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ULTRAVIOLET–VISIBLE SPECTRA OF NAFION MEMBRANE

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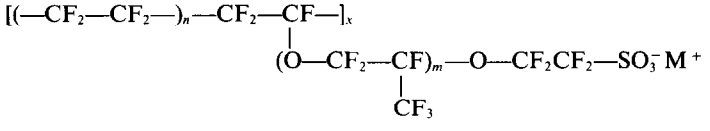
Abstract—The effect of pre-treatment, counterion and electrolyte concentration, temperature and aging of Nafion 117 membrane was investigated by electronic absorption spectroscopy. The band at 196 nm is sensitive to the cluster environment. Its intensity decreases with increasing water content and increases with various countercations according to increasing ionic radius, increase of electrolyte concentration, temperature and time of aging. This behavior may be associated with structural changes induced by membrane hydration. © 1997 Elsevier Science Ltd

INTRODUCTION

Nafion® is a perfluorosulfonate ionomer used extensively as a cation exchange membrane in electrochemical applications, including chloralkali cells [1], fuel cells [2], batteries [3], water electrolysers [3] and as polymer modified electrodes [4, 5].

Nafion ionomers consist of a perfluorinated backbone and ether side-chains terminated with sulfonic groups, SO_3^-. The chemical structure of Nafion 117 is shown below:



(1)

where $n = 6.5$ and M^+ represents an exchangeable cation.

Previous studies [6–11] concluded that the ionic species aggregate to form ionic domains or clusters. Gierke *et al.* [12] have proposed a cluster model (4 nm is diameter) for Nafion membranes and assumed a spherical structure of inverted micelle connected by short and narrow channels.

Nafion membranes are hydrophilic and the water is preferentially sorbed into the clusters due to the hydrophobic character of fluorocarbonic matrix. SAXS results [13] have shown that the Bragg spacing in Nafion membranes increases with water uptake, indicative of cluster size. According to Gierke and Hsu [14], a decrease in the water content in the membrane gives rise to a decrease of the cluster size. On the other hand, pre-treatment of membrane in boiling water induces an increase in cluster size.

The exact amount of absorbed water depends on membrane pretreatment, countercation hydration and electrolyte concentration. The water content of Nafion 117 membrane can be varied up to 22 molecules of H_2O per sulfonic group [15].

In this paper the effects of the alkaline cation, electrolyte concentration, pre-treatment, temperature and aging were investigated on Nafion 117 membrane by ultraviolet and visible (UV/Vis) absorption spectroscopy.

EXPERIMENTAL

Nafion 117 membrane (1100 equivalent weight and 0.180 mm thick) in the acid form (Nafion-H) from Du Pont was used in this investigation. The study was performed on Nafion membrane in both acid form and salt forms, including Na^+, K^+, Rb^+ and Cs^+.

Nafion-H was boiled in distilled water for 30 min. Samples in salt form were obtained by soaking the Nafion-H in appropriate aqueous solutions for 24 hr, rinsing in distilled water to remove excess electrolyte, and wiping with filter paper.

The membrane equilibrated in water or aqueous electrolyte absorbs water. These materials are referred to as hydrated samples.

UV/Vis spectra were recorded using a Beckman DU 70 spectrophotometer, in the range 190–500 nm.

Studies were carried out on samples as-received, on Nafion-H membranes that were boiled or soaked in water and those that were neutralized with monovalent alkaline cations. The effect of temperature was investigated on samples treated in temperatures from 120° to 250°C for 15 min.

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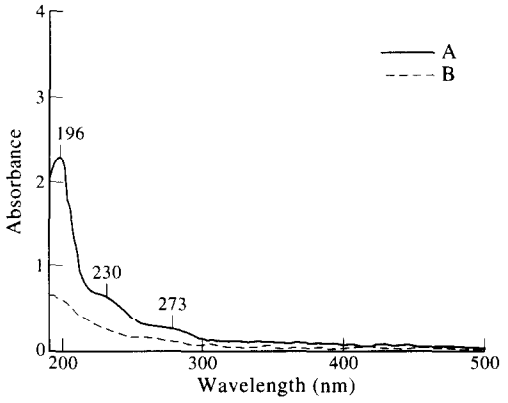

Fig. 1. UV/Vis spectra of Nafion-H 117 as-received (A) and hydrated (B).

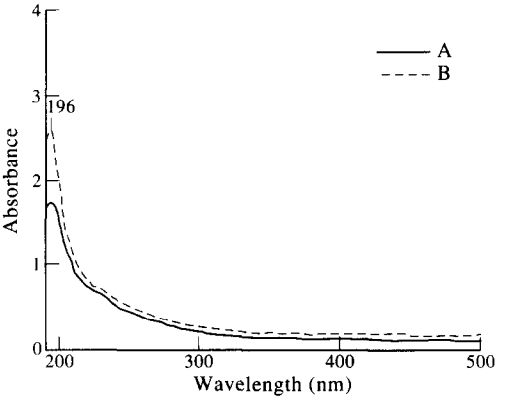

Fig. 2. UV/Vis spectra of Nafion-Na hydrated (A) and Nafion-Cs hydrated (B), neutralized in 0.5 M NaBr solutions of respective cations.

After measurements, treated samples were stored under atmospheric conditions and protected from light, their spectra were periodically recorded to detect changes during aging.

RESULTS AND DISCUSSION

The UV/Vis spectrum of Nafion-H is shown in Fig. 1. This sample shows a strong absorption at 196 nm and two shoulders at 230 and 273 nm.

Effect of pre-treatment

The Nafion-H membrane submitted to pre-treatment (boiled in water for 30 min) exhibit spectral changes, particularly in the position and intensity of the band around 196 nm (Fig. 1). A similar behavior was also observed in Nafion-H membranes that were soaked in water at room temperature, although with less changes observed for the sample treated in boiled water (Table 1). This result can be interpreted in terms of the difference in water uptake by the two samples. It has been reported that the boiled sample has a higher water content than those only soaked [16].

Comparing the results of Fig. 1 and Table 1 we can conclude that the water absorbed by membrane induce considerable decrease in absorbance at 196 nm and is strongly associated with water contents in membrane. This behavior can be assigned to reorganization between the clusters and polymer reorientation, as suggested in previous studies [12, 18, 19]. It is known that addition of water in ionomers affects its morphology, partially dissociates the ions and can also change the local structure of the aggregate [20].

The UV/Vis absorption bands of Nafion membranes are difficult to interpret. A tentative assignment is presented in this study.

Table 1. Absorption band at 196 nm in UV/Vis spectra of Nafion-H membrane

Nafion-H	Absorbance
As-received	2.2
Soaked[a]	0.9
Boiled[b]	0.7

[a]Immersed in water at room temperature for 30 min.
[b]Immersed in boiling water for 30 min.

The absorption at 196 nm could be associated to the carbon–carbon double bond which is produced during the polymerization or modification reactions of Nafion membrane. In the hydrated Nafion-H, the ions are fully solvated and the sulfonate anions shielded from the strong electrostatic effects of the counterion [21], reducing the interactions among the cluster and the polymer chains, and the absorption band may occur at a region lower than 190 nm. The dehydration may induce increasing interactions among the cluster and the double bond segment of polymeric chain, shifting and increasing the intensity of absorption band that appears at 196 nm, due to an auxochrome group (probably OH group). This band could be associated with the perfluorinated backbone of Nafion membrane. The absorption at 230 nm is usually assigned to the diene structure. This chromophore may be produced by a radical during the polymerization or modification reactions, and it remains trapped for a long time, particularly in the crystalline region within the membrane structure. The band at 273 nm may be assigned to a chromophore containing a carbonyl group derived from a radical group which is transformed to a peroxy radical in the atmosphere. The concentrations of these chromophores are very reduced. The absorptions bands at 196, 230 and 273 nm are not associated with the sulfonic group of Nafion.

Effect of counterions

Spectra of hydrated membranes in sodium and cesium ion forms are shown in Fig. 2. The results obtained for samples neutralized with various cations (Table 2) showed a decrease in the absorption at 196 nm with decreasing ionic radius of the countercations. Water absorbed data with various cations

Table 2. Absorption band at 196 nm in UV/Vis spectra of Nafion salt forms (neutralized in 0.5 M bromide solution)

Cation	Ionic radius (Å)	Absorbance
Na^+	0.97	1.7
K^+	1.33	2.0
Rb^+	1.47	2.3
Cs^+	1.67	2.5

Table 3. Absorption band at 196 nm in UV/Vis spectra of Nafion at different concentration of NaOH

Concentration (M)	Absorbance
0.5	1.1
1.0	1.2
2.0	1.5

reported in the literature [17, 22, 23] correlate well with the decrease in the absorption at 196 nm observed in this study (Table 2).

Similar spectra were observed with samples equilibrated in several electrolytes at various exposure times (24 or 72 hr), indicating no dependence on neutralization time. Additional measurements were performed on samples that were first submitted to a pre-treatment prior to the neutralization process. In this case, we observed a higher decrease in the absorption intensity at 196 nm as compared to the samples neutralized without pre-treatment. This result is related to the fact that pre-treated membrane has higher water content than untreated membrane, as observed previously [24].

Effect of electrolyte concentration

The data concerning the effect of electrolyte concentration are listed in Table 3. The results show that the absorbance at 196 nm increases with increasing electrolyte concentration. Considering the literature data [24–27], the water content increases with decreasing electrolyte concentration. This confirms that the spectral changes are associated with the water absorbed by membrane.

On the other hand, we observed that membranes equilibrated in electrolyte containing several anions (OH^-, Cl^- and Br^-) showed a decrease in intensity at 196 nm with increasing the degree of hydration of the anions (Table 4). This effect can be explained considering the sorbed electrolyte formed by large molecules such as Br^- occupies a large volume inside the cluster, causing a decrease in the available volume to water sorption as compared with electrolyte containing OH^-. To confirm this hypothesis, the sample equilibrated in NaBr electrolyte was immersed in water for 24 hr. After this treatment, the membrane was considered to contain no sorbed electrolyte. The spectrum recorded for this sample was similar to that neutralized with NaOH solutions.

Effect of temperature

Figure 3 shows the effect of temperature on Nafion-H membrane treated at various temperatures. Nafion-H heated at 120°C for 15 min shows an UV/Vis spectrum profile similar to the untreated sample. Sample heated at 160°C for 15 min shows an increasing intensity for bands at 196, 230 and 273 nm,

Table 4. Absorption band at 196 nm in UV/Vis spectra of Nafion-Na equilibrated in solution (1 M) containing sodium ion and different anions

Anions	Absorbance
OH^-	1.2
Cl^-	1.3
Br^-	2.5

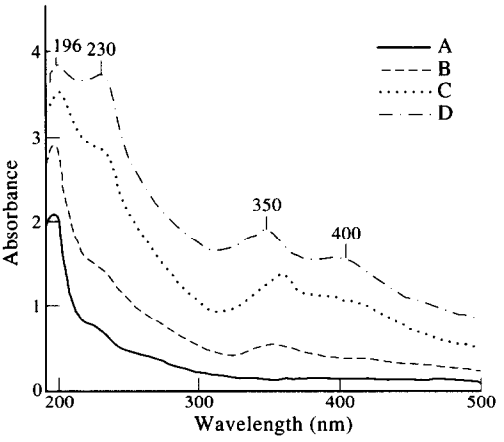

Fig. 3. UV/Vis spectra of Nafion-H treated at different temperatures (for 15 min). (A) 120, (B) 160, (C) 200 and (D) 235°C.

and the appearance of a new weak band at 350 nm. Sample heated at 200°C shows an intensity increasing for bands at 230, 273 and 350 nm, and the appearance of a shoulder at 400 nm. Sample heated at 235°C shows an intensity increasing for bands at 230, 273, 350 and 400 nm. The band at 196 nm shows an intensity increasing with increasing temperature, but at lower rate than that observed for other bands. Several studies [28, 29] have reported that Nafion membranes submitted to high temperatures during the drying process, exhibited structural changes described as shrinkage of clusters and polymeric reorientation.

In contrast, Nafion-Na sample heated from 120 to 250°C exhibits no spectral changes (not shown) as compared to the untreated Nafion-Na sample, showing high thermal stability in comparison to Nafion-H. It has been shown that the thermal stability of Nafion-K is also higher than that of Nafion-H [30].

The intensity change of the band at 196 nm is associated with loss of water content in Nafion-H. Increasing the heating temperature, increases the degree of dehydration and lowers the intensity increasing rate.

The intensity of other bands (230, 273, 350 and 400 nm) increase with increasing heating temperature, and could be partially associated to radical species formed by the scission of the C—S bond of the sulfonic acid group. It is known that when Nafion-H is heated between 35° and 280°C, about 5% weight loss occurs, and the gases are identified as H_2O, SO_2 and CO_2 [30]. The increasing intensity of the band at 230 nm could be due to a chromophore generated by a fluorocarbon radical. The band at 273 nm is associated with a carbonyl chromophore which is also derived from the carbon-based radical in the atmosphere. The bands at 350 and 400 nm could be associated with the chromophore of a $\cdot SO_3H$ radical. This last radical cleaves to produce SO_2 and a hydroxyl radical [30]. The chromophore responsible for absorptions at 350 and 400 nm is uncertain, probably they are associated with a sulfur-based group that remains trapped

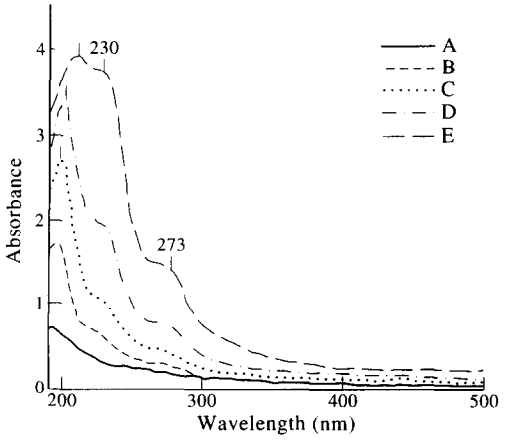

Fig. 4. UV/Vis spectra of hydrated Nafion-H at different times of aging. (A) hydrated sample before aging, (B) 1 month, (C) 4 months, (D) 1 yr and (E) 2 yr.

within the membrane bulk after cleavage of the C—S bond.

Effect of aging

Figure 4 shows the spectra of hydrated Nafion-H at different times of aging. The spectra show a progressive increase in the intensity of the band at 196 nm, with a small red-shift with aging time. The bands at 230 and 273 nm also show an intensity increase with aging time. Similar results are also observed for aged samples with several countercations, but this effect was more pronounced for samples with a higher degree of hydration.

After 1 yr of aging Nafion-Na membrane was immersed in boiling water for 30 min, and the resulting spectrum was similar to that obtained before the immersion. Similar behavior was observed for Nafion-H. These results show that structural changes induced by aging dehydration are irreversible.

The aging after hydration treatment is due to a gradual loss of water content. The decreasing of the degree of hydration increases the interactions among the auxochromic group and the chromophore shifting, and increases the absorption intensity of band in the region of 200 nm. During aging the dehydration process is gradual, but it is not complete because Nafion membrane is slightly hygroscopic [31]. The loss of water by aging induces a conformational change that is different compared to the loss of water by heating.

The band at 230 nm could be due to the presence of the primary radicals that remains trapped during aging. The absorption at 273 nm assigned to a carbonyl group increases its intensity with aging and could be interpreted as being produced by the transformation of a primary radical to a peroxy radical in the atmosphere. It is clear in Fig. 4, spectrum E that the relative intensity of the band at 230 nm decreases and that at 273 nm increases. Furthermore, these changes may be related mainly to the effects of hydration rather than only to aging of the sample, because the as-received Nafion-H, that was kept as a control, after two years exhibited a similar spectrum to the untreated sample.

CONCLUSIONS

The intensities of the band at 196 nm, in the UV/Vis spectra of pre-treated Nafion membrane decreases with increasing absorbed water content and increases with various countercations according to increasing ionic radius, increasing electrolyte concentration, temperature and aging time. These behaviors may be related to reorganization between the clusters and polymer chains induced by water hydration contents.

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