

Short communication

High-performance electrolyte in the presence of dextrose and its derivatives for aluminum electrolytic capacitors

Ming-Liao Tsai^{a,*}, Yi-Fang Lu^a, Jing-Shan Do^{b,1}

^aDepartment of Chemical Engineering, National Chin-Yi Institute of Technology, Taichung 411, Taiwan, ROC

^bDepartment of Chemical Engineering, Tunghai University, Taichung 40704, Taiwan, ROC

Received 28 May 2002; accepted 16 August 2002

Abstract

Dextrose and its derivatives (e.g. glucose, gluconic acid and gluconic lactone) are added to modify the characteristics of electrolytes used in aluminum electrolytic capacitors. The results show that the conductivity and sparking voltage of the electrolytes are severely affected by the concentration of dextrose gluconic acid and gluconic lactone. In addition, the pH of the electrolyte is only slightly affected by the quantity of gluconic acid and gluconic lactone. The capacitance, dissipation factor, and leakage current of capacitors impregnated with the electrolytes prepared in this work are periodically measured under storage conditions and loading at 105 °C.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Aluminum electrolytic capacitors; Sparking voltage; Capacity; Dissipation factor; Leakage current; Dextrose

1. Introduction

Electrolytic aluminum capacitors have been widely employed in the electronics industry [1–4]. The demand of these capacitors is estimated to increase by 8–12% per year by the Industrial Technology Research Institute (ITRI) in Taiwan. Electrolytic aluminum capacitors are mainly used as power supplies for automobiles, aircraft, space vehicles, computers, monitors, motherboards of personal computers, and other electronics. Recent studies on electrolytic aluminum capacitors have focused on achieving smaller size, higher capacitance, greater reliability, and increased safety. In general, the materials and surface morphologies of electrodes, the composition of electrolytes, and the assembly of capacitors determine the performance of the electrolytic aluminum capacitors. It is believed that the composition of electrolytes is one of the most important factors that affect the characteristics of electrolytic aluminum capacitors [5–13].

Studies of solvents for electrolytic aluminum capacitors reported previously [5–19] have mainly focused on ethylene glycol, γ -butyrolactone, and solid electrolytes. Kazuhiko

et al. [8] proposed that the addition of organic and inorganic acids and their derivatives into the electrolyte could reduce the internal resistance of aluminium electrolytic capacitors and broaden the temperature range for applications. Roland [9] devised non-toxic aluminum electrode capacitors in which the electrolyte is a solution in ethylene glycol solution which contains the neutralization product of isophthalic acid (or terephthalic acid) and dialkylamine (or piperidine). Akihiko and Tetsushi [10] made an electrolytic capacitor with an organic and aqueous mixing solvent, the electrolyte included carboxylic acids and salts, inorganic acids and salts, and chelate compounds. Preferably, an organic acid or its salt and an inorganic acid or its salt were used in combination. The chelate compounds were selected from a group that consisted of ethylenediamine-*N,N,N',N'*-tetraacetic acid, *trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid monohydrate, etc. [10]. With a γ -butyrolactone as solvent, a long life and high reliability electrolyte for an aluminum electrolytic capacitor was developed in the presence of a salt composed of carboxylic acid and a quaternary compound which contained a *N,N,N'*-substitute amidine group [11]. Shoichiro et al. [12] reported an electrolyte for use in an aluminum electrolytic capacitor that comprised a quaternary phosphonium salt and an aprotic solvent. The characteristics of aluminum electrolytic capacitors have been found [5–12] to be strongly influenced by the composition of the electrolytes.

* Corresponding author. Tel.: +886-4-2392-4505x7510; fax: +886-4-2392-6617.

E-mail address: mltsai@chinyi.ncit.edu.tw (M.-L. Tsai).

¹ Tel.: +886-4-3590262x114; fax: +886-4-3590009.

For a high-performance electrolytic aluminum capacitor, the electrolyte must have the following physicochemical properties: (i) high ionic conductivity; (ii) a wide operation temperature range (including high thermal stability); and (iii) high ability towards self-restoration (healing) of the aluminum oxide film. To enhance the performance of electrolytic aluminium capacitors, it is very important to prepare electrolytes with various additives. In our previous investigations [5–7], the performance of electrolytes used in the aluminum electrolytic capacitor has been significantly improved by adding various additives such as tetraalkammonium salts and carbohydrates. It was demonstrated that both the sparking voltage and the pH value of the aluminum electrolytic capacitor could be increased by the addition of carbohydrates to the electrolytes when ethylene glycol/H₂O was used as solvent. Nevertheless, the resistance of the electrolyte is increased in the presence of carbohydrates [6]. In the work reported here, dextrose and its derivatives are added to electrolytes based on an ethylene glycol/H₂O mixed solvent to improve the characteristics of the electrolytes. The performance of electrolytic aluminum capacitors with these electrolytes is investigated.

2. Experimental

The raw electrolyte solution, Her Mei 2001, was supplied from Her Mei Electronic Co. Ltd (Taiwan). All the chemicals (e.g. dextrose extra pure grade >99% Wako), gluconic acid (50% aqueous solution, Merck), gluconic lactone (extra pure grade >99%, Sigma), and ethylene glycol (100% J.T. Baker) were not purified further before usage. Electrolytes prepared by adding the desired amount of additives to the commercial electrolyte Her Mei 2001 were used for measuring characteristics such as conductivity, pH, and sparking voltage. The capacitors were prepared by impregnating a condenser element (Her Mei) with the electrolytes under vacuum for 40 min.

The pH, conductivity (κ), dissipation factor (DF) and leakage current (L_c) of the electrolytes were measured by means of a pH meter (SUNTEX SP-701), a conductivity meter (Mettler Toledo MC 126), LCR meter (Motech MT 4080A), and a leakage current tester (Zentech CLC-203), respectively. The values of capacity (C_p) and DF were measured at a frequency of 120 Hz, and the value of L_c was obtained at the loading of 11.5 V for 60 s.

2.1. Sparking voltage

Two aluminum foils (>99.7% AXX1005) were placed into the suitable volume of electrolyte prepared as above. A constant current density of 10 mA cm⁻² was applied by a power source (Chroma 6208K-500) and the cell potential was recorded until sparking occurred at the anode surface.

2.2. Capacitor durability

The durability of electrolytes prepared in this work was tested under the conditions of low-temperature storage, high-temperature storage, and high-temperature with loading. The characteristics of capacitors, including C_p , DF and L_c , were periodically measured under these various conditions. For low- and high-temperature storage, the capacitors impregnated with various electrolytes were placed in a refrigerator maintained at -4 °C and in an oven at 105 °C, respectively. Some of the capacitors were maintained at 105 °C with a voltage loading of 11.5 V for testing of durability.

3. Results and discussion

3.1. Effect of dextrose

The effect of the concentration of dextrose on the properties of the electrolytes is shown in Figs. 1–3. The influence on pH is insignificant, the value remains at around 6.70. This behaviour is due to the fact that dextrose molecules cannot dissociate to alter the concentration of H⁺ in the solution.

The sparking voltage of the electrolyte increases sharply from 106 to 226 V with increase in dextrose concentration from 6.85 to 7.95 wt.%, as illustrated in Fig. 2. A stable, insulating oxide film is grown on the aluminum foil surface in the presence of dextrose, and dextrose can also function as an inhibitor to depress hydrogen evolution at the surface of the aluminum foil [7]. A stable oxide film on the aluminum foil in the presence of dextrose increases the sparking voltage. With further increase in dextrose concentration above 7.95 wt.%, the sparking voltage remains at a constant value of 233 V (Fig. 2).

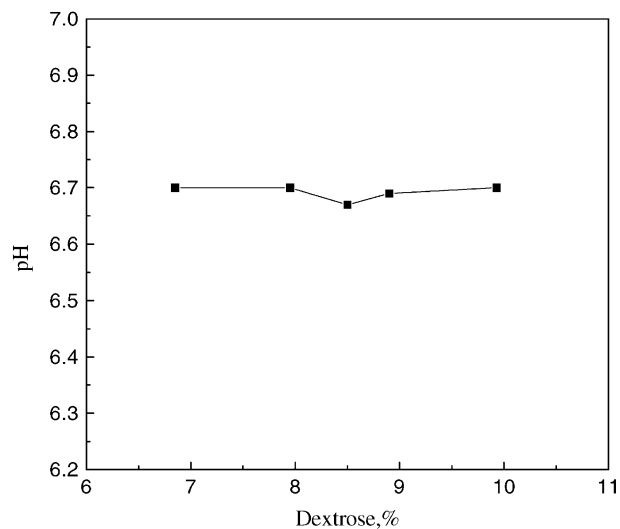


Fig. 1. Effect of concentration of dextrose on pH of electrolyte solution. Temperature: 299 K.

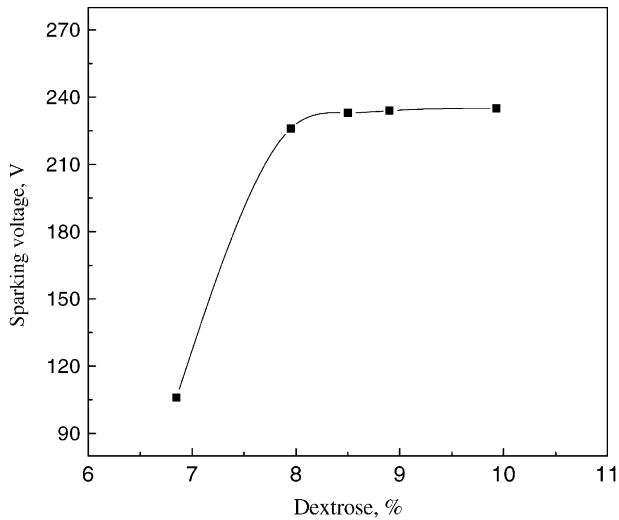


Fig. 2. Effect of concentration of dextrose on sparking voltage. Temperature: 299 K.

The mobility of ions in the electrolyte decreases due to the increase in the viscosity of the solution when the concentration of dextrose is increased. Hence, it appears that the conductivity of the electrolyte decreases with increase in the concentration of dextrose. This deduction is confirmed the experimental data shown in Fig. 3. The conductivity decreases from 26.0 to 21.2 mS cm^{-1} when the concentration of dextrose increases from 6.85 to 9.93 wt.%.

3.2. Effect of gluconic acid

Unlike the effect of dextrose, gluconic acid decreases the pH of electrolyte, i.e. from 6.08 to 5.88 with the increase in the concentration from 8.22 to 9.59 wt.% (Fig. 4). Otherwise, the pH is kept at 6.06 and 5.88 for concentrations of

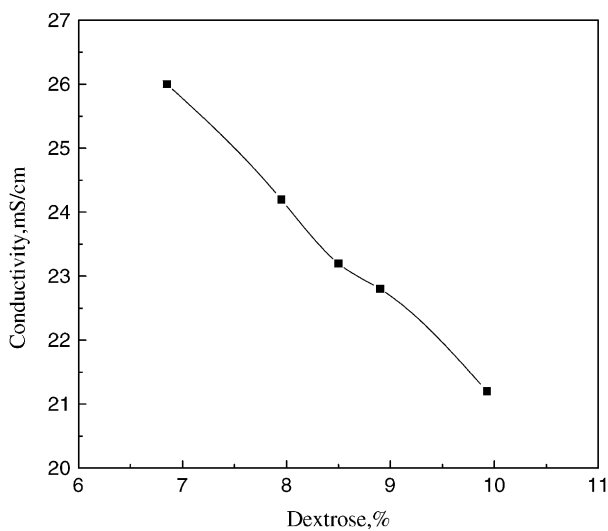


Fig. 3. Effect of concentration of dextrose on conductivity of electrolyte solution. Temperature: 299 K.

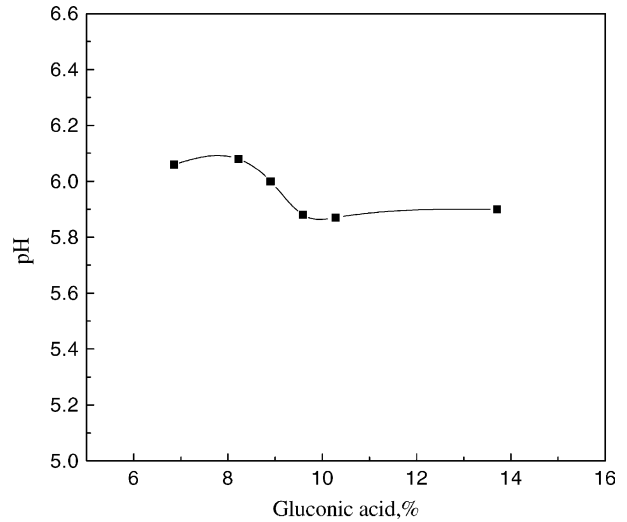


Fig. 4. Effect of concentration of gluconic acid and pH of electrolyte solution. Temperature: 299 K.

gluconic acid less than 8.22 wt.% and greater than 9.59 wt.%, respectively, as shown in Fig. 4. The decrease in pH between 8.22 and 9.59 wt.% gluconic acid results in an increase in the side reactions (e.g. the evolution of gases) and the destruction of the passive film on the aluminum during charging and discharging of the capacitor.

The relationship between the sparking voltage and the concentration of gluconic acid displays two linear region, as shown in Fig. 5. These experimental results suggest that a difference in the growth rate and the stability of the aluminum oxide film occurs in the presence of various concentrations of gluconic acid. The experimental results also correlate well with the two stable pH values found for various concentrations of gluconic acid (Fig. 4). First, the sparking voltage increases rapidly from 218 to 231 V on

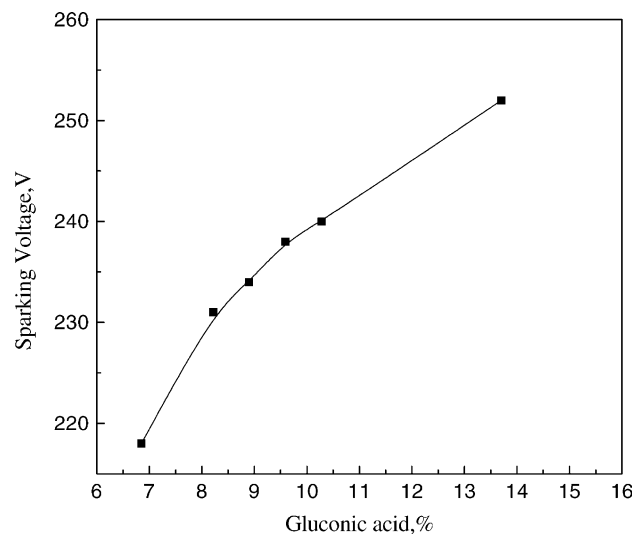


Fig. 5. Effect of concentration of gluconic acid on sparking voltage. Temperature: 299 K.

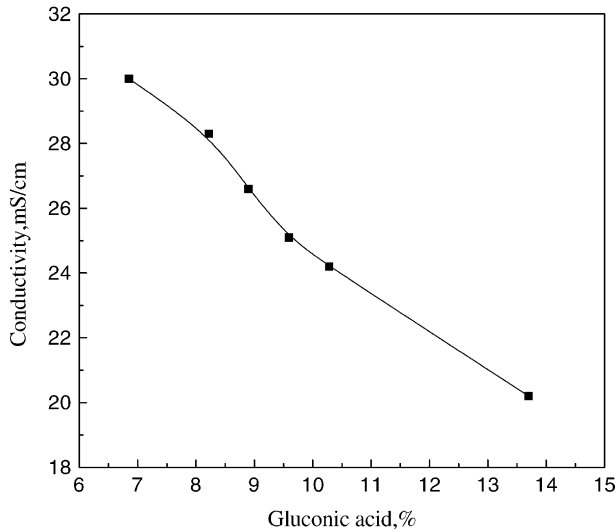


Fig. 6. Effect of concentration of gluconic acid on conductivity of electrolyte solution. Temperature: 299 K.

increasing the content of gluconic acid from 6.85 to 8.22 wt.%. In the second stage, the sparking voltage increases from 231 to 252 V when the concentration of gluconic acid is increased from 8.22 to 13.7 wt.%. The dependence between the sparking voltage and the concentration of gluconic acid was deduced from the differing pH values in the presence of various concentrations of gluconic acid. When the concentration of gluconic acid is less than 8.22 wt.%, the pH is kept at a relative high value and this favours the growth of a stable oxide film on the aluminum foil. On the other hand, the rate of growth of the film is smaller at lower pH values when the concentration of gluconic acid is greater than 9.59 wt.% (Figs. 4 and 5). The gluconic acid in the electrolyte acts as a surfactant which promotes the formation of an insulating oxide film

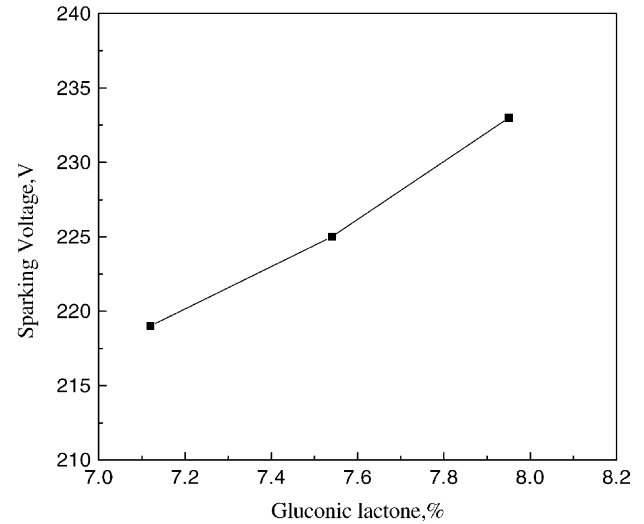


Fig. 8. Effect of concentration of gluconic lactone on sparking voltage. Temperature: 299 K.

and increases its stability on the aluminum surface [13]. Therefore, the greater the amount of gluconic acid added, the higher is the sparking voltage.

The conductivity of the electrolyte decreases from 30.00 to 20.20 mS cm⁻¹ with increase in concentration of gluconic acid from 6.85 to 13.7 wt.% (Fig. 6). This behaviour is due mainly to the low dissociation constant and bulky anion of the gluconic acid compared with other electrolytes.

3.3. Effect of gluconic lactone

The pH changes slightly with increase in the concentration of gluconic lactone from 7.12 to 7.95 wt.%, as shown in Fig. 7. Similar to the effect of dextrose, gluconic lactone is a neutral molecule and does not influence the pH of the

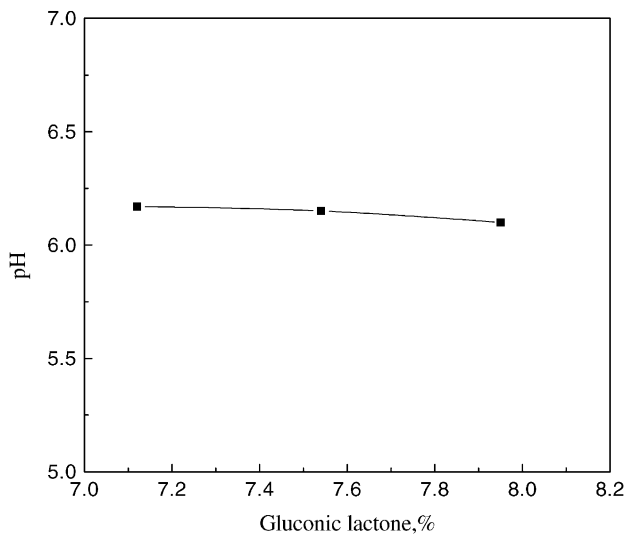


Fig. 7. Effect of concentration of gluconic lactone on pH of electrolyte solution. Temperature: 299 K.

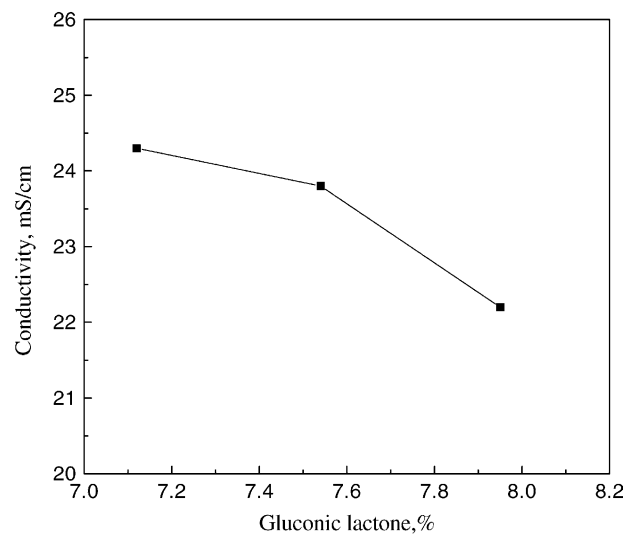


Fig. 9. Effect of concentration of gluconic lactone on conductivity of electrolyte solution. Temperature: 299 K.

Table 1
Properties of electrolytes

Additive	Conductivity (mS cm ⁻¹) ^a	Sparking voltage (V)	pH	Stability at 269 K ^b	Stability at 378 K ^c
Raw electrolyte	26.3	70	6.06	Precipitation	Failure
Dextrose	26.0	130	6.10	OK	>750 h
Gluconic acid	29.0	218	6.07	Precipitation	Failure
Gluconic lactone	24.3	218	6.17	Precipitation	Failure

^a Conductivity measured at 299 K.

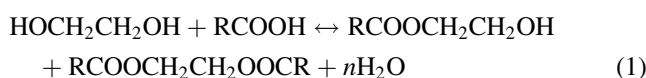
^b Stability tested by storing capacitor impregnated with electrolyte at 269 K for 7 days.

^c Stability tested by storing capacitor impregnated with electrolyte at 378 K for 750 h. Failure is due to expansion of the capacitor can and explosion.

electrolyte. On the other hand, the sparking voltage increases from 219 to 233 V when the concentration of gluconic lactone is increased from 7.12 to 7.95 wt.%, as indicated in Fig. 8. The increase in sparking voltage may be due to an increase in the stability of the insulating oxide film on the aluminum in the presence of gluconic lactone [13]. Since gluconic lactone cannot dissociate to increase the concentration of ions in the solution but may increase the viscosity of the electrolyte, the conductivity of electrolyte decreases with increasing concentration of gluconic lactone. As shown in Fig. 9, the conductivity of the electrolyte decreases from 24.3 to 22.2 mS cm⁻¹ when the concentration of gluconic lactone is increased from 7.12 to 7.95 wt.%.

3.4. Performance of electrolyte

The performance of the electrolyte prepared in this work is displayed in Table 1. Although the electrolyte with 7.85 wt.% gluconic acid displays good conductivity and a sparking voltage of 29.0 mS cm⁻¹ and 218 V, respectively, but the stability at 269 and 378 K is not acceptable. The electrolyte with 7.12 wt.% gluconic lactone also does not pass the stability test. The conductivity of the electrolyte in the presence of dextrose is almost the same as that of the original electrolyte (Her Mei 2001). On adding dextrose, the sparking voltage increases by 85% compared with the original electrolyte, and the good stability is found at 269 and 378 K (Table 1). This good stability is due to hydrogen bonding between the ethylene glycol and the multi-hydroxyl branch of the skeleton of the dextrose structure. When the temperature is decreased to 269 K, the resulting decrease in the solubility of the raw electrolyte causes unstable performance of the electrolyte. Precipitates form in the electrolyte in the presence of gluconic acid and gluconic lactone at 269 K. Esterification of carboxylic acid and ethylene glycol could occur during the high-temperature (378 K) storage test, i.e.



The high vapour pressure of esters and water creates a high internal pressure in the capacitor and this results in failure of the capacitor in a stability test at 378 K when gluconic acid and gluconic lactone is added to the electrolyte.

3.5. Capacitor durability

The durability of capacitors impregnated with electrolyte which contained dextrose was performed at 378 K without and with a loading voltage (11.5 V). The capacity of the capacitors decreases from 1.394 and 1.399 μF to 1.140 and 1.200 μF with increase in the time from 0 to 750 h when stored at 378 K without and with a voltage loading (Tables 2 and 3). The DF value increases with storage time. There are not significantly differences on storage without and with a voltage loading, as indicated in Tables 2 and 3. On the other hand, the leakage current for capacitors stored at 378 K with a voltage loading is significantly less than that without loading. When the capacitor is stored at 378 K with a 11.5 V loading, the leakage current decreases from 46.5 to 10.8 μA with increase in testing time from 0 to 750 h (Table 3). Contrarily to storage with loading, the leakage current increases from 44 to 890 μA with increase in testing time from 0 to 750 h on storing at 378 K without loading (Table 2). When the capacitor is stored without loading, the passive oxide film is attacked with electrolyte and the leakage current increases. By contrast, the passive film on the aluminum foil can be repaired during storage with loading and the leakage current hence decreases.

Table 2
Characteristics of capacitor impregnated with electrolyte containing dextrose during stability test at 378 K

Time (h)	C _p (μF)	DF (%)	L _c (μA)
0	1.394	6.91	44
250	1.209	7.37	1250
500	1.176	7.26	770
750	1.140	7.35	890

Table 3
Characteristics of capacitor impregnated with electrolyte containing dextrose during stability test with loading at 378 K

Time (h)	C _p (μF)	DF (%)	L _c (μA)
0	1.399	6.40	46.5
500	1.257	7.50	33.6
750	1.200	8.30	10.8

4. Conclusions

The performance of electrolyte solutions which contain dextrose, gluconic acid or gluconic lactone have been studied and the capacitors impregnated with the electrolytes have been tested. Experimental results show that the capacitor impregnated with an electrolyte containing dextrose exhibits satisfactory durability. Compared with the original commercial electrolyte, the sparking voltage increases by 85% when the electrolyte has 7.0 wt.% dextrose as an additive. The capacity of the capacitor impregnated with electrolyte containing 7.0 wt.% dextrose increases slightly, and the DF value increases slightly with storage time with and without a loading at 378 K. The leakage current increases from 44 to 890 μA and decreases from 46.5 to 10.8 μA , respectively, when the capacitor is stored at 378 K without and with a 11.5 V loading. Reparation of the passive oxide film form on the aluminum foil causes a decrease in leakage current for a capacitor stored with loading. On the other hand, the passive film is attacked by the chemicals in the electrolyte when capacitor was stored without loading.

Acknowledgements

The authors are very grateful to Her Mei Electronic Co. Ltd. for co-operation during the present work. We also thank

National Chin-Yi Institute of Technology and Tunghai University.

References

- [1] A. Nishino, *J. Power Sources* 60 (1996) 137.
- [2] R. Kotz, M. Carlen, *Electrochimica. Acta* 45 (2000) 2483.
- [3] B.E. Conway, *J. Electrochem. Soc.* 138 (1991) 1539.
- [4] B.E. Conway, in: *Proceedings of the 19th International Power Sources Symposium*, Brighton, UK, *Power Sources* 15 (1995) 65.
- [5] M.L. Tsai, S.Y. Lin, J.S. Do, *J. Technol.* 17 (1) (2002) 123–132.
- [6] M.L. Tsai, G.Z. Chen, *J. Chin-Yi* 19 (2001) 133.
- [7] M.L. Tsai, in: *Proceedings of the Annual Meeting and Conferences*, ChIChE (2001) 165.
- [8] I. Kazuhiko, M. Shoichiro, U. Makoto, US Patent 4786429 (1988).
- [9] F.D. Roland, US Patent 4408258 (1983).
- [10] K. Akihiko, O. Tetsushi, US Patent 6288889 (2001).
- [11] M. Munehiro, US Patent 6128179 (2000).
- [12] M. Shoichiro, I. Kazuhiko, U. Makoto, US Patent 4774011 (1988).
- [13] N. Ryutaro, *Jpn. Patent* 06124852 (1994).
- [14] S. Niwa, Y. Taketani, *J. Power Sources* 60 (1996) 165.
- [15] H. Yamamoto, M. Oshima, M. Fukuda, I. Isa, K. Yoshino, *J. Power Sources* 60 (1996) 173.
- [16] H. Yamamoto, M. Oshima, T. Hosaka, I. Isa, *Synth. Met.* 104 (1999) 33.
- [17] J.M. Brian, T.K. John, M.L. Philip, US Patent 005853794 (1999).
- [18] T. Nishiyama, T. Sakata, A. Fukaumi, S.A. Kobayashi, US Patent 005853794 (1995).
- [19] K. Naoi, M. Takede, H. Kanno, M. Sakakura, A. Shimada, *Electrochim. Acta* 45 (2000) 3413.