Application of micro Raman spectroscopy to industrial FC membranes

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Abstract. Raman spectra of as-received and protonated membranes (Nafion® NRE-212, Fumapem® F-14100 and Fumasep® FAA) were measured with He-Cd and Ar laser. For the first time the Raman and IR spectra are reported of Fumasep membranes. Most of peaks in vibration spectra active in Raman and IR of membranes are interpreted with C-F, C-S, C-O-C, SO₃, C-C bonds. The vibration region connected with protons and H-O bond in both types of membranes is found in Raman and IR spectra.

1. Introduction
Fuel cells promise to be clean alternative energy sources for variety of power applications ranging from mobile phones, notebook computers, residential power production, automotive and stationary energy power systems [1]. Polymer electrolyte membrane (PEM) fuel cell technology is on the forefront of commercialization efforts in comparison with other fuel cell technologies [2]. The cost is the main factor on the way of the PEM fuel cells, and membranes as well as catalyst are two components with highest expenses from time when fuel cells have been established [3].

The commonly used perflourinated solid polymer electrolyte membrane, Nafion® is a sulfonated tetrafluorethylene copolymer discovered in the late 1960s by Walther Grot of DuPont de Nemours [4]. This first class of synthetic polymers with ionic conductivity is called ionomers. Nafion's unique ionic properties are a result of incorporating perfluorovinyl ether groups terminated with sulfonate groups onto a tetrafluoroethylene (Teflon) backbone [4]. Nafion® proton exchange membrane consists of hydrophobic and hydrophilic domains; both are coming in contact with the catalyst and reactants on the electrode surface. The combination of fluorinated backbone, sulfinic acid groups, and the stabilizing effect of the polymer matrix make Nafion acidic, with pKa ~ -6 [5]. Nafion has received a considerable amount of attention as a proton conductor for PEM fuel cells because of its excellent thermal and mechanical stability, high ionic conductivity ensured by the presence of water in reactant gases [4]. Room temperature polymer electrolyte fuel cell (PEFC) is based on ion exchange polymer membrane functioning as a proton conductor, which also separates the reactants from each other.
Nafion membranes have been studied earlier by infrared and Raman spectroscopy [6-10]. Attention was focused mainly on the $\nu_{OH}$ stretching modes, intensity variation of the sulfonate symmetric stretching mode as a function of the alkali ions. Little attempt has been made so far to combine both techniques and to compare with different membranes.

Many research groups are actively engaged in developing alternative membranes with less expensive chemistries. For example, per-fluorinated sulfonic acid (PFSA)/PTFE copolymer membranes (F-930, F-950) with excellent chemical stability and superior ionic conductance have been developed by FuMaTech for fuel cell applications [11].

In this work Raman and FTIR spectra of Nafion PFSA Membrane NRE-212 and different membranes from FuMA-Tech GmbH are presented. The aim of this investigation was to characterize the nature of the proton exchange sites during treatment in acidic/alkali environment which plays a crucial role in the performance of fuel cells.

2. Experimental

Raman spectra were recorded using following Raman spectrometers: “Nanofinder S” 3D confocal spectrometer (purchased from Belorussia, excitation with 441.6 nm radiation from a He-Cd laser operating at about 20 mW) and Spex Ramalog Raman spectrometer (514 nm Ar laser, 671 nm YAG laser). IR spectra of Absorption and Diffuse Reflectance were recorded using Bruker Equinox 55 FTIR spectrometer with resolution of 0.5 cm$^{-1}$. In microscopic mode Raman spectra were recorded for membranes placed horizontally. Laser beam illuminated membrane from below.

Different industrial membranes were investigated. Nafion® NRE-212 (DuPont) with thickness 50.0 $\mu$m was purchased from DuPont (USA). Perfluorinated sulfonic acid polymer cation-exchange membrane Fumapem® F-14100 (thickness 120 $\mu$m) and anion-exchange membrane Fumasep® FAA (thickness 130 $\mu$m) was purchased from FuMA-Tech GmbH (Germany) [11].

All membranes were measured as received on both - IR and Raman equipment. The protonation was done as follows:

1) Fumapem® F-14100: immersed for 3 hours in 10% HNO$_3$ (chemical grade) water solution at 90°C, rinsed and kept in distilled water at 90°C for 1 hour;
2) Fumasep® FAA: in 2M NaOH (chemical grade) solution at room temperature (RT) for 24 hours; rinsed and kept in distilled water at RT for 1 hour;
3) Nafion® NRE-212 immersing for 1 hour in 18% H$_2$O$_2$ solution at 80°C, rinsed and kept in distilled water at 80°C for 0.5 hour; kept 1 hour in 2M H$_2$SO$_4$ (chemical grade) solution at 80°C and finally kept in distilled water for 1 hour.

3. Results and analysis

Raman spectra from as-received and protonated membranes measured with Ar laser differs fundamentally in case of Nafion® NRE-212 (Figure 1a), and only small in case of Fumasep F-14100 (Figure 1b).

Raman spectra of anion exchange membrane from Fumasep® FAA in as-received condition is poor resolved due to very high luminescence under excitation with He-Cd or Ar laser (514 nm). Nevertheless after process of ion exchange in alkaline media the peaks in spectra are well-resolved and new features appear in the region of O-H vibrations around 3000 cm$^{-1}$.

Considerable changes in the IR spectra for Fumasep® FAA (Figure 2) is noticed in the region 3500-2500 cm$^{-1}$, were O-H vibrations are located. All measured vibration peaks both in Raman and IR spectra are collected in Tables 1-3. The material from literature [6-10] was used to interpret the peaks and assign to defined molecules and bonds and databases on web. Most peaks in vibration spectra of membranes are interpreted with C-F (region 380-797 cm$^{-1}$ for symmetric vibrations, and region 1154-1158 cm$^{-1}$ for asymmetric vibrations), C-S (region 806-812 cm$^{-1}$), C-O-C (region 969-989 cm$^{-1}$), SO$_3$ (region 1058-1059 cm$^{-1}$) and C-C (region 1297-1374 cm$^{-1}$) bonds. In the IR spectrum, the appearance of new peaks was noticed after protonation procedures. The ionic character of the chains connected
with protons can promote the disorder in polymer structure after protonation procedures, which is responsible for the broadening of existing peaks and appearance of new ones.

**Figure 1.** Raman spectra of membranes Nafion® NRE-212 (a) and Fumapem® F-14100 (b) (as-received and protonated)

**Figure 2.** Infrared spectra of membrane Fumasep® FAA; - as received and protonated.

For the first time the Raman and IR spectra are reported for Fumapem® and Fumasep® membranes in this work. The new vibration peaks appeared in the membrane Fumasep® FAA after protonation in the regions 3700-3800 and 1600-1700 cm⁻¹ (Figure 2), while the peak at 1679 cm⁻¹ in as-received membrane disappeared after protonation process. An assignment of vibration peaks to specific vibrations in proton exchange membranes are hard due to the lack of complex calculations and measurements. In future it is planned to investigate the membranes using different laser wavelength and sample geometry. It will provide better insight in membrane protonation.
Table 1. Raman and IR peaks of as-received and protonated membrane Nafion® NRE-212.

| Raman spectra | IR spectra | Interpretation |
|---------------|------------|----------------|
| As-received   | Protonated | As-received    | Symmetry class | Assignment |
| 325           | 385        | 432            | A<sub>1</sub>   | δ(CF<sub>2</sub>) |
| 388           |            | 444            |                |              |
|               |            | 463            |                |              |
|               |            | 530            |                |              |
|               |            | 555            | ρ(CF<sub>2</sub>) |              |
|               |            | 635            | ω(CF<sub>2</sub>) |              |
|               |            | 654            |                |              |
|               |            | 719            | ν<sub>s</sub> (CF<sub>2</sub>) |              |
| 735           |            | 782            | A<sub>1</sub>   | ν<sub>s</sub> (CF<sub>2</sub>) |
|               |            | 780            | ν<sub>s</sub> (CF<sub>2</sub>) |              |
| 804           |            | 806            | ν (C - S)       |              |
| 850           |            |                |                |              |
| 975           |            | 969            | ν<sub>d</sub> (C-O-C) |              |
|               |            | 983            | ν<sub>s</sub> (C-O-C) |              |
| 1060          |            | 1058           | ν<sub>s</sub> (SO<sub>3</sub><sup>-</sup>) |              |
| 1070          |            |                |                |              |
| 1299          |            | 1297           | E<sub>2</sub>    | ν(C-C)       |
| 1355          |            | 1337           |                |              |
| 1374          |            |                | A<sub>1</sub>   | ν (C–C)      |
| 1419          |            |                |                |              |
| 1499          |            |                |                |              |
|               |            | 1734           |                |              |
|               |            | 2220           |                |              |
|               |            | 3405           |                |              |

Table 2. Raman and IR peaks of as-received and protonated membrane Fumapem® F-14100

| Raman spectra | IR spectra | Interpretation |
|---------------|------------|----------------|
| As-received   | Protonation| As-received    | Protonation | Symmetry class | Assignment |
| 387           |            | 441            | A<sub>1</sub> | δ(CF<sub>2</sub>) |              |
|               |            | 719            |                |              |              |
| 735           |            | 735            | A<sub>1</sub>  | ν<sub>s</sub> (CF<sub>2</sub>) |              |
|               |            | 750            |                |              |              |
| 778           |            |                |                |              |              |
| 811           |            | 812            | ν(C-S)         |              |              |
| 843           |            | 846            | υ(C-S)         |              |              |
| 893           |            | 891            |               |              |              |
| 936           |            | 947            |               |              |              |
| 972           |            | 989            | υ(C-O-C)       |              |              |
| 1056          |            | 1059           | υ(SO<sub>3</sub><sup>-</sup>) |              |
|               |            | 1076           |                |              |              |
| 1102          |            | 1167           |                |              |              |
|               |            | 1186           |                |              |              |
Table 2. (Continued)

| Raman spectra | IR spectra | Interpretation |
|---------------|------------|----------------|
| As-received   | Protonation| As-received    | Protonation | Symmetry class | Assignment |
| 1299          | 1323       | E<sub>2</sub>   |             |                |            |
| 1374          | 1419       | A<sub>1</sub>   | 1417        |                | ν (C–C)    |
|               | 1432       |                | 1434        |                |            |
|               | 1470       |                | 1472        |                |            |
|               | 1510       |                | 1495        |                |            |
|               | 1634       |                |             |                |            |
|               | 1686       |                |             |                |            |
|               | 2472       |                | 2217        |                |            |
|               | 2817       |                |             |                |            |
|               | 2880       |                |             |                |            |
| 2952          | 2989       |                | 2979        |                |            |
| 3030          | 3022       |                | 3022        |                |            |
| 3116          |            |                | 3392        |                |            |

Table 3. Raman and IR peaks of as-received and protonated membrane Fumasep® FAA

| Raman spectra | IR spectra | Interpretation |
|---------------|------------|----------------|
| As-received   | Protonation| As-received    | Protonation | Assignment |
| 470           |            | 564            | 564         |            |
|               |            | 607            | 606         |            |
|               |            | 631            | 631         | ω(CF<sub>2</sub>) |
|               |            | 661            | 664         |            |
|               |            | 694            | 694         |            |
|               |            | 713            | 716         |            |
|               |            | 747            | 746         | ν<sub>s</sub> (CF<sub>2</sub>) |
|               |            | 789            | 797         | ν<sub>s</sub> (CF<sub>2</sub>) |
| 843           | 843        | 840            | 837         |            |
|               | 854        | 855            | 854         |            |
|               | 874        | 874            |             |            |
| 936           | 989        | 989            |             | ν<sub>s</sub> (C-O-C) |
|               | 1014       | 1014           |             |            |
|               | 1058       | 1058           |             | ν<sub>d</sub> (SO<sub>3</sub>) |
| 1077          | 1073       | 1074           |             |            |
| 1119          | 1119       | 1106           | 1107        |            |
| 1151          | 1154       | 1154           | 1158        | ν<sub>as</sub>(CF<sub>2</sub>) |
| 1192          | 1196       | 1171           | 1170        |            |
|               |            | 1208           |             |            |
| 1255          | 1263       |                |             | ν<sub>m</sub>(CF<sub>2</sub>), ν<sub>m</sub>(SO<sub>3</sub>) |
| 1280          | 1296       | 1294           |             | ν(C-C)    |
| 1340          | 1320       | 1321           |             |            |
Table 3. (Continued)

| Raman spectra | IR spectra | Interpretation |
|---------------|------------|----------------|
| As-received   | Protonation| As-received   | Protonation | Assignment |
| 1367          | 1376       |               |             |            |
| 1404          | 1407       |               |             |            |
| 1489          | 1465       |               |             |            |
| 1493          | 1493       |               |             |            |
| 1502          |            | 1502          |             |            |
| 1570          |            | 1570          |             |            |
| 1585          | 1585       |               |             |            |
| 1626          | 1626       | 1633          |             |            |
| 1643          |            | 1679          |             |            |
| 1679          |            | 1905          |             |            |
| 2843          | 2889       | 2892          |             |            |
| 2989          | 2958       | 2970          |             |            |
| 3078          | 3077       | 3062          |             |            |
| 3164          |            | 3164          |             |            |
| 3350          |            | 3350          |             |            |
| 3607          |            | 3607          |             |            |

4. Summary
FTIR and Raman spectra of as-received and protonated commercial membranes were measured. It was found that PFSA membrane Nafion® NRE-212 after protonation in HNO₃ water solution reveals intense molecular vibration peaks in the spectral region were O-H bond vibrations are located. For the first time the Raman and IR spectra are reported of Fumasep® membranes. Raman spectra of anion exchange membrane FAA in dry condition are poor resolved due to very high luminescence under excitation with Ar laser, but after protonation the molecular vibration peaks in spectra are well-resolved. Most of peaks in vibration spectra of membranes are interpreted with C-F, C-S, C-O-C, SO₃, C-C bonds. Vibration spectra of membranes after protonation are firstly reported.

5. References
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