New Sulfonated Pentablock Copolymer Membranes and Modified Gas Diffusion Layers for the Improvement of Water Splitting Processes

S. Filice ¹, G. Urzì ², R.G. Milazzo ¹, S. Privitera ¹, S.A. Lombardo ¹, G. Compagnini ² and S. Scalese ^{1,*}

- ¹ CNR-IMM, Zona Industriale Strada VIII n.5, I-95121 Catania, Italy; simona.filice@imm.cnr.it (S.F.); gabriella.milazzo@imm.cnr.it (R.G.M.); stefania.privitera@imm.cnr.it (S.M.S.P.); salvatore.lombardo@imm.cnr.it (S.A.L.)
- ² Dipartimento di Scienze Chimiche, Università degli Studi di Catania, Viale A. Doria n.6, I-95125 Catania, Italy; giulia.urzi15@outlook.it (G.U.); gcompagnini@unict.it (G.C.)
- * Correspondence: silvia.scalese@imm.cnr.it

Supporting Information:

FT-IR Analysis

FT-IR spectra of the two polymers are reported in Figure S1. For Nafion[®], there is a peak at 1056 cm⁻¹ due to SO₃⁻⁻ symmetric stretching and peaks at 1147 and 1203 cm⁻¹ due to an overlapping of the signals of asymmetric SO₃⁻⁻ stretching and CF₂ stretching. Peaks at 982 and 970 cm⁻¹ are due to C-O-C symmetric stretching [1].

For the Nexar polymer, the IR spectrum shows absorptions at 1033 cm⁻¹ and 1124 cm⁻¹ resulting from the symmetric and antisymmetric stretching vibration of SO₃H groups, respectively. In particular, the absorption at 1124 cm⁻¹ was demonstrated to be dependent on the amount of sulfonilic groups [2,3]. Similarly to Nafion, the absorption at 1169 and 1200 cm⁻¹ of Nexar can be attributed to asymmetric stretching of SO₂ in the sulfonilic groups. The shifts of these peaks between the two polymers are due to the different environment of the SO₃⁻ functionalization, i.e., the shifts to lower wavelengths for Nexar are due to a more rigid structure of the polymer, thus requiring higher energy to induce the vibrations. Furthermore, for Nexar, three other absorption peaks at 2858, 2924, and 2958 cm⁻¹ are observed and ascribed to asymmetric and symmetric CH stretching [2,3].

The absorptions at 1645 cm⁻¹ and in the region between 3000 and 3600 cm⁻¹, observed for both the polymers, are due to water molecules inside the polymer. Using a model consisting of solvated $H_5O_{2^+}$ ions, Buzzoni et al. interpreted the band at 1650 cm⁻¹ as resulting from bending vibrations of water molecules of the solvation sphere around the protonated species $H_{2n+1}O_{n^+}$ [4]. This peak is absent for dry polymers (not shown here).

The relative intensity of the peak related to the symmetric stretching of SO₃⁻ (at 1033 and 1056 cm⁻¹ for Nexar and Nafion, respectively) with respect to the peaks related to water molecules (1645 cm⁻¹ and the region 3000–3600 cm⁻¹) is higher for the Nexar polymer than for Nafion, in agreement with the difference between the λ values (the calculated amount of water molecules for each sulfonilic group) reported in Table 1.



Figure S1. FT-IR spectra of Nafion and Nexar polymers.

SEM/EDX Analysis

SEM analysis with chemical mapping performed by energy dispersive X-ray analysis on pristine GDL, GDLs covered by TiO₂, Pt (after water splitting test), TiO₂ + Nafion layer, and Pt + Nafion layer are reported in Figures S2, S3, S4, S5, and S6, respectively.



Figure S2. (a) SEM image of the pristine GDL. (b) C and F elemental maps acquired in the box in (a).



Figure S3. (a) SEM image of GDL covered by Titanium dioxide. (b) Element maps acquired in the box of (a).



C K series



Pt M series



F k series



Figure S4. (a) SEM image of GDL covered by Platinum after water splitting tests and (b) the corresponding elemental maps.



Figure S5. SEM images of a detail of GDL covered by TiO₂ and Nafion showing one of the rare regions where Nafion was not uniform, leaving uncovered the fibers below. The elemental maps are also reported.



Figure S6. SEM image and the element maps of GDL covered by Platinum and Nafion.

References

- Adjemian K.T.; Lee S.J.; Srinivasan S.; Benziger J.; Bocarsly A.B. Silicon Oxide Nafion Composite Membranes for Proton-Exchange Membrane Fuel Cell Operation at 80–140 °C. *J. of the Electrochem. Soc.* 2002, 149, A256–A261.
- Truong P.V.; Shingleton S.; Kammoun M.; Black R.L.; Charendoff M.; Willis C.; Ardebili H.; Stein G.E. Structure and Properties of Sulfonated Pentablock Terpolymer Films as a Function of Wet-Dry Cycles. *Macromol.* 2018, *51*, 2203–2215.
- 3. Fan Y.; Cornelius C. Raman Spectroscopic and Gas Transport Study of a Pentablock Ionomer Complexed with Metal Ions and its Relationship to Physical Properties. *J. of Mater. Sci.* **2013**, *48*, 1153–1161.
- 4. Ludvigsson M.; Lindgren J.; Tegenfeldt J. FTIR Study of Water in Cast Nafion Films. *Electrochim. Acta* **2000**, 45, 2267–2271.