

## Synthesis, Characterization and Transport Properties of Novel Ion-exchange Nanocomposite Membrane Containing In-situ Formed ZnO Nanoparticles

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### Abstract

A new type of cation-exchange nanocomposite membranes was prepared by in-situ formation of ZnO nanoparticles in a blend containing sulfonated poly (2,6-dimethyl-1,4-phenylene oxide) and sulfonated polyvinylchloride via a simple one-step chemical method. As-synthesized nanocomposite membranes were characterized using Fourier transform infrared spectroscopy, scanning electron microscopy and X-ray diffraction. The SEM images showed that ZnO nanoparticles were uniformly dispersed throughout the polymeric matrices. The effect of additive loading on physicochemical and electrochemical properties of prepared cation-exchange nanocomposite membranes was studied. Various characterizations revealed that the incorporation of different amounts of ZnO nanoparticles into the basic membrane structure had a significant influence on the membrane performance and could improve the electrochemical properties.

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## 1. Introduction

The significance of membrane processes for the treatment of wastewater and drinking water is still growing. The expense of membranes continues to decrease and it is possible to predict that membranes will be in extensive use in water treatment facilities. Ion-exchange membranes are one of the most advanced membranes, which have

been used in various industrial separation fields [1]: chlor-alkali process, electrodialysis (ED), electro-membrane reactors, electro-deionization and diffusion dialysis [2,3]. Recently, the number of applications that use ion-exchange membranes has gained increasing interest. The use of ion-exchange membranes in fuel cells and separation processes stands out owing to the significant environmental

and economical advantages that they can bring to the society [4,5]. The features of ion-exchange membranes specify to a great extent the performance of electro dialysis processes. These membranes have charged groups attached to their structure which under the influence of an electric field, allow the permeation of ions with opposite charge through the membrane and reject ions with the same charge sign [5]. The development of ion-exchange membranes with improved permselectivity, lower electrical resistance and better chemical and thermal stability at lower cost is one of the most urgent requirements. However, the evaluation of new materials for membrane fabrication opens up the opportunity to further related processes improvement. The composite membranes represent the essential properties of organic polymeric matrix and inorganic fillers and put forward specific advantages for the fabrication of new membranes with suitable separation performances [6]. Thus, organic-inorganic composite materials have attracted more concern [7-9]. Many studies explain fabrication of adsorptive membranes via polymers blending and additive loading procedures using nanomaterials such as metal oxide nanoparticles to enhance membranes performance for wastewater treatment [10, 11]. The polymers are considered the important materials in fabrication of composite membranes due to the benefits of its desirable membrane forming ability, flexibility and low cost. Poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) is a poly-aryl compound which has suitable membrane-forming properties, appropriate thermal and chemical stability. Among the PPO derivatives, aryl substituted sulfonated PPO (SPPO) is an appropriate structure which has been used as a membrane for reverse osmosis, gas separation, ultra-filtration and cation-exchange membranes.

However, SPPO contains plenty of  $-\text{SO}_3\text{Na}$  groups and is highly hydrophilic, so, it can swell strongly in water if the degree of sulfonation is above 28%. The dimensional instability of SPPO is a disadvantage which prevents its practical applications in fuel cells and electro-membrane processes [12]. One of the attractive procedure for improving the membrane properties (e.g., water swelling and dimensional stability) is blending of a mechanical and dimensional stable material into hydrocarbon based polymers; thus, blending of two polymers such as sulfonated polyvinyl chloride (SPVC) and SPPO can generate a structure with novel properties and the membranes are expected to be ion exchangeable and dimensionally stable. Polyvinyl chloride (PVC) is an outstanding material because of its high mechanical strength, reasonable cost and excellent chemical properties (resistance against acid, alkali and organic solvents). The PVC- $\text{SO}_3\text{H}$  structures have applications as a sorbent, based on cation-exchange and hydro-phobicity simultaneously [13]. Zinc oxide is a type of plentiful mineral and one of the most oxide under ambient conditions, exists chiefly in soil and sediment [14-16]. Preparing the new type of cation-exchange nanocomposite membranes with appropriate physicochemical properties for application in electro dialysis process was main target in this work. For the purpose, ZnO nanoparticles were in situ formed in polymer binders matrix and SPPO+SPVC /ZnO nanocomposites were synthesized using the one-step synthetic method. Moreover, sonication was employed in membranes fabrication technique to achieve better homogeneity in the matrix and also to obtain better electrochemical properties and mechanical integrity. Currently no reports have considered incorporating ZnO nanoparticles into cation-exchange membranes. The effect of ZnO

nanoparticles loading on the physicochemical properties of prepared cation-exchange nanocomposite membranes was studied and evaluated. During this experiment, sodium chloride was employed as monovalent ionic solutions for the membrane characterization. The results are applicable for electro-membrane processes especially in electro-dialysis process for waste water treatment and water recovery.

## 2 Experimental

### 2.1 Materials and characterization

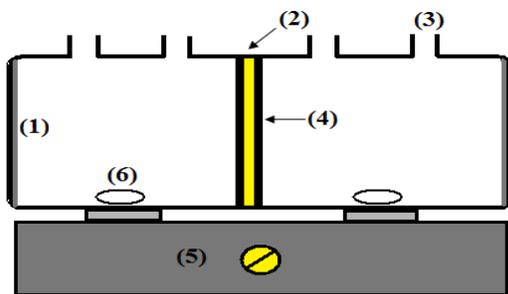
Polyvinylchloride (PVC) purchased from BIPC, Iran, grade S-7054. Poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) with inherent viscosity of 0.57 dl/g in chloroform at 25 °C was obtained from Institute of Chemical Engineering of Beijing (China); SPPO was prepared by sulfonation of PPO according to the literature [17]. Tetrahydrofuran (THF) LR grade as solvent, sodium chloride and sulfuric acid (98%),  $Zn(NO_3)_2 \cdot 4H_2O$  and  $NH_3$  were supplied from Merck Company. Throughout the experiment, distilled water was used. Morphological investigations of the membranes were carried out using scanning electron microscopy (SEM) from Philips Company at an acceleration voltage of 25 kV. The membrane samples were sputtered with gold to obtain a conductive surface. XRD patterns were recorded by a Philips, X-ray diffractometer using Ni-filtered Cu Ka radiation. For preparation of nanocomposite, a multi-wave ultrasonic generator (Bandeline MS 73) equipped with a converter/transducer and titanium oscillator operating at 20 kHz with a maximum power output of 100 W was used for the ultrasonic irradiation. For ion-exchange capacity (IEC) measurements, membranes were first equilibrated in 50 ml of 1M HCl solution for 24 h. After that, they were removed from the solution and washed

with distilled water in order to eliminate excess of the acid. Then, membranes were immersed in 1M NaCl to change hydrogen ions by the sodium ions. The amount of  $H^+$  ions in the solution was determined by titration with 0.01M NaOH. Ion-exchange capacity was expressed in milliequivalents of  $H^+$  per gram of dry membrane. The test cell used in evaluation of membrane electrochemical properties is shown in Fig.1. The cell consists of two cylindrical sections (vessel, each 140 cm<sup>3</sup>) made of Pyrex glass which are separated by membrane. The membrane was fixed between rubber rings. One side of each vessel was sealed by Pt electrode supported with a fragment of Teflon (Polytetrafluoroethylene) and the other side was equipped with a piece of porous medium to support the membrane. There are two orifices on the top of each compartment for feeding and sampling aims. In order to minimize the influence of boundary layer during experiments and to diminish the concentration polarization on the vicinity of membrane's surface, both sections were stirred vigorously by magnetic stirrers (Model: Velp Scientifica Multi 6 stirrer). The membrane area was also 13.85 cm<sup>2</sup>. For measuring membrane potential, the circular membrane was placed between the two half-cells and separated two NaCl solutions of concentrations 0.01 and 0.1 mol dm<sup>-3</sup>. The membrane/solution interface potential was measured using two calomel reference electrodes (through KCl bridges) with the aid of a digital auto multi-meter. The NaCl solutions in the compartments were stirred mechanically. The membrane potential developed between the solutions contacting with both membrane surfaces is expressed via the Nernst equation which was employed to estimate the transport number of ion as follows:

Where  $t_i^m$  is transport number of counter-ions in membrane phase,  $T$  is the temperature,  $R$  is gas constant,  $n$  is the electrovalence of counter-ion and  $a_1$ ,  $a_2$  are electrolyte activities in the solutions specified by Debye–Huckel limiting law. The higher transport number of the counter-ions  $t_i^m$  in a membrane indicates more permselectivity of the IEM. The ionic permselectivity of membranes also is quantitatively expressed on the basis of the counter-ion migration through the IEMs [18].

$$P_s = (t_i^m - t_0) / (1 - t_0) \quad (2)$$

Where,  $t_0$  is the transport number of counter-ions in solution phase.



**Fig. 1.** Schematic diagram of test cell: (1) Pt electrode, (2) membrane, (3) orifice, (4) rubber ring, (5) stirrer, (6) magnetic bar

## 2.2. Sulfonation of PVC

Sulfonated polyvinylchloride (SPVC) was prepared by sulfonation of PVC according to the literature. In order to sulfonate PVC, at first, PVC powder soaked in 1,2-dichloroethane for 4 h to swell the polymer. The pre-swollen PVC was immersed in sulfuric acid (98%) for another 4 h at 60 °C. After the reaction performed, the polymer was washed with high amounts of deionized water to remove excess sulfuric acid and then with acetonitrile to eliminate any possible impurities. Then, the cleaned PVC-SO<sub>3</sub>H polymer was dried at room temperature.

$$E_m = (2t_i^m - 1) (RT/nF) \ln (a_1/a_2) \quad (1)$$

## 2.3. Synthesis of SPPO+SPVC/ZnO nanocomposite

The cation-exchange nanocomposite membranes were prepared by casting solution technique with in-situ formation of ZnO nanoparticles in the polymeric matrix. Typical synthesis process is as follows: The polymer binders (SPPO+SPVC) (7:3 w/w) were dissolved in THF solvent. The mixture was mixed severely at room temperature to obtain a homogenous mixture. Then, a given amount of Zn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O was added to the above mixture under mechanical stirring at room temperature. To this solution, a certain amount of NH<sub>4</sub>OH was then added dropwise, under stirring to reach a mild alkaline pH (~12). The mixture turned from yellow to white, indicating the formation of ZnO. Moreover, for better dispersion of nanoparticles and breaking up their aggregates, the solution was sonicated for 10 min using an ultrasonic instrument. The mixture was then cast onto a clean and dry glass plate at 25 °C and was placed at room temperature. The compositions of casting solutions are shown in Table 1.

Moreover, some nanocomposite samples were prepared by incorporation of previously synthesized ZnO nanoparticles into the casting solution (ex-situ method), but their transport properties were weak in comparison with in-situ method. The SEM images of ZnO nanoparticles are shown in Fig. 2.

## 3. Results and discussion

The XRD pattern of ZnO nanocomposite is shown in Fig. 3. The Zinc oxide peaks that have suitable agreement with reference peaks (JCPDS: 79-0208, crystal system: hexagonal, space group: P63mc).

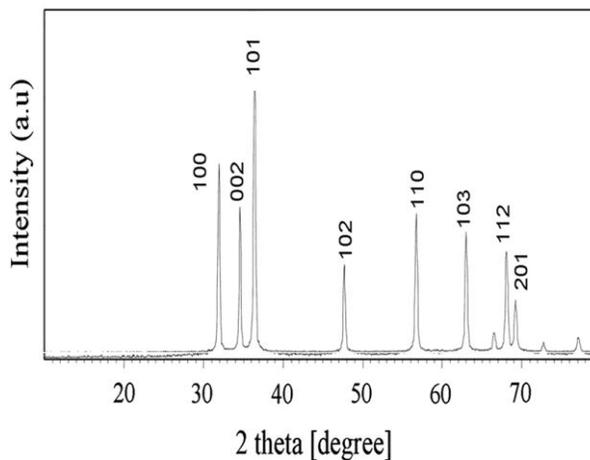
The cross section SEM images of the prepared membranes are presented in Fig. 4, which confirm

the suitable dispersion of nanoparticles in the polymeric matrices.

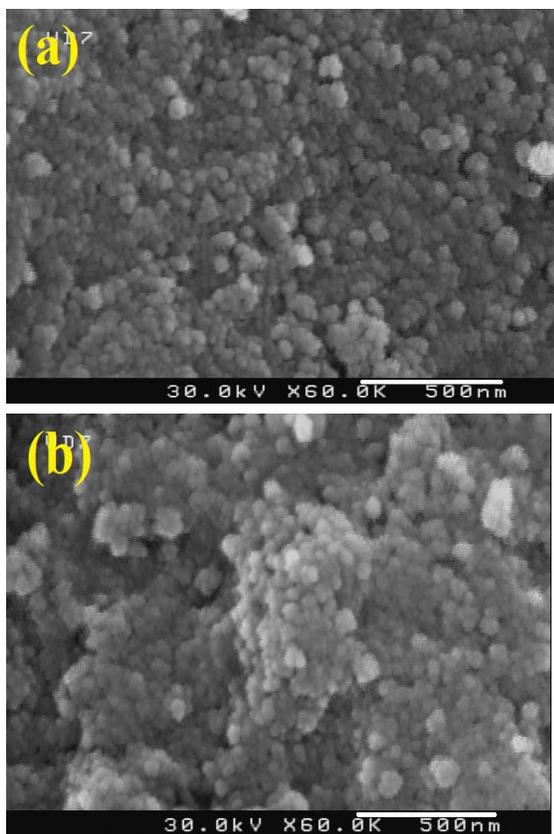
**Table 1.** Compositions of casting solutions for the preparation of ion-exchange membranes.

Membrane	Zn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O (additive:total solid) (w/w)
Sample 1	(0.0:100)
Sample 2	(1:100)
Sample 3	(1.5:100)
Sample 4	(2:100)
Sample 5	(2.5:100)
Sample 6	(3:100)

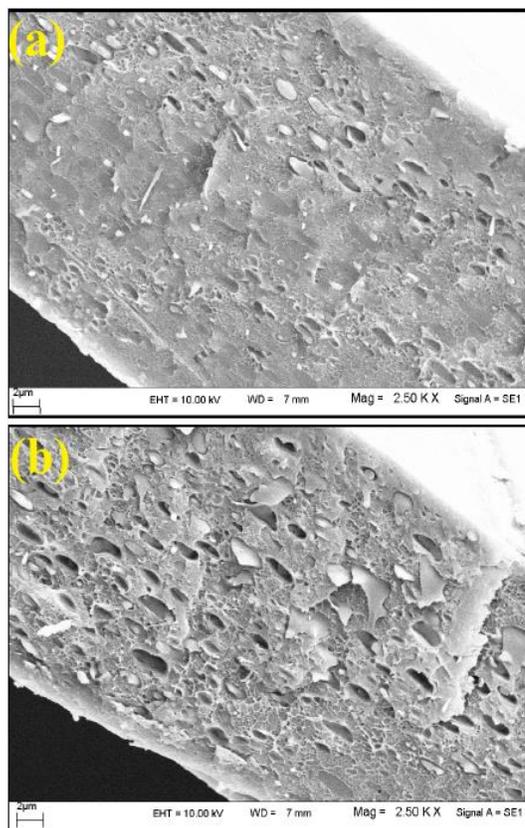
Polymer binder (SPPO:SPVC) (w/w), (7:3);  
solvent (THF:Polymer binder) (v/w), (10:1);



**Fig. 3.** XRD pattern of ZnO nanoparticles



**Fig. 2.** SEM images of ZnO nanoparticles



**Fig. 4.** SEM cross section images of prepared nanocomposite membranes with various loadings of additive (a) 1.5 wt%; (b) 2.5 wt%

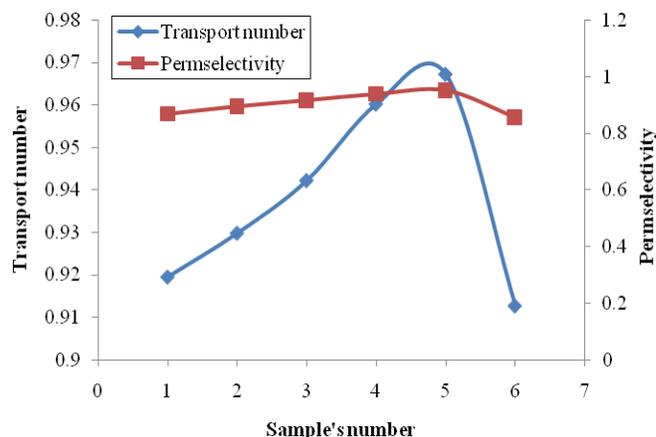
**Table 2.** Ion exchange capacity of prepared membranes.

Sample's number	IEC (meq/gr)
1	0.285
2	0.301
3	0.342
4	0.408
5	0.506
6	0.372

Table 2 presents the ion-exchange capacity of the prepared nanocomposite membranes. The results indicated that the increment of additive loading up to 2.5% wt (sample 5) in the casting solution initially led to an improvement in ion-exchange capacity in prepared nanocomposite membranes. The finding could be attributed to ZnO nanoparticles produced on the membrane surface that might provide more active sites for the ion adsorption due to adsorption characteristic of ZnO nanoparticles. Moreover, the suitable dispersion of in-situ synthesized ZnO nanoparticles provides more accessible active sites for appropriate interaction between ions and membrane surface and so enhances the ion exchange feasibility. However, the highest IEC was not observed at the highest additive content (sample 6). This finding may be probably owing to formation of numerous ZnO nanoparticles on the surface which tend to aggregation, finally leading to reduction of the accessibility of ion-exchange functional groups by their surrounding which in turn leads to IEC decrease.

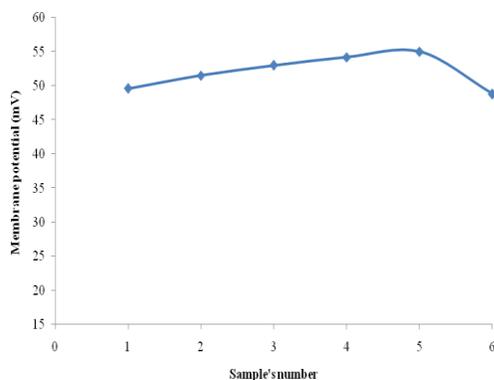
The membrane potential of the prepared membranes is illustrated in Fig. 5. At first, membrane potential was improved with the increase of additive loading (up to 2.5% wt) (sample 5) in the prepared membranes. The increase in membrane IEC value leads to improvement in

surface charge density which supplies additional conducting areas for the membrane. This leads to an improvement in the Donnan exclusion, which is responsible for the increment in membrane potential [19]. The membrane potential was decreased again with more increment in additive concentration from 2.5 to 3 wt.% due to lower membrane surface charge density.

**Fig. 5.** The effect of additive loading on membrane potential

The permselectivity and transport number of membranes are depicted in Fig. 6. At first, both increased with the increment of additive loading to 2.5 wt.% (sample 5) in the casting solution. This trend can be elucidated with respect to the increment in surface charge density with higher control of pathways for ions traffic. Moreover, with the increase of additive concentration (up to 3 wt %), the ionic pathways in the membrane matrix are partially filled via ZnO nanoparticles with high surface hydroxyl groups and so passages are narrowed by them as space limiting factors. This leads to strengthening of the ionic sites control on ions transit and enhances the membrane permselectivity. Moreover, higher increment in additive content reduces the membrane selectivity due to enhancement of nanoparticles density in the

casting solution which leads to discontinuity of polymer chains binder.



**Fig. 6.** The permselectivity and transport number of prepared membranes

#### 4. Conclusion

SPPO+SPVC/ZnO nanocomposites have been successfully prepared by a one-step synthetic method in the presence of  $Zn^{2+}$  and  $OH^-$ . We developed a facile procedure for the in-situ formation of ZnO on polymer binders matrix (SPPO+SPVC) with high uniformity. The SEM images showed uniform nanoparticles distribution and also relatively uniform surface for the prepared nanocomposite membranes. It was found that ZnO nanoparticles could affect overall physicochemical and electrochemical properties.

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