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Preparation and Characterization of Hybrid Nafion/Silica and Nafion/Silica/PTA Membranes for Redox Flow Batteries

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Abstract: *The present work was aimed at the development of a straight-forward method for a multicomponent membranes synthesis, as well as study of electrochemical and ion transport properties of the synthesized membranes. It was shown that introduction of silica and phosphotungstic acid (PTA) into a Nafion membrane composition slightly affects the membrane proton conductivity; however it results in a significant decrease of the ferric ion transfer through the membrane. The addition of PTA was found to result in an increase in the membrane permeability to ferric ions. The membranes converted into* K^+*-form was showed to have a high stability to PTA leaching.*

Keywords: composite membrane, silica, phosphotungstic acid, proton conductivity, ferric ions diffusion coefficient.

1. INTRODUCTION

Recently redox flow batteries, usually used for the storage of electrical energy, have started to gain increasing interest due to their low cost and high efficiency, which opened up a new opportunity for them to be used in a wide range of applications [1-5]. One of the indications of the high potential of redox flow battery technology is a quite recent commercialization of three alternative systems: an all vanadium system manufactured by Austarlian Pinnale VRB, Japon Sumitomo Electric Industries and Canadian VRB Power Systems; a polysulphide-bromine system manufactured by Regenesys Technologies Ltd. and a zinc-cerium system manufactured by Plurion Systems Ltd. A principle of energy storage in those systems is in occurring the oxidation/reduction electrode reactions, while continuously pumping anolyte (electroactive reducing species) and catholyte (electroactive oxidizing species) solutions through a pair of high surface area electrodes. Since these two reactions are separated in space by the ion-exchange membrane, it is one of the battery's key components responsible for efficient functioning. The ideal membrane should be permselective to the charge-carrying ions (protons) in order to provide high ionic conductance and possess low polyvalent metal ions crossover as well as having good chemical stability [6-7]. Despite the excellent results for energy storage efficiency, the long-term stability of most low cost commercial ion exchange membranes (e.g., Selemion CMV) is limited by the oxidizing nature of the ions having high redox potentials [6-8]. Much higher stability along with high proton conductivity are exhibited by perfluorosulfonic membranes such as Nafion, Flemion or Aciplex. However, this kind of membranes suffers from crossover of polyvalent cations, which results in decreases of the electrical efficiency of the redox flow batteries. Currently, a great number of works are being conducted to improve membrane mechanical and electrochemical properties. It is a well-known fact that introduction of different heteropolyacids can significantly enhance proton conductivity of a membrane [9-11]. The introduction of silica into the membrane structure, in turn, allows for significant diminishing the ions crossover [12]. However, an impact of silica on membrane proton conductivity remains controversial: some authors believe that the membrane conductivity increases with an increase in a silica content within the membrane [13, 14], while others lean to a belief that conductivity reduces [15, 16]. Likely, there exists optimum silica concentration resulting in a membrane structure favourable to proton transfer.

For many years we have been developing an alternative redox system based on Fe^{3+}/Fe^{2+} and $2H^+/H_2$ redox couples involving microbial regeneration of ferric ions [17]. Lately, we have come to the point where use of currently available commercial ion-exchange membranes in our system does not allow to have its

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*To whom correspondence should be addressed: Email: vpupkevi@uwo.ca efficient and reliable performance. In this respect, we have made an attempt to synthesize customized membranes, which would have met requirements of our system in more extent. Therefore, the main goal of this work was to study the properties of Nafion based membranes modified by introducing silica or/and PTA.

2. EXPERIMENTAL

2.1. Chemicals

For preparation of the membranes the following reagents were used: Liquion solution LQ-1115, 1100 EW 15% wt. (Ion Power Inc., USA), tetramethyl orthosilicate, 98% (Aldrich), phosphotungstic acid, $H_3PW_{12}O_{40}\cdot 29H_2O$ (Caledon Laboratories Ltd., Canada), N,N-dimethylformamide (Caledon Laboratories Ltd., Canada), isopropyl alcohol (BDH Chemicals, Canada). For studying transport properties sulphuric acid (Caledon Laboratories Ltd., Canada), potassium chloride (Caledon Laboratories Ltd., Canada), and sodium sulphate (Merck, Germany), ferric sulphate (Merck, Germany) were used.

2.2. Membrane Preparation

The membranes under investigation were cast from dimethylformamide (DMFA) solution. For this purpose 15% Nafion solution (Liquion®) was mixed with DMFA at a ratio of 1:1. Certain amounts of additives (silica precursor and/or solution of PTA in isopropyl alcohol) were added, and then the mixture was heated up to the boiling point. When most of the low-boiling solvent was removed, the remainder was transferred into a glass Petri dish, which was placed into an oven and kept there at 150°C for 1.5 hours. For the purpose of completion of tetramethyl orthosilicate hydrolysis, conversion of the membrane into the H^+-form and also washing out remainders of organic solvents, the synthesized membranes were kept in 2 M H_2SO_4 at ambient temperature for 2 weeks.

The silica precursor was prepared by mixing of 5 mL tetramethyl orthosilicate with 50 mL isopropyl alcohol, 2 mL of H_2O and 4 drops of acetic acid. Then the mixture was kept for 2 days at ambient temperature to let tetramethyl orthosilicate partially hydrolyze.

In order to obtain K^+-forms of the membranes, the latter were immersed into 0.1 M solution of KCl and kept at 65°C for ~1 hour.

2.3. Membrane Characterization

The water uptake was determined as the difference between the weight of a swollen membrane and that of dried one at 120°C for 2 hours.

Ion-exchange capacity of the synthesized membranes was determined by acid-base titration. The membrane was dried at 120°C for 2 h, weighed (~0.2 g dry weight) and then dipped in a refluxing 0.1 M Na_2SO_4 solution for 4 h to exchange H^+ ions with Na^+. After that the solution was titrated to the equivalent point with 0.025 M NaOH using a mixture of bromcresol green and methyl red (ratio of 1:2) in ethyl alcohol as an indicator.

To qualitatively estimate PTA leaching from the membranes, the specimens were kept in water and 2M H_2SO_4 at ambient temperature and 30°C (3 weeks), 40°C (24 h) and 100°C (10-15 min). Then, presence of PTA in the extract was registered upon turning the solution to blue (formation of "tungsten blue") after addition of titanium (III) chloride.

Infrared spectra were measured using a Bruker IFS55 FTIR spectrometer equipped with Attenuated Total Reflection (ATR) attachment with germanium crystal.

Membrane conductivities were measured by a direct current two-point-probe method using the technique described earlier [18].

The ferric ions diffusion kinetics was studied by dialysis using the technique analogous to that described by Wiedemann et al. [19]. The membrane (exposed area of 10.4 cm^2) was installed in the dialysis cell having two chambers of 60 mL each. The depletion chamber was filled with 0.15 M $Fe_2(SO_4)_3$ solution, while the enrichment chamber was filled with potassium chloride solution having the same ionic strength (I=2.25). The data obtained by monitoring the iron ions concentration in the enrichment chamber in a course of time, τ, was fairly well fitted to the following equation [19]:

$$C_{\tau}^{E} = C_{\tau=\infty}^{E}\left(1 - e^{-\alpha\tau}\right) \tag{1}$$

where C_{τ}^{E} is the concentration of ferric ions in the enrichment half cell, g L^{-1}, $C_{\tau=\infty}^{E}$ is the final concentration of ferric ions, g L^{-1}, after the system achieved equilibrium, and α is an empirical parameter adjustable to the experimental data. The final concentration was calculated based on the mass balance by the following formula [19]:

$$C_{(\tau=\infty)}^{E} = \frac{V_E C_{(\tau=0)}^{D}}{V_E + V_D} = C_{(\tau=\infty)}^{D} \tag{2}$$

where $C_{(\tau=\infty)}^{D}$ is the initial concentration of ferric ions in the depletion half cell, g L^{-1}, V_E and V_D are the volumes of the enrichment and the depletion half cell, mL, respectively.

The diffusion coefficients were calculated by the following equation [20]:

$$D = \frac{S}{K}\frac{V_D L_m}{A_m} \tag{3}$$

where S is the slope of the C_D/C_E curve vs time; K is the partition coefficient, h^{-1}; L_m is the membrane thickness, cm; A_m is the area of the membrane, cm^2.

For determining the partition coefficient, K, defined as a ratio of the equilibrium ferric ion concentration in the membrane to that in bulk solution, the membrane specimens (0.2-0.3 g) were immersed in the solution with concentrations of ferric ions of 5, 10, and 16 g/L and kept there for 3-5 days until the ion-exchange equilibrium has been achieved. Then, the membranes were taken out of the solution, rinsed with deionized (DI) water and ferric ions were extracted (three times) with 10-15 mL portions of hot (~90°C) 2 M H_2SO_4. The ferric ions content in the cumulative extract were determined using the spectrophotometric method [21]. The values of partition coefficients were calculated as a slope of the linear dependence of the ferric ions concentration in the membrane versus that in an equilibrium bulk solution.

3. RESULTS AND DISCUSSION

The synthesized membranes containing PTA as the only additive were mostly non-transparent, while in the three component systems

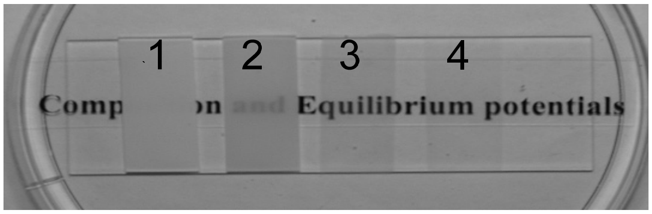

Figure 1. Picture of the synthesized membranes: 1 – 0.3% SiO_2 / 15% PTA / Nafion / (K^+-form), 2 –10% PTA / Nafion, 3 –2.6% SiO_2 / 10% PTA / Nafion, 4 –5%SiO_2 / 10% PTA / Nafion.

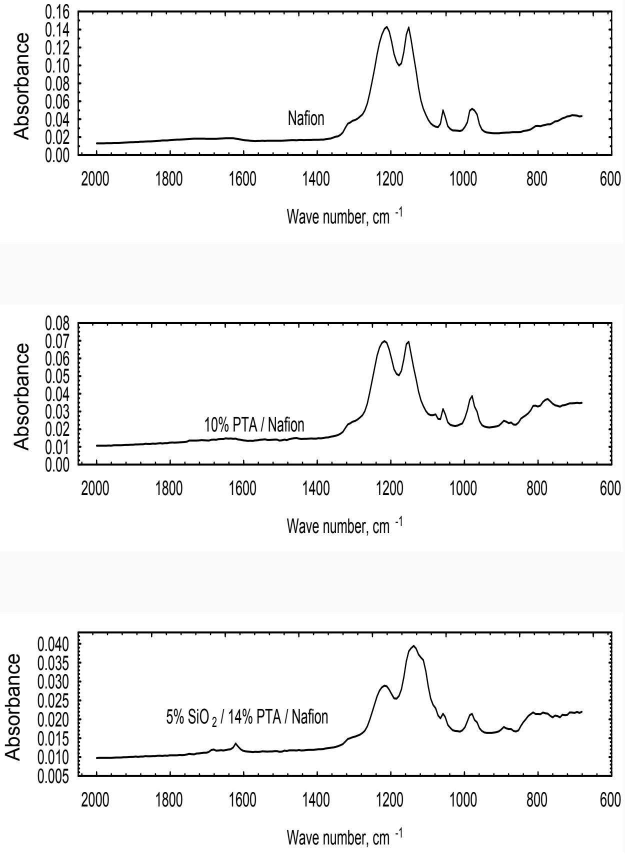

Figure 2. IR-spectra of the synthesized membranes.

(SiO_2 / PTA / Nafion) the membranes were translucent, and tended to become almost fully transparent when a ratio of silica to PTA increased. Unlike the above all the K^+-form membranes were found to be opaque due to formation of potassium salt of PTA that consequently crystallized (Fig. 1). The main reason for such interesting behaviour is an introduction of silica into the membrane composition, which favours formation of smaller PTA crystallites, and therefore the membrane turns to transparent. Similar results of altering crystallite sizes were also obtained for the composite membranes based on sulfonated poly(ether ether ketone) with addition of phosphomolybdic or phosphotungstic acids and ZrO_2 [22]. The authors believe that this can be caused by chemosorption of Keggin-anions by ZrO_2, which results in hindrance of crystallization of the heteropolyacid in a polymeric matrix. In order to prove this suggestion we measured ATR infrared spectra for the synthesized membranes, which are shown in Fig. 2. It can be seen that all the spectra have typical for a Nafion 117 membrane bands at 1212, 1152 and 1057 cm^{-1} [23], and the new bands, caused by an introduction of PTA and SiO_2 into the membranes, appeared in the spectra. For the 10% PTA / Nafion membrane, a comparison of these new bands with those assigned to pure phosphotungstic acid (ν_{intra}(W-O-W), ν_{inter}(W-O-W), ν(W-O) and ν(P-O) usually appearing at 798, 889, 979 and 1078 cm^{-1}, respectively) [24, 25] revealed that in the case of PTA / Nafion membrane ν_{inter}(W-O-W), ν(W-O) vibrations are slightly shifted to the region of higher wavenumbers and ν_{intra}(W-O-W) band splits into the doublet at 775 and 811 cm^{-1}. A similar picture is observed for the 5% SiO_2 / 4.8% PTA / Nafion membrane with the only difference that the split bands appear at 783 and 815 cm^{-1}, which could be an indication of the Keggin ions expansion caused by weakening and elongation of W-O bonds due to the interactions with silica and polymeric matrix. This suggestion is affirmed by a shift of the band ν_s(Si-O-Si) (Fig. 2), typical for the polysiloxane network and appearing at 1130 cm^{-1}, to 1137 cm^{-1} [26] in our particular case. Relatively small band shifts in the spectra of the synthesized membranes testify to the formation of weak interactions between the silica and PTA. An indirect affirmation of this are the results of a series of experiments on the study of leaching of PTA from the membranes. In particular, keeping the membranes in DI water or the solution of sulphuric acid at 40°C resulted in partial leaching of PTA from the membrane structure, while no PTA losses were detected in the solution at ambient temperature. Unlike the above, the membranes stabilized by conversion into the K^+-form did not show any PTA losses even after boiling in water or the solution of sulphuric acid, which is in good agreement with the results reported by Ramani et al. [10, 11].

The additives introduced into the polymer matrices did not have a very high impact on their proton conductivity in 1.1 M sulphuric acid in comparison with that for the recast Nafion membrane (Table 1). The conductivity value for the recast Nafion membrane was found to be much lower than that for a commercial Nafion membrane. This fact can be related to residual presence of organic substances (mainly DMFA), which have negative influence on the conductivity due to their ability to accept protons. However, in the series of self-synthesized composite membranes, conductivity is improved by 15-50% as compared to the recast membrane. The experimental results (Table 1) showed that an introduction of only silica into the membrane has no influence on the conductivity at a content of 10%, however, it leads to its increase at a 5% content. The addition of PTA along with silica results in higher conductivities. It is interesting to note that the highest ionic conductivity was measured for the membranes having a SiO_2:PTA weight ratio close to 1:1. There exists controversial experimental data on the fact of silica influence on proton conductivity. In particular, Jiang et al. [15] and Ren et al. [16] established that the silica modified membrane proton conductivity was considerably lower as compared to a commercial Nafion membrane. They support the opinion that introduction of silica leads to diminishing number of water molecules available for a proton transfer due to their involvement into hydrating the incorporated silica. In contrast, Dimitrova et al. [14] at-

Table 1. Properties of Silica/Nafion and Silica/PTA/Nafion membranes.

Membrane	Thickness (mm)	Ion exchange capacity (mM g^{-1})	Conductivity ($ohm^{-1}\ cm^{-1}$)	Water uptake (wt %)
Nafion-117	0.22	0.909	$2.6\ 10^{-2}$	24.5
Nafion (recast)	0.10	0.911	$1.2\ 10^{-2}$	20.2
5.0% SiO_2 / Nafion	0.15	0.850	$1.8\ 10^{-2}$	22.4
10% SiO_2 / Nafion	0.10	0.800	$1.2\ 10^{-2}$	21.4
10.0% PTA / Nafion	0.15	1.180	$1.4\ 10^{-2}$	19.5
2.6% SiO_2 / 10% PTA Nafion	0.15	1.230	$1.7\ 10^{-2}$	29.3
5.0% SiO_2 / 4.8% PTA Nafion	0.15	0.668	$1.8\ 10^{-2}$	20.0
10.0% SiO_2 / 10.0% PTA Nafion	0.17	0.929	$1.8\ 10^{-2}$	22.2
5.0% SiO_2 / 10.0% PTA Nafion (K^+-form)	0.15	-	$1.5\ 10^{-2}$	-
0.3% SiO_2 / 15.0% PTA Nafion (K^+-form)	0.10	-	$1.4\ 10^{-2}$	-

†Thickness was measured for membranes in swollen state
‡Conductivities were measured in 1.1 M H_2SO_4

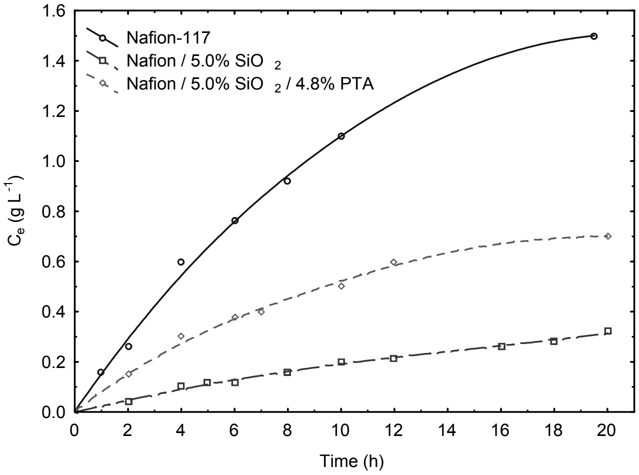

Figure 3. Variation of ferric iron concentration in the enrichment dialysis half cell (C_e) over time.

tained conductivity enhancement upon addition of silica. The authors believe that the silica modified membrane possesses a smaller hydrophobic/hydrophilic interface, favouring proton transfer, which is a result of formation of broader and less tortuous water filled channels within the membrane. Besides, incorporated silica acts as the filler and thereby improves the membrane transport properties in terms of its ability to pass hydrogen ions through.

The results on ferric ions diffusion through the membranes are shown in Fig. 3. As can be seen from the plots, an introduction of the additives has a great influence on the ferric ions transfer in a comparison with that for a commercial Nafion 117 membrane. In particular, introduction of 5.0% SiO_2 resulted in almost 6.5-fold decrease in the ferric ions transfer. The curves presented in Fig. 3 are very well fitted to equation (1) within the timeframe of 8, 10 and 20 h for Nafion 117 (α=0.076), 5.0% SiO_2 / Nafion (α=$6.6\cdot10^{-3}$) and 5.0% SiO_2 / 4.8% PTA / Nafion (α=0.020) membranes, respectively, i.e. the equation works well as long as iron concentration in the depletion chamber is close to the initial one. On the basis of the above-mentioned data and the partition coefficients equal to 4.2 (Nafion 117), 2.4 (5% SiO_2 / Nafion) and 2.8 (5% SiO_2 / 4.8% PTA / Nafion), using equation (3) the iron ions diffusion coefficients were calculated to be $2.2\ 10^{-7}$, $2.5\ 10^{-8}$ and $9.8\ 10^{-8}$ $cm^2\ s^{-1}$ for Nafion-117, Nafion / 5.0% SiO_2 and Nafion / 5.0% SiO_2 / 4.8% PTA, respectively. It should be noted that the diffusion coefficient obtained for a commercial Nafion membrane is consistent with the value ($2\ 10^{-7}$ $cm^2\ s^{-1}$) reported by Ye et al. [26].

4. CONCLUSION

Having analyzed the experimental data obtained, we have come to the following conclusions:

- A simple method for synthesis of multicomponent membranes was proposed;
- The introduction of SiO_2 into the membrane favours the formation of finely dispersed particles of PTA (down to nano-scale);
- The introduction of PTA into a membrane composition has a little effect on the membrane conductivity to protons;
- Conversion of the synthesized membranes into K^+-form prevents PTA leaching;
- The 5.0% SiO_2 / Nafion membrane seems to be the most promising in terms of its use in redox flow batteries due to its low iron diffusion coefficient and fairly high ionic conductivity.

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