

Characteristics of tantalum electrolytic capacitors using soluble polypyrrole electrolyte

Kwan Sik Jang^a, Bongjin Moon^a, Eung Ju Oh^b, Hoosung Lee^{a,*}

^a Department of Chemistry, Sogang University, 1-1 Shinsoo-Dong, Mapo-Gu, Seoul 121-742, South Korea

^b Department of Chemistry, Myongji University, Yongin, Kyonggi-Do 449-728, South Korea

Received 27 February 2003; received in revised form 2 May 2003; accepted 12 May 2003

Abstract

Polypyrrole (Ppy) electrolyte solutions in various organic solvents (dimethylformamide, DMF; *N*-methyl-2-pyrrolidone, NMP; chloroform; trifluoroacetic acid) were prepared using Ppy powder doped with di(2-ethylhexyl)sulfosuccinate sodium salt (Ppy-DEHS) and butyl-naphthalene sulfonate sodium salt (Ppy-BNS), respectively. Several tantalum electrolytic capacitors were fabricated by dip coating in these solutions and their electrical properties such as capacitance and $\tan \delta$ were measured. The capacitors prepared with Ppy-DEHS electrolyte in trifluoroacetic acid showed both high capacitance and low $\tan \delta$. Usage of a Ppy electrolyte solution containing both surfactant and a coupling agent also resulted in high capacitance and low $\tan \delta$. These phenomena were interpreted in terms of electrical conductivity and chemical structure of the electrolyte, and interactions such as hydrogen bonding, radical addition reaction, covalent bonding between the tantalum oxide layer and the solvent.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Soluble polypyrrole; Tantalum electrolytic capacitors; Electrolyte; Surfactant; Coupling agent

1. Introduction

A solid tantalum electrolytic capacitor using a tantalum thin film was developed by Balke in 1929 [1] and a capacitor using MnO_2 as a solid electrolyte was developed by Haring and Taylor in 1965 [2]. Capacitance, loss tangent, and impedance characteristics of tantalum electrolytic capacitors are influenced not only by the property of carbon or silver paste but also by the type of electrolyte and the degree of homogeneity of the coating inside tantalum oxide pores [3–6].

MnO_2 has been widely used as a conventional electrolyte due to its high thermal stability and reliability. However, it has been difficult to achieve large capacitance and low impedance with this material because of its low electrical conductivity ($<10^{-1}$ S/cm) [7,8]. It has been realized that tantalum electrolytic capacitors prepared by electrochemical coating of conducting polymer electrolyte (polyaniline, polypyrrole (Ppy)) showed low impedance and high capacitance at a high frequency region [9,10]. However, this method has several disadvantages such as uneven electrolyte

thickness, complicated manufacturing process and consumption of electric energy during the synthesis and coating of the electrolytes.

Recently, several groups reported tantalum electrolytic capacitors adopting chemically synthesized soluble polyaniline as an electrolyte [11–14]. This soluble polymer electrolyte makes the process easy, simple, and economical. However, the device did not show satisfactory values for the loss tangent and capacitance characteristics, which is attributed to the difficulty in making homogeneous coating inside the tantalum oxide pores. In order to achieve homogeneous coating, several conditions such as concentration of the electrolyte, the number of dipping, the use of additives, were controlled. Among these, the control of the concentration of electrolyte and the number of dipping have a limit to improve the affinity between the electrolyte and the Ta_2O_5 (tantalum oxide) due to the property of the electrolyte itself. So the use of additives to improve the device performance may have not only scientific but also technological importance.

In this work, various additives (surfactants, coupling agents) were added to soluble Ppy solutions in various organic solvents to prepare electrolyte solutions that can enhance the homogeneity of the Ppy film on the surface of tantalum oxide. Tantalum electrolytic capacitors were

* Corresponding author. Tel.: +82-2-705-8446; fax: +82-2-701-0967.
E-mail address: hlee@sogang.ac.kr (H. Lee).

fabricated with these solutions and the effects of the additives on their electrical performances were examined.

2. Experimental

2.1. Preparation of polypyrrole electrolyte

Pyrrole (Tokyo Chemical Industry Co.) was vacuum distilled prior to use. Pyrrole (0.4 mol) and a dopant (0.15 mol, di(2-ethylhexyl)sulfosuccinate sodium salt (DEHSNa) or butylnaphthalenesulfonate sodium salt (BNSNa), Tokyo Chemical Industry Co.) were mixed in distilled water (900 ml in a 1 l beaker) with magnetic stirring and the resulting mixture was cooled to 0 °C. A solution of ammonium peroxydisulfate, (NH₄)₂S₂O₈, (0.10 mol) in 100 ml distilled water was cooled to 0 °C and added to the mixture in ~2 min with magnetic stirring. The resulting mixture was stirred for 20 h at 0 °C for 20 h. The precipitated doped polypyrrole, Ppy-DEHS (or Ppy-DBNS), was filtered through a Buchner funnel with a filter paper and washed with ~2 l distilled water. The filter cake was dried under vacuum (~10⁻³ Torr) for 24 h [15–17].

The dried Ppy powder was dissolved in various solvents (trifluoroacetic acid, dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), chloroform) to make a conducting Ppy electrolyte solution (2% (w/v)). A Ppy electrolyte solution containing surfactant was prepared by adding surfactants, *N*-lauryl-β-aminopropionic acid ((C₁₂H₂₃NHCH₂CH₂COOH), 0.1–1% (w/v)) and sorbitan monolaurate ((C₅H₉O₄CH₂OCOCH₂(CH₂)₉CH₃), 0.1–1% (w/v)), to a polypyrrole solution prepared previously. Structures of the additives (surfactants, coupling agents) are shown in Fig. 1. A Ppy electrolyte solution containing a coupling agent was prepared by adding the coupling agent (0.1% (w/v)), gamma-aminopropyl triethoxysilane ((C₂H₅O)₃Si(CH₂)₃NH₂, coupling agent A) or vinyltrimethoxysilane (CH₂=CHSi(OCH₃)₃, coupling agent B), to the Ppy solution.

2.2. Fabrication of tantalum electrolytic capacitors and measurement of the device performance

A tantalum wire was inserted into tantalum powder in a template. This structure was sintered at 1800 °C, 10⁻⁶ Torr and then electrochemically oxidized to form a Ta₂O₅ film. The inner and outer surface of the tantalum oxide was coated with electrolyte by dipping the structure in a Ppy electrolyte solution for 10 min followed by drying at 90 °C for 10 s. The dipping and drying procedure was repeated eight times. A tantalum electrolytic capacitor was fabricated by coating with carbon paste and then silver paste followed by molding. A schematic structure of the fabricated tantalum electrolytic capacitor is shown in Fig. 2. The loss tangent and capacitance of the devices were measured by an Impedance-Gain-Phase Analyzer (HP 4194A).

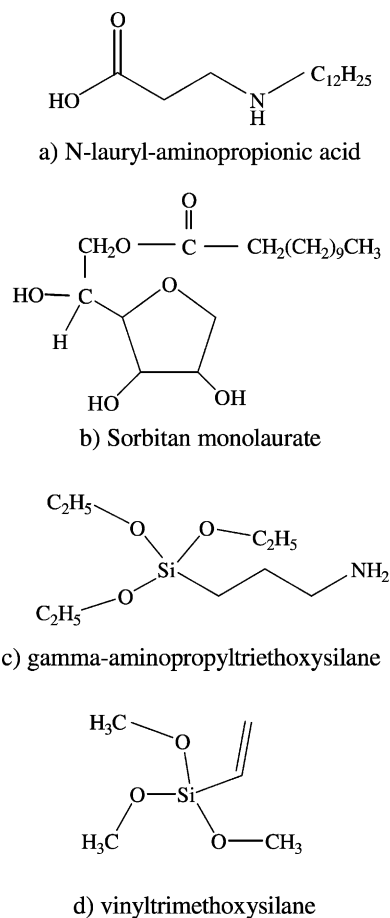


Fig. 1. Structures of the surfactants (a, and b) and the coupling agents (c, and d) used.

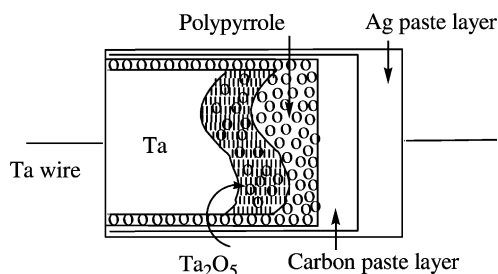


Fig. 2. Structure of tantalum electrolytic capacitor fabricated in this study.

3. Results and discussion

In order to build a tantalum electrolytic capacitor having high capacitance and low loss tangent, the electrolyte should have good affinity to tantalum oxide so that the surface of the pores in tantalum oxide can be uniformly coated [11]. From this point of view, protic solvents seem to be appropriate candidates since they can interact with tantalum oxide strongly through hydrogen bonds [11].

In this study, several surfactants and coupling agents were added to Ppy electrolyte solutions in order to improve the affinity between electrolyte and tantalum oxide. And

Table 1

The capacitance and loss tangent ($\tan \delta$) of the tantalum electrolytic capacitors using Ppy-DEHS and Ppy-BNS electrolyte solutions

	Conductivity (S/cm)	Capacitance (μF , at 120 Hz)	$\tan \delta$ (at 120 Hz)
Ppy-DEHS/DMF	4	74–75	18–17
Ppy-DEHS/NMP	7×10^{-1}	63–64	24–23
Ppy-DEHS/chloroform	3×10^{-2}	50–52	31–30
Ppy-DEHS/trifluoroacetic acid	5×10^{-1}	73–74	19–18
Ppy-BNS/chloroform	6×10^{-1}	62–63	24–23
Ppy-BNS/DMF	6×10^{-2}	55–56	28–27

tantalum electrolytic capacitors (D4 size) were fabricated using these mixed electrolytes.

Di(2-ethylhexyl)sulfosuccinate sodium salt doped Ppy (Ppy-DEHS) was dissolved in various solvents (DMF, NMP, chloroform, trifluoroacetic acid) and butylnaphthalenesulfonate sodium salt doped Ppy (Ppy-BNS) was dissolved in organic solvents (DMF, chloroform) to make electrolyte solutions (Ppy-BNS /chloroform, Ppy-DBNS/DMF).

Tantalum electrolytic capacitors (D4 size) were fabricated by dipping the tantalum oxide into these solutions. Table 1 shows the electrical conductivities of free standing films cast from Ppy-DEHS and Ppy-BNS electrolyte solutions, and the capacitance and loss tangent ($\tan \delta$) at 120 Hz of the capacitors fabricated using these electrolyte solutions.

The tantalum electrolytic capacitor using Ppy-DEHS/DMF solution showed capacitance of 74–75 μF and loss tangent of 18–17 while the capacitor using Ppy-DEHS/chloroform solution showed capacitance of 50–52 μF and loss tangent of 31–30. This result is consistent with the fact that the film cast with Ppy-DEHS/DMF has higher conductivity (4 S/cm) than that with Ppy-DEHS/chloroform [11].

On the other hand, the capacitor prepared with Ppy-DEHS/trifluoroacetic acid electrolyte showed significantly higher capacitance (73–74 μF) and lower loss tangent (19–18) compared to those of the capacitors prepared from Ppy-DEHS/NMP and Ppy-DBNS/chloroform, although the room temperature conductivities of free standing films of these electrolytes are comparable. It seems that the solvent, trifluoroacetic acid, plays a significant role in the performance of the resulting capacitor. We surmise that the electrolyte solution in trifluoroacetic acid can adhere to the surface of the pores of tantalum oxide more strongly than the ones in other solvents because of its enhanced affinity to tantalum oxide resulting from the hydrogen bonding between the protic solvent (trifluoroacetic acid) and tantalum oxide. This may make the effective surface area of tantalum oxide larger and result in high capacitance and low loss tangent of the device [11].

The SEM images of the electrolyte coated on tantalum oxide surfaces in the capacitors prepared from two different electrolyte solutions, Ppy-DEHS/trifluoroacetic acid (a) and Ppy-DEHS/NMP (b), also support the argument that the electrolyte in trifluoroacetic acid coated the pores more efficiently than the one in NMP as shown in Fig. 3.

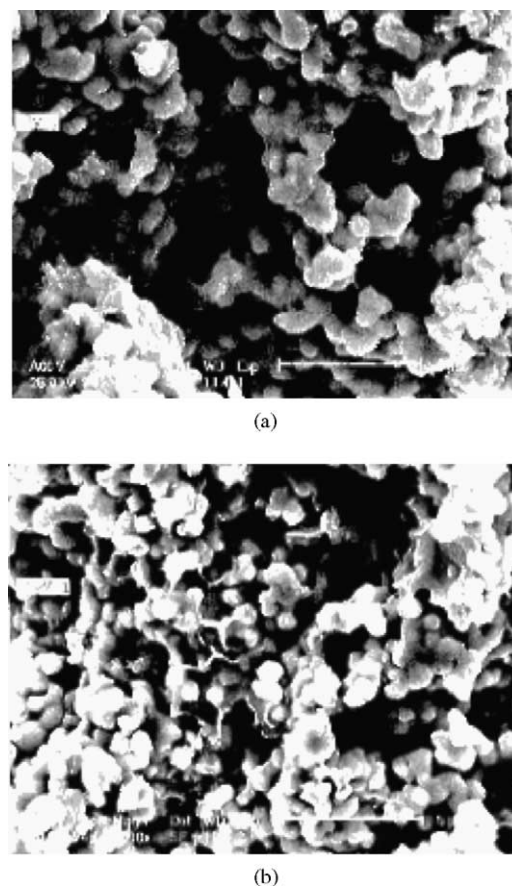


Fig. 3. SEM photographs of the tantalum solid particles in the electrolytic capacitors using. (a) Ppy-DEHS/trifluoroacetic acid, (b) Ppy-DEHS/NMP.

Knowing that the use of electrolyte solution in a protic solvent results in improved device performance, we have chosen Ppy-DEHS/trifluoroacetic acid as an electrolyte solution for the remaining study, and the effect of additives on device performance was investigated.

Surfactant, *N*-lauryl- β -aminopropionic acid ($\text{C}_{12}\text{H}_{23}\text{NHCH}_2\text{CH}_2\text{COOH}$), sorbitan monolaurate ($(\text{C}_5\text{H}_9\text{O}_4\text{CH}_2\text{OCOCH}_2(\text{CH}_2)_9\text{CH}_3)$) and the coupling agents, gamma-aminopropyltriethoxysilane ($(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$; coupling agent A) and vinyltrimethoxysilane ($\text{CH}_2=\text{CHSi}(\text{OCH}_3)_3$; coupling agent B) were used as additives in this study. Tantalum electrolytic capacitors were fabricated using an electrolyte solution doped with one of these additives and their performances were measured by the same method as described above.

When Ppy-DEHS/trifluoroacetic acid electrolyte solution was doped with 0.1–1 wt.% of surfactant and 0.1 wt.% of one of the coupling agents (A and B), the device built with this solution showed better performance than that with undoped Ppy-DEHS/trifluoroacetic acid. The capacitance increased by $\sim 15 \mu\text{F}$ and loss tangent decreased by ~ 11 at 120 Hz.

Figs. 4 and 5 show the capacitance and loss tangent of a tantalum electrolytic capacitor using Ppy-DEHS/trifluoroacetic acid electrolyte solution containing a surfactant and coupling agent.

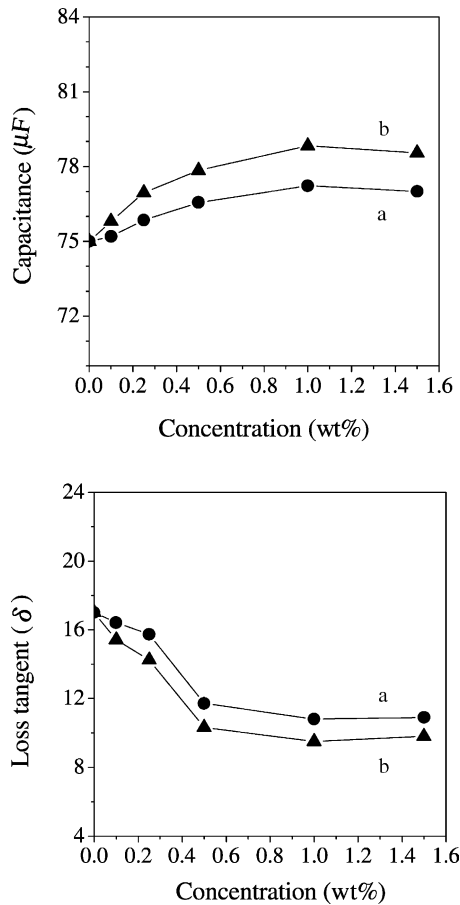


Fig. 4. Capacitance and loss tangent as a function of surfactant concentration of the tantalum electrolytic capacitors using Ppy-DEHS/trifluoroacetic acid electrolyte solution containing surfactant. (a) *N*-lauryl- β -aminopropionic acid, (b) sorbitan monolaurate.

When a surfactant, *N*-lauryl- β -aminopropionic acid or sorbitan monolaurate, that has an affinity with both Ppy and tantalum oxide by hydrophobic interaction and hydrogen bonding was used, high capacitance (78 and 80 μF at 120 Hz) and low loss tangent (11 and 9.5 at 120 Hz) were obtained.

Tantalum electrolytic capacitors prepared with Ppy-DEHS/trifluoroacetic acid electrolyte solution containing coupling agent B (0.1 wt.%) also showed high capacitance (87 μF at 120 Hz) and low loss tangent (11.2 at 120 Hz). In this case, a chemical reaction (radical addition reaction) may occur between the polymer main chain and the vinyl group of the coupling agent (Fig. 6a). In addition, the trimethoxysilyl group of the coupling agent can form a covalent bond with tantalum oxide. By these interactions, the coupling agent seems to improve the affinity of the electrolyte solution with tantalum oxide thereby enhancing electrolyte penetration into the pores of tantalum oxide.

When coupling agent A (gamma-aminopropyltriethoxysilane, 0.1 wt.%) was used as an additive, the capacitance and loss tangent of the resulting device (80 and 14 μF , respectively at 120 Hz) was not as good as those of the

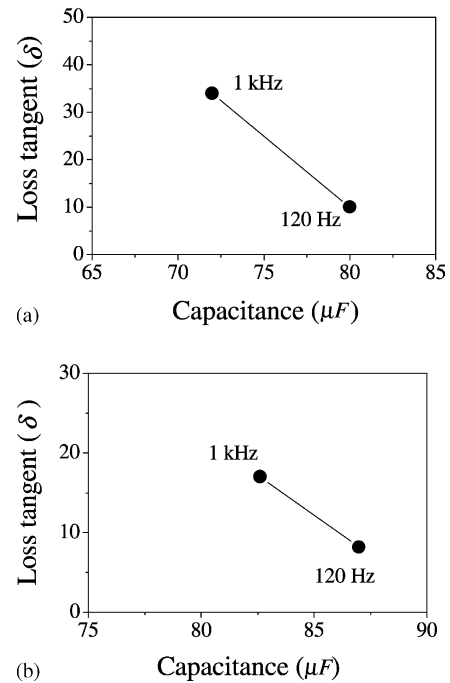


Fig. 5. Capacitance and loss tangent of tantalum electrolytic capacitors using Ppy-DEHS/trifluoroacetic acid electrolyte solution containing coupling agent. (a) Gamma-aminopropyltriethoxysilane, (b) vinyltrimethoxysilane, respectively.

device prepared using coupling agent B (vinyltrimethoxysilane). These results can be explained as follows: when the coupling agent A was added to the electrolyte solution, the chemical interaction (Lewis acid–base type) [18] between

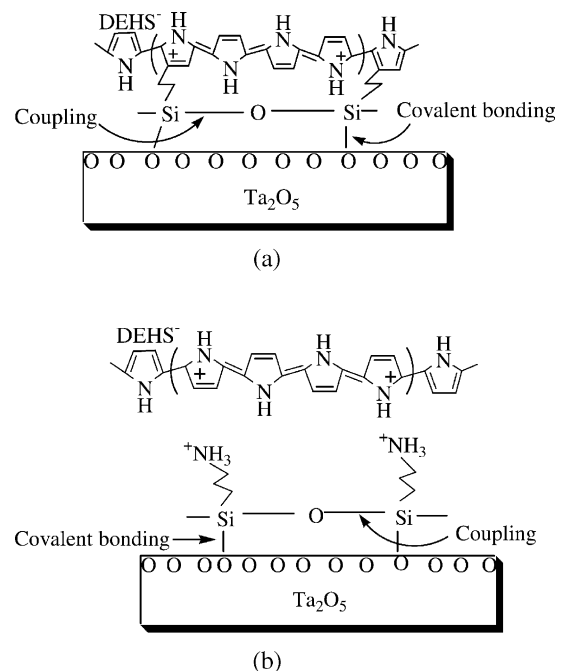


Fig. 6. The interactions formed between the coupling agent, Ppy-DEHS and tantalum oxide upon the addition of the coupling agents. (a) Vinyltrimethoxysilane, (b) gamma-aminopropyl triethoxysilane.

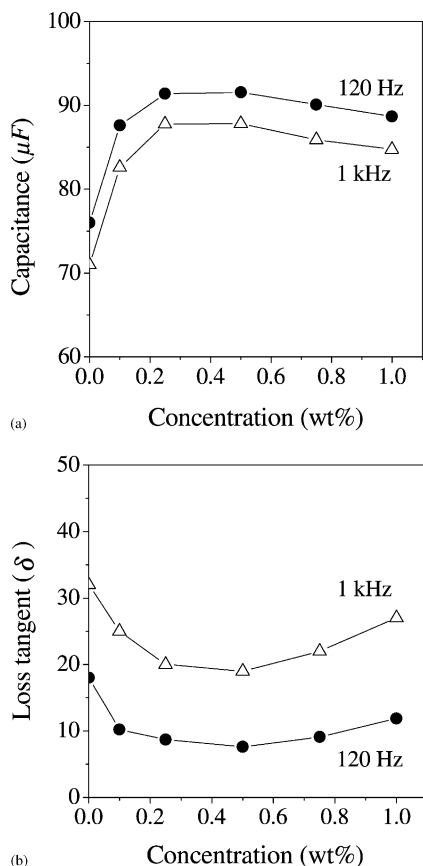


Fig. 7. The capacitance and loss tangent of tantalum electrolytic capacitor as a function of the concentration of the coupling agent B added to the Ppy-DEHS/trifluoroacetic acid electrolyte solution.

the amino groups (donor) in coupling agent A and the N–H bonds or cations (acceptor) in doped Ppy main chain with DEHS can be formed. But considering the acidity of trifluoroacetic acid, the amino groups in the coupling agent should exist as protonated form. Therefore, they will be no longer hydrophobic, which is necessary to anchor to electrolyte polymer chains. In Fig. 6, the above-mentioned interactions between the coupling agent (A or B), Ppy-DEHS, and tantalum oxide in Ppy-DEHS/trifluoroacetic acid are illustrated.

In Fig. 7, the capacitance and loss tangent of tantalum electrolytic capacitor as a function of the concentration of coupling agent B, vinyltrimethoxysilane, are shown.

When 0.5 wt.% of coupling agent B was added to Ppy-DEHS/trifluoroacetic acid electrolyte solution, the device showed the highest capacitance (91 μF at 120 Hz) and the lowest loss tangent (7.6 at 120 Hz) among the capacitors fabricated in this study. This result shows that the optimal amount of coupling agent B can increase the affinity between Ppy-DEHS/trifluoroacetic acid electrolyte solution and tantalum oxide. It is notable that addition of too much coupling agent B (>1 wt.%) to the electrolyte solution results in deterioration of the device performance, which is attributed to the decrease in electrical conductivity of Ppy-DEHS/trifluoroacetic acid electrolyte solution by insu-

lating nature of coupling agent B and formation of insulating layers between the electrolyte and tantalum oxide surface.

4. Conclusion

Polypyrrole powder (Ppy-DEHS, Ppy-BNS) was dissolved in various solvents (DMF, chloroform, trifluoroacetic acid, etc.) to prepare the polymer electrolyte. Tantalum electrolytic capacitors with a small size (D4 size) and high capacitance were fabricated by dip coating in these electrolyte solutions. A device prepared with Ppy-DEHS electrolyte dissolved in a protic solvent, trifluoroacetic acid, showed significantly high capacitance and low $\tan\delta$. Addition of either a surfactant (*N*-lauryl- β -aminopropionic acid, sorbitan monolaurate) or a coupling agent (vinyltrimethoxysilane or gamma-aminopropyl triethoxysilane) to the electrolyte solution also enhanced the performance of the resulting devices compared to the case with no additives.

From this study, it seems to be important in the relevant technologies not only to improve the electrical conductivity of Ppy electrolyte, but also to enhance the affinity between Ppy electrolyte and tantalum oxide by selecting a proper solvent and additives, in order to build a tantalum capacitor with better device performances.

Acknowledgements

This work was supported by Korea Research Foundation Grant (KRF-2002-005-C00013).

References

- [1] C.W. Balke, US Patent no. 1,710,806 (1929).
- [2] H.E. Haring, R.L. Taylor, US Patent no. 3,166,693 (1965).
- [3] M. Satoh, H. Ishikawa, K. Amano, E. Hasegawa, K. Yoshino, *Synth. Met.* 71 (1995) 2259.
- [4] F. Larmat, J.R. Reynolds, Y.J. Qiu, *Synth. Met.* 79 (1996) 229.
- [5] H. Yamamoto, M. Oshima, M. Fukuda, I. Isa, K. Yoshino, *J. Power Sources* 60 (1996) 173.
- [6] H. Yamamoto, M. Oshima, T. Hosaka, I. Isa, *Synth. Met.* 104 (1999) 33.
- [7] M. Hasegawa, US Patent no. 5,486,977 (1996).
- [8] S.E. Libby, US Patent no. 4,780,797 (1988).
- [9] T. Nishiyama, K. Sakata, T. Fukami, A. Kobayashi, S. Arai, US Patent no. 5,428,500 (1995).
- [10] T. Nishiyama, T. Fukami, K. Sakata, S. Arai, A. Kobayashi, US Patent no. 5,455,736 (1995).
- [11] K.S. Jang, J.J. Park, E.J. Oh, J.S. Suh, H.K. Min, *Kor. J. Appl. Phys.* 12 (1999) 444.
- [12] K. Amano, H. Ishikawa, A. Kobayashi, S. Masaharu, US Patent no. 5,672,377 (1997).
- [13] Y. Cao, A.J. Heeger, *Synth. Met.* 52 (1992) 193.
- [14] Y. Cao, J. Qiu, P. Smith, *Synth. Met.* 69 (1995) 187.
- [15] E.J. Oh, K.S. Jang, *Synth. Met.* 199 (2001) 109.
- [16] K.S. Jang, S.S. Han, J.S. Suh, E.J. Oh, *Synth. Met.* 119 (2001) 107.
- [17] E.J. Oh, K.S. Jang, A.G. Macdiarmid, *Synth. Met.* 125 (2001) 267.
- [18] C. Perruchot, M.M. Chehimi, M. Delamar, J.A. Eccles, T.A. Steele, C.D. Mair, *Synth. Met.* 113 (2000) 53.