



Conducting Polypyrrole –Based Film Electrodes for Supercapacitor Application

Enrique Manzano^{1,*}, Brian-Gabriel A. Soan¹, Gerome D. Sy¹, Maria Carla Manzano¹,
Chiara Rosario Julia Lanuza¹, and Reuben Quiroga¹

¹De La Salle University-Manila

* enrique.manzano@dlsu.edu.ph

Abstract: Supercapacitors are energy storage devices suitable for energy harvesting systems, hybrid electric vehicles and power backup supplies among others. In this study, conducting polypyrrole-based film electrodes were fabricated and characterized for supercapacitor applications. The films were electrochemically synthesized in aqueous solution containing sodium p-toluenesulfonate (Na-pTS) as dopant and electrolyte and pyrrole as monomer. The concentration of Na-pTS was varied in order to produce films of various thickness and resistivity. Film resistivity was determined using Van der Pauw Four-Point technique. The measured conductivities of the film electrodes at 0.08M, 0.10M, and 0.12M Na-pTs are 105.21 S/cm, 114.66 S/cm, and 151.71 S/cm respectively. Film thickness and surface morphology were obtained using scanning electron microscopy. The average thickness of the films fabricated is about 24.8 μ m. Using cyclic voltammetry, it was found that the capacitance of the PPY film electrode increases with respect to the concentration of a strong sodium chloride (NaCl) electrolyte. The capacitance values were computed to be 0.01486 F, 0.6784 F, and 0.6751 F at 0.10M, 0.15M, and 0.20M NaCl accordingly. Finally, an electrochemical capacitor prototype was designed and assembled using the fabricated conducting polypyrrole films as electrode and Na-pTS as electrolyte. It was established that increasing the electrolyte concentration enhanced the discharging time of the fabricated electrochemical capacitor. The longest discharging time was 71 minutes, obtained using the film synthesized at 0.20M Na-pTs electrolyte concentration.

Key Words: supercapacitor; conducting polymer; polypyrrole; thin film

1. INTRODUCTION

Supercapacitors have gained attention in today's researches and product development, especially in the field of energy storage, because of their high specific capacitance, long cycle life and high power density. Compared to common storage devices such as batteries and energy sources that utilize limited materials like gasoline and oil,

supercapacitors are promising products to a green energy future.

The usual capacitance of a supercapacitor is about 1000 times higher than the regular dielectric capacitor. In the past, supercapacitors were designed for military and weaponry systems. Today, supercapacitors are considered as energy storage devices used for hybrid electric vehicles and backup power supplies.

Materials being used in the production of supercapacitors are divided into three classes: activated carbons, metal oxides, and conducting polymers. Among these three, conducting polymers have high pseudocapacitance; they are also easy to synthesize, have a high inherent conductivity, and relatively affordable (Choi et. al., 2012). Polypyrrole is a conducting polymer known for its good stability. Recent researches on polypyrrole for supercapacitor applications focus on obtaining high specific capacitance by preparing porous or polypyrrole/carbon composite electrodes by chemical or electrochemical polymerization (Fan and Maier, 2006).

In this study, conducting polypyrrole (PPy) film electrodes were prepared by electrochemical deposition and then characterized by SEM, EDX and cyclic voltammetry. A prototype supercapacitor was fabricated using the PPy film as electrodes and a suitable electrolyte.

2. METHODOLOGY

2.1 Electrodeposition of Conducting Polypyrrole Films

Conducting polypyrrole films were electrochemically synthesized in an aqueous solution containing pyrrole monomer (0.1 M) and sodium *p*-toluenesulfonate (Na-pTs) as anion salt and dopant. The electrolyte solutions were prepared using 200mL pure distilled water with varying dopant concentrations of 0.08M, 0.10M and 0.12M. Both the working and counter-electrodes are made of stainless steel metal plate with dimensions 4 cm x 2.5 cm. A current density of 3.0 mA/cm² was maintained during the polymerization process. All film synthesis was done at room temperature (about 26°C), in a nitrogen and low light environment.

2.2 SEM, EDX and Resistivity Measurements

The surface morphology and thickness of the Ppy films were measured using a Jeol JSM-5310 scanning electron microscope. Also, energy dispersive x-ray spectroscopy was done to determine the elemental composition and concentration of the Ppy films synthesized.

Film resistivity was measured using the Van der Pauw four-point technique. A constant current of 3mA, supplied by a Lodestar DC Power Supply PS-303, was applied through one side of the film as the

voltage is simultaneously measured across the opposite side using a Fluke 75III multimeter.

The Ppy film with the lowest resistivity was then used in the cyclic voltammetry tests and in the fabrication of the prototype PPy-based electrochemical capacitor.

2.3 Cyclic Voltammetry

The basic configuration of an electrochemical capacitor consists of an ionic/electrolyte solution sandwiched between two electrodes. In this study, cyclic voltammetry was used to characterize the PPy film electrode in different concentrations of NaCl (0.10, 0.15 and 0.20M) at a constant scan rate of 100mV/s. The Ppy film was used as the working electrode, a platinum wire as the counter electrode and a Ag/AgCl electrode as reference.

By integrating a segment of the I-V curve (voltammogram), the stored charge over a chosen voltage region was determined. The capacitance was then computed using $C = Q/\Delta V$.

2.4 Fabrication and Characterization of Ppy-based Supercapacitor

The Ppy films with the lowest resistivity were used as electrodes for the prototype supercapacitor. The prototype PPy-based supercapacitor was then characterized using charge-discharge time test to examine the effect of the electrolyte molar concentration on the charging and discharging time of the supercapacitor.

For the charge-discharge time test, the supercapacitor was connected to a 5-V power supply and was allowed to charge for 5 minutes. After the allotted charging time, the power supply was turned off and the discharging time was measured. Charge-discharge time test of the supercapacitor was performed over several cycles.

3. RESULTS AND DISCUSSION

3.1 Elemental Analysis

EDX analysis was performed to identify the elemental composition of the films and their relative concentrations. The elements analyzed and their concentration are carbon (51.72%), nitrogen (20.98%), oxygen (16.68%), sodium (0.34%), and sulfur (10.27%). The presence of sodium confirms the incorporation of the dopant in the PPy film. The

figure below shows the EDX analysis for the PPy film synthesized using 0.12M Na-pTS.

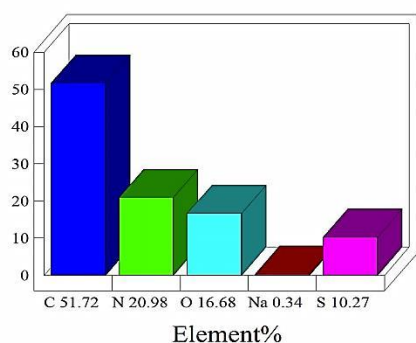


Fig. 1. Elemental composition of PPy film synthesized using 0.12M Na-pTS

3.2 Surface Morphology

Figure 2 shows the SEM images of the three PPy films synthesized using different dopant concentrations. The globular and cauliflower-like structures typical of electrochemically synthesized PPy films are evident in samples B and C.

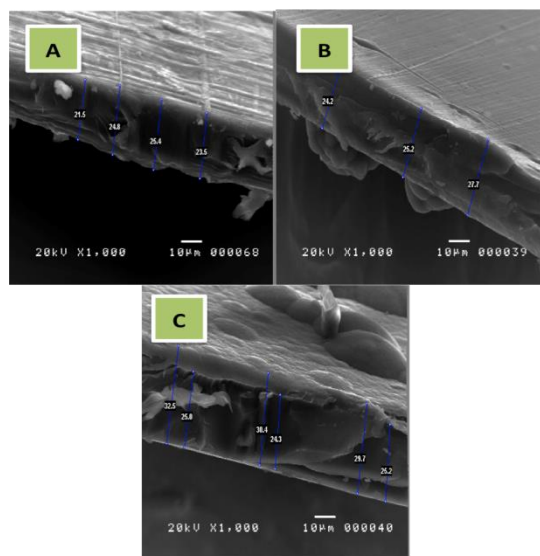


Fig. 2. SEM images at 1000x magnification of PPy films synthesized using Na-pTS dopant concentration of (A) 0.08M, (B) 0.10M, and (C) 0.12M.

The film thickness was also measured using SEM. The average thickness of film A is 23.8 μm, film B is 26.7 μm, and film C is 24.8 μm. Previous

studies have shown that film thickness is dependent on the synthesis time since a longer synthesis time means more time for polymerization and deposition of PPy on the substrate. Since all films were grown for 2 hours, the measured film thicknesses were relatively close to each other (23.8-25.7 μm) regardless of the dopant concentration. Dopant concentration, however, was found to have an effect on the resistivity of the PPy film.

3.3 Ppy Film Resistivity

Using Van der Pauw four-point probe technique, the resistivity of the film was determined. The table below shows the resistivity and thickness of the PPy films grown using different dopant concentrations. It can be seen that as the dopant concentration was increased, the resistivity of the PPy film decreased; i.e. the film becomes more conducting when doped at higher concentrations. Moreover, the calculated conductivities are within the range of typical conducting polypyrrole films.

Table 1. Resistivity and film thickness of Ppy films

Na-pTS Dopant Molarity	0.08M	0.10M	0.12M
Film Thickness (cm)	23.8×10^{-4}	25.7×10^{-4}	24.8×10^{-4}
Resistivity (Ωcm)	9.50×10^{-3}	8.72×10^{-3}	6.59×10^{-3}
Conductivity (S/cm)	105	115	152

The PPy film with the highest conductivity was grown using 0.12M Na-pTS dopant concentration. This was the same film used in fabricating the prototype supercapacitor and in the cyclic voltammetry test.

3.4 Capacitance from C-V Plots

Figure 5.3 presents the cyclic voltammograms of the polypyrrole film electrodes characterized in different concentrations of NaCl electrolyte at a constant scan rate of 100mV/s.

The cyclic voltammograms are typical of capacitive electrochemical cells such as supercapacitors. The shapes of the voltammograms were not rectangular, showing a slow rise in the

current as the voltage is increased. The forward and reverse current plots have the same shape.

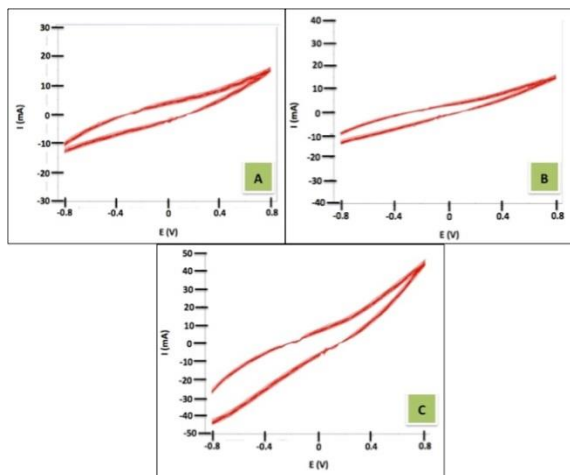


Fig. 3. Cyclic voltammograms of the capacitive electrochemical cell using PPy film as electrode in a solution containing: (A) 0.10M NaCl; (B) 0.15M NaCl; and (C) 0.20M NaCl at a scan rate of 100mV/s for 1 cycle.

The C-V plots above also imply that there was an increase in the peak current as the concentration of the electrolyte in the electrochemical cell was increased. There was a rise in the peak current from 15mA to 45mA when the NaCl electrolyte concentration was raised from 0.10M to 0.20M. The graphs also suggested that the chemical process was quasi-reversible, some indications of which is that the voltammograms were more drawn out as compared to reversible systems. In a quasi-reversible system, both charge transfer and mass transport control the current (Agyeman, n.d). Furthermore, quasi-reversible systems also show irreversible behavior at higher scan rates.

Table 2 below provides the calculated stored charge during charging from 0.4V to 0.8V for the three different NaCl electrolyte concentrations used. The table also shows the computed capacitance for each electrolyte concentration.

Table 3. Capacitance of the electrochemical cell using PPy film as electrode for various concentrations of NaCl.

NaCl electrolyte Molarity	0.10M	0.15M	0.20M
Peak current (mA)	15	15	45
Charge stored (C)	0.0425	0.0467	0.126

Voltage (V)	0.4	0.4	0.4
Capacitance	0.106 F	0.117 F	0.315 F

The charge stored was determined from the area under the curve of the segment of the CV plot from 0.4V to 0.8V. It was found out that a higher electrolyte concentration lead to higher capacitance. Based from the results, the capacitance increased by a factor of 3, from 0.106F to 0.315F, by increasing the electrolyte molar concentration from 0.10M to 0.20M. The difference in capacitance using 0.10M and 0.15M electrolyte is not however significant. Peak current was also found to increase with capacitance, consistent with previous studies on capacitive electrochemical cells.

Related cyclic voltammetry studies on electrochemical capacitors have shown that voltammograms and calculated capacitances from voltammograms depend on scan rate and the voltage region. As scan rate decreases, calculated capacitance increases. The increase in computed capacitance by decreasing scan rate is mainly due to kinetically slow Faradic reactions on the electrode surface and by transmission line behavior caused by electrode porosity (Gamry, n.d.).

3.5 Fabricated PPy-based Supercapacitor

The PPy film that exhibited the lowest resistivity was used as electrode for the prototype supercapacitor. The prototype PPy-based supercapacitor was then characterized using charge-discharge time test.

The design of the PPy-based supercapacitor fabricated in this study consists of an electrolyte sandwiched between the two PPy electrodes. Figure 4 shows the schematic diagram of the supercapacitor.

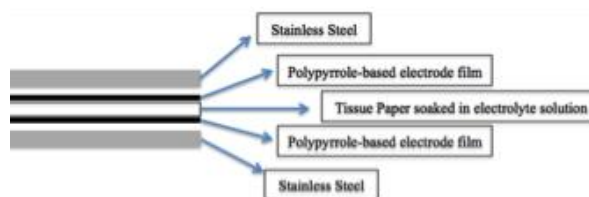


Fig. 4. Schematic diagram showing the layers of the PPy-based supercapacitor prototype.

The prototype PPy-based supercapacitor was characterized using charge-discharge time test to examine the effect of the molar concentration of the electrolyte in the charging and discharging time of

the supercapacitor. The initial charge, final charge and the discharging time for each supercapacitor prototype using different concentrations of the organic Na-pTs electrolyte are given in Table 4.

Table 4. Charge-discharge time of PPy-based supercapacitor in different Na-PTS electrolyte concentrations.

Electrolyte Molarity (Na-PTS)	0.10M	0.15M	0.20M
Charging time	5 minutes	5 minutes	5 minutes
Voltage (mV)	0.950	1.050	1.260
Discharging time	25 minutes	52 minutes	71 minutes

The results from the charge-discharge time test show that as the concentration of the electrolyte was increased from 0.10M to 0.20M, the discharging time of the supercapacitor was enhanced. This might be due to more redox reaction that occurred between the electrode and the electrolyte producing more current. The discharge time was directly recorded without using an LED or a resistor because of current leakage expected from electrochemical capacitors (Niu et. al. 2004). Electrochemical capacitors, unlike parallel-plate and electrolytic capacitors, have relatively high equivalent series resistance (ESR). Also, as the prototype supercapacitor made use of an organic electrolyte, self-discharge could also be attributed to a cell overvoltage (Conway and Pell, 1999) and a faradic impurity reaction (Ricketts and Ton-That, 2000).

4. CONCLUSIONS

Conducting Ppy film electrodes were electrochemically synthesized at different Na-pTs dopant concentrations for supercapacitor application. Also, a prototype supercapacitor using the polypyrrole film with the highest conductivity as electrodes was fabricated and characterized.

The polypyrrole film thicknesses were found to be uniform regardless of dopant concentration with an average thickness of 24.8 μm . Measured polypyrrole film conductivities range from 105 to 152 S/cm. Using cyclic voltammetry, the capacitance of the electrochemical cell using the fabricated PPy film as working electrode and NaCl as electrolyte was found to range from 0.106F to 0.315F. Increasing the electrolyte concentration from 0.10M to 0.20M increased the capacitance by a factor of 3.

The prototype supercapacitors fabricated consist of the synthesized PPy film as electrodes and Na-pTs of varying concentrations as electrolyte. Discharge time was found to be higher for the supercapacitor with higher electrolyte concentration. This might be due to more redox reaction that occurred between the electrode and the electrolyte.

To further analyze the electrochemical properties of the polypyrrole film electrodes, additional test on cyclic voltammetry is recommended such as capacitance and peak current measurement at lower scan rates. Several cycles of CV measurements can also establish if the electrochemical capacitor has poor or useful cycle life. It is also recommended to include electrochemical impedance spectroscopy in the characterization for a more comprehensive study of the PPy-based electrochemical supercapacitor.

5. REFERENCES

- Hussain, A.M.P., Kumar, A. (2006). Enhanced electrochemical stability of all-polymer redox supercapacitors with modified polypyrrole electrodes. *Journal of Power Sources*, 161, 1486–1492.
- Paul, S., Choi, K.S., Lee, D.J., Sudhagar, P., Kang, Y.S. (2012). Factors affecting the performance of supercapacitors assembled with polypyrrole/multi-walled carbon nanotube composite electrodes. *Electrochimica Acta*, 78, 649–655.
- Ingram, M., Staesche, H., Ryder, K. (2004). Activated polypyrrole electrodes for high-power supercapacitor applications. *Solid State Ionics*, 169, 51-57.
- Ramya, R. & Sangaranarayanan, M.V. (2008). Analysis of polypyrrole-coated stainless steel electrodes – Estimation of specific capacitances and construction of equivalent circuits. *J. Chem. Sci*, 120 (1), 25-31.
- Yang, D. (2012). "Application of Nanocomposites for Supercapacitors: Characteristics and Properties", *Nanocomposites - New Trends and Developments*. Retrieved from <http://www.intechopen.com/books/nanocomposites-new-trends-and-developments/application-of-nanocomposites-for-supercapacitors-characteristics-and-properties>
- Muthulakshmi, B., Kalpana, D., Pitchumani, S.,

- Renganathan, N.G. (2006). Electrochemical deposition of polypyrrole for symmetric supercapacitors. *Journal of Power Sources*, 158, 1533–1537.
- Lee, H., Kim, H., Cho, M.S., Choi, J., Lee, Y. (2011). Fabrication of polypyrrole (PPy)/carbon nanotube (CNT) composite electrode on ceramic fabric for supercapacitor applications. *Electrochimica Acta*, 56, 7460–7466.
- Sahoo, S., Dhobar, S., Hatui, G., Bhattacharya, P., Das, C.K. (2013). Graphene/polypyrrole nanofiber nanocomposite as electrode material for electrochemical supercapacitor. *Polymer*, 54, 1033–1042.
- Lu, X., et al. (2012). Polypyrrole/carbon nanotube nanocomposite enhanced the electrochemical capacitance of flexible graphene film for supercapacitors. *Journal of Power Sources*, 197, 319–324.
- Antiohos, D., Romano, M., Chen, J., Razal, J. (2013). Carbon nanotube for energy applications. Retrieved from <http://www.intechopen.com/books/syntheses-and-applications-of-carbon-nanotubes-and-their-composites/carbon-nanotubes-for-energy-applications>
- Miller, J., & Simon, P. (2008). Fundamentals of electrochemical capacitor design and operation. Retrieved from http://www.electrochem.org/dl/interface/spr/spr08/spr08_p31-32.pdf
- Wikimedia Commons (2013). Polypyrrole. Retrieved from <http://commons.wikimedia.org/wiki/File:Polypyrrole.png>
- Dong, Z.H., Wei, Y.L., Shi, W., Zhang, G.A. (2011). Characterisation of doped polypyrrole/manganese oxide nanocomposite for supercapacitor electrodes. *Materials Chemistry and Physics*, 131, 529–534.
- Chemical of the Week. (n.d.). Polymers. Retrieved from: <http://scifun.chem.wisc.edu/chemweek/polymers/polymers.html>
- Arshak, K., Velusamy, V., Korostynska, O., Oliwa-Stasiak, K., & Adley, C. (2009). "Conducting polymers and their applications to biosensors: Emphasizing on foodborne pathogen detection". *IEEE SENSORS JOURNAL*, 9(12), 1942-1951.
- Iqbal, Z., Baughman, R.H., Ramakrishna, B.L., Khare, S., Murthy, N.S., Bornemann, H.J., Mabrook, Pearson, Petty. "Inkjet-printed polypyrrole thin films for vapour sensing." *Inkjet-printed polypyrrole thin films for vapour sensing* 1.1 (2005): 565. Print.
- Cheng, S. (n.d.). Conducting polymer. Retrieved from: http://www.ch.ntu.edu.tw/~sfcheng/HTML/material95/Conducting_polymer.pdf
- Dai, L. (2004). Chapter 2: Conducting polymers. Retrieved from: www.springer.com/cda/content/document/cda_downloaddocument/9781852335106-c1.pdf?SGWID=0-0-45-104548-p17627813
- Hyun, J. (n.d.). Electrical conductivity of materials focused on polymer. Retrieved from <http://electrons.wikidot.com/create-new-page>
- University of Cambridge. (n.d.). About conductivity. Retrieved from <http://www.lehigh.edu/~amb4/wbi/kwardlow/condactivity.htm>
- Electroplating. (n.d.). Retrieved from <http://nzic.org.nz/ChemProcesses/metals/8G.pdf>
- Gale, B. (n.d.). Electrochemical deposition: Principles, methods and applications. Retrieved from: <http://www.eng.utah.edu/~gale/mems/Lecture 12 Electrodeposition.pdf>
- Saville, P. (2005). Polypyrrole: formation and use. Retrieved from www.publicacions.iec.cat/repository/pdf/00000122%5C00000079.pdf
- Swapp, S. (2013). Scanning Electron Microscopy. *Geochemical Instrumentation and Analysis*. Retrieved from http://serc.carleton.edu/research_education/geochemsheets/techniques/SEM.html
- Atterberry, J. (n.d.). How scanning electron microscope works. Retrieved from <http://science.howstuffworks.com/scanning-electron-microscope2.htm>
- Hafner, B. (N.D.). Energy dispersive spectroscopy on the SEM: a primer. Retrieved from http://www.charfac.umn.edu/instruments/eds_on_sem_primer.pdf
- Daghero, D. (n.d.). Resistivity measurements: the conventional and van der Pauw techniques. Retrieved from <http://areweb.polito.it/ricerca/latest/Articoli/vdPauw.pdf>
- UC Davis Chemwiki. (2010). Cyclic Voltammetry. Retrieved from



http://chemwiki.ucdavis.edu/Analytical_Chemistry/Instrumental_Analysis/Cyclic_Voltammetry

N.A. (2002). Cyclic voltammetry procedure. Retrieved from <http://web.nmsu.edu/~snm/classes/chem435/Lab13/procedure.html>

N.A. (1995). Charge Discharge of a Capacitor. Retrieved from <http://faraday.physics.utoronto.ca/1YearLab/capacitor.pdf>

All About Circuits. (n.d.). Capacitor charging and discharging. Retrieved from http://www.allaboutcircuits.com/vol_6/chpt_3/17.html

Dian, Y. et al. (2009). Self-discharge characterization and modeling of electrochemical capacitor used for power electronics applications. *Transactions on power electronics*, vol. 24, no. 2. Retrieved from http://hal.archives-ouvertes.fr/docs/00/36/88/48/PDF/SelfDischarge_Rojat2009.pdf

Conway, B.E. (1999). *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*. Boston, MA/New York: Kluwer/Plenum, pp. 557–595.

Ricketts B.W. & Ton-That, C. (2000). “Self-discharge of carbon-based super-capacitors with organic electrolytes,” *J. Power Sources*, vol. 89, no. 1, pp. 64–69.

Niu, J.J., Conway, B.E. and Pell, W.G. (2004). “Comparative studies of self-discharge by potential decay and float-current measurements at C double-layer capacitor and battery electrodes,” *J. Power Sources*, vol. 135, no. 1/2, pp. 332–343.

Agyeman, A.O. (n.d.). Electrochemistry. Retrieved from <http://www.docstoc.com/docs/113687146/electrochemistry-chem-4700-chapter-2>

Testing electrochemical capacitors. Retrieved 17 April 2014 from <http://www.gamry.com/application-notes/testing-electrochemical-capacitors-part-1-cyclic-voltammetry-and-leakage-current/>