

Effect of varying the amount of binder on the electrochemical characteristics of palm shell activated carbon

Hawaiah Imam Maarof^{1,2}, Wan Mohd Ashri Wan Daud¹, and Mohamed Kheireddine Aroua^{1,*}

¹ Department of Chemical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia.

² Faculty of Chemical Engineering, Universiti Teknologi MARA, 13500 Permatang Pauh, Pulau Pinang, Malaysia.

E-mail: mk_aroua@um.edu.my

Abstract. Polytetrafluoroethylene (PTFE) is among the most common binders used in the fabrication of an electrode, which is used for various electrochemical applications such as desalination, water purification, and wastewater treatment. In this study, the amount of the binder was varied at 10, 20, 30, and 40 wt% of the total mass of palm shell activated carbon (PSAC). The PSAC was used as the active material and carbon black was used as the conductive agent. The effect of different amounts of binder was observed by evaluating the electrochemical characteristics of the electrode through cyclic voltammetry (CV) and potentiometric electrochemical spectroscopy (PEIS). The CV analysis was employed to determine the geometric area normalised electrode double layer capacitance, C_E , and the electrode reaction of the prepared electrode. Meanwhile, the common redox probe, ferro/ferricyanide in 0.5 M NaCl, was employed to estimate the electron transfer resistance through PEIS. The electrochemical characterisation proved that the optimum amount of PTFE was 20 wt% for the 4:1 ratio of active material to conductive agent. On increasing the amount of the binder to 30 wt% and 40 wt%, the estimated value of C_E decreased and remained almost equivalent. Adding more than 30 wt% of binder resulted in pore blockage and reduced the available active site on the PSAC electrode. In addition, the electron transfer resistance of the prepared electrode was found to be in the range of 4-5 $\Omega \cdot \text{cm}^2$.

1. Introduction

There has been growing interest among researchers to explore the performance of porous electrodes in water and wastewater treatment by means of capacitive deionisation (electrosorption), electro-oxidation and electrodeposition [1-8]. A porous electrode provides a high surface area per unit mass and helps increase the rate of electron transfer [9] as well as the electrochemical active site. The use of activated carbon-based electrodes derived from waste and industrial by-products is gaining attention because it is essential to have such a precursor to ensure the economic feasibility of the electrode fabrication process. However, there are only limited works that explore the potential of waste-derived activated carbon electrodes for water and wastewater treatment. Among them are whitewood biochar [10] and palm kernel shell [8, 11, 12]. The waste-derived activated carbon electrodes are in either granular or powdered form as they are placed in a pack bed reactor or preferably fabricated in a form of sheet.

A binder is an essential component in electrode preparation as it helps in the binding of discrete porous particles to form an electrode that facilitates the electrochemical activities in a system. Fluorine-containing resin materials such as polytetrafluoroethylene (PTFE) are widely used as a binder, as they



have excellent chemical and thermal resistance and are best known for their binding properties. PTFE is widely used as a binder for the fabrication of cathode for energy storage, particularly in microbial fuel cell [13-16] and capacitor/supercapacitor [17, 18]. On one hand, Zarei, et al. [19] developed carbon nanotube-PTFE cathode for dye removal under several different operating conditions, while on the other hand, Park, et al. [20] prepared activated carbon-PTFE electrode sheet for desalination. PTFE as a binder was reported to provide high reproducible performance of electrode at low cost as compared to Nafion [14]. Nafion is commonly used as binder in preparing the electrode by brushing method. However, a uniform mixture of active material and PTFE electrode is generally difficult to achieve because of excessive fibrillation due to the PTFE properties [21]. To a certain extent, PTFE is likely to impair the characteristics of the electrode if added in an amount more than adequate. Additionally, PTFE is used in the form of an aqueous dispersion rather than a powder in order to obtain a more uniform mixture.

In this work, a local source of industrial waste, namely palm shell activated carbon (PSAC), was used as the precursor of a porous carbon-based electrode. An optimum amount of PTFE from its aqueous dispersion was determined to bind porous powdered PSAC. Although Misnon, et al. [22] derived an electrode from PSAC and evaluated its electrochemical properties, they merely focused on preparing the electrode as a supercapacitor in which PVDF was used as the binder. In another study by Abbas, et al. [23], PTFE was reported as a better binder compared with PVDF. They reported that PVDF resulted in pronounced reduction of pore volume of activated carbon (Norit® DLC Supra) and lower capacitance was obtained than with PTFE. Hence, the present work aims to explore the feasibility of the local industrial waste, namely PSAC, as the active material for an electrode in which PTFE was used as the binder. There is no available open literature on the electrochemical properties of PSAC-PTFE composite electrode, particularly on the electrochemical active surface area. Therefore, the main objective is to prepare an adequate strength of electrode with an optimum amount of PTFE as the binder. The electrochemical properties of the prepared electrode were further examined to ensure its potential for using as free-standing electrode sheet in water and wastewater treatment.

2. Methodology

2.1. Electrode preparation

The granular PSAC was procured from a local supplier, Bravo Green Sdn. Bhd., Sarawak. It was ground to fine particles and subsequently sieved to obtain the desired particle size ($<100\text{ }\mu\text{m}$). The electrode was prepared by mixing a specific amount of powdered PSAC, carbon black (Super P, Alfa Aesar), and 60 wt% PTFE suspension (Sigma-Aldrich). The mass ratio of PSAC and carbon black was fixed at 4:1. An equal total mass of active material and conductive agent (ca. 0.5 g) was prepared for each type of electrode while varying the percentage of PTFE accordingly. Four different electrodes with pre-determined mass percentage of PTFE were prepared. The mass of PTFE was varied at 10, 20, 30, and 40 wt% and these electrodes were identified as 10PTFE, 20PTFE, 30PTFE, and 40PTFE, respectively. Each mixture was thoroughly hand mixed to produce an electrode paste by the addition of 1,3-propanediol as the solvent. The paste was then kneaded and pressed in a stainless-steel mould prior to drying at 80°C for 2 h, at 125°C for 1 h, and at 250°C for 1 h. When the electrodes are taken out from the oven, they were hand-pressed to increase the mechanical strength. The dried electrodes were then packed into a 5-mm diameter empty electrode tip. The geometrical surface area of the electrode was fixed at 0.196 cm^2 (5 mm diameter). Prior to evaluating the electrochemical characteristics, the electrode surface was polished using the micropad polishing cloth. Each electrode was held vertically and 8-motions were performed for 20 times on the wet polishing pad, which was pre-wetted by distilled water. The electrodes were then dried using hot air blower, cooled at room temperature, and made ready for electrochemical characterisation studies. The morphology of the electrode surface was examined using field emission scanning electron microscopy (FESEM) (AURIGA, Carl Zeiss), equipped with energy dispersive X-ray (EDX) analyser.

2.2. Chronoamperometry (CA)

The experiments were conducted in a single compartment of 100 mL glass cells at room temperature. A three-electrode cell configuration was employed in which a platinum wire and Ag/AgCl (3M KCl) reference electrodes were used for the measurement. The solution was 5 mM potassium ferrocyanide electrolyte in 0.5 M NaCl that acted as the supporting electrolyte. The CA analysis employed a potentiostat (Bio-Logic, SP-300), and the data were analysed using the EC-Lab® software. The electrochemical active surface area was obtained by Cottrell equation (Eq. 1), where I is the current (A), n is the number of electrons transferred, F is Faraday's constant (96485 C/mol), A is the electrochemical active area (cm²), C is the concentration of active species (mol/cm³) and D is the diffusion coefficient (cm²/s).

$$I = \frac{nFACD^{\frac{1}{2}}}{\pi^{\frac{1}{2}}t^{\frac{1}{2}}} \quad \text{Eq. 1}$$

2.3. Cyclic voltammetry (CV)

The CV analysis that was carried out in this study had an identical setup as the CA analysis. The electrolyte was 0.5 M NaCl. The CV experiments and analyses were performed by a potentiostat instrument (Metrohm, Autolab PGSTAT101) controlled by the NOVA 1.10 software. In addition, the solution was stirred in between the experiments to restore initial conditions; however, it was not stirred during the experiment to maintain the flux to the electrode under diffusion-controlled behaviour. Triplicate runs were carried out for each electrode, and the polishing step was performed between each run. The third cycle of each CV was reported unless otherwise stated.

2.4. Potentio electrochemical impedance spectroscopy (PEIS)

The analysis was conducted using a setup and instruments that were similar to that used in the CA analysis. The solution was 5 mM potassium ferrocyanide in 0.5 M NaCl that acted as the supporting electrolyte. PEIS was performed at a potential bias of 0.26 V (vs. Ag/AgCl) over the frequency range of 1 MHz to 1 Hz with an AC perturbation of 10 mV.

3. Result and discussion

3.1. Electrochemical active surface area

Porous properties of the PSAC led to a higher active electrochemical surface area of an electrode when compared with its geometrical area. CA analysis produced a current-time curve as shown in Figure 1. The relationship between the current and the time can be described by the Cottrell equation with the specific known value of the diffusion coefficient, D , of ferrocyanide, i.e. $D = 7.6 \times 10^{-5}$ cm²/s [24]. A linear plot of i vs. $t^{-0.5}$ was obtained, and the electrochemical active surface area of the electrode was estimated from the slope. The electrochemical active surface area was compared to the geometrical surface area, which was 0.196 cm² and listed in Table 1. The 10PTFE was found to have the highest amount of electrochemical active surface area among others with 1.572 cm², which was 8 times higher than its geometrical surface area. The electrochemical active surface area decreased by 42% when the amount of PTFE was increased to 20%. Such an outcome suggests that increasing the amount of PTFE decreases the available high surface area of porous PSAC for electrochemical activities. In addition, almost a similar value of the electrochemical active surface area was observed for 20PTFE, 30PTFE, and 40PTFE, which was between 0.92 and 0.96 cm². It was about more than 5 times greater than its geometrical surface area.

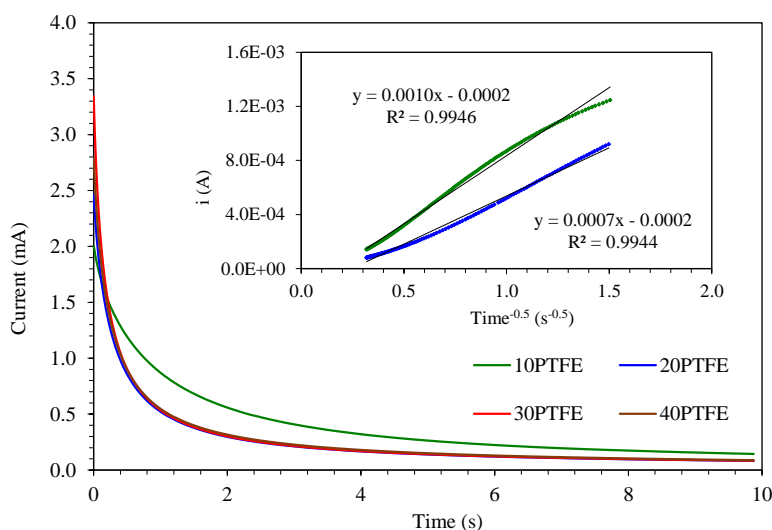


Figure 1. A single-step CA plot of the PSAC electrode using electrodes prepared using different amounts of PTFE at a voltage step from 0 to 0.4 V. Inset shows the plot of i vs. $t^{-0.5}$, which has been employed to deduce the electrochemical active surface area of electrodes.

Table 1. Electrochemical active surface area of prepared electrodes deduced from CA analysis.

Electrode	10PTFE	20PTFE	30PTFE	40PTFE
Electrochemical active surface area, cm ²	1.572	0.917	0.959	0.940
Electrochemical / Geometrical active surface area, cm ² /cm ²	8.0	4.7	4.9	4.8

3.2. Surface morphology

Figure 2 illustrates the FESEM-EDX elemental mapping for the electrodes with a different composition of PTFE. Accordingly, EDX detects the emission of four major elements on the surface of the PSAC electrode, namely carbon, oxygen, fluorine, and a small percentage of silica, as listed in Table 2. These compositions are with reference to the same mapping area as shown in Figure 2. The fluorine element represents the distribution of PTFE on the electrode surface. Generally, all the elements are heterogeneously scattered on the surface of the electrode. It is clearly seen that fluorine dots are sparse (blue colour) in the 10PTFE and are the least concentrated compared to the other electrodes. As the amount of PTFE increases to 40%, the intensity of fluorine dots also increases as the blue spots become denser. This is in agreement with the atomic percentage of fluorine, which increases proportionally as the amount of PTFE increases from 10% to 40%, as listed in Table 2. On the contrary, the percentage of carbon present on the surface of the electrode is inversely proportional to the atomic percentage of fluorine. For instance, in the 10PTFE electrode, the least amount of PTFE introduced in the electrode results in a larger amount of PSAC available on the same area of imaging. This trend is reversed for 40PTFE. The high intensity of fluorine dots in 40PTFE suggests an excess amount of PTFE on the surface which hinders the electrochemically active surface area of the PSAC. Additionally, Figure 3 illustrates a higher magnification of emission scanning on the surface of the PSAC-PTFE composite electrode. It is clearly seen that this composite electrode consists of a wide range of pore sizes, from micro (< 2 nm), meso (2-50 nm), to macro (> 50 nm) pores.

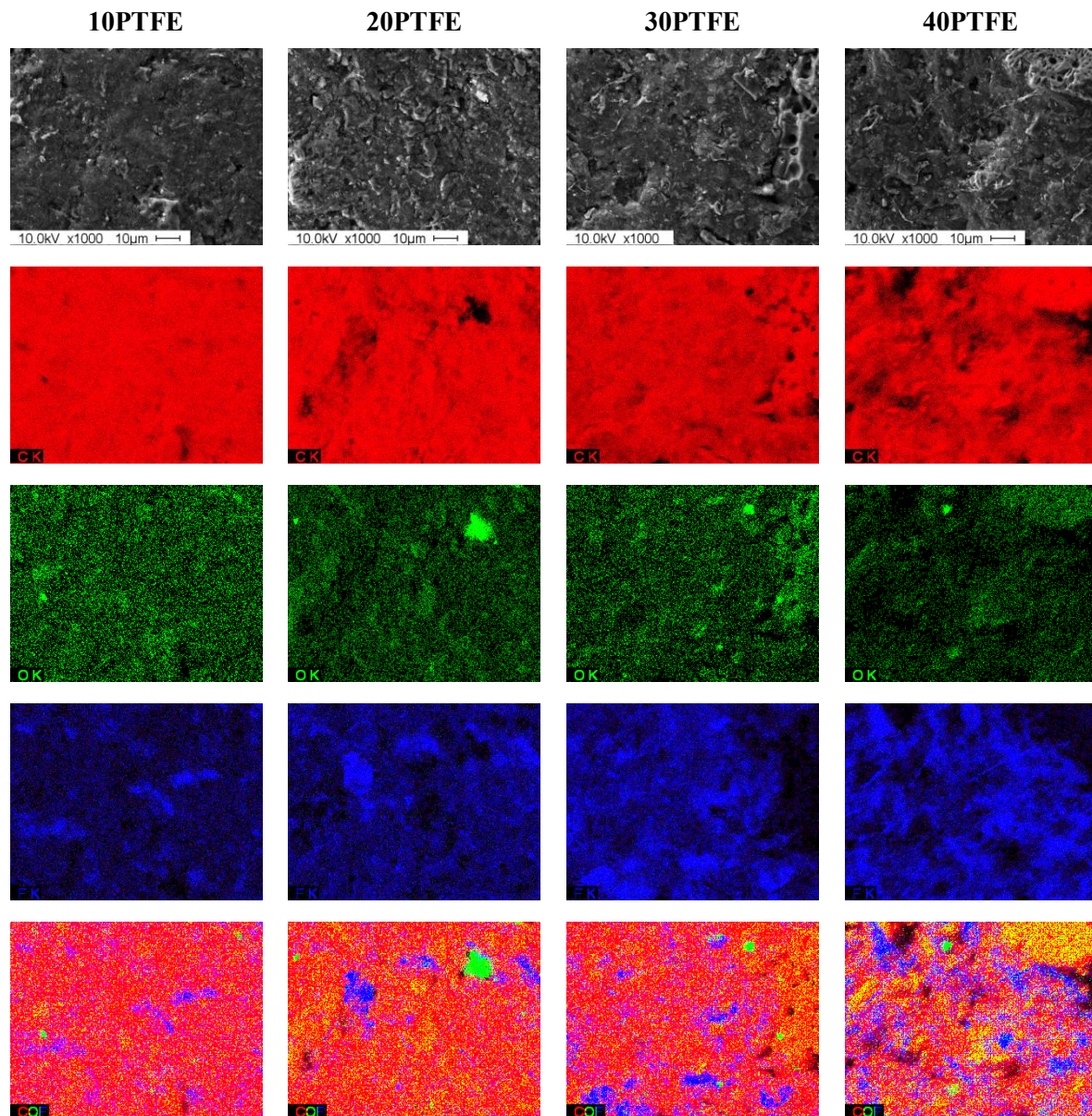


Figure 2. FESEM-EDX elemental mapping of prepared electrodes using different amount of PTFE.

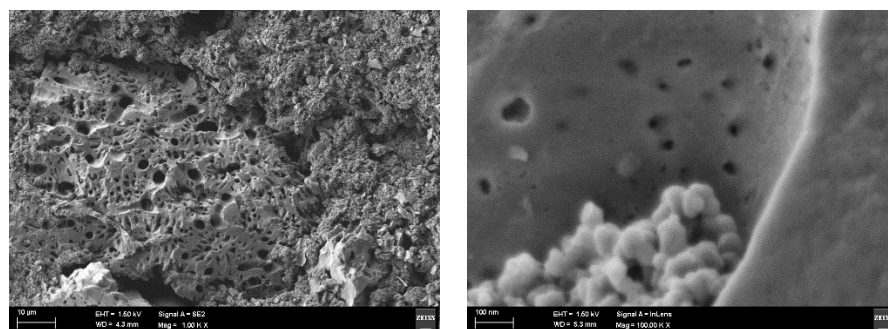


Figure 3. FESEM imaging showing a wide range of pore size available in PSAC-PTFE composite electrode.

Table 2. Elemental composition of electrodes with different composition of PTFE.

Elemental	Atomic percentage, %			
	10PTFE	20PTFE	30PTFE	40PTFE
C	91.47	86.24	84.40	79.81
O	3.79	4.58	3.00	2.82
F	4.58	9.04	12.41	17.11
Si	0.15	0.14	0.18	0.26

3.3. Double layer capacitance, C_E

Figure 4 shows the cyclic voltammogram of the prepared electrodes. The error bar is deduced from the standard deviation of the triplicates run. In between each run, the electrode surface was subjected to a polishing step, as describe in Section 2.3. The average standard deviation for each electrode is listed in Table 3. 10PTFE shows the highest value of average standard deviation ($\pm 91 \mu\text{A}$). After every polishing step in between the CV test, a new surface area on 10PTFE has been introduced, but it leaves a noticeably large amount of carbon particles on the polishing pad. This suggests that 10% of PTFE is not sufficient to bind the PSAC and carbon black. The PSAC and carbon black easily come out from the electrode during typical polishing steps. A lower value of the average standard deviation is found for the electrode with a higher percentage of PTFE, suggesting that sufficient binder is applied in preparing the PSAC-PTFE composite electrode. An about similar finding was reported by Dong, et al. [14], where, when the ratio of PTFE to activated carbon was less than a certain amount, the paste cannot be firmly bound. For this reason, in their study, the ratio of activated carbon/PTFE was varied between 3 and 11. This ratio is equivalent to 9 to 33% of PTFE in each electrode. However, carbon black is not one of the electrode components.

Double layer capacitance for each electrode is estimated from the average value of current produced by the CV analysis. The effect of varying the amount of PTFE on the geometrical area normalised electrode double layer capacitance, C_E is presented by

Figure 5. C_E is calculated using Eq. 2, where E_1 and E_2 are the lower and upper limits of potential, $i(E)$ is the instantaneous current, $\int_{E_1}^{E_2} i(E) dE$ is the total voltammetric charge obtained by integration of forward and backward sweep in CV, (E_1-E_2) is the selected potential width (e.g. 0.2-0.3 V), A is the geometrical surface area of the electrode (0.196 cm^2), and v is the scan rate.

$$C_E = \frac{1}{2(E_2 - E_1)Av} \int_{E_1}^{E_2} i(E) dE \quad \text{Eq. 2}$$

The highest C_E is obtained by 10PTFE and it has the lowest amount of PTFE among the others. As for 20PTFE, the amount of C_E is found to be decreased by 42%. Further increase of PTFE from 30% to 40% does not show a steep reduction in capacitance where it remains in the range of 33 to 34 mF/cm^2 . Thus, this proves that the reduction of C_E is mainly due to the reduction of the electrochemical active surface area. As the amount of PTFE is increased, it impairs the available surface area of PSAC, including its pores. However, all these C_E values are apparently overestimated as the electrode has a large surface area due to its porous characteristics. To take into account the effect of the electrochemical

active surface area on the double layer capacitance, the electrochemical active area normalised electrode double layer capacitance, C_E^* is deduced and presented in Figure 5. The relationship between the capacitance and the electroactive surface area is clearly seen as the C_E^* lies between a small range of C_E^* (6.7 to 8.0 mF/cm²) for all the electrodes which have different compositions of PTFE.

Although the 10PTFE electrode gives the highest active surface area and C_E , the requirement for sufficient strength of binding between the powdered PSAC and carbon black is not achieved. The new surface introduced by 10PTFE after the polishing step, with the apparently high average standard deviation is claimed due to an insufficient amount of binder. On the contrary, Park, et al. [20] reported that the best carbon sheet was prepared using 4 wt% of binder for the desalination purpose, according to the optimum obtained capacitance calculated from the CV analysis. If the optimum capacitance is to become the main criterion by ruling out the requirement of minimum mechanical strength, then 10% of PTFE seems to be the best amount for preparation of the PSAC-PTFE composite electrode. However, due to the physical characteristics of the PSAC and the amount of carbon black used, 20PTFE is better than 10PTFE in providing sufficient binding strength between the active material and conductive agent.

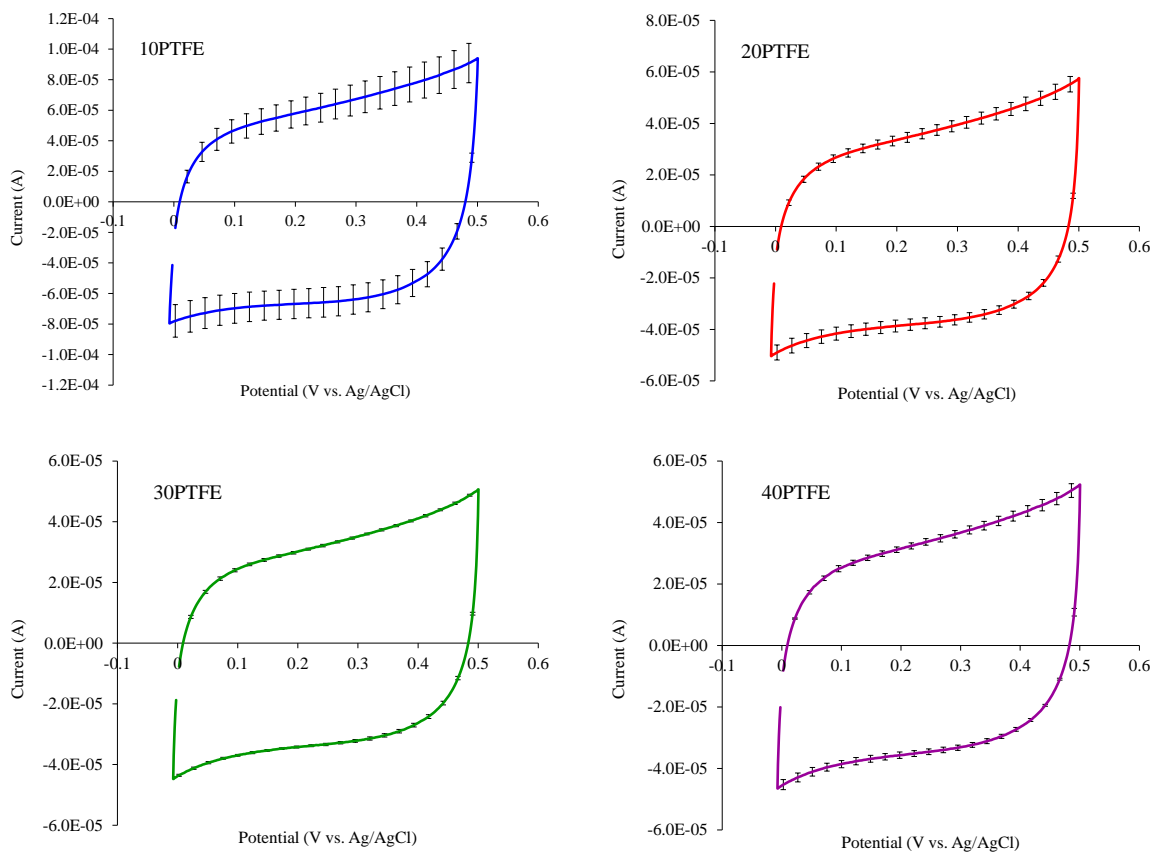
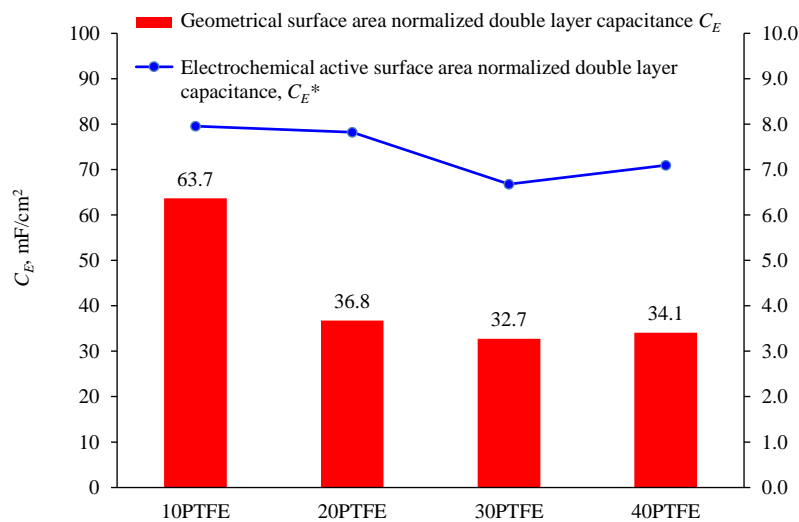


Figure 4. Cyclic voltammograms of 10PTFE, 20PTFE, 30PTFE and 40PTFE.

Table 3. Average standard deviation deduced from the triplicates run of CV by different composition of PTFE.

	10PTFE	20PTFE	30PTFE	40PTFE
Average standard deviation, μA	± 91	± 21	± 0.4	± 10

**Figure 5:** Estimated C_E and C_E^* by using PSAC electrodes with different amount of PTFE.

3.4. Electron transfer resistance

The impedance spectra for 20PTFE, 30PTFE and 40PTFE are compared in Figure 6. The PEIS data are analysed by fitting them into the Randles equivalent electrical circuit, as illustrated in the inset of Figure 6. All the three Nyquist plots similarly display a depressed semicircle over a high frequency range with the centre lying some distance below the x-axis. A depressed semicircle can be explained by the Constant Phase Element (CPE). CPE is the deviation from true capacitor behaviour and it can be attributed to the presence of double layer capacitance [25] and electrode surface roughness [26]. This is in agreement with the rough and non-uniform surface area of PSAC-PTFE electrode, as illustrated by Figure 3. Additionally, the diameter of the depressed loops represents the electron or charge transfer resistance, R_{ct} due to the Faradaic process. R_{ct} is increasing in the following trend, 40PTFE ($3.7 \Omega \cdot \text{cm}^2$) < 30PTFE ($4.6 \Omega \cdot \text{cm}^2$) < 20PTFE ($5.2 \Omega \cdot \text{cm}^2$). The highest electron transfer by 40PTFE can be described by the high conductivity of the prepared electrode due to the durable binding of PSAC and carbon black using a higher amount of PTFE. However, the value of R_{ct} is considered as comparable between the other two. In addition, a straight long line with an angle of 45° to the real axis for all the three electrodes represents semi-finite diffusion impedance, also called the Warburg impedance.

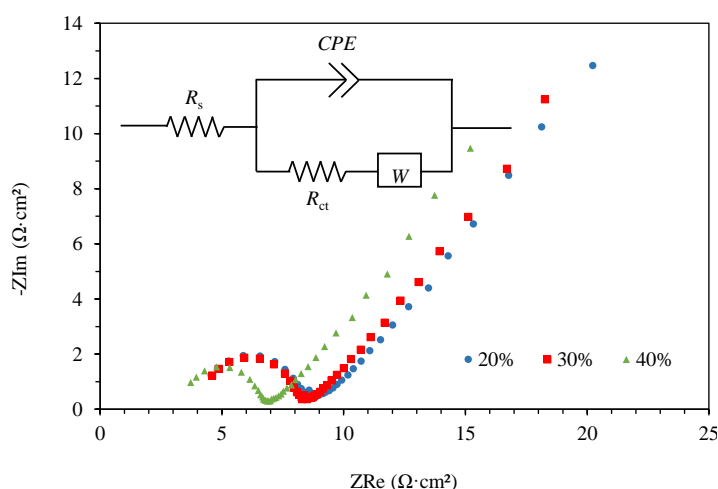


Figure 6: Nyquist plot of PEIS for 20PTFE, 30PTFE and 40PTFE. Inset is the equivalent Randles circuit.

4. Conclusion

This work demonstrates the effect of PTFE composition as a binder in the preparation of the PSAC-PTFE composite electrode. The 10PTFE electrode gives the highest electrochemical active surface area and C_E . However, it was observed that 10% PTFE was not sufficient to firmly bind the PSAC and carbon black for the purpose of preparing a durable free-standing electrode sheet for water or waste-water treatment. On the contrary, 20PTFE has sufficient binding strength between PSAC and carbon black. It produces an acceptable reproducibility in the voltammogram to deduce the double layer capacitance properties of a PSAC-based electrode. It is proven that increasing the amount of PTFE from 10% to 20% in the electrode preparation does impair the electrochemical properties in terms of the electrochemical active surface area and C_E . Further increase of PTFE up to 40% does not significantly help in improving the electrochemical properties of the PSAC-PTFE hybrid electrode. Meanwhile, a comparable electrochemical active surface area, C_E and R_{ct} , were observed between 20PTFE, 30PTFE, and 40PTFE.

Acknowledgement

The authors would like to acknowledge the financial support from the Ministry of Education (MOE), Malaysia for High Impact Research Grant (UM.C/HIR/MOHE/ENG/43), the University of Malaya for PPP grant (PG149-2016A) and the facilities provided at the Centre for Separation Science and Technology (CSST). H.I. Maarof gratefully acknowledges the Ministry of Higher Education (MOHE), Malaysia and Universiti Teknologi MARA, Malaysia for the postgraduate scholarship.

References

- [1] L. Yan, Y.F. Wang, J. Li, H.D. Shen, C. Zhang and T.T. Qu 2016 *Bulletin of the Chemical Society of Japan* **89** 50-7
- [2] R.G. Saratale, K.J. Hwang, J.Y. Song, G.D. Saratale and D.S. Kim 2016 *Journal of Environmental Engineering* **142**
- [3] L. Xu, Y.K. Sun, L.C. Zhang, J.J. Zhang and F. Wang 2016 *Desalination and Water Treatment* **57** 8815-8825
- [4] E.J. Bain, J.M. Calo, R. Spitz-Steinberg, J. Kirchner and J. Axen 2010 *Energy Fuel* **24** 3415-3421
- [5] F. Duan, Y. Li, H. Cao, Y. Wang, J.C. Crittenden and Y. Zhang 2015 *Chemosphere* **125** 205-211
- [6] C.H. Hou and C.Y. Huang 2013 *Desalination* **314** 124-129
- [7] S. Nadakatti, M. Tendulkar and M. Kadam 2011 *Desalination* **268** 182-188

- [8] G. Issabayeva, M.K. Aroua and N.M. Sulaiman 2006 *Desalination* **194** 192-201
- [9] C. Punckt, M.A. Pope and I.A. Aksay 2013 *The Journal of Physical Chemistry C* **117** 16076-16086
- [10] A.M. Dehkhoda, E. Gyenge and N. Ellis 2016 *Biomass and Bioenergy* **87** 107-121
- [11] M.H. Chakrabarti, M. Saleem, M.F. Irfan, S. Raza, D.B. Hasan and W. Daud 2011 *International Journal of Electrochemical Science* **6** 4470-4480
- [12] F. Offei, A. Thygesen, M. Mensah, K. Tabbicca, D. Fernando, I. Petrushina and G. Daniel 2016 *Energies* **9** 1-14
- [13] S. Cheng and J. Wu 2013 *Bioelectrochemistry* **92** 22-26
- [14] H. Dong, H.B. Yu, X. Wang, Q.X. Zhou and J.L. Feng 2012 *Water Research* **46** 5777-5787
- [15] H. Dong, H.B. Yu and X. Wang 2012 *Environmental Science and Technology* **46** 13009-13015
- [16] X.Y. Zhang, X. Xia, I. Ivanov, X. Huang and B.E. Logan 2014 *Environmental Science and Technology* **48** 2075-2081
- [17] A. Gambou-Bosca and D. Belanger 2015 *Journal of The Electrochemical Society* **162** A5115-5123
- [18] Z.T. Zhu, S.H. Tang, J.W. Yuan, X.L. Qin, Y.X. Deng, R.J. Qu and G.M. Haarberg 2016 *International Journal of Electrochemical Science* **11** 8270-8279
- [19] M. Zarei, A. Niaei, D. Salari and A.R. Khataee 2010 *Journal of Electroanalytical Chemistry* **639** 167-174
- [20] K.K. Park, J.B. Lee, P.Y. Park, S.W. Yoon, J.S. Moon, H.M. Eum and C.W. Lee 2007 *Desalination* **206** 86-91
- [21] T. Shimizu, Y. Higashihata and T. Nakamura (1998). United States Patent No. 5707763.
- [22] I.I. Misnon, N.K.M. Zain, R.A. Aziz, B. Vidyadharan and R. Jose 2015 *Electrochimica Acta* **174** 78-86
- [23] Q. Abbas, D. Pajak, E. Frackowiak and F. Béguin 2014 *Electrochimica Acta* **140** 132-8
- [24] J.A. Bard and L.R. Faulkner 2001 *Electrochemical Methods: Fundamentals and Applications* 2nd Ed. (New York: John Wiley & Sons, Inc.) pp 813
- [25] V.F. Lvovich 2012 *Phenomenon Impedance Spectroscopy* ed V.F. Lvovich (New Jersey: John Wiley & Sons, Inc.) pp 37-7
- [26] R. De Levie 1965 *Electrochimica Acta* **10** 113-30