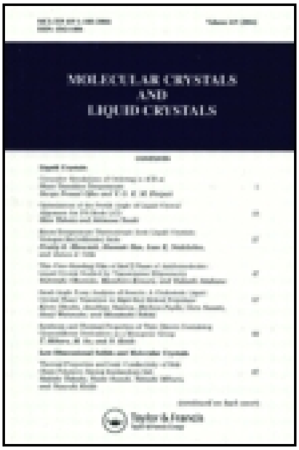

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Materials Science of Conducting Polymers: An Approach to Solid Electrolytic Capacitors with a Highly-Stable Polypyrrole Thin Film

Masao Fukuyama [a] , Yasuo Kudoh [a] , Norishige Nanai [a] & Susumu Yoshimura [a]
[a] Matsushita Research Institute Tokyo, Inc., 3-10-1 Higashimita, Tama-ku, Kawasaki, 214, Japan
Version of record first published: 24 Sep 2006.

Mol. Cryst. Liq. Cryst., 1993, Vol. 224, pp. 61–67
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Materials Science of Conducting Polymers: An Approach to Solid Electrolytic Capacitors with a Highly-Stable Polypyrrole Thin Film

MASAO FUKUYAMA, YASUO KUDOH, NORISHIGE NANAI and SUSUMU YOSHIMURA

Matsushita Research Institute Tokyo, Inc., 3-10-1 Higashimita, Tama-ku, Kawasaki 214, Japan

(Received January 10, 1992; in final form January 14, 1992)

This paper summarizes the present status of materials science of conducting polymers relevant to the their technological applications. This paper also describes the development of solid electrolytic capacitors utilizing conducting-polymer thin films as a solid electrolyte. The capacitors are characterized by excellent frequency, temperature and life stabilities and have been put into commercial use in large quantity.

MATERIALS SCIENCE AND TECHNOLOGICAL APPLICATIONS OF CONDUCTING POLYMERS

During these two score years, various kinds of non-traditional conducting materials have been synthesized, bringing forth an exciting dream to realize artificial or synthetic metals. Since the discovery of high electrical conductivity of doped polyacetylene in 1977,[1] much effort has been devoted to the realization of metallic conductivity ($\sigma > 1$ kS cm^{-1}) through design of molecular and crystal structures of conjugated polymers. The electrical conductivity for highly-oriented and/or high-quality films of polyacetylene,[2,3] polyphenylene[4] and polyphenylenevinylene[5] is now of the order of 10 kS cm^{-1}. The electrical conductivity of electrochemically polymerized polymers such as polypyrrole[6] and poly(3-methylthiophene)[7] has also been enhanced to the order of 1 kS cm^{-1} via control of their structural properties.

For the technological applications of the newly-developed conducting polymers, relevant materials science has to be established, in particular, the improvement in processibility and thermal stability. As for polypyrrole, which are synthesized via electrochemical polymerization,[8] anions of supporting electrolytes are doped to the polymers and their electrical, mechanical and chemical properties are remarkably affected by the dopants. Various kinds of dopants from inorganic anions (Cl^-, Br^-) to very large organic molecules including phthalocyanine and polyelectrolyte (sulfonated PVA, sulfonated polystyrene and polymetacrylic acid) have been adopted, among which sulfonates of naphthalene or anthracene derivatives[9] are thought to

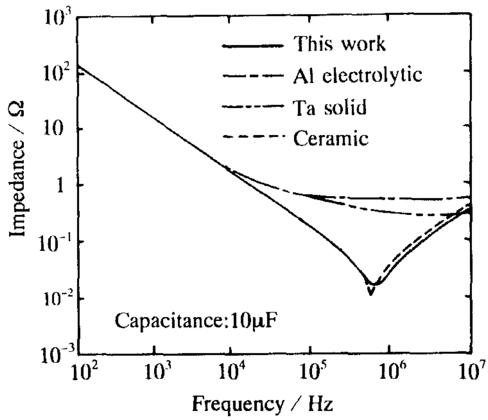

FIGURE 1 Frequency characteristics of impedance for various capacitors.

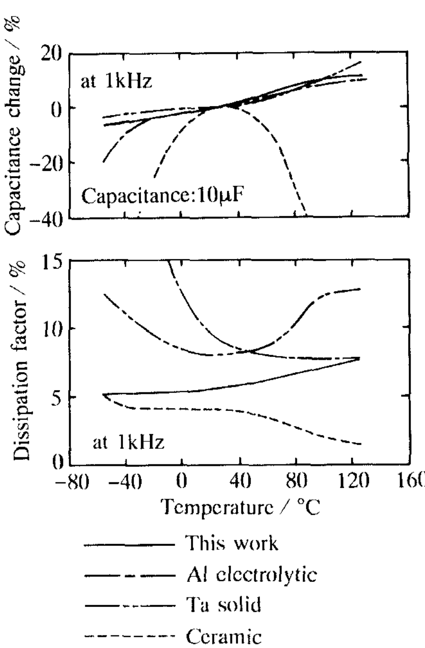

FIGURE 2 Temperature dependence of capacitance of 1 kHz for various capacitors.

be very important dopants that allow the preparation of thermally-stable and highly-conducting polymers.

Advance in the materials science of conducting polymers has yielded various new functional devices which can possibly compete with conventional inorganic devices. Recent examples of such embryos include an all-plastic transistor based on oligo-thiophene[10] and an n-Si Schottky-barrier diode with processible polyacetylene.[11] Electrodes for a secondary battery have been one of major approaches of technological applications of conducting polymers. The first commercial appli-

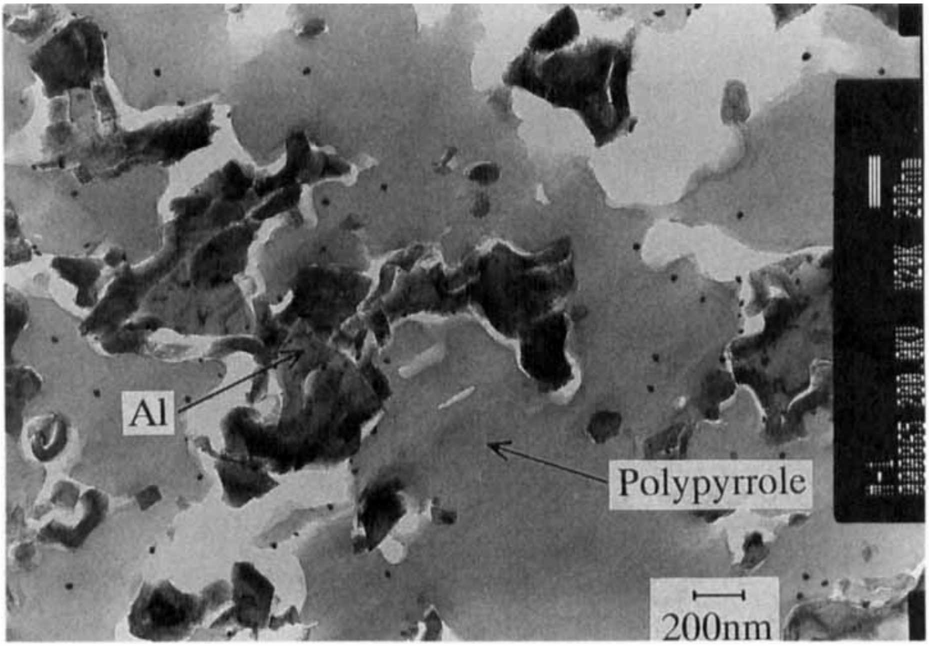

FIGURE 3 Cross-sectional view of polypyrrole solid electrolytic capacitor.

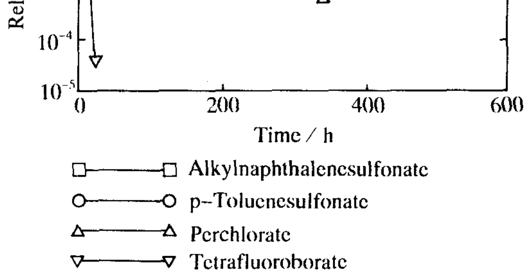

FIGURE 4 Comparison of thermal stability of polypyrrole doped with various dopants.

cation has been made with polyaniline in lithium button-type batteries.[12] Just at the same time as a solid electrolytic capacitor utilizing organic semiconductors based on 7,7,8,8-tetracyanoquinodimethane (TCNQ) was commercialized,[13] proposals were made on the application of conducting polymers to the capacitor.[14]

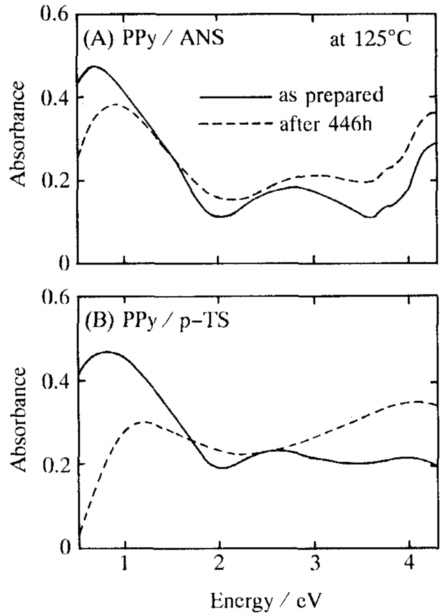

FIGURE 5 Change in optical absorption spectra of polypyrrole doped with alkylnaphthalenesulfonate (ANS) and p-toluenesulfonate (p-TS) at 125°C.

We and other groups in Japan[15,16] have recently developed solid electrolytic capacitors using electrochemically polymerized polypyrrole which characteristics supersede those of multilayer ceramic capacitors. Figures 1 and 2 show the frequency and temperature characteristics for the newly-developed capacitor, respectively, together with those of commercially available capacitors for comparison.[16]

SOLID ELECTROLYTIC CAPACITORS

Electrolytic capacitors are composed of a very thin film of dielectric oxide anodically formed on valve metals (Al and Ta) and a liquid electrolyte. The electrolyte layer serves as a protecting layer for the oxide layer by minimizing the leakage current of the capacitor through electrochemical oxidation of the valve metal at flaw portions of the oxide (known as a self-healing action). However, it has adverse effects on the capacitor performance which are inherent to its ionically conducting and liquid nature. The major disadvantages of the electrolytic capacitors have been a high equivalent series resistance, high impedances at higher frequencies and lower temperatures and relatively short life of operation. There is a long history of the development of a solid electrolytic capacitor starting from the discovery of a solid tantalum capacitor[17] which has a manganese dioxide (MnO_2) layer as the solid electrolyte. Since the electrical conductivity of MnO_2 is low (ca. 0.1 S cm^{-1}) and the self-healing property is considerably lower than that of liquid electrolyte,[18] the tantalum solid capacitors have suffered less perfect performance.

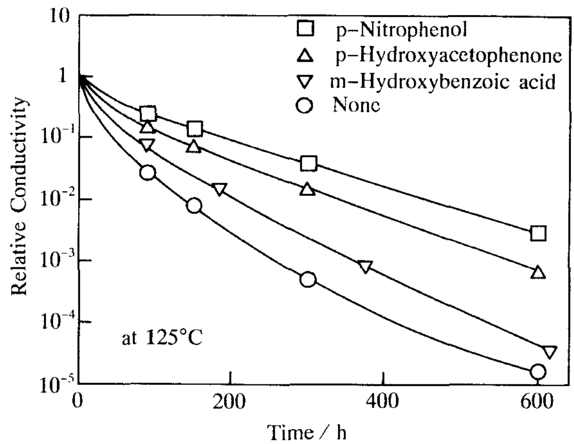

FIGURE 6 Change in conductivity of 125°C for polypyrrole polymerized with various additives in the polymerization electrolyte.

About ten years later, a prototype of new solid electrolytic capacitor was developed using organic semiconductors based on TCNQ[19] which are more highly conductive (1 ~ 10 S cm^{-1}) and have higher self-healing action than MnO_2.[20] The organic semiconductor solid capacitor was recognized to have excellent frequency and temperature characteristics[19,21] coming from the high electrical conductivity of the solid electrolyte. However, it required another decade for the capacitor to be commercialized, until a new method based on the impregnation of molten semiconductors enabled to produce the capacitors in mass quantity.[13]

Since the conductivity of the electrolyte should be as high as possible, conducting polymers are one of the best candidates for the solid electrolyte. One problem was recognized, however, that the oxide cannot conduct electricity when polarized positively, which hampered the formation of a conducting-polymer layer on the insulator via electrochemical polymerization. New methods for forming a conducting polypyrrole layer were devised, which make use of a thin conducting layer pre-coated on the insulator as an anode electrode for the electrochemical polymerization. As the conducting pre-coated layer, we utilized manganese dioxide[22] which was formed by pyrolysis of manganese nitrate. Then an auxiliary electrode was brought into contact with the manganese oxide layer and electrochemical polymerization was carried out potentiostatically. Figure 3 shows a cross-sectional view of an etched aluminium electrode covered with polypyrrole.

IMPROVEMENT IN THE PERFORMANCE OF POLYPYRROLE SOLID ELECTROLYTIC CAPACITORS

An aqueous electrolyte for polymerization was suitable for mass production, so that various kinds of water-soluble sulfonate dopants were examined; dopants of bulky molecules such as alkylnaphthalenesulfonate (ANS) were chosen on account

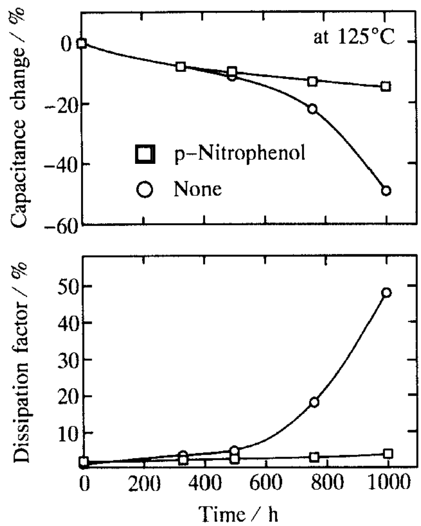

FIGURE 7 Capacitance and dissipation factor as a function of time at 125°C for solid electrolytic capacitors with polypyrrole polymerized with and without p-nitrophenol additive.

of high environmental stabilities. For example, Figure 4 shows the effect of dopants on the thermal stability of polypyrrole left in air at 125°C. Changes in ultraviolet and visible absorption spectra shown in Figure 5 indicate that polypyrrole with the ANS dopant is far more stable against de-doping than that with p-toluenesulfonate but even the former undergoes oxidative degradation at the polymer backbone.[23] As polypyrrole doped with ANS displays no detectable conductivity change in inert atmospheres even at temperatures as high as 150°C, a highly reliable capacitor can be constructed if we employ air-tight encapsulation.[24]

Recently we found that both the electrical conductivity and its stability of polypyrrole were enhanced by the use of organic additives in the electrolyte of polymerization. The conductivity of polypyrrole doped with ANS is of the order of several S cm^{-1}, but it could be enhanced to as high as 100 S cm^{-1} when phenol derivatives were added. Figure 6 shows change in conductivity at 125°C for polypyrrole polymerized with various additives, which implies that a p-nitrophenol additive has the most prominent effect. Solid electrolytic capacitors incorporating the improved polypyrrole electrolyte were also bestowed with extremely high thermal stability even when they are in the bare state (Figure 7). The additives are not doped into the polymer but they may have affected the polymerization to proceed at the α - α' positions and yielded a more regular polymer backbone with a few radical contents. Detailed mechanism for this phenomenon will be published in the near future.

SUMMARY

We have developed a new type of solid electrolytic capacitor which is characterized by (1) ideal frequency characteristics (2) excellent temperature characteristics and

(3) high environmental stability. The development has been conducted with the aid of the materials science established for conducting polymers. Especially the excellent thermal stability could be attained through the choice of supporting electrolytes and additives for the electrochemical polymerization of polypyrrole.

In conclusion the research of conducting polymers is now moved to a new stage and the conducting polymers will surely acquire a position of really technological materials.

Acknowledgment

The authors would like to thank S. Yoshida and J. Ozaki of the Capacitor Division of Matsushita Electronic Components Co., Ltd. for their cooperative work throughout this study. They are also indebted to Professor K. Shimidzu of Keio University for the characterization of the aluminum capacitors with a high-resolution transmission electron microscope.

References

1. H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Ciang and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 578 (1977).
2. H. Naarmann and N. Theophilou, *Synth. Met.*, **22**, 1 (1987).
3. J. Tsukamoto, A. Takahashi and K. Kawasaki, *Jpn. J. Appl. Phys.*, **29**, 125 (1990).
4. D. C. Trivedi, *J. Chem. Soc. Chem. Commun.*, 544 (1989).
5. J. H. Machado, F. E. Karasz, R. F. Kovar, J. M. Burnett and M. A. Druy, *New Polym. Mater.*, **1**, 189 (1989).
6. Z. Cai and C. R. Martin, *J. Am. Chem. Soc.*, **111**, 4138 (1989).
7. J. Roncali, A. Yassar and F. Garnier, *J. Chem. Soc., Chem. Commun.*, 581 (1988).
8. A. F. Diaz, K. K. Kanazawa and G. P. Gardini, *J. Chem. Soc., Chem. Commun.*, 635 (1979).
9. S. Kuwabata, J. Nakamura and H. Yoneyama, *J. Chem. Soc., Chem. Commun.*, 779 (1988); S. Kuwabata, K. Okamoto and H. Yoneyama, *J. Chem. Soc., Faraday Trans. 1*, **84**, 2317 (1988).
10. F. Garnier, G. Horowitz, X. Peng and D. Fichou, *Adv. Mater.*, **2**, 592 (1990).
11. M. J. Sailor, E. J. Ginsburg, C. B. Gorman, A. Kumar, R. H. Grubbs and N. S. Lewis, *Science*, **249**, 1146 (1990).
12. T. Nakajima and T. Kawagoe, *Synth. Met.*, **28**, C629 (1989).
13. S. Niwa, *Syno Tech. Rev.*, 17, 90 (1985); *Synth. Met.*, **18**, 665 (1987).
14. J. S. Shaffer, Jpn. Patent Open 60-70719 (1985).
15. I. Isa, *Nikkei New Mater.*, **1**, 48 (1989); *DENKI KAGAKU*, **58**, 604 (1990).
16. Y. Kudoh, S. Tsuchiya, T. Kojima, M. Fukuyama and S. Yoshimura, *Trans. Inst. Electronics, Information and Communication Eng.*, **J73-C-II**, 172 (1990); *Synth. Met.*, **41–43**, 1133 (1991).
17. D. A. McLean and F. S. Power, *Proc. IRE*, **44**, 872 (1965).
18. D. M. Smith, *J. Electrochem. Soc.*, **113**, 19 (1966).
19. S. Yoshimura, Y. Itoh, M. Yasuda, M. Murakami, S. Takahashi and K. Hasegawa, *IEEE Trans. Parts, Hybrids, Packag.*, **PHP-11**, 315 (1975).
20. S. Yoshimura and M. Murakami, *Bull. Chem. Soc. Jpn.*, **50**, 3153 (1977).
21. Y. Itoh and S. Yoshimura, *J. Electrochem. Soc.*, **124**, 1128 (1977).
22. S. Kondo and K. Takeyama, *Jpn. Patent Open* 62-181415 (1987).
23. O. Nishikawa and H. Kato, *J. Chem. Phys.*, **85**, 6758 (1986).
24. Y. Kudoh, M. Fukuyama, T. Kojima, N. Nanai and S. Yoshimura, Submitted to Denki Kagaku.