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Preparation and characterization of $Ppy/Al_2O_3/Al$ used as solid-state capacitors for microsystems—Effect of amount of electricity passed

Ming-Liao Tsai *

Department of Chemical and Materials Engineering, National Chin-Yi University of Technology, Taiping City, Taichung County 411, Taiwan, ROC

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Abstract

This investigation focuses on the preparation of polypyrrole composite films, $Ppy/Al_2O_3/Al$, 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), dicipation factor (DF) and equivalent series resistance (ESR), were measured in this study. The surface morphology and compositions of the prepared $Ppy/Al_2O_3/Al$ 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 $Ppy/Al_2O_3/Al$ capacitor prepared with 2-NSNa and DBSA as a co-dopant were measured to be $0.029 \pm 0.005\ \mu A\ cm^{-2}$, $688.8 \pm 8.28\ nF\ cm^{-2}$, $14.35 \pm 5.63\%$ and $18.63 \pm 3.48\ \Omega$. Further, the parameters both of R_{ox} and R_{ppy} are 135.5 and 7.047 Ω.
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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 $Ppy/Al_2O_3/Al$ has seldom been reported [41,42]. Hence, this study focuses on the simultaneous preparation of an Al_2O_3 dielectric film and a Ppy

* Tel.: +886 4 23924505x7510; fax: +886 4 23926617.
E-mail addresses: mltsai@mail.ncut.edu.tw, mltsai@chinyi.ncit.edu.tw.

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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 $Ppy/Al_2O_3/Al$ 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 benzylsulfonic 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 distillated 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^{-2} current density for 15 s passed at 298 K.

2.3. Preparation of $Ppy/Al_2O_3/Al$ film

The electrolyte for preparing $Ppy/Al_2O_3/Al$ 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^{-2} 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 $Ppy/Al_2O_3/Al$ prepared is shown in Fig. 1. The capacitive characteristics of dissipation angle (tan δ), ESR, capacity (Cs), and

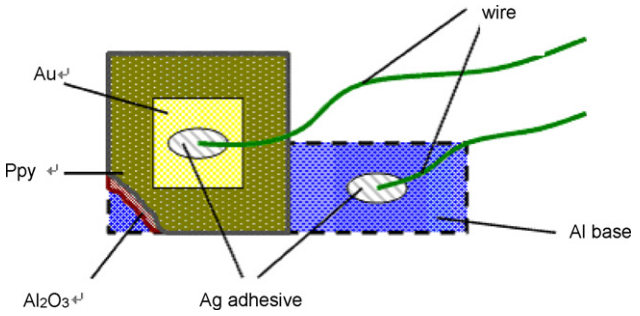

Fig. 1. Assembly of the solid-state $Ppy/Al_2O_3/Al$ capacitor.

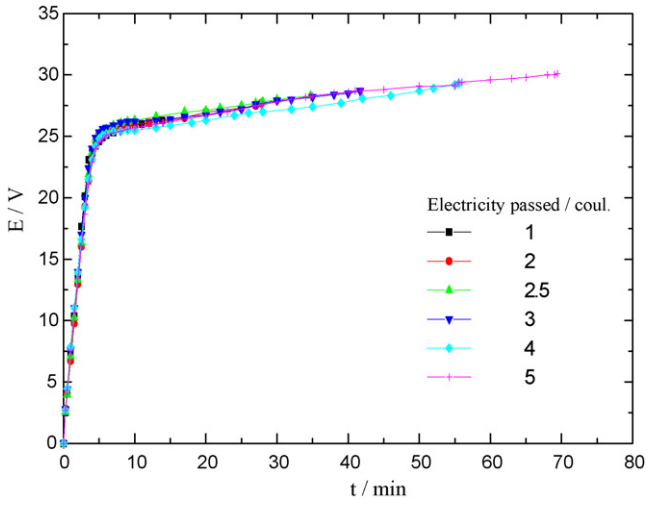

Fig. 2. ESCA spectra of the surface of Al foil. (a) Raw Al plate; (b) pretreatment with 0.1 M NaOH at 30 °C for 1 h; (c) formation at 0.1 M DBSA with the terminated potential of 60 V (calibration for C (1s) at 284.6 eV).

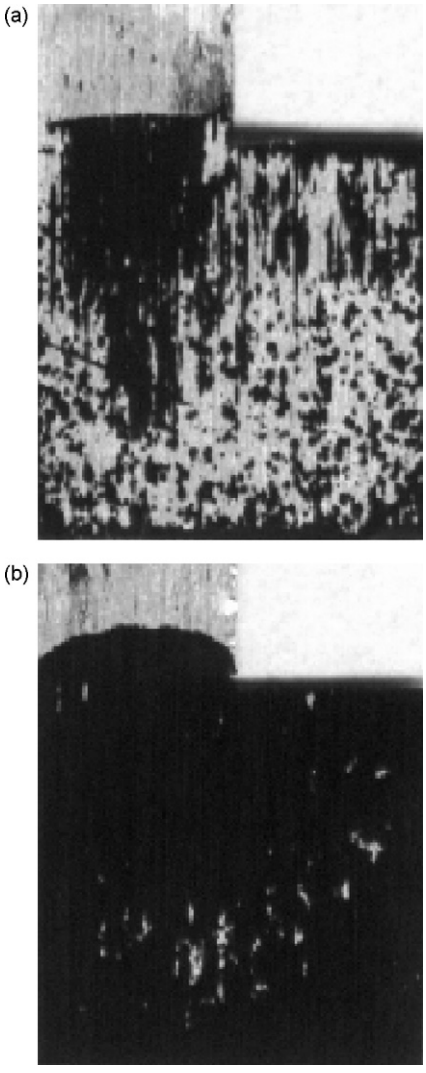

Fig. 3. Diagram of $Ppy/Al_2O_3/Al$. (a) 1 C; (b) 2 C.

leakage current (Lc) 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 (Cs) and tan δ were measured at the frequency of 120 Hz, and the value of Lc was obtained at 100 kHz. The surface morphologies of the aluminum foil substrate and the Ppy/Al_2O_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

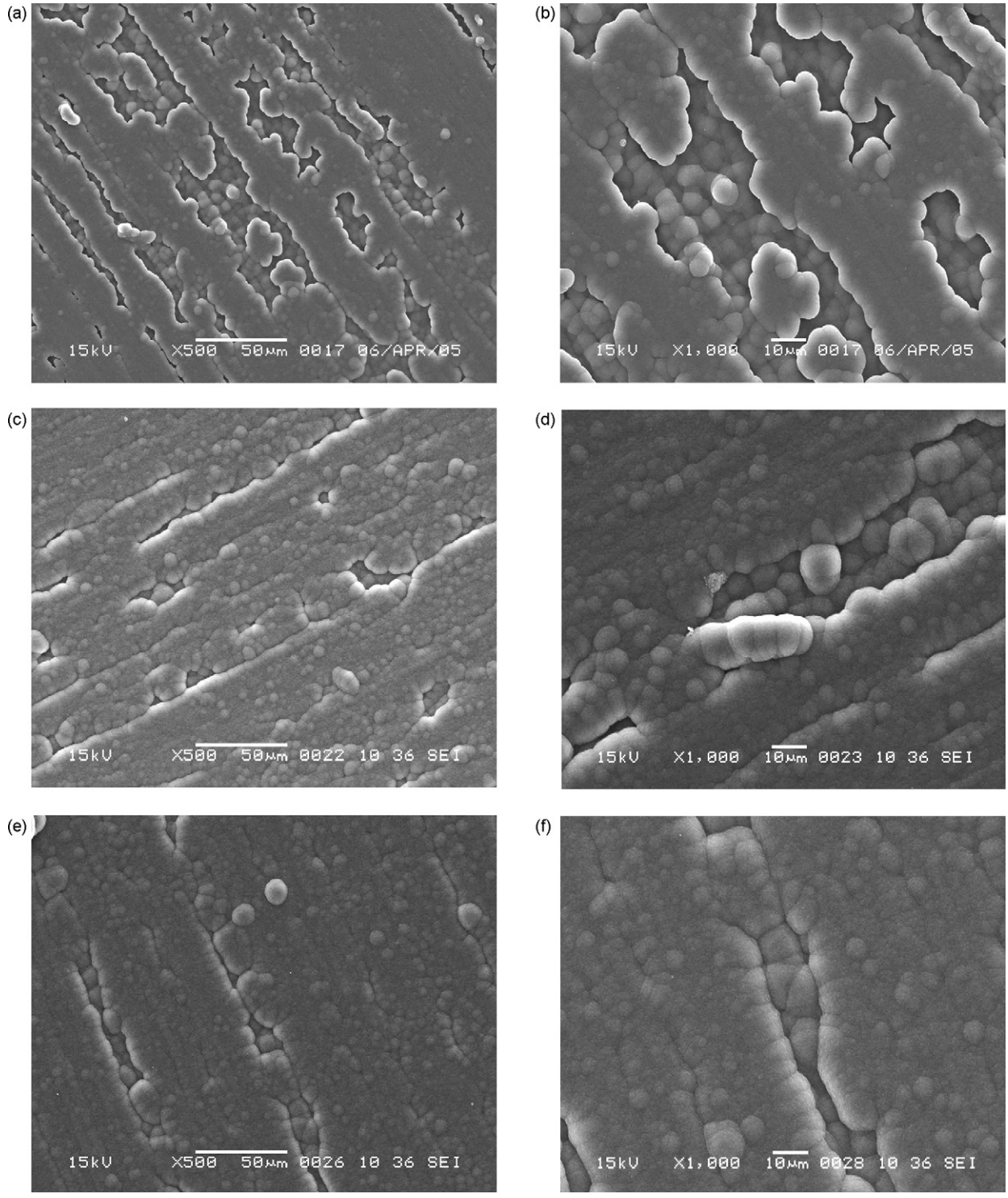

Fig. 4. Morphology of Ppy/Al_2O_3/Al of SEM diagram. (a) 2.5 C, 500×; (b) 2.5 C, 1000×; (c) 3.0 C, 500×; (d) 3.0 C, 1000×; (e) 4.0 C, 500×; (f) 4.0 C, 1000×; (g) 5.0 C, 500×; (h) 5.0 C, 1000×.

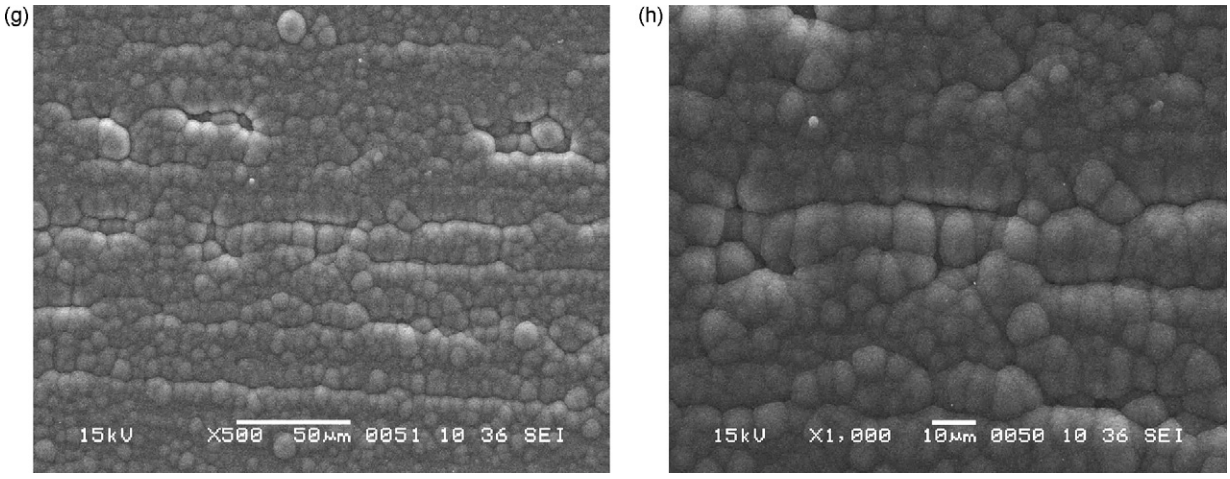

Fig. 4. (*Continued*).

2-NSNa co-dopant, the surface of the Ppy/Al_2O_3/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_2O_3/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_2O_3/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^{-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 °C, counter electrode: 2 cm × 3 cm stainless steel plate. DMSO/H_2O = 10%; I: 0.6 mA cm^{-2}, [2-NSNa] = 0.01 M.

Both CPE_{ox} and CPE_{ppy} are the barrier layer capacitance of Al_2O_3 and Ppy, R_{ox} and R_{ppy} are the parameters of both resistance of aluminum and polypyrrole, and CPE_{tc} is the terminal capacitance and so on. To gather more information on the state of the Ppy/Al_2O_3/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_{ox} and R_{ppy} were the

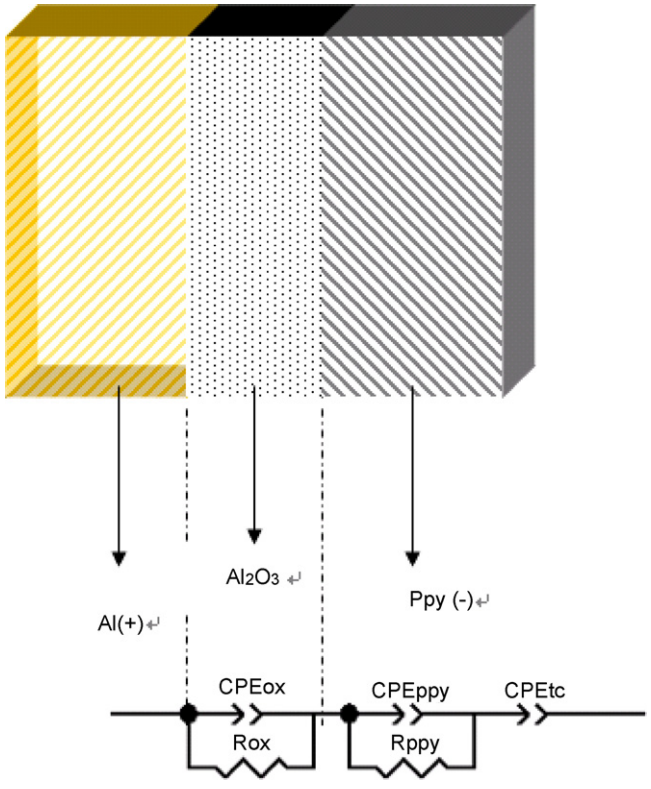

Fig. 5. Equivalent circuit of solid polymer electrolyte aluminum capacitor. CPE_{ox}: barrier layer capacitance (Al_2O_3), R_{ox}: barrier layer resistance (Al_2O_3), CPE_{ppy}: polypyrrole capacitance, R_{ppy}: polypyrrole resistance, CPE_{tc}: terminal capacitance.

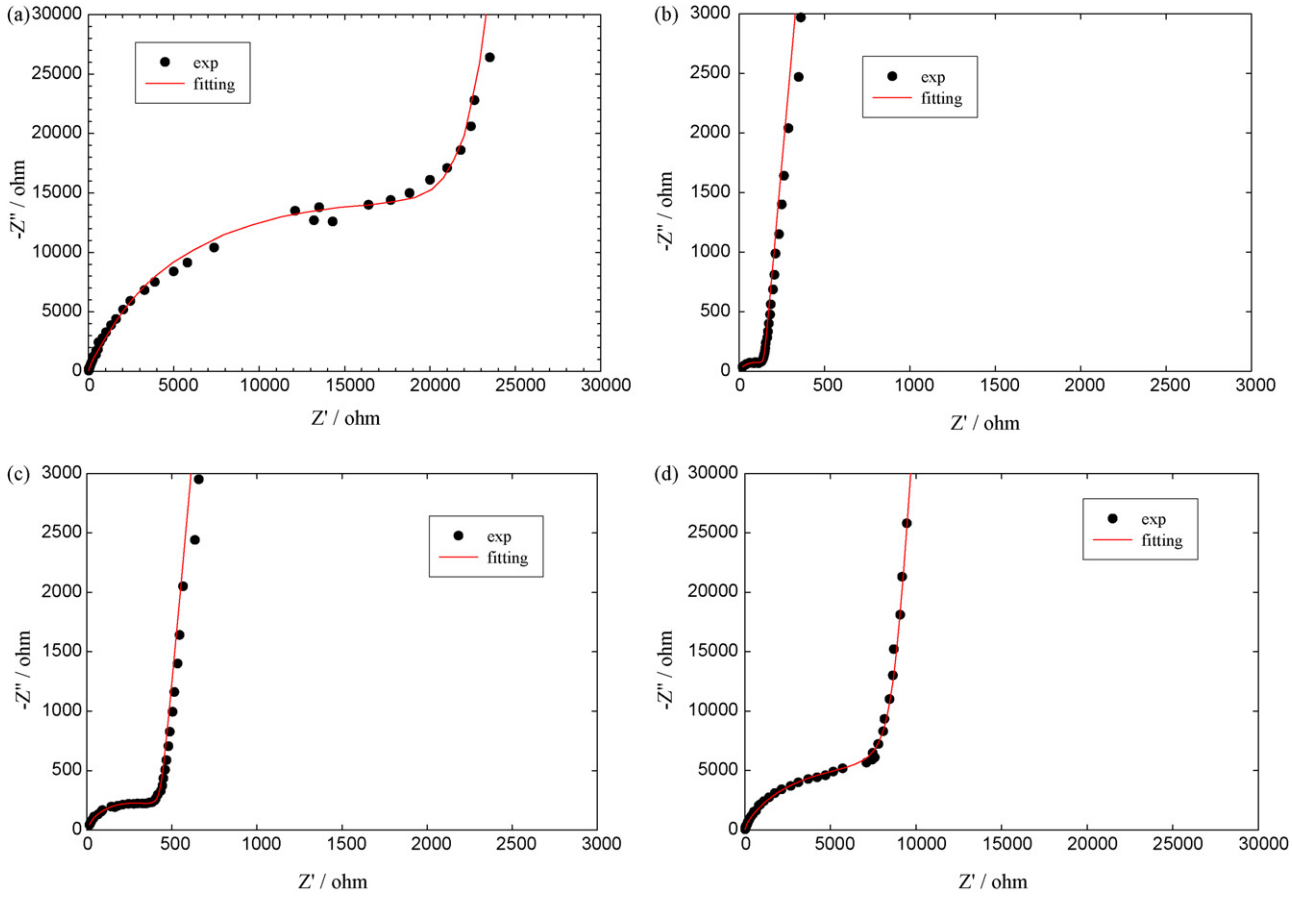

Fig. 6. Effect of the coulombs of electricity passed on the AC impedance diagram: (a) 2.5 C; (b) 3.0 C; (c) 4.0 C; (d) 5.0 C.

largest and were up to 20,216 and 1397 Ω, respectively. Further, the resistance of both R_{ox} and R_{ppy} increased proportionally from 135.5 to 8482 Ω and increased from 7.047 to 122.9 Ω, 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 ± 0.005 to 0.014 ± 0.001 μA 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 ± 8.28 to 464 ± 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 (μA cm^{-2})	Cs (nF cm$^{-2)}$	DF (%)	ESR (Ω)
1	–**	–**	–**	–**
2	–**	–**	–**	–**
2.5	0.024 ± 0.005 (0.170)*	538.1 ± 3.70	102.8 ± 4.56	10.63 ± 1.33
3	0.029 ± 0.005 (0.217)*	688.8 ± 8.28	14.35 ± 5.63	18.63 ± 3.48
4	0.024 ± 0.001 (0.200)*	634.8 ± 22.0	49.33 ± 8.71	12.88 ± 0.74
5	0.014 ± 0.001 (0.146)*	464.1 ± 34.43	69.77 ± 10.44	9.208 ± 0.968

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^{-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 °C, counter electrode: 2 cm × 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 × Cs (μF) × V.

** Cannot be measured.

Table 3
AC impedance parameters

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

[2-NSNa] = 0.01 M; DMSO/H_2O: 10%; Temperature: 293 K; Loading: 0 h.

role, the insulation of the Al_2O_3 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 ± 4.56%, because the Ppy deposited onto the Al surface was not uniformly spread. Further, ESR was mainly in the range of 9.28 ± 0.968 to 18.63 ± 3.48 Ω, 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 Ω 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-

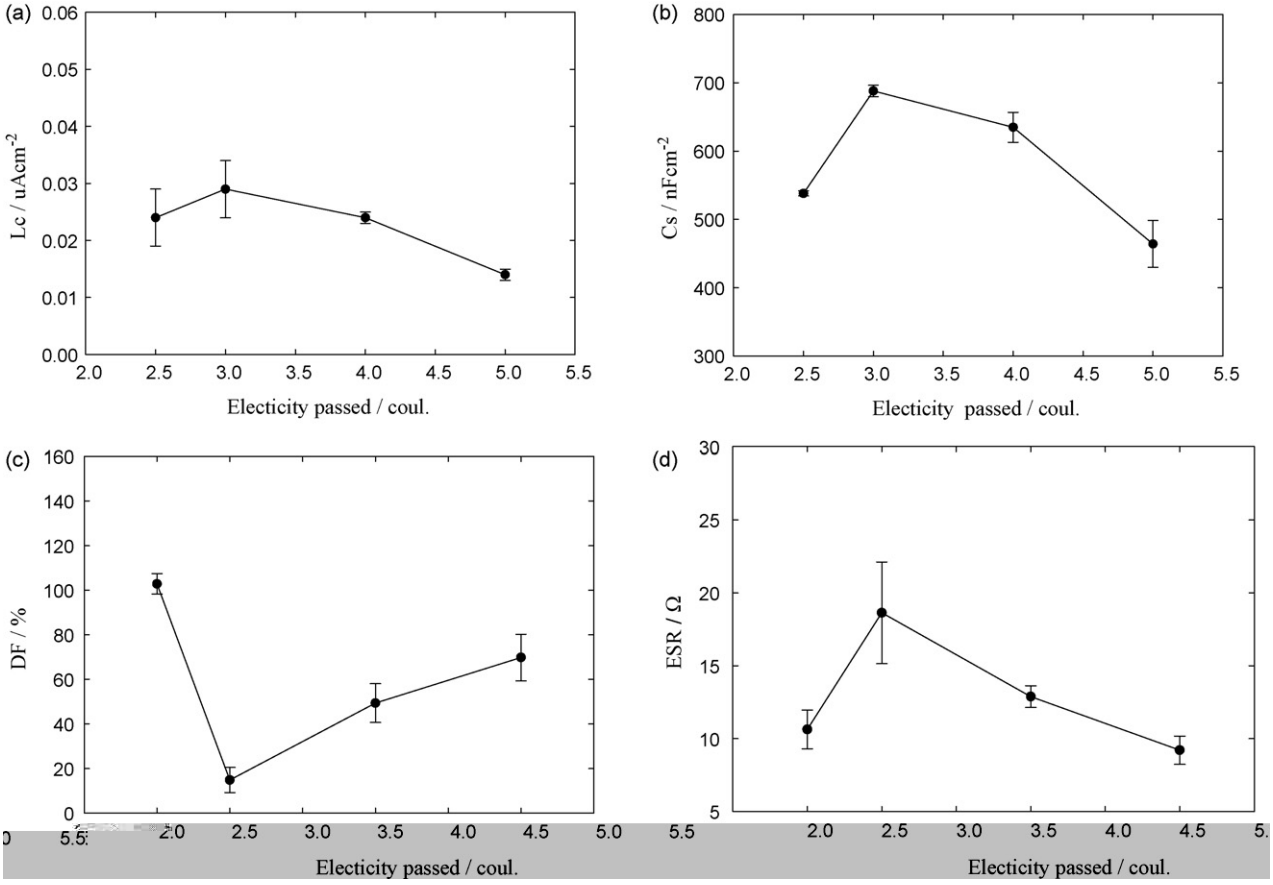

Fig. 7. Effect of the coulombs of electricity passed on the characterization of Ppy/Al_2O_3/Al: (a) Lc; (b) Cs; (c) DF; (d) ESR.