

Novel nanocomposite heterogeneous cation exchange membrane prepared by MWCNTs-co-silver nanolayer composite nanoparticles: Physico/chemical characterization and investigation of concentration effect

Akbar Zandehnam*, Mehrfam Rabieyan*, Sayed Mohsen Hosseini^{**,†}, and Saeideh Mokhtari*

*Thin Film Laboratory, Department of Physic, Faculty of Science, Arak University, Arak 38156-8-8349, Iran

**Department of Chemical Engineering, Faculty of Engineering, Arak University, Arak 38156-8-8349, Iran

(Received 29 May 2014 • accepted 24 August 2014)

Abstract—Nanocomposite polyvinyl chloride/multi walled carbon nano tubes (MWCNTs)-co-silver (Ag) nanolayer composite nanoparticles heterogeneous ion exchange membranes were prepared by solution casting techniques. MWCNTs-co-Ag nanolayer composite nanoparticles were prepared by magnetron sputtering method. The effect of used composite nanoparticles and electrolyte's concentration on physico/chemical properties of membranes was studied. Scanning and transmission electron microscopy and X-ray diffraction results showed uniform distribution and crystalline structure for the composite nanoparticles. Images also showed relatively uniform distribution for the membranes. Membrane transport number, selectivity and electrical conductivity were improved by increase of additive content in membrane matrix. All mentioned parameters were also enhanced by increase of electrolyte concentration. Membranes exhibited lower selectivity/transport number for bivalent ions compared to monovalent type. Membrane average roughness was decreased slightly by increase of additive content. Membrane ionic flux was decreased initially by increase of additive content up to 0.5%wt and then began to increase by more additive concentration. Mechanical stability of membranes was also improved by using of composite nanoparticles in membrane matrix. Modified membrane containing 4%wt composite nanoparticles showed better electrochemical properties compared to others.

Keywords: Mixed Matrix Membrane, Multi Walled Carbon Nano Tubes-co-silver Nanolayer Composite Nanoparticles, Plasma Treatment, Physico/Chemical Characterization, Concentration Effect

INTRODUCTION

Ion exchange membranes (IEMs) are widely used as active separators in various processes such as electrodialysis for desalting brackish waters, reconcentrating brine from seawater and production of table salt. IEMs also are efficient tools in resource recovery and food and pharmacy processing as well as environmental protection [1-13]. In such processes, ion interactions with membrane, water, and with each other occur in complex fashions. So, a knowledge of the physico/chemical properties of IEMs is important behind decisions about their applicability [10,14-18].

Preparing IEMs with special physico-chemical characteristics is a vital step in future chemical and waste treatment application [2, 10,19-21]. Variation of functional groups, selection of different polymeric matrices, polymers blending, use of various additives, alteration of cross-link density and surface modifications are important ways to obtain superior IEMs [1,5,10,14,15,22-28].

Preparing heterogeneous ion exchange membranes with appropriate physico-chemical characteristics for the application in electrodialysis processes related to water recovery and treatment was the primary target of the current research. Polyvinyl chloride (PVC)

based mixed matrix heterogeneous cation exchange membranes were prepared by solution casting techniques using cation exchange resin powder as functional groups agent and tetrahydrofuran as solvent. Multiwall carbon nanotubes (MWCNTs)-co-silver (Ag) nanolayer composite nanoparticle was also employed as inorganic filler additive in membrane fabrication.

Application of inorganic particles or fillers, especially nano-materials, into polymeric matrixes has been examined in many applications to enhance the mechanical, thermal and chemical stabilities of polymeric compounds in severe conditions and also to improve the separation properties of membranes [5,9,23].

Utilizing MWCNTs-co-Ag composite nanoparticle in membrane matrix can dedicate special selective characteristics in prepared membranes with respect to superior electrical, mechanical and adsorption characteristics of MWCNTs [23,32-34] and high electrical/thermal conductivity and natural anti-bacterial property of Ag nanolayer [35,36].

Different methods have been carried out in surface modification/combination of MWCNTs with inorganic materials like nanoparticles such as chemical reduction, radiation, electro-chemical deposition, ion beam assisted deposition, pulsed laser ablation, chemical vapor deposition and etc [37-48].

No research was found by our literature survey for surface modification of MWCNTs by Ag nanolayer through magnetron sputtering technique/plasma treatment. The suitable adhesions of nano-

[†]To whom correspondence should be addressed.

E-mail: sayedmohsen_hosseini@yahoo.com, S-Hosseini@araku.ac.ir
Copyright by The Korean Institute of Chemical Engineers.

particles to substrate, uniformity, good and controllable deposition rate and high purity are some of advantages of this method [49].

Currently, no reports have considered incorporating MWCNTs-co-Ag nanolayer composite nanoparticles into ion exchange membranes and the literature is silent on characteristics and functionality of mixed matrix PVC based/MWCNTs-co-Ag nanolayer heterogeneous cation exchange membranes.

The effects of MWCNTs-co-Ag nanolayer composite nanoparticles in the casting solution and also electrolyte's concentration on physico-chemical characteristics of prepared heterogeneous cation exchange membranes were studied. The results are valuable for electro-membrane processes, especially electrodialysis process for water recovery and treatment.

MATERIALS AND METHODS

1. Materials

Polyvinylchloride (grade S-7054, density: 490 g/lit, viscosity: 105 Cm^3/g) supplied by Bandar Imam Petrochemical Company, Iran, was used as binder. Tetrahydrofuran (THF, solubility: 20 °C, molar mass: 72.11 g/mol, Density: 0.89 g/cm^3) was employed as solvent. Multiwalled carbon nanotubes (MWCNTs, functionalized type: COOH-MWCNT) with 10-20 nm outer diameter, 5-10 nm inner diameter, 0.5-2 μm length and 200 m^2/g specific surface area were provided from NANO-RADBEHAN Company, Iran. Cation exchange resin (Ion exchanger Amberlyst[®] 15, strongly acidic cation exchanger, H^+ form- 4.7 meq/g dry weight) by Supelco was used in membrane preparation. All other chemicals were supplied by Merck. Throughout the experiment, distilled water was used.

2. Synthesis of MWCNT-co-Ag Nanolayer Composite Nanoparticles

To fabricate novel MWCNTs-co-Ag nanolayer composite nanoparticles, silver was sputtered on MWCNTs in a vacuum reactor (with 10^{-6} mbar base pressure) by argon plasma treatment using magnetron sputtering method (planar magnetron sputtering model-12" MSPT, HIND high vacuum. Bangalore, India) at 90 w power (DC MAGNETRON SUPPLY POWER MODEL- PS- 2000). Silver (Ag) with high purity (99.9% purity) and argon (research grade 99.9%) were utilized as target and plasma former in magnetron sputtering system, respectively. The distance between MWCNTs and Ag (cathode, 12.5 cm diameter and 3 mm thickness) was kept 12 cm (optimal distance) in plasma reactor during the process to obtain a uniform film with good packing density. Silver nanoparticles with 0.5 nm/s were deposited on MWCNTs surface with constant thickness of 10 nm. The thickness of coated Ag nanolayer was adjusted by changing the deposition time. Before starting the actual experiment, the target was pre-sputtered for 10 min with a moveable shutter located in between the target and substrate. This shutter is also used to control the period of deposition exactly.

3. Preparation of Nanocomposite Cation Exchange Membranes

The heterogeneous cation exchange membranes were prepared by casting technique/phase inversion method. To undertake membrane preparation, resin particles were dried in oven at 30 °C for 48 h and then pulverized into fine particles in a ball mill and sieved to the desired mesh size. The ion exchange resin with desired particle size (-300 +400 mesh) was used in membrane fabrication.

The preparation proceeded by dissolving the polymer binder into THF solvent ((THF : PVC) (v/w), (20 : 1)) in a glass reactor equipped with a mechanical stirrer (Model: Velp Scientifica Multi 6 stirrer) for more than 6 h. This was followed by dispersing a specific quantity of ground resin particle as functional groups agents ((Resin : PVC) (w/w), (1 : 1)) and MWCNTs-co-Ag nanolayer composite particles as additive (0.0, 0.5, 1.0, 2.0, 4.0, 8.0%wt) in polymeric solution, respectively. The mixture was mixed vigorously at room temperature to obtain uniform particle distribution in the polymeric solution. For better dispersion of particles and breaking up their aggregates, the solution was sonicated for 2 h using an ultrasonic instrument. Sonication of solid particles increases the viscosity of casting solution by reducing aggregation and sedimentation and reduces the evaporation rate of casting solvent. This improves the polymer chain relaxation as well as its conformation with particles surfaces and promotes the compatibility of particles and binder [50,51]. This reduces the amount of cracks and fissures between binder and particles and so improves the membrane selectivity. Moreover, uniform distribution of resin particles on membrane surface and in the bulk of membrane matrix provides superior conducting regions in membrane and generates easy flow channels for counter-ion transport. Also, the presence of more conducting region can strengthen the intensity of uniform electrical field around the membrane and decreases the concentration polarization phenomenon [52]. The mixing process was repeated for another 30 min using the mechanical stirrer. The mixture was then cast onto a clean and dry glass plate at 25 °C. The membranes were dried at ambient temperature (25 °C) and immersed in distilled water. As the final stage, the membranes were pretreated by immersing in 0.5 M NaCl solution for 48 h. The membrane thickness was measured by a digital caliper device (Electronic outside Micrometer, IP54 model OLR) around 60-70 μm .

4. Test Cell

The electrochemical properties for the prepared membranes were measured using the test cell [22,23]. The cell (Fig. 1) consists of two cylindrical compartments made of Pyrex glass which are separated by membrane. One side of each vessel was closed by Pt electrode supported with a piece of Teflon and the other side by membrane. The top of each compartment contained two orifices for feeding and sampling purposes.

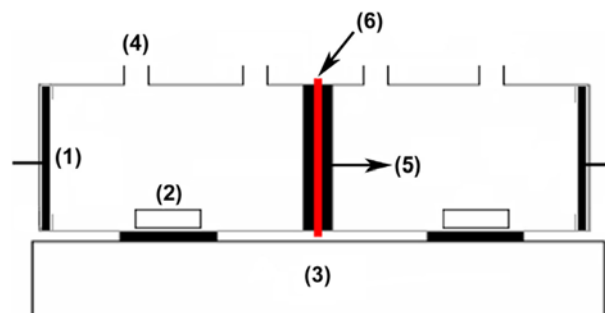


Fig. 1. Schematic diagram of test cell.

- | | |
|------------------|-----------------|
| (1) Pt electrode | (4) Orifice |
| (2) Magnetic bar | (5) Rubber ring |
| (3) Stirrer | (6) Membrane |

5. Composite Nanoparticles Characterization

5-1. Scanning Electron Microscopy/Transmission Electron Microscopy

SEM (EM-3200, model KYKY) and TEM (EM10C, 80 KV) analysis were carried out to characterization of structure and morphology of prepared MWCNT-co-Ag nanolayer composite nanoparticles powders. The prepared samples were sputtered with gold under vacuum conditions for SEM observation. Also dilute mixture of composite nanoparticles/alcohol (droplet, mesh 300) was used for TEM study.

5-2. X-ray Diffraction (XRD)

For micro-structural studies of prepared MWCNT-co-Ag nanolayer composite nanoparticles, X-ray diffraction (XRD) patterns were carried out by X-ray diffractometer (XRD, model X' Pert Pw 3373, $K_{\alpha}=1.54 \text{ \AA}$, Philips, Holland).

6. Membrane Characterization

6-1. Morphological Studies

The behavior of prepared membranes is closely related to their structure, especially the spatial distribution of ionic site. The structures of prepared membranes were examined by scanning optical microscopy (SOM Olympus, model IX 70) in transmission mode with light going through the membrane for scanning purposes. For SOM by SOM device, the samples were cut in small pieces and after mounting between lamellas, observation was made by the optical microscope.

6-2. Mechanical Strength and Roughness

The tensile stress of the prepared nanocomposite membranes was investigated by Universal Testing Machine (UTM, SDLATAS, M 350- 5 KN, 1 mm/min, at ambient temperature). The sample's size was 80 mm×15 mm. Measurements were in triplicate for each sample, and then their average value was reported to minimize the experimental errors. The average roughness of the prepared membranes was determined using the roughness tester (MODEL TR200, high accuracy, resolution of 0.001 μm).

6-3. Membrane Potential, Transport Number and Permselectivity

The membrane potential is the algebraic sum of Donnan and diffusion potentials [4,23,27,53]. This parameter was evaluated for the equilibrated membrane with unequal concentrations of electrolyte solution at ambient temperature. The developed potential across the membrane was measured by connecting both compartments and using saturated calomel electrode (KCl bridges) and digital auto multi-meter (Model: DEC 330FC, Digital Multimeter, China). The measurement was repeated until a constant value was obtained. The membrane potential (E_{Measure}) is expressed for mono (1 : 1) and bivalent (2 : 1) ionic solutions as follows [4,15,21,28,53,54]:

$$E_{\text{Measure}} = (2t_i^m - 1) \left(\frac{RT}{F} \right) \ln \left(\frac{a_1}{a_2} \right) \quad (\text{monovalent solution- 1 : 1 salts}) \quad (1)$$

$$E_{\text{Measure}} = \left(\frac{3}{2}t_i^m - 1 \right) \left(\frac{RT}{F} \right) \ln \left(\frac{a_1}{a_2} \right) \quad (\text{bivalent solution- 1 : 2 salt})$$

where t_i^m is transport number of counterions in membrane phase, R is gas constant, T is the temperature, a_1 , a_2 are solutions electrolyte activities in contact membrane surfaces and F is faraday constant. The ionic permselectivity of membranes also is quantitatively expressed based on the migration of counterion through the IEMs [4,15,53,54]:

$$P_s = \frac{t_i^m - t_0}{1 - t_0}, \quad t_0 = \frac{\lambda_i}{\sum_{i=1}^n \lambda_i} \quad (2)$$

where, t_0 is the transport number of counterions in solution and calculated based on molar ionic conductivity (λ_i) [55].

6-4. Concentration of Fixed Ionic Charge of Membrane

The existence of greater conducting regions on membrane surface can improve the membrane electrochemical properties and strengthen the intensity of uniform electrical field around the membrane, which decreases the concentration polarization phenomenon. The concentration of fixed ionic charge on membrane surface (Y) has been expressed in terms of permselectivity as follows [6,16,53,54]:

$$Y = \frac{2C_{\text{Mean}}P_s}{\sqrt{1 - P_s^2}} \quad (3)$$

where, P_s is the permselectivity and C_{Mean} is the mean concentration of electrolytes.

6-5. Ionic Permeability and Flux

The measurements of ionic permeability and flux were by using a test cell. A 0.1 M NaCl solution was placed on anodic side of the cell and a 0.01 M NaCl solution on its cathodic side. A DC electrical potential (Dazheng, DC power supply, Model: PS-302D) with an optimal constant voltage (10 V) was applied across the cell with stable platinum electrodes. The membrane surface area was also 19.63 cm^2 . The cations pass through the membrane to cathodic section. Also, according to anodic and cathodic reactions the produced hydroxide ions remain in cathodic section and increase the pH of this region.



According to the first Fick's law, the flux of ions through the membrane can be expressed as follows [20-22]:

$$N = P \frac{C_1 - C_2}{d} \quad (4)$$

where, P is coefficient diffusion of ions, d is membrane thickness, N is ionic flux and C is the cations concentration in the compartments.

$$N = - \frac{V}{A} \times \frac{dC_1}{dt} = P \frac{C_1 - C_2}{d} \quad (5)$$

$$C_1^0 = 0.1 \text{ M}, \quad C_2^0 = 0.01 \text{ M}, \quad C_1 + C_2 = C_1^0 + C_2^0 = 0.11 \text{ M} \quad (6)$$

where, A is the membrane surface area. Integrating of Eq. (5) was as follows:

$$\ln \frac{(C_1^0 + C_2^0 - 2C_2)}{(C_1^0 - C_2^0)} = - \frac{2PA t}{Vd} \quad (7)$$

The diffusion coefficient and flux of cations in membrane phase are calculated from Eq. (7) considering pH changes measurements (Digital pH-meter, Jenway, Model: 3510) in cathodic section.

6-6. Electrical Resistance

The electrical resistance of equilibrated membrane was meas-

ured in NaCl solution at ambient temperature [23,28,56]. Measurement was by an alternating current bridge with 1,500 Hz frequency (Audio signal generator, Electronic Afzar Azma Co. P.J.S). The membrane resistance was calculated using difference resistance between the cell (R_1) and electrolyte solution (R_2) ($R_m=R_1-R_2$). The areal resistance was expressed as follows:

$$r=(R_m A) \quad (8)$$

where, is areal resistance and A is the surface area of membrane.

RESULTS AND DISCUSSION

1. Characterization of MWCNT-co-Ag Nanolayer Composite Nanoparticles

The SEM and TEM images of pristine MWCNTs and prepared MWCNT-co-Ag nanolayer composite nanoparticles are shown in Fig. 2. The MWCNTs and Ag nanolayer are clearly seen in the images. Silver nanolayers/nanoparticles are uniformly distributed on the surface of fiber-like multiwalled carbon nanotubes. The uniform distribution of nanolayers/nanoparticles on the surface of MWCNTs provides more and superior conducting regions for the composite nanoparticles and strengthens the intensity of electrical field, which decreases the concentration polarization phenomenon. Also, images indicate that magnetron sputtering method/plasma treatment is an effective producer for preparation of hybrid MWCNT-co-Ag nanolayer composite nanoparticles successfully.

The XRD patterns of pristine MWCNTs and synthesized MWCNT-co-Ag nanolayer composite nanoparticles are given in

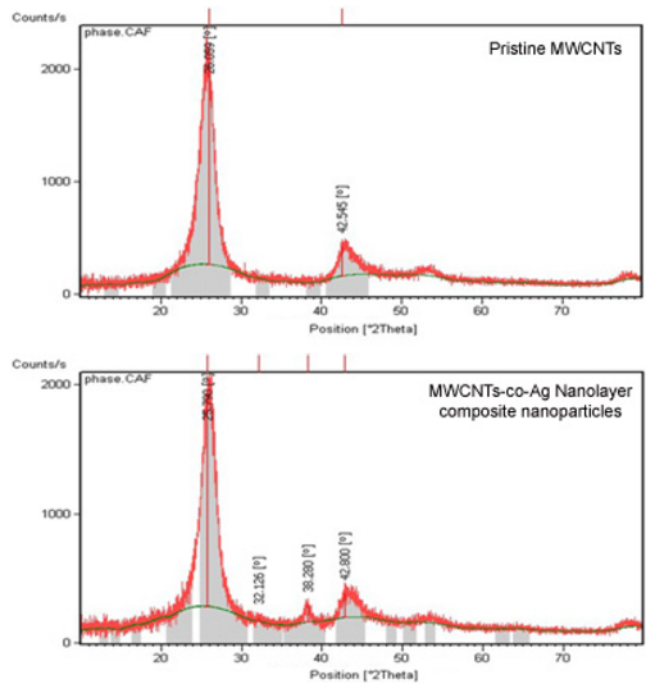
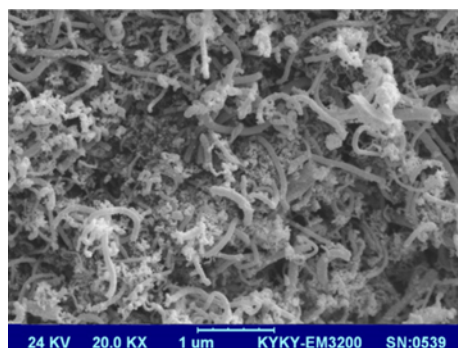
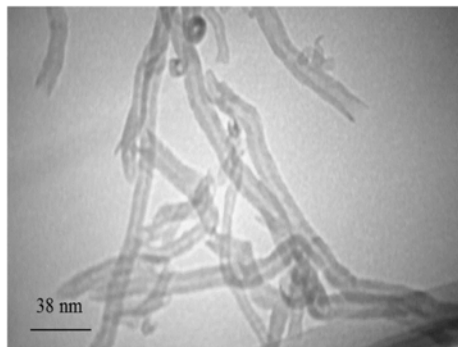


Fig. 3. XRD patterns of (a) pure MWCNTs and (b) synthesized MWCNT-co-Ag nanolayer composite nanoparticles.

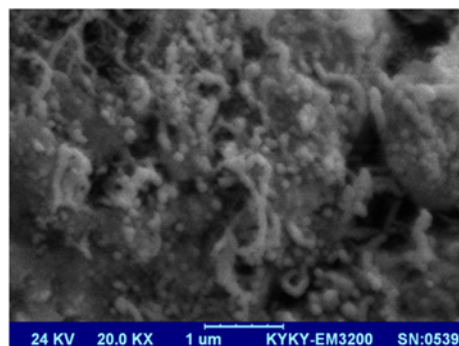
Fig. 3(a) and (b). In the diffraction pattern of pristine MWCNTs, one sharp peak (at $2\theta=26.059^\circ$) and several weak peaks appear, which are assigned to (0 0 2), (1 0 0), (0 0 4) and (1 1 0) planes of



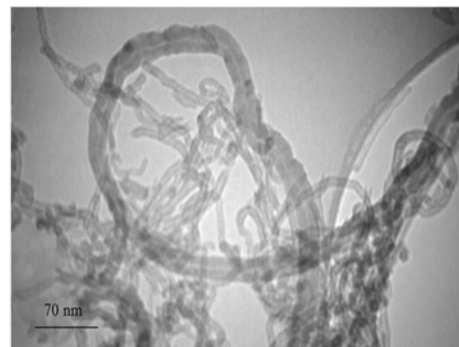
SEM- Pristine MWCNTs



TEM- Pristine MWCNTs



SEM- MWCNT-co-Ag nanolayer



TEM- MWCNT-co-Ag nanolayer

Fig. 2. The SEM and TEM images of pristine MWCNTs and prepared MWCNTs-co-Ag nanolayer composite nanoparticles.

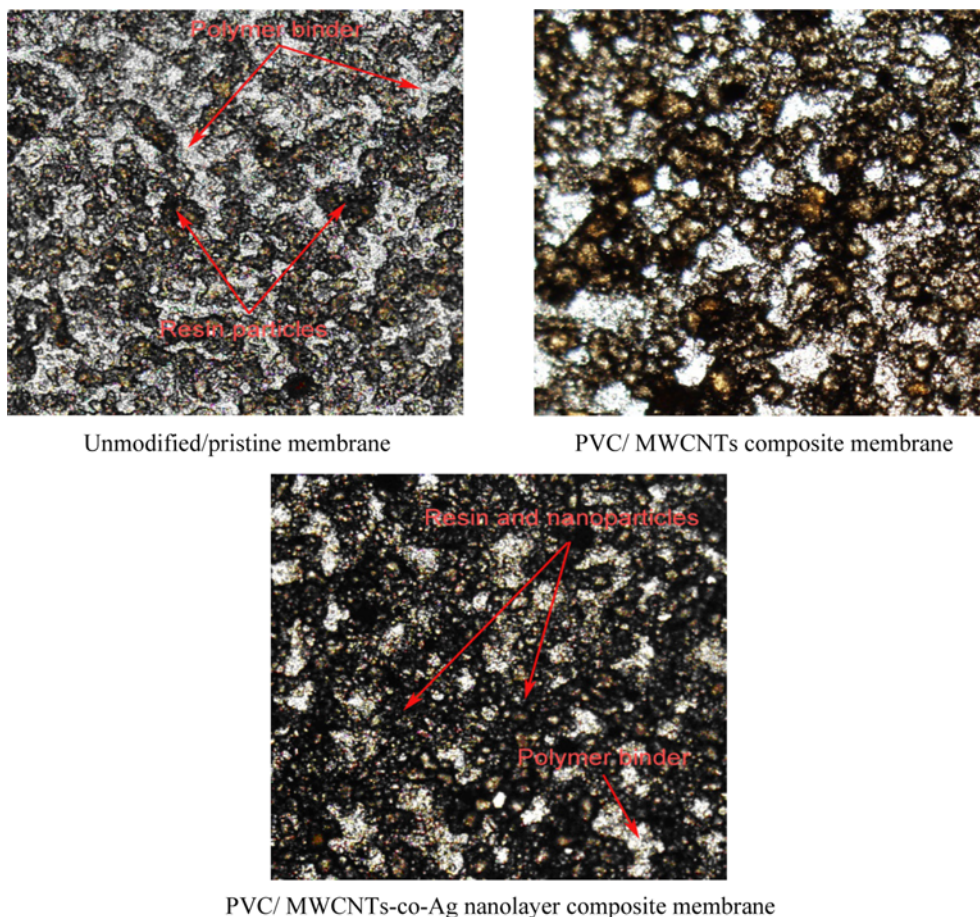


Fig. 4. SOM images of prepared membranes (10 X magnification); (a) unmodified membrane, (b) PVC/MWCNTs composite membrane and (c) PVC/MWCNTs-co-Ag nanolayer composite membrane.

graphitized MWCNTs. For MWCNT-co-Ag nanolayer composite nanoparticles, new diffraction peaks at $2\theta=38.280^\circ$ and 32.126° are observed clearly, which are not visible for pure MWCNTs and correspond to planes of face-centric-cubic of Ag. The results indicated crystalline structure for both MWCNTs and composite nanoparticles.

2. Characterization of Nanocomposite Membranes

2-1. Morphological Studies

SOM studies were conducted to evaluate the morphology and ionic/additive sites condition in prepared membrane. The membranes SOM images in transmission mode with light going through them are depicted in Fig. 4. The polymer binder, resin particles and used additive nanoparticles are seen in the images. The brightness of the images was decreased and dark regions were increased by use of additive in the membrane matrix, which restricts the light transmission through the membranes. The images show a relatively uniform surface for the membranes. As shown, the particles are uniformly distributed in the prepared membranes. As described earlier [51], sonication has a significant effect on the distribution of particles in prepared membranes and results in the formation of more uniform phase. Moreover, SOM images showed more uniform distribution of particles for the composite membrane containing *MWCNTs-co-Ag nanolayer* composite nanoparticles com-

pared to membrane containing pure MWCNTs. The surface modification of MWCNTs with Ag nanolayer increases the interactions between nanoparticles with resin particles, and so improves its distribution throughout the membrane matrix. The uniform distri-

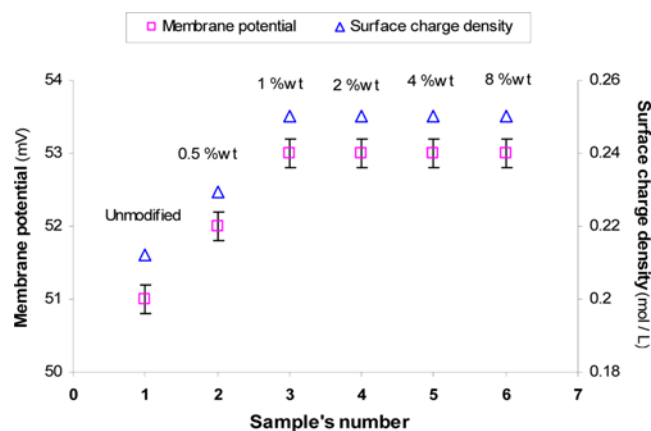


Fig. 5. Membrane potential and surface charge density of prepared ion exchange membranes modified by MWCNTs-co-Ag nanolayer composite nanoparticles in sodium chloride ionic solution.

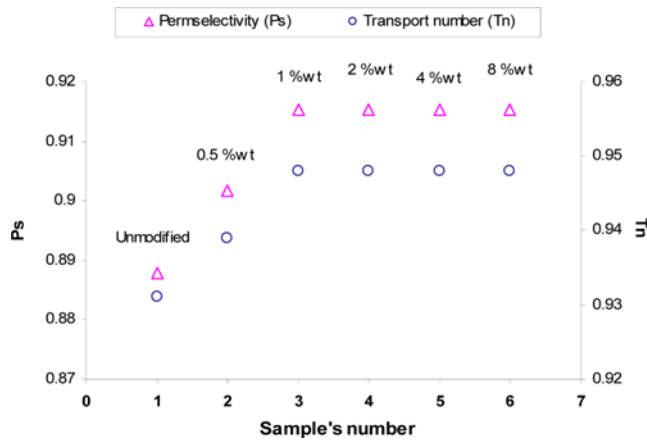


Fig. 6. Comparison between the transport number (Tn) and permselectivity (Ps) of prepared membranes in NaCl ionic solution; pristine membrane and membranes containing MWCNTs-co-Ag nanolayer composite nanoparticles.

bution of particles improves the polymer chains relaxation as well as its conformation with particles surfaces and so enhances the membrane selectivity.

2-2. Membrane Potential, Permselectivity and Transport Number (NaCl)

The membrane potential (Fig. 5) was improved in sodium chloride ionic solution by increase of MWCNTs-co-Ag nanolayer composite nanoparticles in prepared membranes. This may be attributed to increase of membrane surface charge density (Fig. 5), which provides additional conducting regions for the membranes and generates suitable flow channels for easy passage of the counter ions. This leads to enhanced Donnan exclusion that is responsible for the increment of membrane potential [4,15,23,53].

The transport number and permselectivity of membranes in NaCl solution are also depicted in Fig. 6. Obtained results showed that membrane permselectivity and transport number were enhanced by increase of additive concentration in prepared membranes. This happening also can be explained with respect to increase in membrane surface charge density with suitable control of pathways for ions traffic, which improves the selectivity. Also, with increase of additive concentration, the ionic pathways in the membrane matrix are occupied by the additive particles and so they are narrowed by them as space limiting factors. This causes strengthening of the ionic sites domination on ions traffic and increases the membrane transport number and selectivity.

Moreover, as shown in Fig. 7, the membrane average roughness was decreased slightly by increase of additive concentration in the casting solution. A membrane with a rough surface has more abil-

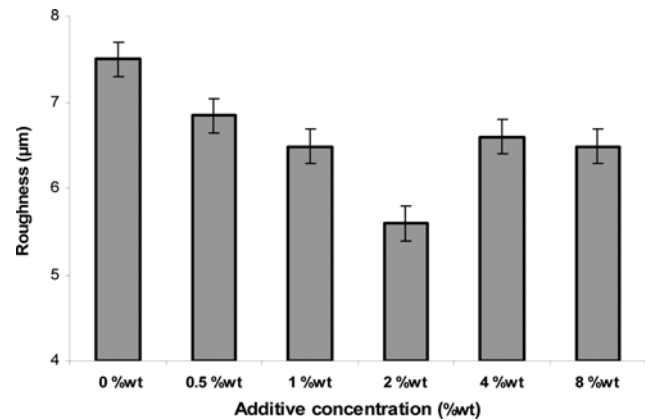


Fig. 7. The average roughness of prepared cation exchange membranes with various ratios of MWCNTs/Ag nanolayers composite nanoparticles.

Table 1. The effect of electrolyte's concentration on membrane potential, transport number and selectivity of PVC/(4%wt) MWCNTs-co-Ag nanolayer mixed matrix membrane

Concentration (M)	Membrane potential (MV)	Transport number (%)	Permselectivity (%)
(0.001/0.01)	51	>93	>88
(0.01/0.1)	53	>94	>91
(0.05/0.5)	48	>90	>84

ity to trap the ions, which leads to lower ionic rejection compared to the membrane with smooth surface. This means that the physical properties of membrane have a crucial effect on its performance.

2-3. The Effect of Electrolyte Concentration on Transport Number and Selectivity

Results showed that (Table 1) membrane potential, transport number and permselectivity were improved initially in sodium chloride ionic solution by increase of electrolyte concentration from (0.001/0.01) M to (0.01/0.1) M. This may be attributed to increase of counterion interactions with the membrane surface, which is possible at higher concentration of electrolyte environment and leads to enhanced Donnan exclusion. Results are significantly in contrast with Donnan equilibrium theory [4,15,53,57].

All mentioned parameters were decreased again by more increase in electrolyte concentration from (0.01/0.1) M to (0.05/0.5) M, which is due co-ions percolation through the membrane at high electrolyte concentration.

2-4. Characterization of Membranes in Bivalent Ionic Solutions

During the ion removal or concentrating of solutions, scale for-

Table 2. Comparison between the membrane potential, transport number and permselectivity of modified membrane containing (4%wt) composite nanoparticles in Mono and Bivalent ionic solutions

Concentration (M)	Membrane potential (MV)		Transport number (%)		Permselectivity (%)	
	NaCl	Pb (NO ₃) ₂	NaCl	Pb (NO ₃) ₂	NaCl	Pb (NO ₃) ₂
(0.001/0.01)	51	24	>93	>92	>88	>85
(0.01/0.1)	53	17	>94	>84	>91	>70

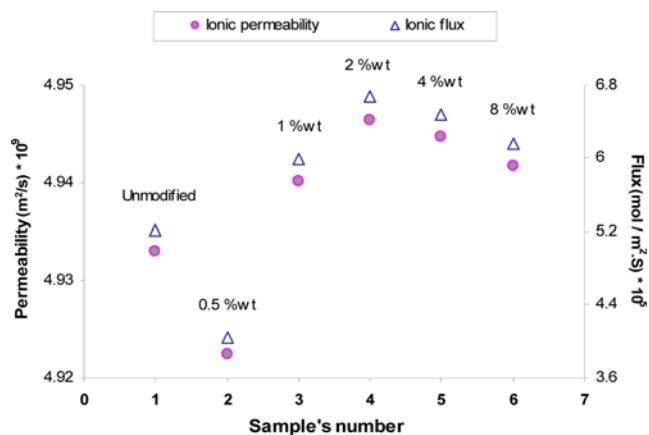


Fig. 8. Ionic permeability and flux of prepared cation exchange membranes with various ratios of additives (MWCNTs/Ag nanolayers) content.

mation of bivalent ions on membrane surface is a serious problem which is due to hydroxide formation. Obtained results showed lower potential, selectivity and transport number for the prepared membranes in bivalent ionic solution ($\text{Pb}(\text{NO}_3)_2$) compared to monovalent type (NaCl) (Table 2). This may be due to stronger bonds of bivalent ions with ion exchange functional groups [15,27], which decreases the membranes electrochemical properties. In fact, bivalent ions have stronger electrostatic attraction with fixed opposite charge sites of membranes and so prevent from their dissociation. Furthermore, the larger radius of bivalent ions and their hydrated size in comparison with monovalent type are other reasons for lower membrane potential, transport number and permselectivity [15,21].

2-5. Ionic Permeability and Flux

During the experiment, ions pass through the membrane and reach to concentration section. Results (Fig. 8) revealed that the ionic permeability and flux were decreased initially by increase of additive concentration up to 0.5%wt in the casting solution. This may be attributed to the pore filling phenomenon by the additive particles, which makes difficult the ion transport and so declines the ionic permeability and flux. The ionic permeability and flux were increased again by more increase in additive content from 0.5 to 8%wt in prepared membranes. This may be due to adsorption characteristic of MWCNTs-co-Ag nanolayer composite nanoparticles at higher nanoparticle concentration, which increases the cation interaction with the membrane surface and facilitates the ion transport. Also, the electrical property of used composite nanoparticles strengthens the intensity of electrical field around the membrane and increases the ionic permeability and flux.

2-6. Electrical Resistance

The areal electrical resistance of prepared membranes in 0.5 M NaCl ionic solution was decreased sharply by increase of additive loading ratio in modified membranes (Fig. 9). This is assigned to electrical property and adsorption characteristic of MWCNTs-co-Ag nanolayer composite nanoparticles, which improves the ions' interaction with membrane surface and so strengthens the intensity of uniform electrical field around the membrane. In general, less selective membranes have lower membrane resistances but this is not always true and depends on the membrane structure and its

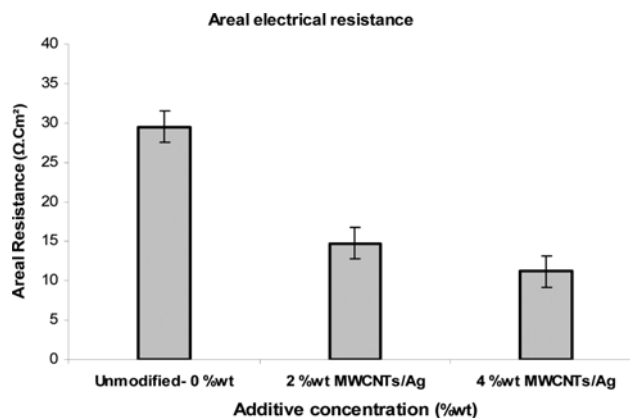


Fig. 9. The areal electrical resistance of prepared cation exchange membranes: Unmodified membrane and modified membranes containing MWCNTs/Ag nanolayers composite nanoparticles.

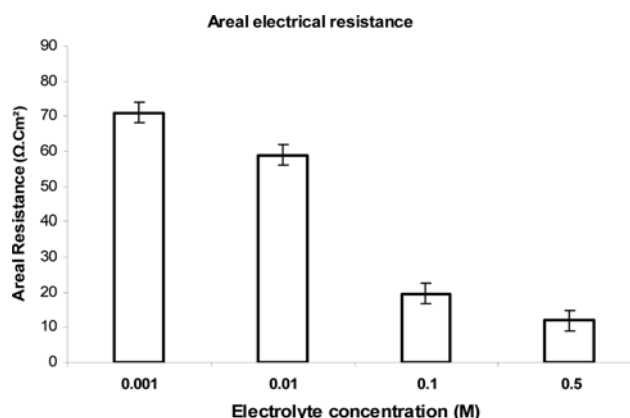


Fig. 10. The effect of electrolyte concentration on electrical resistance of prepared nanocomposite membranes (PVC-co- 4%wt additive).

properties [57].

2-7. The Effect of Electrolyte Concentration on Membrane Electrical Resistance

The effects of electrolyte concentration on electrical resistance of prepared membranes are shown in Fig. 10. The significant increase in membrane resistance at lower salt concentration is attributed to the diffusion boundary layer resistance, which is more significant at lower salt concentration. Moreover, at high electrolyte concentration, the membrane swelling decreases the electrical resistance [17].

2-8. Mechanical Strength of Prepared Membranes

The effect of additive loading on tensile stress behavior of prepared membranes was studied by Universal Testing Machine. Obtained results (Fig. 11) showed that mechanical stability of prepared membranes was improved by increase of additive content up to 1%wt in prepared membranes due to the presence of strong interfacial bonding between the polymers and additive particles, which improves the mechanical property. Moreover, the local heterogeneity in prepared membranes with well dispersed additive particles makes favorable molecular interactions between the additive

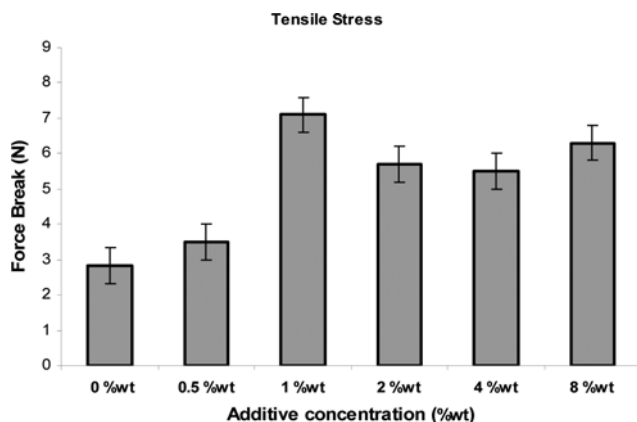


Fig. 11. The effect of additive concentration on mechanical strength behavior of prepared nanocomposite membranes.

particles and binder [23,51,58]. The membrane tensile stress was decreased again by more additive loadings from 1 to 8%wt due to discontinuity of polymer binder, which tends to form discrete phase.

3. Superior Membrane

The modified cation exchange membrane containing 4%wt MWCNTs-co-Ag nanolayer composite nanoparticles showed better electrochemical properties compared to other prepared membranes. A comparison between the electrochemical properties of modified membrane containing 4%wt MWCNTs-co-Ag nanolayer composite nanoparticles, membrane containing 4%wt pure MWCNTs and pristine one (un-modified membrane) is given in Table 3. Also, a comparison with some commercial membranes is given in Table

4. The obtained results revealed that modified membranes in this study are comparable with commercial ones.

CONCLUSION

SEM and TEM images of prepared MWCNT-co-Ag nanolayer composite nanoparticles showed uniform distribution of Ag nanolayers on the surface of fiber-like multiwalled carbon nanotubes. Also, XRD patterns results indicated crystalline structure for the composite nanoparticles. Images showed a relatively uniform surface/particles distribution for the membranes. Moreover, images exhibited more uniform distribution of particles for the composite membrane containing MWCNTs-co-Ag nanolayer composite nanoparticles compared to membrane containing pure MWCNTs. The membrane potential, surface charge density, selectivity and transport number were improved by increase of MWCNTs-co-Ag nanolayer composite nanoparticles in prepared membranes. Membrane potential, transport number and selectivity were improved by increase of electrolyte concentration. The membrane average roughness decreased slightly by increase of additive concentration in the casting solution. A membrane with a rough surface has more ability to trap the ions, which leads to lower ionic rejection compared to the membrane with smooth surface. The ionic permeability and flux decreased initially by increase of additive concentration up to 0.5%wt in the casting solution and then increased again by more increase in additive content. The areal electrical resistance of modified nanocomposite membranes decreased sharply by increase of additive loading in membrane matrix. The electrical resistance of membranes also decreased by increase of electrolyte concentration.

Table 3. Comparison between the electrochemical properties of (PVC/MWCNTs-co-Ag nanolayer composite nanoparticles) membrane, (PVC/MWCNTs) membrane and pristine one

Membrane	Permselectivity (%)	Transport number (%)	Flux (mol/m ² ·S)*10 ⁵	Electrical resistance (Ω cm ²)
Pristine membrane 0%wt additive	>88	>93	5.21	29.5
Modified membrane 4%wt pure MWCNTs	>89	>93	5.75	20.3
Modified membrane 4%wt MWCNTs/Ag	>91	>94	6.49	11.2

Table 4. Comparison between the electrochemical properties of prepared membranes in this research and some commercial membranes [9,19,57]

Membrane	Permselectivity ^a (%)	Electrical resistance ^a (Ω cm ²)
Modified membrane 4%wt MWCNTs/Ag	>91	<11.2
RAI Research Corp., USA R-5010-H	95	8-12
Ionics Inc., USA, CR61-CMP	-	11
Ionics Inc., USA, CR67-HMR	-	7-11
FuMA-Tech GmbH, Germany FKB	-	5-10
Ralex® CMH-PES	>92	<10
Ionics Inc., USA (61CZL386)	-	9
CSMCRI, India (HGC)	87	4-6
Fumasep® FKE	>98	<3
Fumasep® FKD	>95	<3
Neosepta® CMX	>96	1.8-3.8

^aMeasured in sodium chloride ionic solution

Prepared membranes exhibited lower selectivity and transport number for bivalent ions compared to monovalent type. Furthermore, the mechanical stability of prepared membranes improved by increase of additive content up to 1%wt in prepared membranes. The membrane tensile stress decreased again by more additive loadings from 1 to 8%wt due to discontinuity of polymer binder, which tend to form discrete phase. Among the prepared membranes, modified membrane containing 4%wt MWCNTs-co-Ag nanolayer composite nanoparticles showed better electrochemical properties compared to other modified membranes and unmodified ones. The obtained results are valuable for electro membrane processes, especially electro dialysis process for water recovery and water treatment.

ACKNOWLEDGEMENT

The authors gratefully acknowledge Arak University and also Iran Nanotechnology Initiative Council for the financial support during this research.

REFERENCES

1. P. V. Vyas, P. Ray, S. K. Adhikary, B. G. Shah and R. Rangarajan, *J. Colloid Interface Sci.*, **257**, 127 (2003).
2. M. Y. Kariduraganavar, R. K. Nagarale, A. A. Kittur and S. S. Kulkarni, *Desalination*, **197**, 225 (2006).
3. R. K. Nagarale, G. S. Gohil, V. K. Shahi, G. S. Trivedi and R. Rangarajan, *J. Colloid Interface Sci.*, **277**, 162 (2004).
4. V. K. Shahi, S. K. Thampy and R. Rangarajan, *J. Membr. Sci.*, **158**, 77 (1999).
5. M. Zarrinkhameh, A. Zendehtnam and S. M. Hosseini, *Korean J. Chem. Eng.*, **31**, 1187 (2014).
6. R. K. Nagarale, V. K. Shahi, R. Schubert, R. Rangarajan and R. Mehnert, *J. Colloid Interface Sci.*, **270**, 446 (2004).
7. G. J. Hwang, H. Ohya and T. Nagai, *J. Membr. Sci.*, **156**, 61 (1999).
8. C. O. M' Bareck, Q. T. Nguyen, S. Alexandre and I. Zimmerlin, *J. Membr. Sci.*, **278**, 10 (2006).
9. T. Xu, *J. Membr. Sci.*, **263**, 1 (2005).
10. A. Elattar, A. Elmidaoui, N. Pismenskaia, C. Gavach and G. Pourcelly, *J. Membr. Sci.*, **143**, 249 (1998).
11. J. Schauer and L. Brozova, *J. Membr. Sci.*, **250**, 151 (2005).
12. R. W. Baker, *Membrane Technology and Applications*, Wiley, England, 2nd Ed. (2004).
13. S. Koter and A. Warszawski, *Polish Journal of Environmental Studies*, **9/1**, 45 (2000).
14. S. M. Hosseini, S. S. Madaeni and A. R. Khodabakhshi, *J. Membr. Sci.*, **365**, 438 (2010).
15. G. S. Gohil, V. V. Binsu and V. K. Shahi, *J. Membr. Sci.*, **280**, 210 (2006).
16. V. K. Shahi, G. S. Trivedi, S. K. Thampy and R. Rangarajan, *J. Colloid Interface Sci.*, **262**, 566 (2003).
17. P. Dlugolecki, B. Anet, S. J. Metz, K. Nijmeijer and M. Wessling, *J. Membr. Sci.*, **346**, 163 (2010).
18. G. S. Gohil, V. K. Shahi and R. Rangarajan, *J. Membr. Sci.*, **240**, 211 (2004).
19. R. K. Nagarale, G. S. Gohil and V. K. Shahi, *Adv. Colloid Interface Sci.*, **119**, 97 (2006).
20. J. Kerres, W. Cui, R. Disson and W. Neubrand, *J. Membr. Sci.*, **139**, 211 (1998).
21. X. Li, Z. Wang, H. Lu, C. Zhao, H. Na and C. Zhao, *J. Membr. Sci.*, **254**, 147 (2005).
22. S. M. Hosseini, S. S. Madaeni and A. R. Khodabakhshi, *J. Membr. Sci.*, **351**, 178 (2010).
23. S. M. Hosseini, S. S. Madaeni and A. R. Khodabakhshi, *J. Membr. Sci.*, **362**, 550 (2010).
24. A. R. Khodabakhshi, S. S. Madaeni and S. M. Hosseini, *Polym. Int.*, **60**, 466 (2011).
25. J. Balster, O. Krupenko, I. Punt, D. F. Stamatialis and M. Wessling, *J. Membr. Sci.*, **263**, 137 (2005).
26. T. Sata and W. Yang, *J. Membr. Sci.*, **206**, 31 (2002).
27. R. K. Nagarale, G. S. Gohil, V. K. Shahi and R. Rangarajan, *Colloids Surf., A*, **251**, 133 (2004).
28. T. Sata, *Ion Exchange Membranes: Preparation, Characterization, Modification and Application*, Royal Society of Chemistry, Cambridge, UK (2004).
29. E. S. Wiks, *Industrial Polymers Handbook: Products, Processes, Application*, WILEY-VCH Press, Germany (2001).
30. James E. MARK, *Polymer Data Handbook*, Oxford University Press, New York (1999).
31. C. A. Harper, *Handbook of plastic and elastomers*, McGraw-Hill, New York (1975).
32. A. F. Ismail, P. S. Goh, S. M. Sanip and M. Aziz, *Sep. Purif. Technol.*, **70**, 12 (2009).
33. J. M. Thomassin, J. Kollar, G. Caldarella, A. Germain, R. Jerome and C. Detrembleur, *J. Membr. Sci.*, **303**, 252 (2007).
34. S. H. Liao, C. C. Weng, C. Y. Yen, M. C. Hsiao, C. C. M. Ma, M. C. Tsai, A. Su, M. Y. Yen, Y. F. Lin and P. L. Liu, *J. Power Sources*, **195**, 263 (2010).
35. A. Zendehtnam, M. Arabzadegan, S. M. Hosseini, N. Robatmili and S. S. Madaeni, *Korean J. Chem. Eng.*, **30**(6), 1265 (2013).
36. N. Prakash, S. Jayapradeep and P. N. Sudha, *Investigation of antimicrobial properties of silver and copper nanoparticles encapsulated in chitosan*, First International Conference on Nanostructure Material, Kottayam India, April 2009, 311-317.
37. N. Tanaka, H. Nishikiori, S. Kubota, M. Endo and T. Fujii, *Carbon*, **47**, 2752 (2009).
38. D. K. V. Ramana, J. S. Yu and K. Seshaiha, *Chem. Eng. J.*, **223**, 806 (2013).
39. X. Wang, B. Xia, X. Zhu, J. Chen, S. Qiu and J. Li, *J. Solid State Chem.*, **181**, 822 (2008).
40. V. Georgakilas, D. Gournis, V. Tzitzios, L. Pasquato, D. M. Guldi and M. Prato, *J. Mater. Chem.*, **17**, 2679 (2007).
41. F. Wang, S. Arai and M. Endo, *Electrochem. Commun.*, **6**, 1042 (2004).
42. F. Alimohammadi, M. Parvinzadeh Gashti, A. Shamei and A. Kiumarsi, *Superlattices Microstruct.*, **52**, 50 (2012).
43. T. Machino, W. Takeuchi, H. Kano, M. Hiramoto and M. Hori, *Appl. Phys. Express*, **2**, 25001 (2009).
44. C. Kim, B. Lim, B. Kim, U. Shim, S. Oh and B. Sung, *Synth. Met.*, **159**, 424 (2009).
45. T. Laha, A. Agarwal, T. McKechnie and S. Seal, *Mater. Sci. Eng. A.*, **381**, 249 (2004).
46. C. F. Deng, D. Z. Wang, X. Zhang and A. B. Li, *Mater. Sci. Eng. A.*

- 444, 138 (2007).
47. H. Kwon, M. Estili, K. Takagi, T. Miyazaki and A. Kawasaki, *Carbon*, **47**, 570 (2009).
48. W.M. Daoush, B.K. Lim, C.B. Mo, D.H. Nam and S.H. Hong, *Mater. Sci. Eng. A.*, **513**, 247 (2009).
49. M. Ohring, *Material Science of thin films; Deposition and Structure*, 2nd Ed., Academic Press (2001).
50. C. E. Powell and G. G. Qiao, *J. Membr. Sci.*, **279**, 1 (2006).
51. S. M. Hosseini, S. S. Madaeni and A. R. Khodabakhshi, *J. Appl. Polym. Sci.*, **118**, 3371 (2010).
52. M. S. Kang, Y. J. Choi, I. J. Choi, T. H. Yoon and S. H. Moon, *J. Membr. Sci.*, **216**, 39 (2003).
53. R. K. Nagarale, V. K. Shahi, S. K. Thampy and R. Rangarajan, *React. Funct. Polym.*, **61**, 131 (2004).
54. R. K. Nagarale, V. K. Shahi and R. Rangarajan, *J. Membr. Sci.*, **248**, 37 (2005).
55. D. R. Lide, *CRC Handbook of Chemistry and Physics*, CRC Press, 87th Ed., 2006-2007.
56. Y. Tanaka, *Ion Exchange Membranes: Fundamentals and Applications*, *Membrane Science and Technology Series*, 12, Elsevier, Netherlands (2007).
57. P. Długolecki, K. Nymeijer, S. Metz and M. Wessling, *J. Membr. Sci.*, **319**, 214 (2008).
58. S. M. Hosseini, P. Koranian, A. Gholami, S. S. Madaeni, A. R. Moghadassi, P. Sakinejad and A. R. Khodabakhshi, *Desalination*, **329**, 62 (2013).