PROCEEDINGS

Volume II

Organized by:
Department of Chemical & Process Engineering,
Faculty of Engineering & Built Environment,
Universiti Kebangsaan Malaysia

In cooperation with:

Co-sponsored by:

InnoBio

15th
REGIONAL SYMPOSIUM
ON
CHEMICAL ENGINEERING
(RSCE)

SYMPOSIUM OF MALAYSIAN
CHEMICAL ENGINEERS
(SOMCHE)

INNOVATIONS FOR
SUSTAINABLE FUTURE

Impiana KLCC Hotel & Spa,
Kuala Lumpur, Malaysia
2nd & 3rd December 2008
PROCEEDINGS

15th REGIONAL SYMPOSIUM ON CHEMICAL ENGINEERING (RSCE)

in conjunction with the

22nd SYMPOSIUM OF MALAYSIAN CHEMICAL ENGINEERS (SOMCheE)

INNOVATIONS FOR SUSTAINABLE FUTURE

VOLUME II

Impiana KLCC Hotel & Spa,
Kuala Lumpur, Malaysia
2-3 December 2008

Organized by:
Department of Chemical & Process Engineering
Faculty of Engineering & Built Environment
Universiti Kebangsaan Malaysia

In cooperation with IChemE (Malaysia)

Sponsored by:
RSCE-SOMCHE 2008
INNOVATIONS FOR SUSTAINABLE FUTURE
VOLUME II

Proceedings of the 15th Regional Symposium On Chemical Engineering in conjunction with the 22nd Symposium Of Malaysian Chemical Engineers
Kuala Lumpur, Malaysia, 2-3 December 2008

Organized by:
Department of Chemical & Process Engineering
Faculty of Engineering & Built Environment
Universiti Kebangsaan Malaysia

Edited by:
Wan Ramli Wan Daud
Mohd Sabri Talrriff
Abdul Wahab Mohammad
Abu Bakar Mohamad
Meor Zainal Meor Talib
Siti Masrinda Tasirin
Siti Rozaimah Sheikh Abdullah
Jamaliah Md Jahim
Nurina Anuar
Masturah Marhom
Shuhaida Harun

FACULTY OF ENGINEERING AND BUILT ENVIRONMENT
UNIVERSITI KEBANGSAAN MALAYSIA
BANGI • 2008

Kuala Lumpur, 2-3 December 2008
RSCE-SOMChe 2008 is the formal proceedings of the 15th Regional Symposium of Chemical Engineering 2008 and the 22nd Symposium of Malaysian Chemical Engineers 2008 jointly held at the Impiana Hotel & Spa in Kuala Lumpur, Malaysia on the 2-3 December 2008. The combined symposia is a continuation of the two highly successful symposia; the former is an important annual forum for academicians, researchers, and practitioners in the South East and Pacific Asian region and the latter is an equally important forum for their Malaysian counterparts, to exchange knowledge and information in the broad area of chemical engineering science and technology. The RSCE-SOMChe 2008 has a pivotal role in improving chemical engineering research and linkages in the ASEAN region as well as in Malaysia.

The theme Innovation for Sustainable Future reflects the urgent need for chemical engineers to practice their art in a sustainable way to ensure future generations will still enjoy a high quality of life. In general, RSCE-SOMChe 2008 highlights the roles of chemical engineering in meeting the challenges and exploring opportunities in sustainable engineering.

As the chief editor of the proceedings, I am delighted that the response of papers has been overwhelming from so many countries. Exactly 402 abstracts were received and accepted but only 300 papers were finally received and accepted for inclusion in both volumes of the proceedings. I am happy to report that authors from 12 countries, 61 universities and 3 companies are participating in this conference. The countries are Malaysia, Australia, Finland, India, Indonesia, Iran, Japan, Singapore, New Zealand, Philippines, Poland & Thailand.

While RSCE-SOMChe 2008 set the pace for regional collaboration and sustainable development in the field of chemical engineering, the symposium also emphasizes innovative chemical engineering in meeting the goals of sustainable engineering. As the Third World develops at a very fast rate, there is concern that indiscriminate use of unsustainable technology there may destroy the environment at an even faster rate leading to environmental and ecological disasters some of which are already emerging.

The first volume of the proceedings contains the plenary papers and papers in the field of biomolecular and bioprocess engineering, complex fluid engineering, clean production and safe practice and food and product technology. The second volume contains papers in advanced materials and nanotechnology, process system engineering, renewable energy and reaction engineering.

The massive editorial effort has been lightened by untiring efforts of fellow editors. Finally I would like to acknowledge with thanks the efforts of Keynote lecturers and all authors in meeting manuscript deadlines and adhering to the format. I would like to apologize to authors if any errors inevitably have crept into their work during the editorial process.

Prof. Ir. Dr. Wan Ramli Wan Daud, Chief Editor, November 19, 2008

Kuala Lumpur, 2-3 December 2008
ACKNOWLEDGEMENT

RSCE-SOMChE 2008 is grateful to the following organizations for their support as co-sponsors and cooperating organizations:

Universiti Kebangsaan Malaysia

Institute of Chemical Engineers (Malaysia)

Petroleum Nasional Berhad (PETRONAS)

BASF PETRONAS Chemicals Sdn. Bhd.

Inno Biologics Sdn. Bhd (InnoBio)
INTERNATIONAL SCIENTIFIC COMMITTEE
(ADVISORY PANEL)

Chairman: Prof. Ir. Dr. Wan Ramli bin Wan Daud (Malaysia)
Prof. Ir. Dr. Mohamad Azlan Hussain (Malaysia)
Prof. Dr. Suryo Purwono (Indonesia)
Assoc. Prof. Dr. Sanggono Adisasmito (Indonesia)
Prof. Dr. Masaaki Suzuki (Japan)
Prof. Dr. Hiroo Niiyama (Japan)
Prof. Dr. Susan A. Roces (Philippines)
Prof. Dr. Maria Natalia R. Dimaano (Philippines)
Prof. Dr. Ching Chi Bun (Singapore)
Prof. Dr. Xu Rong (Singapore)
Prof. Dr. Piyasan Praserthdam (Thailand)
Chutimon Satirapipathkul (Thailand)
Prof. Dr. Tran Vinh Dieu (Vietnam)
Prof. Dr. Le Cong Hoa (Vietnam)
ORGANISING COMMITTEE

Chairman
Ir. Prof. Dr. Wan Ramli Wan Daud

Co Chairman
Assoc. Prof. Ir. Dr. Mohd Sobri Takriff

Secretary
Dr. Manal Ismail

Treasurer
Assoc. Prof. Dr. Siti Kartom Kamarudin

Technical Chairman
Prof. Ir. Dr. Abdul Wahab Mohammad
COMMITTEE

Prof. Dr. Rakmi Abdul Rahman
Prof. Dr. Abu Bakar Mohammed
Prof. Dr. Abdul Amir Hasan Kadhun
Dr. Mohd. TuSirin Mohd Nor
Assoc. Prof. Dr. Zahedi Fisal
Assoc. Prof. Dr. Siti Masrinda Tasirin
Assoc. Prof. Dr. Meor Zainal Meor Talib
Assoc. Prof. Dr. Mohd Sahaid Kalil
Assoc. Prof. Dr. Zahira Yaakob
Assoc. Prof. Dr. Siti Rozaimah Sheikh Abdullah
Dr. Nurina Anuar
Dr. Jamaliah Md Jahim
Dr. Masturah Markom
Noorhisham Tan Kofli
Shuhaida Harun
Reehan Adne Ab. Rahim
Rosiah Rohani
Muhammad Syukri Abd. Rahaman
Nur Tantiyani Ali Othman
Rahaiza Misnon
<table>
<thead>
<tr>
<th>No.</th>
<th>Title of Paper / Authors</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Nanotechnology : Environmental Applications and Implications</td>
<td>K1</td>
</tr>
<tr>
<td></td>
<td>Hossein Kazemian, Technology Park of Tehran University, Tehran, Iran</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Process Systems Engineering Challenges in the Oil &amp; Gas Industries</td>
<td>K9</td>
</tr>
<tr>
<td></td>
<td>M. M. F. Hasan, Jie Li, I. A. Karimi, National University of Singapore, Singapore</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Erik Birgersson and Arun S Mujumdar, National University of Singapore, Singapore</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nobuyoshi Nakagawa, Gunma University, Japan</td>
<td></td>
</tr>
<tr>
<td>No.</td>
<td>Title of Paper / Authors</td>
<td>Page</td>
</tr>
<tr>
<td>-----</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
</tbody>
</table>
| 1.  | Production of carbon nanofibers (CNFS) on impregnated activated carbon  
Yehya M. Ahmed, Abdullah-Al-Mamun, Suleyman Aremu Muyibi, Ma’an Fahmi R. Al-Khatib, Isam Yasin Qudsiah, Mohammed A. AlSaadi, International Islamic University of Malaysia | 1    |
| 2.  | Effect of agricultural waste fiber as reinforcement to plastics manufactured using rotational molding  
| 3.  | The effect of natural rubber modification on morphology and properties of natural rubber (SR-20)/polypropylene blends  
Bahruddin, F. Kurniawansyah, Sumarno, Gede Wibawa, Nonot Soewarno Institute of Technology Sepuluh Nopember | 13   |
| 4.  | Evaluation of granulometric analyses of narrow particle fractions for chosen materials  
Barbara Pesko & Tomasz Niedoba, University of Science and Technology AGH, Poland | 19   |
| 5.  | Optimization on CNT production using modified domestic microwave oven  
Eka Merdeka Prasetya, Joseph Auresenia, Raymond G.R. Tan, Masaaki Suzuki, De la Salle University, Philippines | 27   |
| 6.  | The study of micron-size polystyrene production using anti-solvent technology  
F. Kurniawansyah, N Rahmansyah, WK Marvinanda, Sumarno, Institute of Technology Sepuluh Nopember, Indonesia | 33   |
<table>
<thead>
<tr>
<th>No.</th>
<th>Title of Paper / Authors</th>
<th>Page</th>
</tr>
</thead>
</table>
| 1.  | Synthesis and characterization the composite organic-inorganic membrane using sol-gel process for proton exchange membrane fuel cell (PEMFC)  
A.Mahreni, Universiti Kebangsaan Malaysia                                                      | 467  |
| 2.  | Performance of nano composite membranes as electrolyte for proton exchange membrane fuel cell (PEMFC)  
A.Mahreni, A.B. Mohamad, A. A. H. Kadhum, W.R. W. Daud, Universiti Kebangsaan Malaysia                    | 473  |
| 3.  | Effects of temperature and solvent concentration to the yield of biogasoline from bagasse  
Sri Haryati1, Yetty Irmayania, Selpianaa, Sri Rizki Putri Primandaria                                | 479  |
SYNTHESIS AND CHARACTERIZATION THE COMPOSITE ORGANIC-INORGANIC MEMBRANE USING SOL-GEL PROCESS FOR PROTON EXCHANGE MEMBRANE FUEL CELL (PEMFC)

A. Mahreni, A. B. Mohamad, A. A. H. Kadhum, W. R. W. Daud
Department of Chemical and Process Engineering, Universiti Kebangsaan Malaysia, (UKM) 43600, Bangi, Selangor DE, Malaysia

Keywords: Heteropolyacid (PWA), Nafion, Nanocomposite, Sol-gel

ABSTRACT

Nafion-silicon oxide (SiO_2)-phosphotungstic acid (PWA) composite membrane has been synthesized for medium temperature Proton Exchange Membrane Fuel Cell (PEMFC) application using sol-gel method. X-ray diffraction (XRD) was used to determine saturated absorption of PWA in the silica matrix. A transparent film was achieved at annealing temperature of 140°C over 10 hours duration. The film than was characterized by Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and Fourier Transform Infrared Spectroscopy (FTIR). The SEM and TEM results indicated homogenous structure of the Nafion-SiO_2-PWA composite membrane with SiO_2 and PWA particles size less then 10 nm. X-Ray Diffraction (XRD) result showed that the maximum loading of PWA in the SiO_2 matrix is in the ratio of PWA/SiO_2 equal to 0.45 (wt/wt.). The vibration absorption peak of Si-O-Si bond at 800 cm\(^{-1}\) and W-O-W at 755 cm\(^{-1}\) were observed thus indicated the inorganic compound was embedded in the Nafion matrix and did not leach out after washing treatment using acid and base solutions.

INTRODUCTION

Perfluorosulfonic acid (PFSA) membrane (e.g. Nafion) is not suitable for low relative humidity PEMFC application because the conductivity of PFSA membrane was dramatically reduced at low relative humidity (RH). Therefore, a need exists to develop membrane for PEMs application that are functional at low operating RHs.

Nafion based organic/inorganic composite membrane with heteropolyacid (phosphotungstic acid, PWA) additive using tetraethoxyorthosilicate (TEOS) as immobilizer to the PWA have been investigated as alternative material for low humidity PEMFC operation.
The aim of this experiment is to prepare the Nafion-SiO₂-PWA composite membrane using solution phase sol-gel method with incorporation of silica and PWA in the Nafion cluster to produce Nafion-SiO₂-PWA nanocomposite membrane. XRD was utilized to determine the maximum PWA loading in the silica matrix. The parameters that have been studied are: (i) annealing time and (ii) ratio of SiO₂/Nafion to the physic-chemical properties of the composite membrane.

MATERIALS AND METHOD

Materials
Nafion solution of 5 wt% (EW 1100 Dupont), TEOS (Si(OEt)₄) 98%, PWA (H₃PW₁₂O₄₀) 96%, Dimethylformamide (DMF), Sulfuric acid (H₂SO₄) 98%, Hydrogen Peroxide (H₂O₂) 30% were all purchased from Aldrich. Deionized water was used as solvent in all the experiments.

Method
Membrane Preparation.
Appropriately 5% wt Nafion solution was evaporated at room temperature to obtain solid Nafion. Solid Nafion was dissolved in DMF solvent to obtain 5% wt Nafion solution in DMF. PWA was also dissolved in deionized water and then mixed with TEOS at weight ratio of PWA:SiO₂ = 4:10. Subsequently, it was stirred in an ultrasonic bath for 30 min, and added to the Nafion-DMF solution and further stirred in an ultrasonic bath for 6 hours. The mixture was allowed to stand at room condition to release trapped air bubbles for another 24 hours without mixing. This solution was casted in a Petri dish and heated at 80°c for 2 hours to remove the solvent. In order to enhance the mechanical properties of the composite matrix, heating was continuously applied at 140°c at different periods of 2, 4, 6 and 10 hours until transparent membrane was obtained. Then, the recast composite membrane was made to detach from the Petri dish by boiling it in the de-ionized water. Finally, the membrane was cleaned by heating at 80°c in the solution of 3 wt. % H₂O₂, de-ionized water, 0.5M H₂SO₄ and again in de-ionized water until the pH of the washing water becomes almost neutral. These composite membranes are designated NS10W, NS15W and NS20W, whose specifications in ratio of Nafion/TEOS/PWA are 100:10:1.1538; 100:15:1.7303 and 100:20:2.3072 (wt./wt./wt.), respectively.

RESULTS AND DISCUSSION

Saturated Loading of PWA Particle in the SiO₂ Matrix
The XRD pattern of pure silica, pure PWA and the mixture of Silica-PWA are as show in Fig 1. The amount of heteropolyacid (PWA) loaded on silica was limited
The aim of this experiment is to prepare the Nafion-SiO₂-PWA composite membrane using solution phase sol-gel method with incorporation of silica and PWA in the Nafion cluster to produce Nafion-SiO₂-PWA nanocomposite silica matrix. XRD was utilized to determine the maximum PWA loading in the membrane. The parameters that have been studied are: (i) annealing time and (ii) ratio of SiO₂/Nafion to the physic-chemical properties of the composite membrane.

MATERIALS AND METHOD

Materials
Nafion solution of 5 wt% (EW 1100 Dupont), TEOS (Si(OH₂)₄) 98%, PWA (H₃PW₁₂O₄₀) 96%, Dimethylformamide (DMF), Sulfuric acid (H₂SO₄) 98%, Hydrogen Peroxide (H₂O₂) 30% were all purchased from Aldrich. Deionized water was used as solvent in all the experiments.

Method
Membrane Preparation.
Approximately 5% wt Nafion solution was evaporated at room temperature to obtain solid Nafion. Solid Nafion was dissolved in DMF solvent to obtain 5% wt Nafion solution in DMF. PWA was also dissolved in deionized water and then mixed with TEOS at weight ratio of PWA:SiO₂ = 4:10. Subsequently, it was stirred in an ultrasonic bath for 30 min, and added to the Nafion-DMF solution and further stirred in an ultrasonic bath for 6 hours. The mixture was allowed to stand at room condition to release trapped air bubbles for another 24 hours without mixing. This solution was casted in a Petri dish and heated at 80°C for 2 hours to remove the solvent. In order to enhance the mechanical properties of the composite matrix, heating was continuously applied at 140°C at different periods of 2, 4, 6 and 10 hours until transparent membrane was obtained. Then, the recast composite membrane was made to detach from the Petri dish by boiling it in the de-ionized water. Finally, the membrane was cleaned by heating at 80°C in the solution of 3 wt. % H₂O₂, de-ionized water, 0.5M H₂SO₄ and again in de-ionized water until the pH of the washing water becomes almost neutral. These composite membranes are designated NS10W, NS15W and NS20W, whose specifications in ratio of Nafion/TEOS/PWA are 100:10:1.1538; 100:15:1.7303 and 100:20:2.3072 (wt./wt./wt.), respectively.

RESULTS AND DISCUSSION

Saturated Loading of PWA Particle in the SiO₂ Matrix
The XRD pattern of pure silica, pure PWA and the mixture of Silica-PWA are as show in Fig 1. The amount of heteropolyacid (PWA) loaded on silica was limited
by the uptake characteristics of silica. Fig 1(a-b) show consecutively the XRD pattern of PWA crystalline and silica amorphous phase. While Fig 1(c-e) show the XRD pattern of the PWA entrapped on silica with the ratio of PWA/SiO$_2$ is 0.45, 0.6 and 0.15 (wt/wt.), respectively. The selected of PWA loaded amount correspond to uniform distribution of the PWA on the silica pore shows overlapping between the typical crystalline structure of PWA and the amorphous structure of silica at ratio of PWA/SiO$_2$ is (0.15) and (0.45) (wt/wt.).

![Figure 1. XRD Pattern of (a) Pure PWA, (b) Pure SiO$_2$, (c) Ratio of PWA/SiO$_2$ (0.45), (d) Ratio PWA/SiO$_2$ (0.6) and (e) Ratio PWA/SiO$_2$ (0.15).](image)

Fig 1(c) and Fig 1(e) revealed an overlapping between the typical crystalline structure of PWA and the amorphous structure of silica. The results indicated that at the ratio of PWA/SiO$_2$ (0.15) until 0.45 all of the PWA particles have inserted in the silica pores and the peak assign to the PWA particle has disappeared. If the ratio of PWA/SiO$_2$ increase to 0.6, a different spectral pattern is obtained that the sharp spectral peak attributed to the presence of PWA crystalline in the SiO$_2$-PWA mixture appear. It means that a part of PWA particle is not insert in the silica pores cause the silica pore has been full filled by PWA particles and saturated loading has been reached. Therefore it can be conclude that the saturated PWA loading on the silica pore is best at the ratio of 0.45 (wt/wt.) as show by Fig 1 (c). This ratio will be used for the designed of the composition of NS10W, NS15W and NS20W composite membrane prepared using sol-gel method.

Clarity analysis to optimize annealing time and temperature
The time required to produce transparent membrane is 10 hours at annealing temperature 140°C for all the composite membranes. After the post treatment of
washing and drying, the membrane was analyzed using UV-VIS spectrophotometer, to determine qualitatively the amount of inorganic phase distribution in the organic polymer matrix. The transparency of the composite membrane is a measure of inorganic phase distribution in the range of nanoscale dimension in the organic polymer matrix [Khana, P.K. et al. 2005]. If phase dissociation has taken place, the composite membrane formed is neither transparent nor translucent. Phase separation and homogeneity of the particle distribution also influence the mechanical strength properties of the membrane. Physical visibility of Nafion 112 (commercial) and all the composite membranes are transparent in the UV-VIS spectrum at the annealing time of 10 hours and temperature of 140°C, which indicated the absence of the phase separation of both the inorganic and organic phase (The UV-VIS) result is shown in [Mahreni, A et al. 2008].

The result also showed that there are chemical interactions taking place between the organic and inorganic compounds through the hydrogen bonding between the sulfonate group of Nafion polymer and the hydroxyl (OH) group of the silanol Si(OH) produced via the hydrolysis of TEOS molecules. On the other hand, the electrostatic interactions between the ions of H₃PW₁₂O₄₀ and SiOH took place in the composite membrane material. Therefore, the composite membrane has strong bonding between organic-inorganic compounds, which could have been responsible for the transparency and homogeneous distribution of the inorganic phase in the organic matrix.

SEM and TEM analysis
The morphology of the composite Nafion-SiO₂ recasted membrane are shown in Fig 2. It can be seen that the solid SiO₂ and PWA are uniformly distributed within the membrane and do not form any agglomerate structures. The thickness of composite membrane is measured to be 70 ± 5 μm.

![Figure 2.](image)

(a) SEM Cross Section Image of Nafion 112 (Commercial)  
(b) NS15W With Magnification 10,000 X, (c) TEM Cross Section Image of NS15W Membrane With Magnification 60,000 X, (NS10W and NS20W are not shown)

FTIR analysis
The interactions between SO₃H and SiOH and PWA were studied by FTIR which were used to monitor the formation of Nafion/SiO₂/PWA nanocomposite film [Ramani, V. et al. 2005]. The FTIR spectra at 4000-400 cm⁻¹ were shown in Fig.
3. The major vibration associated with the Nafion membrane (Fig. 3a) were found in N112, NS10W, NS20W nano-composite membranes. The two C–F stretching vibrations of the PTFE backbone can be observed at 1194 cm⁻¹ and 1134 cm⁻¹. The peaks observed at 1054 cm⁻¹ and 9670 cm⁻¹ were attributed to the stretching vibration moieties of SO₃⁻ and C–O–C, respectively. IR spectra for bonding structure of C-O-C of Nafion membrane at wave number (967 cm⁻¹) shifts to lower wave number of 967 cm⁻¹ for NS15W composite membranes. This phenomenon can be attributed to the strong interactions of SiO₂ component and sulfonate groups in side chain of the Nafion polymer [Ramani V. et al. 2004] [Shao Z.G. et al. 2004]

The observable peak at 980 cm⁻¹ represents the vibration moiety of the W=O functional group. Therefore, it is evident from these data that the SiO₂ and PWA are indeed present in the composite membranes even after these membranes had undergone the pretreatment process of washing using 3wt % H₂O₂ and 0.5 M H₂SO₄ solution at the temperature of 80°C for 1 hour. It is apparent that the SiO₂ and PWA are compatible with Nafion membrane and the PWA is able to be immobilized into the SiO₂ media.

![Figure 3](image_url)

FTIR Spectra of (a) N112 Commercial Membrane, NS10W and NS20 Composite Membrane for NS15W is not shown (b) NS20W Composite Membrane
CONCLUSION

Nafion-SiO₂-PWA composite membrane has been successfully made using sol-gel method at solvent evaporation temperature of 80°C and annealing temperature of 140°C for 10 hours at fixed ratio of PWA/SiO₂ = 0.4 (wt./wt.). All of the composite membrane synthesized at above conditions showed transparent visibility and suggested that the homogeneous distributions of the inorganic particles in the nano dimension of the organic matrix. The SEM and TEM measurements showed homogeneous structure of the composite and the particle size of less than 10 nm is obtained. The observable peak at 980 cm⁻¹ represents the vibration moiety of the W=O functional group. Therefore, it is evident that the SiO₂ and PWA are indeed present in the composite membranes even after these membranes had undergone the pretreatment process. It is apparent that the SiO₂ and PWA are compatible with Nafion membrane and the PWA is able to be immobilized into the SiO₂ media.

REFERENCE


