Microstructural studies of poly (perfluorosulfonic acid) membrane doped with silver nanoparticles using positron annihilation spectroscopy

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Abstract. The Nafion -117 (H+ form) was converted to Ag+ form by ion exchange. The silver nanoparticles were formed in the membrane by reduction of Ag+ (of Ag+ form membrane) using an ionic reducing agent, NaBH₄, and a neutral reducing agent, formamide. The free volume hole sizes in the nanoparticle doped and undoped Nafion were measured by positron annihilation lifetime spectroscopy (PALS). The surface modifications in the membrane by incorporation of nanoparticles were investigated using slow positron beam. The changes in the bulk free volume of Nafion with presence of nanoparticles were found to be nominal. In contrast, the surface microstructure appears to have undergone significant change.

1. Introduction

Poly (perfluorosulfonic acid) membrane (Nafion®) is one of the most studied synthetic membranes for various applications [1,2]. The Nafion-117 consists of polytetrafluoroethylene backbone and perfluoro ether side chains terminated by SO₃⁻H⁺ group. The technological importance of the Nafion is due to its selective permeability to cations, low resistance to current flow and excellent chemical, mechanical and thermal stability. The various properties of Nafion are dependent on its microstructure. The free volume properties of Nafion were shown to be strongly correlated to the diffusion of gases through the membranes [3]. Incorporation of nanoparticles into the membranes has been shown to change the properties of the membranes drastically [4]. The properties of nanoparticles in the matrix are strongly related to their size, shape and their spatial distribution in the matrix. In this regard, Nafion has received much attention as a host for variety of nanoparticles [5,6]. The incorporation of metal oxide nanoparticles in the Nafion was shown to improve proton conductivity and water retention properties [6]. The Nafion stabilized nanoparticles were also used as sensors [7,8]. Although there are many studies on the correlations of the physicochemical properties with the free volume structure of Nafion [3,9,10], the microstructural changes that may occur with incorporation of nanoparticles in the membrane have not been reported so far. The positron annihilation spectroscopy (PAS) is the powerful tool to study the free volume hole properties in the membranes [11]. The variable energy slow positron beam is used to probe the microstructure of the surfaces of thin films.

In the present work, Nafion-117 in H⁺ form is converted to Ag⁺ form by ion exchange method. The Ag⁺ ions were reduced, to form nanoparticles in the membrane, using either sodium borohydride (NaBH₄) or formamide. The resulting microstructural changes were studied using PAS.
2. Experimental

2.1. Sample preparation
Nafion-117 ion exchange membrane having thickness of 178 μm, IEC of 0.91 mmol/g and density 1.95 g/cc was purchased from Aldrich. The H⁺ form of the Nafion was equilibrated with 0.5 M NaCl solution for 30 h to convert to the Na⁺ form. It was further converted to Ag⁺ form by immersing in 0.25 M AgNO₃ for 48 h [12]. The silver nanoparticles were formed in the Nafion membrane by reduction of Ag⁺. For this purpose Ag⁺ form of the membranes were immersed in 0.66 M NaBH₄ or formamide for 30 mins, with continuous stirring. The membrane samples were washed with boiled water to remove any unwanted residue.

2.2. Positron annihilation studies
The PALS measurements were performed at room temperature using a fast-fast coincidence system consisting of two BaF₂ scintillation detectors. The time resolution of the spectrometer was 350 ps. For PALS measurements, 20 Ci source of ²²Na deposited on 8 μm Kapton film was sandwiched between stack of Nafion membrane with four pieces on each side and wrapped in an aluminum foil. Total area under each lifetime spectra was about 10⁶. The positron lifetime spectra were fitted using PATFIT-88. The continuous distribution of lifetime was obtained using CONTIN. The free volume hole radii were calculated from o-Ps lifetimes. The details of the data analysis are given elsewhere [13].

Depth dependent Doppler broadening measurements of the surface of the membrane were carried out using a slow positron beam at BARC, in the energy range 200 eV- 10 keV. A 30% relative efficiency high purity germanium detector with a resolution of 2 keV at 1332 keV photo peak of ⁶⁰Co was used for Doppler broadening measurements and spectra with 2×10⁵ counts were acquired at each energy. The ratio of the counts within ~ 2.0 keV energy window centered at 511keV and total photo peak area was used to evaluate the S-parameter. The 3γ/2γ ratio or relative Ps yield was estimated as the ratio of total counts in the 375-480 keV region of the annihilation gamma-spectra to counts under the 511 keV peak.

3. Results and discussion
The two reducing agents used in the present study to reduce Ag⁺ in the membrane to silver nanoparticles are NaBH₄ and formamide. The Nafion is a cation exchange membrane and does not allow negative ions to permeate into it. When borohydride (BH₄⁻) is used as a reducing agent, Ag⁺ ions at the ion exchange sites are replaced with Na⁺ ions as represented below,

\[ [-R - SO₂⁻, Ag⁺]_{\text{mon}} + [NaBH₄]_{\text{aq}} \rightarrow [-R - SO₂⁻, Na⁺]_{\text{mon}} + [BH₄⁻]_{\text{aq}} + [Ag⁺]_{\text{mon}} \]

and the replaced Ag⁺ ions moving out of the membrane are reduced to Ag nanoparticles near the surface regions of the membrane by BH₄⁻ as

\[ [BH₄⁻]_{\text{aq}} + [Ag⁺]_{\text{mon}} + 3H₂O \rightarrow [H₂BO₃]_{\text{aq}} + [Ag⁺]_{\text{mon}} + \frac{3}{2} H₂(g) \]

Thus, the use of borohydride as reducing agent renders the Nafion membrane in the Na⁺ form with nanoparticles concentrated near the surface regions extending up to ~15 μm [12] from the surface. Formamide, on the other hand, is neutral and it can invade the matrix of the Nafion. The reduction of silver ions in the membrane by formamide can be represented as

\[ 2[-R - SO₂⁻, Ag⁺]_{\text{mon}} + [HCONH₂]_{\text{aq}} + [H₂O]_{\text{mon}} \rightarrow 2[-R - SO₂⁻, H⁺]_{\text{mon}} + [NH₂COOH]_{\text{aq}} + 2[Ag⁺]_{\text{mon}} \]

The carbamic acid decomposes NH₂COOH → CO₂(g) + NH₃. Thus, the use of formamide as reducing agent gives the Nafion with homogeneously distributed nanoparticles within the membrane and leaves the backbone in the H⁺ form. Further details about the spatial distributions of silver nanoparticles in Nafion with preparation method are described by Kumar et al. [14]. The Nafion membranes with silver nanoparticles produced using NaBH₄ and formamide as reducing agents are referred to as Na⁺/Ag and H⁺/Ag, respectively, while the Nafion without nanoparticles are referred to with cation present in the ion exchange sites. The formation of nanoparticles in these membranes was confirmed.
by XRD measurements and the size of the nanoparticles estimated using Debye-Scherrer formula were found to be 15±5 nm and 10±3 nm respectively. The results are in agreement with the sizes reported in the literature [14].

The o-Ps lifetimes and intensities in the Nafion samples with and without nanoparticles are shown in figure 1. The pore radius distributions calculated from the lifetime distributions are given in figure 2. The o-Ps lifetime in the H⁺ form of Nafion is in reasonable agreement with the reported values [5,9]. The Nafion in Na⁺ form showed marginally lower o-Ps lifetime than the H⁺ form. The Ps lifetimes in the Nafion were shown to be sensitive to water retention in the membrane [9]. The shorter o-Ps lifetime in the Na⁺ exchanged Nafion than the H⁺ form might be due to less retention of water in the former because of the larger ionic size of Na⁺. The Ag⁺ form showed significantly lower o-Ps lifetime and intensity. The Ag⁺ ions are known to be good scavengers of electron and hence inhibit the positronium formation [15]. The changes in the o-Ps lifetimes and intensities in Ag⁺ loaded membrane might be due to chemical effects of Ag⁺ rather than the free volume changes. The changes in the distribution of bulk o-Ps lifetimes or pore radii distributions in the membrane on introduction of nanoparticles are found to be marginal (Figure 2). However, the lowering in the intensity of o-Ps is significant and well beyond the statistical uncertainties (Figure 1). This shows that the nanoparticles are blocking some of the free volume holes in the Nafion membrane, though this fraction seems to be very small.

The slow positron beam studies have been carried out to understand the microstructural changes on the surface of the membrane. The energy dependent S-parameter in the membranes is shown in Figure 3. The mean implantation depth of the positrons in the film is also shown in the figure. The implantation depth (in µm) is calculated as 0.040×E^{1.6/ρ}, where E is the positron energy in keV and ρ is the density of the membrane in g/cc. The density differences that can arise due to incorporation of nanoparticles are ignored here in calculating the mean implantation depth. It can be seen from the figure that the maximum depth probed is ~1µm. Hence, the probing region only corresponds to a small part of surface nanoparticles even in the borohydride reduced samples where nanoparticles are spread over ~15µm [12]. It is interesting to note that the surface S-parameters in the nanoparticles doped membranes (in both H⁺ and Na⁺) are significantly higher than their counter parts without nanoparticles. The relative 3γ/2γ ratio in the surface of the membranes in the nanoparticles doped samples is also higher than the undoped samples as shown in figure 4, with exception of the Ag⁺ form of Nafion. The higher S-parameter and higher Ps yield (3γ/2γ ratio) in the surface layers of the nanoparticles doped membranes suggest an increase in the free volumes in these regions contrary to the average bulk. The higher S-parameter in the surface of Ag⁺ form of membrane with lower Ps yield might be due to formation of a metallic layer of silver on the surface of the membrane when the
sample is stored in air for a longer duration. The possible increase in the free volumes or open porosity near the surface regions might be due to the release of gaseous byproducts during reduction of Ag⁺ to silver nanoparticles.

![Figure 3. The \( S \)-parameter as a function of positron energy and mean implantation depth.](image1)

![Figure 3. The \( \gamma/2\gamma \) ratio as a function of positron energy and mean implantation depth.](image2)

4. Conclusion

The microstructural changes in the Nafion-117 membrane with the formation of silver nanoparticles have been monitored using conventional positron annihilation lifetime spectroscopy and slow positron beam. The studies indicate reduction in the number of free volume holes without much change in the average hole radii with formation of nanoparticles in both H⁺ and Na⁺ forms of Nafion. However, the surface of the Nafion membrane undergoes significant microstructural changes i.e. becomes more porous on formation of nanoparticles as indicated by high Ps yield and high \( S \)-parameter. This is probably caused by release of gaseous byproducts during the reduction of Ag⁺ ions to nanoparticles.

5. References

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