Effects of Mesoporous Silica Addition on Electrochemical Properties of Carbon Electrode

Noramira Saad, Mohammad Noor Jalil, Zaini Haryati Mohd Zain, Hamizah Mohd Zaki

Abstract: ***Mesoporous silica is material that possesses the pore sizes between 2 nm to 50 nm which had expanded their applications rapidly. In this study, mesoporous SBA-15 and SBA-16 were synthesized via surfactant templating approach using triblock copolymer as directing agent and tetraethyl orthosilicate (TEOS) as silica source. The synthesized materials were characterized by X-ray diffraction (XRD) spectroscopy, scanning electron microscopy (SEM) and nitrogen absorption-desorption tests. The pore diameters are 5.5 nm and 3.2 nm for SBA-15 and SBA-16 respectively, were determined with BJH method based on adsorption data. Three different electrodes were fabricated, carbon paste electron (CPE) and two modified carbon paste electrodes (MCPE): SBA-15/MPCE and SBA-16/MPCE. The fabricated electrodes were tested using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). SBA-16/MCPE showed better adsorption, enhanced the response signal to 81% and a lower resistance (4.04KΩ). The synthesized mesoporous materials have the potential to be used in the development of high performance, lightweight and flexible devices in electrochemistry***

Keywords**:** ***Electrochemical properties, mesoporous silica, mesoporous silica-carbon electrode, SBA-15, SBA-16***

I. INTRODUCTION

The discovery of surfactant template silica such MCM-41, MCM-48 and SBA-15 was first reported in early 1990's led to a new class of materials that offers high thermal and mechanical stabilities [1], [2]. Due to the continuity of mesoporous silica development, studies on their properties are very actively conducted [3]. Unique properties of the mesoporous materials such as uniform pores size and large surface area have resulted in excellent surface enhancement effects [4], [5]. These materials are useful for application in emergent areas such as energy storage in double layer supercapacitors, catalytic supports in fuel cell electrodes, adsorption of bulky molecules in liquid phase, improvement of selectivity in electro analysis, and enhancement of drug release rate [6]–[11].

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Previous research has proved that mesoporous silica carbon paste enhanced the current signal compared to carbon electrode [12]–[14]. The materials that are made from silica such as SBA-15 and SBA-16 provide 2D and 3D pore structure. Apparently, a loop has been observed with SBA series compared to closed silica mesostructured, the MCM series. The mechanism of electrode's surface during electrical charging is still under debate particularly regarding the effect of silica pore structure with the current signal obtained. In this study, the mesoporous silica (SBA-15&16) were synthesized and characterized followed by analysis study of the electrochemical behaviours of the material towards frequencies and voltage are analysed. The electrochemical performance of the mesoporous silica-carbons was then compared to reference microporous carbon.

II. MATERIALS AND METHOD

A. Chemicals Raw Materials

The chemicals used were analytical grade and purchased from; Tri-block copolymer Pluronic P123, $EO_{20}PO_{70}EO_{106}$ and F127 ($EO_{106}PO_{70}EO_{106}$) (Sigma-Aldrich), tetraethyl orthosilcate, TEOS (98%, Aldrich), graphite powder (<20µm, Aldrich), paraffin oil (Biobasic), hydrochloric acid,HCl (36%, Aldrich), Methanol, CH_4O, ethanol, C_2H_6O, deionized water, copper wire, glass tube, epoxy glue.

B. Instrumentations

Synthesized mesoporous silicas characterized by X-Ray diffraction (Rigaku D/max-2500), FE-SEM from SUPRA 40 and for N_2 adsorption desorption (Micromeritics, ASAP 2060). The electrochemical measurements carried out using an Auto-lab PGSTAT101 potentiostat which working electrode (CPE and SBA-15/MCPE), reference electrode (Ag/AgCl) and counter electrode (platinum).

C. Synthesis of Mesoporous Silica

1) SBA-15

Mesoporous silica was prepared via surfactant templating technique. Pluronic P123(4g) was dissolved in deionized water (30mL) and HCl (2M, 120mL) and stirred in closed container for 20 hours. The TEOS (8.5g) was added slowly to the mixture then being stirred vigorously for 15 minutes and kept under static condition at temperature 35°C for 20 hours. Thus, the substance was transferred to oven at 90°C for 24 hours. The precipitate obtained was filtered, wash using deionized water and dried for 3 days at 45°C. Obtained silica then calcined at 500°C in air for 6 hours [15].

2) *SBA-16*

The SBA-16 was prepared in acidic condition employing a non-ionic surfactant,

Pluronic F127 ($EO_{106}PO_{70}EO_{106}$) as structure-directing agent. Pluronic F127 (2.3 g) dissolved in concentrated HCl (0.6 mL) and methanol (100 mL) with continuous stirring for 2 hours at 35 °C. In a separate beaker, TEOS (10 mL), ethanol (5 mL) and deionized water (4 mL) mixed as second mixture and stirred for 30 minutes at room temperature. The second mixture was added to the first mixture and stirred for an hour at 35 °C. The mixture kept in static condition for 20 hours (hydrothermal treatment) at 80 °C. Cooled down at ambient temperature for 4 hours before transferred into a closed container and heated for 24 hours at 90°C to enhance the formation of silica crosslink. The sample finally filtered then calcined at 550°C for 6 hours.

3) *Electrode fabrication*

Three types of electrodes were prepared for cyclic voltammetry and electrochemical impedance. CPE was prepared by mixing graphite powder with paraffin oil. Mesoporous silicas were mixed with graphite powder and bind together using a few drops of paraffin oil to obtain MCPE paste (SBA-15&16). The pastes were packed tightly into the glass tube's cavity. Implementation of copper wire inside the tube provides electrical contact for the system. Bottom surface of the electrodes were polished using smooth paper and washed with deionized water.

4) *Electrochemical measurement*

The electrochemical measurements on electrodes were performed using cyclic voltammetry (CV) at scan rate 0.1 Vs^{-1} and recorded between -0.4V – 0.6V. The electrochemical impedence spectroscopy (EIS) measurements were performed using potentiostat at frequencies 1mHz to 10 MHz [14].

III. RESULT AND DISCUSSION

A. Mesoporous Silica Structural Characterization

Powder X-Ray diffractogram of synthesized mesoporous SBA-15 and SBA-16 are shown in Fig. 1 shows three resolved peaks of SBA-15 at 2θ ≈ 1.02°, 1.72° and 1.96°, corresponding (100), (110) and (200) respectively which reflects as well-ordered mesoporous silica structured with d_{100}=8.83 nm [16].The presence of peaks can be assigned the diffractions from 2-d symmetry associated with the hexagonal structure [17]. The peaks resolved for SBA-16 from the diffractogram at low angle may be assigned as (110), (220) and (211) diffraction with $d_{(110)}$ = 10.7 nm. The diffraction pattern indicates 3D symmetry which associated with cubic structures.

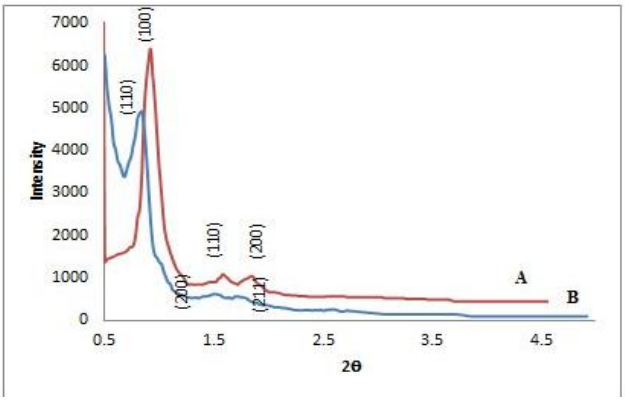
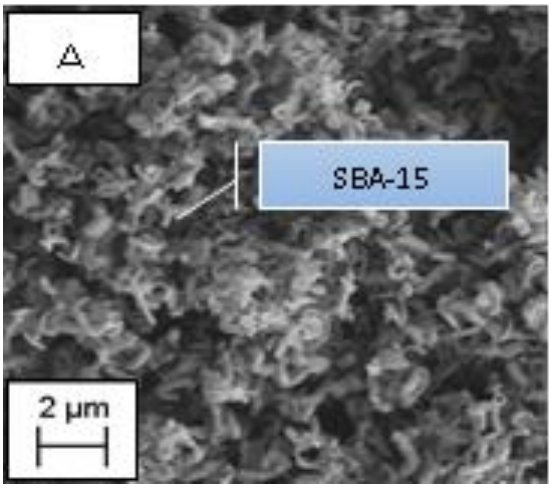
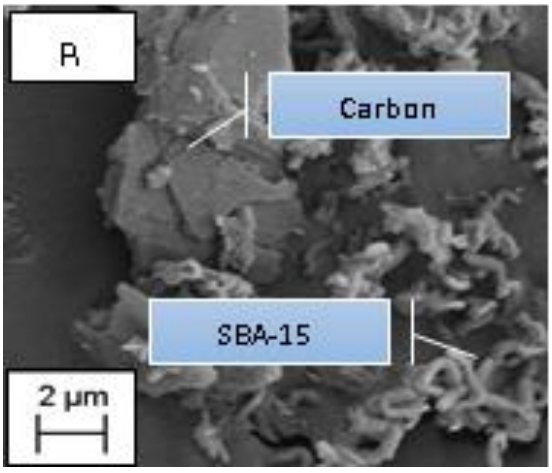
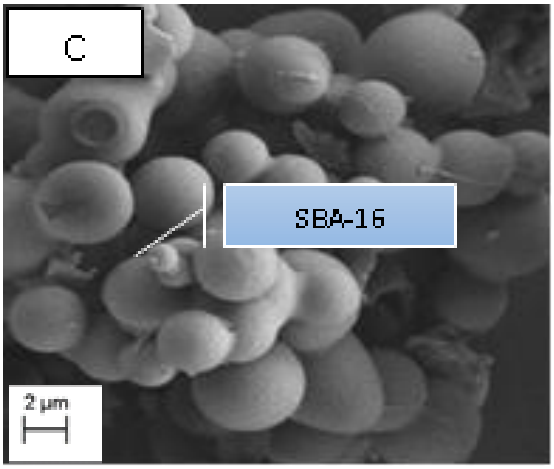


Fig. 1 XRD diffraction pattern of synthesised (A) SBA-15 and (B) SBA-16

Fig. 2 shows FESEM micrographs of calcined mesoporous silica morphologies in 10k× of magnification and hybrid of SBA and carbon sample. The micrographs show that the production of SBA-15 possessing hexagonal-rod-like-shape to the material and SBA-16 with 3D cubic shape [16], [18].







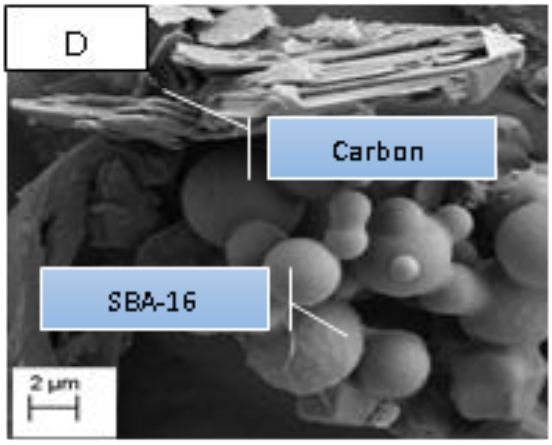


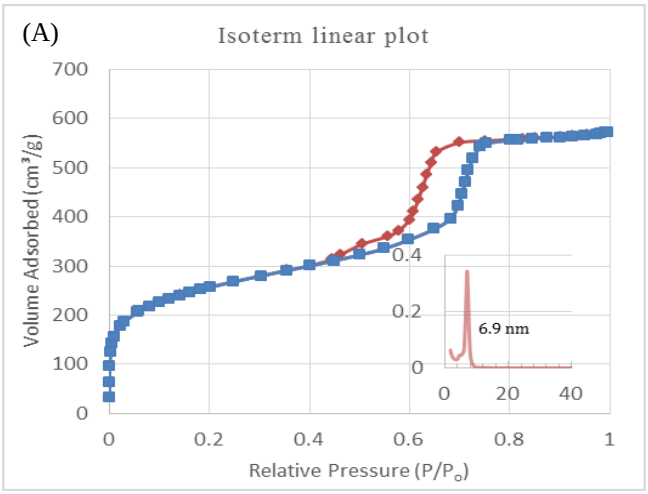
Fig. 2 Micrograph images of A) calcined SBA-5 B) hybrid of SBA-15 and carbon for MCPE/SBA-16 C) calcined SBA-16 and D) hybrid of SBA-16 and carbon for MCPE/SBA-16.

The pores structure of prepared mesoporous materials was characterized by nitrogen adsorption measurements. The isotherm and pore size distributions of synthesized materials are show in Fig. 3. Calcined SBA-15 and SBA-16 exhibit type-IV curves according to IUPAC classification with hysteresis loop at relative pressure (P/P_o) at about 0.46 to 0.76 (SBA-15) and 0.3-0.7 (SBA-16), which indicate mesoporosity. The pore size distributions (PSD) curves (insert) as determined by BJH method show well-defined peaks at pore diameter between 6.0 nm to 9 nm for SBA-15 and as SBA-16 between 3 nm to 4.5 nm. The presence of a low distributed peak between 4 nm to 6 nm of SBA-15 could be the interconnected pore of SBA-15 [18]. The BET surface area, pore volume and pore width of SBA-15 are summarized in Table I.

Table I Pore analysis of SBA-15 and SBA-16

SBA-	*1* (m^2/g)	*2* (cm^3/g)	*3* (nm)	*4* (nm)	*5* (nm)
15	913	0.8341	5.4271	4.9021	8.83
16	450.	0.2594	3.1830	3.0972	10.7

1. Specific surface area determined by BET method
2. Total pore volume
3. Pores diameter (Dp) as determined by BJH from adsorption data
4. Pores diameter (Dp) as determined by BJH from desorption data
5. Pore size distribution of silica



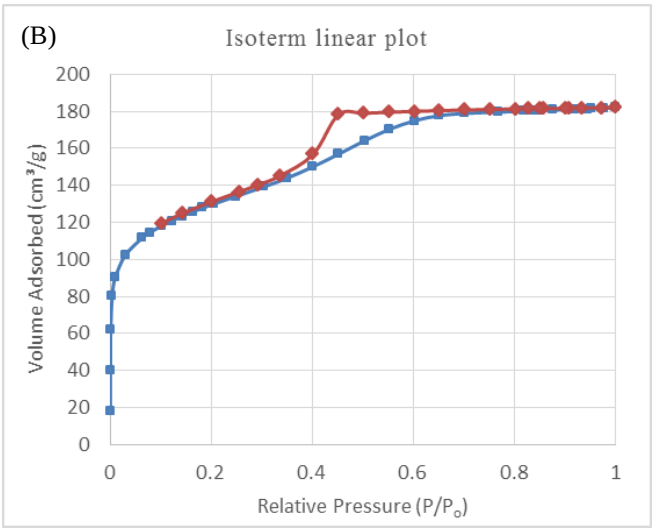


Fig. 3 Isoterm linear plot of A) SBA-15 and B) SBA-16 and pore size distribution of silica (insert)

The BET surface areas of the mesoporous silicas are 913.26 m2/g and 450.37 m2/g for SBA-15 and SBA-16 respectively and as for the respective total pore volumes are 0.83 cm3/g and 0.26 cm3/g. The results show that SBA-15 has a larger surface area and a larger total pore volume.

B. Electrochemical Behaviors Study of Mesoporous Silica

Cyclic voltammetry (CV) and electrochemical impedence spectroscopy (EIS) used to study the electrochemical behaviours of mesoporous silica-carbon. Fig. 4 shows the cyclic voltammogram of $5.0x10^{-3}$ M of potassium ferrocyanide by three different working electrodes that indicate the presence of redox process [14]. The voltammogram in Fig. 4 shows that the electrode with mesoporous silicas (SBA-15/MCPE and SBA-16/MCPE) exhibit current enhancement by 70% and 81% respectively at oxidation peak compared to CPE which unmodified carbon paste. The same trend can be observed at the reduction peaks.

The nyquist plot in Fig. 5 indicates the frequency response of electrode. By fitting the data using Randles circuit (inset), Rct of CPE, SBA-15/MCPE and SBA-16/MCPE can be estimated to be 21.25 KΩ, 6.298 KΩ and 4.038 KΩ respectively.

The results show that the presence of SBA-15 and SBA-16 improves electrochemistry behaviors of the surface. This suggest the addition provides meso-sites to the surface which form good electron pathway between the electrode and the electrolyte. Silica is known as non-conducting material and the introduction of silica to the carbon contribute to self-assembled micro-electrode array that attributed by conducting and non-conducting surface [19]. Thus, better electron pathway result in low electron-transfer resistance towards the surface thus significantly improves the response signal [20].

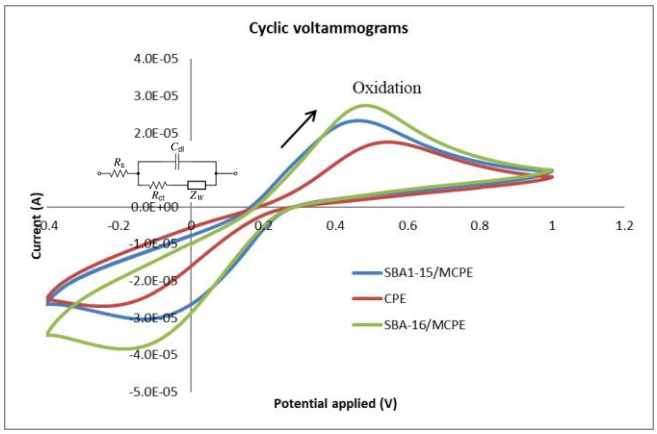


Fig. 4 Cyclic voltammograms of $Fe(CN)_3^{-4/-6}$ containing 0.1 M KCl at CPE and MCPE

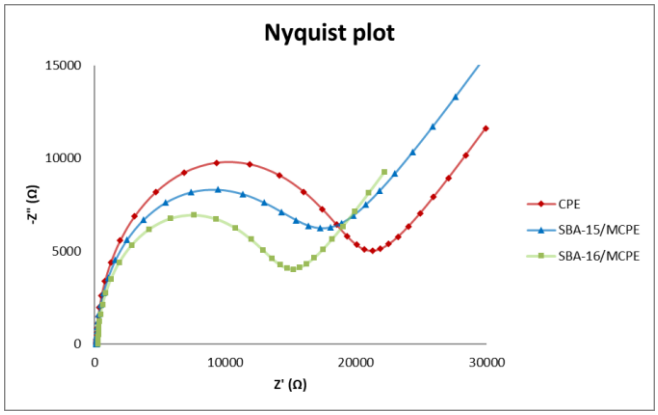


Fig. 5 Nyquist plot at CPE, SBA-15/MCPE and SBA-16/MCPE in 5.0x10-3 Fe(CN)3-4/-6 containing 0.1 M KCl

As a comparison, SBA-16/MCPE has better signal response towards electrolyte and lower resistance in Randles circuit than SBA-15/MPE. This may attribute from different structures that possessed by mesoporous silica SBA-15 and SBA-16. The 3D cubic structure of SBA-16 may efficiently establish the electric conduction pathways throughout the entire system and accommodate the volume expansion [21]. Hence, the response signal of the electrode SBA-16/MCPE increases immensely and higher than electrode SBA-15/MCPE that is composed of 2D hexagonal ordered [22].

IV. CONCLUSION

The mesoporous material SBA-15 and SBA-16 were successfully synthesized with 5.5 nm and 3.2 nm pore size using surfactant templating technique. Electrochemical study indicates that SBA-16/MCPE results highest current by 81% and lower resistance compared to CPE. From the results obtained, the MCPE which combined mesopores materials with carbon shows improvement in electrochemical behaviors due to unique characteristics of mesoporous silica material which prohibit uniform pore, large pores size and high pore volume. Higher fraction of mesopores in the carbon paste (MCPE) mixture supplied higher current densities on the surface which provide many favorable sites for electron transfer and shows a smaller resistance with respect to mainly carbons paste. This study demonstrates that the mesoporous silica can be considered as promising material in the development of high performance, lightweight and flexible devices in electrochemistry. The carbon electrode features can be potentially improved by introducing mesoporous material as meso-sites addition and better understanding in ion transport process through the mesoporous silica carbon pores. The selection of mesoporous material with different structure may affect the behaviors and performance of the electrode.

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