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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, SO_3, 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, note book 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, sulfonic 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 νOH 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 μm was purchased from DuPont (USA). Perfluorinated sulfonic acid polymer cation-exchange membrane Fumapem® F-14100 (thickness 120 μm) and anion-exchange membrane Fumasep® FAA (thickness 130 μm) 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_2O_2 solution at 80°C, rinsed and kept in distilled water at 80°C for 0.5 hour; kept 1 hour in 2M H_2SO_4 (chemical grade) solution at 80ºC 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.

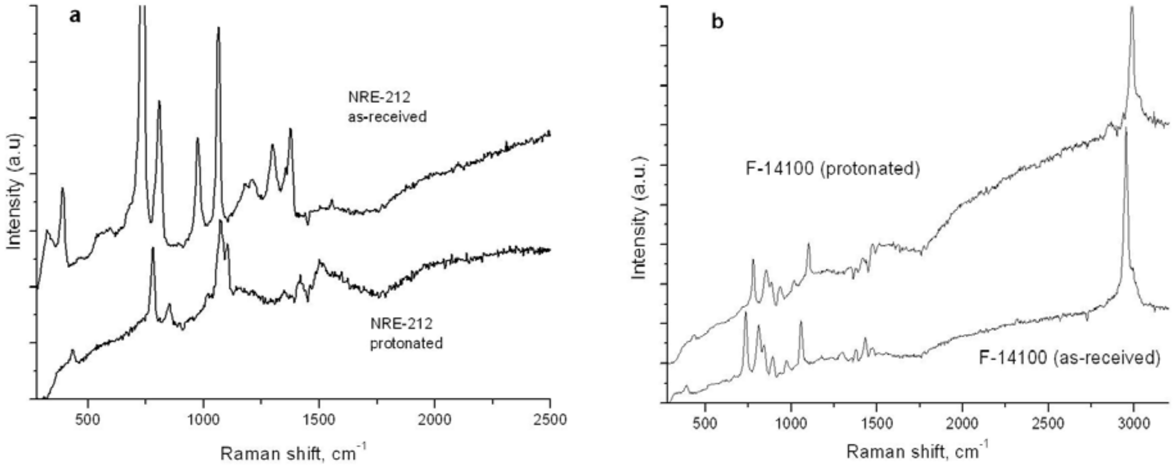

Figure 1. Raman spectra of membranes Nafion® NRE-212 (a) and Fumapem® F-14100 (b) (as-received and protonated)

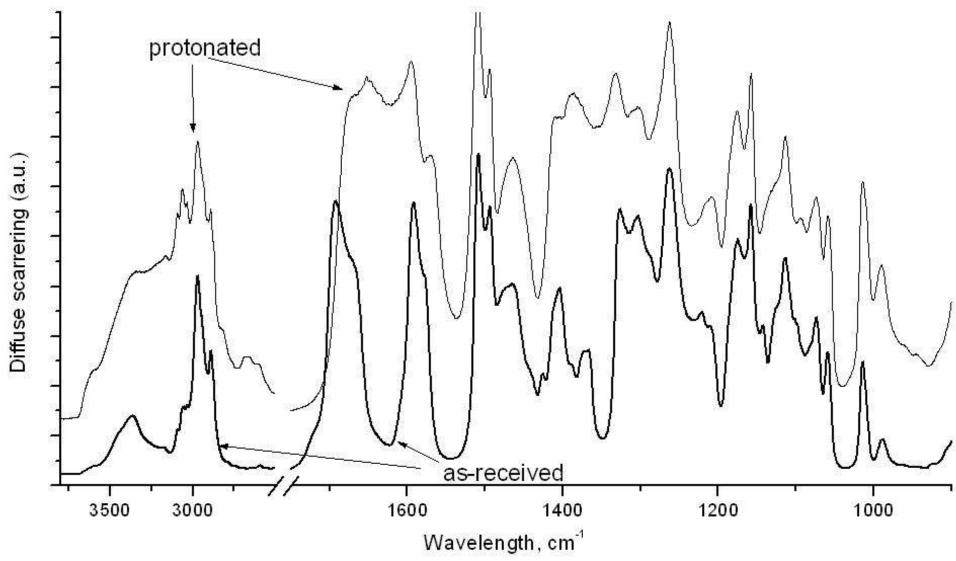

Figure 2. Infrared spectra of membrane Fumasep® FAA; - as received and protonated.

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	Interpretation	
As-received	Protonated	As-received	Symmetry class	Assignment
325				
388		385	A_1	$\delta(CF_2)$
	432			
		444		
		463		
		530		
		555		$t(CF_2)$
		635		$\omega(CF_2)$
		654		
		719		$\nu_s\ (CF_2)$
735			A_1	$\nu_s\ (CF_2)$
	782	780		$\nu_s\ (CF_2)$
804		806		ν (C - S)
	850			
975		969		ν_s(C-O-C)
		983		ν_s(C-O-C)
1060		1058		$\nu_s(SO_3^-)$
	1070			
1299		1297	E_2	ν(C-C)
1355		1337		
1374			A_1	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				A_1	$\delta(CF_2)$
		441			
		719			
735		735		A_1	$\nu_s\ (CF_2)$
		750			
	778				
811		812			ν(C-S)
843	854	846	846		
893	887	891	891		
	936	947			
972		989	989		ν_s(C-O-C)
1056			1059		$\nu_s(SO_3^-)$
		1076	1076		
	1102	1167			
		1186			

Table 2. (Continued)

Raman spectra		IR spectra		Interpretation	
As-received	Protonation	As-received	Protonation	Symmetry class	Assignment
1299		1323		E_2	
1374				A_1	ν (C–C)
	1419	1417	1417		
1432		1434	1434		
1470		1472			
		1510	1495		
		1634			
		1686			
			1711		
		2472	2217		
		2817			
		2880			
2952	2989	2979	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	$\omega(CF_2)$
		661	664	
		694	694	
	713	715	716	
		747	746	ν_s (CF_2)
	789	797	797	ν_s (CF_2)
843	843	840	837	
	854	855	854	
		874	874	
	936			
		989	989	ν_s(C-O-C)
		1014	1014	
		1058	1058	$\nu_s(SO_3^-)$
	1077	1073	1074	
1119	1119	1106	1107	
1151	1154	1154	1158	$\nu_{as}(CF_2)$
1192	1196	1171	1170	
			1208	
	1255	1263		$\nu_{as}(CF_2)$, $\nu_{as}(SO_3^-)$
	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	
			1570	
		1585	1585	
1626	1626		1633	
	1643			
		1679		
			1905	
	2843	2889	2892	
2989	2958	2967	2970	
3078	3077	3373	3062	
			3164	
			3350	
			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 HNO_3 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, SO_3, C-C bonds. Vibration spectra of membranes after protonation are firstly reported.

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