

# Preparation and characterization of Ppy/Al<sub>2</sub>O<sub>3</sub>/Al used as solid-state capacitors for microsystems—Effect of amount of electricity passed

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Received 5 January 2007; received in revised form 9 April 2007; accepted 15 April 2007

Available online 25 April 2007

## Abstract

This investigation focuses on the preparation of polypyrrole composite films, Ppy/Al<sub>2</sub>O<sub>3</sub>/Al, used as solid-state capacitor with electrochemical polymerization in the presence of DBSA, co-dopant and co-solvent. The parameters of the solid-state capacitor, i.e. leakage current (Lc), capacitor (Cs), dielectric factor (DF) and equivalent series resistance (ESR), were measured in this study. The surface morphology and compositions of the prepared Ppy/Al<sub>2</sub>O<sub>3</sub>/Al electrolyte were examined using SEM and EDS, respectively. Further, for 3 C of electricity passed, the values of Lc, Cs, DF and ESR of the Ppy/Al<sub>2</sub>O<sub>3</sub>/Al capacitor prepared with 2-NSNa and DBSA as a co-dopant were measured to be  $0.029 \pm 0.005 \mu\text{A cm}^{-2}$ ,  $688.8 \pm 8.28 \text{ nF cm}^{-2}$ ,  $14.35 \pm 5.63\%$  and  $18.63 \pm 3.48 \Omega$ . Further, the parameters both of  $R_{\text{ox}}$  and  $R_{\text{ppy}}$  are 135.5 and 7.047  $\Omega$ .

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**Keywords:** Polypyrrole; Aluminum solid-state capacitor; Aluminum oxides; Co-dopants

## 1. Introduction

In recent years, conducting polymers, such as polypyrrole, polyaniline, polythiophene and so on have been synthesized via chemical polymerization [1–4], and electrochemical polymerization [5–16]. Electrochemical polymerization of pyrrole is an alternative method that can provide conducting polymer coatings without involving toxic or excess chemicals. In addition, another advantage of electrochemical polymerization is safety because the reaction is controlled at mild condition [7–13,16]. Conductive polypyrrole which shows thermal stability, short response time, and high conductivity has been extensively studied due to its wide applications in electronic equipment [17], material of batteries [18], solid polymer electrolyte for capacitor [19,20], sensors [21–23], and as a conducting heat-melted adhesive for EMI shielding applications [24].

Previous modifications of different kinds of materials used in the micro-electronic system have been published

[7,10,13,25–28]. Iroh et al. postulated the formation of polypyrrole coatings on stainless steel in aqueous benzene sulfate solution and electrochemical polymerization of polypyrrole onto Al 2024 substrate in aqueous oxalic acid solution [28,29]. Kim et al. also investigated a model enzyme to be entrapped in the electrochemically grown Ppy/Pt film [30]. Sabbatini et al. showed that the thin layer of native oxide film that grows on the surface of both titanium and its alloys matches these requirements, leading to a thin protective layer on Ppy growth [26]. In addition, Hwang et al. also showed that the electropolymerization of pyrrole and 4-(3-Pyrrolyl) butane-sulfonate is carried out on Pt substrates [27]. Aluminum, which is a stable commercialized product, is one of the suitable materials used as the capacitor base, because it had many advantages, such as the highest unit capacity, easy micro-production for a dc power supply displayer, lower price and so on. Previously, the simultaneous formation of Ppy and aluminum oxide on an aluminum substrate in the presence of a single dopant has been reported [25,26,30–40]. Nevertheless, the effect of co-dopant on the capacitive characteristics of the simultaneous formation of Ppy/Al<sub>2</sub>O<sub>3</sub>/Al has seldom been reported [41,42]. Hence, this study focuses on the simultaneous preparation of an Al<sub>2</sub>O<sub>3</sub> dielectric film and a Ppy

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solid polymer electrolyte onto the Al foil by adding DBSA and 2-NSNa as a co-dopant system. The coulombs of electricity passed that affect the structure and morphology of preparation of the Ppy/Al<sub>2</sub>O<sub>3</sub>/Al film and the characteristics of the resulting solid-state capacitor are investigated.

## 2. Experimental

### 2.1. Materials

All of the chemicals (e.g., pyrrole extra pure grade >99.99% ACROS), dodecyl benzenesulfonic acid (DBSA, pure grade, TCI), sodium 2-naphthalenesulfonic acid (GR grade >99%, MERCK), sodium hydroxide (GR grade >99%, MERCK), HCl (GR grade, 37%, MERCK), and methyl alcohol (99.98%, TEDIA) used in this work were not further purified before usage.

### 2.2. Treatment of Al

Aluminum foil was purchased from Kaimei Electronic Corp (40PFA92, 40 μm). The film of aluminum oxide deposited onto the surface of Al foil was eroded with a 1.0 M NaOH solution for 15 min at 298 K. Next, the surface of Al was washed many times with distilled water (Millipore). Then, the Al foil was electrochemically etched in a 0.664 M HCl aqueous solution by an electricity supply of 200 mA cm<sup>-2</sup> current density for 15 s passed at 298 K.

### 2.3. Preparation of Ppy/Al<sub>2</sub>O<sub>3</sub>/Al film

The electrolyte for preparing Ppy/Al<sub>2</sub>O<sub>3</sub>/Al was obtained by mixing the desired amount of pyrrole monomer, DBSA, and 2-naphthalenesulfonic acid (2-NSNa) in the suitable concentration of acid aqueous solution. Before the electrolysis, the aluminum foil was impregnated in 0.1 N NaOH for 1 h to remove the native oxide film on the surface. The aluminum foil after the pretreatment was immediately placed onto the electrolyte that had been purged with nitrogen to remove the dissolved oxygen and the electrolysis was controlled at a 0.6 mA cm<sup>-2</sup> constant current by a dc power supply (Keithley 237).

### 2.4. Assembly and properties of solid-state capacitor

The assembly of the solid-state capacitor using the Ppy/Al<sub>2</sub>O<sub>3</sub>/Al prepared is shown in Fig. 1. The capacitive characteristics of dissipation angle (tan δ), ESR, capacity (Cs), and

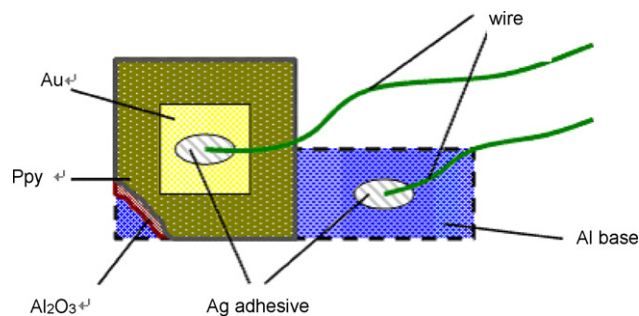


Fig. 1. Assembly of the solid-state Ppy/Al<sub>2</sub>O<sub>3</sub>/Al capacitor.

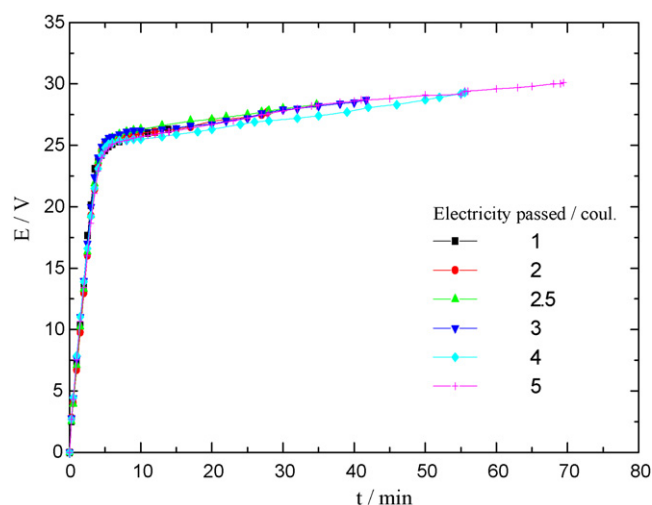


Fig. 2. ESCA spectra of the surface of Al foil. (a) Raw Al plate; (b) pretreatment with 0.1 M NaOH at 30 °C for 1 h; (c) formation at 0.1 M DBSA with the terminated potential of 60 V (calibration for C (1s) at 284.6 eV).

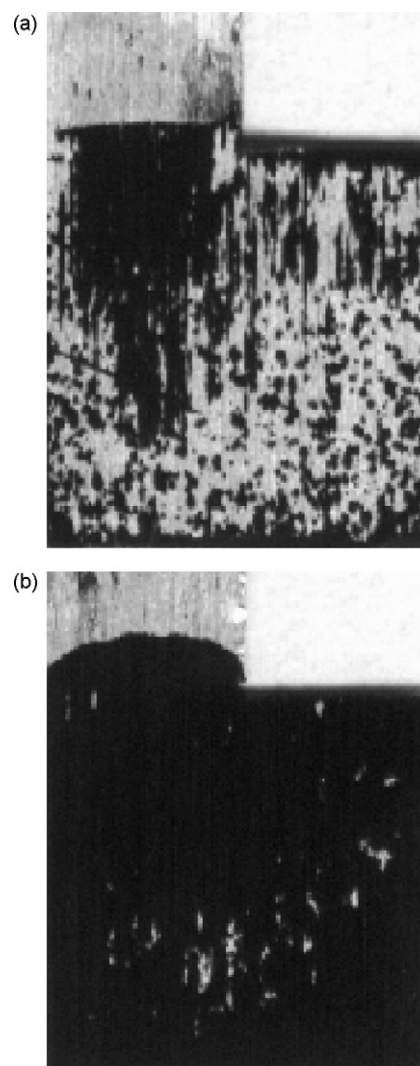


Fig. 3. Diagram of Ppy/Al<sub>2</sub>O<sub>3</sub>/Al. (a) 1 C; (b) 2 C.

leakage current ( $I_c$ ) of the solid-state capacitor were measured by the LCR meter (Motech MT 4080A) and leakage current tester (Zentech CLC-203), respectively. The values of capacity ( $C_s$ ) and  $\tan \delta$  were measured at the frequency of 120 Hz, and the value of  $I_c$  was obtained at 100 kHz. The surface morphologies of the aluminum foil substrate and the Ppy/ $\text{Al}_2\text{O}_3$ /Al prepared were analyzed by SEM (JOEL, JSM-5400).

### 3. Results and discussion

#### 3.1. Surface morphology

Effect of the amount of electricity passed on the morphology of Ppy onto Al was shown in Fig. 2. To examine the morphology of the polypyrrole film grown in the presence of DBSA and

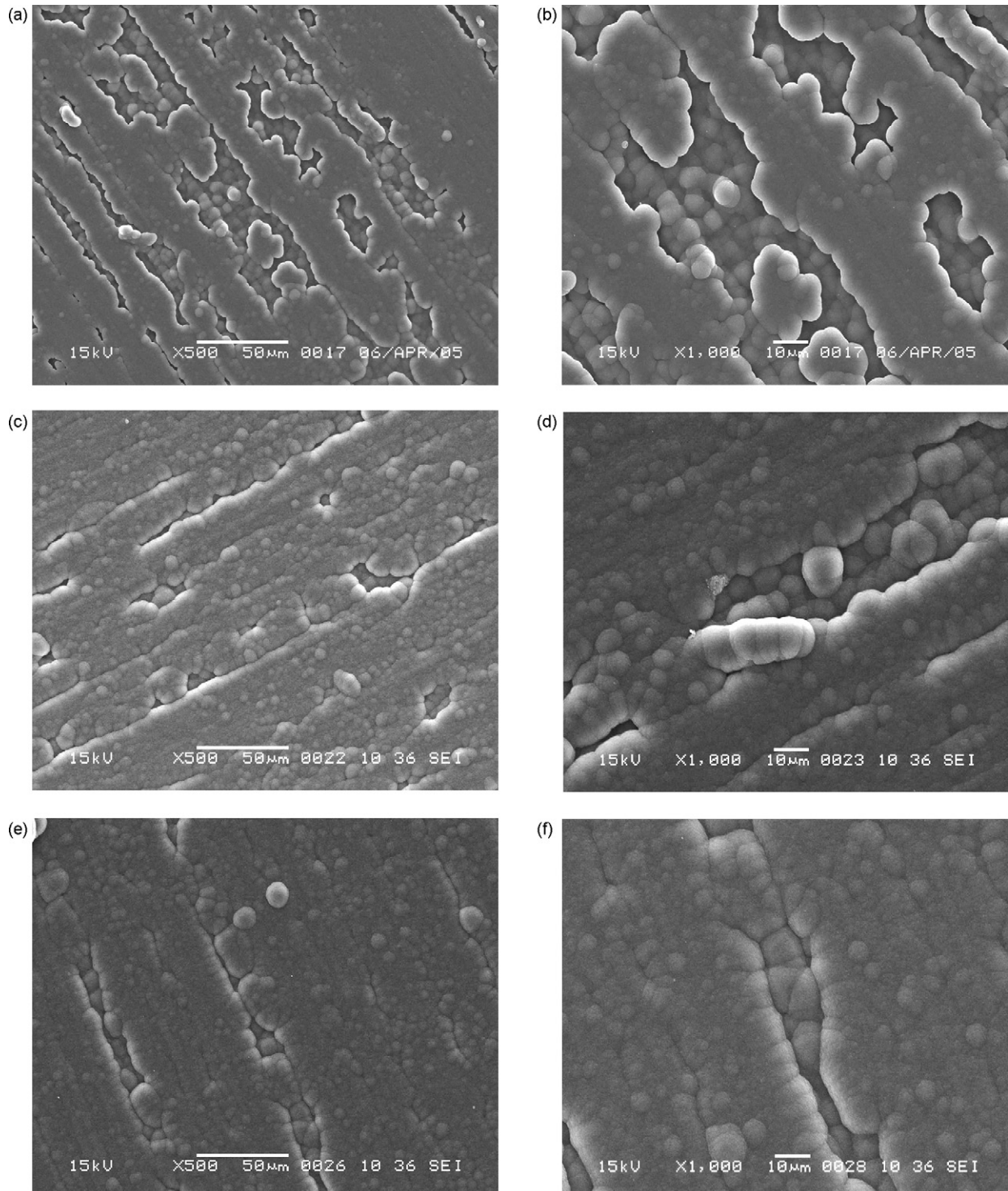


Fig. 4. Morphology of Ppy/ $\text{Al}_2\text{O}_3$ /Al of SEM diagram. (a) 2.5 C, 500 $\times$ ; (b) 2.5 C, 1000 $\times$ ; (c) 3.0 C, 500 $\times$ ; (d) 3.0 C, 1000 $\times$ ; (e) 4.0 C, 500 $\times$ ; (f) 4.0 C, 1000 $\times$ ; (g) 5.0 C, 500 $\times$ ; (h) 5.0 C, 1000 $\times$ .

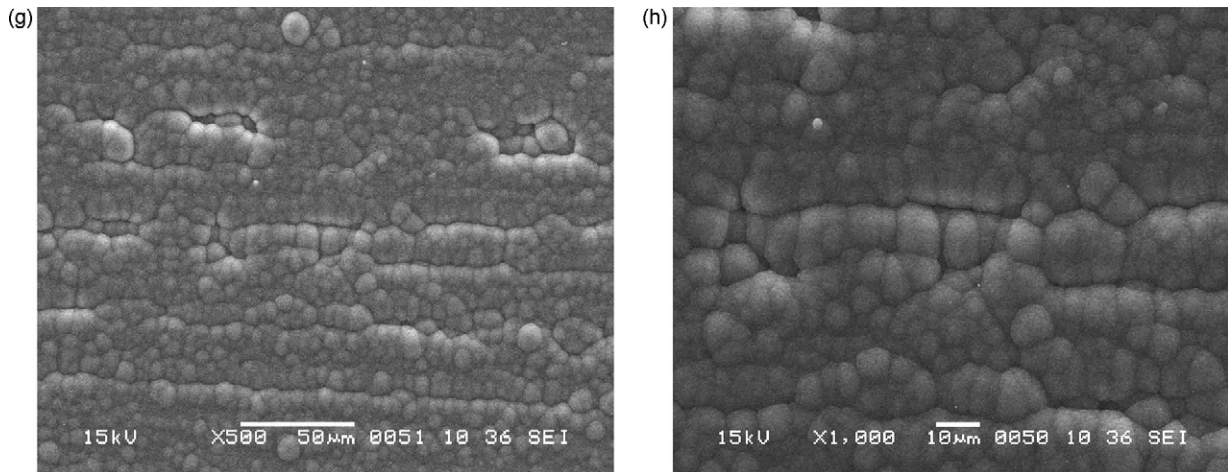


Fig. 4. (Continued).

2-NSNa co-dopant, the surface of the Ppy/Al<sub>2</sub>O<sub>3</sub>/Al film was observed using a scanning electron microscope. Fig. 2 shows the typical variations in cell voltage with the electrolysis time recorded during the formation of Ppy/Al<sub>2</sub>O<sub>3</sub>/Al film onto Al in the presence of 0.1 M DBSA and 0.01 M 2-NSNa as co-dopant. For 10-min electrolysis, the cell voltages appeared at the range of 25.5–26.3 V, and the terminated voltages increased from 26.3 to 30.8 V when the amount of electricity passed increased from 1 to 5 C, as shown in Fig. 2 and Table 1.

According to the literature, the film thickness of aluminum oxide increased 14 Å per voltage supplied [43]. Hence, the thickness of aluminum oxide increased from 368.2 to 431.2 Å when the amount of electricity passed was increased from 1 to 5 C. On the other hand, with less than 2 C of electricity passed, Ppy could not form a uniform film on the Al surface. In this case, the performance and the characterization data of the capacitor could not be obtained, as shown in Fig. 3(a) and (b) and Table 2. Furthermore, the Al surface was fully covered with Ppy when the amount of electricity passed exceeded 2.5 C, as shown in Fig. 4(a)–(h).

### 3.2. AC impedance analysis

The electrode interface of conducting polymer films onto Al, may be simulated by the electrical equivalent circuit of Fig. 5.

Table 1  
Effect of the coulombs of electricity passed on the formation of Ppy/Al<sub>2</sub>O<sub>3</sub>/Al

Electricity passed (C)	Volt (V)
1	26.3
2	27.7
2.5	28.3
3	28.7
4	29.3
5	30.8

Area of Al foil = 1 cm × 1 cm, thickness of Al foil = 40 µm; conditions for pre-treatment of Al foil: [NaOH] = 1 M, T = 25 °C, t = 0.5 h; [HCl] = 0.664 M, 25 °C, 200 mA cm<sup>-2</sup>, 15 s conditions for preparing Ppy/Al<sub>2</sub>O<sub>3</sub>/Al/Al: [pyrrole] = 0.1 M, [DBSA] = 0.1 M, initial pH 1.3, T = 6 °C, counter electrode: 2 cm × 3 cm stainless steel plate. DMSO/H<sub>2</sub>O = 10%; I: 0.6 mA cm<sup>-2</sup>, [2-NSNa] = 0.01 M.

Both CPE<sub>ox</sub> and CPE<sub>ppy</sub> are the barrier layer capacitance of Al<sub>2</sub>O<sub>3</sub> and Ppy, R<sub>ox</sub> and R<sub>ppy</sub> are the parameters of both resistance of aluminum and polypyrrole, and CPE<sub>tc</sub> is the terminal capacitance and so on. To gather more information on the state of the Ppy/Al<sub>2</sub>O<sub>3</sub>/Al film, further investigation was made using ac impedance spectroscopy measurements. The electrode interface of conducting polymer films onto Al surface was well simulated and the effect of the amount of electricity passed on the impedance spectra is illustrated in Fig. 6(a)–(d) for 2.5 C of electricity passed, the resistance of both R<sub>ox</sub> and R<sub>ppy</sub> were the

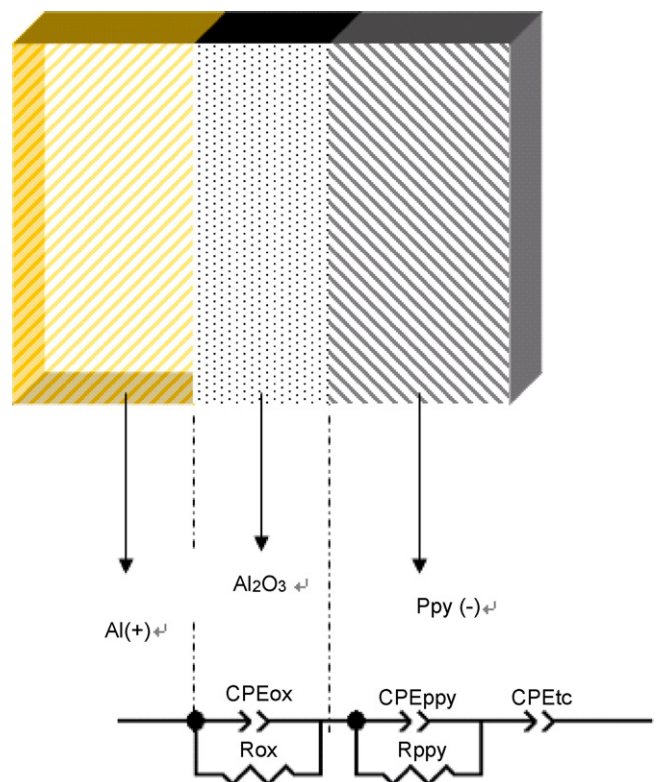


Fig. 5. Equivalent circuit of solid polymer electrolyte aluminum capacitor. CPE<sub>ox</sub>: barrier layer capacitance (Al<sub>2</sub>O<sub>3</sub>), R<sub>ox</sub>: barrier layer resistance (Al<sub>2</sub>O<sub>3</sub>), CPE<sub>ppy</sub>: polypyrrole capacitance, R<sub>ppy</sub>: polypyrrole resistance, CPE<sub>tc</sub>: terminal capacitance.

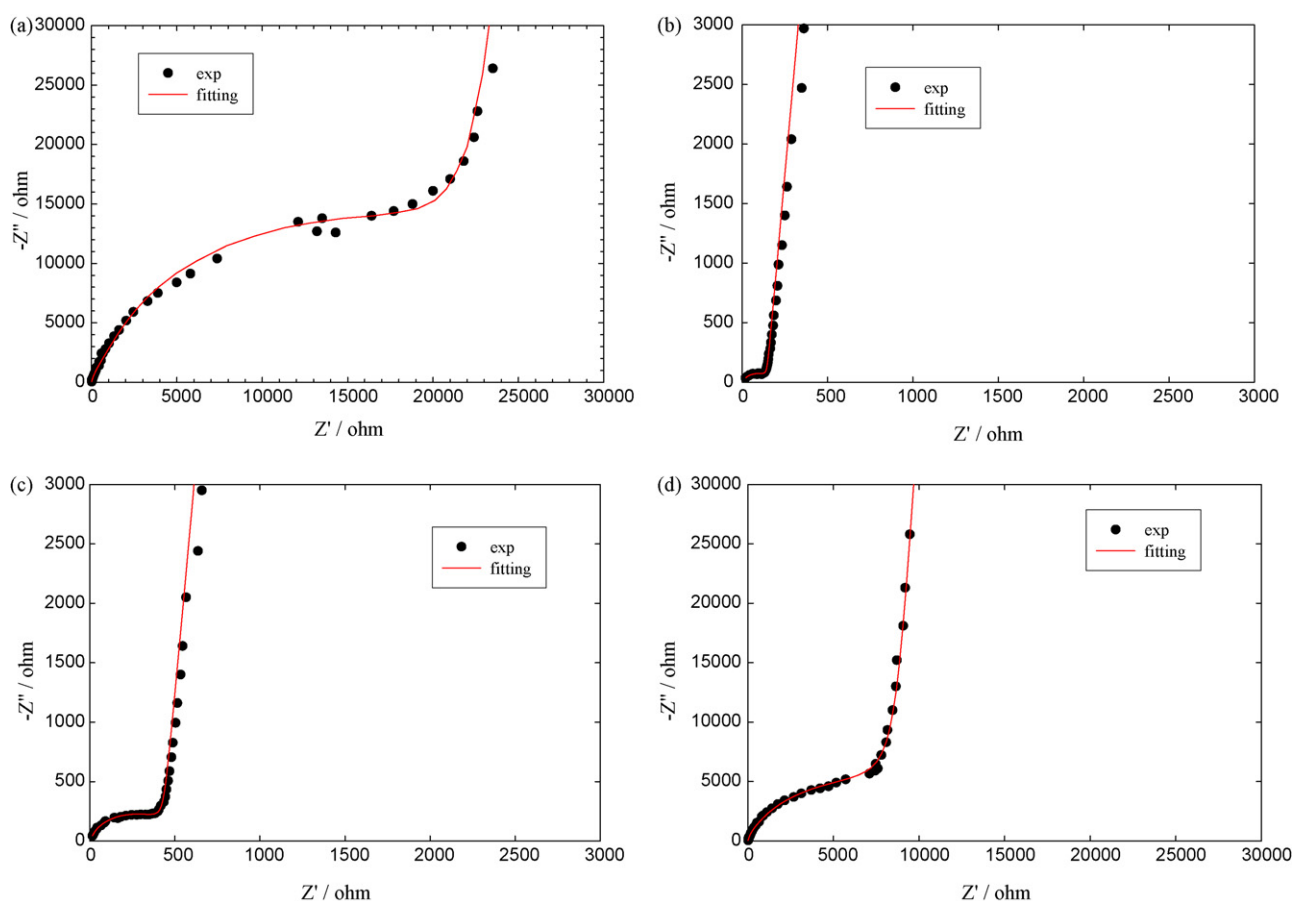


Fig. 6. Effect of the coulombs of electricity passed on the AC impedance diagram: (a) 2.5 C; (b) 3.0 C; (c) 4.0 C; (d) 5.0 C.

largest and were up to 20,216 and 1397  $\Omega$ , respectively. Further, the resistance of both  $R_{ox}$  and  $R_{ppy}$  increased proportionally from 135.5 to 8482  $\Omega$  and increased from 7.047 to 122.9  $\Omega$ , respectively by increasing the amount of electricity passed from 3.0 to 5.0 C as shown in Table 3 and Fig. 6(b)–(d). For a run with 2.5 C of electricity passed, the morphology covered by Ppy was not uniform; hence, the resistance of the composite solid polymer electrolyte was higher. In addition, the resistance increased proportionally because the film of both Ppy and aluminum oxide became thicker. Further, the conjugated double bond on the conducting polymer might be destroyed for a longer electrolysis run.

### 3.3. Performance and characterization

The Lc data was lower than that of the little marked data as shown in Table 2 that were calculated from the empirical equation ( $Lc = 0.05 CsV$ ), and the Lc data decreased from  $0.029 \pm 0.005$  to  $0.014 \pm 0.001 \mu A cm^{-2}$  when the amount of electricity increased from 3 to 5 C as shown in Fig. 7(a) and Table 2, respectively. Further, when the amount of electricity passed exceeded 2.5 C, the capacity decreased from  $688.8 \pm 8.28$  to  $464 \pm 34.43 nF cm^{-2}$  by increasing the amount of electricity passed from 3 to 5 C, as shown in Fig. 7(b) and Table 2. For a longer electrochemical polymerization of pyr-

Table 2  
Effect of the coulombs of electricity passed on the characterization of Ppy/ $Al_2O_3$ /Al

Electricity passed (C)	Lc ( $\mu A cm^{-2}$ )	Cs ( $nF cm^{-2}$ )	DF (%)	ESR ( $\Omega$ )
1	—**	—**	—**	—**
2	—**	—**	—**	—**
2.5	$0.024 \pm 0.005$ (0.170)*	$538.1 \pm 3.70$	$102.8 \pm 4.56$	$10.63 \pm 1.33$
3	$0.029 \pm 0.005$ (0.217)*	$688.8 \pm 8.28$	$14.35 \pm 5.63$	$18.63 \pm 3.48$
4	$0.024 \pm 0.001$ (0.200)*	$634.8 \pm 22.0$	$49.33 \pm 8.71$	$12.88 \pm 0.74$
5	$0.014 \pm 0.001$ (0.146)*	$464.1 \pm 34.43$	$69.77 \pm 10.44$	$9.208 \pm 0.968$

Area of Al foil = 1 cm  $\times$  1 cm, thickness of Al foil = 40  $\mu m$ ; conditions for pre-treatment of Al foil: [NaOH] = 1 M,  $T = 25^\circ C$ ,  $t = 0.5$  h; [HCl] = 0.664 M,  $25^\circ C$ , 200 mA  $cm^{-2}$ , 15 s conditions for preparing Ppy/ $Al_2O_3$ /Al/Al: [pyrrole] = 0.1 M, [DBSA] = 0.1 M, initial pH 1.3,  $T = 6^\circ C$ , counter electrode: 2 cm  $\times$  3 cm stainless steel plate. DMSO/ $H_2O = 10\%$ ;  $I = 0.6$  mA  $cm^{-2}$ , [2-NSNa] = 0.01 M, Lc: 6.3 V, Cs, DF: 120 Hz, ESR: 100 kHz.

\*  $Lc = 0.05 \times Cs (\mu F) \times V$ .

\*\* Cannot be measured.

Table 3  
AC impedance parameters

Parameter	Electricity pass (C)			
	2.5	3.0	4.0	5.0
$CPE_{ox}$ ( $\mu F$ )	$1.147 \times 10^{-7}$	$1.331 \times 10^{-7}$	$1.085 \times 10^{-7}$	$2.588 \times 10^{-7}$
$\beta_{ox}$	0.978	0.913	0.924	0.856
$R_{ox}$ ( $\Omega$ )	20,216	135.5	417.1	8482
$CPE_{ppy}$ ( $\mu F$ )	$5.352 \times 10^{-7}$	$1.107 \times 10^{-7}$	$8.265 \times 10^{-6}$	$1.406 \times 10^{-7}$
$\beta_{ppy}$	0.835	$2.219 \times 10^{-3}$	$1.672 \times 10^{-4}$	1.146
$R_{ppy}$ ( $\Omega$ )	1397	7.047	7.653	122.9
$CPE_{tc}$ ( $\mu F$ )	$8.430 \times 10^{-7}$	$8.473 \times 10^{-7}$	$8.609 \times 10^{-7}$	$7.306 \times 10^{-7}$
$\beta_{tc}$	0.954	0.961	0.960	0.973

[2-NSNa] = 0.01 M; DMSO/H<sub>2</sub>O: 10%; Temperature: 293 K; Loading: 0 h.

role, the insulation of the Al<sub>2</sub>O<sub>3</sub> film became thicker. Hence, both Lc and capacity decreased. Furthermore, when 2.5 C of electricity were passed, the variation in DF was increased to  $102.8 \pm 4.56\%$ , because the Ppy deposited onto the Al surface was not uniformly spread. Further, ESR was mainly in the range of  $9.28 \pm 0.968$  to  $18.63 \pm 3.48 \Omega$ , as shown in Fig. 7(c) and (d) and Table 2.

### 3.4. Life test

The life test of capacitors composted with solid polymer electrolyte in the presence of 2-NSNa and DBSA co-dopants was

determined at 293 K with a loading voltage of 4 V. When 2.5 C of electricity were passed, the resistance of aluminum oxide,  $R_{ox}$ , increased from 20,016 to 306,900  $\Omega$  when the test time of solid polymer electrolyte capacitor lasted from 0 to 1000 h at 293 K under 4 V loading, as shown in Fig. 8. The resistance of aluminum oxide increased 14.33-folds because for a 1000 h testing, the surface onto Al foil has not been covered with Ppy for a 2.5 C electrolysis run. Further, another reason accounting for the increase in  $R_{ox}$  is the increasing film thickness of aluminum when more coulombs of electricity were passed. Fig. 9 shows that the variation in resistance of Ppy was still smooth for a 2.5 C polymerized Ppy electrolyte. Fur-

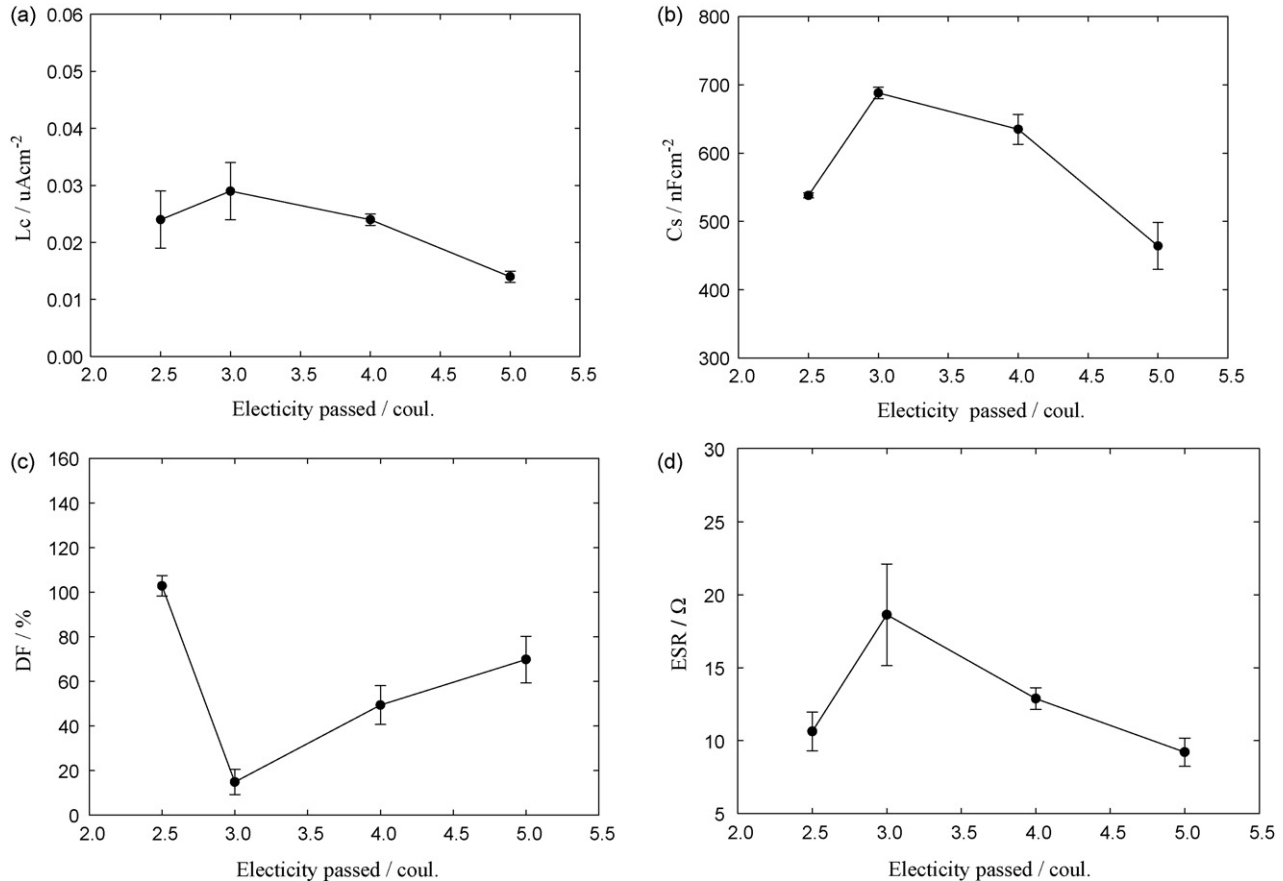


Fig. 7. Effect of the coulombs of electricity passed on the characterization of Ppy/Al<sub>2</sub>O<sub>3</sub>/Al: (a) Lc; (b) Cs; (c) DF; (d) ESR.

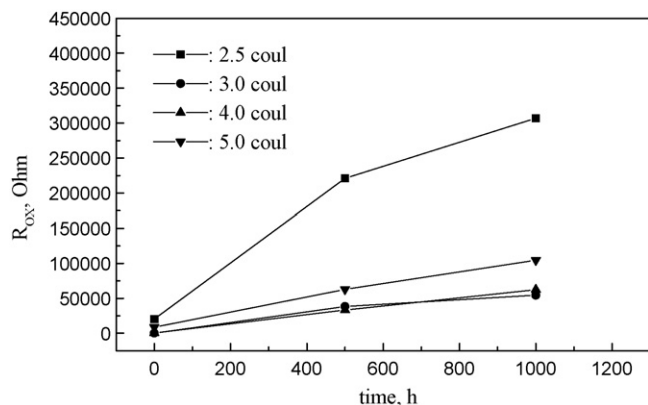


Fig. 8. Resistance variation of aluminum oxide vs. loading time plot. Loading voltage: 4 V; temperature: 293 K.

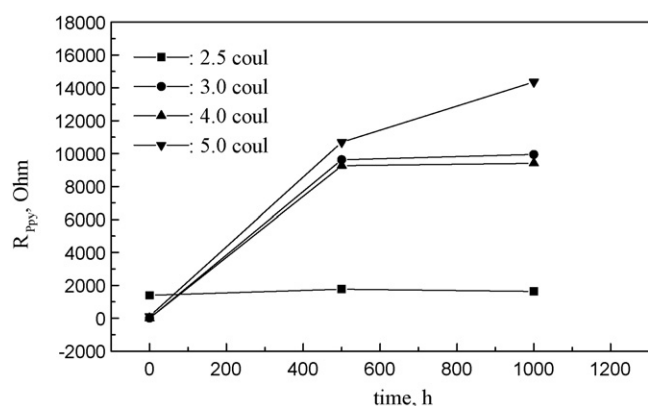


Fig. 9. Resistance variation of Ppy vs. loading time plot. Loading voltage: 4 V; temperature: 293 K.

thermore, the resistance of Ppy increased about 116-folds. The main reason for this change in  $R_{\text{ppy}}$  was either the increase in de-doping of 2-NSNA and DBSA or weight of conducting polymer, Ppy, increased after a longer polymerization, as shown in Fig. 10.

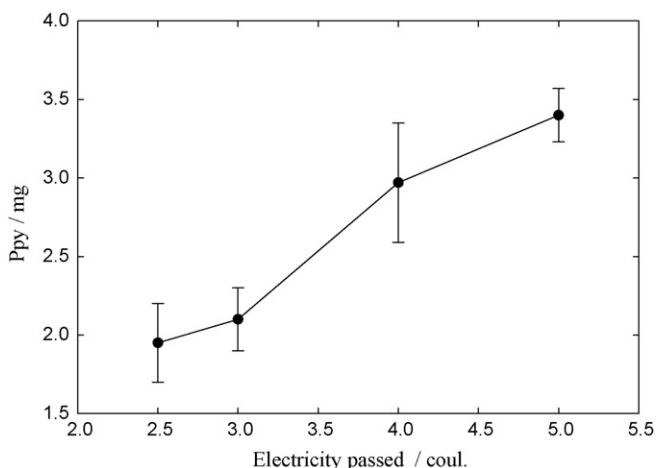


Fig. 10. Ppy weight of Ppy/Al<sub>2</sub>O<sub>3</sub>/Al vs. electricity passed plot.

#### 4. Conclusions

The effect of the amount of electricity passed on the preparation of Ppy/Al<sub>2</sub>O<sub>3</sub>/Al film in the presence of 2-NSNa and DBSA co-dopants used as a solid-state capacitor for microsystems have been successfully explored. The surface morphology onto Al observed via SEM was perfect spread with Ppy when the amount of electricity passed exceeded 2.5 C. In addition, for 3.0 C of electricity passed, the capacitance was up to  $688.8 \pm 8.28 \text{ nF cm}^{-2}$ , DF value was  $14.35 \pm 5.63\%$ , ESR was  $18.35 \pm 3.48 \Omega$ , and Lc was  $0.029 \pm 0.005 \mu\text{A cm}^{-2}$ . On the other hand, the assume ac impedance model via computer simulated was well matched from the experimental result and theoretical analysis. During 3.0 C of electricity passed, the parameters both  $R_{\text{ox}}$  and  $R_{\text{ppy}}$  are 135.5 and 7.047  $\Omega$ . Furthermore, the resistance of aluminum oxide increased 14.33-folds for a 1000 h life testing and the resistance of Ppy increased about 116-folds for a 2.5 C electrolysis run.

#### Acknowledgements

The author is very grateful for the financial support from GSM Electronic Co. Ltd., and National Chin-Yi University of Technology.

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