High-performance membranes with full pH-stability

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Figure S1. EDX mapping (C, O, F, S) of PVDF-g-PSSA-3 top view.



Figure S2. EDX mapping (C, O, F, S) of PVDF-g-PSSA-3 cross-section.



Figure S3. ATR-FTIR spectra of PVDF, PVDF-PSSA-1 and PVDF-PSSA-3 (both prior to sulfonation).

Sample	At% C	At% F	At% S	At% O	At% N	At% Ca	At% Na	At% Si	At% Al	At% Cl
PVDF	64.20 ± 0.23	21.46 ± 0.13	0.41 ± 0.04	9.90 ± 0.15	3.34 ± 0.18	0.24 ± 0.03	/	0.45 ± 0.13	/	/
PVDF-g- PSSA-1	62.56 ± 0.19	14.47 ± 0.12	1.09 ± 0.04	16.34 ± 0.12	3.80 ± 0.16	0.17 ± 0.03	/	0.32 ± 0.05	1.12 ± 0.08	0.19 ± 0.03
PVDF-g- PSSA-2	65.83 ± 0.18	14.87 ± 0.10	2.56 ± 0.04	13.89 ± 0.13	2.22 ± 0.16	0.22 ± 0.03	0.41 ± 0.04	/	/	/
PVDF-g- PSSA-3	64.18 ± 0.20	18.25 ± 0.10	1.87 ± 0.04	12.96 ± 0.12	2.44 ± 0.16	0.15 ± 0.03	/	/	0.16 ± 0.13	/

Table S1. Surface composition of different membranes as determined by XPS. Values in grey are due to sample contamination.

The origin of the different contaminating species is explained as follows. Calcium, sodium and chlorine contamination can come from the various treatments with demi-water to which the membranes were subjected. The presence of silicon can be explained by the use of a silicon grease to ensure the vacuum during the XPS measurements. The origin of aluminum remains unclear. The nitrogen presence can be attributed to residual N-methyl-2-pyrrolidone, left in the membranes from the casting solvent or from remnants of the initiator (ammoniumpersulfate). Although sulfur is also present in the pristine PVDF membrane, this value is much lower than that seen in the grafted and sulfonated samples. The sulfur 2p signal (Fig. S3) shows that there is a single sulfur environment at a binding energy of 168.2 eV, which is consistent with high oxidation state sulfur, such as sulfate or sulfonic acid, similar to that indicated for the PSSA products (Fig. S4 to S6).^{1,2} Finally, the presence of oxygen in the pristine membrane can have different origins: (1) sulfate groups, (2) silicone grease, (3) NMP or (4) oxidation under air of the carbon framework.³





Figure S4. XPS spectra of pristine PVDF: (a) wide scan, (b) C 1s, (c) F 1s, (d) O 1s, (e) S 2p.





Figure S5. XPS spectra of pristine PVDF-g-PSSA-1: (a) wide scan, (b) C 1s, (c) F 1s, (d) O 1s, (e) S 2p.





Figure S6. XPS spectra of pristine PVDF-g-PSSA-2: (a) wide scan, (b) C 1s, (c) F 1s, (d) O 1s, (e) S 2p.





Figure S7. XPS spectra of pristine PVDF-g-PSSA-3: (a) wide scan, (b) C 1s, (c) F 1s, (d) O 1s, (e) S 2p.



Figure S8. Cross-section SEM images before and after pH-treatment for (a) pristine PVDF membrane and (b) PVDF-g-PSSA-3 membrane.

References

- P. Louette, F. Bodino and J.-J. Pireaux, *Surf. Sci. Spectra*, 2005, **12**, 127–132.
- 2 M. M. Nasef and H. Saidi, *Appl. Surf. Sci.*, 2006, **252**, 3073–3084.
- 3 N. Fairley, Lorentzian Asymmetric Lineshape.