



Preparation and characterization of PVdF nanofiber ion exchange membrane for the PEMFC application

Won Gi Jang, Jian Hou, Hong sik Byun*

*Department of Chemical Engineering, Keimyung University, Daegu, Republic of Korea
Email: hsbyun@kmu.ac.kr*

Received 3 September 2010; Accepted 3 January 2011

ABSTRACT

This paper reports the preparation and characterization of polyvinylidene fluoride (PVdF) nanofiber ion exchange membrane for the application in polymer electrolyte membrane fuel cells (PEMFC). The composite membrane of PS/PVdF was prepared by using the electrospinning method with PVdF solution in a mixed solvent of DMAc and acetone by pore-filling with a mixture of styrene and PS using DVB as cross-linking reagent. Ion exchange membrane (SPS/PVdF) was then manufactured by introducing sulfonate ($-\text{SO}_3\text{H}$) groups using sul-furic acid on the prepared PS/PVdF membranes. The modified membranes were characterized by fourier transform infrared (FTIR), scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), water uptake, ion exchange capacity (IEC), electrical conductivity and membrane & electrode assembly (MEA). By controlling the content of PS, characteristics comparable to Nafion which has water uptake, IEC and electrical conductivity values suited for the application in PEMFC could be observed in modified membranes. In particular, not only water uptake values (90–550%) were much higher than that of Nafion 115, but also IEC values were more than double the values of Nafion 115. As of the results of electrical conductivity measurements and MEA tests, SPS/PVdF membranes showed the possibility of being an alternative membrane for Nafion 115 due to their improved properties.

Keywords: PEMFC; Nanofiber; PVdF; Pore-filling; PS; DVB; Electrospinning

1. Introduction

PEMFC has recently become popular as a power source for cars and electric components because of good characteristics of energy conversion and power density [1,2]. The requirements for the polymer electrolyte membrane which is one of the major parts in PEMFC are high proton conductivity, chemical stability and good mechanical strength. It has been known that Nafion, a perfluorinated membrane used for PEMFC, satisfies those requirements. However, Nafion shows

several drawbacks such as decrease of electric conductivity and efficiency of catalyst after using for a long time and a high price when it is used for PEMFC [3–5]. Many studies have focused on the development of new membranes such as hydrocarbon polymer electrolyte membranes [6,7], modification of a perfluorinated polymer [8], a surface modification between electrode and membrane and the preparation of a composite membrane with hydrocarbon polymer and PVdF having the good mechanical properties and thermal stability [9–11].

This study is focused on the research regarding ion exchange membranes for the application in PEMFC. The porous and thin substrate was manufactured by

*Corresponding author.

electrospinning method using PVdF having good mechanical and thermal stability. In order to improve the capacity of the membrane, the PS/PVdF membranes were prepared by pore-filling and the SPS/PVdF membranes were then manufactured by introducing sulfonate ($-\text{SO}_3\text{H}$) groups using sulfuric acid. In the end, possibility of the application in PEMFC was discussed.

2. Experiments

2.1. Materials

Materials used to manufacture the polymer nanofibers were PVdF powder (Arkema, Kynar 761), acetone (>99.5%) and DMAc (N,N-Dimethylacetamide, >99%) purchased from DUKSAN PURE CHEMICALS CO., Ltd. Materials used to manufacture the pore-filling solution were polystyrene PS ($M_w = 280,000$), styrene monomer and DVB (Divinylbenzene) after elimination of the polymerization inhibitors and NMP (N-Methyl-2-pyrrolidone, >99%) and BPO (Benzoyl peroxide, Lancaster, 97% (dry wt.)) purchased from Aldrich. In order to introduce sulfonate groups ($-\text{SO}_3\text{H}$) into PS/PVdF membranes, sulfuric acid (H_2SO_4 , DUKSAN, >96%) was used.

2.2. Preparation of PVdF nanofiber substrate membranes

The PVdF nanofiber substrate membranes were prepared by the electrospinning method [12], after the electrospinning solution had been prepared by mixing PVdF powder (wt. 19%) with DMAc (wt. 24.3%) and acetone (wt. 56.7%) as solvent. After then the prepared solution was filled into a 5 ml syringe with a 22 gauge needle. The syringe was positioned vertically for 30 min or more so that bubbles might be allowed to rise. By pushing the end of the syringe, the air was completely removed. The ejection speed was controlled by using KDS100 (KD Scientific Inc.) and the voltage supply equipment used was a CPS 60K02VIT (CHUNGPA EMT co., Ltd.). The electrospinning conditions were as following: flow rate 0.5 ml/h, voltage 10 kV, TCD (tip to collector distance) 10 cm, duration 3 h.

2.3. Preparation of PS/PVdF composite membranes

The pore-filling solution was prepared by mixing PS and the refined styrene monomers, DVB, BPO with NMP as the solvent. The composition of the pore-filling solution is indicated in Table 1. This solution was dispersed evenly on the PVdF substrate membranes using a Teflon roller. In order to polymerize the styrene monomers dispersed on the membranes, they were heated in the an oven at 110° for 20 h and at 130° for 2 h. After this,

Table 1
Composition of the pore-filling solutions

Styrene (wt. %)	DVB (wt. %)	Polystyrene (wt. %)	NMP (wt. %)	BPO (wt. %)
55.38	2.40	10	31.72	0.5
52.29	2.27	15	29.94	0.5
46.1	2	25	26.4	0.5

the membranes were cleaned using ethanol and in order to eliminate remaining solvents, they were dried in the oven at 100° for at least a day.

2.4. Preparation of SPS/PVdF ion exchange membranes

The manufactured PS/PVdF membranes were sulfonated with sulfuric acid (wt. 98%) for at least a day until the sulfonate groups were completely introduced into the membranes [12–15]. At the beginning, some problems occurred related to the cleaning of the sulfonated membranes. In case that those were directly dropped into distilled water or the experiment was conducted at low temperature, destruction of pores and cracking of the surface were generated because of the heat of dilution and the osmotic pressure effect. The sulfonated membranes were cleaned using a gradual reduction of the concentration of the solution and in the end, they were cleaned in distilled water for at least a day and all experiments were conducted at 80° .

2.5. Analysis of the structure and surface of the SPS/PVdF ion exchange membranes

FTIR (JASCO, FT/IR–620) was used to detect sulfonate groups ($-\text{SO}_3\text{H}$) in the network. SEM and EDS (Hitachi, S-480) were used both to observe the surface and to compare it to that of the PVdF membrane.

2.6. Water uptake measurement

SPS/PVdF membranes were wetted in distilled water at room temperature for about a day. After the membranes were picked up with tongs, wiped with tissue to remove water on the surface and then the wet membrane weight (W_1) was measured. To determine the dry membrane's weight (W_2), the wet membranes were dried in the oven at 100° for a day and then W_2 was measured. The average water uptake values were determined by repeatedly six times conducting all the procedures mentioned above. Water uptake was determined according to the following Eq. (1) [15].

$$\text{water uptake \%} = \frac{w_1 - w_2}{w_2} \times 100\% \quad (1)$$

2.7. IEC (Ion exchange capacity) and electrical conductivity measurements

The sulfonated membranes were placed in 1N HCl solution for about 12 h to replace Na⁺ by H⁺. After the membranes had dried in the oven they were weighed, placed in 0.5N NaCl solution for about 12 h and the proton content was then determined by titration with 0.01N NaOH solution using phenolphthalein as the indicator. The IEC was calculated as following Eq. (2).

$$\text{IEC}(\text{meq} / \text{g}) = \frac{C_{\text{NaOH}}(\text{meq} / \text{l}) \times V_{\text{NaOH}}(\text{l})}{W_{\text{dry}}(\text{g})} \quad (2)$$

The surface resistance was measured using four point probe arranged at intervals of 1 mm. By using this probe, the values of resistances (ohm) were calculated as measuring currents (*I*) and voltages (*V*) after then the value of surface resistance (ohm/sq) was measured by adjusting to calibration constant (C.F). The factors of calibration constants (C.F) are sample size (*cf1*), thickness (*cf2*) and temperature (*cf3*). The sample size constant is 4.532 where the size is over 40 mm and the thickness constant is close by 1 where the thickness is under 400 μm and the temperature constant is close by 1 where temperature is about 23°. After drying the 4 cm × 4 cm samples in the vacuum oven the electrical conductivity data was obtained from repeatedly six times conducting surface resistance measurements (AIT Co., Ltd., CMT-SR100N).

$$\begin{aligned} V / I &= \text{ohm} \\ \text{ohm} \times \text{C.F} &= \text{ohm} / \text{sq} \\ \text{C.F} &= cf1 \times cf2 \times cf3 \end{aligned} \quad (3)$$

2.8. Membrane electrode assembly (MEA) measurement

In order to confirm the actual application for PEMFC, MEA tests were performed. The MEA is produced according to the following procedures. The catalyst material is first prepared in liquid “ink” form by thoroughly mixing of catalyst (a powder of Pt dispersed on carbon) and a solution of the membrane material dissolved in alcohols. Once the ink is prepared, it is applied to the surface of the solid membrane. That method involves painting the catalyst “ink” directly onto a dry, solid piece of membrane. The wet catalyst layer and the membrane are heated until the catalyst layer is dry. The membrane is then turned over and the procedure is repeated on the other side. The dry MEA is next rehydrated by immersing in lightly boiling dilute acid solution to also ensure that the membrane is in the H⁺ form needed for fuel cell operation. The final step is a thorough rinsing in distilled water.

The MEA used in this study was assembled in accordance with Fuel Cell Power’s (Korean company) producing process, which was the company’s confidential method. The experiment conditions were as follows: the full humidity, operating temperature of 60°, ambient pressure and the active area of 25 cm².

3. Results and discussion

3.1. Analysis of the structure and surface of SPS/PVdF membranes

In order to confirm the existence of sulfonate groups and the composition of the SPS/PVdF membranes manufactured in the sulfonation process, FTIR and EDS tests were performed and the results are shown in Fig. 1 and Fig. 2. According to the FTIR spectra, the observed structures were similar regardless of the concentration of PS. The existence of sulfonate groups (–SO₃–) which cause the ion conductivity was confirmed in the SPS/PVdF membranes because the sulfonate groups were shown in 1040⁻¹ and 1120 cm⁻¹ peaks. The existence of sulfonate groups could be also confirmed by detecting sulfur atoms in the EDS spectra.

The micrographs of the top surfaces of PVdF and SPS/PVdF membranes are shown in Fig. 3. The thickness of the manufactured membranes was 40–50 micron, the pore size was 0.5 micron. So the thickness was smaller than that of Nafion. On the SEM images, it can clearly be seen that the PVdF membranes formed a porous structure whereas the sulfonated SPS/PVdF membranes formed a filled structure. This situation was regularly observed regardless of the composition of styrene and DVB.

3.2. Water uptake measurements

Water uptake is an important factor which affects the swelling effects and flexibility of the membrane and

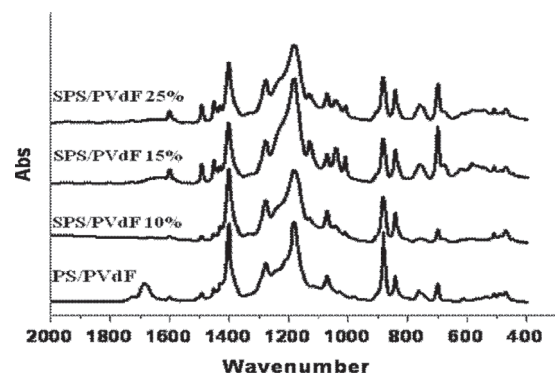


Fig. 1. ATR-FTIR spectra of PS/PVdF and SPS/PVdF membranes.

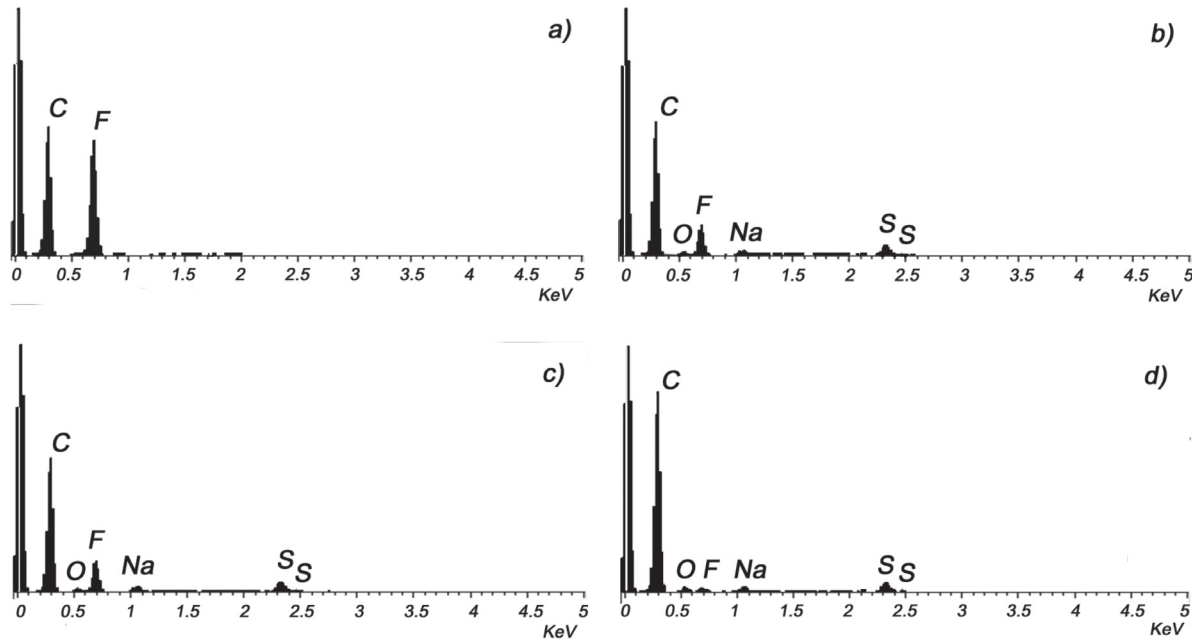


Fig. 2. EDS Spectra: (a) PS/PVdF (b) SPS/PVdF (PS 10%) (b) SPS/PVdF (PS 15%) (c) SPS/PVdF (PS 25%).

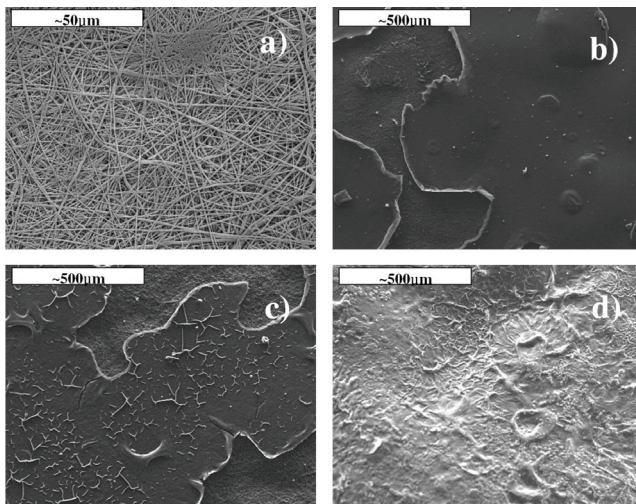


Fig. 3. SEM micrographs of the top surface of PVdF and SPS/PVdF composite membranes; (a) PVdF membrane (b) SPS/PVdF (PS 10%) (c) SPS/PVdF (PS 15%) (d) SPS/PVdF (PS 25%).

proton conductivity while PEMFC is operated. Water uptake data of Nafion and SPS/PVdF membranes are shown in Fig. 4. In the SPS/PVdF membranes, the water uptake increased with increasing content of PS. And it can clearly be seen that all obtained values for water uptake of SPS/PVdF membranes were higher than that of Nafion (17.19%). The highest water uptake (550%) was achieved when the amount of PS was 25%.

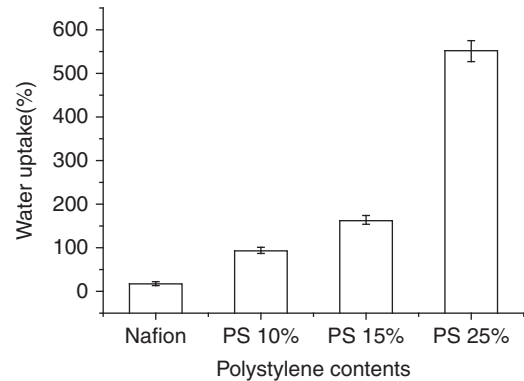


Fig. 4. Water uptake of SPS/PVdF membranes with varied PS content and of Nafion.

3.3. IEC and Electrical conductivity measurements

The IEC values of Nafion in comparison to the manufactured SPS/PVdF membranes are shown in Fig. 5 (a). The higher the amount of PS, the more the IEC values increased, but the results remained constant for concentrations of more than 15 weight percent of PS. However, in this test, the IEC values of the prepared membranes were higher than that of Nafion. Similarly to the results of the water uptake test, the number of sulfonate groups that were introduced into the membranes increased along with increasing amount of PS.

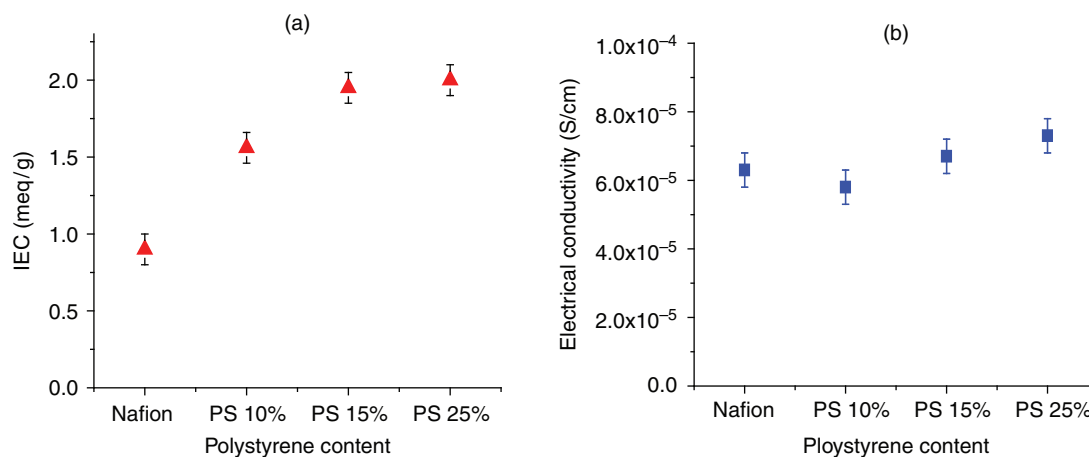


Fig. 5. (a) IEC of SPS/PVdF membranes with varied PS content and of Nafion (b) Electric conductivity of SPS/PVdF membranes with varied PS content and of Nafion.

The electrical conductivity of Nafion and the manufactured SPS/PVdF membranes is shown in Fig. 5 (b). The results corresponded with the IEC values and the values for the SPS/PVdF membranes were similar to that of Nafion or even higher. It can be expected that the manufactured SPS/PVdF membranes has a possibility of an alternative membrane for Nafion.

3.4. MEA test

In order to confirm the possibility of the application in PEMFC due to the positive results of the previous tests, MEA test was performed. The results are shown in Fig. 6.

Because of the results of IEC and electrical conductivity measurements, it was expected that the

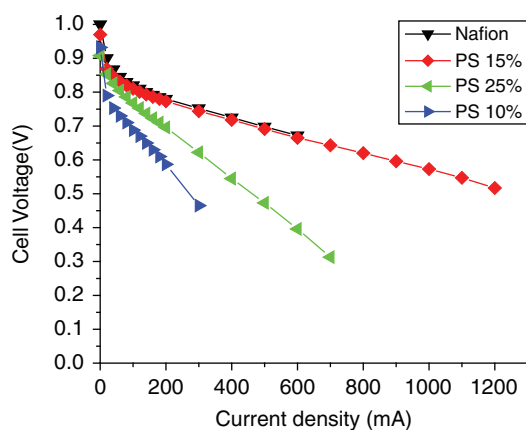


Fig. 6. MEA tests of SPS/PVdF membranes and Nafion.

MEA values of the modified membranes would be higher than those of Nafion, but actual MEA values were lower. For the SPS/PVdF membranes pore-filled with 15 wt. % PS the results were almost similar to that of Nafion. This situation was explained by the microvoid effects [16] which were generated in the manufacturing procedures. Therefore, complementary studies are required to commercialize the SPS/PVdF membranes.

4. Conclusions

In this study, PVdF nanofibers were prepared by using the electrospinning method. In order to improve the capacity performance of the membrane, the PS/PVdF membranes were prepared by pore-filling and the SPS/PVdF membranes were then manufactured successfully by introducing sulfonate ($-\text{SO}_3\text{H}$) groups using sulfuric acid. Sulfonate groups in the network could be confirmed through EDS, FTIR and SEM. By controlling the concentration of PS, characteristics comparable to Nafion which has water uptake, IEC and electrical conductivity values suited for PEMFC application could be observed in modified membranes. In particular, not only water uptake values (90–550%) were much higher than that of Nafion 115, but also IEC values were more than double that of Nafion 115. In MEA tests, for the SPS/PVdF membranes pore-filled with 15 wt. % PS, the results were almost similar to those of Nafion. If drawbacks such as the microvoid effects can be solved, modified SPS/PVdF membranes will be able to be an alternative material for Nafion.

References

- [1] K. Sopian and W.R. Wan Daud, Challenges and future developments in proton exchange membrane fuel cells, *Renewable Energy*, 31 (2006) 719–727.
- [2] S.M.J. Zaidi, S.D. Mikhailenko, G.P. Robertson, M.D. Guiver and S. Kaliaguine, Proton conducting composite membranes from polyether ether ketone and heteropolyacids for fuel cell applications, *J. Membr. Sci.*, 173 (2000) 17–34.
- [3] P. Costamagna and S. Srinivasan, Quantum jumps in the PEMFC science and technology from the 1960s to the year 2000: Part I. Fundamental scientific aspects, *J. Power Sources*, 102 (2002) 242–252.
- [4] P. Staiti, F. Lufrano F. Lufrano, A.S. Aricò, E. Passalacqua and V. Antonucci, Sulfonated polybenzimidazole membranes-preparation and physic chemical characterization, *J. Membr. Sci.*, 188 (2001) 71–78.
- [5] A. Schechter and R.F. Savinell, Imidazole and 1-methyl imidazole in phosphoric acid doped polybenzimidazole, electrolyte for fuel cells, *Solid State Ionics*, 147 (2002) 181–187.
- [6] M. Rikukawa and K. Sanui, Prog. Proton-conducting polymer electrolyte membranes based on hydrocarbon polymers, *Polym. Sci.*, 25 (2000) 1463–1502.
- [7] Q. Li, R. He, J.O. Jensen and N.J. Bjerrum, Approaches and Recent Development of Polymer Electrolyte Membranes for Fuel Cells Operating above 100°, *Chem. Mater.*, 15 (2003) 4896–4915.
- [8] K. Lunkwitz, U. Lappan and U. Scheler, Modification of perfluorinated polymers by high-energy irradiation, *J. Fluor. Chem.*, 125 (2004) 863–873.
- [9] C. Hasiotis, V. Deimede and C. Kontoyannis, New polymer electrolytes based on blends of sulfonated polysulfones with polybenzimidazole, *Electrochimia Acta*, 46 (2001) 2401–2406.
- [10] A.H.C. Sirk, J.M. Hill, S.K.Y. Kung and V.I. Birss, Effect of Redox State of PtRu Electrocatalysts on Methanol Oxidation Activity, *J. Phys. Chem. B*, 108 (2004) 689–695.
- [11] S. Haufe and U. Stimming, Proton conducting membranes based on electrolyte filled microporous matrices, *J. Membr. Sci.*, 185 (2001) 95–103.
- [12] S. Ramakrishna, K. Fujihara, W.E. Teo, T. Yong, Z. Ma and R. Ramaseshan, Electronpun nanofibers: solving global issues, *Mater. Today*, 9 (2006) 40–50.
- [13] N. Chanunpanich, B. Lee and H. Byun, Macromolecular Research, A study of electrospun PVDF on PET sheet, 3 (2008) 212–217.
- [14] J.P. Shin, B.J. Chang, J.H. Kim, S.B. Lee and D.H. Suh, Sulfonated polystyrene/PTFE composite membranes, *J. Membr. Sci.*, 251 (2005) 247–254.
- [15] S. Xue and G.P. Yin, Proton exchange membranes based on poly(vinylidene fluoride) and sulfonated poly(ether ether ketone), *Polymer*, 47 (2006) 5044–5049.
- [16] L. Du and S.C. Jana, Hygrothermal effects on properties of highly conductive epoxy/graphite composites for applications as bipolar plates, *J. Power Sources*, 182 (2008) 223–229.