Understanding the fingerprint region in the infra-red spectra of perfluorinated ionomer membranes and corresponding model compounds: Experiments and theoretical calculations

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ABSTRACT

We present an ATR-FTIR study of three major perfluorinated ionomers that are used as proton exchange membranes in fuel cells (FCs) and that differ in their side chains: Nafion, Aquivion and 3M membrane. The choice of the following low-molecular-weight model compounds (MCs) that mimic the membrane side chains was essential for FTIR band assignment: perfluoro(3-methyl-2,4-dioxahexane)sulfonic acid for Nafion, perfluoro(2-ethoxyethane)sulfonic acid for Aquivion, and perfluoro(2-ethoxybutane)sulfonic acid for the 3M membrane. The major goal was to identify spectral bands that can be used for recognizing bonds involved in membrane fragmentation. A major focus was on the signals from the C–O–C bonds, which were assigned in some papers for Nafion and Aquivion membranes. Our ATR-FTIR results for 3M membranes did not conform to these assignments, and DFT calculations of the vibrational frequencies for the MCs were used to resolve this conundrum. The ATR-FTIR spectra of membranes and MCs and the DFT calculations led to an understanding of the fingerprint region of all membranes, and to a re-examination and re-assignment of results for Nafion and Aquivion membranes. The low intensity of the spectral bands for the ether link connected to the backbone (for all membranes) and also in the side chain (for Nafion) suggests that these bands cannot be used for the determination of the extent of degradation.

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1. Introduction

Perfluorinated ionomers are the membranes of choice as proton-exchange membranes (PEMs) for fuel cell (FC) applications, because of their superior mechanical properties and their chemical and thermal stability [1]. While Nafion was the benchmark membrane for some time, additional perfluorinated membranes are now available, as shown in Chart 1. The major structural variation in the membranes shown in Chart 1 is the side chain. Indeed, recent work in our laboratory has indicated the greater stability of the 3M and Aquivion membranes, a result that was explained by the absence of the tertiary carbon and ether bond in the side chain, compared to Nafion [2].

Major ideas on the degradation mechanism in perfluorinated membranes have undergone significant modifications in the last few years. Initial results were explained by attack of hydroxyl radicals, HO•, on the terminal –COOH end groups in the polymer backbone, leading to the unzipping mechanism [3,4]. Recent studies, however, have emphasized the susceptibility of the *side chains* to hydroxyl radical attack, a process that becomes even more important in chemically stabilized membranes, in which the number of –COOH is significantly reduced [5].

Our studies, based on direct electron spin resonance (ESR) and spin trapping ESR, demonstrated the centrality of the hydroxyl radical, HO•, as the most aggressive oxygen radical that can attack both the main- and the side chains in PEMs, examined the difference between ex situ and in situ experiments based on experiments in a FC inserted in the ESR resonator, and developed methods for the detection of early events and for identification of membrane fragments [6–10]. Taken together, these studies have formulated three main degradation paths for the PEMs: main chain unzipping and side chain attack (both by attack of hydroxyl radicals), and main chain and side chain scission by hydrogen atoms at the tertiary carbon atoms.

Numerous studies on the degradation of perfluorinated ionomers have been carried out by various experimental techniques. Solid state NMR studies have confirmed the idea that the side chain is vulnerable to hydroxyl radical attack [11–13]. Current studies have suggested that in Nafion the C–O–C bond in the middle of the side chain is preferentially cleaved at low humidity conditions: ATR (attenuated total reflection)-FTIR studies of perfluorinated ionomers with different equivalent weights exposed to

Chart 1. Structures of perfluorinated membranes (Nafion, Aquivion, 3M), and corresponding model compounds (PFMHSA, PFEESA, PFEBSA).

H_2O_2 were interpreted in terms of the loss of sulfonic group and the rupture of the C–O–C linkage in the side chain [14].

The Nafion absorption bands at 969 and 982 cm^{-1} were assigned to the C–O–C group connecting the side chain to the main chain, and to the C–O–C group in the side chain, respectively; the absence of the 982 cm^{-1} band in Dow membranes (which have the same side chain as the Aquivion membranes) was considered as a support for this assignment [15,16]. The band at 982 cm^{-1} was attributed to the C–O–C linkage at the backbone chain, and that at 969 cm^{-1} to the C–O–C bond in the side chain of Nafion membrane. Some questions on the assignments of the Nafion 969 and 982 cm^{-1} bands were raised in our preliminary FTIR study of perfluorinated membranes that also included, for the first time, the 3M membranes: In this study the frequencies of the ether linkages in the Nafion and Dow/Aquivion membranes were confirmed by results for the membranes and two of the model compounds (MCs). However, we emphasized that "*Further studies are needed in order to understand some of the results presented above for the 3M membranes, in particular the absence of the band at 967 cm^{-1}*" [17].

We present here an ATR-FTIR and density functional theory (DFT) study of Nafion, Aquivion, 3M membranes, and of the corresponding MCs: perfluoro(4-methyl-3-oxaoctanoic)sulfonic acid (PFMHSA, for Nafion), perfluoro(2-ethoxybutane)sulfonic acid (PFEESA, for Aquivion), and perfluoro(2-ethoxybutane)sulfonic acid (PFEBSA, for the 3M membrane), as seen in Chart 1. This complete study of the three major perfluorinated membranes and of corresponding MCs led to a better understanding of the fingerprint FTIR region 700–1100 cm^{-1}, and to a re-examination and re-assignment of FTIR bands included in the current published literature. An important conclusion of this study is that a good indicator for evaluating the extent of membrane degradation is the sulfonic band at $\approx$1060 cm^{-1} for the membranes and MCs, not the ether linkages as originally thought.

2. Experimental

2.1. Materials

The Nafion membrane was a gift from Frank D. Coms of General Motors. The 3M and PFIA membranes were supplied by

M.S. Schaberg of 3M. The Aquivion membrane was a gift from Solvay Solexis, Bollate, Italy. The membranes were: 3M (thickness 25 μm), Aquivion E87-03S (thickness 30 μm), and Nafion 117 (thickness 175 μm). The MCs perfluoro(3-oxahexanoic)sulfonic acid (PFEBSA) and perfluoro(4-methyl-3-oxaoctanoic)sulfonic acid (PFMHSA) were a gift from David Schiraldi of Case Western Reserve University who used the notation MC7 (for PFEBSA) and MC8 (for PFMHSA) in their study [5]. PFEESA was purchased from Matrix Scientific. All materials were used as received.

2.2. ATR-FTIR spectra

The spectra were collected at ambient temperature on Perkin Elmer Spectrum 2000 and Spectrum 100 spectrometers equipped with a Harrick MPV-Pro Star single reflection ATR diamond crystal. The membranes were pressed against the crystal with the pressure applicator at the maximum setting. The model compounds were measured as thin films. The baseline in all spectra was corrected automatically. Plotting and analysis of the FTIR spectra was performed using the Microcal Origin software. The water content in the investigated materials was not determined; however, the FTIR spectra indicated the presence of water in the membranes and the MCs

2.3. DFT calculations

All calculations presented here were performed with a multicore version of the Gaussian 03W package [18]. The structures and frequencies were calculated at the DFT level by applying B3LYP hybrid functional [19,20] and the 6-311G(2d,2p) basis set [21,22] in vacuo and in solution. The solvent effect was included via the polarizable continuum model (PCM) [23] as implemented in Gaussian package, and the solvent was water. It was demonstrated that in many cases the calculated PCM frequencies are able to reproduce the experimental data [24,25]. In our studies, however, PCM model calculations underestimated the observed frequencies. The best overall agreement between theory and experiment was obtained in gas phase calculations and only these results are presented. According to Webber et al. the effect of including the dielectric medium in the calculations is rather small compared to sequential addition

of water molecules to the solvation sphere [26]. We note that the calculated frequencies are slightly lower than experimental ones. Since the scaling factors used are <1, the calculated frequencies were not scaled.

3. Results and discussion

3.1. ATR–FTIR spectroscopy

Fig. 1A presents the spectra of Nafion and Aquivion membranes measured at ambient temperature [17]. Interpretation of the spectra was performed in the earlier literature by comparison with the IR spectrum of polytetrafluoroethylene (PTFE, teflon) [27–29]. The major difference between Nafion and PTFE is the appearance of the strong band at 1056 cm^{-1} which was assigned to the SO$_3^-$ symmetric stretch, and of the two bands at 969 and 982 cm^{-1}, which were assigned in the literature to C–O–C linkages connected to the main chain and in the side chain, respectively [14–16]. The 969 cm^{-1} band is also seen in the spectrum of Aquivion membrane, and was taken as a verification of the assignment of the C–O–C linkage in Nafion. The asymmetric C–O–C stretching mode is expected to contribute a band around 1130 cm^{-1} in a spectral region more difficult to interpret because of the C–F bands. A very weak band at 806 cm^{-1} was attributed to the C–S stretching vibration [30]. The assignments, based on published data, are summarized in Table 1.

The ATR–FTIR spectra of the corresponding MCs, PFMHSA for Nafion and PFEESA for Aquivion, are shown in Fig. 1B. We note that PFEESA was considered an MC for Nafion by Warren and McQuillan [31] and in our study of MCs fragmentation [8]. At this stage we propose that PFMHSA is the more appropriate MC for Nafion because of the presence of the *two* ether links, and PFEESA is the ideal MC for Aquivion, because of the *one* ether linkage and the two CF$_2$ groups in the side chain between the oxygen and the sulfonic group. The ATR–FTIR spectrum of PFMHSA and PFEESA are presented in Fig. 1B and the band assignments are listed in Table 1, also based on published data. The similar, even identical, fingerprint region for the membranes and the corresponding MCs suggests that the MCs are well chosen and their vibrational modes calculated by DFT methods, see below, can also describe the expected bands in the spectra of the membranes.

In order to validate the interpretation of FTIR spectra for the Nafion and Aquivion membranes and for the corresponding MCs, we performed experiments with the 3M membrane and its MC,

Table 1
Assignment of the absorption bands of Nafion and Aquivion membranes, and of corresponding model compounds PFMHSA and PFEESA, respectively.[a]

Nafion	PFMHSA	Aquivion	PFEESA	Band assignment
			1461 w	
1350 vw	1407 vw			$\nu_{as}(SO_2)$
1320 vw	1349 vw	1320 vw		$\nu_{as}(CF_3)$
	1310 v			$\nu_{as}(CF_3)$
1301 vw		1301 vw	1307 vw	$\nu_s(C-F)$
1280 vw		1280 vw		$\nu_{as}(SO_3^-)$
	1229 s		1235 w	$\nu_s(CF_3)$
1199 s	1195 s	1199 s	1195 s	$\nu_{as}(CF_2)$
	1155 s		1155 s	
1143 s		1143 s		$\nu_s(CF_2)$
1134 s	1135 s	1134 s	1135 s	$\nu_{as}(C-O-C)$
	1098 s		1098 s	$\nu_s(CF_2)$
1056 s	1057 s	1056 s	1057 s	$\nu_s(SO_3^-)$
993 sh	998 sh			
982 s	986 s			$\nu_s(C-O-C)$
969 s	968 s	969 s	975 s	$\nu_s(C-O-C)$
				$\nu_s(SO-H)$
	810 sh			
806 vw	801 vw	806 vw	801 vw	$\nu_s(C-S)$
	750 vw			$\nu_s(CF_3)$

s, strong; w, weak; vw, very weak; sh, shoulder.

[a] Assignment of localized bands is based on published literature [14,15,27,28].

PFEBSA. The ATR–FTIR spectrum of the 3M membrane in the range 1500–700 cm^{-1} is presented in Fig. 2A. The major difference compared to the Nafion and Aquivion FTIR spectra is the *absence* of band around 969 cm^{-1}, which was detected in Aquivion membranes and was previously assigned to the C–O–C linkage between the backbone and the side chain. Fig. 2B presents the ATR–FTIR spectrum of PFEBSA as the MC (one ether group, mimics the 3M membrane side chain, Chart 1) in the range of 1500–700 cm^{-1}. The spectrum of PFEBSA is typical for the ionized (dissociated) sulfonic acid. The very weak band at 1408 cm^{-1} is assigned to the SO$_2$ asymmetric stretching mode [31]. The 1300–1100 cm^{-1} region is dominated by the strong C–F bands. Bands at 1343 cm^{-1} and 1289 cm^{-1} can be assigned to asymmetric vibrations of CF$_3$ and SO$_3^-$ groups, respectively. Strong bands at 1225, 1197 and 1150 cm^{-1} can be assigned to the C–F vibrations in CF$_2$. The band at 1136 cm^{-1} is assigned to the asymmetric C–O–C vibrations. Bands at 1069 cm^{-1} and 1062 cm^{-1} are assigned to SO$_3$ vibrations and are typical for the dissociated sulfonic groups. As for the 3M membrane, the band due to the symmetric vibration of C–O–C observed for Aquivion at 969 cm^{-1} is

F$_3$C-CF$_2$-O-CF$_2$-CF-O-CF$_2$-CF$_2$-SO$_3$H
CF$_3$

F$_3$C-CF$_2$-O-CF$_2$-CF$_2$-SO3H

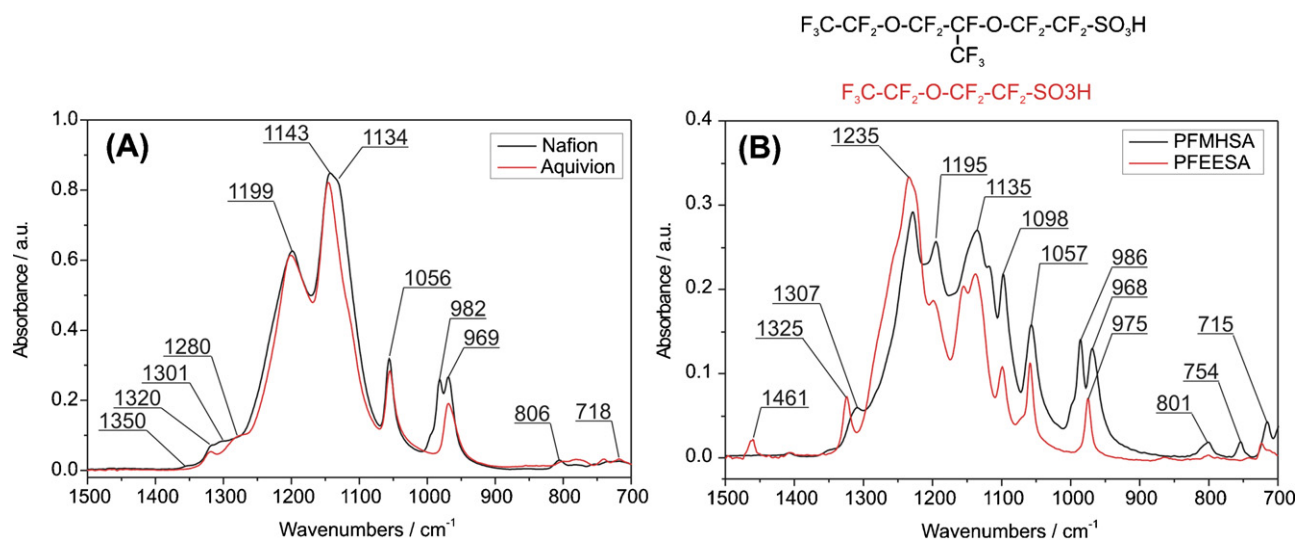**Fig. 1.** ATR–FTIR spectra in the 1500–700 cm^{-1} range of Nafion and Aquivion membranes in (A), and of the corresponding model compounds PFMHSA and PFEESA, respectively, in (B).
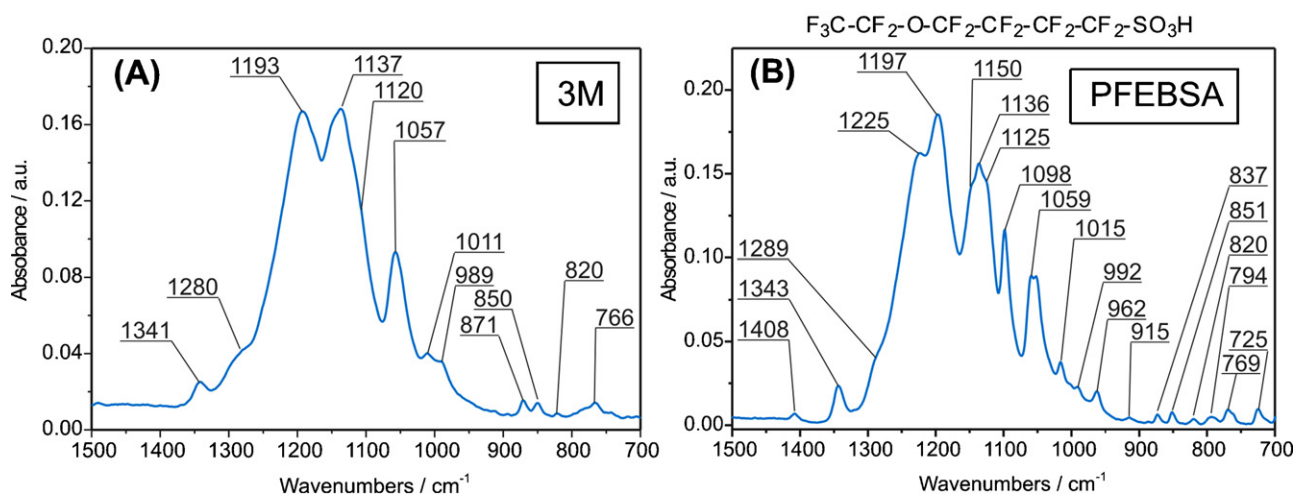
Fig. 2. ATR–FTIR spectra in the 1500–700 cm^{-1} range of the 3M membrane in (A), and of the corresponding model compound PFEBSA in (B).

(A) PFMHSA, acidic form
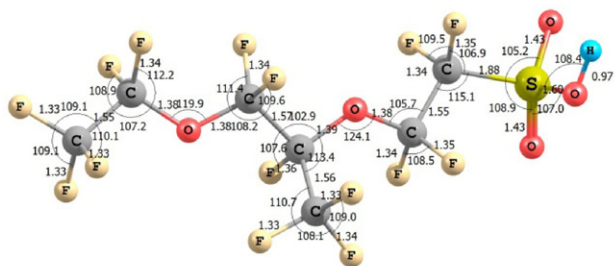
(B) PFMHSA, ionic form
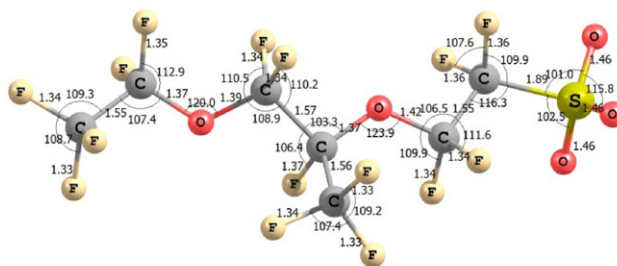
(C) PFEESA, acidic form
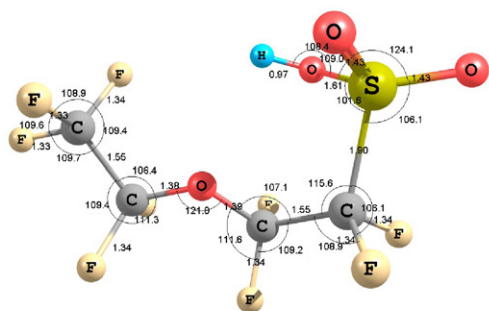
(D) PFEESA, ionic form
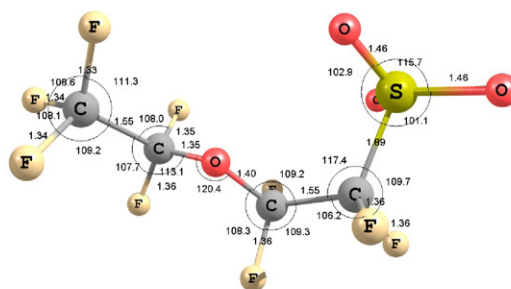
(E) PFEBSA, acidic form

(F) PFEBSA, ionic form

Fig. 3. B3LYP/6-311(2d,2p) optimized structures of PFMHSA, PFEESA, and PFEBSA: (A), (C) and (E) in acidic form (–SO$_3$H), and (B), (D) and (F) in ionic form (–SO$_3^-$). All angles are in degrees and the bond lengths in Å. Geometries are presented using the ChemCraft program (http://www.chemcraftprog.com).

Table 2
Calculated vibrational modes of PFMHSA, the model compound for Nafion.

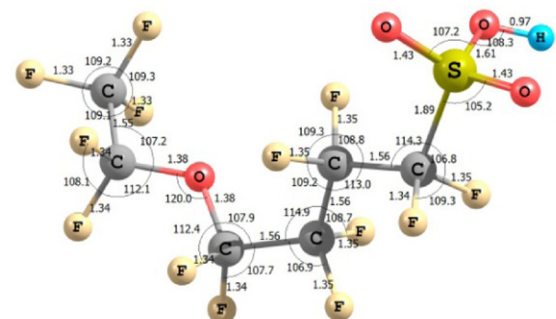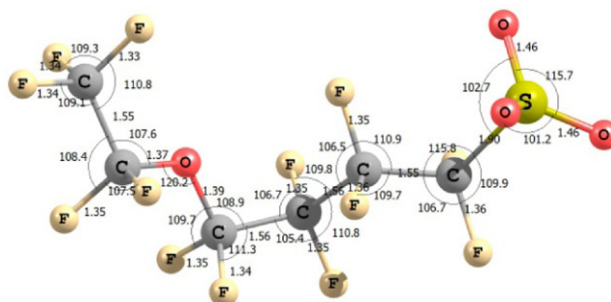| −SO_3H (acidic form)			−SO_3^- (ionic form)		
ν (cm^{-1})	Intensity (km mol^{-1})	Assignment	ν (cm^{-1})	Intensity (km mol^{-1})	Assignment
1427	212.0	δ(SO–H)	1400	2.9	ν(C–C)
1400	7.8	ν(C–C)	1325	86.5	ν(C–C)
1327	127.3	ν(C–C)	1319	54.5	ν_s(CF$_2$) + ν(C–C)
1290	159.9	ν_s(CF$_2$) + ν(C–C)	1293	324.9	ν_s(CF$_2$) + ν(C–C)
1252	305.6	ν_{as}(CF$_3$) + ν_s(CF$_2$)	1271	370.1	ν_{as}(SO$_3$)
1239	933.6	ν_{as}(CF$_3$) + ν_s(CF$_2$)	1250	209.0	ν_{as}(CF$_3$) + ν_s(CF$_2$)
1230	269.7	ν_{as}(CF$_3$)	1217	244.9	ν_{as}(CF$_3$) + ν_s(CF$_2$)
1207	194.5	ν_{as}(CF$_3$) + ν_{as}(CF$_2$) + ν_{as}(SO$_3$H)	1191	145.4	ν_s(CF$_2$)
1200	209.6	ν_{as}(CF$_2$)	1179	116.1	ν_{as}(CF$_3$) + ν_s(CF$_2$)
1196	61.6	ν_{as}(CF$_2$)	1176	307.9	ν_{as}(CF$_2$)
1187	97.9	δ(SO–H)	1139	119.2	ν_{as}(CF$_2$)
1169	100.7	δ(SO–H)	1124	358.6	ν_{as}(C–O–C) + ν_s(CF$_2$)
1165	94.2	ν_{as}(CF$_2$)	1122	100.6	ν_s(CF$_3$) + ν_s(CF$_2$)
1135	486.3	ν_{as}(C–O–C) + ν_s(CF$_2$)	1110	129.9	ν_{as}(C–O–C) + ν_s(CF$_2$)
1130	201.0	ν_s(CF$_2$)	1063	462.0	ν_s(SO$_3$) + ν_s(CF$_2$)
1110	98.7	ν_{as}(C–O–C) + ν_s(CF$_2$)	1019	17.6	ν(C–S)
1001	94.5	ν_s(CF$_3$)	998	80.0	ν_s(CF$_2$)
974	46.5	ν(C–S)	928	173.4	ν_s(CF$_3$)
828	14.3	ν_s(C–O–C) + ν_s(CF$_2$)	827	1.3	ν_s(C–O–C)
780	11.8	ν_s(C–O–C) + ν_s(CF$_2$)	774	4.3	ν_s(C–O–C) + ν_s(CF$_2$)
804	10.2	ν(C–F) + δ(SO–H)	706	29.7	ν(C–F)
747	18.3	ν(C–F) + (SO$_3$H)str	997	80.0	ν_s(CF$_2$)

not observed in the spectrum of PFEBSA. Several weak bands below 962 cm^{-1} are difficult to assign.

3.2. DFT calculations of IR bands for the MCs

These calculations were performed in order to understand the ATR-FTIR spectra of the three membranes, in particular the absence of the band at 969 cm^{-1} expected for the 3M membrane. Since all experiments were performed on samples containing water (samples were used *as received*), it seems reasonable to also consider in the calculations the ionic forms of the model compounds. Optimized geometries (with the lowest energy) for acidic (−SO$_3$H) and ionic (−SO$_3^-$) forms of PFMHSA, PFEESA, and PFEBSA are shown in Fig. 3. The SO$_3^-$ group in the ionized molecules has $C_{3\upsilon}$ symmetry, as expected. Warren and McQuillan reported the formation of the hydrogen bond in PFEESA between the O–H group and one of the fluorine atoms of the CF$_3$ group, a result that is confirmed in our calculations, see Fig. 3C: the F–H distance is 2.66 Å vs 2.70 Å in Ref. [31]. The formation of an intramolecular hydrogen bond is expected to stabilize the structure [31].

Comparison of the experimental FTIR spectrum with the calculated vibrational modes for PFMHSA, the MC for Nafion, is shown in Fig. 4 and the calculated band assignments are listed in Table 2; the intensity units are discussed in part (a) of the supporting information. Because of the non-localized vibrational modes, the listed assignments are for dominant bands only. All bands are quite well reproduced in the calculated spectra, and the difference between calculated and experimental frequencies is of the order of <5%. As seen in Fig. 4, the major difference between acidic and anionic forms is due to the presence of the sulfonic group. In the calculated spectrum of the acidic form the relatively strong absorption at 1427 cm^{-1} is visible. This mode is not observed in the ionic molecule; instead, a new strong band at 1063 cm^{-1} appears. This band is a combination of the symmetric vibrations of SO$_3^-$ and CF$_2$ groups. Two bands at 986 and 968 cm^{-1} in the experimental spectrum of PFMHSA, previously assigned to C–O–C bridges, are at 974 cm^{-1} for the SO$_3$H form, and at 998 and 1019 cm^{-1} in the SO$_3^-$ form in the calculated spectra. The bands around 1000 cm^{-1} result from the symmetric vibration of the CF$_3$ group in the middle of the MC, and the bands at 974 cm^{-1} in the acidic form and 1019 cm^{-1} in the ionic form are due to the C–S stretching vibrations. Calculated

symmetric vibrations of C–O–C bridges in PFMHSA are represented by very weak modes at ≈830 cm^{-1} and 780 cm^{-1}.

Comparison of the experimental FTIR spectrum with the calculated vibrational modes for PFEESA, the MC for Aquivion, is shown in Fig. 5 and the calculated band assignments are listed in Table 3. The major difference in the calculated spectra of PFEESA is due to the presence of the sulfonic group. In acidic form a relatively strong band due to the SO–H vibration is observed at 1426 cm^{-1}. This band is associated with the non-dissociated sulfonic group and is not observed in the ionic form. In the experimental spectrum this mode is represented by a very weak band at 1407 cm^{-1}. The other band associated with −SO$_3$H vibrations is expected at ≈913 cm^{-1} but is not observed in any experimental spectra. Calculated bands at 1399.3 and 1316.1 cm^{-1} are due to the C–C vibrations and are not visible in FTIR but can be observed in Raman spectra. The spectral range 1300–1100 cm^{-1} is obscured by C–F vibrations. The band at 1235 cm^{-1} is due to the CF$_3$ group symmetric vibrations and cor-
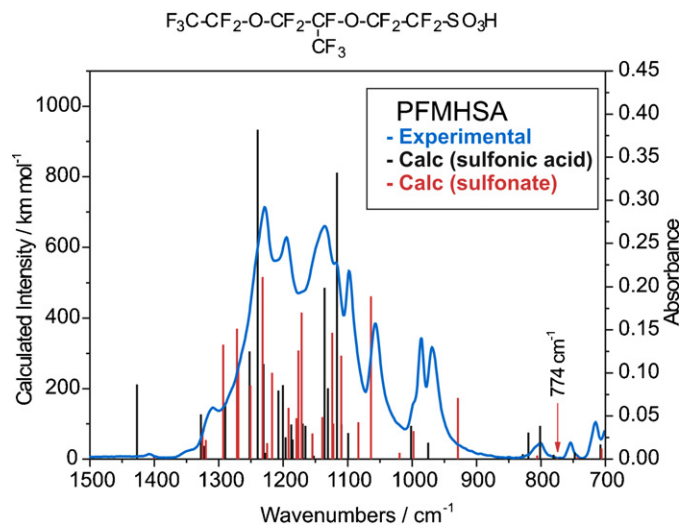

Fig. 4. Experimental and calculated ATR-FTIR spectra of PFMHSA, the model compound for Nafion. Blue line is the experimental spectrum, black bars are calculated modes for the acid form, −SO$_3$H, and red bars are calculated modes for the ionic form, −SO$_3^-$. Experimental data are for the ionic form.

Table 3
Calculated vibrational modes for PFEESA, the model compound for Aquivion.

−SO$_3$H (acidic form)			−SO$_3^-$ (ionic form)		
ν (cm^{-1})	Intensity (km mol^{-1})	Assignment	ν (cm^{-1})	Intensity (km mol^{-1})	Assignment
1426.3	224.2	δ(SO–H)	1404.2	1.3	ν(C–C)
1399.3	19.1	ν(C–C)	1316.4	235.2	ν(C–C)
1316.1	141.3	ν(C–C)	1270.1	273.2	ν_{as}(SO$_3$)
1245.8	302.3	ν_{as}(CF$_3$)	1267.8	334.0	ν_{as}(SO$_3$)
1226.8	286.1	ν_{as}(CF$_3$) + ν_{as}(CF$_2$) + ν_{as}(SO$_3$H)	1234.4	249.9	ν_{as}(CF$_3$)
1216.6	669.0	ν_{as}(CF$_2$)	1224.9	279.8	ν_s(CF$_2$)
1199.6	145.2	ν_{as}(CF$_3$)	1200.1	275.7	ν_{as}(CF$_3$)
1196.1	103.5	ν_{as}(CF$_3$) + ν_{as}(CF$_2$)	1162.4	426.6	ν_{as}(CF$_2$)
1193.7	20.5	ν_{as}(SO$_3$H)	1149.3	150.9	ν_{as}(CF$_2$)
1176.4	38.3	δ(SO–H)	1137.3	149.9	ν_{as}(CF$_2$)
1172.6	4.4	δ(SO–H)	1123.7	292.3	ν_{as}(C O C) + ν_s(CF$_2$)
1138.4	331.8	ν_{as}(C–O–C) + ν_s(CF$_2$)	1115.1	84.9	ν_{as}(CF$_2$)
1107.1	362.2	ν_{as}(CF$_2$)	1068.8	90.2	ν_s(CF$_3$) + ν_s(CF$_2$)
1098.6	71.3	ν_s(CF$_2$) + ν_s(CF$_3$)	1022.5	44.8	ν_s(SO$_3$)
966.0	76.6	ν(C–S)	945.6	76.0	ν_s(C–S)
822.8	17.3	ν_{as}(C–O–C) + ν_s(CF$_2$)	821.9	18.2	ν_s(C–O–C) + ν_s(CF$_2$)
815.7	106.1	ν(C–F) + δ(SO–H)	790.2	18.8	ν_s(CF$_2$) + ν_s(CF$_3$)
791.5	63.7	ν_s(CF$_2$) + ν_s(CF$_3$)	713.1	56.4	ν_s(CF$_2$) + ν_s(CF$_3$)
719.8	35.7	ν_s(CF$_2$) + ν_s(CF$_3$)			

responds to calculated modes at 1245.8 and 1234.4 cm^{-1} in acidic and ionic form, respectively. The band at 1195 cm^{-1} is due to the asymmetric vibration of CF$_2$; in both calculated spectra this band is at 1200 cm^{-1}. The calculated band at 1122.5 cm^{-1} corresponds to the measured band at 1155 cm^{-1} and is associated with asymmetric vibrations of SO$_3^-$. The strong band at 1035 cm^{-1} is due to the asymmetric vibrations of the C–O–C group. In the calculated spectra these modes are coupled with the symmetric vibration of CF$_2$ and appear at 1138.4 cm^{-1} in the acidic form and 1123.7 cm^{-1} in the anionic form. The band at 1098 cm^{-1} can be assigned to asymmetric vibrations of CF$_2$ and corresponds to calculated modes at 1107.1 and 1115.1 cm^{-1} in the acidic and ionic forms, respectively. Similarly to other materials, the band due to the symmetric vibrations of the sulfonate group SO$_3^-$ is at 1057 cm^{-1}. In the calculated spectrum this band is shifted to lower frequency and is located at 1022.5 cm^{-1}. According to literature data, the strong band at 975 cm^{-1} can be assigned to symmetric vibrations of C–O–C bridges. In our calculation this band appears at 966.0 cm^{-1} in the acidic and 945.6 cm^{-1} in the ionic form, and is associated with the

strong ν_s(C–S) vibration. Weak calculated modes of ν_s(C–O–C) at 822.8 cm^{-1} in the acidic form and 821.9 cm^{-1} in the anionic form correspond to a very weak band at 801 cm^{-1} previously assigned to symmetric vibrations of C–S.

The comparison of the experimental ATR-FTIR spectrum and calculated vibrational modes for PFEBSA is shown in Fig. 6, and the corresponding assignments are listed in Table 4. The calculated modes are in good agreement with the experimental spectrum. As for PFMHSA and PFEESA, the major difference between the calculated spectra for the acidic and ionic forms is related to the sulfonic group. In the acidic form of PFEBSA the strong absorption at 1425 cm^{-1} is due to the bending mode of SO–H. In the calculated spectrum for the anionic form this band disappears and the new intense band at 1030 cm^{-1} assigned to the symmetric vibration of SO$_3^-$ is observed. In both forms the bands due to the symmetric vibrations of C–O–C bridges are at ≈820 cm^{-1}. This assignment is confirmed by the ATR-FTIR spectrum of the perfluoroimide acid (PFIA) membrane [32], Fig. 7, where the C–O–C symmetrical mode is represented by a very weak band at 825 cm^{-1}.

To summarize: The calculated backbone C–O–C band is at 827 cm^{-1} for PFMHSA (the MC for Nafion), at 822 cm^{-1} for PFEESA
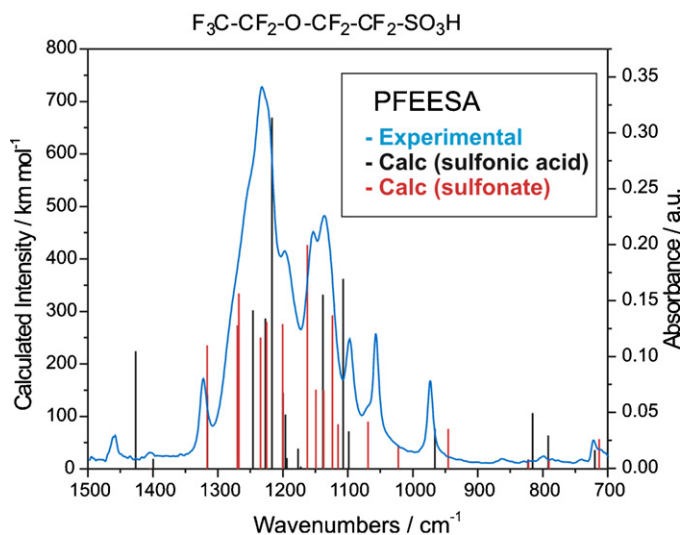

Fig. 5. Experimental and calculated ATR-FTIR spectra of PFEESA, the model compound for Aquivion. Blue line is the experimental spectrum, black bars are calculated modes for the −SO$_3$H form and red bars are calculated modes for the −SO$_3^-$ form. Experimental data are for the ionic form.
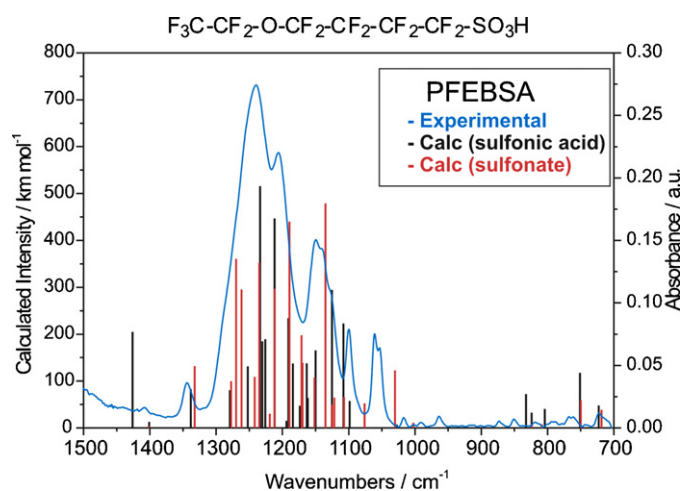

Fig. 6. Experimental and calculated ATR-FTIR spectra of PFEBSA, the model compound for the 3M membrane. Blue line is the experimental spectrum, black bars are calculated modes for the −SO$_3$H form and red bars are calculated modes for the −SO$_3^-$ form. Experimental data are for the ionic form.

Table 4
Calculated vibrational modes for PFEBSA, the model compound for the 3M membrane.

−SO$_3$H (acidic form)			−SO$_3^-$ (ionic form)		
ν (cm^{-1})	Intensity (km mol^{-1})	Assignment	ν (cm^{-1})	Intensity (km mol^{-1})	Assignment
1425	207.4	δ(SO–H)	1402	5.3	ν(C–C)
1401	16.5	ν(C–C)	1335	119.5	ν(C–C)
1331	73.3	ν(C–C)	1278	143.2	ν(CF$_2$) + ν(C–C)
1277	57.7	ν_s(CF$_2$) + ν(C–C)	1269	298.7	ν_{as}(SO$_3$)
1232	554.6	ν_{as}(CF$_3$)	1262	331.4	ν_{as}(SO$_3$)
1231	301.9	ν_{as}(CF$_3$)	1235	297.6	ν_{as}(CF$_3$)
1226	397.1	ν_{as}(CF$_3$) + ν_s(CF$_2$)	1216	425.8	ν_{as}(CF$_3$) + ν_s(CF$_2$)
1207	79.7	ν_{as}(CF$_3$) + ν_{as}(CF$_2$)	1211	114.0	ν_{as}(CF$_3$) + ν_s(CF$_2$)
1197	210.1	ν_{as}(CF$_2$)	1184	230.8	ν_{as}(CF$_2$)
1191	51.6	ν_{as}(CF$_2$) + ν_{as}(SO$_3$)	1183	169.3	ν_{as}(CF$_2$)
1183	45.2	δ(SO–H)	1165	253.2	ν_{as}(CF$_2$)
1169	141.7	ν_{as}(CF$_2$) + δ(SO–H)	1136	532.0	ν_{as}(C–O–C) + ν_s(CF$_2$)
1149	286.9	ν_{as} (CF$_2$)	1084	47.0	ν_s(CF$_3$) + ν_s(CF$_2$)
1123	182.9	ν_{as}(C–O–C) + ν_s(CF$_2$)	1030	129.9	ν_s(SO$_3$) + ν_s (CF$_2$)
1108	259.7	ν_{as}(C–O–C) + ν_s(CF$_2$)	1002	4.5	ν_s(SO$_3$)
1101	57.0	ν_s(CF$_3$) + ν_s (CF$_2$)	824	8.2	ν_s(C–O–C)
832	54.11	ν_s(C–O–C) + ν_s(CF$_2$)	808	10.0	ν(C–F)
826	16.0	ν_s(C–O–C) + ν_s(CF$_2$)	754	53.2	ν(C–F)
804	65.1	ν(C–F) + δ(SO–H)	718	48.0	ν(C–F)
756	127.9	ν(C–F) + (SO$_3$H)str			

(the MC for Aquivion), at 824 cm^{-1} for PFEBSA (the MC for the 3M membrane), and at 827 cm^{-1} for PFIA. The C–O–C group near the tertiary carbon in PFMHSA appears at 774 cm^{-1}, Fig. 4.

The calculated bands for PFEESA in the presence of one water molecule based on the 6-311G(d,p) [31] and on the 6-331G(2d,2p) level of theory used in this study are listed in Table S1, part (b) of supporting information. Both methods reproduce the vibrational modes of PFEESA. However the vibrational frequencies derived from the B3LYP/6-311G(2d,2p) level calculation are slightly higher.

3.3. SO$_3^-$ bands

The ATR-FTIR spectra of Nafion and Aquivion membranes presented here are in good agreement with literature data. In all membranes the region of 1300–1100 cm^{-1} is dominated by the C–F vibration. The band at around ≈1060 cm^{-1} observed in all membranes and in the MCs is assigned to the symmetric stretching mode of SO$_3^-$ [28–30]. This assignment is supported by the DFT calculations for the MCs: The symmetric mode of the SO$_3^-$ group are at

1063 and 1030 cm^{-1} for PFMHSA (Table 2) and PFEBSA (Table 4), respectively, and are combined with CF$_2$ symmetric vibrations. For PFEESA this mode is at 1022.5 cm^{-1} (not mixed with CF$_2$). DFT data for the MCs show that the SO$_3^-$ group has $C_{3\upsilon}$ symmetry, as seen in Fig. 3, in agreement with literature data [33]. All S–O bonds lengths in this group are 1.46 Å and the O–S–O angles are 115.8°.

The asymmetric SO$_3^-$ mode is expected around ≈1300 cm^{-1}, a region obscured by the strong C–F absorption; this band is observed as a shoulder at 1280 cm^{-1} in the MCs. Based on the theoretical calculations, this band is located at ≈1270 cm^{-1} in the MCs, in good agreement with the experimental value.

3.4. FTIR spectra of the 3M membrane

The most striking results were obtained for 3M membrane. As seen in Fig. 2A, the bands at 986 and 968 cm^{-1} are not observed in the ATR-FTIR spectrum of the 3M membrane. This result was verified with the PFEBSA model compound (Fig. 2B), which mimics the 3M membrane side chain. Cable et al. assigned these modes to the ether C–O–C linkage, based on comparing ATR-FTIR spectra of Nafion and Dow (here Aquivion) membranes. The higher frequency 986 cm^{-1} band was attributed C–O–C linkage at the backbone chain, while the lower frequency 968 cm^{-1} was assigned due to the C–O–C bond in the side chain of Nafion membrane. The low frequency band is also seen in the Aquivion membrane, and the slight shift of this peak to lower wavenumbers was explained by the proximity of the –SO$_3$H group and its electron withdrawing character [16].

In our DFT calculations for the acidic form of PFMHSA, the calculated frequency 998 cm^{-1} (the symmetric stretching mode of CF$_2$) corresponds to the measured band at 986 cm^{-1}. The calculated mode at 928 cm^{-1} (the symmetric vibration of CF$_3$) corresponds to the measured band at 968 cm^{-1}. In the calculated spectrum for PFEESA and PFEBSA, which have no –CF$_3$ group in the middle of the side chain, this band is not observed.

Most importantly, the calculated C–O–C band at the backbone is at 827 cm^{-1} for PFMHSA (the MC for Nafion), at 822 cm^{-1} for PFEESA (the MC for Aquivion), at 824 cm^{-1} for PFEBSA (the MC for the 3M membrane), and at 827 cm^{-1} for the PFIA. Taken together, these results imply that the data for the 3M membrane and corresponding MC PFEBSA require a reassignment of the Nafion and Aquivion (or Dow) membranes bands at 986 and 968 cm^{-1}.
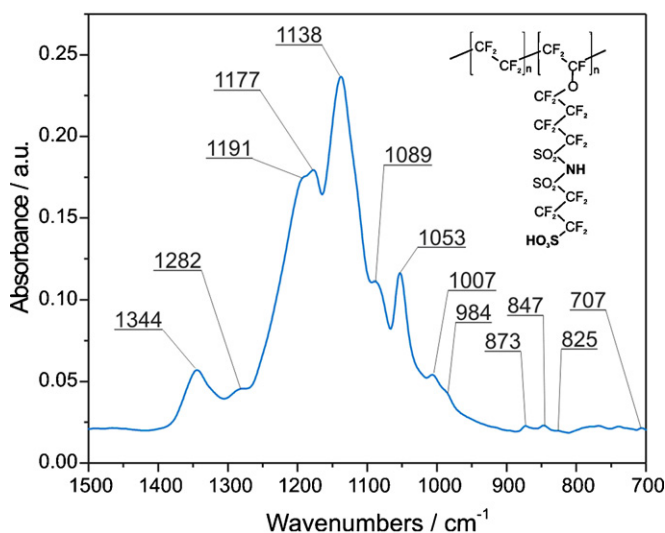

Fig. 7. ATR-FTIR spectrum of the perfluoroimide acid (PFIA) membrane in the 1500–700 cm^{-1} range.

We note that alternative assignments of the 986 and 968 cm^{-1} bands in Nafion and Dow (or Aquivion) membranes have been discussed in the literature: Ostrowska and Narewska have assigned the 986 cm^{-1} band to the −CF$_2$CF(CF$_3$)− group [28,29]. Tang et al. assigned this band to the C−F vibration in CF$_3$ groups [34], in agreement with Pacansky et al. in their study of Krytox [35]. Some questions related to the assignments of the 986 and 968 cm^{-1} bands were also raised in theoretical studies. In all cases there is an agreement in the assignment on the C−F vibrations; however, there are discrepancies in the assignments of the symmetric C−O−C vibrations and SO$_3^-$ vibrations. Using the B3LYP/6-31++G(d,p) theory level, Okamoto assigned the 989 and 1060 cm^{-1} bands to the symmetric vibrations of SO$_3^-$ and asymmetric stretching of C−O−C, respectively. The lower frequency band, at 968 cm^{-1}, was assigned to the vibration of the −CF$_3$ group in the middle of the Nafion side chain [36], *in line with our findings*. This assignment of the 989 and 1060 cm^{-1} bands is reversed compared to available literature data, where the 1060 cm^{-1} mode is assigned to the sulfonic group. The assignment of the 968 cm^{-1} mode to vibrations of the −CF$_3$ group located in the middle of the side chain of Nafion is in agreement with early literature data [35].

Warren and McQuillan used DFT at the B3LYP/6-311G+(d,p) level for perfluoro(2-ethoxyethane)sulfonic acid (PFEESA, named PES in their paper), assigned the 971 cm^{-1} mode to the C−S stretching vibration in the acidic form, and observed the disappearance of this band in the dissociated form [31]. In agreement with our results, the symmetric stretching modes of the C−O−C group were assigned to the calculated band at ≈820 cm^{-1}.

Based on calculations at the X3LYP/6-311++(d,p) level, Webber et al. suggested that the 1060 cm^{-1} band is dominated by C−O−C vibrations while SO$_3^-$ is a major contributor to modes at 983 and 970 cm^{-1} [26].

In summary, the FTIR study of the ionomer membranes and of the corresponding MCs, together with the DFT calculations of the MCs, have provided the necessary information for a fingerprint region assignment that includes the *three* perfluorinated membranes. The crucial role was played by the FTIR spectra of the 3M membrane and the corresponding MC, PFEBSA. This study also led to additional confidence in the assignment of the band at ≈1060 cm^{-1} to the SO$_3^-$ group.

4. Conclusions

We presented an ATR-FTIR study of three major perfluorinated ionomers that are used as proton exchange membranes in fuel cells (FCs) and that differ in the structure of the side chains: Nafion, Aquivion and 3M. The following low-molecular-weight model compounds (MCs) that mimic the membrane side chains were essential for FTIR band assignment: perfluoro(3-methyl-2,4-dioxahexane)sulfonic acid (PFMHSA) for Nafion, perfluoro(2-ethoxyethane)sulfonic acid (PFEESA) for Aquivion, and perfluoro(2-ethoxybutane)sulfonic acid (PFEBSA) for the 3M membrane.

The major goal was to identify spectral bands that can be used for recognizing the specific bonds involved in the membrane fragmentation process. The focus was on the IR signals from the C−O−C bonds, which were assigned in some papers for Nafion and Dow/Aquivion membranes; our ATR-FTIR results for the 3M membranes did not conform to these assignments. DFT calculations of the vibrational frequencies for the MCs were essential for an understanding of the fingerprint FTIR region.

Taken together, the ATR-FTIR spectra of the membranes and of the model compounds and the DFT calculations led to an understanding of the fingerprint region of all three membranes, and to a re-examination and re-assignment of results for Nafion and Aquivion membranes in the existing literature. The low intensity of the spectral bands for the ether link connected to the backbone (for all membranes) and also in the side chain (for Nafion) suggests that these bands cannot be used for the determination of the extent of degradation. A preferable quantitative approach for the determination of the extent of degradation could be based on the sulfonic group absorption, which appears at ≈1060 cm^{-1} in the three membranes.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2011.05.067.

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