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(54) Title: FORWARD OSMOSIS HOLLOW FIBER MEMBRANE

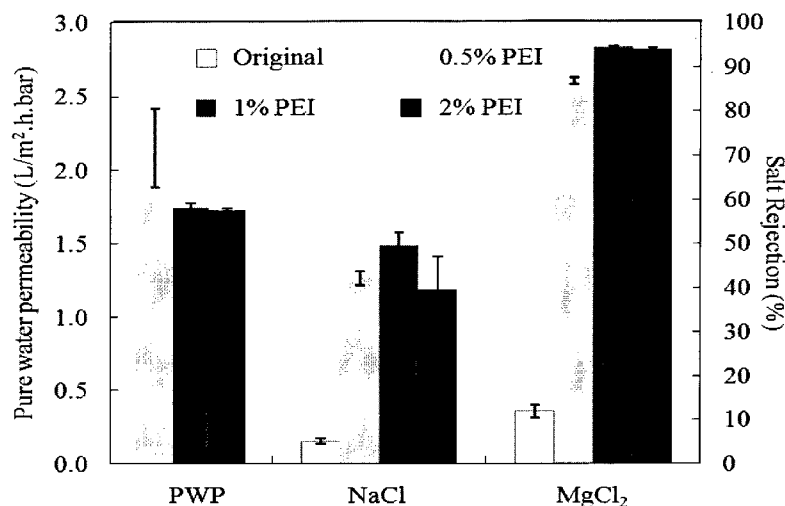


FIGURE 2

(57) Abstract: Present invention relates to a method for forming a nanofiltration hollow fiber membrane comprising a poly(amide-imide) (PAI) hollow fiber substrate having a polyethyleneimine (PEI)-cross-linked PAI surface layer. This membrane is suitable for forward osmosis applications. The method comprises contacting the PAI hollow fiber substrate with an aqueous solution of polyethyleneimine (PEI) under conditions suitable for cross-linking PAI in the surface layer of the PAI hollow fiber substrate by PEI.



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FORWARD OSMOSIS HOLLOW FIBER MEMBRANE

Cross-Reference to Related Application

[0001] This application claims the benefit of priority of United States of America Provisional Patent Application No. 61/417,758, filed 29 November 2010, the contents of which being hereby incorporated by reference in its entirety for all purposes.

Technical Field

[0002] The invention relates to a method of forming a nanofiltration hollow fiber membrane, and in particular, a poly(amide-imide) hollow fiber membrane, which is suitable for use in forward osmosis applications.

Background

[0003] Forward osmosis (FO) process is a natural phenomenon, which can be defined as the net movement of water molecules across a semi-permeable membrane from a less concentrated solution to a more concentrated solution. FO process utilizes an osmotic pressure gradient instead of hydraulic pressure or temperature as a driving force, thus it has the potential to produce water with less energy consumption and is well suited for a wide range of potential applications, including wastewater treatment, water purification, seawater desalination, as well as power generation.

[0004] However, the main drawback of FO system is the permeate flux decline due to internal concentration polarization in the dense substrate when conventional reverse osmosis (RO) membranes were used.

[0005] As an alternative option, nanofiltration (NF) membranes have been explored for use in FO process due to their properties of 'loose' RO and high rejections to

multivalent salts. For instance, it has been reported that polybenzimidazole (PBI) NF hollow fiber membranes with a desirable mean pore size can be used for FO process. Under FO tests using 1M MgCl_2 as the draw solution, these membranes showed water flux of 4 and 6 $\text{L/m}^2\cdot\text{h}$ for the configurations of active layer facing feed water (AL-facing-FW) and active layer facing draw solution (AL-facing-DS), respectively. PBI, however, has poor mechanical strength for fabrication of self-standing membranes.

[0006] In another example, cellulose acetate NF hollow fiber membrane was fabricated and explored for its FO application. The membrane exhibited water flux in the range of 2.7 to 7.3 $\text{L/m}^2\cdot\text{h}$ with 0.5 to 2.0 M MgCl_2 draw solutions for the AL-facing-DS orientation and 1.8 to 5.0 $\text{L/m}^2\cdot\text{h}$ with the same draw solutions for the AL-facing-FW orientation. Hydrophilic polymers such as cellulose and its derivatives exhibit good properties as membrane materials in desalination applications. However, these polymers are very sensitive to thermal, chemical and biological degradation. Hydrolysis of this type of materials occurs very rapidly in alkaline conditions. The separation process using cellulose-based membranes must therefore be carried out at an optimum pH of 4 to 6.5 at ambient temperature.

Summary

[0007] Various embodiments provide for a poly(amide-imide) (PAI) hollow fiber membrane with improved properties and performance.

[0008] According to a first aspect of the invention, there is provided a method for forming a nanofiltration hollow fiber membrane comprising a PAI hollow fiber substrate having a polyethyleneimine (PEI)-cross-linked PAI surface layer, the method comprising contacting the PAI hollow fiber substrate with an aqueous solution of PEI

under conditions suitable for cross-linking PAI in the surface layer of the PAI hollow fiber substrate by PEI.

[0009] According to another aspect of the invention, there is provided a nanofiltration hollow fiber membrane comprising poly(amide-imide) (PAI) hollow fibers, wherein the surface of the PAI hollow fibers comprises PAI cross-linked by polyethyleneimine (PEI).

[0010] According to a further aspect, the use of the nanofiltration hollow fiber membrane in a forward osmosis process is provided.

Brief Description of the Drawings

[0011] In the drawings, like reference characters generally refer to the same parts throughout the different views. The drawings are not necessarily drawn to scale, emphasis instead generally being placed upon illustrating the principles of various embodiments. In the following description, various embodiments of the invention are described with reference to the following drawings.

[0012] **Figure 1** shows the cross-section morphology of PAI hollow fiber substrates of Example 1 at (a)(i) 30X and (a)(ii) 200X, Example 2 at (b)(i) 30X and (b)(ii) 200X, and Example 3 at (c)(i) 30X and (c)(ii) 200X.

[0013] **Figure 2** shows salt rejections of Example 1 membranes immersed in various concentrations of PEI solution at 70°C for 120 min.

[0014] **Figure 3** shows the effect of post-treatment time on filtration performance of treated Example 1 membrane (test conditions: 1.0 bar, room temperature and 500ppm salt aqueous solution; post-treatment conditions: 70°C and 1 wt% PEI solution).

[0015] **Figure 4** shows the cross-section morphology of Example 1 PAI hollow fiber after post treatment: (a) enlarged at 30X; (b) enlarged at 200X; Outer surface

morphology of Example 1 PAI hollow fiber: (c) after post treatment, enlarged at 20KX; (d) before post treatment, enlarged at 20KX. (Post-treatment condition: 1 wt% PEI solution at 70°C for 2h).

[0016] **Figure 5** shows ATR-FTIR spectra of the Example 1 substrate before post-treatment (top) and after post treatment (bottom). The inset is the spectra in the wave number region of 1520-1670 cm^{-1} . (Post-treatment conditions: 1 wt% PEI solution at 70°C for 2h).

[0017] **Figure 6** shows the reaction scheme between (a) poly(amide-imide) (PAI) and (b) polyethyleneimine (PEI); (c) cross-linked PAI.

[0018] **Figure 7** shows zeta potential of Example 1 hollow fiber membrane before and after post-treatment (*post-treatment conditions: 1 wt% PEI solution at 70°C for 2h).

[0019] **Figure 8** shows the rejection behaviors of treated Example 1 membrane to various salts (test conditions: 1.0 bar, room temperature and 500ppm salt aqueous solution; post-treatment conditions: 1 wt% PEI solution at 70°C).

[0020] **Figure 9(a), (b)** show FO experimental results of (i) water flux and (ii) J_S/J_V in two configurations (▲ AL-facing-DS; ■ AL-facing-FW) for the membranes of Example 2 and 3, respectively.

[0021] **Figure 10** shows an illustration of effective osmotic pressure difference in a positively charged FO membrane (a) AL-facing-FW; (b) AL-facing DS.

Description

[0022] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practised. These embodiments are described in sufficient detail to enable those skilled in the art to practise the invention. Other embodiments may be utilized and

structural, logical, and electrical changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0023] Various embodiments of the present invention provide a poly(amide-imide) (PAI) hollow fiber membrane.

[0024] Hollow fiber membranes have large lumen with an inner diameter of more than 1mm. A larger lumen of the membrane is favorable to the fluid flow inside the lumen with less resistance. Further, hollow fiber membranes are suitable for FO processes because they are self-supported and possess a flow pattern necessary for FO process. Additionally, it is much simpler to fabricate a hollow fiber module with a high packing density. Accordingly, the present invention offers a simple fabrication process, a tailorable membrane structure and a promising membrane performance in the AL-facing-FW configuration for FO applications.

[0025] PAIs are thermoplastic amorphous polymers possessing a positive synergy of properties from both polyamides and polyimides and thus have exceptional mechanical, thermal and chemical resistant properties. PAI presents a good chemical stability at a wide pH range and a high resistance to many organic solvents because of its ability to form intra- and inter-chain hydrogen bonding. In addition, PAI can be utilized in hollow fiber membrane fabrication using non-solvent induced phase separation (NIPS) technique. PAIs are mainly produced by Solvay Advanced Polymers under the trademark Torlon (Torlon®). There are three types of Torlon® PAI materials that can be used in membrane fabrication: Torlon 4000T-LV (low viscosity), MV (medium viscosity), and HV (high viscosity). In one embodiment, Torlon 4000T-MV is used in the present invention. Torlon® PAI powders are suitable for use in other high

performance forms. For example, these powders are soluble in dipolar aprotic solvents such as N-methyl pyrrolidone (NMP), dimethylacetamide (DMAC), dimethylsulfoxide (DMSO) and dimethylformamide (DMF). Solutions of these systems are spun into fibers to form hollow fiber membrane substrates.

[0026] Hollow fiber spinning technique is well established in the art and has been reported in detailed by Shi *et al.* (*J Membrane Sci.* 305 (2007) 215-225), for example. Briefly, the dope was dispensed under pressure through a spinneret at a controlled rate, and went through an air gap before immersing into a coagulation bath. Tap water was used as external coagulant while the mixtures of Milli-Q Water and NMP with different ratios were used as the bore fluid. The nascent hollow fiber was taken up by a roller at a certain velocity and stored in a water bath to remove residual solvent for at least 2 days. A post-treatment was performed to alleviate the membrane substrate shrinkage and pores collapse during drying process at ambient condition. The membrane substrate was immersed into a water/glycerol mixture for 24 h. This process allowed the glycerol to replace water gradually in the membrane substrate pores. The membrane substrates were subsequently dried at room temperature prior to the characterization tests and further applications. The glycerol inside the membrane substrate pores can act as the pore supporter to alleviate the collapse of pores during membrane substrate drying process.

[0027] In various embodiments, the nanofiltration hollow fiber membrane includes a PAI hollow fiber substrate having a polyethyleneimine (PEI)-cross-linked PAI surface layer. The PAI-PEI cross-linked selective layer is supported on the PAI hollow fiber substrate which provides the mechanical strength to the resultant hollow fiber membrane. Asymmetric microporous hollow fibers made of Torlon® PAI material are used as the porous substrate. The present invention has utilized the unique feature of

PAI, i.e. the imide group in PAI interacts with an amine-functionalized polyelectrolyte (i.e. PEI) by forming cross-linking to form a positively charged diamine on the membrane surface. The PAI-PEI cross-linked selective layer is NF-like, i.e. the nominal pore size of the PAI-PEI cross-linked selective layer is in the nanometer range, such as about 0.5 to about 2 nm, similar to pore sizes of nanofiltration membranes.

[0028] Figure 6 shows in one embodiment (a) a poly(amide-imide) (PAI), (b) polyethyleneimine (PEI), and (c) the cross-linked PAI-PEI.

[0029] The hollow fiber membrane is formed by contacting the hollow fiber substrate with an aqueous solution of PEI under conditions suitable for cross-linking PAI in the surface layer of the PAI hollow fiber substrate by PEI.

[0030] In various embodiments, the hollow fiber substrate is immersed in the aqueous PEI solution. Alternatively, the aqueous solution of PEI is circulated around the hollow fiber substrate by using a pump. In one embodiment, PEI ethylenediamine end-capped was used to perform the chemical post-treatment of the hollow fiber substrate. For example, about 500mL of PEI aqueous solution may be used.

[0031] In certain embodiments, the concentration of the aqueous PEI solution ranges from between about 0.2 to about 5 wt%. For example, the concentration of the aqueous PEI solution may be about 1 wt%.

[0032] According to various embodiments, the hollow fiber substrate is contacted with the aqueous PEI solution at a temperature of between about 50°C and about 80°C for the cross-linking reaction between the PAI hollow fiber substrate and PEI to occur. For example, the reaction temperature may be about 70°C.

[0033] In further embodiments, the hollow fiber substrate is contacted with the aqueous PEI solution for a period of between about 1 and about 180 min, such as about 120 min.

[0034] As mentioned above, the hollow fiber substrates may be formed by spinning technique. In one embodiment, the hollow fiber substrate is formed by dry-jet wet spinning. The dry-jet wet spinning includes dispensing a polymer dope solution and a bore fluid through a spinneret into a coagulation bath and removing the spun hollow fiber substrate from the coagulation bath.

[0035] In certain embodiments, the polymer dope solution includes poly(amide-imide) dissolved in a solvent selected from the group consisting of N-methyl-2-pyrrolidone (NMP), dimethylacetamide (DMAc), dimethylsulfoxide (DMSO) and dimethylformamide (DMF).

[0036] Additionally, the polymer dope solution may further include additives such as a pore former. Any pore formers are suitable so long as they can dissolve in the respective solvents for PAI. For example, suitable pore formers include, but are not limited to, organic pore formers such as PEG, polyvinylpyrrolidone (PVP), pluronic, alcohol (methanol, ethanol, iso-propanol, glycerol), and ethylene glycol, inorganic salt pore formers such as lithium chloride (LiCl), LiBr, KClO₄, or water. In one embodiment, the pore former may be LiCl.

[0037] In various embodiments, the bore fluid may be water or a mixture of NMP and water.

[0038] In order that the invention may be readily understood and put into practical effect, particular embodiments will now be described by way of the following non-limiting examples.

Examples

Experiments and Methods

Materials

[0039] Torlon® 4000T (copolymer of amide and imide) (PAI), supplied by Solvay Advanced Polymers (Alpharetta GA), was used to make porous hollow fiber substrates. N-Methyl-2-pyrrolidone (NMP, > 99.5%, CAS#872-50-4, Merck Chemicals, Singapore) and lithium chloride (LiCl, anhydrous, CAS#7447-41-8, MP Biomed) were used as a solvent and pore former, respectively. Purified water by a Milli-Q system (18MΩcm) was used as the internal coagulant. Dextrans with different molecular weights (from 6,000 to 500,000 Da, (C₆H₁₀O₅)_n, CAS#9004-54-0, Sigma) were used to characterize the molecular weight cut off (MWCO) of hollow fiber membranes. Polyethyleneimine (PEI) ethylenediamine end-capped (Sigma Aldrich) was used to perform chemical post-treatment of the hollow fiber substrate. For filtration experiments, sodium chloride (NaCl, ≥ 99%), magnesium chloride (MgCl₂, hexahydrate), sodium sulfate (Na₂SO₄, anhydrous), magnesium sulfate (MgSO₄, heptahydrate) were purchased from Merck. All the reagents were used as received.

General Scheme for Fabricating Hollow Fiber Membrane Substrate

[0040] PAI was dried in a 50°C vacuum oven for at least 12 h to remove moisture prior to the preparation of dope solutions. The polymer was then dissolved into NMP in a jacket flask equipped with a mechanical stirrer in a temperature of about 60 °C for 3 days. Once the polymer was dissolved completely, a desired amount of LiCl was added and stirred until homogeneous solution can be attained, followed by filtering and degassing prior to spinning.

[0041] Hollow fiber spinning technique is well established in the art and has been reported in detailed by Shi *et al.* (*J Membrane Sci.* 305 (2007) 215-225), for example. Briefly, the dope was dispensed under pressure through a spinneret at a controlled rate, and went through an air gap before immersing into a coagulation bath. Tap water was

used as external coagulant while the mixtures of Milli-Q Water and NMP with different ratios were used as the bore fluid. The nascent hollow fiber was taken up by a roller at a certain velocity and stored in a water bath to remove residual solvent for at least 2 days. A post-treatment was performed to alleviate the membrane substrate shrinkage and pores collapse during drying process at ambient condition. The membrane substrate was immersed into a water/glycerol mixture for 24 h. This process allowed the glycerol to replace water gradually in the membrane substrate pores. The membrane substrates were subsequently dried at room temperature prior to the characterization tests and further applications. The glycerol inside the membrane substrate pores can act as the pore supporter to alleviate the collapse of pores during membrane substrate drying process.

[0042] In the following examples, the hollow fiber membrane substrates were prepared using PAI dissolved in NMP or DMAc solvent. The concentrations of the polymer range from about 12 to about 25 wt.%. Water, LiCl or poly(ethylene glycol) (PEG) with a concentration ranging from about 1 to about 10 wt.% is adopted as a non-solvent additive in the dope solution. A mixture of NMP and water of certain weight ratios of between about 0/100 and about 50/50 is adopted as the bore fluid.

[0043] The temperature of the spinneret is controlled at between about 15 °C and about 40 °C. An air gap of about 0.2 cm to about 20 cm is used. The hollow fiber membrane substrate preferably has an outer diameter of about 800 μm to about 2000 μm, more preferably about 1000 μm to about 1500 μm, and an inner diameter of about 500 μm to about 1300 μm, more preferably about 800 μm to about 1200 μm.

General Scheme for Forming A Dense Skin Layer of the Hollow Fiber Membrane

[0044] The formation of a NF-like skin layer on the outer surface of the PAI hollow fiber membrane substrate was made based on chemical cross-linking reaction, which was conducted by immersing the hollow fiber membrane substrate into a 500 mL of PEI aqueous solution at temperature of about 50 °C to about 80 °C. The reaction time was varied from about 0 to about 180 min and the PEI concentration was varied from about 0.2 % to about 5 % (wt/wt). Next, the membranes were rinsed using purified water and stored for characterization.

Example 1

[0045] PAI hollow fiber membrane substrates (ST#1) were made of a polymer dope solution consisting of 20 wt.% PAI in NMP. The dope extrusion rate was 6 g/min, while the bore fluid composition used was purely water (i.e. NMP and water ratio is 0/100 vol.%) with a flow rate of 4 ml/min. Tap water with room temperature around 23 °C was used as the coagulant. The air gap used was 5 cm. The details of dry-jet wet spinning conditions are listed in **Table 1**.

[0046] After spinning, the hollow fiber membrane substrate was immersed in a 500 mL of PEI aqueous solution at temperature of 70 °C. The reaction time was 120 min and the PEI concentration was 1 % (wt/wt). Next, the membranes were rinsed using purified water and stored for characterization.

Example 2

[0047] PAI hollow fiber membrane substrates (ST#2) were made of a polymer dope solution consisting of 15 wt.% PAI in NMP with 2 wt.% LiCl. The dope extrusion rate was 6 g/min, while the bore fluid composition used was a mixture of NMP and water

(25/75 vol.%) with a flow rate of 8 ml/min. Tap water with room temperature around 23 °C was used as the coagulant. The air gap used was 5 cm. The details of dry-jet wet spinning conditions are listed in **Table 1**. The chemical cross-linking conditions are the same as those used in Example 1.

Example 3

[0048] PAI hollow fiber membrane substrates (ST#3) were made of a polymer dope solution consisting of 15 wt.% PAI in NMP with 3 wt.% LiCl. The dope extrusion rate was 6 g/min, while the bore fluid composition used was a mixture of NMP and water (25/75 vol.%) with a flow rate of 8 ml/min. Tap water with room temperature around 23 °C was used as the coagulant. The air gap used was 5 cm. The details of dry-jet wet spinning conditions are listed in **Table 1**. The chemical cross-linking conditions are the same as those used in Example 1.

Parameters	ST#1	ST#2	ST#3
Dope composition (PAI/LiCl/NMP) (wt.%)	20/0/80	15/2/83	15/3/82
Dope flow rate (g min ⁻¹)	6.0	6.0	6.0
Bore fluid (NMP/H ₂ O) (vol.%)	0/100	25/75	25/75
Bore fluid flow rate (mL min ⁻¹)	4.0	8.0	8.0
Air gap (cm)	5.0	5.0	5.0
Take up speed	free fall	free fall	free fall
External coagulant	tap water	tap water	tap water
Spinning temperature (°C)	23	23	23
Spinneret diameter (mm)	1.50	1.50	1.50
ID of bore fluid needle (mm)	0.70	0.70	0.70

Table 1. Spinning conditions and parameters used in Examples 1, 2, and 3

Characterization of PAI Hollow Fiber Membrane Substrates

[0049] The structure and morphology of the resultant membranes were examined by a Zeiss EVO 50 SEM. The average overall porosity of the membrane was determined by gravimetric method which measures the weight of isopropyl alcohol as the wetting solvent contained in membrane pores. Tensile strength test of the hollow fiber membranes was performed using a Zwick 0.5kN Universal Testing Machine at room temperature. To perform pure water permeability (PWP) and molecular weight cut-off (MWCO) measurement, two hollow fiber modules were made. Every module consisted of four fibers with an effective length of 25 cm. Compaction was carried out at 1 bar for 2h prior to measurement. DI water was circulated through the shell and lumen side of the membrane module at 1 bar to get PWP. MWCO of PAI hollow fiber substrate was determined by the filtration method using a 2000 ppm dextran solution and analyzed by gel permeation chromatography (GPC) on a Polymer Laboratories-GPC 50 plus system (double PL aquagel-OH Mixed-M 8 μ columns). The dextran solution was made by a mixture of several different molecular weights from 6,000 Da to 500,000 Da.

Membrane Surface Charge

[0050] Membrane surface charge (zeta potential) was observed based on the streaming potential measurement by using a SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria). An electrolyte solution of 10 mM potassium chloride (KCl, Merck, Singapore) solution was circulated through a cylindrical measuring cell containing the membrane sample. The streaming potential was detected by Ag/AgCl electrodes located at both ends of the sample. Automatic titration was performed using a 0.1 M hydrochloric acid (HCl, Qrec) solution and a 0.1 M sodium hydroxide (NaOH, Merck, Singapore)

solution to investigate the effect of pH on membrane surface charge. The Fairbrother-Mastin approach was used to determine the zeta potential of the membrane.

Confirmation of the Chemical Reaction in the Post-Treatment

[0051] The chemical reaction occurring in the post-treatment was confirmed by a fourier transformed infra red spectrometer (FTIR, Perkin Elmer, Spectrum 2000) using the attenuated total reflection (ATR) with ZnSe crystal method. The hollow fiber membranes were dried in a vacuum oven overnight before the analysis.

PWP and Salt Rejection

[0052] Four pieces of hollow fibers were potted into a tube (effective length of 25 cm) and sealed by epoxy. The performance of PWP and salt rejection of chemically modified PAI hollow fibers was tested in a bench scale cross-flow filtration unit. The hydraulic pressure up to 1.5 bar was applied on the shell side of hollow fiber membrane module to obtain water permeability coefficient (A) using DI water. The salt rejection experiment was carried out using a 500 ppm salt solution based on conductivity measurements (Ultrameter II, Myron L Company, Carlsbad, CA) of permeate and feed water.

Performance in FO Process

[0053] The same modules used for PWP and salt rejection measurements were used for FO experiment. Two-variable-speed gear pumps were used to supply feed (purified water) and draw solutions (MgCl_2 , etc.), respectively. The volumetric flow rates of the shell side and lumen side were 1500 mL/min and 450 mL/min, respectively, to ensure a similar Reynolds number (around 2600) of the liquid flowing both in the module shell

and fiber lumen. FO experiments were performed in two configurations: active layer facing draw solution (AL-facing-DS) and active layer facing feed water (AL-facing-FW). The draw solution either flowed in the shell side of the module (AL-facing-DS) or in the lumen of the hollow fibers (AL-facing-FW). The volumetric water flux, J_v , was determined at a certain time interval by measuring the weight changes of the feed tank with a digital mass balance connected to a data logging system. The FO test was conducted at room temperature of 23 °C.

Results and Discussion

Morphology and Property of PAI Hollow Fiber Membrane Substrates

[0054] Figure 1 shows the cross-section morphologies of SEM for three PAI hollow fiber membrane substrates (ST#1, ST#2, and ST#3) prepared by a variation of dope composition and spinning parameter, as indicated in **Table 1**. It can be seen that these substrates exhibited similar cross-section morphologies in which the finger-like structures were developed simultaneously beneath the inner and outer surfaces without forming large macro-voids. However, the ST#1 hollow fiber substrate presented the thickest sponge-like structure in the middle of the cross-section, followed by the ST#2 and ST#3 hollow fiber substrates, as shown in Figure 1(a)(ii), (b)(ii) and (c)(ii). Moreover, the difference in wall thickness of the fibers can be easily observed. The thinner walls for the ST#2 and ST#3 substrates are mainly attributed to the higher flow rate of the bore fluid used (for ST#2 and ST#3) during the membrane fabrication. A thinner substrate and less sponge-like structure are favorable to the FO process, which will be discussed in later paragraphs.

[0055] The properties of the PAI hollow fiber membrane substrates in terms of dimension, PWP, MWCO and porosity are listed in **Table 2**.

Properties	ST#1	ST#2	ST#3
Fiber ID/OD (mm/mm)	0.87/1.27	1.19/1.50	1.17/1.45
Fiber wall thickness (μm)	835	155	140
PWP ($\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$)	27	122	134
Outer skin MWCO (KDa)*	20	23	< 6
Inner skin MWCO (KDa) ⁺	37	44	24
Porosity (%)	51	70	85

*dextran filtration was performed from the shell side

⁺dextran filtration was performed from the lumen of the fiber

Table 2. Properties of PAI Hollow Fiber Membrane Substrates of Example 1, 2, and 3

[0056] From **Table 2**, the ST#2 and ST#3 hollow fiber membrane substrates possessed quite large dimensions (ID/OD around 1.2/1.5 mm/mm) in comparison with conventional NF hollow fibers. A larger fiber lumen is favorable to the fluid flow inside the lumen with less resistance based on the Hagen-Poiseuille's law.

[0057] From **Table 2**, it can also be seen that the ST#1 has the lowest PWP compared to ST#2 and ST#3 substrates as the polymer concentration in the original dope composition decreased from 20% to 15%, leading to increased membrane porosity. It seems that ST#3 hollow fiber substrate possessed an excellent pore structure, which is indicated by the low MWCO (<6 KDa, dextran filtration was performed from the shell side), high pure water flux (134 $\text{L/m}^2 \cdot \text{h} \cdot \text{bar}$) and high porosity (85%). The MWCO experiment was repeated to confirm the correctness of the measurement. The possible reason responsible for the low MWCO may be linked to the dope composition of ST#3 substrate (PAI/LiCl/NMP: 15/3/82). Since the concentration of the additive is high (higher than ST#2), the thermodynamic stability of the initial dope composition was reduced, so instantaneous demixing might take place in the phase inversion process,

resulting in a denser surface but a more porous support. These properties are believed to be relevant to the subsequent chemical post-treatment and FO application.

[0058] Table 3 shows the mechanical properties (tensile modulus, tensile stress at break and tensile strain) of the PAI hollow fiber substrates along with the counterparts of polyethersulfone (PES) hollow fiber membranes reported previously. The PAI hollow fibers possessed tensile modulus of 151 MPa to 239 MPa, which is much higher than that of PES hollow fibers (57.5 MPa to 138.9 MPa). A high tensile modulus suggests a high rigidity of the membrane. While the tensile stress and strain at break measured for the PAI hollow fibers can reach as high as 6.4 MPa to 12.2 MPa and 26% to 50%, respectively, the combination of high tensile stress and strain at break allows the membrane to have a high toughness.

Sample	Tensile Modulus (MPa)	Stress at break (MPa)	Strain at break (%)
ST#1	239 ± 16	9.8 ± 0.5	42 ± 4
ST#2	224 ± 7	12.2 ± 1.1	50 ± 7
ST#3	151 ± 4	6.4 ± 0.2	26 ± 4
PES ^a	81.9 – 88.4	4.1 – 5.4	34.0 – 58.6
PES ^b	57.5 – 104.0	0.9 – 1.7	9.9 – 16.9
PES ^c	107.0 – 138.9	2.8 – 3.4	29.5 – 43.8

^aWang *et al.*, *J Membrane Science*, 355 (2010) 158-167

^bChung *et al.*, *Chemical Engineering Science*, 55 (2000) 1077-1091

^cQin *et al.*, *J Membrane Science*, 157 (1999) 35-51

Table 3. Mechanical Properties of PAI Hollow Fiber Membrane Substrates of Example 1, 2, and 3

Optimal Conditions for Chemical Post-treatment

[0059] The optimal post-treatment temperature was determined by varying the temperature from 60°C to 80°C using the ST#1 hollow fiber as the model substrate

while the PEI concentration was fixed at 1% and the post treatment time was controlled at 2h. The temperature effect on the PWP and salt rejections of the modified membrane can be observed from **Table 4**. Before the post treatment, the original membrane had the PWP of 26.7 L/m².h.bar and the rejection of 11.9% to MgCl₂. As the temperature of post-treatment increased, the PWP decreased to 1.8 L/m².h.bar while the salt rejection to MgCl₂ increased to 94% at 70°C due to more surface pores being sealed as a result of cross-linking reaction between the PAI and PEI. The chemical reaction has been confirmed by ATR-FTIR experiments and will be discussed later paragraphs. The mechanical strength of the membranes modified at 60°C and 70°C remained almost unchanged. However, when the post-treatment temperature increased to 80°C, the reaction might be too severe, resulting in a membrane with a very poor mechanical strength. Hence, the post-treatment temperature of 70°C was selected as an optimal condition applied for the treatment of other hollow fiber substrates.

Post treatment Temperature (°C)	Tensile strength (MPa)	PWP (L m ⁻² h ⁻¹ bar ⁻¹)	Salt rejection (%)	
			NaCl	MgCl ₂
Original-ST#1	9.8 ± 0.5	26.7 ± 1.5	5.1 ± 0.7	11.9 ± 1.5
60	9.9 ± 0.2	14.6 ± 0.1	7.9 ± 0.7	46.3 ± 8.8
70	9.7 ± 0.2	1.8 ± 0.03	49.4 ± 3.0	94.4 ± 0.4
80	N/A	N/A	N/A	N/A

*Post treatment condition: 1 wt.% PEI solution for 2h

Table 4. Effect of Post Treatment Temperature on Membrane Properties.*

[0060] In order to determine the optimal PEI concentration, three PEI aqueous solutions of 0.5 wt%, 1 wt% and 2 wt% were prepared. As observed in **Figure 2**, the ST#1 hollow fiber membranes modified with a 0.5 wt% PEI solution gave the lowest salt rejection to MgCl₂ and the highest PWP as compared to those modified with 1 wt% and

2 wt% PEI solutions. When 1 wt% and 2 wt% PEI solutions were used, there was no significant difference in the PWP of the modified membranes, but the membrane treated in a 1 wt% PEI solution presented the highest rejection of NaCl. Thus, the PEI solution with 1 wt% concentration was used for the post-treatment.

[0061] **Figure 3** shows the effect of post-treatment time on the filtration performance of modified ST#1 membrane using a 1 wt% PEI solution at 70°C. Obviously, a longer post-treatment time allowed more PEI molecules to crosslink with PAI, leading to an increase in the thickness of dense outer layer. Consequently, the PWP decreased and the salt rejection (R_s) increased. The membranes immersed in the PEI solution for 60 min showed $MgCl_2$ rejection of 47% and the PWP of 12 L/m².h.bar. Increasing the immersion time to 120 min enhanced the $MgCl_2$ rejection significantly to 94% and dropped the PWP to 1.74 L/m².h.bar.

Characteristics of Modified PAI Hollow Fiber Membranes

[0062] **Figure 4(a) to (c)** show the cross-section and outer surface morphology of ST#1 modified PAI hollow fiber. It can be seen that there is no visible difference on the cross-section morphology as compared to the original ST#1 hollow fiber substrate depicted in **Figure 1(a)(i) and (a)(ii)**. However, the difference in the outer surface morphology for modified and unmodified membranes can be noticed as shown in **Figure 4(c) and (d)**. The outer surface became denser after the post treatment.

[0063] The chemical reaction between the PAI and PEI was verified by ATR-FTIR measurements as shown in **Figure 5**. The typical imide bands can be detected at 1778 and 1717 cm⁻¹ (symmetric and asymmetric C=O stretching, respectively), 1379 cm⁻¹ (C-N-C stretching), 1109 and 725 cm⁻¹ (imide ring) for the ST#1 PAI hollow fiber substrate. It can be seen clearly that after the post-treatment, the imide peaks

disappeared while amide peaks became stronger ($\text{C}=\text{O}$ at 1641 cm^{-1} and $\text{C}-\text{N}$ at 1532 cm^{-1}). This confirms that the cross-linking has effectively taken place as depicted in **Figure 6** where the imide rings were opened and a bond between the amine functional group in PEI and the imide rings in PAI has been formed.

[0064] The charge characteristics of the ST#1 hollow fiber membrane before and after the post-treatment were determined in terms of zeta potential. It can be seen in **Figure 7** that the original PAI membrane had an isoelectric point of 4.4. At a pH below the isoelectric point, the membrane were positively charged due to amine protonation, while at a pH above the isoelectric point the membrane was negatively charged because of the deprotonation of the carboxyl group. However, it was noticed that after the post-treatment the isoelectric point was shifted to 10.4 due to more amine groups attached to the surface. This means that the membrane presented positive charges in a wide pH range, which could be beneficial to some applications.

[0065] The rejection behaviors of the modified ST#1 membrane to various salts are depicted in **Figure 8**. The chemical reaction between the PAI and PEI resulted in a positively charged membrane due to amine groups attaching on the membrane surface. Thus, a high rejection of MgCl_2 is expected. It was also observed that the membrane presented a higher rejection to divalent cations than monovalent cations. The MgCl_2 rejection was the highest at all post-treatment time while Na_2SO_4 had the lowest rejection though the diffusion coefficients for those salts are comparable (MgCl_2 : $1.25 \times 10^{-9}\text{ m}^2/\text{s}$; Na_2SO_4 : $1.23 \times 10^{-9}\text{ m}^2/\text{s}$). These results may be attributed to the combination of several factors: (1) the contributions of the co-ion and counter-ion to the ionic strength, (2) the electric charge on the membrane, and (3) the hydrated radius of the ions. Especially, when a charged membrane was placed in an electrolyte solution, the concentration of the co-ion near the membrane surface was lower than that in the bulk

solution, while the counter-ion concentration was higher near the membrane surface than in the bulk solution. Since the counter-ion valency of SO_4^{2-} is higher than that of co-ion (Na^+) in the Na_2SO_4 solution, the positive charges of the membrane may be shielded. Therefore, the contribution from the electric interaction to the selective rejection behavior (Donnan repulsion effect) of the membrane was weakened, leading to a lower rejection to Na_2SO_4 .

PAI Hollow Fiber Membranes with a Positively Charged NF-Like Selective Layer for FO Application

[0066] The intrinsic properties of PAI hollow fiber membranes with a positively charged NF-like selective layer (hereinafter denoted as PAI FO hollow fibers) such as water permeability A and MgCl_2 rejection measured in an RO cross-flow filtration setup are tabulated in **Table 5**. It can be seen that the PAI FO hollow fibers presented a water permeability ranging from 1.74 to 2.25 $\text{L}/\text{m}^2\cdot\text{h}\cdot\text{bar}$ which is higher than commercial Hydration Technology Innovations' (HTI) FO flat sheet membranes (HTI's FO membrane: A value of 0.8 to 1.13 $\text{L}/\text{m}^2\cdot\text{h}\cdot\text{bar}$). The three PAI FO hollow fibers also exhibited a high MgCl_2 rejection over 91.1% at 1 bar pressure.

Sample	Water permeability, A ($\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$)	MgCl_2 Rejection @ 1 bar, R_s (%)
ST#1	1.74	94.4
ST#2	2.25	92.7
ST#3	2.19	91.1

Table 5. Intrinsic Properties of Hollow Fiber Membranes of Example 1, 2, and 3

[0067] The performance of three different PAI FO hollow fiber membranes in FO process was determined using a 1.5M MgCl_2 solution as the draw solution and de-ionized water as the feed water at 23°C, and the results are listed in **Table 6**. It was found that in the configuration of the AL-facing-DS, the ST#1, ST#2, and ST#3 PAI FO hollow fibers showed a water flux of 6.34, 17.28, and 17.15 $\text{L/m}^2\cdot\text{h}$, respectively. The ST#2 and ST#3 PAI FO membranes presented almost three-time higher water flux as compared to the ST#1. Since the water flux in the FO process is determined by both the skin layer and the substrate structure, and the water permeability of the ST#2 and ST#3 membranes is only ~ 1.3 times of the ST#1 membrane, the three-time higher water flux presented by the ST#2 and ST#3 membranes is believed to be mainly attributed to their much thinner and more porous substrate structure, as shown in **Figure 1** and **Table 2**.

Sample	AL-facing-DS		AL-facing-FW	
	$J_v (\text{L m}^{-2} \text{h}^{-1})$	$J_s/J_v (\text{g L}^{-1})$	$J_v (\text{L m}^{-2} \text{h}^{-1})$	$J_s/J_v (\text{g L}^{-1})$
ST#1	6.34	0.48	4.15	0.46
ST#2	17.3	0.96	11.7	0.33
ST#3	17.2	2.19	12.9	0.37

*Draw solution: 1.5M MgCl_2 solution.

Table 6. Performance of PAI FO membranes applied in FO process.*

[0068] The experimental FO water flux and the ratio of salt flux over water flux (J_s/J_v) as a function of draw solute concentration are shown in **Figure 9** for the ST#2 and ST#3 PAI FO hollow fiber membranes. It was found that the two membranes exhibited similar water flux profiles. The water flux increased steadily as the concentration of the draw solution increased. For both the AL-facing-DS and AL-facing-FW configurations,

the ST#2 and ST#3 PAI FO membranes presented similar performance. This result is a bit surprising, as the ultra-filtration (UF) substrates of the ST#2 and ST#3 had different MWCOs and porosities (ϵ) though the fiber wall thickness (l) of the two membranes is similar. The difference in the pore size of the outer surface may be mitigated by the chemical crosslink reaction. In the substrate, porosity, fiber wall thickness and tortuosity (τ) are the main parameters to affect the FO flux. Since the ST#2 substrate had bigger pores, it might have better pore interconnections, i.e., a smaller value of tortuosity as compared with the ST#3 substrate. Though the ST#2 substrate has a lower porosity than the ST#3 substrate, the structural parameters $S = \tau l / \epsilon$ of these two substrates might be similar.

[0069] The J_S/J_V profiles as a function of the draw solute concentration for the ST#2 and ST#3 PAI FO hollow fiber membranes are illustrated in **Figure 9(a)(ii)** and **(b)(ii)**, respectively. Overall, in the configuration of the AL-facing-FW, the ST#2 and ST#3 membranes show similar J_S/J_V profiles. The J_S/J_V of the two membranes is smaller than 0.4 g/L, which is lower than in the AL-facing-DS configuration for both membranes. This value is also lower than the data for HTI's FO membrane which is 0.85 g/L. Surprisingly, when the orientation changed, a significant difference in the J_S/J_V profile occurred between the two membranes. The J_S/J_V of the ST#2 PAI FO hollow fiber membrane increased slightly as the draw solute concentration increased to 2.0 M and then it maintained almost unchanged. In contrast, the J_S/J_V of the ST#3 membrane was much higher than the ST#2 PAI FO hollow fiber membrane, and it raised sharply with an increase in draw solute concentration.

[0070] To understand this behavior, schematic concentration profiles in a positively charged membrane are depicted in **Figure 10** to illustrate the salt transportation in the

FO process. The PAI FO hollow fiber membrane consists of two parts: (1) a dense active skin layer (shaded) which contains most of the charge; and (2) a porous substrate (white) which may contain less charge, as the membrane substrate was immersed in a PEI solution after both fiber ends were sealed. In the AL-facing-FW configuration (**Figure 10(a)**), the C_1 and C_4 are the salt concentrations of the bulk feed and the draw solution, and the C_2 and C_3 are the salt concentrations at the interfaces between the feed and the membrane surface, and between the active layer and the porous substrate, respectively. The difference between the C_3 and C_4 was caused by water permeation (dilution effect) for a neutral membrane, which is so-called ICP effect. However, the C_3 in a positively charged membrane substrate may be smaller than in a neutral membrane substrate due to the Donnan exclusion that tended to expel the $MgCl_2$ back to the draw solution. In addition, the charges in the dense-active surface also imposed a repulsive force to the salt penetration through the membrane (salt flux and salt repulsion are in opposite directions). Thus, there were double electrical repulsions to the salt transfer in a positively charged FO membrane under the configuration of AL-facing-FW.

[0071] However, in the AL-facing-DS configuration (**Figure 10(b)**), when some of the salt penetrated through the dense-active layer into the porous substrate, a salt concentration of C_2 at the interface of the active layer with the porous substrate was built up. The positive charges in the support layer tended to expel the ions to the feed side because of a less mass transfer resistance in the substrate. Thus the salt transportation through a positively charged FO membrane was facilitated in the configuration of AL-facing-DS (salt flux and salt repulsion are in the same direction). That is why the J_s/J_v in the AL-facing-FW is lower than in the AL-facing-DS for both membranes.

[0072] Comparing the ST#2 PAI FO hollow fiber membrane with the ST#3 PAI FO hollow fiber membrane, the main difference lies in the substrate porosity (70% for ST#2 vs. 85% for the ST#3). In the AL-facing-DS configuration, a highly porous substrate would significantly reduce the hindrance of mass transfer, making the facilitated ion transportation imposed by the positive charges in the substrate easily realized. Thus, the J_S/J_V of the ST#3 PAI FO membrane was much higher than the ST#2 PAI FO membrane, and it increased sharply with an increase in draw solute concentration.

[0073] Table 7 lists the water flux of various membranes with a NF-like selective layer used for FO process. It seems the performance of the ST#2 and ST#3 PAI FO hollow fiber membranes in the configuration of AL-facing-FW are better than most of other NF membranes reported in literature. In addition, the ST#2 and ST#3 PAI FO hollow fiber membranes exhibited the largest fiber lumen, which is a desirable feature for liquid processes.

Sample	ID/OD (mm mm ⁻¹)	PWP (L m ⁻² h ⁻¹ bar ⁻¹)	R _s MgCl ₂ (%)	FO water flux (L m ⁻² h ⁻¹)	DS: MgCl ₂ (M)	Orientation
ST#2	1.24/1.58	2.25	92.7	13.1	0.5	AL-facing-DS
				15.4	1.0	
ST#2	1.24/1.58	2.25	92.7	8.36	0.5	AL-facing-FW
				10.4	1.0	
ST#3	1.24/1.54	2.19	91.1	13.2	0.5	AL-facing-DS
				14.6	1.0	
ST#3	1.24/1.54	2.19	91.1	9.74	0.5	AL-facing-FW
				11.0	1.0	
PBI ^a	0.14/0.27	0.50	86.0	9.02	2.0	AL-facing-DS
PBI ^a	0.14/0.27	0.50	86.0	5.20	2.0	AL-facing-FW
4m-PBI ^{b,*}	0.21/0.29	1.34	92.0	11.0	1.0	AL-facing-DS
4m-PBI ^{b,*}	0.21/0.29	1.34	92.0	5.00	1.0	AL-facing-FW
9m-PBI ^{b,*}	0.21/0.29	1.25	96.0	5.00	1.0	AL-facing-DS

9m-PBI ^{b,*}	0.21/0.29	1.25	96.0	1.70	1.0	AL-facing-FW
DL-PBI ^{c,#}	0.54/0.95	1.74	87.0	15.7	1.0	AL-facing-DS
DL-PBI ^{c,#}	0.54/0.95	1.74	87.0	7.50	1.0	AL-facing-FW
CA ^d	0.35/0.55	0.47	97.0	2.70	0.5	AL-facing-DS
CA ^d	0.35/0.55	0.47	97.0	1.80	0.5	AL-facing-FW

^aWang *et al.*, *J Membrane Science*, 300 (2007) 6-12

^bWang *et al.*, *Chemical Engineering Science*, 64 (2009) 1577-1584

^cYang *et al.*, *Environmental Science & Technology*, 43 (2009) 2800-2805

^dSu *et al.*, *J Membrane Science*, 355 (2010) 36-44

*Chemically modified PBI; #Dual-layer PBI

Table 7. Comparison of Various Membranes Used in FO Process

Conclusion

[0074] In summary, based on the present method, PAI FO hollow fiber membranes having a large lumen with an inner diameter > 1mm and a wall thickness of about 0.15 to about 0.17 mm have been obtained. The hollow fiber substrate has a high porosity of about 70 to about 85%. The hollow fiber membranes also possess a high pure water permeability of about 2.19 to about 2.25 L m⁻²h⁻¹bar⁻¹ and reasonable rejections of about 49% and about 94% at 1 bar pressure for NaCl and MgCl₂, respectively. In the FO process, when using a 0.5 M MgCl₂ as a draw solution and DI water as the feed in the AL-facing-FW configuration at 23°C, the water fluxes of the ST#2 and ST#3 PAI FO hollow fiber membranes are 8.36 and 9.74 L m⁻²h⁻¹, respectively, and the J_S/J_V of the two membranes is smaller than 0.4 g L⁻¹, which is lower than the data of 0.85 g L⁻¹ for HTI's FO membrane.

[0075] Different from a neutral membrane, the positively charged FO membrane provides double electric repulsions to the salt transfer through the membrane in the AL-

facing-FW configuration, leading to a reduction of salt penetration, while in the AL-facing-DS configuration, the positive charges facilitate salt transportation.

[0076] The membrane structure and surface property can be carefully tailored by adjusting polymer dope composition, spinning conditions and the post-treatment parameters.

[0077] By "comprising" it is meant including, but not limited to, whatever follows the word "comprising". Thus, use of the term "comprising" indicates that the listed elements are required or mandatory, but that other elements are optional and may or may not be present.

[0078] By "consisting of" is meant including, and limited to, whatever follows the phrase "consisting of". Thus, the phrase "consisting of" indicates that the listed elements are required or mandatory, and that no other elements may be present.

[0079] The inventions illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms "comprising", "including", "containing", etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the inventions embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

[0080] By "about" in relation to a given numerical value, such as for temperature and period of time, it is meant to include numerical values within 10% of the specified value.

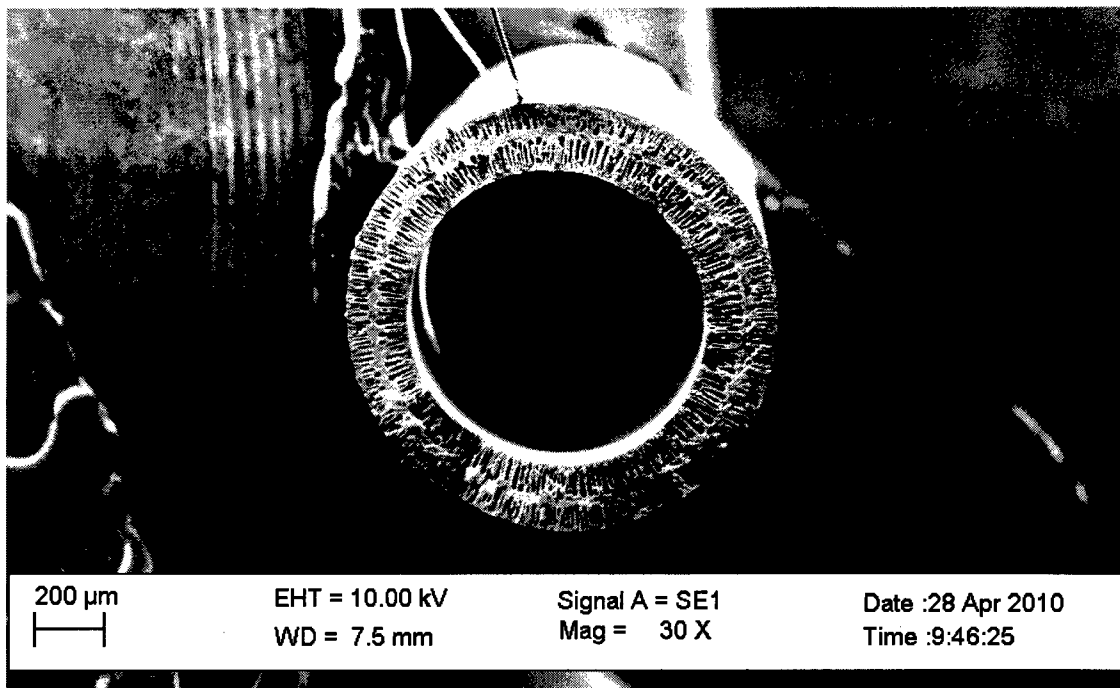
[0081] The invention has been described broadly and generically herein. Each of the narrower species and sub-generic groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

[0082] Other embodiments are within the following claims and non-limiting examples. In addition, where features or aspects of the invention are described in terms of Markush groups, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

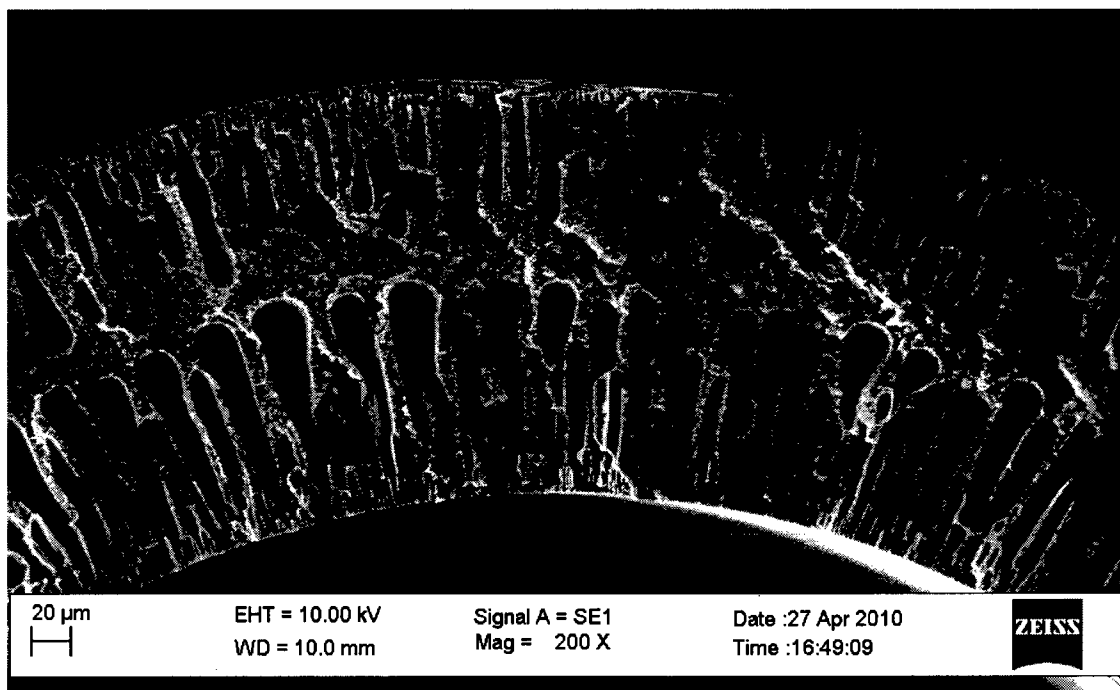
Claims

1. A method for forming a nanofiltration hollow fiber membrane comprising a poly(amide-imide) (PAI) hollow fiber substrate having a polyethyleneimine (PEI)-cross-linked PAI surface layer, the method comprising contacting the PAI hollow fiber substrate with an aqueous solution of polyethyleneimine (PEI) under conditions suitable for cross-linking PAI in the surface layer of the PAI hollow fiber substrate by PEI.
2. The method of claim 1, wherein contacting comprises immersing the PAI hollow fiber substrate in the aqueous PEI solution.
3. The method of claim 1 or 2, comprising contacting the PAI hollow fiber substrate with the aqueous PEI solution at a temperature of between about 50°C and about 80°C.
4. The method of claim 3, comprising contacting at about 70°C.
5. The method of any one of claims 1 to 4, comprising contacting the PAI hollow fiber substrate with the aqueous PEI solution for a period of between about 1 and about 180 min.
6. The method of claim 5, comprising contacting for about 120 min.
7. The method of any one of claims 1 to 6, wherein concentration of the aqueous PEI solution ranges from between about 0.2 to about 5 wt%.

8. The method of claim 7, wherein the concentration is about 1 wt%.
9. The method of any one of claims 1 to 8, wherein the PAI hollow fiber substrate is made of asymmetric microporous hollow fibers made of PAI material.
10. The method of claim 9, wherein the PAI material is Torlon® PAI.
11. Nanofiltration hollow fiber membrane comprising poly(amide-imide) (PAI) hollow fibers, wherein the surface of the PAI hollow fibers comprises PAI cross-linked by polyethyleneimine (PEI).
12. The nanofiltration hollow fiber membrane of claim 11 obtained by the method of any one of claims 1-10.
13. Use of the nanofiltration hollow fiber membrane of claim 11 or 12 in a forward osmosis process.

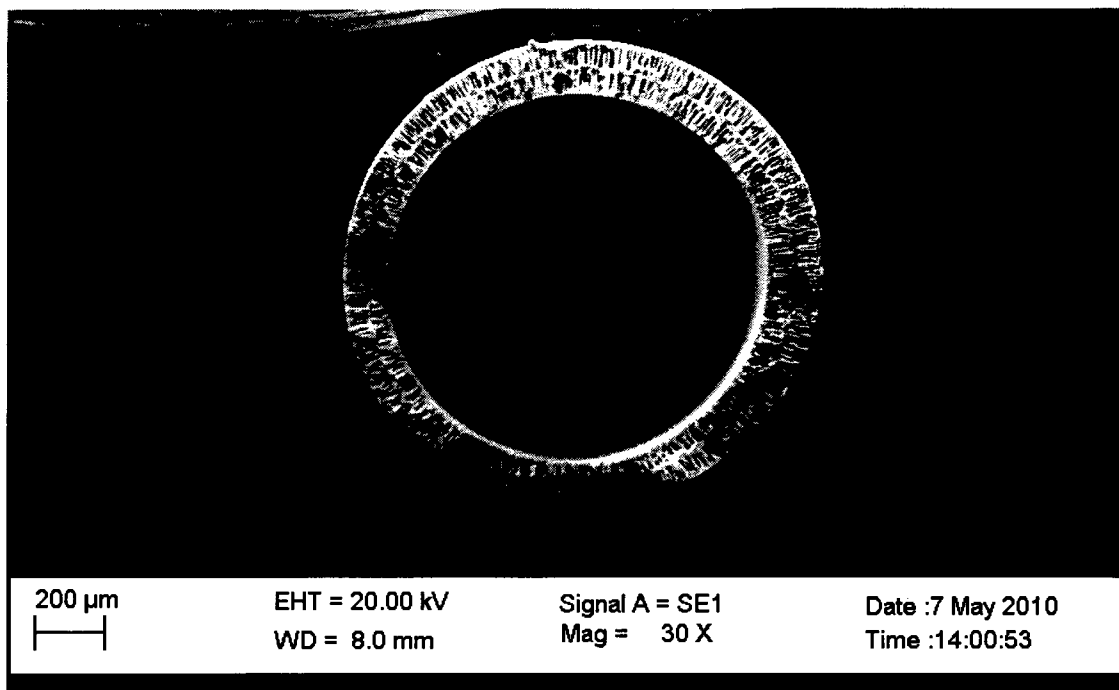


(a)(i)

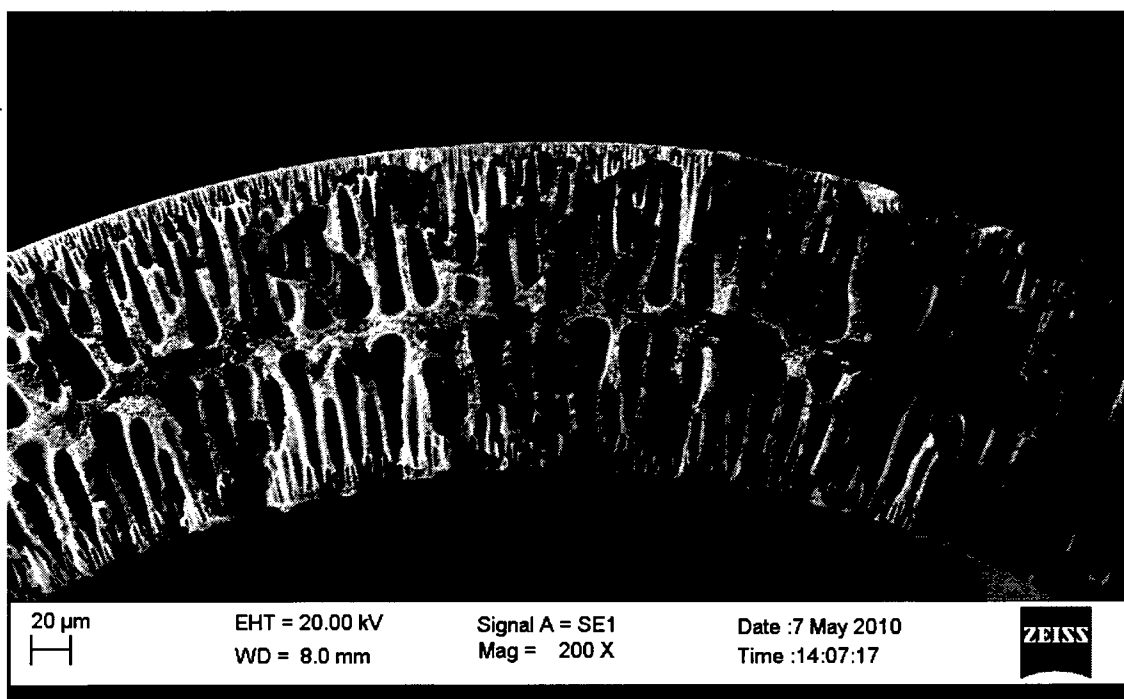


(a)(ii)

FIGURE 1

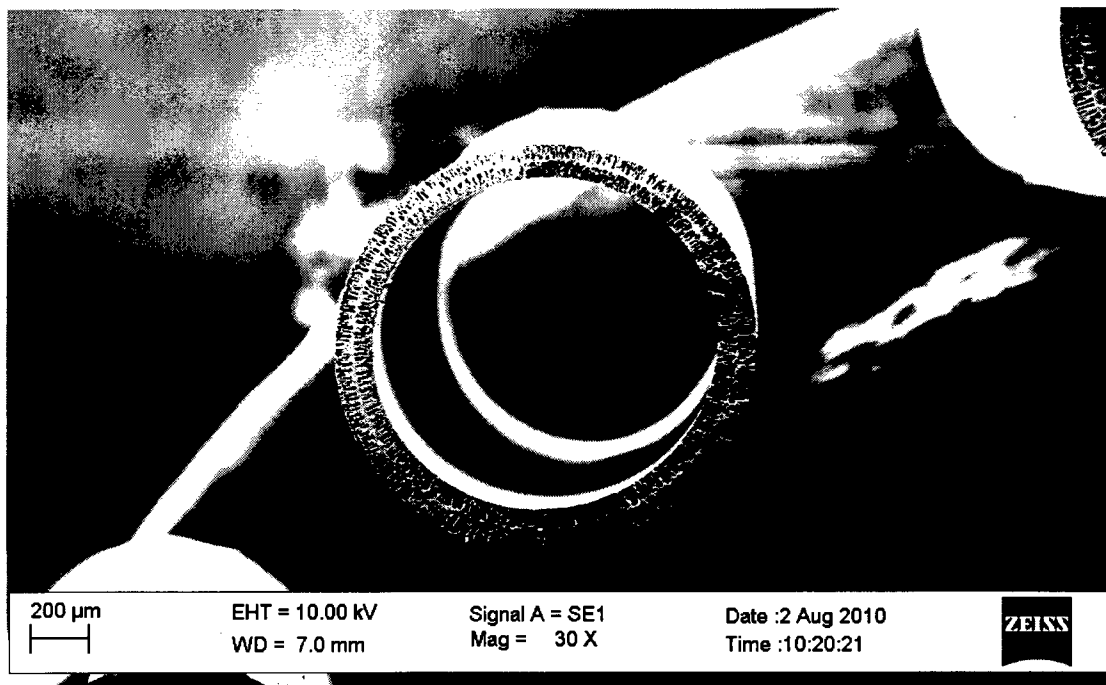


(b)(i)

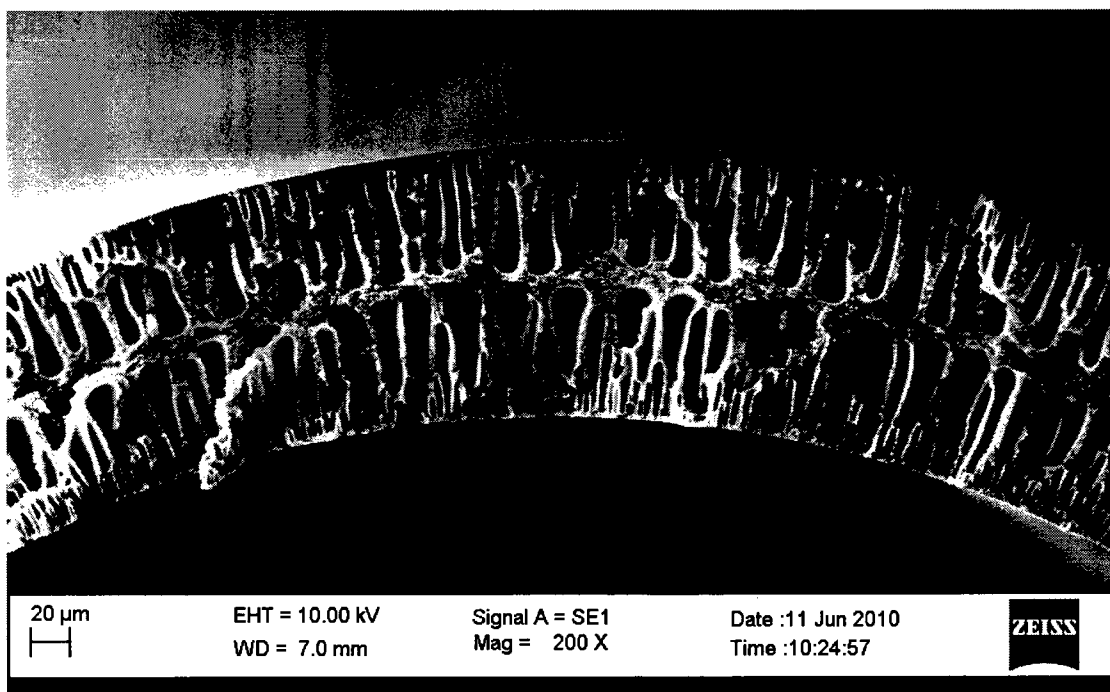


(b)(ii)

FIGURE 1 (cont)



(c)(i)



(c)(ii)

FIGURE 1 (cont)

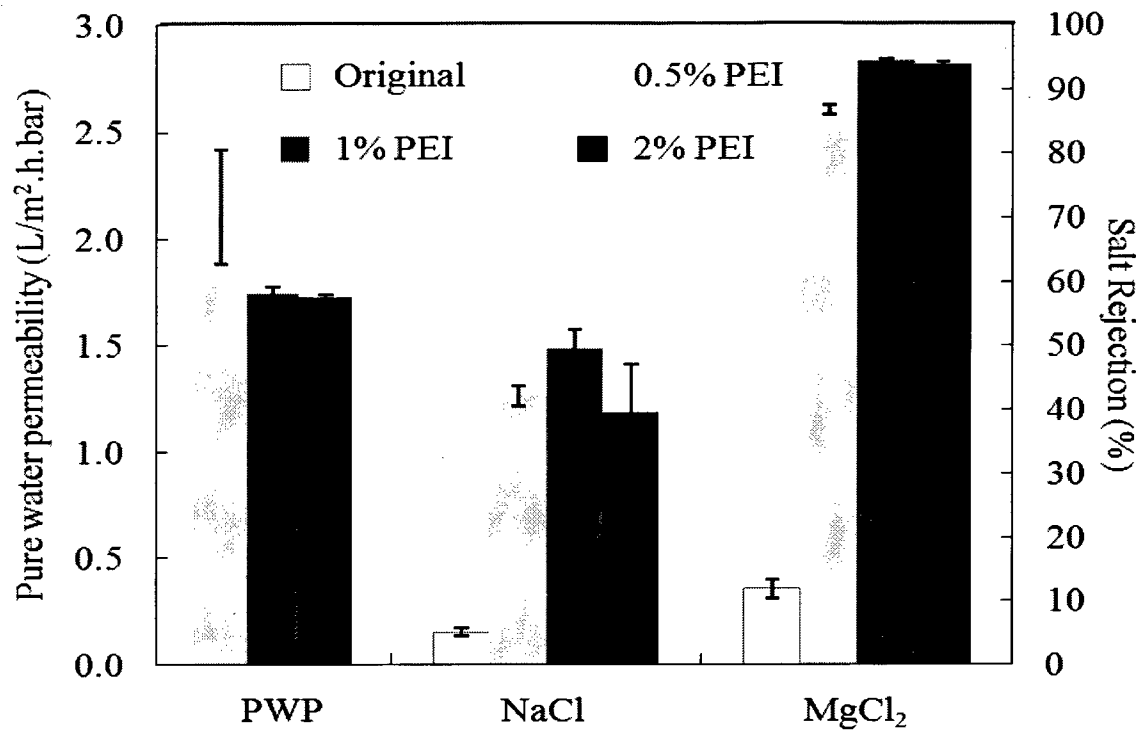


FIGURE 2

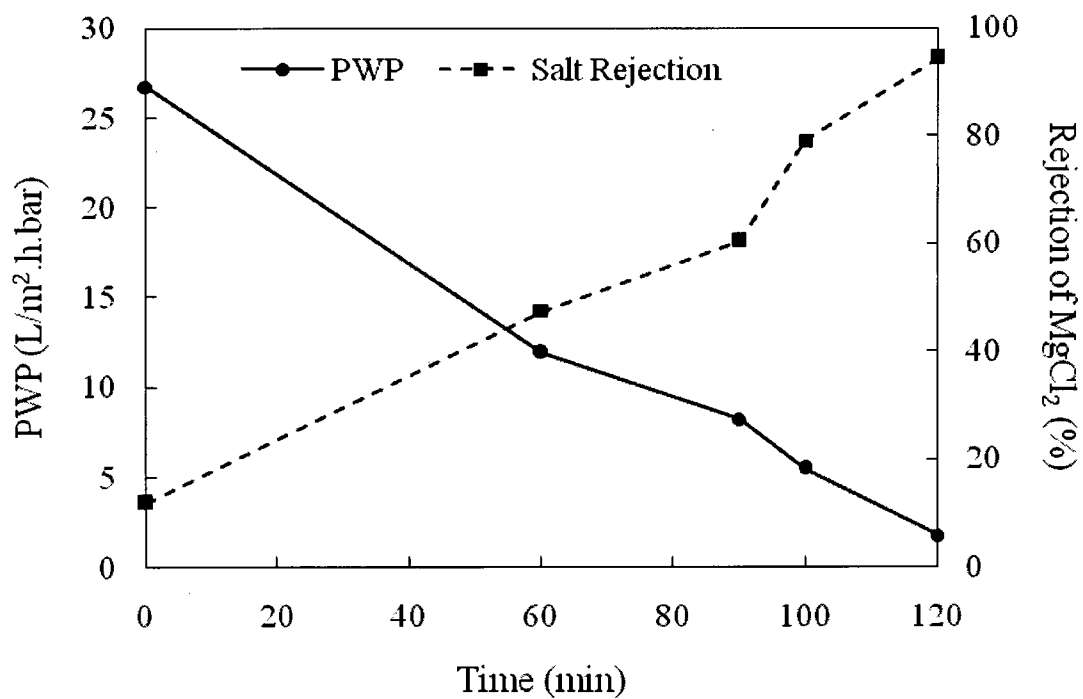
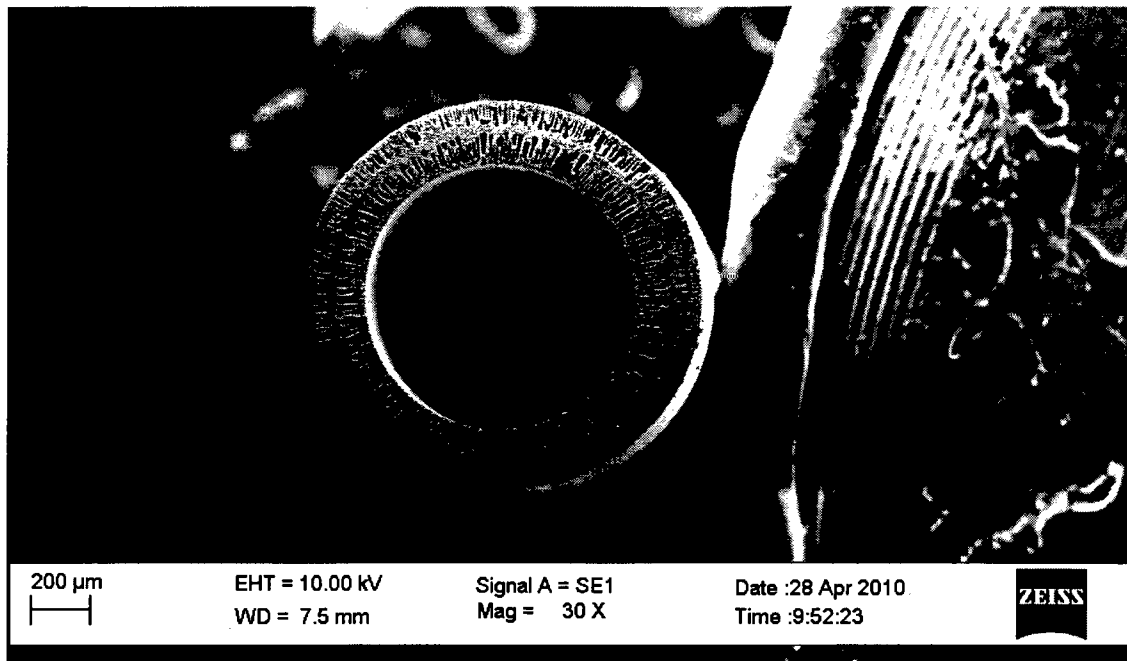
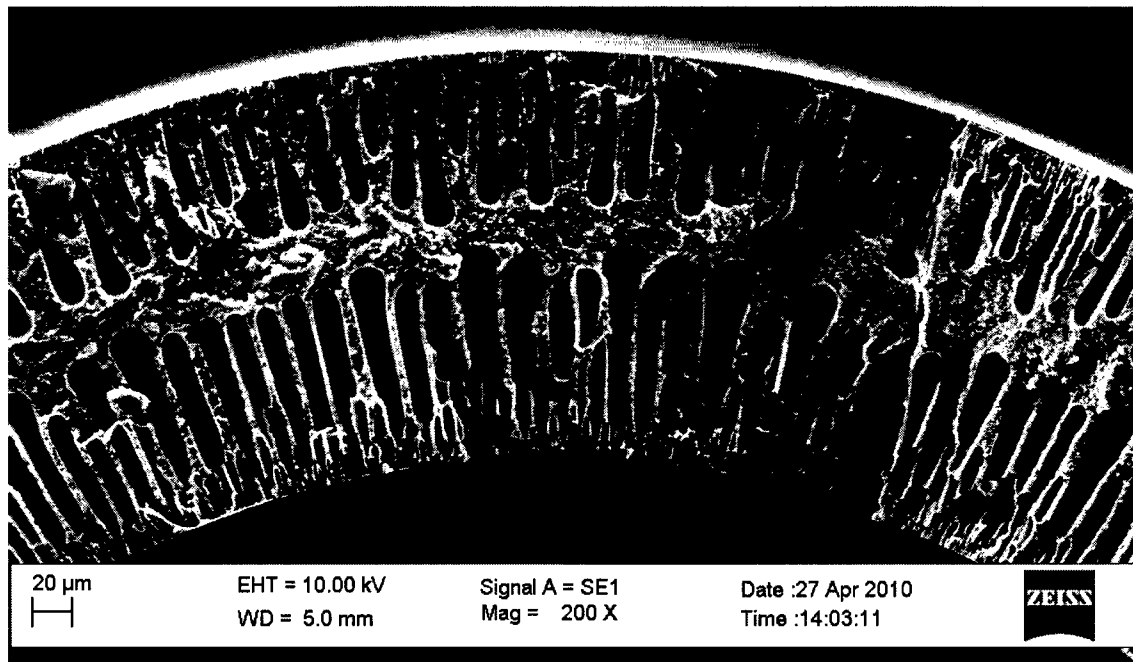


FIGURE 3

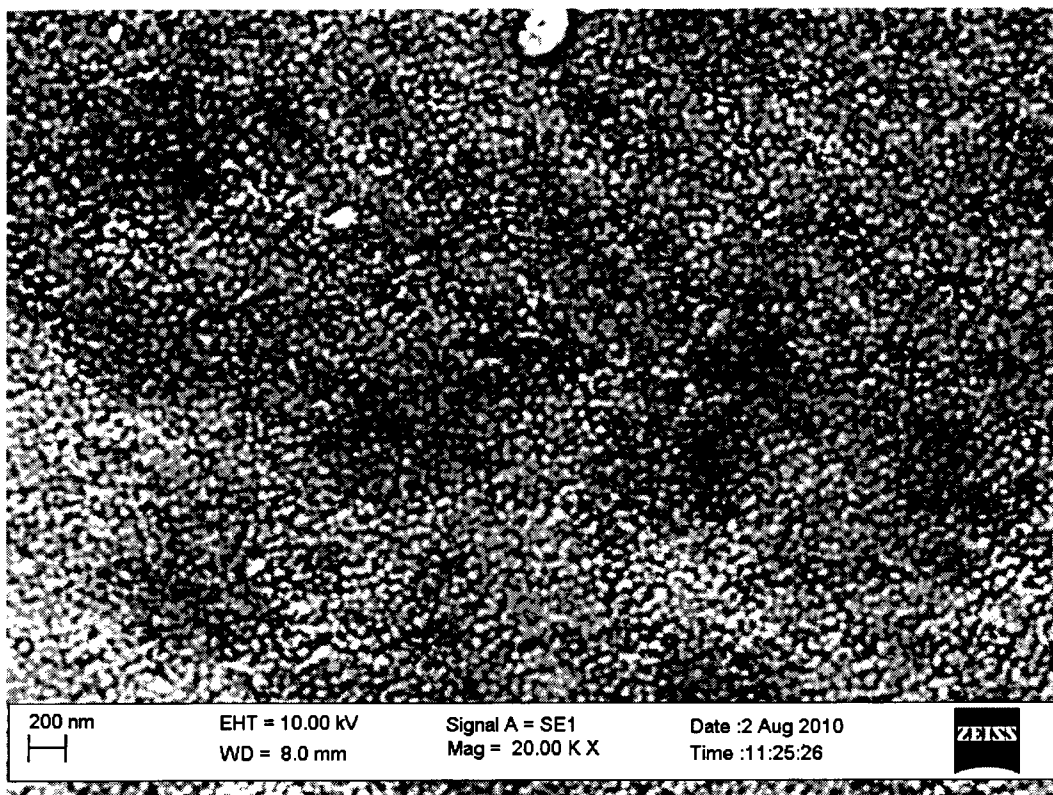


(a)

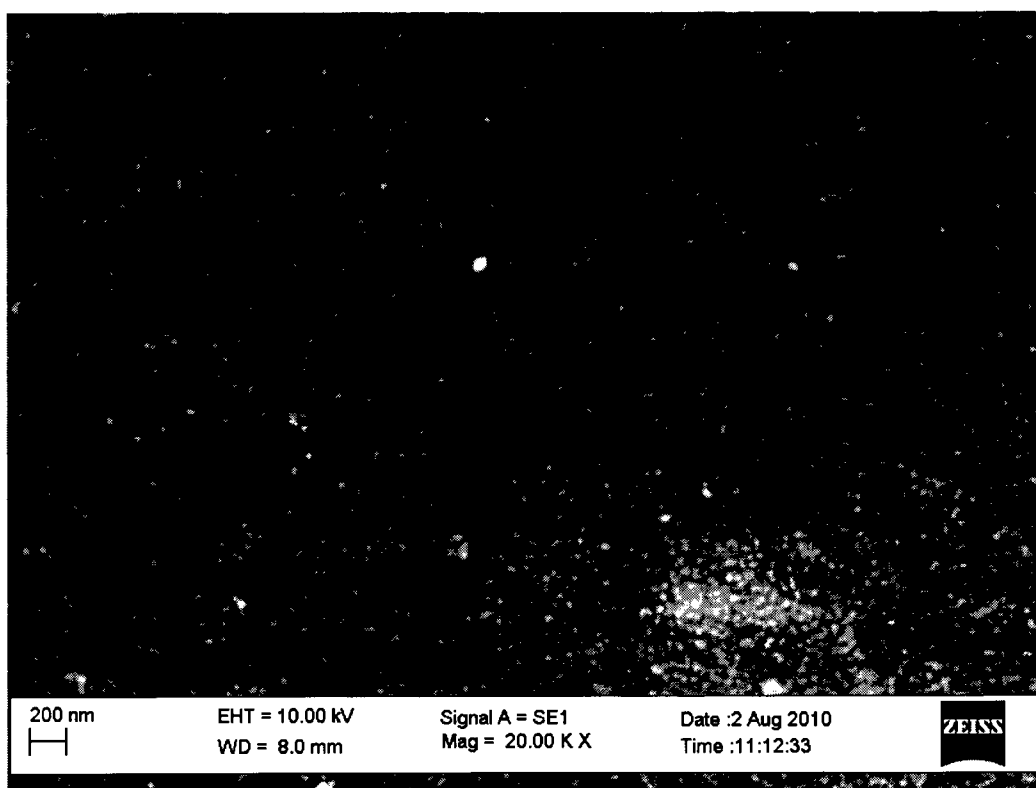


(b)

FIGURE 4

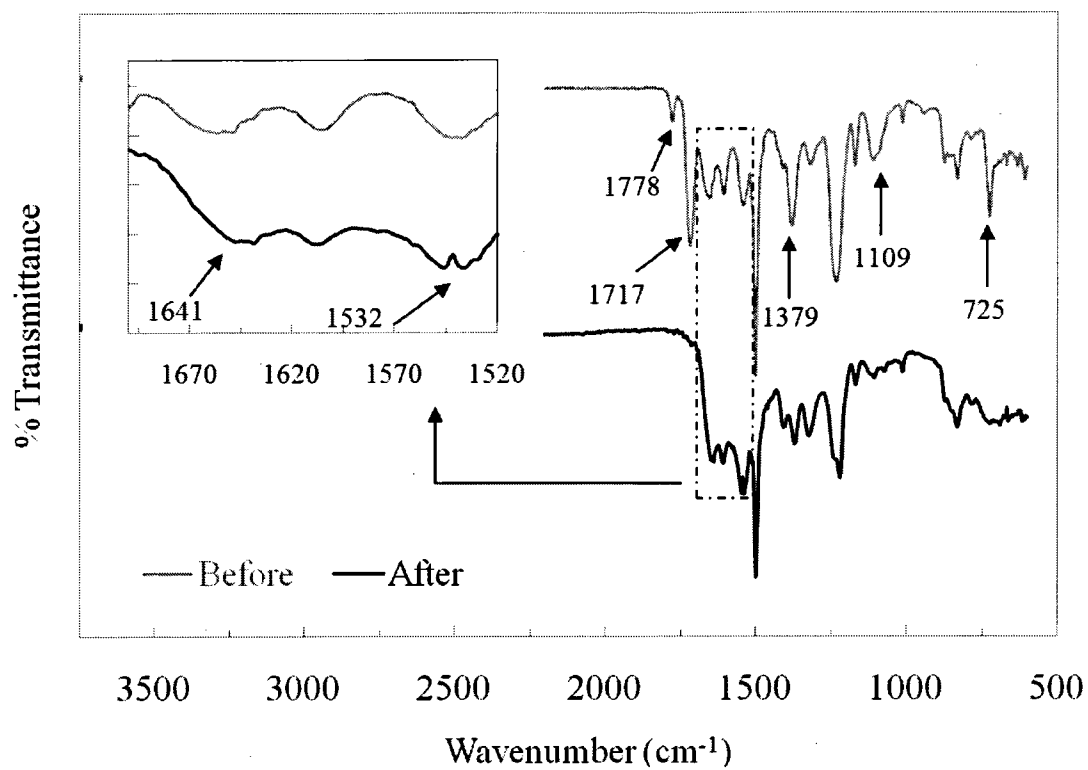
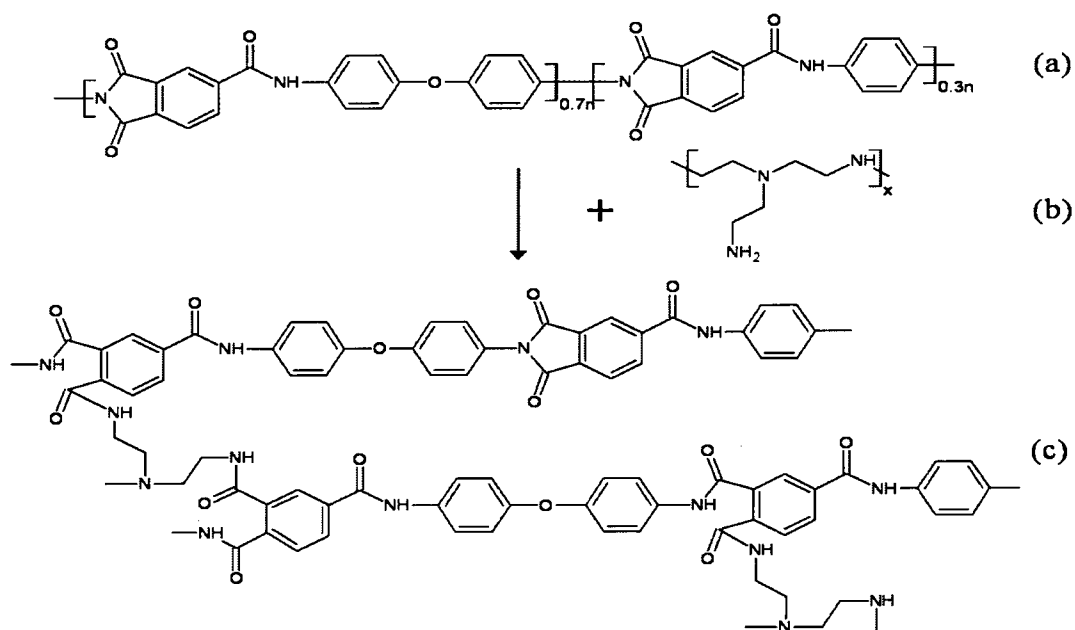


(c)



(d)

FIGURE 4 (cont)

**FIGURE 5****FIGURE 6**

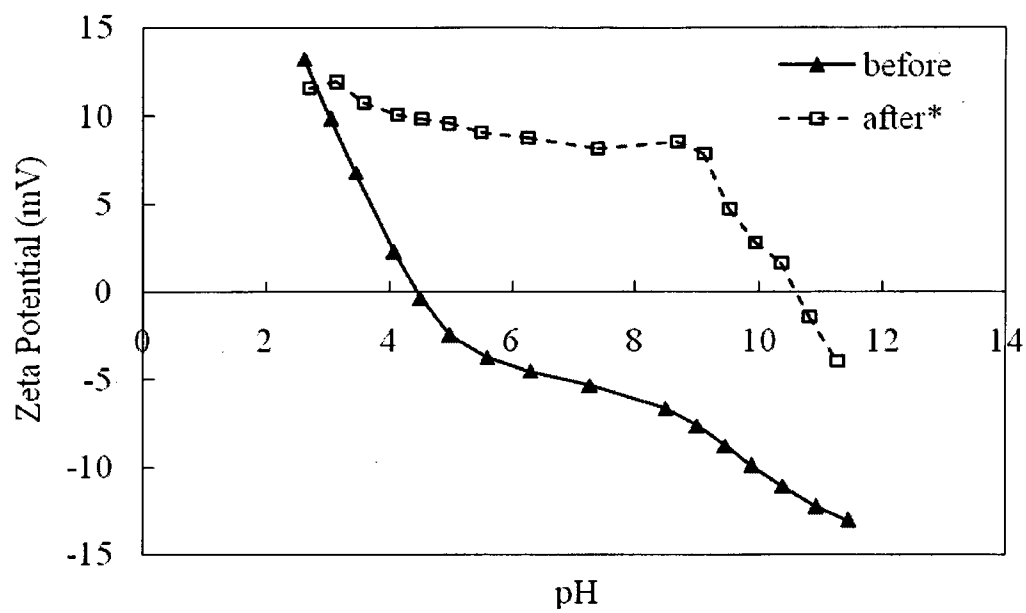


FIGURE 7

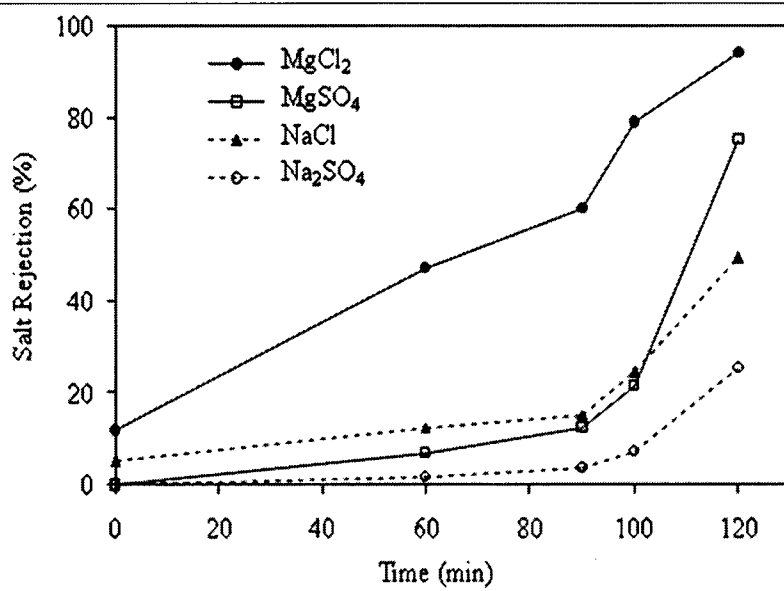
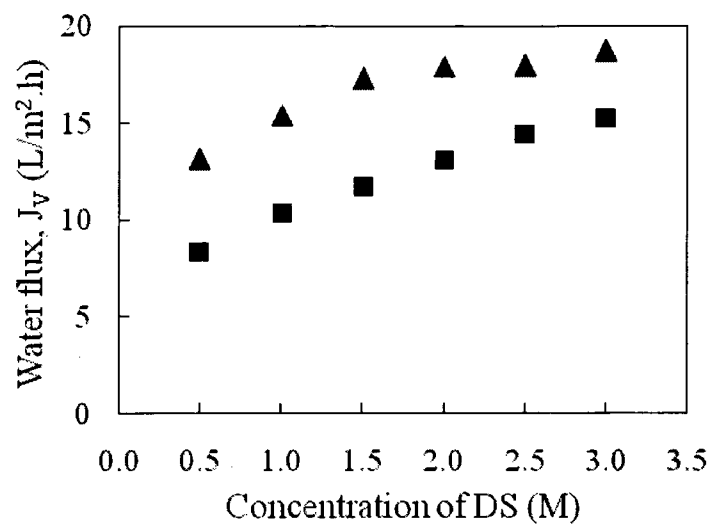
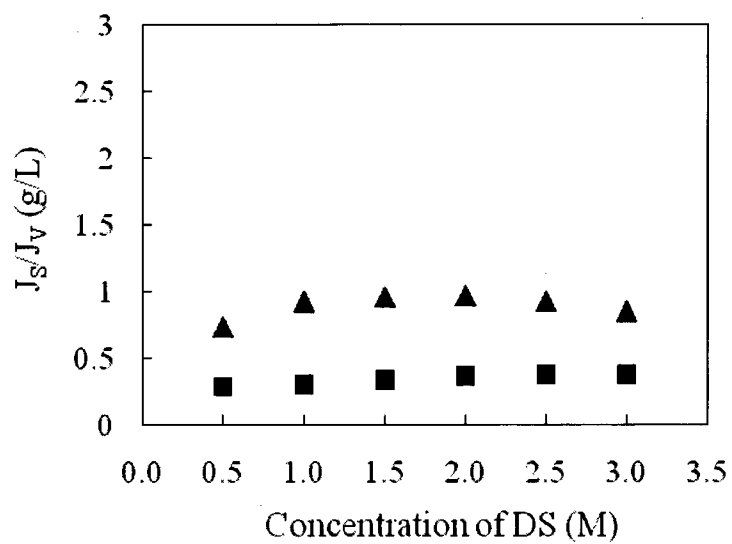


FIGURE 8

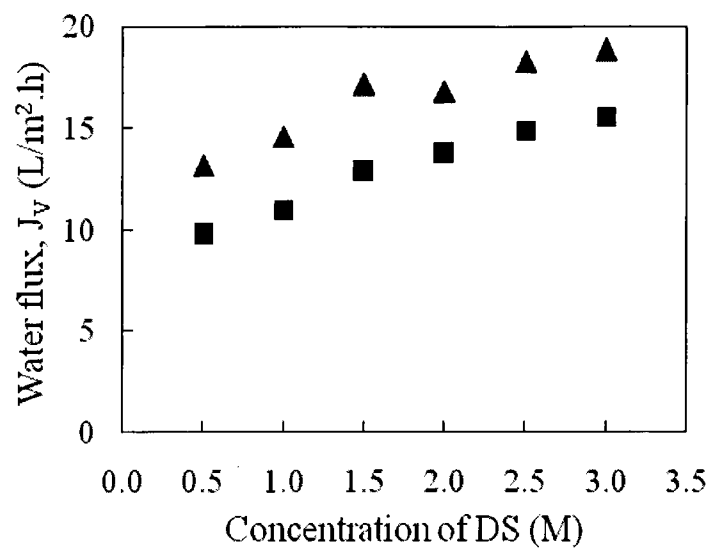


(a)(i)

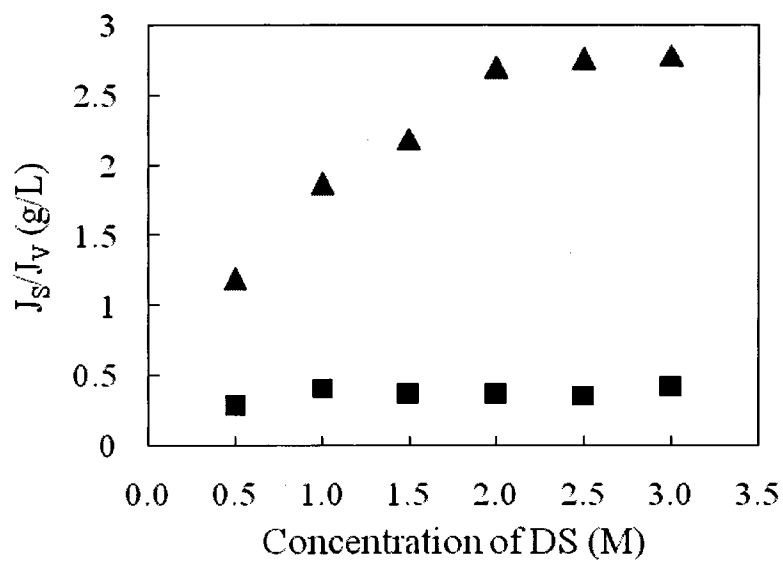


(a)(ii)

FIGURE 9



(b)(i)



(b)(ii)

FIGURE 9 (cont)

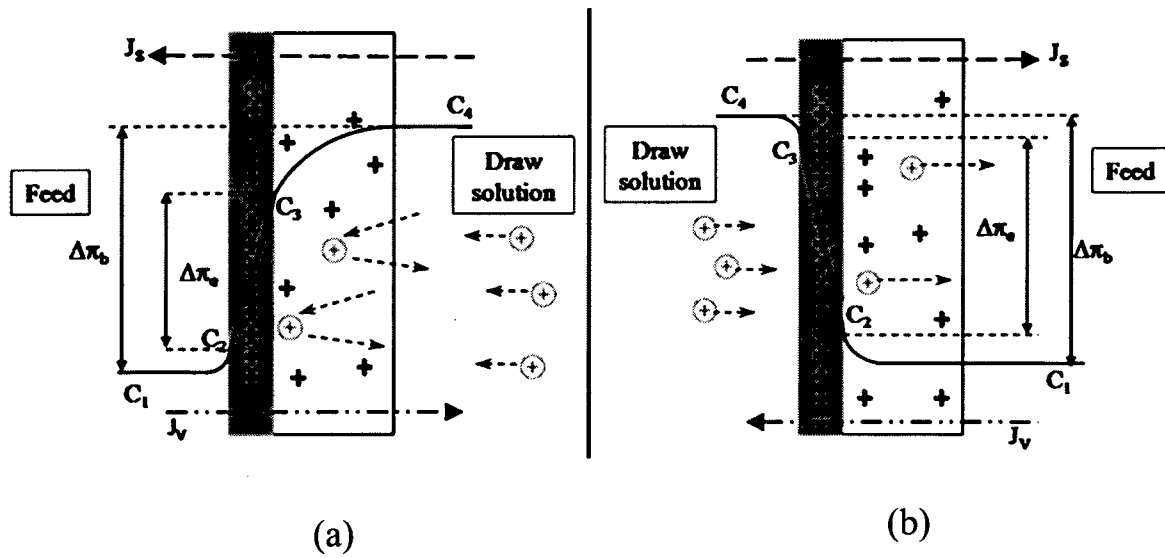


FIGURE 10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2011/000418

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

B01D 69/00 (2006.01)

B01D 61/02 (2006.01)

B01D 71/06 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI/EPODOC: B01D and keywords membran+, nano+, hpolyamide-imide+, PAI, polyamide_imide+, substrate+, base+, support+, layer+. Google Patent, Espace and Web of Science NPL keyword searches with keywords: nanofiltration, membrane, polyamide-imide, PAI, polyethyleneimine, polyaziridine, poly(iminoethylene), torlon.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2010/111755 A2 (KATHOLIEKE UNIVERSITEIT LEUVEN – K.U.LEUVEN R & D) 07 October 2010 See Abstract, pages 10-11, 13, claims	1-13
A	US 2010/0181253 A1 (VANDEZANDE ET AL.) 22 July 2010 See Abstract, para. [0019], claims	1-13
A	WO 2003/013708 A2 (CREAVIS GESELLSCHAFT FUR TECHNOLOGIE & INNOVATION MBH) 20 February 2003 English Abstract retrieved from EPODOC database See whole Abstract	1-13



Further documents are listed in the continuation of Box C



See patent family annex

* Special categories of cited documents:
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Date of the actual completion of the international search
17 January 2012

Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2011/000418

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2001-120968 A (NOK CORP) 08 May 2001 English Abstract retrieved from EPODOC database See whole Abstract	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/SG2011/000418

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report			Patent Family Member				
WO	2010111755	NONE					
US	2010181253	CA	2687382	CN	101678286	EP	2164615
		JP	2010526919	RU	2009145936	WO	2008138078
WO	03013708	AU	2002321292	DE	10139559		
JP	2001120968	NONE					
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.							
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