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Supplementary Materials

A review of proton exchange membranes modified with inorganic nanomaterials for fuel cells

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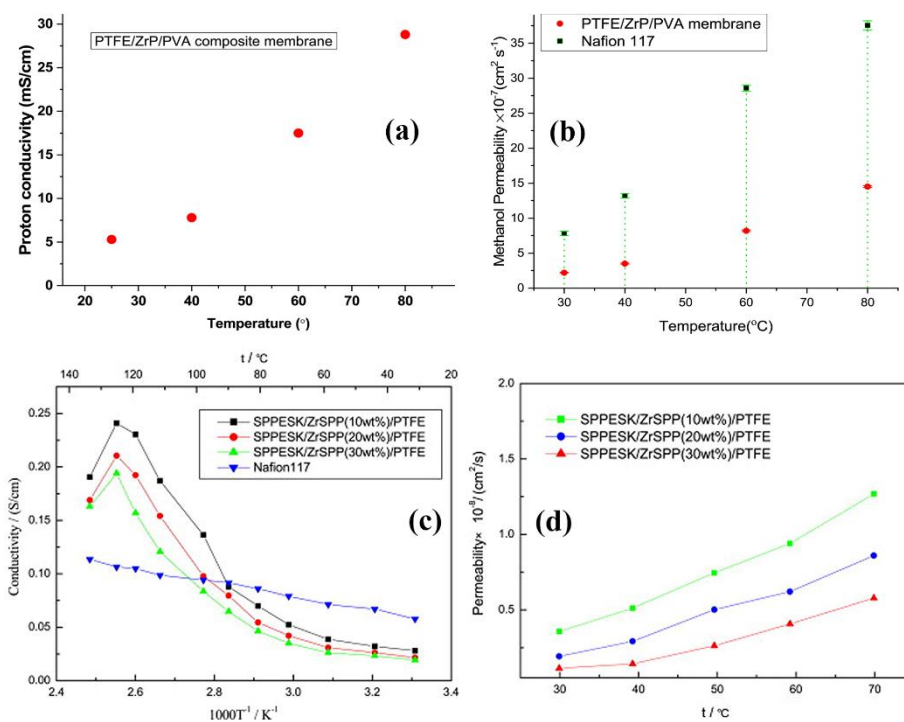


Fig. S 1 Temperature vs. proton conductivity curves for (a) polymer blend membranes (b) polymer blend membrane and Nafion 117 membrane (c) Arrhenius plots of membranes containing SPESK, ZeSPP and PTFE (d) methanol permeability value of SPESK/ZrSPP/PTFE supported membranes ¹². With copyright permission 2020, 2010. Elsevier.

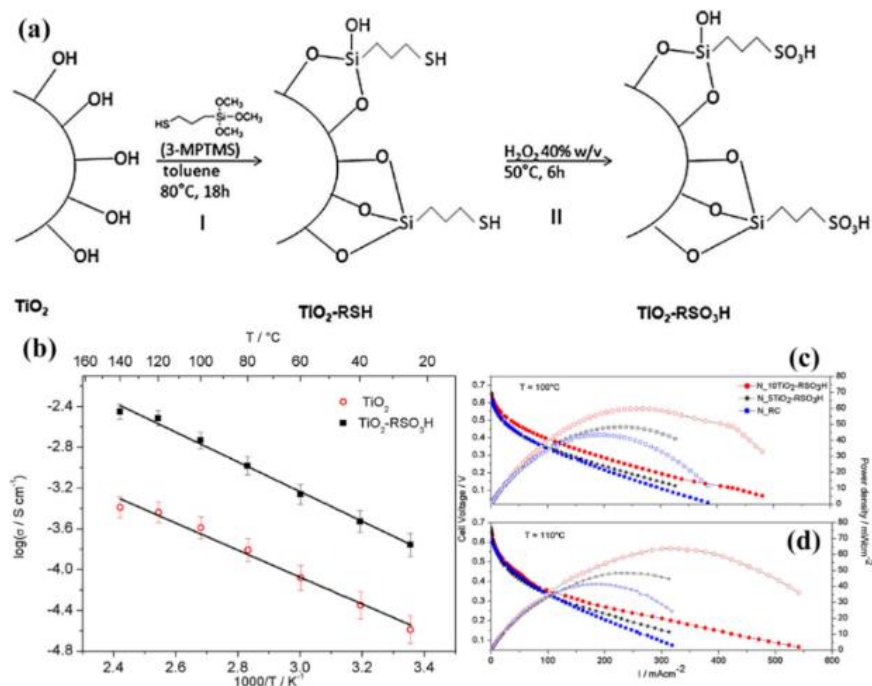


Fig. S 2 (a) Synthesis procedure of the surface functionalization of TiO_2 nanoparticles. (b) Arrhenius plots of TiO_2 and $\text{TiO}_2\text{-RSO}_3\text{H}$ based composite membranes at 100% RH. (c) Polarization as well as PD plots of recasted Nafion and titania and functionalized titania based composite membranes at 100°C (c) and 110°C (d) ³. With copyright permission 2014, Elsevier.

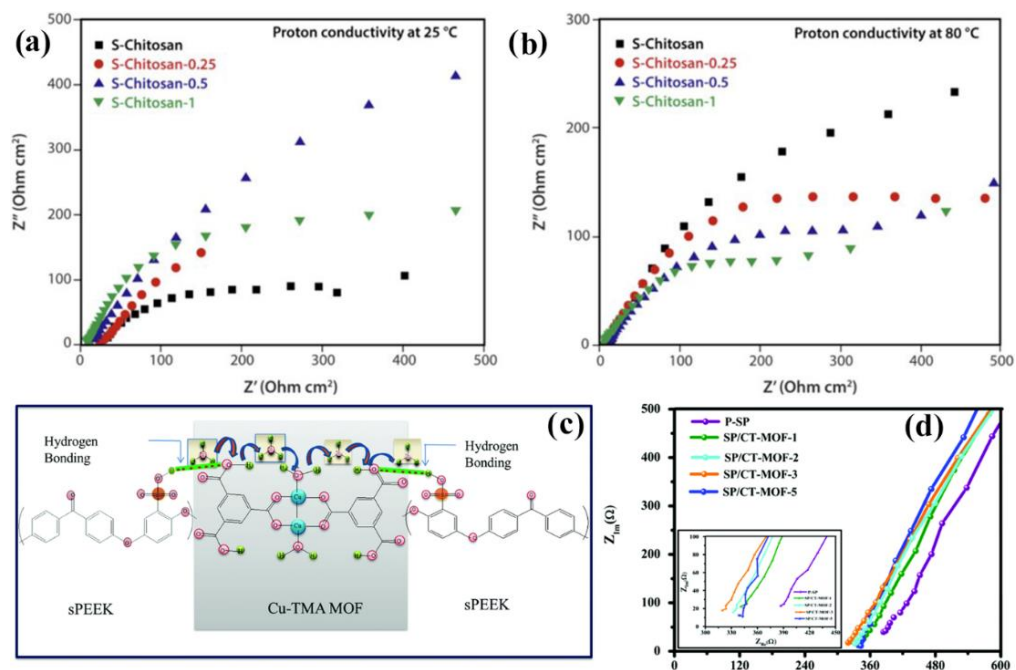


Fig. S 3 AC impedance values of sulphonated Chitosan and blended Sulphonated chitosan and HKUST-1 hybrid membranes at the temperature of (a) 25°C and (b) 80°C. (c) Explanation of proton transfer mechanism through copper and trimesic based MOF embedded composite membrane. (d) AC impedance plot of pristine SPEEK and SPEEK/MOF composite membranes with different amounts of MOF temperature of 70 °C and RH 98 %⁴⁵. With copyright permission 2018, 2022, John Wiley and Sons and Royal Society of Chemistry.

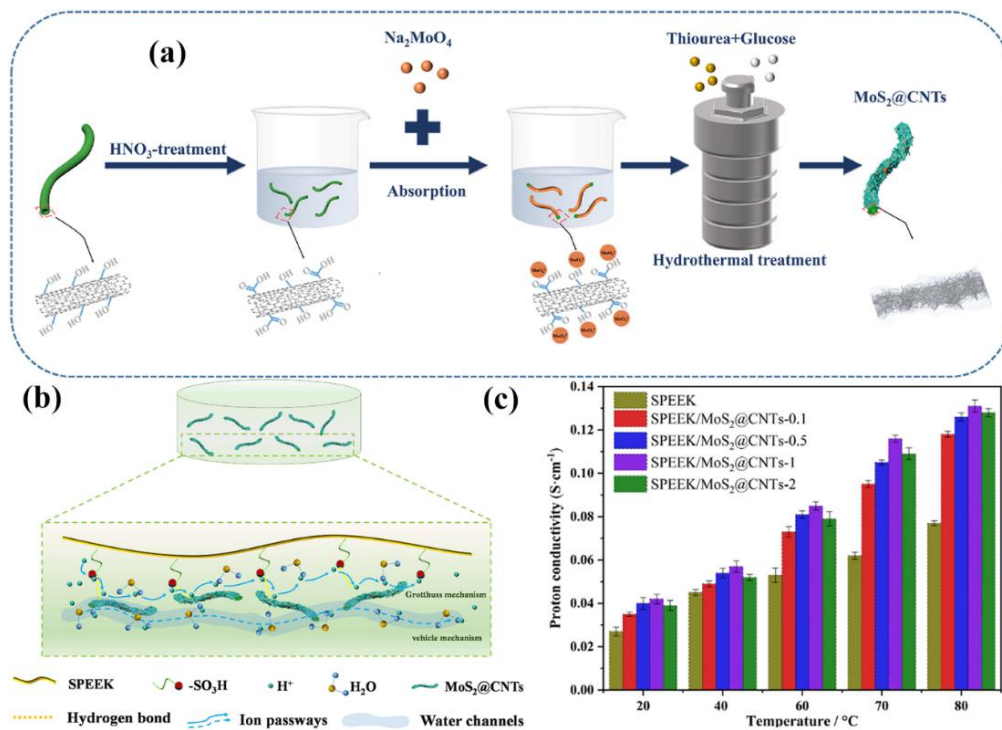


Fig. S 4 (a) Schematic illustration of synthesis procedure of MoS₂ based CNTs. (b) Schematic Explanation of proton transfer mechanism within MoS₂@CNTs based SPEEK membranes. (c) Temperature Vs Proton Conductivity values of pristine SPEEK and composite membranes containing different amounts of MoS₂@CNT⁶. With copyright permission 2022, Elsevier.

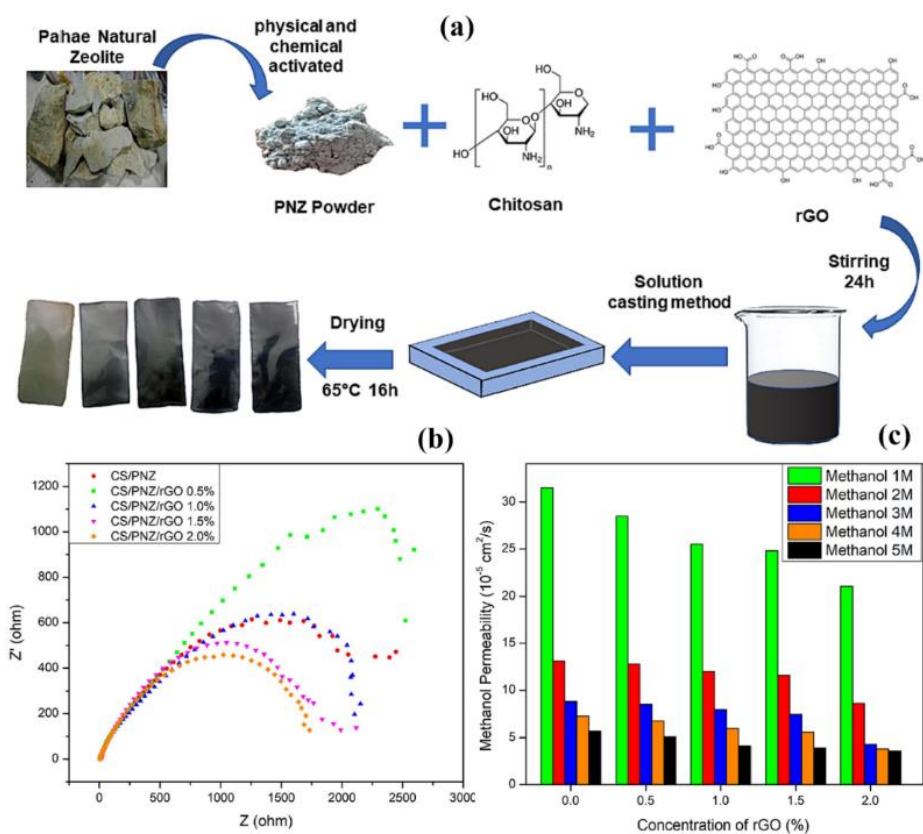


Fig. S 5 Schematic illustrations of CS/PNZ/rGO composite membrane manufacturing procedure. (b) AC impedance curves of composite membranes with different amounts of reduced graphene oxide. (c) different concentrations of reduced graphene oxides in the composite membranes Vs methanol permeability values⁷. With copyright permission 2023, Elsevier.

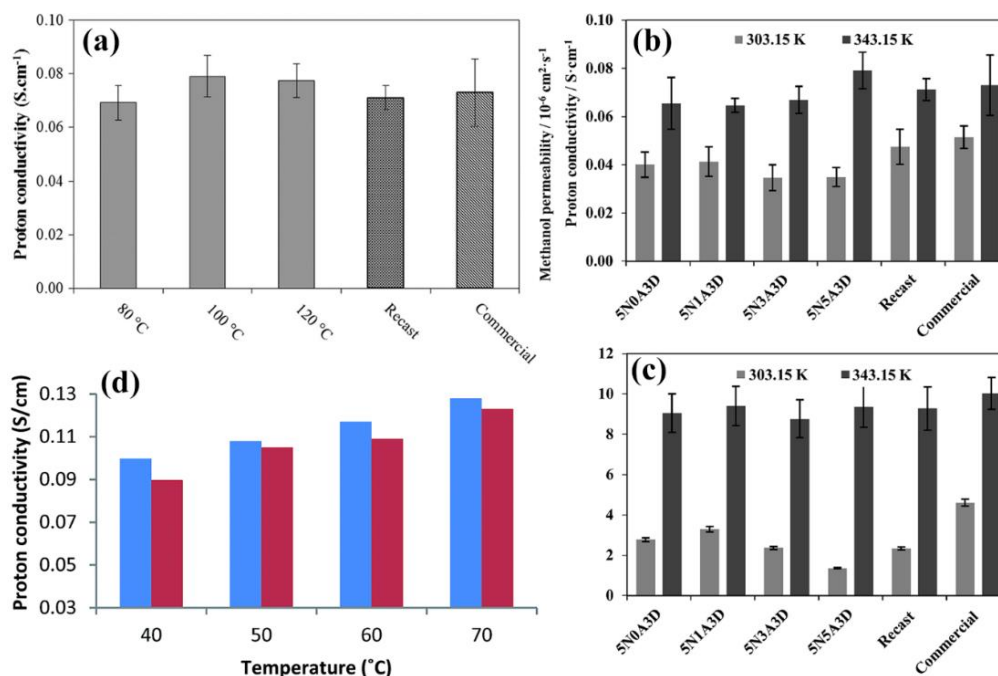


Fig. S 6 (a) Proton conductivity values [70 °C] of commercial, 0 wt.% and 5 wt. % GMPT functionalized Mordenite and 0wt.% GMPT functionalized Mordenite composite membranes at casting temperature of 80, 100 and 120 °C. (b) Proton Conductivity and (c) Methanol permeability of Nafion/Mordenite composite membranes checked at 303.15 K and 343.15 K temperatures. (d) Temperature Vs Proton Conductivity Values of ■ Nafion 117, ■ 0.5% Mordenite loaded Nafion membrane ⁸⁹¹⁰. With copyright permission 2015, 2016 and 2020, Elsevier and Royal Society of Chemistry.

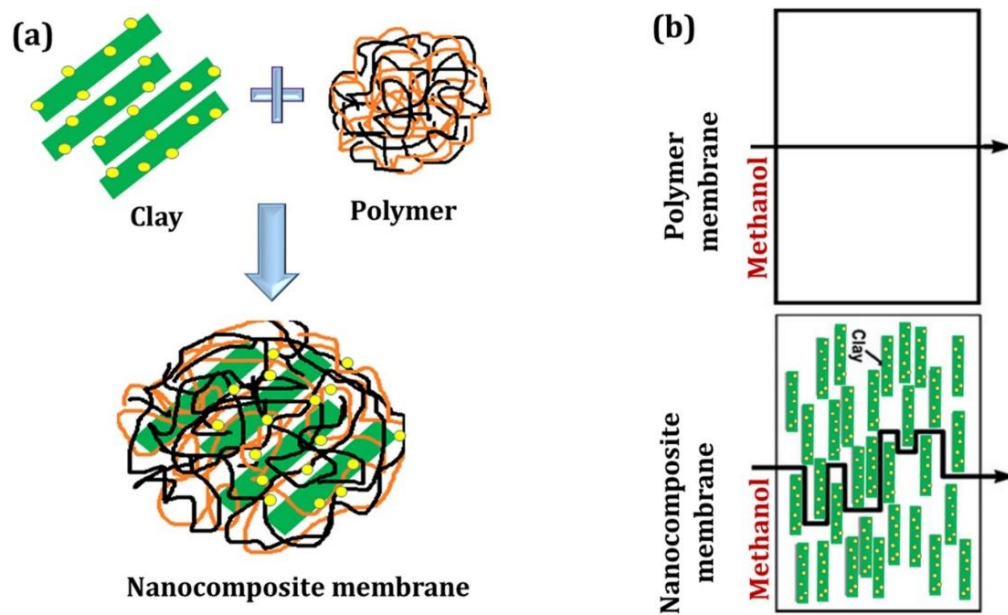


Fig. S 7 (a) Procedure of preparation of Nanocomposite membrane [Clay + Polymer] (b) illustration of ionic channel ways developed by incorporation of exfoliated clay nano-platelets within polymer matrix¹¹. With copyright permission 2022, Elsevier.

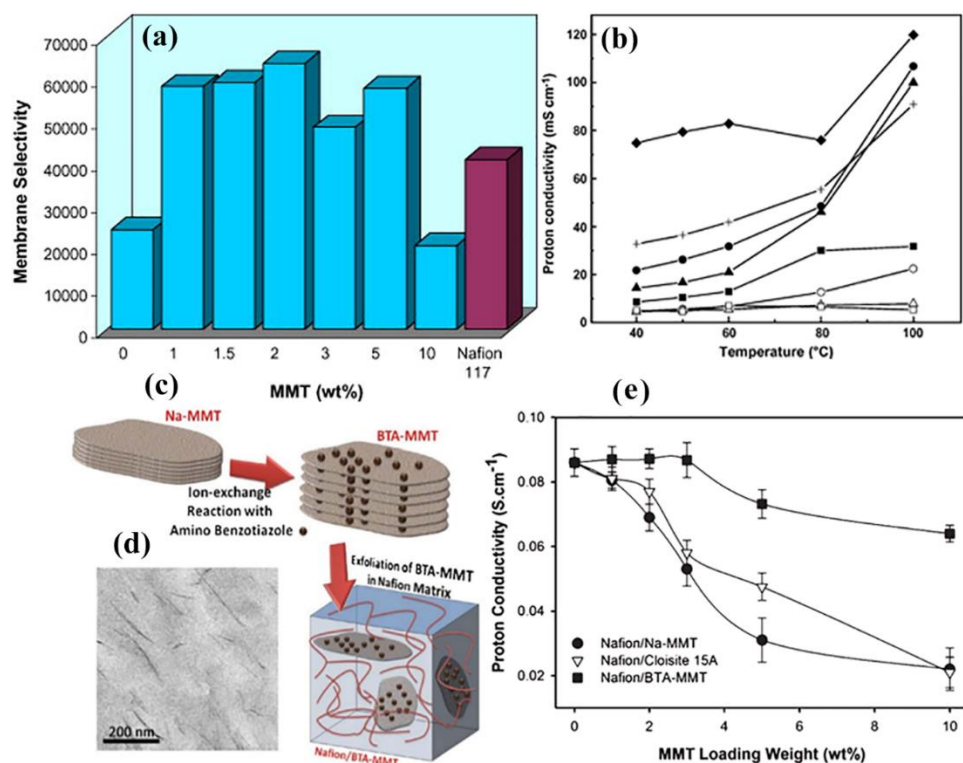


Fig. S 8 (a) MMT weight percentage Vs membrane selectivity Curves of pristine Nafion 117 and different amounts of MMT in sulphonated PPO. (b) Temperature Vs Proton conductivity Values of SPEEK (+), Nafion® 117 (◆), and the SPEEK/SMMT composite membranes. With Amount of MMT (Empty symbols) for 1 wt. % (●), 3 wt.% (▲) and 5 wt.% (■). (c) Schematic diagram of BTA-MMT preparation with BTA molecules (d). TEM image of Nafion and BTA-MMT blended nano-composite membranes (e) MMT weight Vs Proton conductivity values of different types of Nafion membrane with NA-MMT, Cloisite 15A and BTA-MMT¹²¹³. With copyright permission 2008 and 2014, Elsevier and Royal Society of Chemistry.

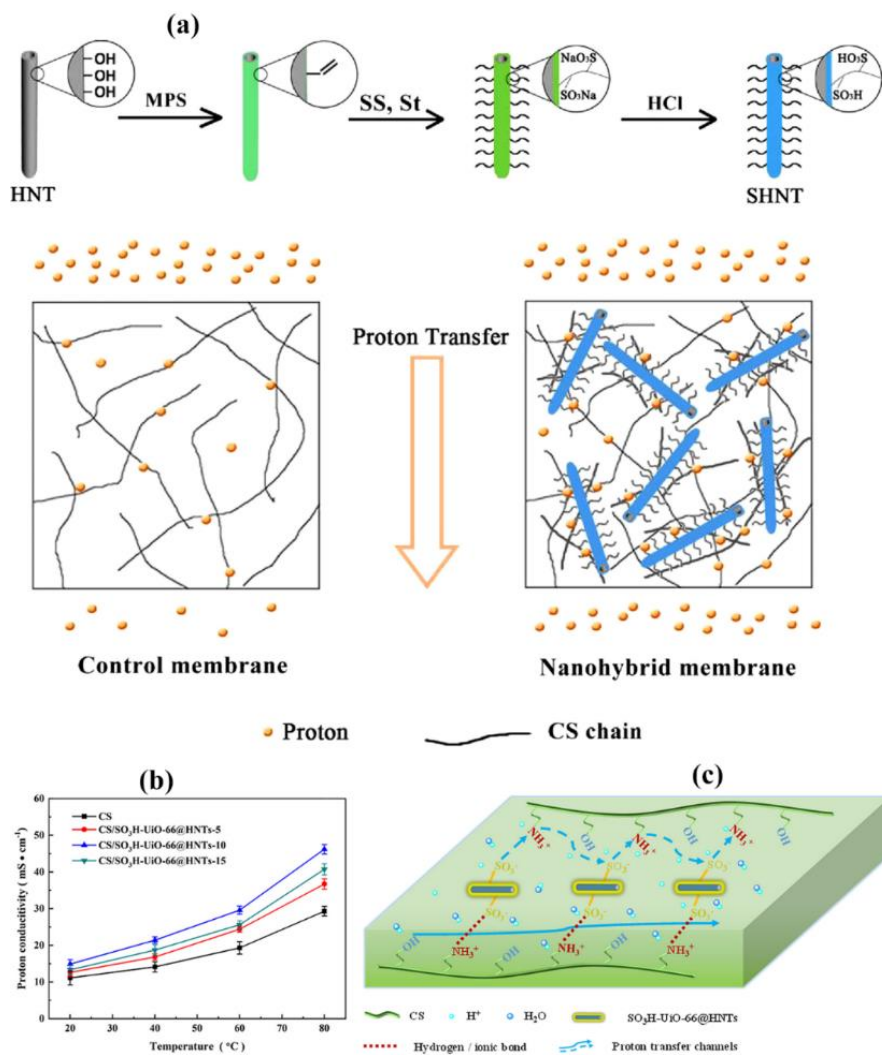


Fig. S 9 (a) Schematic diagram of synthesis of sulfonated HNT and sulphonated HNT based chitosan nano hybrid membranes. (b) Temperature Vs Proton conductivity values of Pristine chitosan membrane and 5-15 w.% sulfonated UiO-66@HNT based chitosan membranes (c) Schematic explanation of possible protons transport channels and interactions within the composite membrane¹⁴¹⁵. With copyright permission 2014 and 2021, Elsevier.

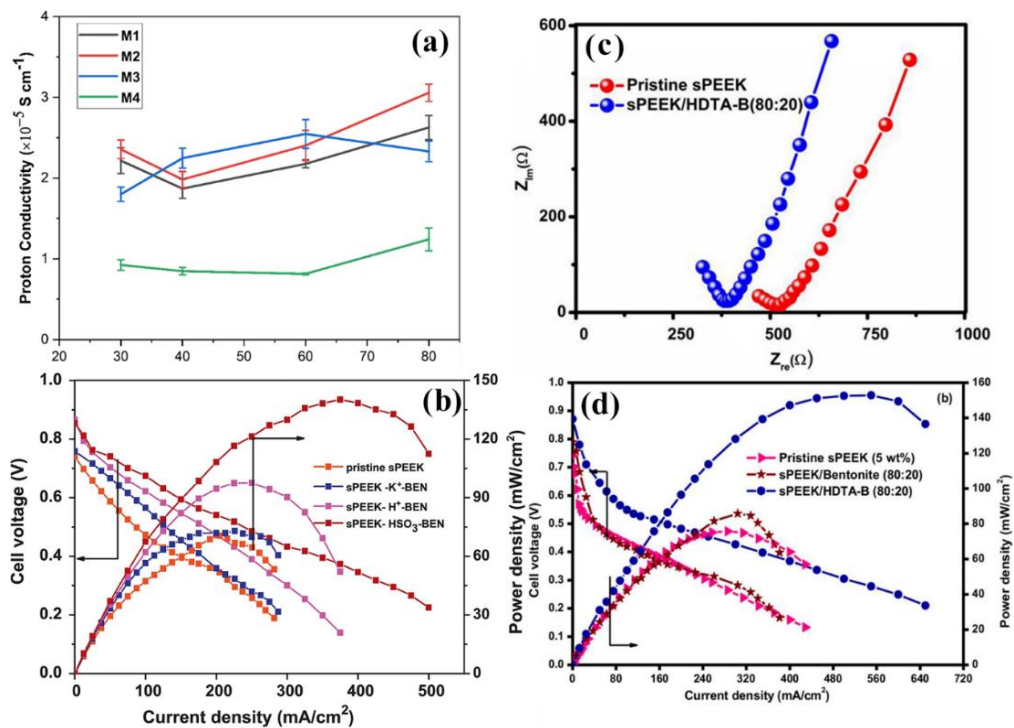


Fig. S 10 (a) Temperature Vs Proton Conductivity values of different composite membranes containing SPEEK, Cloisite and Bentonite (b) DMFC single cell Performance with Polarization and Power density curves of pristine SPEEK, K⁺-BEN, H⁺-BEN and HSO₃-BEN based SPEEK composite membranes at the temperature of 70 °C. (c) AC impedance curves and (d) RH (%) Vs Proton conductivity values curves of pristine SPEEK and HDTA based SPEEK composite membrane. [70°C under 100% RH]¹⁶¹⁷¹⁸. With copyright permission 2014, 2018 and 2023, Springer, Elsevier and IOP Science.

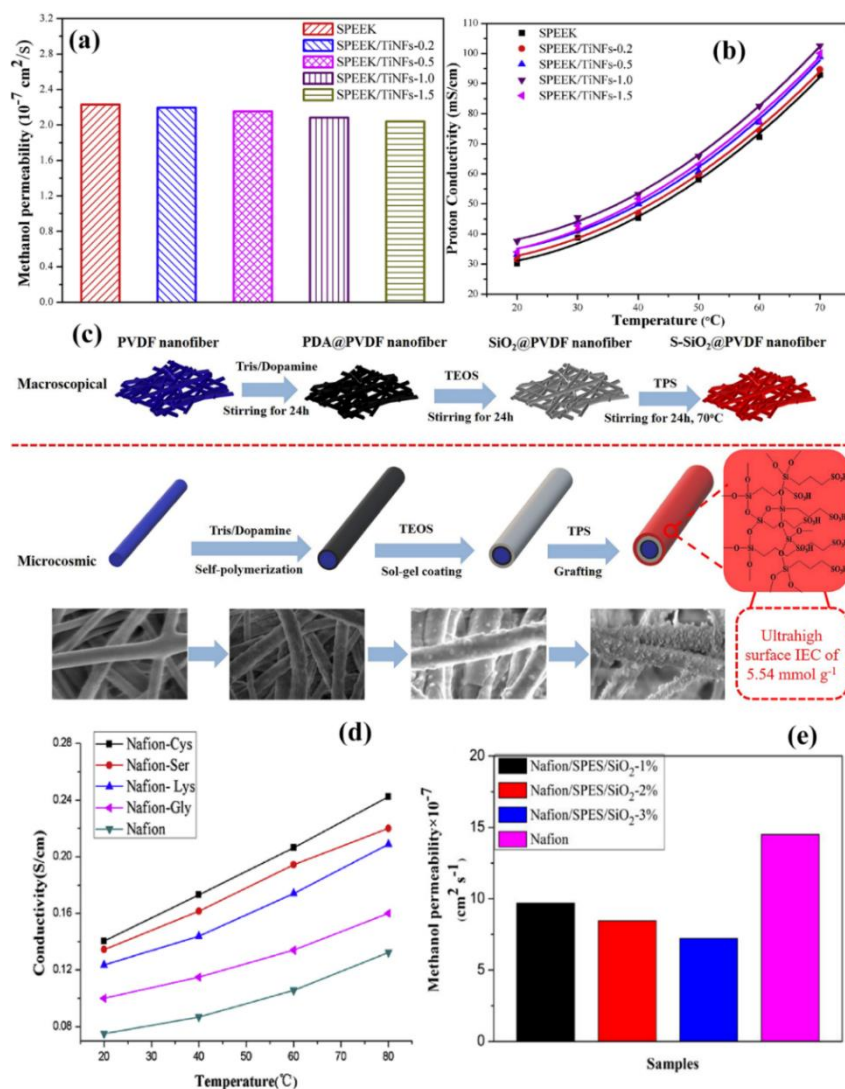


Fig. S 11 (a) Methanol permeability and (b) Proton Conductivity values of pristine SPEEK and SPEEK with different contents of Titania nanofiber (c) Schematic explanation of synthesis procedure of sulfonated silica coated PVDF nanofibers (d) Temperature Vs Proton conductivity values of Nafion with Cys, Ser, Lys and Gly along with pristine Nafion membranes (e) Methanol permeability values of Nafion/SPES composite membrane incorporated with 1-3 wt.% SiO_2 ^{19 2021,22}. With copyright permission 2017 and 2020, Elsevier.

Abbreviations

PEM: Proton exchange membrane
 GO: Graphene Oxide
 SGO: Sulfonated Graphene Oxide
 PEG: Polyethylene glycol
 F-silica: Functionalized silica
 ZrP: Zirconium phosphate
 UiO-66 : Zirconium based metal organic framework
 UiO-66-NH₂: Zirconium based metal organic framework-Ammonia
 GO@UiO-66: Graphene oxide coated zirconium based metal organic framework
 MILs- MOFs: Materials of the institute Lavoisier metal organic frameworks
 MOFs: Metal organic frameworks

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ZrSPP: zirconium sulfophenyl
PDHC: 1, 4-phenyldiamine hydrochloride
Co₃O₄: Cobalt Oxide
ZIF: Zeolitic imidazolate framework
S(ZIF-C): Sulfonated zeolitic imidazolate framework-derived porous carbon
SiO₂: Silicon dioxide
SSiO₂: Sulfonated silicon dioxide
Zr-Cr-SO₃H: Zirconium-chromium sulfonic groups
SiO₂@GO: Graphene oxide coated silicon dioxide
TiO₂: Titanium dioxide
GO: Graphene oxide
SiO₂-Al₂O₃: Silicon dioxide-aluminum Oxide
Al₂O₃: Aluminum Oxide
TiSiO₄: Titanium silicate
MOS₂: Molybdenum sulfide
E-MOS₂: Exfoliated molybdenum sulfide
MOS₂@CNT: Carbon nanotube coated molybdenum sulfide
Pd-GO: Palladium -graphene oxide
F-GO: Functionalized graphene Oxide
rGO: Reduced graphene oxide
MPTES: 3-mercaptopropyl triethoxysilane
GMPTS: Gamma-glycidoxypropyltrimethoxysilane
MPTES: 3- mercaptopropyl triethoxysilane
S-MMT: Sulfonated montmorillonite
BTA: Benzotriazole
SHNT: Sulfonated halloysite nanotubes
HDTA: Hexadecyltrimethylammonium chloride
PTFE: Polytetrafluoroethylene
PVDF: Polyvinylidene Fluoride
LBL: Layer by layer
SPAEK: Sulfonated poly(arylene ether ketone)
SSiO₂: Sulfonated silica
SBN: Sulfonated boron nitride
BN: Boron nitride
GMPT: Gamma-glycidoxypropyl trimethoxysilane
TAP: 2,4,6-triaminopyrimidine
TPS: 3-trihydroxysilyl-1-propanesulfonic
TTIP: Titanium tetraisopropoxide
SiWA: Tungstosilicic acids
QA: Quaternary ammonium
SBMA: Sulfobetaine methacrylate
SPPEK: Sulfonated poly(phthalazinone ether sulfone ketone)
ZrSPP: Zirconium sulfophenyl
SEM: Scanning electron microscopy
SPEEK: Sulfonated poly (ether ether ketone)
TEOS: Tetraethyl orthosilicate
H₂SO₄: Sulfuric acid
ITO: Indium Tin Oxide
PVDF-HFP: Poly(vinylidene difluoride-co-hexafluoropropylene)
QPEI: Quaternized polyethyleneimine
PVA: Polyvinyl alcohol
SA: Sodium alginate
PWA: Phosphotungstic acid
ZrP: Zirconium Phosphate
Tin (IV) oxide: SnO₂
Ph-CA: phosphorous-functionalized cellulose acetate
DNA: Deoxyribonucleic Acid
PVDF-PS: Polyvinylidene fluoride grafted polystyrene
S(ZIC-C): sulfonated zeolitic imidazolate framework-derived porous carbon

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