



Synthesis of novel ion-conducting materials for fuel cell application

Nodar Dumbadze

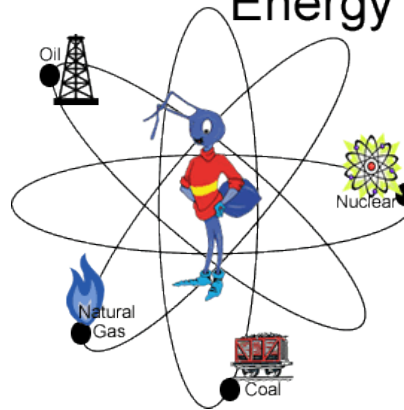
Agricultural University of Georgia

Institute of Chemistry and Molecular Engineering

Introduction



Non-Renewable Energy



Introduction



Fuel cells

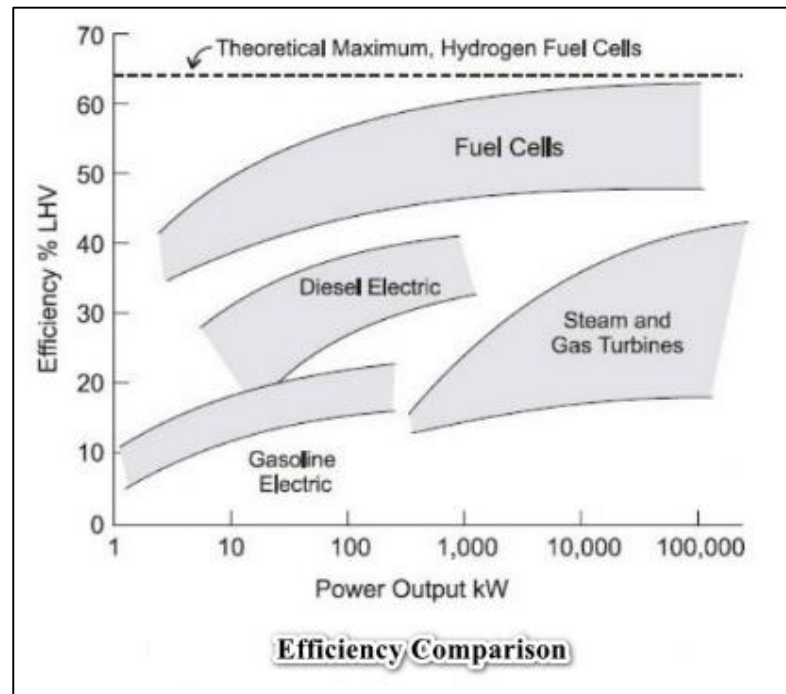


Introduction



Fuel cells

1. Higher energy efficiency;
2. Less CO₂ emissions.

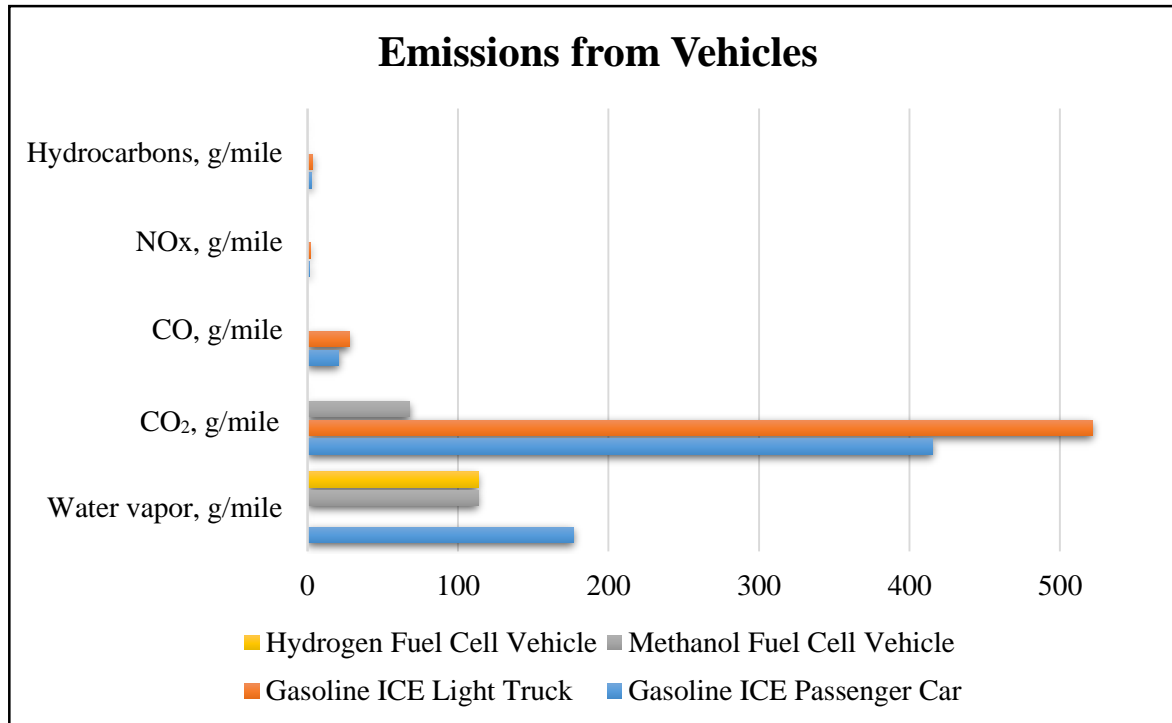


Introduction



Fuel cells

1. Higher energy efficiency;
2. Less CO₂ emissions.



Introduction



Introduction



Fuel cells

1. Polymer electrolyte membrane/proton exchange membrane fuel cells (PEMFC);
2. Phosphoric acid fuel cells (PAFC);
3. Alkaline fuel cells (AFC);
4. Solid oxide fuel cells (SOFC);
5. Molten carbonate fuel cells (MCFC).

Introduction



Proton exchange membrane fuel cells (PEMFC)



Introduction



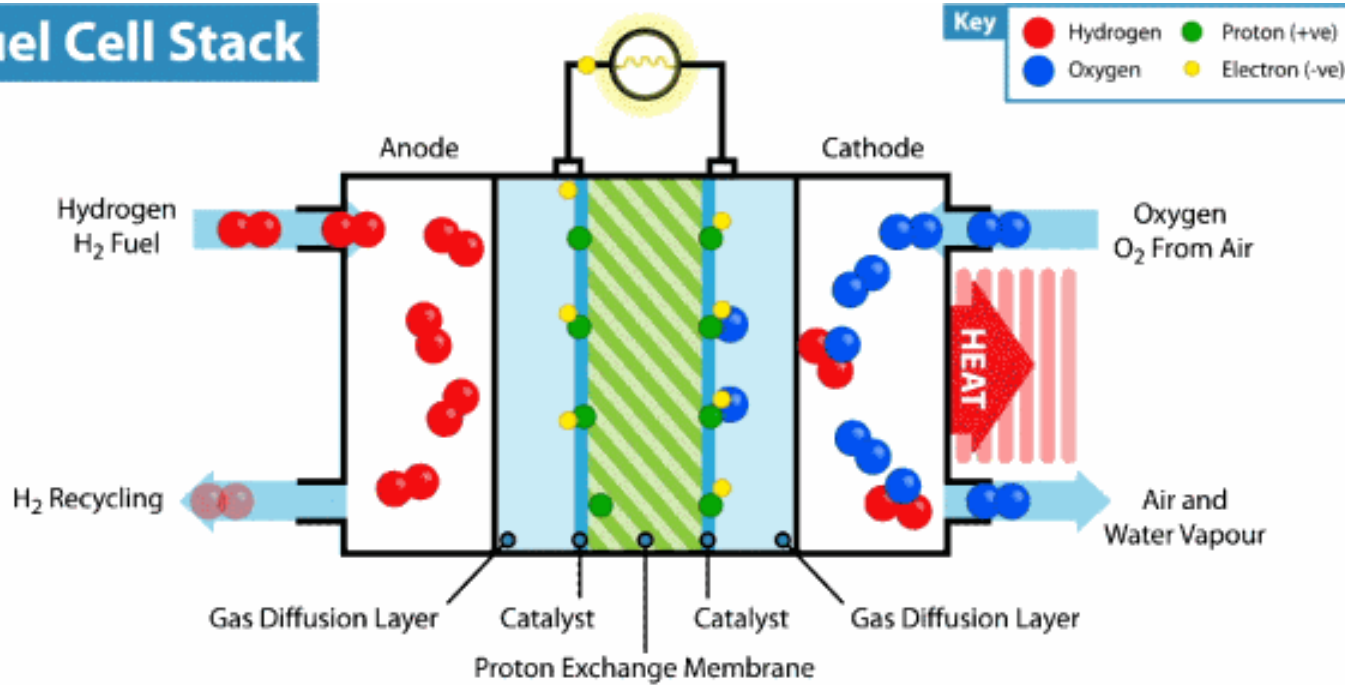
Proton exchange membrane fuel cells (PEMFC)

- Low operation temperature;
- Higher energy density compared to batteries;
- Quiet operation;
- Fast startup;
- Zero local pollutant emission;
- High energy conversion efficiency.

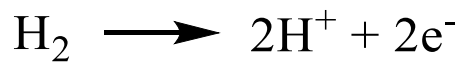
Proton exchange membrane fuel cells (PEMFC)



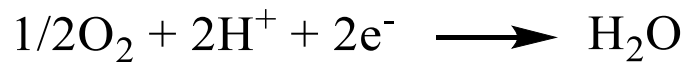
Fuel Cell Stack



• **Anode:**



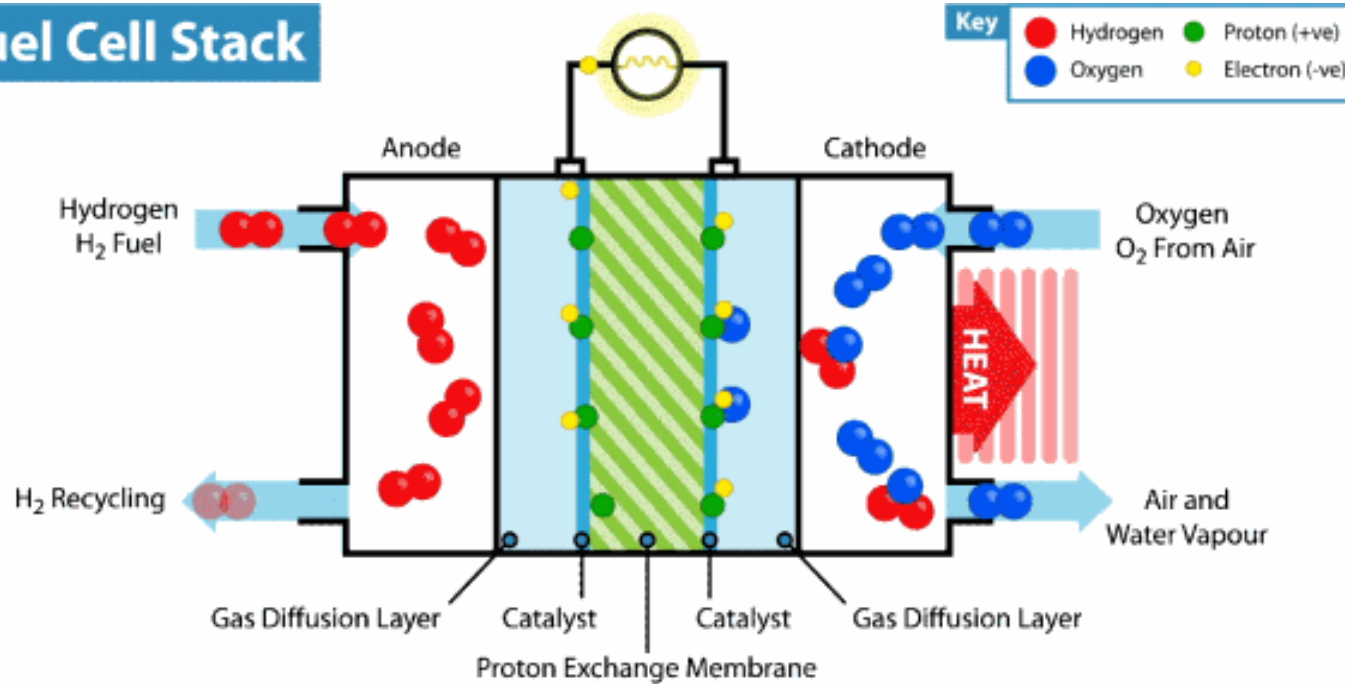
• **Cathode:**



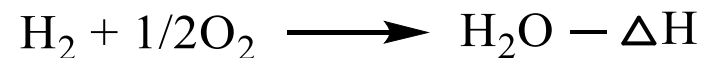
Proton exchange membrane fuel cells (PEMFC)



Fuel Cell Stack



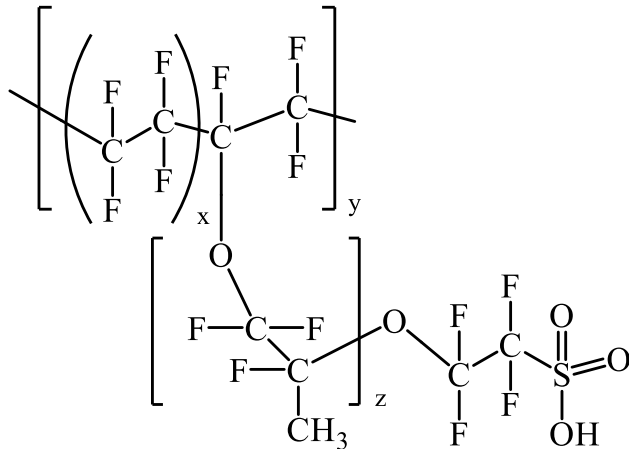
Overall reaction:



Proton exchange membrane fuel cells (PEMFC)



Chemical structure of Nafion®



Advantages:

- Good mechanical properties (< 90 °C);
- Chemical stability;
- High proton conductivity.

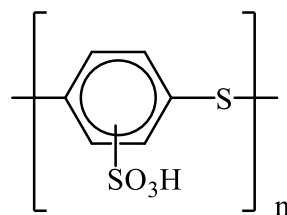
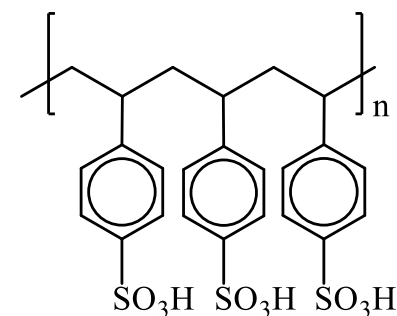
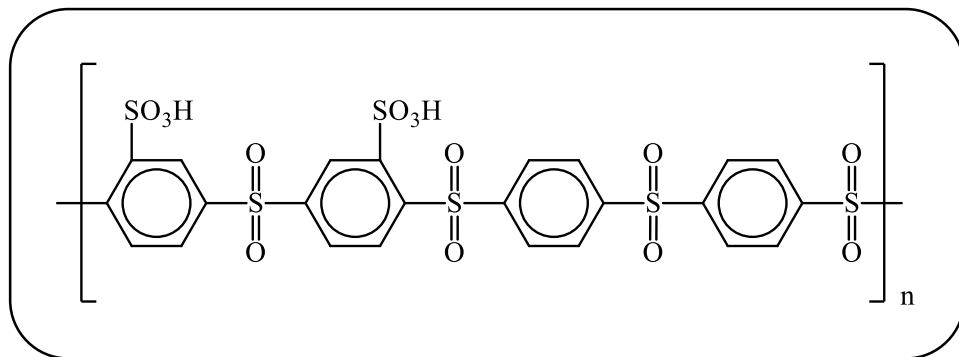
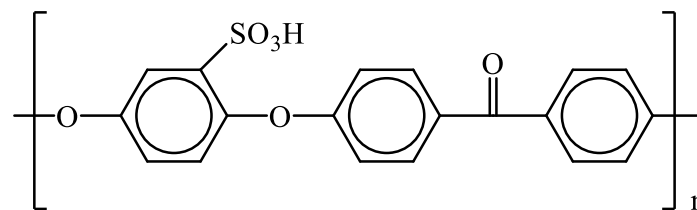
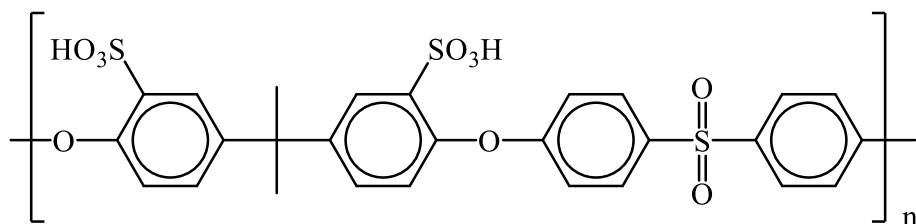
Disadvantages:

- Low operation temperature (< 90 °C);
- Environmental incompatibility;
- High gas permeability;
- High electroosmotic drag of water from the anode to the cathode;
- Deterioration of mechanical properties at high temperature and low humidity.

Proton exchange membrane fuel cells (PEMFC)



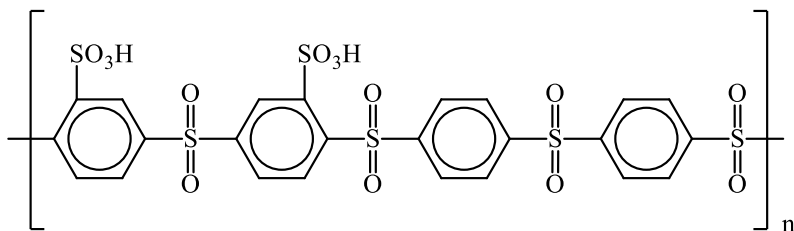
Chemical structures of sulfonated aromatic polymers



Proton exchange membrane fuel cells (PEMFC)

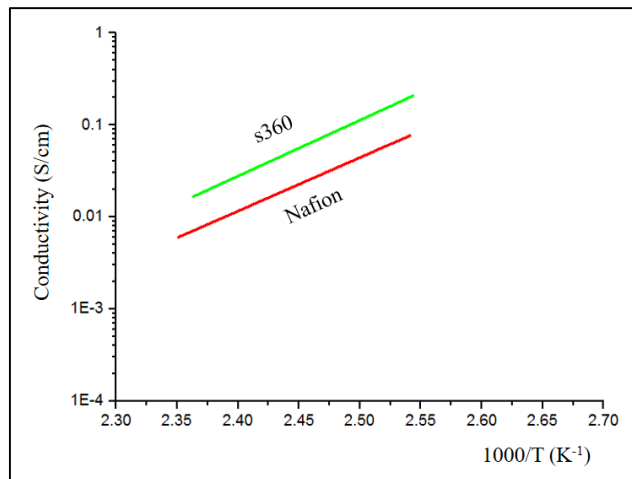


Chemical structure of sPSO₂-360



Advantages:

- High IECs and proton conductivities compared to fluorinated ionomers (PFSA)s;
- Oxidative stability;
- Thermal stability;
- Low electroosmotic drag of water from the anode to the cathode;
- Good mechanical properties at moderate humidity.



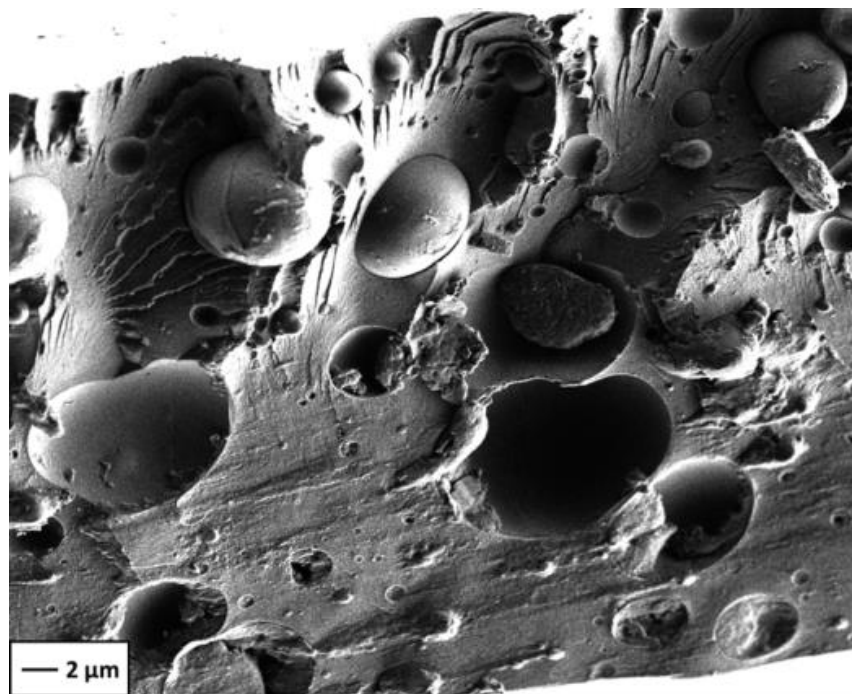
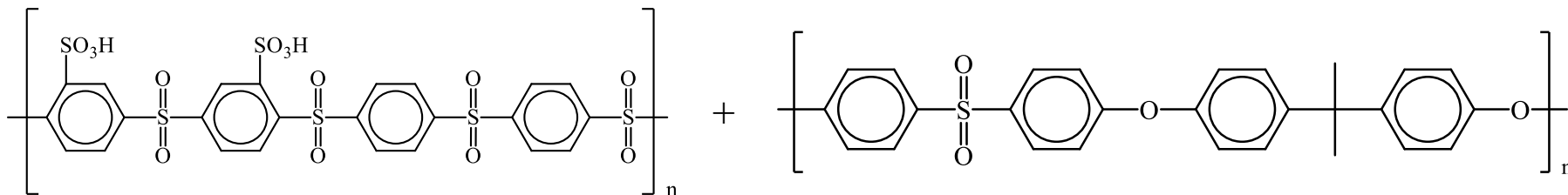
Disadvantages:

- Brittleness in the dry state;
- Unsatisfactory mechanical properties at high humidity.

Proton exchange membrane fuel cells (PEMFC)



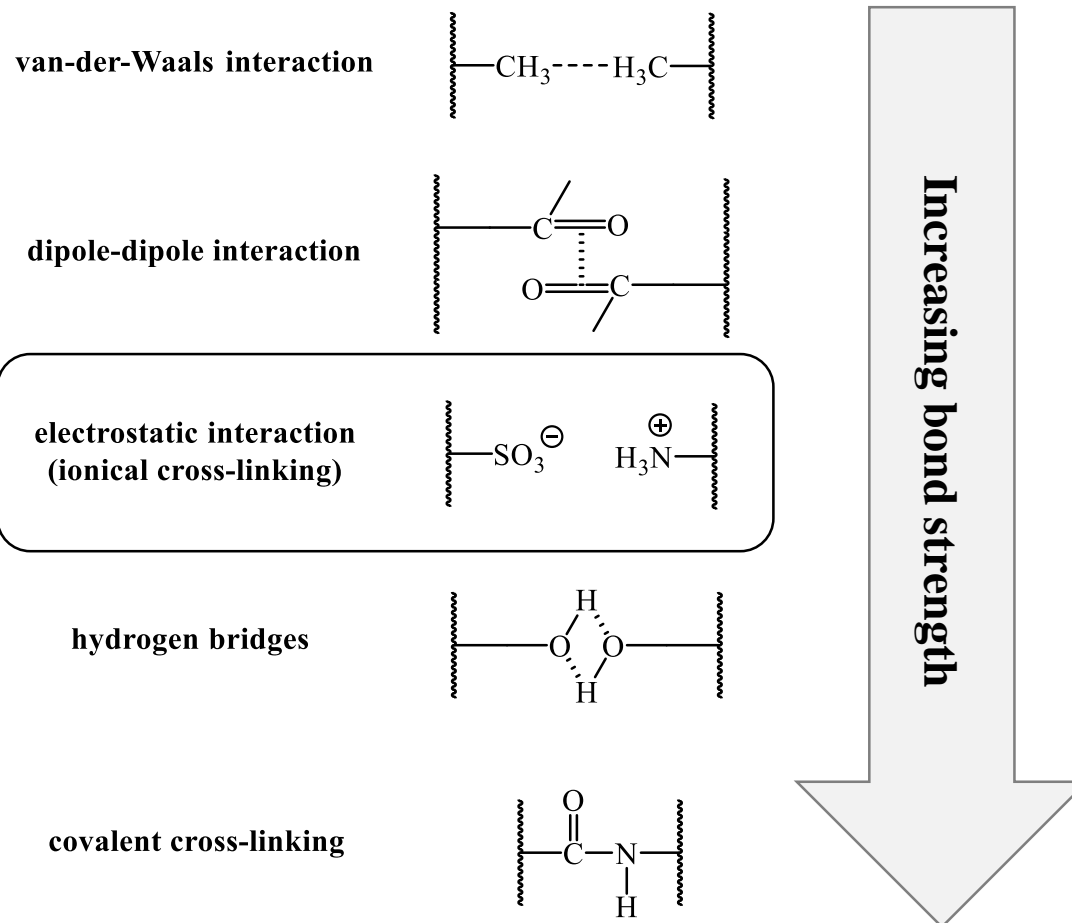
Blend of sPSO₂-360 with PSU



Proton exchange membrane fuel cells (PEMFC)



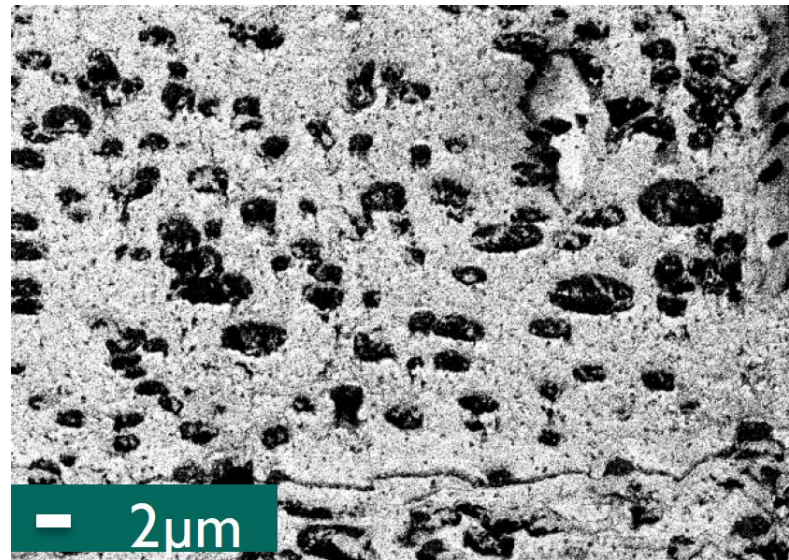
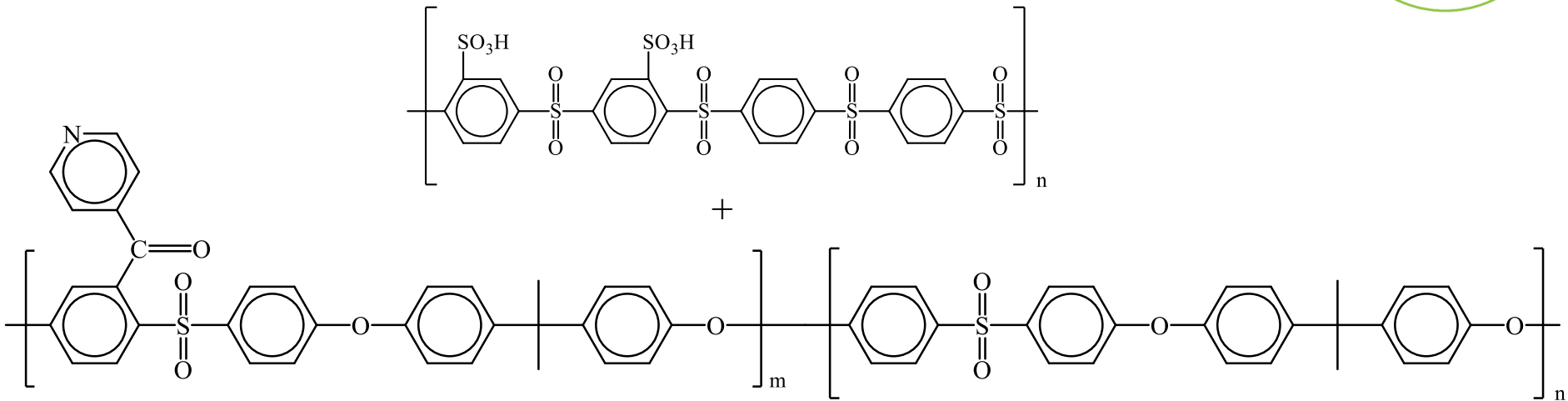
Specific interactions between macromolecules



Proton exchange membrane fuel cells (PEMFC)



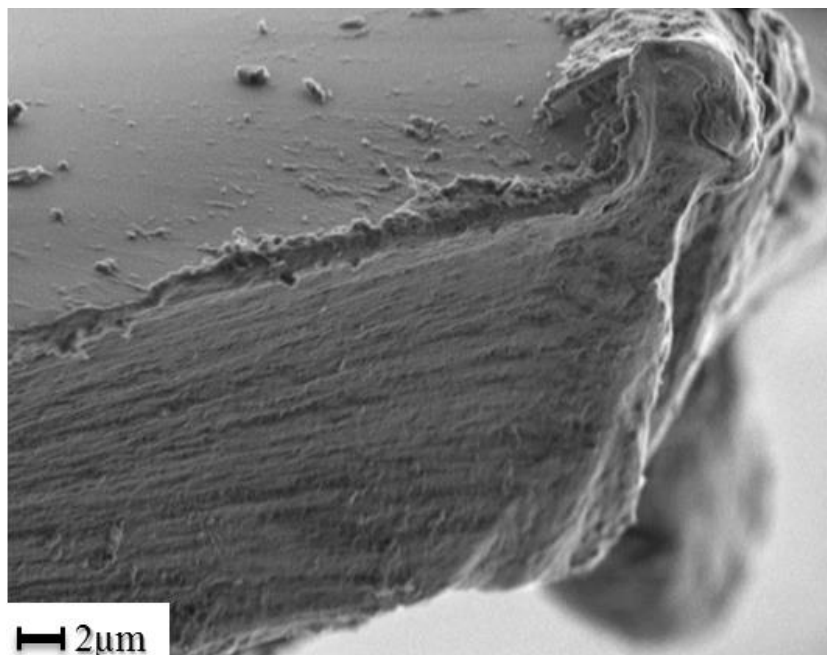
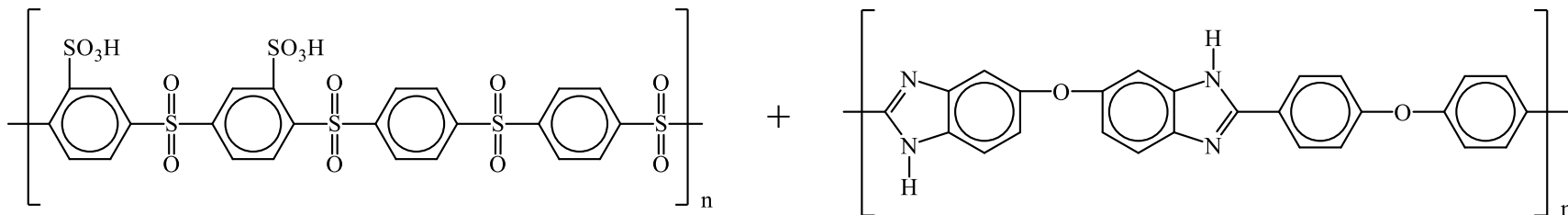
Blend of sPSO₂-360 with PSU-py



Proton exchange membrane fuel cells (PEMFC)



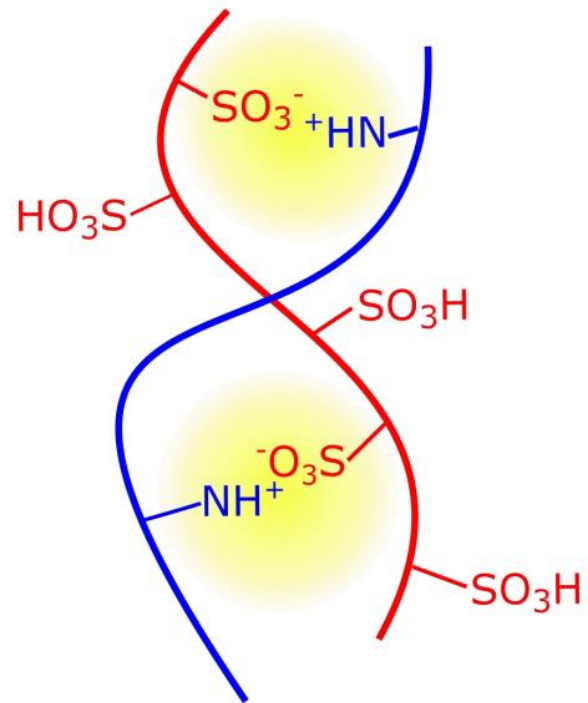
Blend of sPSO₂-360 with PBI-OO



Proton exchange membrane fuel cells (PEMFC)



Scheme of ionic crosslinking of a sPSO₂-360 (red) with a PBI-OO (blue)



- Increase of mechanical strength;
- Decrease of proton conductivity;
- Decrease of ion exchange capacity.

Proton exchange membrane fuel cells (PEMFC)



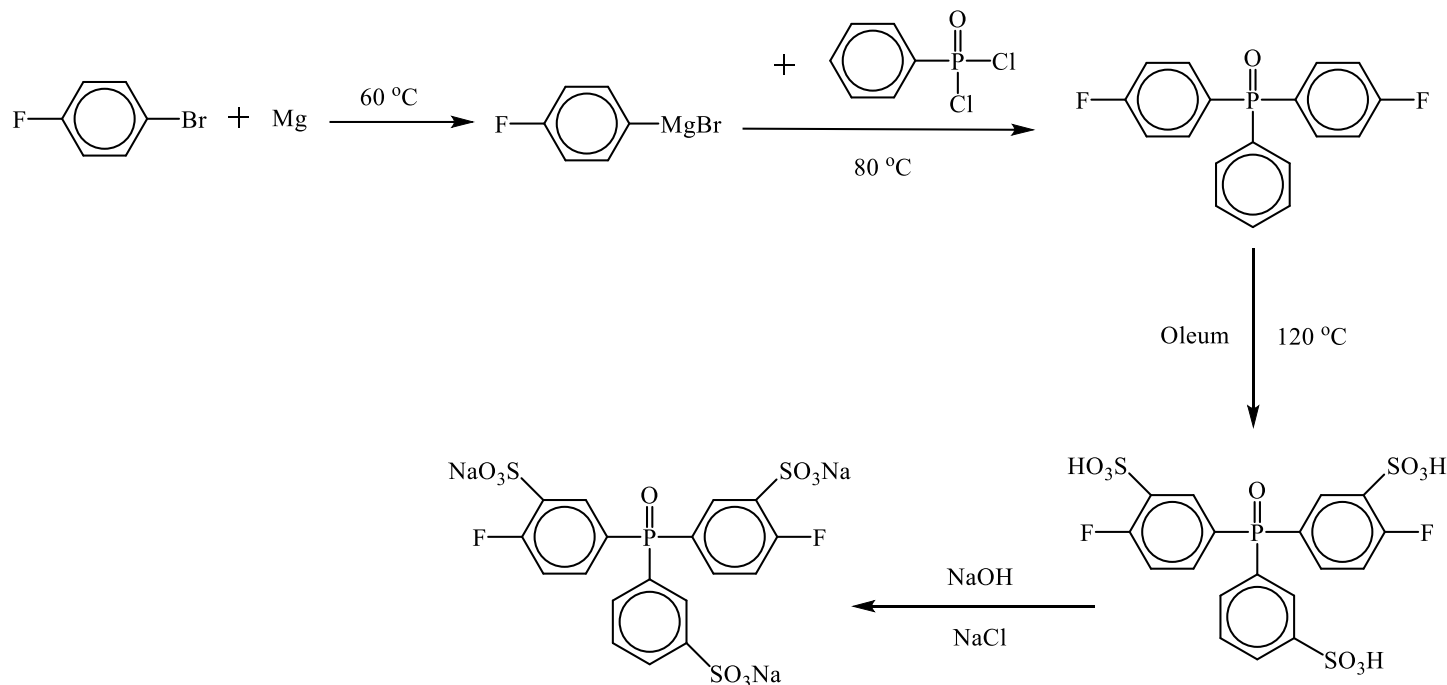
Research objective:

**Synthesis of monomer and polyelectrolyte
with high sulfonation degree**

Proton exchange membrane fuel cells (PEMFC)



Synthesis scheme of sodium 5,5'-((3-sulfonatophenyl)phosphoryl)bis(2-fluorobenzenesulfonate)^{1,2}



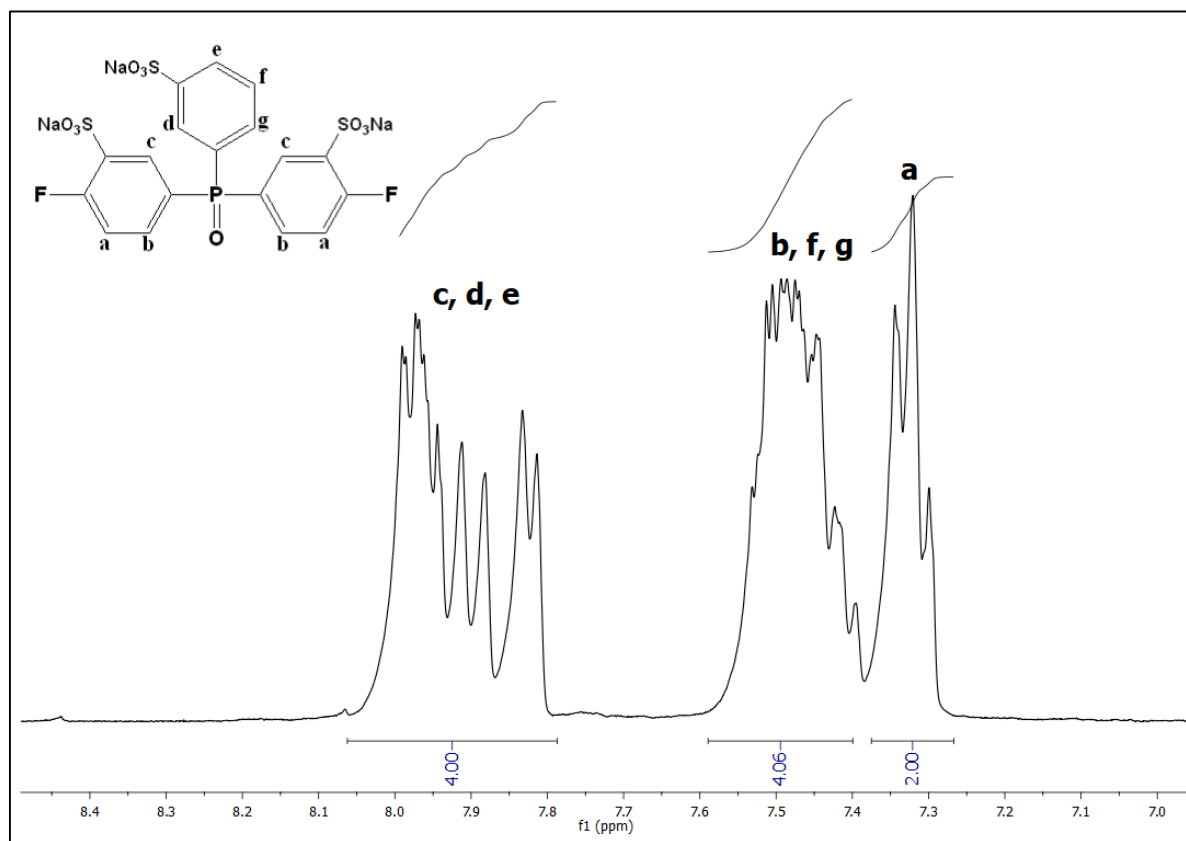
1. X. Ma, C. Zhang, G. Xiao, D. Yan, G. Sun, Synthesis and characterization of sulfonated poly(phthalazinone ether phosphine oxide)s by direct polycondensation for proton exchange membranes, *J. Polym. Sci. Part A Pol. Chem.* 46 (2008) 1758-1769;

2. Liao, H.; Zhang, K.; Tong, G.; Xiao, G.; Yan, D. Sulfonated Poly(arylene Ether Phosphine Oxide)s with Various Distributions and Contents of Pendant Sulfonic Acid Groups Synthesized by Direct Polycondensation. *Polym. Chem.* 2014, 5, 412-422.

Proton exchange membrane fuel cells (PEMFC)



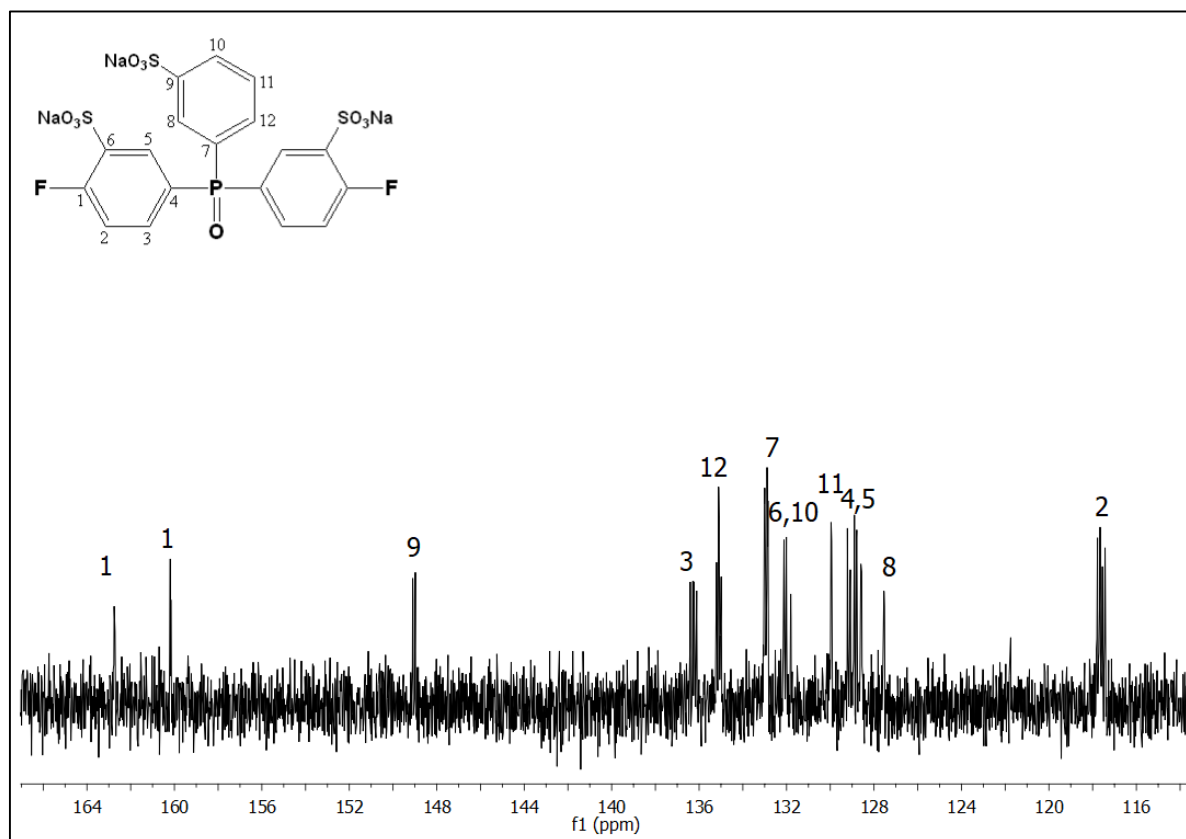
^1H NMR Spectra of sodium 5,5'-((3-sulfonatophenyl)phosphoryl)bis(2-fluorobenzenesulfonate)



Proton exchange membrane fuel cells (PEMFC)



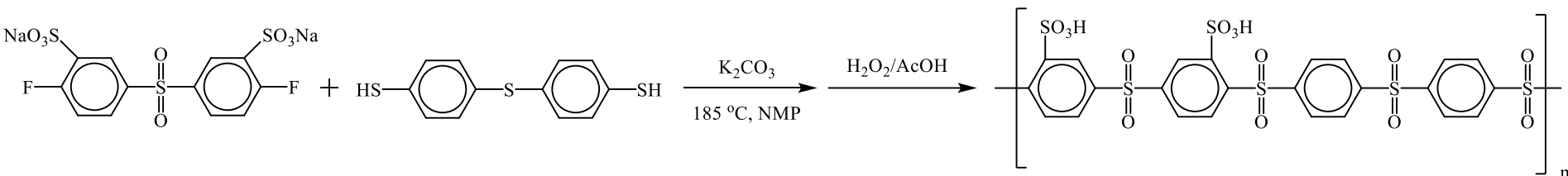
^{13}C NMR Spectra of sodium 5,5'-((3-sulfonatophenyl)phosphoryl)bis(2-fluorobenzenesulfonate)



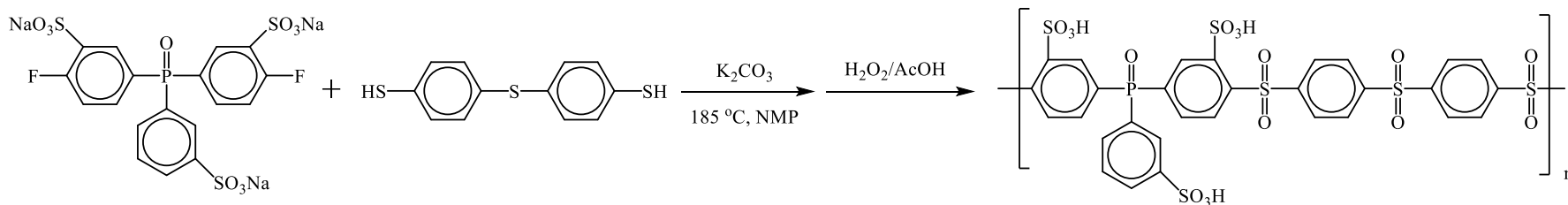
Proton exchange membrane fuel cells (PEMFC)



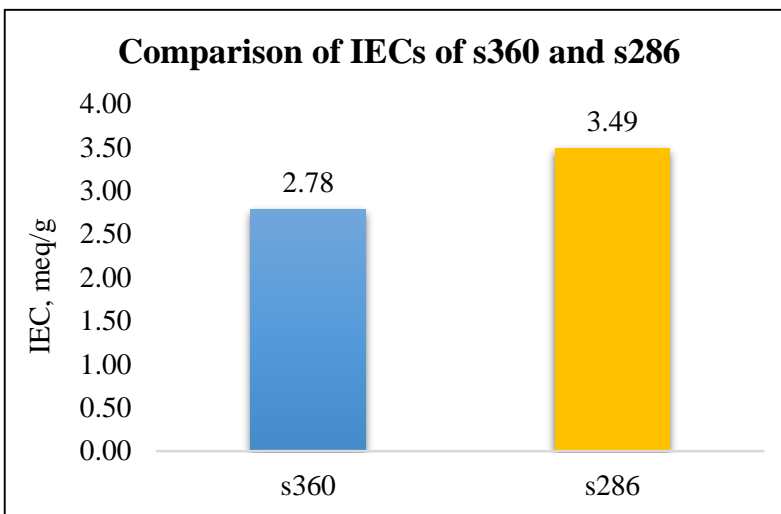
Synthesis scheme of sPSO₂-360



Synthesis scheme of sPSO₂PO-286

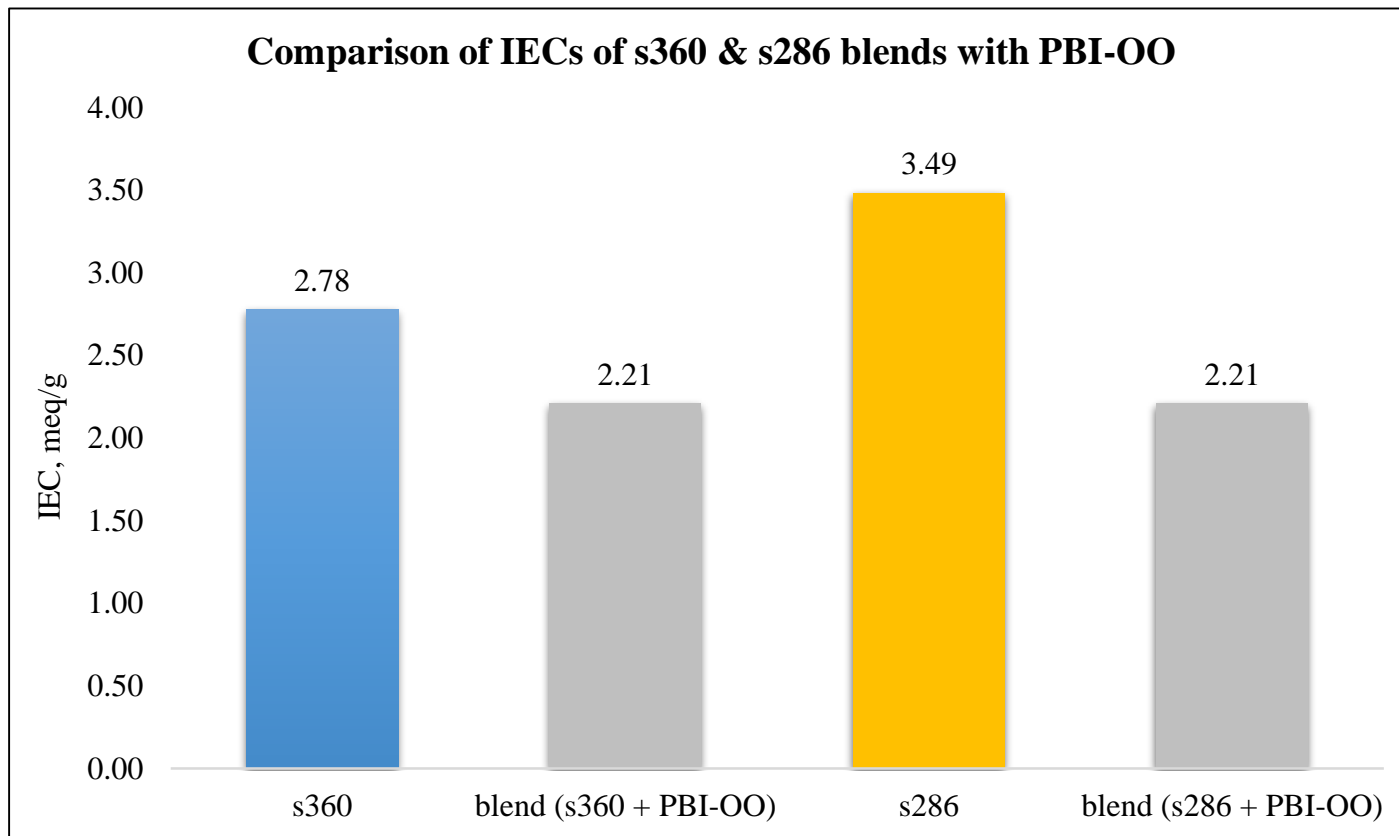


Comparison of IECs of s360 and s286



➤ IEC increases by ≈ 25 %

Proton exchange membrane fuel cells (PEMFC)



PBI-OO = 7.5 %



PBI-OO = 15.39 %

Acknowledgments



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Volkswagen**Stiftung**

References



- Kreuer, K.D. (2001), “On the development of proton conducting polymer membranes for hydrogen, methanol fuel cells”, *Journal of Membrane Science*, Vol. 185 No. 1, pp. 29-39;
- Kreuer, K., Paddison, S. J., Spohr, E. & Schuster, M. Transport in proton conductors for fuel-cell applications: simulations, elementary reactions, and phenomenology. *Chem. Rev.* 104, 4637–4678 (2004);
- Alkire, R. C.; Gerischer, H.; Kolb, D. M.; Tobias, C. W., Eds. *Advances in Electrochemical Science and Engineering*; Johy Wiley & Sons: New York, 2002;
- G. Maier, J. Meier-Haack, In *Fuel Cells II*; Springer-Verlag Berlin, Berlin, 216 (2008) pp. 1–62;
- J.A. Kerres, *Fuel Cells* 5 (2005) 230-247;
- K.-D. Kreuer, Proton conductivity: materials and applications, *Chem. Mater.* 8 (3) (1996) 610–641;
- S. Bose, T. Kuila, T.X.H. Nguyen, N.H. Kim, K. Lau, J.H. Lee, Polymer membranes for high temperature proton exchange membrane fuel cell: recent advances and challenges, *Prog. Polym. Sci.* 36 (2011) 813-843;
- X. Ma, C. Zhang, G. Xiao, D. Yan, G. Sun, Synthesis and characterization of sulfonated poly (phthalazinone ether phosphine oxide)s by direct polycondensation for proton exchange membranes, *J. Polym. Sci. Part A Pol. Chem.* 46 (2008) 1758-1769;
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Acknowledgments



Thank you for attention!