

Short communication

Triethanolamine as an additive of high water content electrolyte to enhance the capacitor's performance

Kun-Li Wang^{a,*}, Rong-Fu Chang^b

^a Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei, No. 1, Section 3, Chung-Hsiao E. Road, Taipei 106, Taiwan

^b Habor Electronics Co. Taichung, No. 77, Industrial 20th Road, Tai-ping City, Taichung 411, Taiwan

Received 4 May 2006; received in revised form 30 August 2006; accepted 31 August 2006

Available online 5 October 2006

Abstract

Triethanolamine (TEA) has been evaluated as an additive to a commercial electrolyte to enhance the properties of aluminum electrolytic capacitors. The results showed 1–3 wt.% TEA additive can prevent the pH and conductivity of the electrolytes from decreasing for 5000 h at 60 °C. The anodic restoration ability of an anode aluminum film in the electrolyte with TEA additive showed more efficient than the electrolyte without TEA additive. Low temperature electric characteristics of capacitors showed that TEA additive can prevent the electrolyte inside capacitors from freezing and losing electric characteristics even at –40 °C. Load life test of capacitors impregnated with electrolytes with or without TEA additive showed remarkable differences. The TEA additive promoted 105 °C load life time from 3019 h up to 5624 h and from 2144 h up to 3621 h for 125 °C load life time test.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Aluminum electrolytic capacitor; Electrolyte; Triethanolamine; Load life; Additive

1. Introduction

Various applications of aluminum electrolytic capacitors include home appliances, computer motherboards and peripherals, power supplies, industrial electronics, communication products and automobiles [1,2]. The capacitors are mainly used to provide filtering, bypassing, rectifying, coupling, blocking, flash light or transforming functions, which play an important role in the electric and electronic products [3].

A typical aluminum electrolytic capacitor includes an anode foil and a cathode foil processed by surface-enlargement and/or formation treatments. The surface-enlargement treatment is performed by etching a high purity aluminum foil to increase its surface area so that a miniaturized electrolytic capacitor with high capacitance can be obtained. The anode aluminum foil is then subjected to form a dielectric surface film (Al₂O₃). The thickness of a dielectric film is related to the working volt-

age of the aluminum electrolytic capacitor. After cutting to a specific size according to the design specification, a laminate made up of an anode foil, a cathode foil which is opposed to the dielectric film of the anode foil and possesses etched surfaces, and a separator interposed between the anode and cathode foils, is wound to provide an element. The wound element does not have any electrical characteristics of electrolytic capacitor yet until completely dipped in an electrolyte for driving and housed in a metallic sheathed package in cylindrical form with a closed-end equipping a releaser. Furthermore, a sealing material made of elastic rubber is inserted into an open-end section of the sheathed package, and the open-end section of the sheathed package is sealed by drawing, whereby an aluminum electrolytic capacitor is constituted [4].

In fact, the electrolytic capacitor utilizes the mobility of ions in the electrolyte to obtain electric characteristics; therefore, the conductivity of the electrolyte is an important factor for deciding the performance of an electrolytic capacitor. Such that, it is an important issue for how to promote the conductivity of an electrolyte to maintain the electrolytic capacitor with high-temperature stability between the electrolyte and the materials

* Corresponding author. Tel.: +886 2 27712171x2558; fax: +886 2 27317117.

E-mail addresses: klwang@ntut.edu.tw (K.-L. Wang), rfchang@ntu.edu.tw (R.-F. Chang).

used in the capacitors, especially the stability of the electrolyte and the aluminum foils [5].

The capacitor is always required to have a low equivalent series resistance (ESR) in applications in order to sufficiently show the high performance. Recent studies [6–8] on electrolyte focus on high conductivity, higher stability under operation conditions, and higher reliability for capacitor using the electrolyte. One of the easy way to promote its conductivity is to increase its water-content in the EG/water solvent ratio. However, the disadvantages of high water-content electrolyte are as follows: (1) it possesses lower boiling point and higher saturated vapor pressure, which causes damage on the capacitor structure. (2) Water may react with the aluminum oxide to form hydroxide and hydrogen at high temperature, so that the dielectric film may be destroyed and cause rapid decay on voltage endurance and ascent on leakage current. (3) The low temperature electric characteristics of the electrolyte may be not good due to the high water content [9].

The pH of the electrolyte in the aluminum electrolytic capacitor should be prevented from decreasing, in order to obtain an aluminum electrolytic capacitor with high reliability. Nakada et al. [10] used a solid compound comprising a metal for keeping the pH of the electrolyte constant. Szaraz et al. [11] proposed that the acid forms esters with ethylene glycol EG at low pH and high temperature. The high vapor pressure of esters and water increases high internal pressure in the capacitor and results in failure of the capacitors [12,13].

One approach to solve the disadvantages of high water-content electrolyte is to prevent the pH from decreasing during using by subjoining an additive with a high boiling point, stable with capacitor element, basic, and soluble in electrolyte.

The physical properties of triethanolamine are as follows: molecular weight 149.2, melting point 21.6 °C, boiling point 335.4 °C, pH 10.5. It is soluble in EG/water based electrolyte and can promote the boiling point of the electrolyte. Therefore, triethanolamine is a good candidate for being the additive. In this paper, we subjoin triethanolamine in a commercial high water-content electrolyte to evaluate its performance.

2. Experimental

2.1. Electrolyte test

The origin electrolyte (A0) was supplied by Habor Electronics Co. (Taiwan) containing mainly ethylene glycol EG, water, ammonium adipate, citric acid, ammonium formate, ammonium phosphate and a small amount of *p*-nitrobenzoic acid. The water content of A0 is around 50 wt.%, triethanolamine (TEA, Mallinckrodt, 99 wt.% CAS:102-71-6) was added to the origin electrolyte with a weight percent of 1% (A1) and 3% (A3). TEA was well stirred in a beaker at 60 °C for 1 h and was dissolved completely. The pHs and conductivities of the solutions were measured at 25 ± 3 °C and also monitored at a specific period of time at 60 °C. The conductivities and pHs of these samples were measured with a conductivity meter (WTW cond 330i/SET, Germany) and a pH meter (WTW pH 330i/SET, Germany).

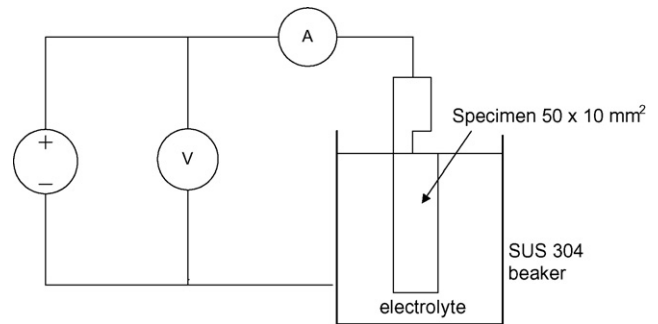


Fig. 1. Voltage–time curve measurement circuit.

The anodic formation of the aluminum oxide film (580 formation voltage, Foiltec, Taiwan) was tested in these samples using an SUS 304 1000 mL beaker as the counter electrode at 25 ± 3 °C. The aluminum oxide film specimen was cut into a specimen as indicated in Fig. 1 and immersed 50 mm × 10 mm area beneath the electrolyte. A constant current density of 0.2 mA cm⁻² was applied and the voltage–time curve was recorded [14].

2.2. Low temperature test of capacitor

Capacitors with 6.3 V, 1000 μF, 8 mm × 20 mm (diameter × height) were used as the examples in this study. The elements were kindly provided by Habor electronics Co., Taiwan. The capacitor element included: (1) the anode aluminum foil, model LA80A1, capacitance 65 μF cm⁻², 11.5 AV, 119 mm × 14 mm (length × width), thickness 80 μm produced by Liton company, Taiwan; (2) the cathode aluminum foil, model FT520, capacitance 200 μF cm⁻², 134 mm × 14 mm (length × width), thickness 50 μm produced by Foiltec company, Taiwan; (3) the separator, model RTZ30-40, thickness 40 μm, 288 mm × 16 mm (length × width) produced by NKK company, Japan; (4) lead type 15120 (KLF Co., Taiwan).

The comparison of low temperature electrical characteristics were carried out by showing the ratio of capacitance (*C*), the ratio of dissipation factor ($\tan \delta$), and the ratio of impedance (*Z*) at 120 Hz and 100 kHz at different temperatures.

The capacitance and $\tan \delta$, leakage current (LC) and ESR of the capacitors were measured at 25 ± 3 °C by an LCR meter (Zentech 100 LCR meter, Taiwan) at a frequency of 120 Hz, a leakage current tester (Zentech CLC 201, Taiwan) and a component analyzer (Zentech 3305 automatic component analyzer, Taiwan) at a frequency of 100 kHz [15].

2.3. Capacitor load and shelf life test

According to Japanese industrial standard (JIS) method [15], a load life test was performed to measure the electrical characteristics of the aluminum electrolytic capacitor at a specific temperature, such as 105 and 125 °C, with applying a working voltage from a dc power supplier (IDRC CHP Q500A, Taiwan) and measured the electrical characteristics at 25 ± 3 °C every specific time period.

Table 1
Conductivities and pHs of electrolytes

Entry	TEA (wt.%)	pH ^a	Conductivity (mS cm ⁻¹) ^a
A0	0	5.9	91.7
A1	1.0	6.0	90.5
A3	3.0	6.3	85.4

^a pH and conductivities were measured at 25 ± 3 °C.

3. Results and discussion

3.1. Electrolyte test

The pHs and conductivities of the solution were measured at 25 ± 3 °C and listed in Table 1. As the TEA content increased from 0 to 3 wt.%, the conductivities slightly decreased from 91.7 to 85.7 mS cm⁻¹ due to the much lower dissociation constant (1.73×10^{-8}) comparing to other components (about 10^{-4}) in the electrolyte formula and higher viscosity of TEA. The basicity of TEA made the pHs of the solution increasing from 5.9 to 6.3.

The anodic oxidation behavior of an anode aluminum film was tested by A0, A1, A3 electrolytes. Fig. 2 shows the voltage–time curve with a constant current density of 0.2 mA cm⁻² applied. The voltage increased with time because of the growth of an insulation oxidation layer on the cutting surface of the anode foil film. While the oxidation layer and the electrolyte cannot withstand the voltage rising in the electric field, sparking spots occurred on the film surface and broke down voltage rising. From Fig. 2, we can find that electrolyte A3 restoration rate is more efficient than electrolyte A1 and A0. The final sparking voltage of these three electrolytes shows no obvious differences. The results indicate that TEA is a constructive compound for restoration, but the real reason is not understood yet. The basicity of TEA avoids the pH decreasing, which retards the formation of esters [11].

The pHs and conductivities of the electrolytes changing with time were performed at 60 °C to test the stability of the electrolytes and are illustrated in Figs. 3 and 4. From Fig. 3, the pHs with TEA additive changed from 6.00 to 6.10 for A1 and

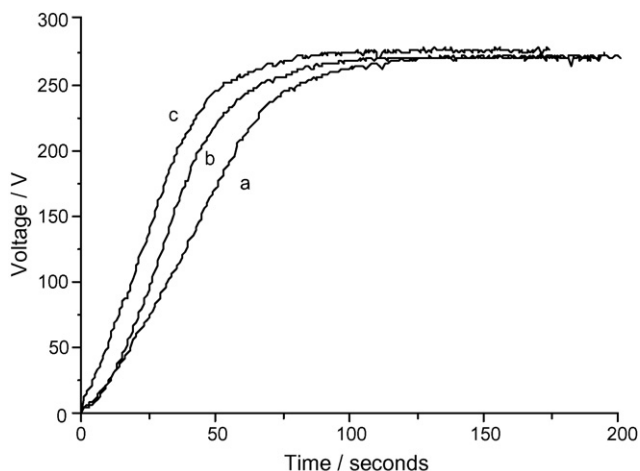


Fig. 2. Voltage–time curve in (a) electrolyte A0, (b) electrolyte A1, and (c) electrolyte A3.

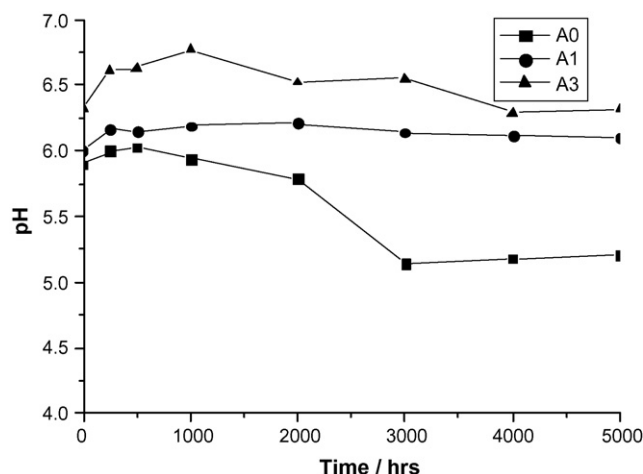


Fig. 3. The pH changes with time of the electrolytes.

from 6.30 to 6.31 for A3, respectively, while A0, without TEA additive, changed seriously from 5.90 to 5.21. The more TEA content, the pH is higher and more stable. It indicates that TEA has the function to inhibit changing on pH. From Fig. 4, the conductivities with TEA additive changed from 90.5 and 85.4 mS cm⁻¹ to 84.3 and 83.2 mS cm⁻¹ for A1 and A3, respectively, while A0, without TEA additive, changed violently from 91.7 to 45.8 mS cm⁻¹. The more TEA content, the decay of conductivity is less. This result suggests that TEA is a good compound to keep conductivity from decreasing. However, the higher TEA content has lower conductivity at the beginning. Szaraz et al. [11] have reported that esters formed and adsorbed on the aluminum oxide surface at low pH and high temperature. The conductivity of A0 decreased more rapidly than A1 and A3 because of the low ionizing ability of the esters. The results showed that TEA additive can keep pH and conductivity almost constant for 5000 h.

3.2. Low temperature test of capacitor

The results of low temperature test of the electrical characteristics are summarized in Table 2. The capacitance ratios

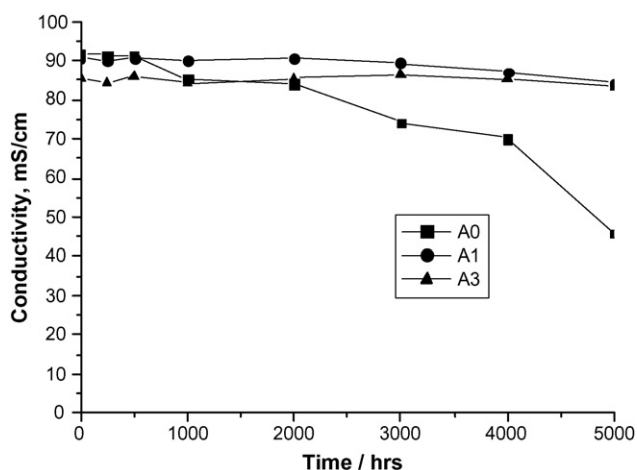


Fig. 4. The conductivity changes with time of the electrolytes.

Table 2
Low temperature properties of the capacitors impregnated with the electrolytes

Temperature (°C)		A0	A1	A3
−20/25	Z, 120 Hz	1.06	1.09	1.06
	Z, 100 kHz	1.02	1.02	1.03
	C, 120 Hz (%)	94.1	91.5	91.4
	tan δ , 120 Hz	1.23	1.15	1.11
−30/25	Z, 120 Hz	1.16	1.18	1.10
	Z, 100 kHz	3.37	3.14	2.73
	C, 120 Hz (%)	82.4	81.9	86.6
	tan δ , 120 Hz	7.76	4.66	2.79
−40/25	Z, 120 Hz	5.50	3.33	2.67
	Z, 100 kHz	29.31	20.53	18.96
	C, 120 Hz (%)	6.7	15.7	21.6
	tan δ , 120 Hz	61.74	30.48	28.60

(relative to 25 °C) for capacitors impregnated with A0 measured at −20, −30 and −40 °C were 94.1%, 82.4% and 6.7%, respectively, while the capacitance ratios for capacitors impregnated with A1 and A3 were 91.5%, 91.4% at −20 °C, 81.9%, 86.6% at −30 °C, and 15.7%, 21.6% at −40 °C. Lower ratio of impedance Z and tan δ , and higher ratio of capacitance at low temperature mean a capacitor has better electrical characteristics. The electrolyte containing higher TEA content had the lower impedance ratio and tan δ , and higher ratio of capacitance. The capacitors impregnated with electrolytes containing TEA exhibited better electrical characteristics. These results show that TEA additive can effectively prevent the electrolytes inside the capacitors from losing electrical characteristics at low temperature. It maybe results from the extra addition of TEA, which lower the freezing point of electrolyte.

3.3. Capacitor load and shelf life test

The initial electrical characteristics of the capacitors measured from 10 samples average using A0, A1, A3 as impregnated electrolytes were listed in Table 3. The initial capacitance shows a positive TEA content dependence, but dissipation factor shows a negative TEA content dependence. The results indicate that electrolytes containing TEA can alter more effective surface area on the aluminum foil. The initial ESR for the capacitors impregnated with A0, A1 and A3 are 0.012, 0.013 and 0.013 Ω respectively due to the differences in conductivities.

The failure modes of capacitors are defined in the following two conditions [16]:

Table 3
The initial electrical characteristics of capacitors impregnated with the electrolytes

Characteristics	A0	A1	A3
C, 120 Hz (μ F)	896.8	919.1	927.0
tan δ , 120 Hz (%)	4.97	4.21	4.03
LC (μ A)	2.0	2.4	2.2
ESR, 100 kHz (Ω)	0.012	0.013	0.013

All values were measured at 25 \pm 3 °C.

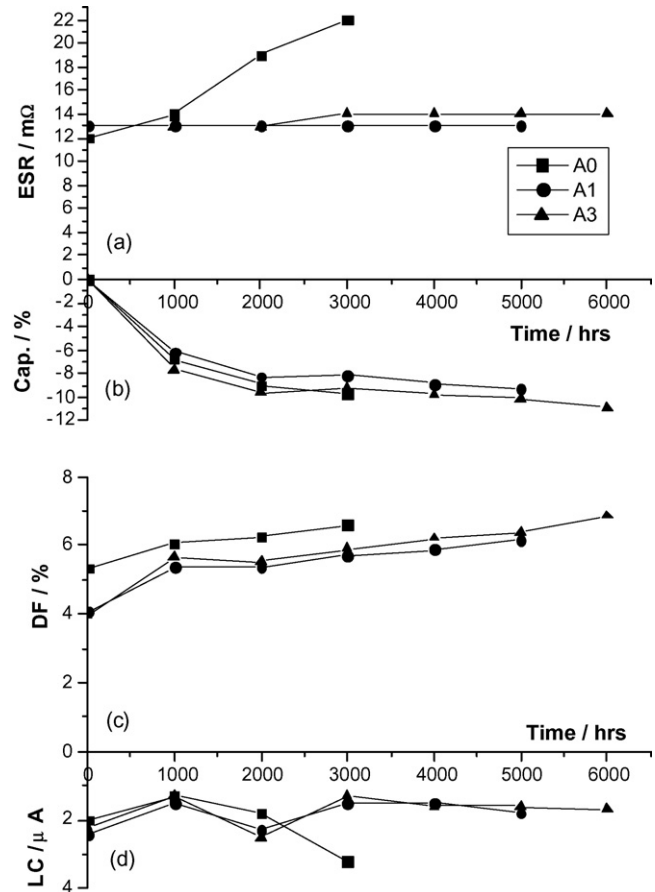


Fig. 5. Load life test at 105 °C of capacitors: (a) ESR, (b) capacitance reduction, (c) dissipation factor, tan δ , and (d) leakage current. The load life time for the capacitors was 3019 h for A0 electrolyte, 5105 h for A1 electrolyte and 5624 h for A3 electrolyte.

1. *Catastrophic failure.* When a capacitor completely lost its function due to a short or open circuit.
2. *Degradation failure.* The gradual deterioration of electrical characteristics of a capacitor.

The judging criteria for degradation failure are defined as follows: (1) capacitance drops 25% from its initial capacitance, (2) tan δ increases over 30%, (3) pressure relief vent operation. In this study, if one of these three criteria happened, the capacitor was treated as failure.

The high temperature life results are illustrated in Figs. 5 and 6. According to these criteria, the 105 °C load life was 3019 h for electrolyte A0, while it expands to 5170 and 5624 h for electrolyte A1 and electrolyte A3, respectively. Moreover, the 125 °C load life enlarges to 3621 h for electrolyte A3 from 2144 h for electrolyte A0. All failed capacitors were due to the catastrophic failure. The capacitors life time were related to the TEA contents of the electrolytes, which kept the pHs and conductivities almost constant during the capacitor's serving life. This indicates the capacitors impregnated with TEA additive electrolyte have longer serving life performance.

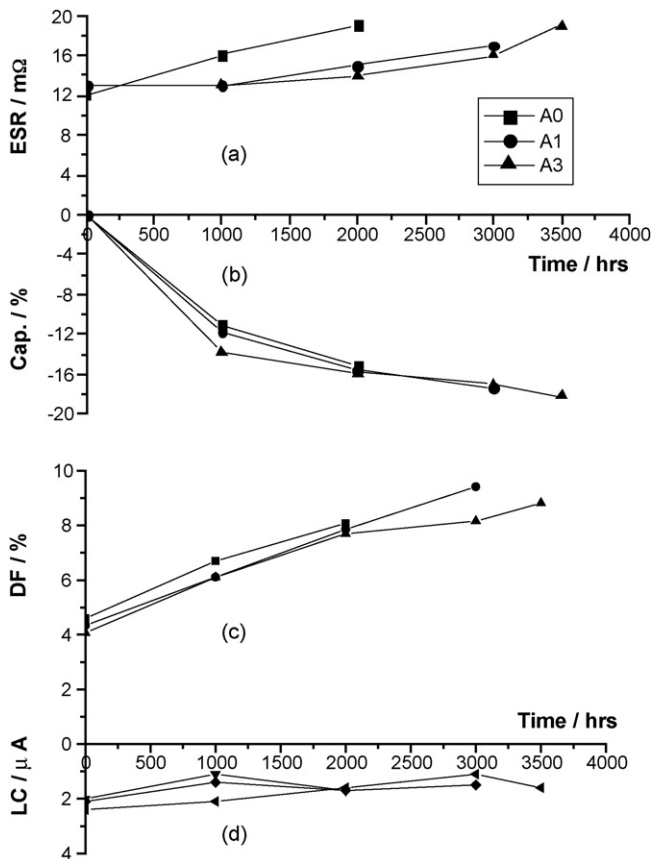


Fig. 6. Load life test at 125 °C of capacitors: (a) ESR, (b) capacitance reduction, (c) dissipation factor, $\tan \delta$, and (d) leakage current. The load life time for the capacitors was 2144 h for A0 electrolyte, 3126 h for A1 electrolyte and 3621 h for A3 electrolyte.

4. Conclusion

A new electrolyte system adding TEA as an additive has been proposed for aluminum electrolytic capacitors. Experimental results obtained in the present work are summarized as follows:

1. The TEA additive in a commercial high water-content electrolyte will raise the pH and lower the conductivity a bit. It can

keep pHs and conductivities of capacitors from dramatically decreasing with time.

2. The capacitors impregnated with electrolytes containing TEA will exhibit better low temperature electrical characteristics. TEA can effectively prevent the electrolytes inside the capacitors from freezing and losing electrical characteristics.
3. The TEA additive electrolyte makes the anodic restoration ability behavior more efficient.
4. The electrolyte containing TEA can maintain the pHs and conductivities almost constant for long serving life.
5. The 1–3% TEA additive to a commercial high water-content electrolyte can enhance the service life without failure.

Acknowledgements

The authors are grateful to Habor electronics Co. for supporting through this investigation. The financial support provided by Mr. Habor Hsu is gratefully acknowledged.

References

- [1] Dennis Zogbi, Passive Component Industry, Paumanok Publications, September/October 2003, pp. 8–11.
- [2] R. Kotz, M. Carlen, *Electrochim. Acta* 45 (2000) 2483.
- [3] A. Bruce Carlson, David G. Gisser, *Electrical Engineering Concepts and Applications*, 2nd ed., Addison Wesley, 1990, pp. 113–147.
- [4] I. Nagata, *Aluminum Dry Electrolytic Capacitors*, Japan Capacitor Industry, Tokyo, 1983.
- [5] J.-K. Chang, C.-M. Liao, C.-H. Chen, W.-T. Tsai, *J. Power Sources* 138 (2004) 301–308.
- [6] A. Komatsu, T. Ogawara, US Patent 6,288,889 (2001).
- [7] A. Komatsu, US Patent 6,349,028 (2002).
- [8] T. Sugiyama, M. Ozawa, H. Itoh, K. Tamamitsu, M. Sakakura, US Patent 6,493,211 (2002).
- [9] A. Komatsu, T. Ogawara, US Patent 6,285,543 (2001).
- [10] Y. Nakada, M. Tanahashi, E. Igaki, M. Shimada, US Patent 6,542,784 (2002).
- [11] I. Szaraz, W. Forsling, *Appl. Spectrosc.* 57 (6) (2003) 622–627.
- [12] M.-L. Tsai, Y.-F. Lu, J.-S. Do, *J. Power Sources* 112 (2002) 643–648.
- [13] M. Ue, M. Takeda, Y. Suzuki, S. Mori, *J. Power Sources* 60 (1996) 185–190.
- [14] EIAJ RC-2364, Electronic Industry Association of Japan, 1998.
- [15] JIS C 5101-4, Japanese Standard Association, 2002.
- [16] Technical note CAT8101D, Nichicon Co., Japan.