Chapter -2

Metal nanoparticles in Nafion by direct reduction

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2.1. Introduction

The cluster-network model of water-swollen Nafion, proposed by Geirke, is shown in Fig 1.2. It proposes that Nafion microstructure is divided into a hydrophobic domain consisting of the fluorinated backbones and a hydrophilic domain consisting of the ionic clusters. These ionic clusters are made of fixed sulfonic groups, their counter ions, and water. Elliott et al. proposed morphology of Nafion consists of independent bicontinuous networks of ionic clusters and fluorocarbon chains as shown in Fig 2.1 [123-125].

![3D morphology showing continuous network of ionic clusters](image)

The presence of ionic water clusters in Nafion membrane makes it a promising host for nanoparticles (nps). A variety of monometallic, bimetallic, and ceramic nanoparticles have been incorporated in the Nafion membrane [184-186,189,203-207]. Jalani et al. synthesized Nafion/ZrO₂, Nafion/SiO₂, and Nafion/TiO₂ nanocomposite membranes via in situ sol–gel technique to improve water uptake and proton conductivity for fuel cell application [203]. Nafion/organic silica modified TiO₂ composite membrane was prepared by in situ sol–gel method for Vanadium redox flow battery [204]. Liu et al. prepared TiO₂ nano crystals in the nafion by hydrolysis of varying concentration of lower titanium alkoxide for photo catalytic applications [205]. Watanabe et al. modified Nafion by the incorporation of hygroscopic
oxides such as SiO$_2$ and TiO$_2$ to increase water uptake [176,208]. They were prepared by casting from a Nafion solution with TiO$_2$/SiO$_2$ colloids prepared by the hydrolysis of Titanium/Si tetraisopropoxide. Thampan et al. modified Nafion by the incorporation of hygroscopic oxides or inorganic solid acids such as ZrO$_2$/SO$_4$ [209]. Malhotra et al. incorporated inorganic solid acids (such as heteropolyacids) in Nafion for improving water retention as well as providing additional acidic sites [210]. Mauritz et al. and Adjemian et al. introduced nanosized SiO$_2$ into pores of Nafion by in situ sol-gel method [211,212]. Krishnan et al. prepared CdS in Nafion by incorporating Cd$^{2+}$ in the membrane by ion exchange followed by exposing the membrane to H$_2$S [213]. Similarly Rollins et al. prepared Ag$_2$S nanoparticles in nafion in silver form by reaction of Na$_2$S [186]. Sun et al. and Sachdeva et al. prepared silver nanoparticles in Nafion by borohydride reduction of silver form of Nafion [184,189]. Watanabe et al. synthesized platinum nanocrystallites, dispersed in the Nafion membrane, by the cation exchange treatment of Nafion with a [Pt (NH$_3$)$_4$] Cl$_2$ followed by reduction with hydrazine [176,208]. Ramon et al. synthesized bimetallic Ag–Au nanostructures homogeneously distributed on Nafion membranes by galvanic substitution reaction of silver island deposition on to the Nafion films [206].

Synthesis of nanocomposite membranes either by casting a bulk mixture of powder or colloidal state of inorganics with a polymer solution or in-situ formation of inorganic particles utilizing the membrane as template is very promising [212]. The advantage of in-situ method is that the particle size and dispersion of these solid particles can be controlled by the concentration of precursors. More often, the sizes of nanoparticles formed in the matrix of Nafion are much larger than the size of water clusters (4-5 nm) present in it [184,186,189,203-207]. Recently, Ag nanocubes have been synthesized by adenosine-5’-triphosphate (ATP) mediated reduction of Ag$^{+}$ ions in the Nafion membrane [214].
results so far seem to suggest that the shape and size of nanoparticles in Nafion may not be dependent only on the dimensions of water clusters.

The synthesis of metal nanoparticles generally involves transfer of the desired metal ions by the ion-exchange process to the membrane matrix and subsequent reduction of metal ions by appropriate reductant in the membrane matrix [184,186,206,207]. The reductant plays an important role in the spatial distribution of metal nanoparticles in the ion-exchange membrane. Nafion is a cation-exchange membrane and, therefore, the anionic reductant would not enter in bulk matrix of the membrane due to “Donnan exclusion”. Wang et al. have observed that CdS nanoparticles in the Nafion membrane were confined to surface when Na$_2$S was used as a precursor [185]. Contrary to this, the CdS nanoparticles in Nafion have been found to be uniformly distributed across thickness of the membrane when thioacetamide used as a precursor. This has been attributed to the fact that non-ionic thioacetamide could diffuse into the cation-exchange membrane much more uniformly [185]. It has also been reported that the Ag nanoparticles formed in Nafion-117 membrane by reduction with BH$_4^-$ ions were located mostly to a few $\mu$m surface layer of the membrane [189].

The transport properties of the Nafion-117 membrane were not found to be affected by the formation of Ag nanoparticles by BH$_4^-$ ions reduction [189]. However, the proton conductivity was decreased significantly when SiO$_2$ nanoparticles were formed in matrix of the Nafion-115 membrane [215]. This indicates that the tortuosity of diffusion channels (three dimensional network connecting water swollen clusters) in membrane increases by incorporation of nanoparticles in the matrix.

In this chapter, the synthesis of nanoparticles by in situ chemical reduction of metal (Ag$^+$ & Rh$^{3+}$) ions in Nafion-117 membrane with borohydride (BH$_4^-$), formamide (HCONH$_2$), and dimethyl formamide (HCON(CH$_3$)$_2$), as reductant, have been studied. Formamide and dimethyl formamide (DMF) are non-ionic and can invade the membrane matrix [216-219].
The fraction of Ag\(^+\) ions loaded in the membrane, that has been reduced, have been quantified using radiotracer. Shape, size, and spatial distribution of nanoparticles have been obtained by transmission electron microscopic (TEM) analyses of the cross-section of membrane samples. The membrane morphology strongly influences diffusion mobility of the counterions. Therefore, the self-diffusion coefficients of different valence counterions (Na\(^+\), Cs\(^+\), and Eu\(^{3+}\)) in the nanoparticles embedded membrane have been measured to understand the effects of inclusion of nanoparticles on diffusion mobility of the counterions.

2.2. Experimental

2.2.1. Reagents and apparatus

Analytical grade chemicals (NaNO\(_3\), AgNO\(_3\), CsNO\(_3\), Eu\(_2\)O\(_3\), NaBH\(_4\), DMF, and formamide) from BDH (Poole, England) and deionized water (18 M\(\Omega\).cm) purified by model QuantumTM from Millipore (Mumbai, India) were used throughout the studies. Nafion-117 ion-exchange membrane with an equivalent weight of 1100 and thickness of 178 \(\mu\)m (Ion Power Inc.) was used after conditioning. The membrane samples were preconditioned by boiling in conc. HNO\(_3\) for 3-4 h. to remove organic impurities introduced during manufacturing process. It was followed by washing and boiling the membrane samples in distilled water for one hour. Subsequently, the membrane samples were equilibrated with 0.5 mol L\(^{-1}\) NaOH and 0.5 mol L\(^{-1}\) HCl at room temperature (27 \(^\circ\)C) for converting the membrane into the proton form [33,220]. Radiotracers \(^{22}\)Na, \(^{137}\)Cs, and \(^{110m}\)Ag were obtained from the Board of Radiation and Isotope Technology, Mumbai, India. Radiotracer \(^{154}\)Eu was prepared by irradiating known amount of Eu\(_2\)O\(_3\) (having 99.1 % enriched \(^{153}\)Eu obtained from Euriso-top, France) for appropriate time in Dhruva reactor at BARC, Mumbai, India. \(^{154}\)Eu radiotracer solution was prepared by dissolving the irradiated Eu\(_2\)O\(_3\) in concentrated HCl and evaporating it to near dryness. The acidity of stock solution of \(^{154}\)Eu was adjusted to pH = 2 for preventing any hydrolysis during the period of storage. The \(\gamma\)-activity of \(^{22}\)Na, \(^{137}\)Cs,
$^{110m}$Ag, and $^{154}$Eu in the membrane was monitored by a well-type NaI(Tl) detector connected to a multi-channel analyser. All the samples and standard containing radioactivity were counted in identical sample-detector geometry. The thickness of the membrane samples was measured using a digital micrometer (Mitutoyo, Japan) with a precision of ± 0.001mm.

2.2.2. Preparation of the nanoparticles

The conditioned membrane sample (2×2 cm) in Na$^+$ form was equilibrated with 25 mL of 0.25 mol L$^{-1}$ of AgNO$_3$ solution to convert it into Ag$^+$ form. The Na$^+$ ions tagged with $^{22}$Na radiotracer were used to study the quantitative replacement by Ag$^+$ ions. It was observed that > 98% of Na$^+$ ions in membrane was replaced by the Ag$^+$ ions from aqueous solution having 0.25 mol L$^{-1}$ AgNO$_3$. Similarly the membrane was converted to Rh$^{+3}$ from by ion exchange process. The metal ion loaded membrane samples were reduced by equilibrating it with 15 mL of reductant at fixed temperature for a known period of time with constant stirring. NaBH$_4$ (0.2 mol L$^{-1}$), formamide, and DMF were used as reductant. For formamide and DMF reduction, fully Ag$^+$ ions loaded samples were used. In case of BH$_4^-$ reduction, the amount of Ag$^+$ ions was kept 15% of ion-exchange sites by equilibrating fully Ag$^+$ ions loaded membrane samples in the well-stirred 0.25 mol L$^{-1}$ NaNO$_3$ for 45 s as described elsewhere [189]. Rh$^{+3}$ loaded nafion membrane was reduced with formamide at 65°C for 30 min. After reduction, the membrane samples were thoroughly washed with water and equilibrated with NaNO$_3$ (0.25 mol L$^{-1}$) to remove unreduced metal ions, if any, from the membrane matrix.

2.2.3. Characterization

2.2.3.1. UV-Vis spectroscopy

Ag nanoparticles gives color due to surface plasmon resonance of electrons. UV-Vis spectra of Ag nanoparticles embedded membrane samples were recorded using UV-Vis Spectrophotometer (V-530, JASCO, Japan). The absorbance measurements were carried out
by mounting the sample (1x2 cm) on to the inside wall of a (1x1x3 cm) quartz cell and placing it in a spectrophotometer to record spectrum with respect to air.

2.2.3.2. TEM

For TEM analyses of cross-section of membrane, the membrane samples were sectioned under cryogenic conditions in Leica ultramicrotome to 70 nm thickness. The sections were picked on 200 mesh Cu grids. The grids were examined in an FEI Technai G2 electron microscope in IIT Bombay [Central Facility at SAIF], Mumbai at 120 KeV without any staining or post-treatment. The sizes of nanoparticles were measured manually using the image analyser software (Image Z, version 1.33 U). The size distribution was obtained from 5-8 images obtained by TEM of samples from different locations of the membrane.

2.2.3.3. Determination of fractional conversion of Ag$^+$ ions to nps

In order to quantify Ag$^0$ content after the reduction of membrane, the membrane samples (2 x 2 cm pieces) were equilibrated with 0.1 mol L$^{-1}$ AgNO$_3$ stock solution containing known activity of $^{110m}$Ag radiotracer for 24 h. After equilibration, the membrane samples were thoroughly washed with de-ionized water to remove equilibrating solution clinging to the surface of the samples. These samples were subjected to reduction as described above. Post reduction, the membrane samples were equilibrated with 0.25 mol L$^{-1}$ NaNO$_3$ for 30 min to remove un-reduced Ag$^+$ ions. This ensured that $^{110m}$Ag radioactivity in the samples represent only content of Ag$^0$ and not Ag$^+$ ions, if any. The membrane samples were counted before and after reduction in a well type NaI(Tl) detector to monitor the $\gamma$-activity of $^{110m}$Ag in the membrane samples. The percentage of Ag$^+$ ions reduced to Ag$^0$ in the sample was obtained as:

$$\text{Ag}^0 \ (\% \ of \ ion \ exchange \ sites) = \frac{A_t}{A_b} \times 100$$

(2.1)

where $A_t$ and $A_b$ are the $\gamma$-activity of $^{110m}$Ag before and after reduction followed by equilibration with NaNO$_3$, respectively.
2.2.3.4. Ion exchange capacity

Ion exchange capacity of membrane is defined as the number of equivalents of counter ions present in per unit mass of membrane. The total exchangeable sites (IES, in moles) available in the membrane samples (1 x 2 cm pieces) were measured by equilibrating them for 24 h with 0.05 mol L\(^{-1}\) NaCl stock solution containing known activity of \(^{22}\)Na. After equilibration, the membrane samples were thoroughly washed with deionized water to remove equilibrating solution clinging to the surface of the samples. Filter paper standards were prepared by taking pieces of filter paper of the same dimensions (1 x 2 cm) as the membrane samples and adding known volume (50, 100 and 200 \(\mu\)L) of the radiolabeled 0.05 mol L\(^{-1}\) NaCl stock solution. NaCl stock solution used for preparing standard samples contained same \(^{23}\)Na (natural) to \(^{22}\)Na (radioactive) ratio as the solution used for equilibrating the membrane samples. Each standard was prepared in duplicate. The soaked filter papers were dried at room temperature and counted in a well type NaI(Tl) detector in a similar counting geometry as the membrane samples. The amount of Na\(^{+}\) ion in the membrane sample was obtained by comparing the \(\gamma\)-activity of \(^{22}\)Na in the membrane samples with filter paper standards as given below:

\[
\text{Ion Exchange capacity} = \frac{A_{(\text{mem})} \times M_{(\text{std})}}{A_{(\text{std})} \times W_{\text{mem}}} \tag{2.2}
\]

where \(A_{(\text{mem})}\) and \(A_{(\text{std})}\) are \(^{22}\)Na \(\gamma\)-radioactivities (counts min\(^{-1}\)) in membrane sample and standard, respectively. \(M_{(\text{std})}\) is moles of Na\(^{+}\) in the standard and \(W_{\text{mem}}\) is the weight of the membrane.

2.2.3.5. Water-uptake capacity

The water uptake capacity and dimensional changes after the reduction of the membrane samples were also measured. The water uptake capacity of the membranes, defined as the amount of water absorbed per unit dry weight of the membrane, was obtained from the difference in weight of wet and vacuum dried membrane samples in appropriate ionic form.
For measurements of water uptake capacity, the membrane samples were equilibrated with 0.25 mol L\(^{-1}\) relevant salt solution for 24 h. The water uptake capacity of the membranes was determined by using the following equation:

\[
\text{Water uptake capacity (\%) } = \frac{(W_{\text{wet}} - W_{\text{dry}})}{W_{\text{dry}}} \times 100
\]  

(2.3)

Where, \(W_{\text{wet}}\) is the weight of the wet membrane sample and \(W_{\text{dry}}\) is the weight of the same membrane sample dried under vacuum.

### 2.2.3.6. EDXRF analyses

Energy Dispersive X-ray Fluorescence (EDXRF) measurements of membrane samples were carried out using Total Reflection X-ray Fluorescence Spectrometer IX-2000 provided with EDXRF geometry (ITAL STRUCTRES, Italy). \(W L_\alpha\) (8.398 keV) radiation was used as excitation source for EDXRF measurements.

**Fig. 2.2 Arrangement for dead end cell experiment**

### 2.2.4. Dead end cell experiment

In order to study the penetration of reducing agent formamide across the thickness of membrane, the \(Ag^+\)-loaded membrane was exposed to formamide from one side in a dead end cell as shown in Fig. 2.2 for 24 hrs. After reduction, the membrane samples were equilibrated
with the 0.25 mol L\(^{-1}\) NaNO\(_3\) to ensure the removal unreduced Ag\(^+\) ions from the membrane, if any.

2.2.5. Measurement of self-diffusion coefficients of the counterions

The self-diffusion coefficients of Na\(^+\), Cs\(^+\), and Eu\(^{3+}\) ions were obtained from analyses of the isotopic-exchange rate profiles as described in chapter 1, section 1.5.1 [33,34]. The measurements of isotopic-exchange rates of (M\(^{n+}\)=Na\(^+\), Cs\(^+\), and Eu\(^{3+}\)) were carried out using 2 x 2 cm pieces of the Nafion-117 membrane. The membrane samples in appropriate ionic forms were placed in 25 mL of respective equilibrating salt solution (0.25 mol L\(^{-1}\)) containing radioactivity tagged counterions. These radiotracer loaded membrane samples were again equilibrated with salt solution (0.25 mol L\(^{-1}\)) having same ions as the counterions in the membrane samples. The solution (at 25\(^\circ\)C) containing membrane sample was stirred vigorously (\(\approx 52\) rad s\(^{-1}\)) to minimize the concentration gradient of counterions in the equilibrating solution. The amount of radiotracer counterions desorbed from the membrane sample was monitored by taking out the membrane sample from the equilibrating solution at regular time intervals. The membrane samples were washed with de-ionized water to remove traces of equilibrating solution adhering to its surface and then radioactivity in the membrane was counted with a \(\gamma\)-ray spectrometry in a fixed geometry. The membrane sample was again placed in the equilibrating solution after counting. The actual residence time of the membrane in the equilibrating solution was considered as time for the isotopic exchange of counterions.

2.3. Results and discussion

2.3.1. Formation of the metal nanoparticles

The formation of metal nanoparticles in the membrane matrix is a two steps process. First, the membrane samples have been loaded with M\(^{n+}\) ions by ion-exchange mechanism shown below:
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\[ n[-\text{R-SO}_3\text{H}^+]|_{\text{mem}} + [\text{M}^{n+}]_{\text{aq}} \rightleftharpoons [(\text{R-SO}_3^-)]_n \text{M}^{n+} + n[\text{H}^+]_{\text{aq}} \]  
\[ \text{(2.4)} \]

Next metal ions in the loaded membranes have been reduced using a reducing agent. For formamide reduction, reaction is shown below:

\[ 2[(\text{R-SO}_3^-)]_n \text{M}^{n+} |_{\text{mem}} + n[\text{HCONH}_2]_{\text{aq}} + n[\text{H}_2\text{O}]_{\text{mem}} \rightleftharpoons n[\text{NH}_2\text{COOH}]_{\text{aq}} + 2n[-\text{R-SO}_3\text{H}^+]_{\text{mem}} + 2n[\text{M}^0]_{\text{mem}} \]  
\[ \text{(2.5)} \]

The conversion of metal ion to its zero valent state in the membrane matrix is highly dependent on nature of the reductant as well as on the ion-exchange process operating during the reduction. Formamide and DMF are non-ionic reductants and the membrane matrix is swelled in them. They are, therefore, expected to invade the interior of Nafion-117 membrane.

In the case of Ag\(^{+}\) ions, the reduction process occurring in the membrane matrix has been studied by tagging Ag\(^{+}\) ions with \(^{110}\text{Ag}\) radiotracers and results of this study are summarized in the Table 2.1. It has been observed that the rate of formation of Ag nanoparticles in the membrane is quite slow with DMF at room temperature. The membrane sample has started dissolving on increasing the temperature of DMF and hence formamide has been used for reduction of Ag\(^{+}\) ions in the membrane. The rate of formation of Ag nanoparticles has increased when formamide is used as reducing agent. As shown in Table 2.1, the amount of Ag nanoparticles formed with both formamide and DMF at room temperature are 2-3\% of Ag\(^{+}\) ions loaded in the membrane samples. This is due to loss of Ag\(^{+}\) ions from the membrane sample to reducing solution as colour of reducing solution has been also changed. In order to increase the reduction rate as well as amount of Ag nanoparticles in the membrane, the Ag\(^{+}\)-loaded membrane samples have been equilibrated with formamide at 40°C and 65°C. It is evident from the Table 2.1 that the formation of nanoparticles has enhanced considerably on increasing the temperature i.e. 16 \% of Ag\(^{+}\) ions present in the ion-exchange sites have been converted to Ag\(^0\) within 15 min at 65°C. The amount of Ag\(^0\) formed in the membrane during
reduction with formamide at 65°C has been found reproducible within ±1% in five experiments. Unlike formamide and DMF reduction, the reduction of Ag\(^{+}\)-loaded membrane samples with BH\(_4\)\(^{-}\) ions is quite fast and quantitative. 15% Ag\(^{+}\) ions loaded membrane samples, prepared by controlled by desorption of Ag\(^{+}\) ions from ion-exchange sites of the membrane with Na\(^{+}\) ions [189], are reduced by BH\(_4\)\(^{-}\) ions. Nearly 94 % of Ag\(^{+}\) ions present in the membrane have been converted to Ag\(^{0}\) within 5 min.

The ion-exchange capacity of the membrane has not changed significantly after reduction of Ag\(^{+}\) ions in the membrane. After reduction with BH\(_4\)\(^{-}\), the dimensions of the membrane have not changed significantly. However, the area of the membrane has reduced after formamide reduction and increased by 5-8 % after DMF reduction of the membrane. The thickness of the membrane has changed corresponding to change in the area. Similarly, Rh nanoparticles have been prepared in Nafion by the reduction of Rh\(^{3+}\)-loaded membrane with formamide at 65°C for 30 min.

2.3.2. Size and spatial distribution of Ag nps

The size and spatial distributions of Ag nanoparticles have been studied by ultra-thin sectioning of the cross-section of membrane samples reduced with BH\(_4\)\(^{-}\), DMF at room temperature, and formamide at 65°C. The choice for these samples are based on the fact that Ag\(^{+}\) reduction rates in these cases are slowest and fastest as given in Table 2.1 and also they represent ionic and non-ionic reductants. The TEM analyses of the cross-section of the membrane samples are given in Figs. 2.3-2.5 and the results of statistical analyses of TEM micrographs are summarized in Table 2.1. It is seen from Table 2.1 that size distributions of Ag nanoparticles in the samples varied significantly depending upon the reducing conditions. It is clear from the TEM micrographs analyze that the shape of Ag nanoparticles is nearly spherical in all the cases.
Table 2.1 Results of the reduction of Ag$^+$ ions in Nafion-117 membrane with different reducing agents.

<table>
<thead>
<tr>
<th>Reducing Reagent</th>
<th>Temp. (°C)</th>
<th>Equilibration Time</th>
<th>Amount of Ag$^+$ reduced (%)</th>
<th>Average size (nm)</th>
</tr>
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<tbody>
<tr>
<td>HCON(CH$_3$)$_2$</td>
<td>25</td>
<td>7 days</td>
<td>2-3</td>
<td>5±1 &amp; 18±5</td>
</tr>
<tr>
<td>HCONH$_2$</td>
<td>25</td>
<td>24 h</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>HCONH$_2$</td>
<td>40</td>
<td>30 min</td>
<td>7</td>
<td>-</td>
</tr>
<tr>
<td>HCONH$_2$</td>
<td>65</td>
<td>15 min</td>
<td>16</td>
<td>9±2</td>
</tr>
<tr>
<td>BH$_4^-$</td>
<td>25</td>
<td>5 min</td>
<td>94</td>
<td>15±4</td>
</tr>
</tbody>
</table>

Fig. 2.3 TEM analyses of Ag nanoparticles in BH$_4^-$ reduced membrane samples. (a) Ag nanoparticles distributions at the surface, (b) Ag nanoparticles distributions in the interior, & (c) statistical analysis of Ag nanoparticles.
As can be seen from Fig. 2.3(a & b), the Ag nanoparticles are mostly located at the surface of the BH$_4^-$ ions reduced membrane samples. Sachdeva et al. showed that Ag nanoparticles, formed by reduction with BH$_4^-$, were mostly positioned at the surface layer of the membrane [189]. This is due to inability of BH$_4^-$ ions to invade interior matrix of the cation-exchange membrane. However, few Ag nanoparticles are observed throughout the matrix of membrane. In present experiment, 0.2 mol L$^{-1}$ concentration of NaBH$_4$ solution is used. This concentration is high enough to produce leakage of BH$_4^-$ ions in the matrix of membrane [221-223]. This, in turn, reduces some amount of Ag$^+$ ions in the bulk matrix. The average size of Ag nanoparticles in this sample is found to be 15 nm, which is close to 13.4 ± 2.2 nm reported by Sun et al. for Ag nanoparticles formed by BH$_4^-$ reduction in Nafion-117 membrane under similar conditions [184].

The TEM of cross-section of membrane samples reduced with DMF under ambient conditions does not also show uniform distribution of Ag nanoparticles. It is seen from Fig. 2.4(a) & 2.4(b) that the Ag nanoparticles are slightly more concentrated at the surface of the membrane than the bulk matrix. The statistical analysis given in Fig. 2.4(c) indicated that there was a bimodal size distribution of Ag nanoparticles. The smaller nanoparticles are in significantly larger number having 5 nm size and bigger nanoparticles (18 nm) are lesser in number but dispersed throughout the matrix. DMF is a mild reducing agent and require 7 days to form 2-3 % nanoparticles in the membrane matrix. As DMF swells Nafion membrane readily, the physical structure of the membrane changes continuously during reduction from water swollen membrane having water cluster-channel network to that corresponding to DMF swollen homogenous membrane. Swelling and ion-exchange processes operating during prolong equilibration with DMF seems to be responsible for non-uniform bimodal size distribution in the membrane matrix. It appears that bigger nanoparticles have been formed.
Fig. 2.4 TEM analyses of Ag nanoparticles in DMF reduced membrane samples. (a) Ag nanoparticles distributions at the surface, (b) Ag nanoparticles distributions in the interior, & (c) statistical analysis of Ag nanoparticles.

during initial reduction of Ag$^+$ nanoparticles in membrane sample still containing water cluster-channel network structure. This was based on the fact that the size of bigger nanoparticles (18 nm) is comparable to that of the Ag nanoparticles (15 nm) formed by BH$_4^-$ reduction in the membrane. As reduction time progress, the swelling of membrane samples with DMF would destroy the cluster-channel network structure. This would lead to the homogeneous matrix that might restrict the growth of nanoparticles to a smaller size. The radiotracer studies indicate that there is considerable loss of Ag content from the membrane
sample to equilibrating DMF solution. H\(^+\) ions formed during reduction occurring both in membrane matrix and DMF solutions would displace Ag\(^+\) ions from the ion-exchange sites at interior of membrane to the surface leading to slightly higher reduction at the surface of membrane as seen in Fig. 2.4(a).

Fig. 2.5 TEM analyses of Ag nanoparticles in formamide reduced membrane samples. (a) Ag nanoparticles distributions at the surface, (b) Ag nanoparticles distributions in the interior, (c) enlarged view of b, & (d) statistical analysis of Ag nanoparticles.
It is seen from Fig. 2.5(a, b, & c) that the Ag nanoparticles of average size 9 nm are uniformly distributed across the thickness of membrane sample reduced with formamide at 65°C with constant stirring. This indicates that fast reduction produced nanoparticles uniformly throughout the membrane. However, the sizes of Ag nanoparticles are considerably higher than the expected size of water cluster (4-5 nm) in Nafion-117 membrane [109,224]. The number of Ag⁺ ions in any of the initial water domains is small. In a typical hydrophilic domain of 4-5 nm there may not be more than 100 cations. So reducing all the Ag⁺ ions in that domain would produce Ag nanoparticles that would have ~ 1 nm size. The particles observed are ≈ 10-15 times larger. There is a possibility that the Ag⁰ atoms form adjacent clusters may be diffusing fairly rapidly to the site of seeding. The growth of Ag nanoparticles leads to strain at different location along the cluster where seeding of nanoparticles has occurred. Due to this strain, a point comes when the cluster cannot take further strain and either the channel structure is disrupted or the silver nps is excluded out of the channel due to rearrangement of physical structure by hydration forces. It is known that the Nafion-117 membrane rearrange its physical structure depending upon the pretreatment conditions and counterions [33].

2.3.3. Characterization of the reduced samples

The variation of intensity of surface plasmon absorption bands (SPB) of nanoparticles as a function of reduction time in a well stirred formamide at 65°C has been studied. It is seen form UV-Vis spectra given in Fig. 2.6 that the intensity of SPB was quite high though only 15-16 % of Ag⁺ ions present in the ion-exchange sites of membrane sample was converted to Ag nanoparticles. In order to study the penetration of reducing agent formamide across the thickness of membrane, dead end cell experiment has been carried out. The EDXRF analyses of both the surfaces of membrane samples have been carried out. The EDXRF spectra are shown in Fig. 2.7. It is seen from the comparison of the EDXRF spectra that the Ag content
Fig. 2.6 Variation of UV-Vis spectra corresponding to growth of Ag nanoparticles as a function of equilibration time of Ag\(^+\)-loaded membrane sample in well-stirred formamide solution at 65 °C.

Fig. 2.7 Comparison of EDXRF spectra of both the surfaces of Ag\(^+\)-loaded membrane samples before reduction (broken lines) and after reduction (solid lines) with a formamide at 65 °C.
in membrane decreased considerably after reduction but the intensity of S K$_\alpha$ peak has not changed. As intensities of S K$_\alpha$ peak representing -SO$_3$ groups are same, the lower intensity of Ag in the reduced sample with that in nascent sample has been attributed to loss of Ag$^+$ ions during reduction process. However, the distributions of Ag contents on both the surfaces of the dead end cell reduced membrane sample have been almost same. This indicated that formamide could diffuse to unexposed side of membrane and reduced Ag$^+$ ions in bulk matrix of the membrane. In case of BH$_4^-$ reduction under similar conditions, the Ag$^+$ ions have been found to reduce only on the side of the membrane that was exposed to the reductant [189].

2.3.4. Size and spatial distribution of Rh nps

TEM of the cross section of formamide reduced Rh$^{+3}$ loaded membrane are shown in Fig. 2.8. It is evident from the TEM image given in Fig. 2.8 that the clusters containing Rh nanoparticles of size 2-4 nm have been formed. It is seen in TEM image given in Fig. 2.8(a & b) that the most of Rh nanoparticles aggregated in the clusters throughout the matrix. The fractal dimension (D) of the two dimensional cluster has been calculated by the power law relationship between no. of particles and radius, $N(r) \propto r^D$ where r is the radius of the searching circle assuming the centre of mass of the cluster as the origin. The fractal dimension of cluster has been found to be 1.8 (Fig. 2.8 c). It has been reported that the self-diffusion mobility of the trivalent counterions in the Nafion-117 membrane is quite slow [35,225]. This would lead to the reaction-limited as well as diffusion limited aggregation of Rh atoms. This would produce fractals normally observed in diffusion controlled growth of crystals [226-229]. However, the exact reason for the formation of clusters in the membrane matrix could not be understood.
Fig. 2.8  a) TEM image showing cross-section of membrane containing Rh cluster formed by in situ reduction of Rh$^{3+}$ ions in the membrane with formamide at 65°C, (b) enlarged view of a, and (c) plot for fractal dimension.

2.3.5. Self-diffusion coefficients of the counterions

The self-diffusion of ions in a homogeneous medium is due to continuous random motions that give rise to a definite probability of their arrival at some point within a given time. The precise information about the matrix effect on mobility of the ions can be obtained from the self-diffusion coefficient of the ions. Self-diffusion coefficients of ions in ion-exchange membranes provide information about the physical as well as the electrostatic interactions between the fixed charged sites and the diffusing ions [225]. In
order to study the effects of formation of nanoparticles on the membrane morphology and matrix, the isotopic-exchange rate profiles of Na\(^+\), Cs\(^+\), and Eu\(^{3+}\) counterions have been measured in the Ag nanoparticles embedded membrane samples formed by reduction with formamide at 65°C. The choice for this membrane sample was based on the fact that Ag nanoparticles are uniformly dispersed in it. The self-diffusion coefficients of Na\(^+\), Cs\(^+\), and Eu\(^{3+}\) counterions have been measured as Na\(^+\) and Cs\(^+\) ions lead to extreme of water contents in the membrane (see Table 2.2), and Eu\(^{3+}\) ions represent higher valence counterions.

**Table: 2.2 Effects of Ag nps formation on the water uptake capacity and the self-diffusion coefficients (D) of the counterions in nascent Nafion-117 membrane and Ag nps dispersed Nafion-117 membrane formed after reduction at 65°C.**

<table>
<thead>
<tr>
<th>Ionic form</th>
<th>Water uptake (wt. %)</th>
<th>D (x 10(^{-6}) cm(^2) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without Ag nps</td>
<td>With Ag nps</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>17.2(^\text{a})</td>
<td>18±1</td>
</tr>
<tr>
<td>Cs(^+)</td>
<td>8.2(^\text{a})</td>
<td>10±1</td>
</tr>
<tr>
<td>Eu(^{3+})</td>
<td>13.2(^\text{b})</td>
<td>15±1</td>
</tr>
</tbody>
</table>

\(^{a}\): taken from Ref. 24; \(^{b}\): taken from Ref. 29; \(^{c}\): average of three experiments

The profiles of isotopic-exchange rate of \(^*\)Na\(^+\)\(_\text{(mem)}\) ⇌ Na\(^+\)\(_\text{(aq)}\), \(^*\)Cs\(^+\)\(_\text{(mem)}\) ⇌ Cs\(^+\)\(_\text{(aq)}\), and \(^*\)Eu\(^{3+}\)\(_\text{(mem)}\) ⇌ Eu\(^{3+}\)\(_\text{(aq)}\) (* represents radioactivity tagged ions) isotopic exchanges were analysed by using an analytical solution of Fick’s second law described in chapter 1, section 1.5.1 [33-35]. The equation 1.5 was used for deducing self-diffusion coefficients from isotopic-exchange rate profile. The variation of the fractional attainment of isotopic-exchange equilibrium F(t) as a function of square root of equilibration time t\(^{1/2}\) for the Ag nanoparticles embedded membrane samples with the different counterions are shown in the Fig. 2.9. It is evident from the figure that the F(t\(_k\)) varies linearly with t\(^{1/2}\) during initial stages of the exchange process, which is a characteristics of the Fickian diffusion. The value of D has been
obtained by a non-linear least-square fit of experimental profile with equation 1.5. The comparisons of experimental data point for the isotopic-exchange rate for Ag nanoparticles embedded membrane and calculated isotopic-exchange rate profiles for nascent membrane are shown in Fig. 2.9. The values of D, thus obtained are given in Table 2.2. It is seen from

![Graph](image)

**Fig. 2.9** Fractional attainment of isotopic-exchange equilibrium ($F(t)$) as a function of square root of equilibration time $t$. The symbols x, o, and Δ represent $^{*}\text{Na}^+(\text{mem}) \rightleftharpoons \text{Na}^+(\text{aq})$, $^{*}\text{Cs}^+(\text{mem}) \rightleftharpoons \text{Cs}^+(\text{aq})$, and $^{*}\text{Eu}^{3+}(\text{mem}) \rightleftharpoons \text{Eu}^{3+}(\text{aq})$ isotopic-exchange rate profiles between Ag nps embedded Nafion membrane in contact with a well stirred aqueous salt solution. The solid lines 1, 2, and 3 represent isotopic-exchange rate profiles of Na$^+$, Cs$^+$, and Eu$^{3+}$ ions, respectively, calculated using self-diffusion coefficients of ions in the nascent Nafion-117 membrane and equation 1.5.
experimental isotopic-exchange profiles shown in Fig. 2.9 that the Na\(^+\)-exchange profile in membrane is not affected by the formation of Ag nanoparticles in the membrane. However, the Cs\(^+\) and Eu\(^{3+}\) exchange rates have been considerably enhanced in Ag nanoparticles embedded membrane as compared to that in nascent membrane.

As can be seen from Table 2.2, there is no significant difference in the D values of Na\(^+\) and water contents in the nascent and Ag nanoparticles embedded membrane samples. However, there is a significant difference in the D values of Cs\(^+\) and Eu\(^{3+}\) in the membrane samples with and without Ag nanoparticles. The value of D has increased 2 and 5 times for Cs\(^+\) and Eu\(^{3+}\), respectively, after the formation of Ag nanoparticles in the membrane. The water content in Cs\(^+\) form of membrane has been found to increase from 8 wt.% to 10 wt.% on formation of Ag nanoparticles in the membrane by reduction with formamide at 65°C. Similarly water content in Eu\(^{3+}\) form of membrane has been increased from 13.2 wt.% to 15 wt.% due to the formation of Ag nanoparticles. It appears that the inclusion of Ag nanoparticles prevents the dehydration of membrane with least hydrated counterions like Cs\(^+\) ions. It has been reported that increase in the water fraction of the Nafion-117 membrane, which leads to the morphological change, is responsible for higher self-diffusion coefficients of the counterions [33].

2.4. Conclusion

The present study indicated that the fast reduction of silver ions with non-ionic reductant produced Ag nanoparticles monodispersed throughout the bulk matrix of the Nafion-117 membrane. It has been achieved by increase in the reaction temperature and using formamide as reducing agent. Contrary to this, the anionic reductant BH\(_4^-\) produced Ag nanoparticles near the surface of the membrane due to Donnan exclusion of anions in the fixed negative charged membrane. DMF, being slow reductant, produced a bimodal distribution of nanoparticles throughout the membrane matrix. In case of slow moving ion Rh\(^{3+}\), formation
of fractal was observed. The diffusion properties of the membrane changed significantly when nanoparticles were uniformly dispersed in the membrane matrix. For example, the self-diffusion coefficients of the slow moving counterions like Cs$^+$ and Eu$^{3+}$ increased significantly membrane samples. The inclusion of Ag nanoparticles in the membrane leads to the higher water content than the corresponding ionic form of the nascent Nafion-117 membrane. This, in turn, leads to higher diffusion mobility of less hydrated ions.