The Effects of Parameters for Preparing Conducting Polymer and Modification of Carbon Nanotubes on Electrochemical Characteristics of Aluminum Capacitors

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ABSTRACT

Carbon nanotubes (CNTs) which are directly grown on nanoporous alumina templates by chemical vapor deposition are modified by acid-treatment or/and annealing and then a negative electrode is obtained. Next, alumina is deposited onto the nanoporous alumina templates with the grown as well as modified CNTs by a chemical liquid phase deposition method and then a positive electrode is obtained. Finally, the negative electrode coated with solid electrolyte polymerized by changing weight ratios between iron(III) p-toluenesulfonate hexahydrate-6 H2O and 3,4-ethylenedioxythiophene is assembled with the positive electrode into an aluminum capacitor. The capacitance of the aluminum capacitor reaches a maximum at 6 of the weight ratio between iron(III) p-toluenesulfonate hexahydrate-6 H2O and 3,4-ethylenedioxythiophene. Furthermore, the highest capacitance as well as operation potential of the aluminum capacitor and the lowest leakage current density of the aluminum capacitor at the 10000th cycle of potential cycling are obtained by the CNTs being treated with acid and annealed. Moreover, the decreasing rates of the capacitance as well as operation potential of the aluminum capacitor and the increasing rate of the leakage current density of the aluminum capacitor for the raw CNTs are quicker than those for the CNTs treated with acid or/and annealed.

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1. Introduction

Aluminum electrolytic capacitors have been widely used as power supplies for all types of electronic equipment including automobiles, computers, monitors, and other electronic components. The aluminum electrolytic capacitor consists of aluminum anode foil—on which an oxide is prepared by an electrochemical oxidation process—a suitable electrolyte, and aluminum cathode foil. The capacitance of the aluminum cathode foil is much higher than that of the aluminum anode foil so that the applied potential appears mainly on the aluminum anode foil, which determines the operation potential and capacitance. Thus, we were concerned principally with the anode electrode.

For conducting polymer used as solid electrolyte of aluminum capacitors, an electrically conductive polymer layer (monomer: ethylenedioxythiophene, oxidant: iron(III) p-toluenesulfonate hexahydrate, and solvent: n-butanol, i-propanol, as well as pure water) is disposed on the oxide dielectric layer on the sinter by impregnation of the oxide dielectric layer with a polymer solution or chemical polymerization. In our previous study, carbon nanotubes (CNTs) which were directly grown on nanoporous alumina templates by chemical vapor deposition were modified by radio frequency nitrogen-plasma at different time. In order to reduce cost, simply physicochemical methods of acid-treatment or/and annealing were instead of nitrogen-plasma in this study. Methods for the modification of the physical and chemical properties of carbon materials include acid treatment and annealing. The tips of multi-walled CNTs were opened by boiling 69 wt% nitric acid during 15 to 45 min and then the multi-walled CNTs were annealed in CO2 at 525°C during 60 to 100 min for the elimination of the disordered carbon coming from the tip destruction. CNTs were refluxed in 16 M nitric acid for 3 h and then the CNTs were annealed in nitrogen or hydrogen for 3 h at 450 or 950°C. CNTs were firstly oxidized by H2O2 for opening tube ends as well as shortening CNT’s length, then treated by HCl for removing the residual oxidized catalyst particles as well as other carbonaceous materials, and finally annealed in air at 450°C for 45 min for maximizing the CNT tip destruction as well as further reducing the amorphous carbon. Single-walled CNTs were annealed in air at increasing temperatures in the range from 300 to 550°C for 1 h. In order to improve the organized carbon, specific surface area, or hydrophilic nature of carbonaceous materials, CNTs were modified by acid treatment or/and annealing in this study. This paper examines the effects of weight ratios between iron(III) p-toluenesulfonate hexahydrate-6 H2O as well as 3,4-ethylenedioxythiophene and the CNTs treated with acid or/and annealed on the capacitance, operation potential, leakage current density, and long-term operational stability of aluminum capacitors in this study.

2. Experimental

Aluminum foil (10 × 5 × 0.001 cm², purity 99.98%) was degreased in acetone for 5 min. In order to remove the oxide layer from its surface, it was then immersed in 1 M aqueous NaOH for 2 min and subsequently rinsed with de-ionized water. Next, it was rinsed ultrasonically with alcohol for 15 min. Finally, in order to fabricate well-ordered nanoporous anodic aluminum oxide (AAO) templates through a two-step anodization process, it was electro-polished in a solution of sulfuric acid:phosphoric acid:de-ionized water in ratios of 2:2:3. AAO templates were fabricated through a two-step anodization process. For the first anodization of the aluminum foil, 25 V was applied for 30 min in a 0.5 M sulfuric acid solution at 5°C. Etching of the anodized film followed in a mixture of chromic acid (1.8 wt%)
and phosphoric acid (6 wt%) for 40 min at 60°C. The second anodization was performed under the same conditions as the first anodization except 210 s of time. At the end of the second anodization, the previous value of the current density was halved and then the sample was re-anodized until reaching stable potential. This process was repeated 8 times until reaching almost 0 V of potential.

In order to completely remove aluminum oxide (barrier layer) on the pore bottom tips of AAO templates and then electrochemically deposit catalyst particles at the pore bottom tips of AAO templates, the pores of AAO templates were further widened after the second anodization by etching in phosphoric acid (5 wt%) for 20 min.

Before carbon nanotube growth, the cobalt (Co) catalyst particles were electrochemically deposited at the pore bottom tips of AAO templates in an electrolyte of CoSO4·7H2O (5 wt%) and H3BO3 (2 wt%) by applying an alternating current potential 10.5 V (frequency: 60 Hz) for 60 s. Next, CNTs were grown on the Co-coated nanoporous alumina templates using thermal CVD with the gas mixture (C2H2 = 50 cm³·min⁻¹ and Ar = 100 cm³·min⁻¹) at 600°C for 60 min.

The CNT electrodes were immersed in 61 wt% HNO3 for 20 min or/and annealed at 450°C in Ar (200 cm³·min⁻¹) for 45 min. Then negative electrodes of aluminum capacitors were obtained.

The saturated solution of Al2(SO4)3 was prepared as a source liquid. The suspended particles are hydrolytes of Al³⁺, and could be filtered out by the 0.2 μm filter. Sodium bicarbonate fine powder was added slowly to obtain a pH value of 2.89 for the growth solution. As soon as the reaction was completed, de-ionized (DI) water was immediately added in order to increase the pH to 3.80. After being filtered again by the 0.2 μm filter, the solution was now ready for alumina thin film growth on the nanoporous alumina templates with grown CNTs for 3 h at ambient temperatures. Then positive electrodes of aluminum capacitors were obtained.

Finally, the negative electrodes coated with solid conducting polymer electrolyte (PEDOT: poly-3,4-ethylenedioxythiophene) polymerized by varying weight ratios (5, 6, and 7) between iron(III) p-toluenesulfonate hexahydrate-6 H2O (oxidant) and 3,4-ethylenedioxythiophene (monomer) were assembled with the positive electrodes into aluminum capacitors by a coin cell manual crimping machine (CR2032, Taiwan).

Capacitance and resistance measurements were made at 120 Hz (frequency) with a LCR (inductance, capacitance, and resistance) meter (Hioki, 3522-50, Japan). In addition, operation potential and leakage current density measurements were made by applying direct current with a Capacitor leakage current/IR meter (Chroma, Model 11200, and Taiwan). Furthermore, surface morphologies of pristine CNTs grown on nanoporous alumina templates, CNTs (grown on nanoporous alumina templates) annealed, alumina deposited onto the nanoporous alumina templates with grown pristine CNTs, alumina deposited onto the nanoporous alumina templates with grown CNTs treated with acid or/and CNTs (grown on nanoporous alumina templates) annealed, alumina deposited onto the nanoporous alumina templates with grown pristine CNTs, alumina deposited onto the nanoporous alumina templates with grown CNTs treated with acid or/and alumina deposited onto the nanoporous alumina templates with grown CNTs annealed were conducted by a field emission scanning electron microscope (FE-SEM, JEOL JSM-6700F, Japan). Moreover, the intensity ratios of the C-C stretching mode to the disorder-induced mode of graphite structure for pristine CNTs, CNTs treated with acid or/and CNTs annealed were investigated by a microscope Raman spectrometer (inVia, Renishaw, England). The UV-vis absorption spectra of the PEDOT polymerized at 5, 6, and 7 of weight ratio between iron(III) p-toluenesulfonate hexahydrate-6 H2O and 3,4-ethylenedioxythiophene were recorded with a UV/VIS spectrophotometer (PerkinElmer precisely, Lambda 850, USA). Contact angles for pristine CNTs, CNTs treated with acid or/and CNTs annealed were measured by a CONTACT-ANGLE METER (KYOWA INTERFACE SCIENCE CO., LTD., CA-D, Japan).

Figure 1. The effects of weight ratios between iron(III) p-toluenesulfonate hexahydrate-6 H2O and 3,4-ethylenedioxythiophene on the capacitance of aluminum capacitors with solid electrolyte (PEDOT) for CNTs without modification.

3. Results and Discussion

Figure 1 shows the effects of weight ratios between iron(III) p-toluenesulfonate hexahydrate-6 H2O and 3,4-ethylenedioxythiophene on the capacitance of aluminum capacitors with solid electrolyte (PEDOT) for CNTs without modification. The capacitance reached a maximum at 6 of the weight ratio between iron(III) p-toluenesulfonate hexahydrate-6 H2O and 3,4-ethylenedioxythiophene. The reason behind this behavior may be explained as following. The UV-vis absorption spectra of the PEDOT polymerized at 5, 6, and 7 of weight ratios between iron(III) p-toluenesulfonate hexahydrate-6 H2O and 3,4-ethylenedioxythiophene are shown in Figs. 2(a), 2(b), and 2(c), respectively. The broad absorbance in the wavelength region around 600 and 650 nm corresponds to the peaks of PEDOT. The absorbance of the PEDOT polymerized at 6 of the weight ratio between iron(III) p-toluenesulfonate hexahydrate-6 H2O and 3,4-ethylenedioxythiophene was the highest among the PEDOT polymerized at 5, 6, and 7 of weight ratios between iron(III) p-toluenesulfonate hexahydrate-6 H2O and 3,4-ethylenedioxythiophene (See Fig. 2), thus the amount of the PEDOT polymerized at 6 of the weight ratio between iron(III) p-toluenesulfonate hexahydrate-6 H2O and 3,4-ethylenedioxythiophene was the highest and then the capacitance was the highest (See Fig. 1). A similar result has been published in previous literature where the weight ratio between iron(III) p-toluenesulfonate hexahydrate and ethylenedioxythiophene was 5 due to iron(III) p-toluenesulfonate hexahydrate being instead of iron(III) p-toluenesulfonate hexahydrate-6 H2O. Furthermore, at 6 of the weight ratio between iron(III) p-toluenesulfonate hexahydrate-6 H2O and 3,4-ethylenedioxythiophene, the capacitance (642 μF cm⁻²) for CNTs without modification and aluminum capacitors with solid electrolyte was higher than that (330 μF cm⁻²) for CNTs without modification and aluminum capacitors with solid electrolyte (6 of the weight ratio between iron(III) p-toluenesulfonate hexahydrate-6 H2O and 3,4-ethylenedioxythiophene) as well as electrolytic paper. The reason behind this picture may be explained as following. Resistance is inversely proportional to contact area which is proportional to capacitance (C = εε₀A/L, where ε is the relative dielectric constant, ε₀ is permittivity, A is the contact area between PEDOT and as well as alumina, and L is the thickness of alumina), so equivalent series resistance is inversely proportional to capacitance. The inverse proportion between equivalent series resistance and capacitance was also observed. The electrolytic paper (nonconductor) led to an increase in equivalent series resistance of aluminum capacitors, therefore the capacitance of aluminum capacitors with solid...
electrolyte (6 of the weight ratio between iron(III) p-toluenesulfonate hexahydrate-6 H$_2$O and 3,4-ethylenedioxythiophene) and electrolytic paper decreased.

Figure 3 shows the effects of weight ratios between iron(III) p-toluenesulfonate hexahydrate-6 H$_2$O and 3,4-ethylenedioxythiophene on the operation potential of aluminum capacitors with solid electrolyte for CNTs without modification. The operation potential was constant due to the same thickness of alumina. Furthermore, Fig. 4 shows the effects of weight ratios between iron(III) p-toluenesulfonate hexahydrate-6 H$_2$O and 3,4-ethylenedioxythiophene on the leakage current density of aluminum capacitors with PEDOT for CNTs without modification. The curve of Fig. 4 was similar to the curve of Fig. 1 since the leakage current density is proportional to the product of capacitance by operation potential (See Figs. 1, 3, and 4).

Therefore, the weight ratio between iron(III) p-toluenesulfonate hexahydrate-6 H$_2$O and 3,4-ethylenedioxythiophene at 6 was chosen as a better/superior condition due to the highest capacitance, constant operation potential, and almost unchangeable leakage current density (See Figs. 1, 3, and 4).

Figure 5 shows the effects of the pristine CNTs treated with acid or/and annealed and different charge-discharge cycles on the capacitance for aluminum capacitors with solid electrolyte (6 of the weight ratio between iron(III) p-toluenesulfonate hexahydrate-6 H$_2$O and 3,4-ethylenedioxythiophene). At the beginning of potential cycling, the capacitances of the aluminum capacitors for the raw CNTs and the CNTs treated with acid were lower than those for the CNTs treated with acid as well as annealed and the CNTs annealed (See Fig. 5). The reason behind this behavior may be explained as following. By the CNTs treated with acid or/and
Moreover, Fig. 7 shows the effects of the pristine CNTs treated with acid or/and annealed and different charge-discharge cycles on the capacitance for aluminum capacitors with solid electrolyte (6 of the weight ratio between iron(III) p-toluenesulfonate hexahydrate-6 H₂O and 3,4-ethylenedioxythiophene).

The effects of the pristine CNTs treated with acid or/and annealed and different charge-discharge cycles on the capacitance for aluminum capacitors with solid electrolyte (6 of the weight ratio between iron(III) p-toluenesulfonate hexahydrate-6 H₂O and 3,4-ethylenedioxythiophene).

Table 1. The contact angle, amount of chemical liquid phase deposition of aluminum oxide, and I_D/I_D of the CNTs treated with acid or/and annealed.

<table>
<thead>
<tr>
<th>CNTs modified by different methods</th>
<th>Contact angle (°)</th>
<th>Amount of chemical liquid phase deposition of aluminum oxide (mg cm⁻²)</th>
<th>I_D/I_D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine CNTs</td>
<td>136</td>
<td>0.485</td>
<td>0.890</td>
</tr>
<tr>
<td>CNTs treated with acid</td>
<td>4</td>
<td>0.820</td>
<td>0.983</td>
</tr>
<tr>
<td>CNTs annealed</td>
<td>135</td>
<td>0.490</td>
<td>0.972</td>
</tr>
<tr>
<td>CNTs treated with acid and annealed</td>
<td>4</td>
<td>0.760</td>
<td>0.983</td>
</tr>
</tbody>
</table>

The curve of Fig. 5 was the inversion of the curve of Fig. 7 because of capacitance being inversely proportional to resistance.

Figure 8 shows the effects of the pristine CNTs treated with acid or/and annealed and different charge-discharge cycles on the operation potential for aluminum capacitors with solid electrolyte (6 of the weight ratio between iron(III) p-toluenesulfonate hexahydrate-6 H₂O and 3,4-ethylenedioxythiophene).

The curve of Fig. 7 was the inversion of the curve of Fig. 8 due to operation potential being inversely proportional to resistance.

Figure 9 shows the effects of the pristine CNTs treated with acid or/and annealed and different charge-discharge cycles on the leakage current density for aluminum capacitors with solid electrolyte (6 of the weight ratio between iron(III) p-toluenesulfonate hexahydrate-6 H₂O and 3,4-ethylenedioxythiophene).

Figure 5. The effects of the pristine CNTs treated with acid or/and annealed and different charge-discharge cycles on the capacitance for aluminum capacitors with solid electrolyte (6 of the weight ratio between iron(III) p-toluenesulfonate hexahydrate-6 H₂O and 3,4-ethylenedioxythiophene).

Figure 6. FE-SEM micrographs of (a) pristine CNTs grown on nanoporous alumina templates, (b) CNTs (grown on nanoporous alumina templates) treated with acid, (c) CNTs (grown on nanoporous alumina templates) annealed, and (d) CNTs (grown on nanoporous alumina templates) treated with acid and annealed.

Figure 7. The effects of the pristine CNTs treated with acid or/and annealed and different charge-discharge cycles on the equivalent series resistance for aluminum capacitors with solid electrolyte (6 of the weight ratio between iron(III) p-toluenesulfonate hexahydrate-6 H₂O and 3,4-ethylenedioxythiophene).

Figure 8. The effects of the pristine CNTs treated with acid or/and annealed and different charge-discharge cycles on the operation potential for aluminum capacitors with solid electrolyte (6 of the weight ratio between iron(III) p-toluenesulfonate hexahydrate-6 H₂O and 3,4-ethylenedioxythiophene).

Figure 9. The effects of the pristine CNTs treated with acid or/and annealed and different charge-discharge cycles on the leakage current density for aluminum capacitors with solid electrolyte (6 of the weight ratio between iron(III) p-toluenesulfonate hexahydrate-6 H₂O and 3,4-ethylenedioxythiophene).
Alumina deposited onto the nanoporous alumina templates with grown pristine CNTs treated with acid as well as annealed, and (d) alumina deposited onto the nanoporous alumina templates with grown pristine CNTs treated with acid as well as annealed.

Figure 10. FE-SEM micrographs of (a) alumina deposited onto the nanoporous alumina templates with grown pristine CNTs, (b) alumina deposited onto the nanoporous alumina templates with grown CNTs treated with acid, (c) alumina deposited onto the nanoporous alumina templates with grown CNTs annealed, and (d) alumina deposited onto the nanoporous alumina templates with grown CNTs treated with acid as well as annealed.

Figure 9. The effects of the pristine CNTs treated with acid or/and annealed and different charge-discharge cycles on the leakage current density for aluminum capacitors with solid electrolyte (6 of the weight ratio between iron(III) p-toluenesulfonate hexahydrate-6 H₂O and 3,4-ethylenedioxythiophene).

The effects of the pristine CNTs treated with acid or and annealed and different charge-discharge cycles on the leakage current density for aluminum capacitors with solid electrolyte (6 of the weight ratio between iron(III) p-toluenesulfonate hexahydrate-6 H₂O and 3,4-ethylenedioxythiophene).

The lowest leakage current density of the aluminum capacitor at the 10000th cycle of potential cycling (See Figs. 5, 8, and 9).

Figure 11 shows the effects of different charge-discharge cycles on the capacitance of the aluminum capacitor with liquid electrolyte (organic ammonium, ethylene, etc.) and electrolytic paper for the CNTs treated with acid. From a comparison of Figs. 5 and 11, the capacitance of the aluminum capacitor with solid electrolyte (6 of the weight ratio between iron(III) p-toluenesulfonate hexahydrate-6 H₂O and 3,4-ethylenedioxythiophene) for the CNTs treated with acid was higher than that of the aluminum capacitor with solid electrolyte at the beginning of potential cycling since the conductivity (100 S cm⁻¹) of solid electrolyte (PEDOT) is higher than that (0.01 S cm⁻¹) of liquid electrolyte. The long-term operational stability for the aluminum capacitor with solid electrolyte was obviously better than that for the aluminum capacitor with liquid electrolyte. This picture may be attributed to the CNTs dispersing into the liquid electrolyte after cycling, as evidenced by the liquid electrolyte changing from light yellow to light black for the aluminum capacitor with liquid electrolyte.

4. Conclusion

At the beginning of potential cycling, the capacitances of the aluminum capacitors for the raw CNTs and the CNTs treated with acid were lower than those for the CNTs treated with acid as well as annealed and the CNTs annealed. Furthermore, at the beginning of potential cycling, the leakage current densities of the aluminum capacitor for the CNTs treated with acid and the CNTs treated with acid as well as annealed were lower than those for the raw CNTs and the CNTs annealed. Moreover, the capacitance for the aluminum capacitor with solid electrolyte was higher than that for the aluminum capacitor with liquid electrolyte at the beginning of potential cycling and the long-term operational stability for the aluminum capacitor with solid electrolyte was obviously better than that for the aluminum capacitor with liquid electrolyte.

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References

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