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Covering anodized aluminum with electropolymerized polypyrrole via manganese oxide layer and application to solid electrolytic capacitor

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Abstract

A new technology for covering an etched and anodized aluminum (Al) foil with polypyrrole (PPy) was developed. PPy was electropolymerized from an external electrode via an extremely thin semiconducting manganese oxide layer prepared on the etched and anodized Al foil in advance. Pyrolytic and reduced manganese oxide could be used with little difference in the performance of the PPy layer growth. To obtain a high coverage ratio, the optimal starting materials were manganese nitrate for the pyrolysis process and sodium permanganate for the reduction process. On the basis of the technology, two kinds of Al solid electrolytic capacitors, in which the PPy layers are used as electrolytes, were produced and characterized. These capacitors showed almost equal ideal impedance–frequency characteristics, excellent temperature characteristics and environmental stability, and independence of the manganese oxide synthesis route.

Keywords: Polypyrrole; Aluminium; Manganese oxide; Electropolymerization; Capacitors

1. Introduction

Many kinds of electroconducting polymers having π-conjugated double bonds have been attracting much attention as advanced materials. In particular, polypyrrole (PPy) is one of the most interesting objects of study because it has a relatively high conductivity and an environmental stability in the oxidative (conductive) state. Although PPy can be synthesized by both the chemical method [1] and the electrochemical method [2], the latter, whereby it is easy to form a thin and durable film [3], is thought to be more useful in the application field of electronics.

'Organic semiconductor capacitor', which is a kind of aluminum (Al) solid electrolytic capacitor using tetracyanoquinodimethane (TCNQ) complex salt as the electrolyte, was developed and commercialized. It is known that the capacitor shows improved impedance–frequency characteristics [4,5]. Since electropolymerized PPy has a higher conductivity and a thermal stability than the TCNQ complex salt and if the PPy layer is formed on the etched and anodized Al foil, it can probably yield a capacitor with higher performance than the organic semiconductor capacitor. Actually, there have been a few reports that mentioned covering anodized valve metals directly with electropolymerized PPy, and the resultant electroconducting-polymer capacitors [6,7]. However, it seems to be possible to form the PPy layer on the anodized valve metals only in limited polymerization conditions, moreover, it is thought to be difficult to obtain reproducible results. To overcome these difficulties, there are some proposals to give the surface of the anodized valve metals conductivity with electroconducting materials, for example, electrodeposited manganese oxide [8], pyrolytic manganese oxide [9] and chemically synthesized electroconducting polymers [10,11]. We have reported previously a new type of Al solid electrolytic capacitor using PPy as the electrolyte that is electropolymerized on the surface of the etched and anodized Al foil via an extremely thin pyrolytic manganese oxide layer [9,12]. As the PPy has a high conductivity and an environmental stability, the capacitor showed ideal impedance–frequency characteristics comparable with those of a multilayer ceramic capacitor; it had excellent endurance characteristics at 125 °C and, at 95% RH and 80 °C. Moreover, the capacitor had also flat temperature characteristics.

Recently, we developed a new manufacturing method for the electroconducting-polymer capacitor in which PPy was formed via a reduced manganese oxide layer. This paper describes: (i) the influence of the preparation conditions of the pyrolytic and reduced manganese oxide layers on the performance of covering the etched and anodized Al foil with electropolymerized PPy, and (ii) the characteristics of the two kinds of electroconducting-polymer capacitors using the pyrolytic and reduced manganese oxide layers.

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Table 1
Influence of manganese compounds and pyrolysis on capacitor performance

Manganese compound	Mn concentration (wt.%)	Solvent	Number of pyrolysis times	Electrode	Capacitance [a] (μF)	tan δ [b] (%)	LC [c] (μA)
Manganese nitrate	0.9	Water	1	Al foil [d]	4.26	3.3	0.18
	9.2	Water	1	Al foil	5.58	1.8	0.07
	15.3	Water	1	Al foil	4.77	5.5	0.13
Manganese acetate	9.5	Water	1	Al foil	4.83	3.0	0.16
Manganese naphthenate	2.3	Toluene	1	Al foil	4.5	2.5	
	3.8	Toluene	1	Al foil	4.93	1.8	
Manganese (II) acetylacetonate	2.5	Ethanol	1	Al foil	4.57	1.9	
Manganese (III) acetylacetonate	2.0	Ethanol	1	Al foil	4.21	2.2	
	2.0	Ethanol	3	Al foil	4.71	2.2	
	2.0	Ethanol	5	Al foil	4.39	2.2	
Manganese ethylate	1.0	Ethanol	1	Al foil	3.57	1.3	
	1.0	Ethanol	2	Al foil	4.57	1.2	
	1.0	Ethanol	3	Al foil	4.46	1.7	
Manganese caprylate	2.4	Toluene	1	Al foil	4.4	1.3	
	4.8	Toluene	1	Al foil	5.1	2.3	
Manganese anthranilate	2.2	Ethanol	1	Al foil	[e]	[e]	

[a] Capacitance at 1 kHz.
[b] Dissipation factor at 1 kHz.
[c] LC: leakage current, data obtained for samples re-anodized after preparation of the manganese oxide layer.
[d] Dimension:4 mm × 6 mm, anodization voltage: 47 V.
[e] Impossible to cover with PPy.

2. Experimental

2.1. Materials

Manganese compounds examined to prepare pyrolytic and reduced manganese oxide layers are as follows: manganese nitrate; manganese acetate; manganese naphthenate; manganese (II) acetylacetonate; manganese (III) acetylacetonate; manganese ethylate; manganese caprylate; manganese anthranilate; potassium permanganate, and sodium permanganate.

Pyrrole monomer and the supporting electrolytes of sodium triisopropylnaphthalenesulfonate (TIPNS) were purchased in their refined grades and used without any further purification. In addition, water and reagent grades of toluene, ethanol, methanol and nitric acid were appropriately used as a solvent or reductant. Although water was deionized, all other substances were used in the as-purchased state.

An electrochemically etched Al foil for the capacitor anode was prepared as the Al specimen. After being cut to a rectangular shape, the Al foil was anodized in a 3% aqueous solution of ammonium adipate at 47 V and 70 °C.

2.2. Preparation of manganese oxide and polypyrrole on the surface of anodized aluminum foil

A pyrolytic manganese oxide layer was formed by heating the etched and anodized Al foil saturated with a solution of a manganese compound at 200–300 °C for about 30 min. Reduced manganese oxide layers were prepared using two kinds of methods:

(i) while the Al foil was immersed in an aqueous solution containing permanganate at about 60 °C, methanol and 0.1 M nitric acid were added drop by drop [13], and

(ii) the Al foil was dipped in an aqueous solution of permanganate and a solution for electropolymerization (treated below).

In both experiments, the area of the Al foil prepared manganese oxide was kept constant and an anode lead was connected at the noncovered part. The combinations of the examined manganese compound and the solvent are shown in Table 1. The several grams' scales of the pyrolytic and reduced manganese oxide were separately synthesized.

Electropolymerization was carried out potentiostatically in a solution containing 0.25 M pyrrole monomer and 0.1 M TIPNS at 2.0 V in ambient conditions and room temperature. To apply the potential of the electropolymerization, a stainless-steel external electrode was brought into contact with the surface of the etched and the anodized Al foil prepared manganese oxide layer.

2.3. Characterization of manganese oxide layer and electroconducting-polymer capacitor

The morphology of the Al foil prepared manganese oxide and PPy was observed through a Nihon Denshi JSM-T300 scanning electron microscope (SEM), a Nihon Denshi JEM-4000EX transmission electron microscope (TEM) and a Nihon Denshi JEM-2000FXII TEM. The MnO_x content of the synthesized manganese oxide and the x value of MnO_x were analyzed by chelate titration using disodium ethylenediaminetetraacetate (EDTA) and redox titration using oxalic acid and potassium permanganate. Infrared (IR) spectra were recorded using a Hitachi I-5040 FT-IR spectrometer. The quality of the manganese oxide layer was evaluated by means of the capacitance and dissipation factor of the capacitor unit that was prepared by applying colloidal graphite and silver paint on the surface of the PPy layer and by connecting a cathode lead. The capacitance and dissipation factor were measured with a Yokogawa Hewlett-Packard 4192A impedance analyzer.

Further characterization, such as, impedance–frequency characteristics, capacitance, dissipation factor and equivalent series resistance (ESR)–temperature characteristics and environmental stability were carried out by using capacitors encapsulated with epoxy resin. The impedance–frequency characteristics were measured with a Hewlett-Packard 4194A impedance/gain-phase analyzer. Two kinds of endurance tests in which rated voltage stresses were applied were carried out using several samples at 125 °C, and at 85% RH and 85 °C. During these tests, the capacitance, dissipation factor and leakage current were intermittently measured at room temperature. The leakage current, which is defined as the current observed after 2 min while applying the rated voltage, was obtained using a Yokogawa 3873 data logger.

3. Results and discussion

3.1. Influence of preparation conditions of pyrolytic manganese oxide layer on characteristics of electroconducting-polymer capacitor

Table 1 shows the characteristics of electroconducting-polymer capacitor units which were prepared using manganese oxide pyrolyzed under various conditions. Relatively high capacitances are obtained by using manganese nitrate, manganese acetate, manganese naphthenate and manganese caprylate as the starting materials. However, since manganese acetate aqueous solution is apt to show precipitation caused by hydrolysis during a certain period of time, it is difficult to realize a stable high capacitance unless a fresh solution of manganese acetate is used. Furthermore, manganese naphthenate and manganese caprylate also seem to be rather unsuitable for a mass-production process, because of the toxicity and the flammability of toluene used as the solvent. By contrast, a manganese nitrate aqueous solution was safe and was proved to be stable and gave highly reproducible results. Hence, manganese nitrate is thought to be the optimal starting material. The maximum capacitance was obtained when a manganese nitrate solution containing 9.2 wt.% of manganese was used. Here, the coverage ratio, which is defined as the ratio of capacitance observed after being covered with PPy to that after the anodization in the solution, was about 85%. The decrease in the capacitance observed when a manganese nitrate solution, having a lower concentration of manganese than the optimal that was used, is most likely caused by the uneven formation of the manganese oxide layer. On the other hand, the decrease in capacitance and the increase in dissipation factor are shown by using a manganese nitrate solution having excessively high concentration of manganese. These factors seem to be ascribed to the blockage of some etching pits and the formed thick manganese oxide layer whose conductivity is much lower than the PPy layer.

However, because the pyrolysis which brings thermal stress and/or erosive gas leads to heavy damage to the dielectric layer of the Al foil, to obtain a high-quality capacitor having small leakage current, it is necessary to re-anodize the anodized Al foil after pyrolysis.

Fig. 1 is a TEM photograph of the anodized Al foil formed with a pyrolytic manganese oxide layer prepared with manganese nitrate solution containing 9.2 wt.% of manganese. It is found that a very thin manganese oxide layer with a thickness of 20–30 nm is formed. Fig. 2 shows an SEM photograph that exhibits the PPy layer growing along the surface of the etched Al foil prepared with the pyrolytic manganese oxide layer. The smooth upper part is the surface of PPy, and the rough lower part is that of the noncovered etched Al foil. It seems that the PPy layer goes ahead with filling the etching pits. Fig. 3 displays a cross-sectional SEM photograph of the etched Al foil completely covered with PPy. From Figs. 2 and 3, it is clear that the growth rate of PPy in the surface direction is much greater than that in the perpendicular direc-

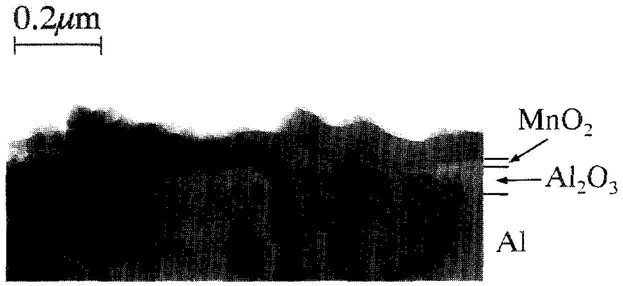

Fig. 1. TEM photograph of anodized aluminum foil formed pyrolytic manganese oxide prepared with manganese nitrate.

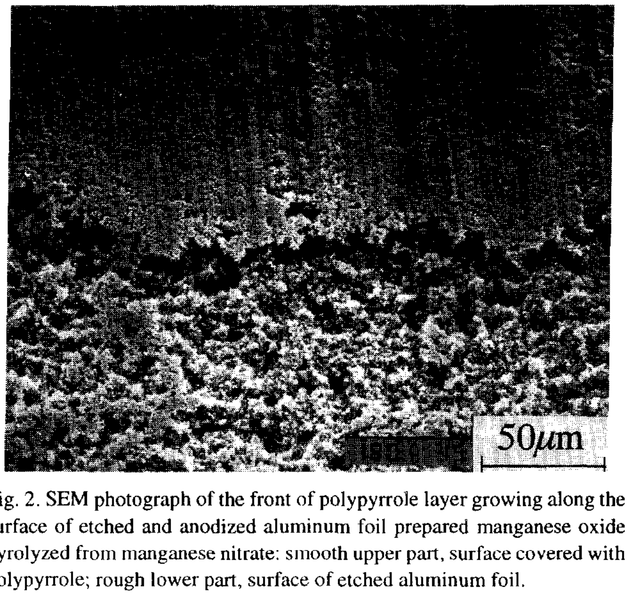

Fig. 2. SEM photograph of the front of polypyrrole layer growing along the surface of etched and anodized aluminum foil prepared manganese oxide pyrolyzed from manganese nitrate: smooth upper part, surface covered with polypyrrole; rough lower part, surface of etched aluminum foil.

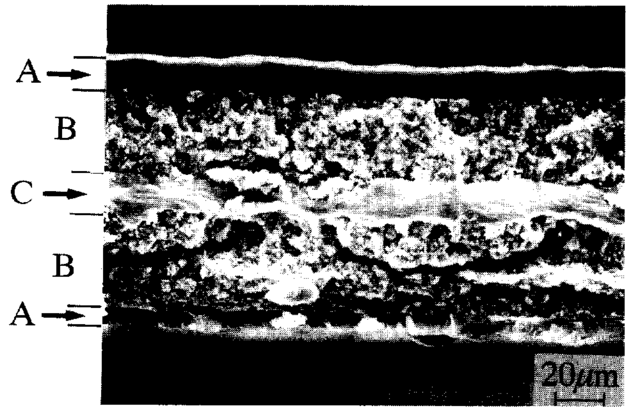

Fig. 3. Cross-sectional SEM photograph of the etched and anodized aluminum foil electrode completely covered with electropolymerized polypyrrole: (A) polypyrrole layer; (B) etched layer of aluminum foil, and (C) core of etched aluminum foil.

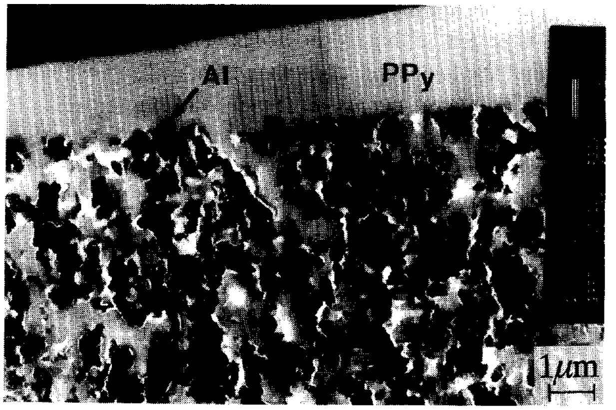

Fig. 4. TEM photograph of etching pits of aluminum foil filled with electropolymerized polypyrrole.

tion. Although the detailed mechanism of the anisotropic growth rate of PPy is unknown, the manganese oxide layer is believed to play a role. Furthermore, Fig. 4 displays a more magnified TEM photograph instead of the SEM photograph shown in Fig. 3. As can be seen, the etching pits of the Al foil are uniformly filled with PPy. Fig. 4 explains clearly why the developed electroconducting-polymer capacitors show such high coverage ratios.

3.2. Influence of preparation conditions of reduced manganese oxide layer on characteristics of electroconducting-polymer capacitor

Table 2 summarizes the characteristics of electroconducting-polymer capacitor units that were prepared using manganese oxide reduced under various conditions. It is possible to cover the etched and anodized Al foils with PPy via the reduced manganese oxide layer as well as via the pyrolytic one. However, we could hardly obtain highly reproducible results using the combination of methanol and nitric acid as the reductant compounds. It may be due to the blockage of some etching pits with formed manganese oxide whose quantity increases with the progress of the reduction reaction. The problem was solved by the newly developed method in which, after being saturated with a permanganate solution, the anodized Al foil is immersed into a solution for the electropolymerization. The reason why the reproducibility is improved is that the reduction reaction of permanganate occurs only adjacent to the surface of the Al foil. When a potassium permanganate solution was used, it was difficult to obtain a high coverage ratio unless the coat of manganese oxide was carried out repeatedly. The complexity is settled by using sodium permanganate whose solubility is higher than that of potassium permanganate. From Table 2, it is found that manganese concentrations of 5.7 wt.% and more give the saturated coverage ratios. In this process, the following electropolymerization was hardly affected, because the reduction reaction occurs only at limited places as aforementioned, therefore, consuming very little pyrrole monomer and TIPNS.

It was expected that the increase in defects of dielectric layer was prevented, because the reduced manganese oxide

Table 2
Influence of permanganate compounds and reduction conditions on capacitor performance

Manganese compound	Mn concentration (wt.%)	Reductant	Number of reduction times	Electrode	Capacitance [a] (μF)	tan δ [a] (%)	LC [b] (μA)
Potassium permanganate	1.1	CH_3OH/HNO_3	1	Al foil [c]	2.18	0.8	
Potassium permanganate	1.1	Pyrrole/TIPNS	1	Al foil	1.77	0.5	0.20
Potassium permanganate	1.1	Pyrrole/TIPNS	2	Al foil	1.94	0.6	0.17
Potassium permanganate	11	Pyrrole/TIPNS	3	Al foil	2.25	0.8	0.18
Sodium permanganate	2.5	Pyrrole/TIPNS	1	Al foil	1.77	0.8	
Sodium permanganaete	3.7	Pyrrole/TIPNS	1	Al foil	1.94	0.8	
Sodium permanganate	4.7	Pyrrole/TIPNS	1	Al foil	2.24	0.7	
Sodium permanganate	5.7	Pyrrole/TIPNS	1	Al foil	2.34	1.0	
Sodium permanganate	6.3	Pyrrole/TIPNS	1	Al foil	2.39	0.7	0.06
Sodium permangante	7.3	Pyrrole/TIPNS	1	Al foil	2.38	1.0	

[a] at 1 kHz.

[b] Data obtained for samples without re-anodization after preparation of the manganese oxide layer.

[c] Dimension:3 mm × 4 mm, anodization voltage: 47 V.

[d] Sodium triisopropylnaphthalenesulfonate.

Table 3
Analytical data for manganese oxide

	MnO_x content (%)	x value of MnO_x
Pyrolytic product from manganese nitrate	104	2.28
Reduced product from potassium permanganate (reductant: CH_3OH, HNO_3)	85.8	2.15
Reduced product from potassium permanganate (reductant: pyrrole, TIPNS)	77.3	1.54

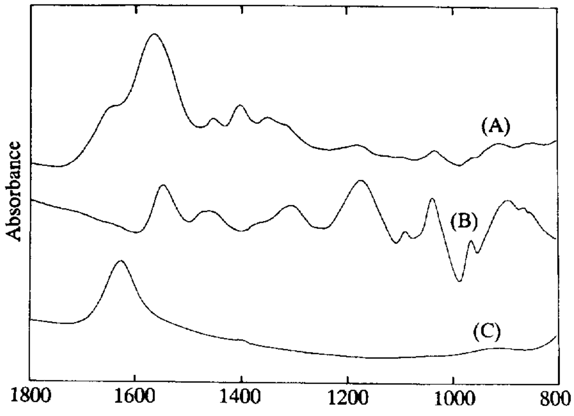

Fig. 5. IR spectra of the reduced product of permanganate prepared in a solution for (A) electropolymerization, (B) chemically synthesized polypyrrole using ferric sulfate as an oxidant and (C) reduced product of permanganate prepared with methanol and nitric acid.

layer was prepared under mild conditions, for example from room temperature to 60 °C. Actually, small leakage-current capacitors were obtained without the re-anodization of the anodized Al foil after preparation of manganese oxide (Table 2).

Table 3 shows the analytical data for pyrolytic and reduced products containing manganese oxide prepared under various conditions. Although the MnO_x content of the reduced products from potassium permanganate was lower than that of the pyrolytic product from manganese nitrate, it is most likely caused by manganese oxide prepared in an aqueous solution that is hydrated [14]. Furthermore, it should be also mentioned that there was a great difference in the MnO_x content and the x value of MnO_x between the two kinds of reduced product prepared with various reductants. Fig. 5 displays IR spectra of those reduced products from potassium permanganate along with that of PPy-chemically synthesized using ferric sulfate. The spectrum of the reduced product of permanganate using methanol and nitric acid as the reductant gives peaks at 920, 1400 and 1628 cm^{-1}. On the other hand, the spectrum of the reduced product from permanganate prepared in a solution for the electropolymerization not only has the above-mentioned peaks but also peaks at 964, 1038, 1184, 1304, 1352, 1404, 1454 and 1566 cm^{-1}. The latter peaks are nearly identical with those of the spectra of chemically synthesized PPy and those of electrochemically polymerized PPy reported by Hyodo and MacDiamid [15]. We also observed that an Al foil thickly coated with reduced manganese oxide changes color from brown to black, when it was immersed in a solution for the electropolymerization. As Hupe also mentioned [16], we therefore conclude that PPy is synthesized at the surface of reduced manganese oxide that has a higher activity than pyrolytic manganese oxide [14]. This can explain why the reduced product from permanganate prepared in a solution for the electropolymerization has such low MnO_x content and the x value of MnO_x.

3.3. Comparison of electroconducting-polymer capacitors using pyrolytic and reduced manganese oxide

Since we reported previously the characteristics of the electroconducting-polymer capacitor in which PPy was prepared via pyrolytic manganese oxide [9,12], the comparison of the electroconducting-polymer capacitors prepared with both the reduced and the pyrolytic manganese oxide are given. As for the former, the manganese oxide layer was prepared with a manganese nitrate solution containing 9.2 wt.% of manganese. On the other hand, about the latter, the coat of manganese oxide was repeated three times by using a potassium permanganate solution containing 1.1 wt.% of manganese and a solution for the electropolymerization. Figs. 6 and 7 show the impedance–frequency characteristics, and capacitance, dissipation factor and ESR–temperature characteristics of the two kinds of capacitor whose nominal capacitances are 2.4 μF. As can be seen from these figures, that there is no essential difference in the performance between two kinds of capacitor. This results because the thickness of the manganese

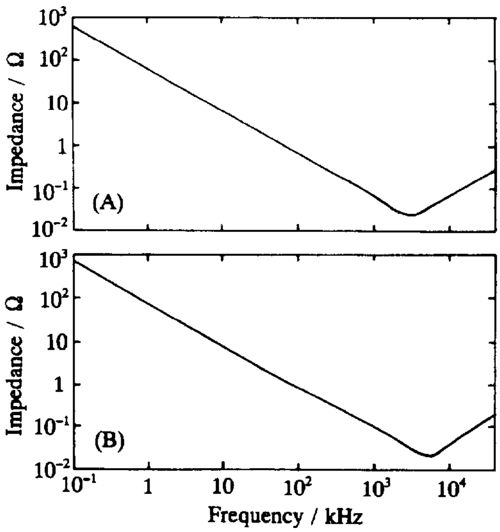

Fig. 6. Comparison of impedance-frequency characteristics for capacitors using electropolymerized polypyrrole via reduced manganese oxide prepared with (A) permanganate and (B) pyrolytic manganese oxide prepared with manganese nitrate; capacitance, 2.4 μF.

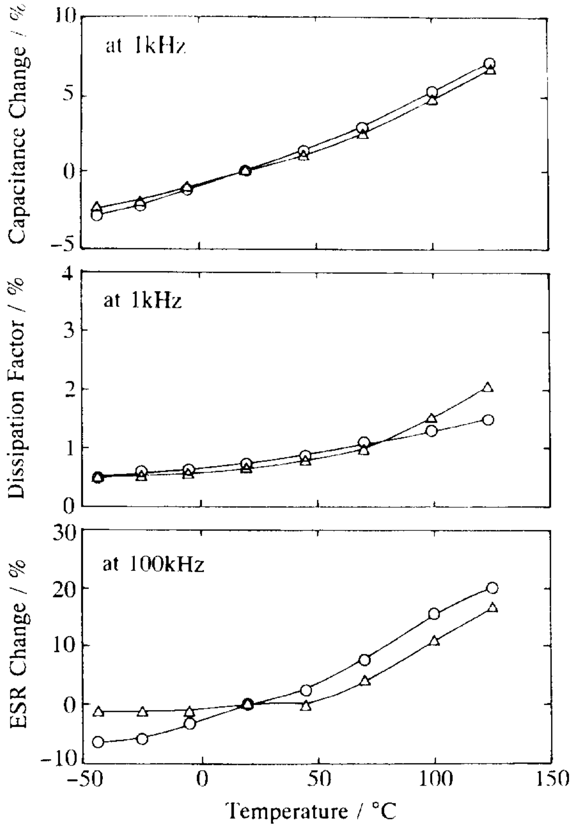

Fig. 7. Comparison of capacitance–dissipation factor and equivalent series resistance (ESR)–temperature characteristics for capacitors using electropolymerized polypyrrole via reduced manganese oxide prepared with (△) permanganate and (○) pyrolytic manganese oxide prepared with manganese nitrate.

oxide layer compared with that of laminated PPy layer is so small, for example, shown in Figs. 1 and 3, so that performance of the electrolyte is mainly dominated by that of PPy.

Figs. 8 and 9 present the comparison of endurance tests, which were carried out at 125 °C and at 85% RH and 85 °C, for the above-mentioned two kinds of capacitor. The capacitors having the reduced manganese oxide layers showed lower leakage currents at the beginning, in spite of the omission of the re-anodization. The steep decrease in capacitance that is observed in the first 50 h at 125 °C (Fig. 8) seems to be ascribed to the desorption of water that was adsorbed at the surface of electrode noncovered with PPy, when kept for a long time at ambient conditions. As for the capacitors having the reduced manganese oxide layer, since the deterioration rate of capacitance observed after 500 h at 125 °C (Fig. 8) is less than 3% except the change at an early stage, it is not believed to be a serious problem. On the other hand, as shown in Fig. 9, although the almost similar increase in capacitance and dissipation factor is observed for both the capacitors, this phenomenon is most likely brought about by the adsorption of water to the surface of the electrode noncovered with PPy. Hence, the electroconducting-polymer capacitor using reduced manganese oxide has excellent thermal and moisture stabilities comparable with that using pyrolytic manganese oxide.

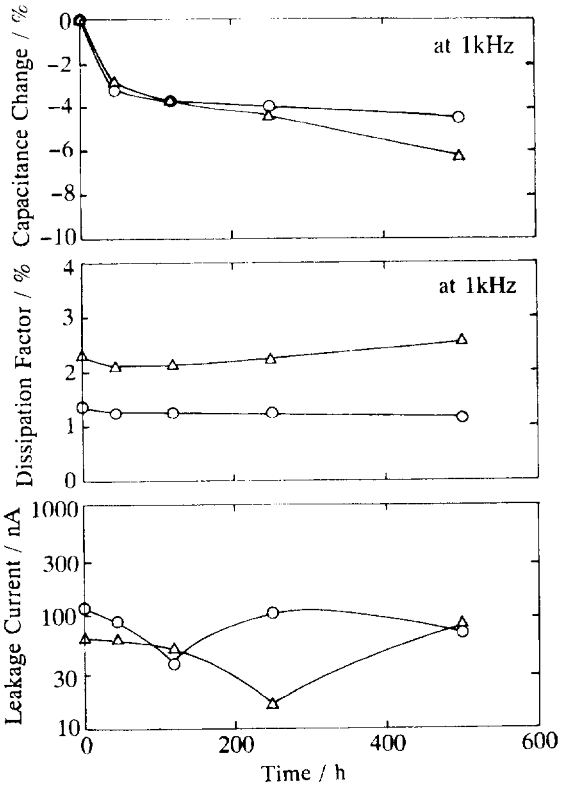

Fig. 8. Comparison of endurance characteristics for capacitors using electropolymerized polypyrrole via reduced manganese oxide prepared with (△) permanganate and (○) pyrolytic manganese oxide prepared with manganese nitrate applied at a rated voltage of 13 V at 125 °C.

From the viewpoint of mass production, the process using reduced manganese oxide has great advantages as follows: (i) it is unnecessary to re-anodize the anodized Al foil after preparation of the manganese oxide layer, and (ii) it is possible to prepare the manganese oxide and PPy layer in the same solution, because the consumption of pyrrole monomer and supporting electrolyte are negligibly small and the rate of the reduction reaction is higher than that of the PPy layer growth. These help the mass-production process of the electroconducting-polymer capacitor to be extremely simple. Furthermore, since the damage to the dielectric layer is prevented, it is possible to enhance the rated voltage and to decrease the ratio between forming voltage and rated voltage so as to miniaturize the size of the electroconducting-polymer capacitor.

4. Conclusions

The etched and anodized Al foils were proved to be covered with electropolymerized PPy via the manganese oxide layer prepared in advance. The manganese oxide layers synthesized either by pyrolysis and reduction could be used with little differences in their performance. The optimal starting materials were manganese nitrate for the pyrolysis process and sodium permanganate for the reduction process. On the basis of these results, two kinds of electroconducting-poly-

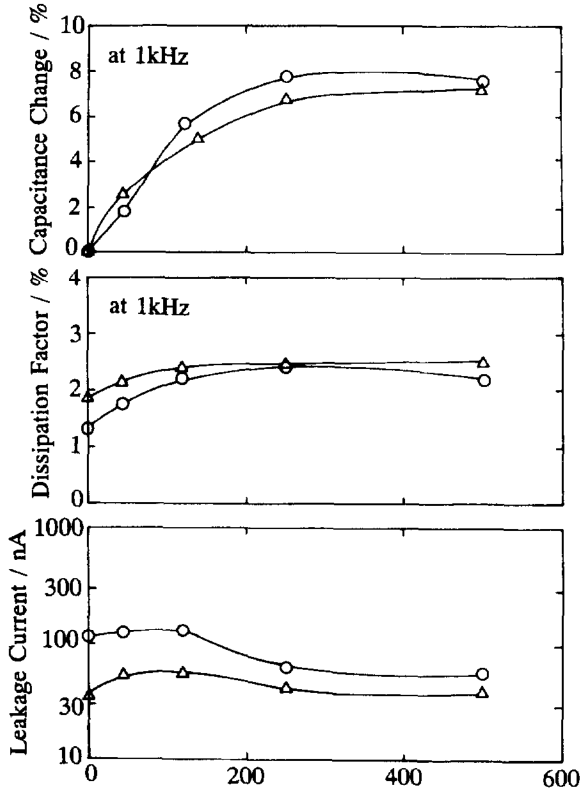

Fig. 9. Endurance characteristics for capacitors using electropolymerized polypyrrole via reduced manganese oxide prepared with (△) permanganate and (○) pyrolytic manganese oxide prepared with manganese nitrate applied at a rated voltage of 13 V at 85% RH and 85 °C.

mer capacitors in which electropolymerized PPy is formed via the pyrolytic and reduced manganese oxide layers were developed. Independent of the manganese oxide synthesis route, these capacitors show almost the same excellent impedance–frequency characteristics, temperature characteristics and environmental stability.

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