepared by the methods described in our previous papers [8,9]. The following abbreviations were used for these solutes: trimethylethylammonium hydrogen maleate (TMEAM), triethylmethylammonium hydrogen maleate (TEMAM), tetraethylammonium hydrogen maleate (TEAM), triethylammonium hydrogen maleate (MA.TEA), tetramethylammonium hydrogen phthalate (TMAP), triethylmethylammonium hydrogen phthalate (TEMAP), tetraethylammonium hydrogen phthalate (TEAP), triethylammonium hydrogen phthalate (PA.TEA); triethylmethylammonium benzoate (TEMAB), tetraethylammonium benzoate (TEAB) and triethylammonium benzoate (BA.TEA).

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2.2. Ampule test

Each electrolyte was filled in a 100 ml liquefied gas sampling tube (Taiatsu Scientific Glass Co., A-2) shown in Fig. 1(a). The tubes were placed at 115 °C under dry air stream in an oven (Tabai Espec Corporation, IPH-200). After regular intervals, the tubes were cooled to room temperature and parts of the electrolytes were taken out. The electrolytic conductivity of these samples was measured by a conductivity meter (Toa Electronics, CM-60S/CGT-511B) at 25 °C. They were also diluted with methanol and analyzed by a liquid chromatograph (Waters, Model 510). The analytical conditions for each electrolyte were as follows:

(i) *Phthalate electrolytes*. Column: Shimadzu, SCR101H (diameter 7.9 mm and length 300 mm), eluent: 0.1% trifluoroacetic acid aqueous solution, flow rate: 1 ml min^{-1}, temperature: 60 °C, detector: UV (254 nm).

(ii) *Maleate electrolytes*. The same conditions as for phthalate electrolytes except the wave length of UV is 220 nm.

(iii) *Benzoate electrolytes*. Column: GL Sciences, Intersil ODS-2 (diameter 4.6 mm and length 150 mm), eluent: 0.1% aqueous phosphoric acid/acetonitrile (56/44) (v/v), flow rate: 1 ml min^{-1}, temperature: 40 °C, detector: UV (254 nm).

A 200 ml portable reactor (Taiatsu Scientific Glass, Co., TVS) was also used instead of the tube; the gas phase was analyzed by gas chromatography. The analytical conditions for each gas were as follows:

(i) *Amines and alcohols*. Apparatus: Perkin-Elmer, Σ2000, column: Nishio Industry, 5% PEGHT/Adsorb P-1 (80/100, diameter 3 mm and length 1200 mm), carrier gas: He, flow rate: 30 ml min^{-1}, temperature: 140 (3 min)–20 °C min^{-1}–200 °C (12 min), injection temperature: 200 °C, detector: FID (250 °C).

(ii) *C_2H_4 and CO_2*. Apparatus: Shimadzu, GC-9A, column: Waters Porapak QS (80/100, diameter 3.2 mm and length 3100 mm), carrier gas: He, flow rate: 40 ml min^{-1}, temperature: 70 °C, injection temperature: 200 °C, detector: TCD (200 °C).

Identification of the products was carried out by GC/MS (Hitachi, L-6000/JEOL, JMS-SX102) and LC/MS (Hewlett-Packard, 5890A/JEOL, JMS-SX102).

(iii) *Polymeric products* were analyzed by gel permeation chromatography. Apparatus: Shimadzu, LC-6AD, column: Toso, TSKgel GMHXL (diameter 7.8 mm and length 300 mm), eluent: DMF, flow rate: 1 ml min^{-1}, temperature: 25 °C, detector: RI. The structure of the isolated polymeric products were analyzed by a CHN elemental analyzer (Perkin-Elmer, 240C), FT-IR (Nicolet, DX510), ^{1}H and ^{13}C-NMR (Varian Instruments, Gemini 300), and pyrolysis–GC/MS (pyrolyzer; Yanagimoto, GP-1018).

2.3. Model capacitor test

A model capacitor was assembled by using a 6 ml glass vial with a polytetrafluoroethylene (PTFE)-coated butyl
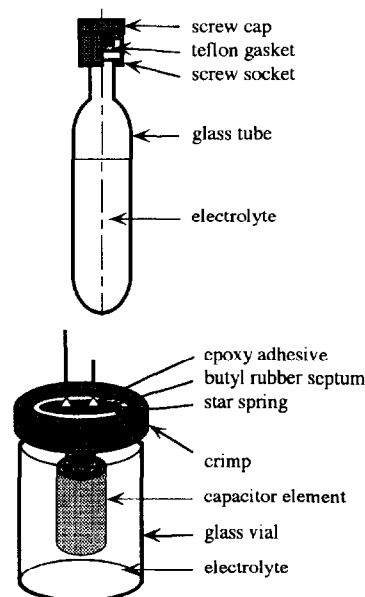

Fig. 1. Schematic view of (a) ampule tube, and (b) model capacitor.

rubber septum (Perkin-Elmer) as depicted in Fig. 1(b). A capacitor element with 25 WV, 340 μF, whose lead wires were stuck through the closure and glued with an epoxy adhesive, was immersed into 8 ml of an electrolyte in the vial and crimped tightly. With or without applying 25 V on the model capacitors from a d.c. power source (Kikusui Electronics Co., PAD110-1.5L) at 115 °C in the oven, the deterioration of the electrolytes was examined at regular intervals by the measurement of the electrolytic conductivity and liquid chromatography analysis as described above.

3. Results and discussion

Thermal stability of the GBL-based electrolytes was examined by leaving the electrolytes in the sealed tubes (Fig. 1(a)) at 115 °C.

3.1. Electrolytic conductivity

Fig. 2(a)–(c) shows the change in electrolytic conductivities of the phthalate, maleate and benzoate systems, respectively. Decrease in conductivity indicates the deterioration of the electrolytes caused by the decrease of ionogens. It is apparent from Fig. 2 that the deterioration behavior is mainly dependent on the kind of carboxylate anion.

(i) Phthalate electrolytes were stable at 115 °C over 15 000 h regardless of the kind of ammonium cation. Although there was a large difference in electrolytic conductivity between quaternary and tertiary ammonium salts [9], no difference in stability was observed at 115 °C.

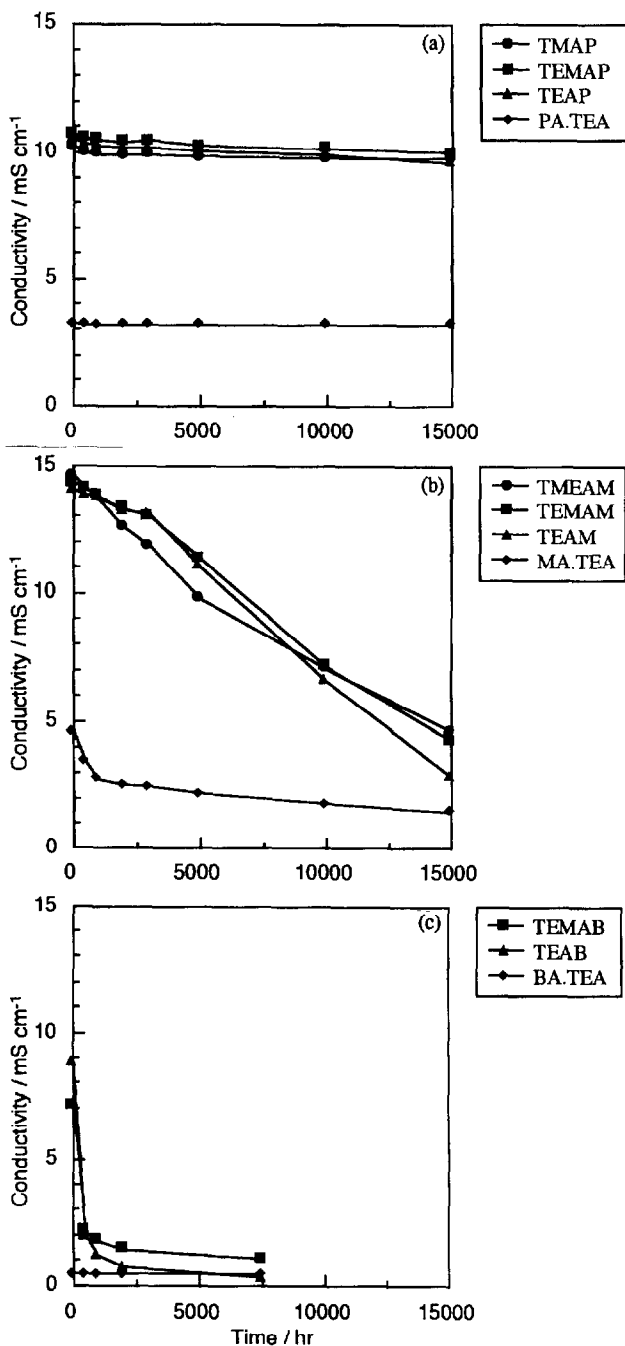(ii) Maleate electrolytes showed a decrease in electrolytic conductivity. Quaternary ammonium salts gradually deteri-

Fig. 2. Conductivity change of GBL-based electrolytes at 115 °C: (a) phthalate/GBL; (b) maleate/GBL, and (c) benzoate/GBL systems.

Fig. 3. Chromatograms for the deteriorated electrolytes at 115 °C: (a) TMAP/GBL, 15 000 h; (b) TETAM/GBL, 15 000 h, and (c) TEMAB/ GBL, 500 h.

orated with time, while tertiary ammonium salts exhibited initial degradation.

(iii) Quaternary ammonium benzoate electrolyte deteriorated rapidly within 100 h, while tertiary ammonium benzoate electrolyte kept its low conductivity constant.

3.2. Product analysis

In order to clarify the decomposition mechanisms, the deteriorated electrolytes were analyzed by liquid chromatography. Fig. 3(a)–(c) shows the chromatograms of the dete-
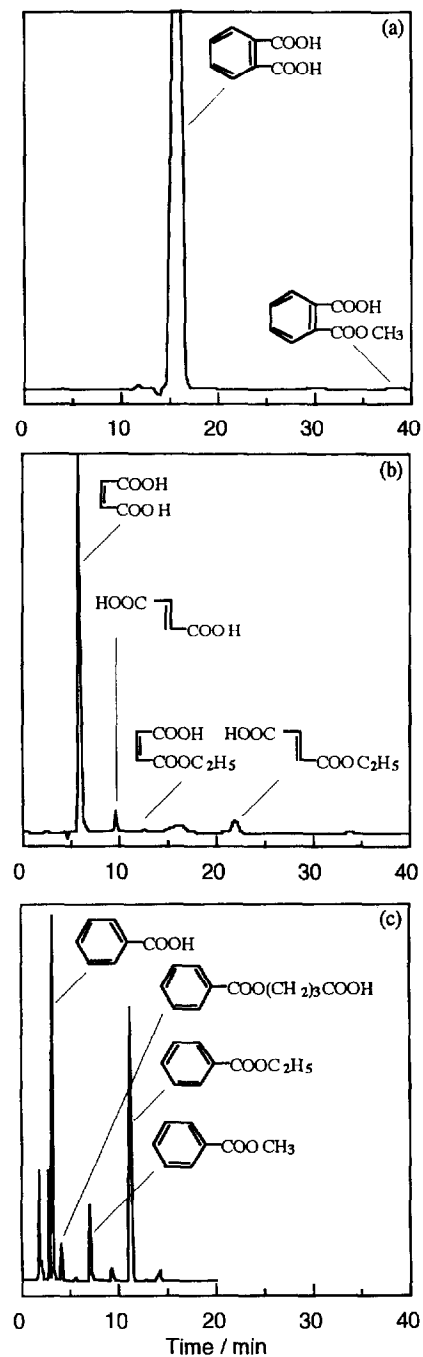
riorated electrolytes at 115 °C for phthalate (TMAP), maleate (TEMAM) and benzoate (TEMAB) electrolytes, respectively. The phthalate and maleate electrolytes gave a small amount of converted products even after 15 000 h, while the benzoate electrolyte after 500 h contained not only a significant amount of alkyl benzoates but also a condensation product between benzoic acid and γ-butyrolactone.

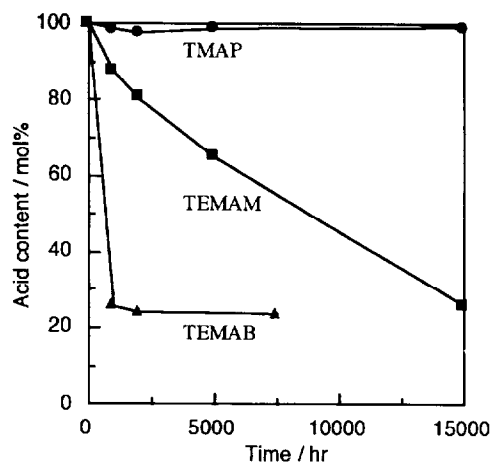In Fig. 4, the decrease in carboxylic acid contents versus time analyzed by liquid chromatography is given. The

Fig. 4. Decrease in acid content in GBL-based electrolytes at 115 °C.

Table 1
Analytical results for TEMAM/GBL electrolyte after 188 h at 150 °C

Products	mol% [a]	Products	mol%
COOH COO (structure)	79.3	$(C_2H_5)_3CH_3N^+$	80.3 [b]
CO_2	15.8	$(C_2H_5)_2CH_3N$	7.0
		C_2H_5OH	5.8
		$CH_2=CH_2$	0.9
HOOC—COOC₂H₅ (structure)	1.0	$(C_2H_5)_3N$	3.0
(H_2O)	21.5)	CH_3OH	2.6

[a] Calculated by assuming initial TEMAM to be 100 mol%.
[b] Estimated from acid content.

decrease in acid content correlates strongly with the decrease in electrolytic conductivity, which was shown in Fig. 2.

To elucidate the decomposition routes accurately, quantitative analyses of the products included in both gas and liquid phases were carried out.

(i) From TMAP electrolyte heated at 130 °C for 250 h, only small amounts of trimethylamine and monomethyl phthalate were detected and no further investigation was performed.

(ii) Since the decomposition rate of TEMAM electrolyte at 115 °C was not severe enough to give an appropriate amount of products for their characterization, the reaction temperature was raised to 150 °C using a portable reactor. Analytical results are given in Table 1, where 90% in mass balance was obtained. The amounts of products were represented in mol% when the initial content of TEMAM was assumed to 100 mol%. The formation of carbon dioxide accounted for 76 mol% of the loss of maleate anion and the generation of amines and alcohols accounted for 51 mol% of the loss of triethylmethylammonium cation, respectively. Isomerization of maleate to fumarate proved to be a minor pass, despite this conversion has been considered to be a main reason to lose conductivity in tertiary ammonium maleate/ GBL electrolytes [5]. Although acrylate anion, which can be a decarboxylated product of maleate anion, was not detected in the deteriorated electrolyte, an unknown polymeric product

was detected by gel permeation chromatography. This polymer, which was isolated by evaporating the solvent followed by washing with water, was analyzed by several methods. Elemental analysis revealed low nitrogen content in the polymer (C: 61.56, H: 6.62, N: 0.37), however, NMR and pyrolysis–GC/MS suggested the existence of the triethylmethylammonium cation. FT-IR afforded a strong peak at 1740 cm^{-1} and shoulder at 1600 cm^{-1}, which are assigned to an ester and carboxylate anion, respectively. Pyrolysis–GC/MS also showed strong CO_2 and GBL peaks, which are strong indications of the existence of polyester structures. About 5 wt.% loss of GBL in the deteriorated electrolyte also supports this speculation. According to these results, the decarboxylation of maleic acid is a main reaction followed by the formation of polymeric compounds containing polyester and polyacrylate structures as shown in Fig. 5. The reason of water formation is unclear, this amount being nearly equivalent to the loss the of maleate anion.

(iii) Analytical results for TEMAB electrolyte are given in Table 2, where 97% in mass balance was obtained. It became apparent that quaternary ammonium benzoate salts decompose by SN2 attack at the carbon atoms on quaternary ammonium cation by carboxylate anion as shown in Fig. 6. The large difference in chemical stability between the phthalate and benzoate electrolytes can be attributed to the difference in the extent of ionic association as reported previously [8].
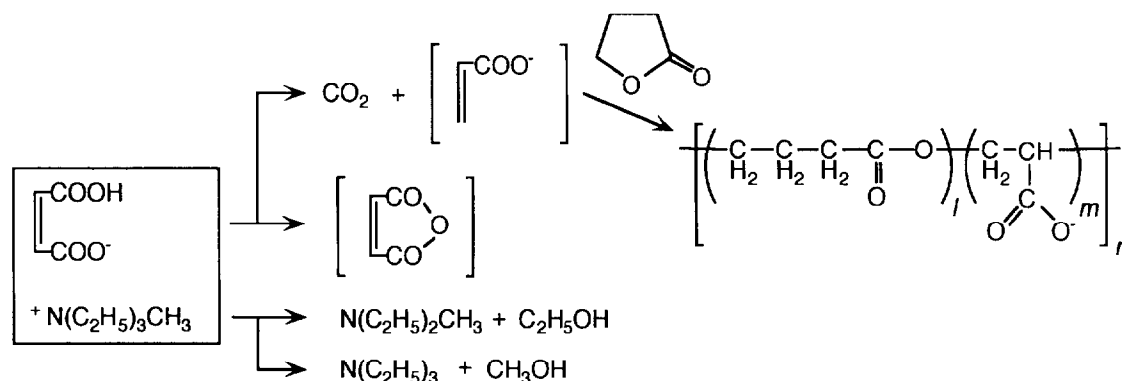

Fig. 5. Scheme of the deterioration of TEMAM/GBL electrolyte.
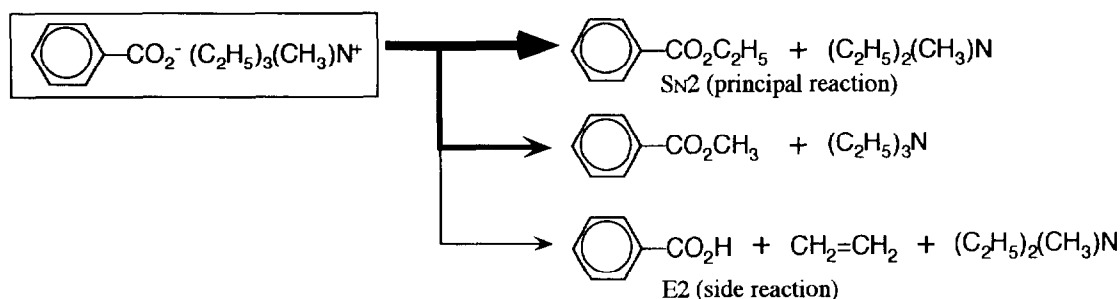
Fig. 6. Scheme of the deterioration of TEMAB/GBL electrolyte.
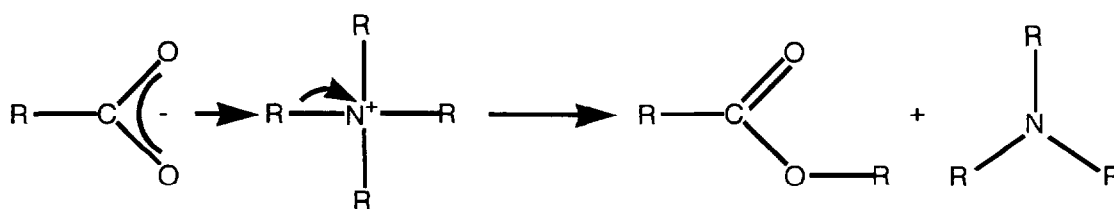

Fig. 7. Effect of ion-pair formation vs. decomposition of a quaternary ammonium carboxylate.

Table 2
Analytical results for TEMAB electrolyte after 250 h at 110 °C

Products	mol% [a]	Products	mol%
⬡—COO⁻	26.4	$(C_2H_5)_3CH_3N^-$	26.4 [b]
⬡—COOC₂H₅	46.9	$(C_2H_5)_2CH_3N$	46.8
		C_2H_5OH	1.9
⬡—COOCH₃	16.7	$(C_2H_5)_3N$	31.7
		CH_3OH	2.4

[a] Calculated by assuming initial TEMAB to be 100 mol%.
[b] Estimated from acid content.

It seems that a strong ion-pair formation accelerates the decomposition reaction according to the reaction scheme shown in Fig. 7, because the shorter distance between a carboxylate anion and a quaternary ammonium cation enhances the probability of collisions between these ions.

3.3. Model capacitor test

The life of aluminum electrolytic capacitors is usually evaluated by examining the changes in capacity and dissipation factor at an elevated temperature with or without applying a nominal voltage [3]. It was reported that the life of capacitors can be easily estimated by their weight, because the weight loss of the capacitors by solvent evaporation correlates with the capacity decrease or dissipation factor increase [10]. However, there is no report on the chemical change of the electrolytes inside the capacitors due to technical difficulties. We adopted a model capacitor, which consisted of a glass vial, a PTFE-coated butyl rubber septum and a capacitor element with 25 WV, 340 µF (Fig. 1(b)). This model capacitor contained a large excess amount of the electrolyte, which
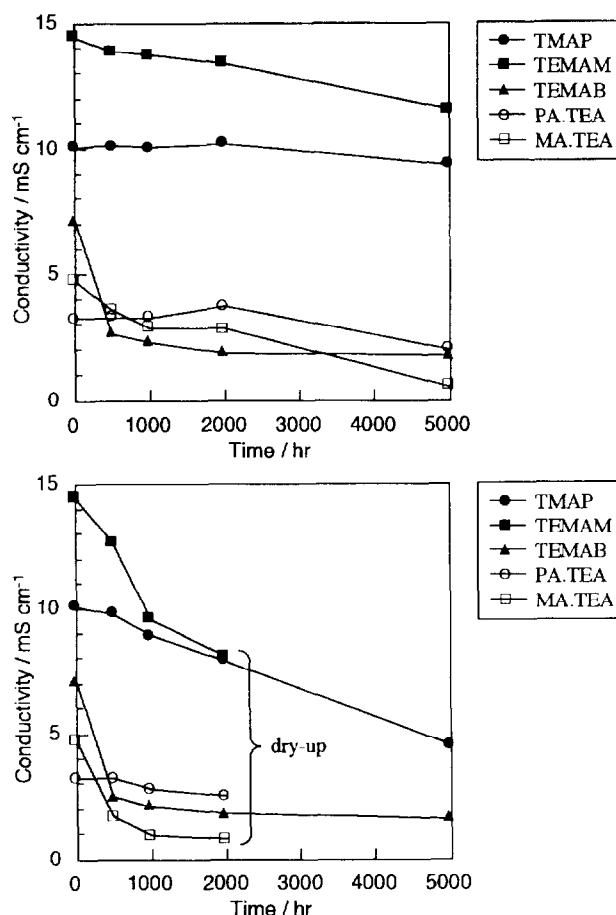

Fig. 8. Life tests at 115 °C of model capacitors employing GBL-based electrolytes: (a) shelf test, and (b) load test.

enabled the measurement of electrolytic conductivity and the analysis of the composition of the deteriorated electrolytes.

Fig. 8 shows the decreases in conductivity of phthalate, maleate and benzoate electrolytes including quaternary and tertiary ammonium salts, when the model capacitors were left

at 115 °C without or with applying a d.c. 25 V. The features of Fig. 8(a) were almost equal to those of Fig. 2, which indicates no catalytic effect of aluminum or aluminum oxide occurred during the decomposition reaction. Applying a d.c. voltage accelerated evidently the deterioration of phthalate and maleate electrolytes and resulted in dry-up of the electrolytes. The investigation on the detailed mechanisms by electrolysis is in progress.

4. Conclusions

1. In quaternary ammonium hydrogen maleate/GBL electrolytes, the maleate anion decomposed by decarboxylation resulting in a complex polymer containing polyester and polyacrylate structures.
2. Quaternary ammonium benzoate deteriorated in GBL by SN2 reaction giving alkyl benzoates and trialkylamines.
3. Decomposition of carboxylate salts in GBL was accelerated by electrolysis.

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