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# Overcoming the Trade-Off between Methanol Rejection and Proton Conductivity via Facile Synthesis of Crosslinked Sulfonated PEEK Proton Exchange Membranes

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**Abstract:** In this work, homogeneous, thin-film proton exchange membranes (PEMs) with superior proton conductivities and high methanol rejection were fabricated via a facile synthesis procedure. Sulfonated polyether ether ketone (sPEEK) was crosslinked via a Friedel–Crafts reaction by $\alpha,\alpha'$-dichloro-p-xylene, a non-hazardous and hydrophobic compound. PEMs with varying crosslinking and sulfonation degrees were fabricated to overcome the traditional trade-off between methanol rejection and proton conductivity. The sulfonation of PEEK at 60 °C for 24 h resulted in a sulfonation degree of 56%. Those highly sulfonated backbones, in combination with a low membrane thickness (ca. 20 µm), resulted in proton conductivities superior to Nafion 117. Furthermore, X-ray photoelectron spectroscopy proved it was possible to control the crosslinking degree via the crosslinking time and temperature. The PEMs with the highest crosslinking degree showed better methanol rejection compared to the commercial benchmark. The introduction of the crosslinker created hydrophobic membrane sections, which reduced the water and methanol uptake. Subsequently, the membrane became denser due to the crosslinking, hindering the solute permeation. Those two effects led to lower methanol crossovers. This study proved the successful fabrication of PEMs overcoming the trade-off between proton conductivity and methanol rejection, following a facile procedure using low-cost and non-hazardous materials.

**Keywords:** electrochemistry; membrane synthesis; cation exchange membrane; proton conductivity; polyether ether ketone; methanol retention

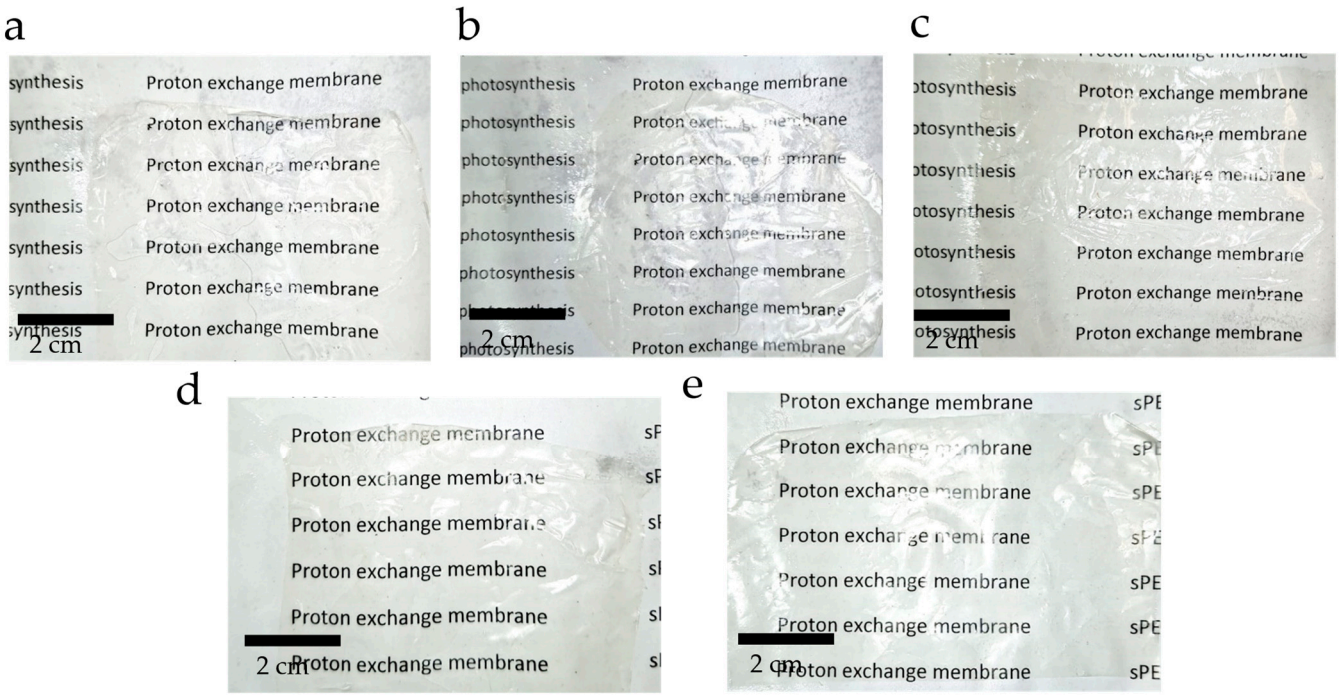


**Figure S1:** Pictures of the sPEEK/DCX membranes: (a) sPEEK, (b) sPEEK/DCX, (c) sPEEK/DCX-s90°C, (d) sPEEK/DCX-CX24h, (e) sPEEK/DCX-CX190°C

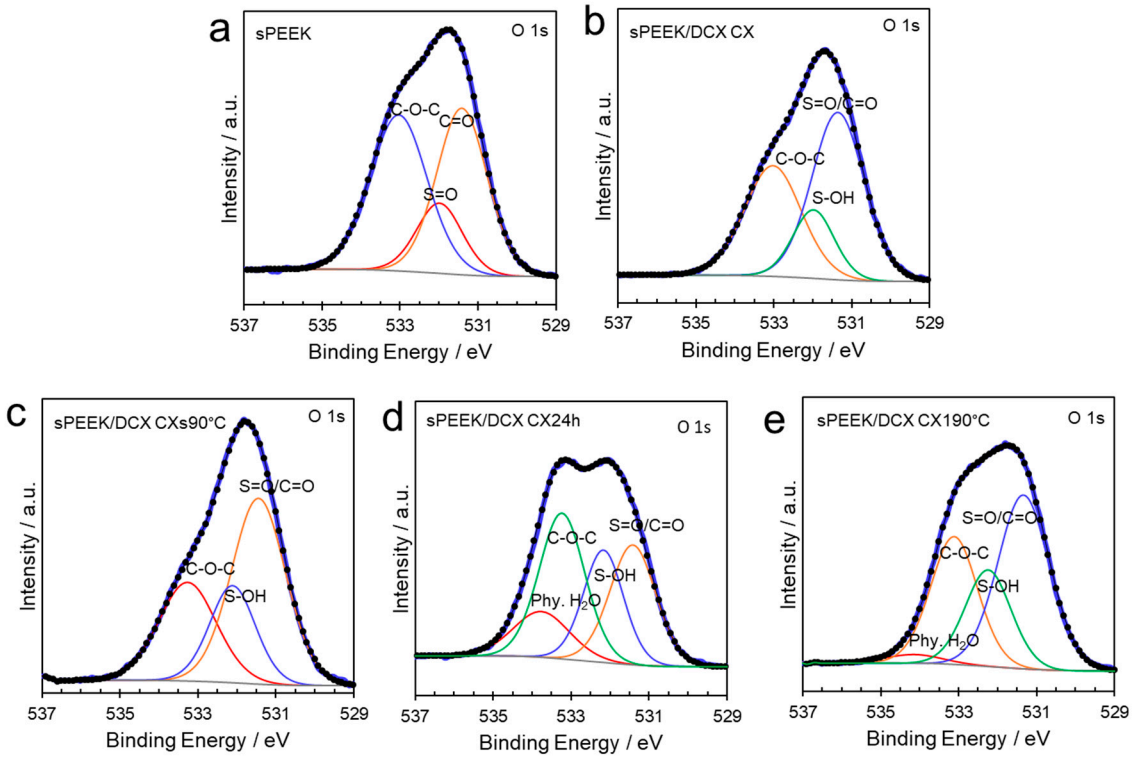


**Figure S2**. High resolution O 1s XPS spectra of the self-synthetized membranes; (a) sPEEK, (b) sPEEK/DCX, (c) sPEEK/DCX-s90°C, (d) sPEEK/DCX-CX24h, (e) sPEEK/DCX-CX190°C.

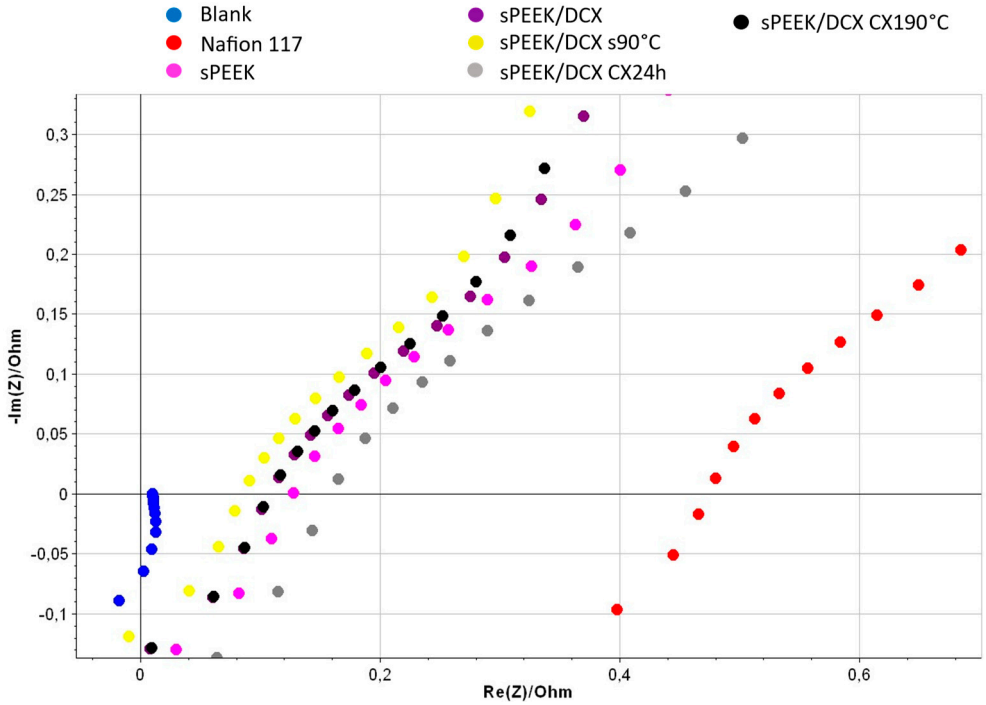


**Figure S3:** The impedance spectroscopy data of the proton resistance experiment. The resistance value is derived from the intersect at high frequencies on the complex impedance plane with the Re(Z) axis.